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FINAL REPORT ON CEN/TC264/WG38 STATIONARY SOURCE EMISSIONS - STANDARD METHOD TO DETERMINE FUGITIVE AND DIFFUSE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE

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Approved on behalf of NPL by
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EXECUTIVE SUMMARY

The aim of CEN/TC264/WG38 is the development and validation of standardised test methods for the determination of diffuse and fugitive emissions of volatile organic compounds (VOC) from oil and gas facilities. The standard should be complementary to the existing standard for the determination of leaks from piping and equipment EN 15446:2008.

Initially, a report summarising the available techniques for fugitive VOC monitoring was completed, providing a comprehensive description of the options along with their advantages and disadvantages, suitability of particular applications. From this initial report five methods were selected to participate in the two different measurement campaigns as part of WG38. The methods selected were: OGI, DIAL, SOF, tracer and RDM.

The first measurement campaign was carried out at a decommissioned area of a refinery in France during September 2016. During this campaign a controlled release facility was used to create known quantities of VOC and validate the selected techniques. A second measurement campaign, to assess the application of techniques at an active industrial site, took place in June 2017 in the Netherlands. The same five techniques (OGI, DIAL, SOF, tracer and RDM) were deployed. The final results from both these studies are detailed in this report (see Section 5 and Section 6).

Overall, the two validation studies were successfully executed. The first campaign independently validated the different techniques ability to quantify VOC emissions. The second campaign assessed the test protocol for each technique and showed that a real site could be surveyed and key messages on emissions developed using the protocols. The combined outputs of the studies are being fed into the final standard.

1. INTRODUCTION

This project requires the development and validation of standardised test methods for the elaboration of a European Standard, "Stationary source emissions — Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere".

The European Commission’s standardisation mandate M/514 under the Directive 2010/75/EU on industrial emissions, was accepted by CEN/BT, and a decision was taken to establish this standardisation work within CEN/TC 264/WG 38.

1.1 BACKGROUND

The control of the emissions of VOCs to atmosphere due to their losses during storage or transport is covered by both EU legislation and international protocols. The legislation on industrial emissions (Directive 2010/75/EU) is supported by the Best Available Techniques Reference documents (BREFs), which set out at an EU level the best available techniques for defined industrial activities and/or across these activities. Several BREFs also cover the prevention and control of fugitive and diffuse emissions of VOCs from industrial storage and transfer activities, in particular the BREFs concerned with mineral oil and gas refineries, large volume organic chemicals, and the “horizontal” BREF on the emissions from storage. The mandate for this work requests the European standardisation organisations to develop a European Standard that can be used in the determination of VOC emissions to be regulated within permits that are issued according to the Directive.

Total VOC emissions are also regulated at the EU and Member States levels under the National Emission Ceilings Directive (2001/81/EC) which sets total emission ceilings for such emissions at specific levels to be met from 2010 onwards.

VOCs are emitted by a wide range of sources including transport and industrial processes, as well as biogenic and other natural sources, and also by associated storage and handling activities, and the industrial and domestic use of VOC containing products.

VOCs are emitted to a significant extent by fugitive and diffuse sources (including non-point sources) and these emissions are difficult to quantify accurately. This requirement for more accurate determination of these important VOC emissions creates a challenge because of the complex nature of their emissions, and they require specific measurement and estimation methods that are currently not standardised. However, improving the accuracy of determining these VOC emissions should enable an improved assessment of these losses and may provide an incentive to reduce such losses, as well as the benefits to their effects on the environment and human health. This is intended to also contribute to the more uniform application of EU regulations and EU guidance documents.

2. OBJECTIVES

Mandate M/514 requires CEN to prepare and validate a standard for the determination of diffuse and fugitive emissions from oil and gas facilities. It should be complementary to the existing standard for the determination of leaks from piping and equipment EN 15446:2008.

Validation will cover techniques which are regarded under the EU Commission's BAT Conclusions - 2014/738/EU: Commission Implementing Decision of 9 October 2014 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions, for the refining of mineral oil and gas, and additional techniques included by CEN/TC 264/WG 38 (listed above).

Two validation studies were required to be undertaken. The first used a controlled release, able to replicate typical industrial emission levels, at an industrial location to challenge the remote sensing techniques with a known release of VOC under typical industrial conditions. A second validation study deployed the suite of techniques at an industrial facility to validate the combined framework of techniques defined in the standard and demonstrate their operation at a typical site.

3. WORK PACKAGES SUMMARY

In this section of the report a brief summary (and additional sign-posting) of the different work packages (WP) is given.

3.1 WP1 - RESEARCH INTO PERFORMANCE OF MONITORING TECHNIQUES

This work package was composed of two tasks:

- Collation and review of available technical information and stakeholder consultations
- Specifications for the initial performance requirements of the remote monitoring methods

A report reviewing the available monitoring techniques, examples of field measurement data and recommendations for the future together with an extensive set of references for available field work has been delivered by NPL to meet the requirements for the first of these tasks. The required performance characteristics have been presented to the working group, discussed and put into the draft standard to meet the requirements of the second task.

Section 4 presents a summary of performance for the monitoring techniques selected as part of the WG38 standard, the full report is included in Annex A.

3.2 WP2 - PLANNING AND COORDINATION OF THE FIELD MEASUREMENT PROGRAMME

This work package was composed of three tasks:

- Initial consultation with suitable candidate industrial site operators and planning
- Support for the first field validation programme (controlled release at an industrial site
- Support for the second field validation programme (application of the techniques at an industrial site)

Jonathan Martinez (Bureau Veritas – France) was appointed coordinator of the field measurement programme. A list of potential validation sites was identified and after discussion by the working group a site in the south of France and one in the Netherlands, were chosen for the two field campaigns (See Annex B).

A decommissioned area of a refinery in Southern France was selected as the location for the first validation study, taking place from 19th-30th September 2016. Testing used a controlled area release facility provided by NPL to measure a known quantity of VOC. An operational refinery in the Netherlands was selected as the location for the second validation study, taking place from 8th to 22nd June 2017. During both the campaigns four measurement providers participated in the tests (NPL, Bureau Veritas, FluxSense and Total), using a total of five different methods (see Section 4). The results and conclusions from both these validation studies are summarised in Sections 5 and 6.

3.3 WP3 - SPECIFICATION OF METEOROLOGICAL MEASUREMENTS (WITH WIND SPEED AND DIRECTION)

This work package was composed of one task:

- Specification of the number of wind sensors and their locations, a specification for a portable wind LIDAR and the subsequent deployment of the agreed facilities during the validation studies.

Following a review of available wind LIDARs, a Leosphere Windcube wind LIDAR sensor was selected and used for the validation studies. Additionally, three fixed meteorological masts fitted with ultrasonic meteorological stations were also deployed. See Annex C for details.

3.4 WP4 - OPTICAL GAS IMAGING CAMERA

This work package was composed of two tasks:

- Specification of the optical gas imaging camera with validation requirements
- Utilise the selected OGI at the selected sites and report the results

A number of manufacturers of OGI systems were approached for specifications of their systems, resulting in the selection of the FLIR GF320 IR camera was selected and used at the validation site tests.

The results from the OGI testing at both validation studies are found in Annex D.

3.5 WP5 - IMPLEMENTATION OF THE REMOTE MONITORING METHODS AT A SITE WHERE A CONTROLLED EMISSION SOURCE OF VOCS CAN BE LOCATED AND OPERATED IN THE FIELD

This work package was composed of eleven tasks:

- Assessment of the suitability of the test plan, including a visit to the site and discussion with the plant operators
- Identification of the location for the controlled release source
- Assessment of a suitable controlled release facility and its deployment for the field testing campaigns
- Deployment of the meteorology equipment at suitable locations for the field testing
- Implementation of the validation work programme including measurement of the controlled releases by DIAL, SOF and tracer techniques
- Where possible make measurements of the background sources at the test site in order to add value to the results
- Development and implementation of a work plan for linked measurement with OGI monitoring under WP4 and other technologies
- Possible requirements for any additional supplementary measurements
- Completion of the monitoring exercise at Site 1 using the monitoring techniques deployed
- Data processing and reporting of results by operators monitoring during the first field test
- Draw conclusions from the first field trial at Site 1.

The final results were presented by the four participants at WG38 meetings in Jan 2018. These results from each technique are reported in Section 5 (and Annex E). Additionally, the results from the controlled release facility (CRF) are also found in Section 5 (and Annex E).

3.6 WP6 - IMPLEMENTATION OF THE REMOTE MONITORING METHODS AND ESTIMATION/CALCULATION METHODS AT THE SECOND INDUSTRIAL SITE

This work package was composed of six tasks:

- Assessment of the suitability of the test plan, including a visit to the site and discussion with the plant operators

- Finalisation of the work plan, including specification of the area of the site to be monitored and for how long, for each remote monitoring method, ideally so that the total flux of emissions from the entire plant is achievable. Requirement for linking remote monitoring methods with the estimation methods and linked OGI monitoring, plus any additional supplementary measurements
- Deployment of the meteorology equipment at suitable locations for the field testing
- Completion of the monitoring exercise at the second industrial site, implementing the validation work programme, using SOF, DIAL, tracer and OGI (under WP4) techniques where required, over a campaign of around three weeks
- Data processing and reporting of results by operators monitoring during the first field test
- Draw comprehensive conclusions from the second field trial.

The preliminary results were presented by the four participants at WG38 meetings in December 2017 (19th – 20th) and May 2018 (23rd and 24th). The final results from each technique are reported in Section 6 (and Annex F).

3.7 WP7 - SYNTHESIS AND STATISTICAL EVALUATION OF THE MONITORING DATA AVAILABLE AFTER THE FIELD TRIALS

This work package was composed of four tasks:

- Drawing together and summarising the results in a number of data sets for different techniques
- Comparisons of all the results and conclusions with those investigated as part of WP1, regarding specifications and stakeholder views
- Statistical assessment of the performance of the techniques

The results of the statistical assessment were assessed and discussed in WG38 meetings and during a teleconference call in Feb 2018 from WP7 are reported in Section 7 (and Annex G).

3.8 WP8 - DEVELOP SPECIFICATIONS OF THE PERFORMANCE REQUIREMENTS FOR REMOTE MONITORING METHODS FOR USE WITH THE STANDARD

This work package was composed of one task:

- Report defining comprehensive specifications of the performance requirements for the remote monitoring methods (DIAL and SOF) for use with this European Standard

The Working Group has discussed the recommended specifications / protocols for the techniques that have been incorporated into the most recent draft of the new standard. The protocols have been revised using the information from the validation studies completed; the updated protocols can be found in Annex H. In addition a separate summary report of WP8 has been written

3.9 WP9 - DEVELOP SPECIFICATION OF THE PERFORMANCE REQUIREMENTS FOR REMOTE MONITORING METHODS FOR USE WITH THE STANDARD

This work package is composed of three tasks:

- An interim report on progress of the project after 18 months
- Final report covering the final results of the two field validation programmes with conclusions and recommendations, performance specifications for the selected methods and a summary on the status of the drafting of the European standard

- Reporting to the Commission on preparation of the standard

The interim report was delivered in January 2017, which has fed into this final report. This final report meets the requirements of the second and third tasks and will in turn feed into the finalised standard.

4. SUMMARY OF PERFORMANCE ASSESSMENT FOR AVAILABLE MONITORING TECHNIQUES

A report has been compiled by NPL examining the available monitoring techniques for detection of VOCs, including examples of field measurement data and references where possible. Initially, eight techniques were reviewed. However, only five technique were selected to feed into the standard. These were: DIAL, SOF, tracer correlation, RDM and OGI. The first four of these methods are used for identifying and measuring plumes and fence line or whole site surveying. The final technique (OGI) is generally utilised for leak detection; although, there is research into using this technique for plume quantification. A summary of performance assessment for the available monitoring techniques is presented below, the full report is included in Annex A.

4.1 DIFFERENTIAL ABSORPTION LIDAR (DIAL)

DIAL is a laser based remote sensing technique which enables measurements of range resolved concentrations to be made of a wide range of atmospheric species. Mass emission fluxes from large areas, e.g. an industrial site, can be calculated by combining DIAL and wind measurements. The DIAL is able to make measurements of a wide range of volatile organic compounds (VOC) (one or two at a time) in the UV (benzene, toluene and other non-VOC species) and in the IR (C2+, methane, ethane, ethene, ethyne, methanol and other non-VOC species). DIAL estimated uncertainty for a single emission rate measurement is about 10-30%, although a set of measurements is usually made which reduces the uncertainty typically below 20%.

The method is affected by atmospheric conditions, but in general this does not prevent its use. Fog reduces the maximum working range, but enhances the signal to noise ratio within that working range. Light rain and snow, both, enhance the signal to noise ratio and increase the maximum working range. Heavy rain and heavy snow usually require stopping the measurements to avoid deterioration of the scanner mirrors. Clear atmospheric conditions with few particles would reduce the signal to noise ratio and the maximum working range.

4.2 SOLAR OCCULATION FLUX (SOF)

The SOF technique is based upon using the sun as the light source to detect gas species that absorb in the solar spectrum. SOF measurements are carried out both in the infrared and UV visible regions using an infrared spectrometer and UV-spectrometer that are connected to a solar tracker. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. Mass fluxes/emissions are obtained by combining SOF and wind measurements. The method is used to quantify and map the location of various gas emission sources with a spatial coverage going from industrial conglomerates down to sub-areas in individual plants. Flux measurements that are carried out at the fence line of the industries, or further away, have the smallest uncertainties (20-30 %). Measurements close to single tanks have larger uncertainties (~50%). The method only works in daylight in sunny conditions.

SOF is able to make simultaneous measurements of a wide range of gas species in the infrared spectral region. Key pollutants that can be measured include alkanes (C_2-C_{10}), alkenes (ethene, propene, butadiene), alcohols (methanol, ethanol), alkynes (ethyne) and other non-VOC species. Methane and Aromatic VOCs can be measured but with limited sensitivity due to the high atmospheric background levels in the former case and weak absorption properties and cross interference with CO_2 in the latter case.

4.3 TRACER CORRELATION TECHNIQUES

Time correlation tracer (TCT) uses an instrument such as an FTIR to detect plant emissions, scaled by the measured quantity of an inert tracer gas released at a known rate close to the leak location. These techniques are only used for quantification of existing identified emission sources. Whole site measurements are possible with a standoff distance for the instrument of several kilometres. By deploying the instrument closer it would be possible to resolve multiple sources from a smaller area, however multiple tracer releases would be required to cover larger sites.

The method works best when the tracer source is located as close to the analyte emission source as possible. The main source of uncertainty is then from any differences in behaviour of the analyte and tracer in the same atmospheric conditions. Emission rates can be calculated with 15-30% precision.

4.4 REVERSE DISPERSION MODELLING (RDM)

Currently, modelling tools are widely used in environmental monitoring to solve problems of chronic impact and for the evaluation of accidental impacts. Generally, the purpose of a model is to solve a "direct" problem, which is to obtain an estimate of concentrations of pollutants in the atmosphere from a set of input parameters that are mainly the weather conditions and the sources of emissions.

For reverse dispersion modelling (RDM), concentration measurements are carried out downwind of the source. Meteorological quantities are determined and conclusions are drawn, with the help of dispersion calculations, about the emission rate and, if necessary, the emission structure. The reverse dispersion modelling inverts the classical way of a dispersion calculation. Therefore, it is also termed inverse dispersion calculation. The RDM method is able to determine a wide range of VOC compounds, depending on the conventional ambient measurement methods available, which are carried out downwind of the source: total VOC, methane, ethane, ethene, ethyne, methanol, benzene, toluene, xylene and others. From this measured concentration and meteorological data, quantitative mass emission fluxes can be produced by reverse dispersion modelling. The overall uncertainty depends on measurement uncertainty of downwind/upwind VOC-measurements, the complexity of the industrial site (as this impacts upon the complexity of wind field modelled) and the dispersion model.

4.5 OPTICAL GAS IMAGING (OGI)

OGI involves using optical camera systems to render certain VOCs to be visible in real time, allowing identification of leaks in real time. VOC plumes will be visible on the camera if they absorb energy in the wavelength range that the filter allows to pass, if the plume and background radiation emissions are different and if there is sufficient movement of the plume. OGI systems use IR cameras that provide a real time visualisation of gases and recording video, with standard and high sensitivity modes where consecutive images are subtracted from each other to accentuate the movement of VOC plumes. In some cases there will also be the ability to take pictures in visible and IR of the leaking equipment, recording of the detection time and date and the GPS coordinates of the leaking component.

OGI can detect leaks from a distance allowing surveying of inaccessible areas for techniques like sniffing, however the method is qualitative so cannot provide a leak rate. Inexperienced operators may miss smaller leaks or need to be closer to the source to identify some leaks. Depending on background conditions it may be easier or harder to detect leaks.

OGI has been shown to be as efficient as the EPA Method 21 for detection of leaks from components above a 500ppm total hydrocarbon threshold, although it can miss some smaller leaks detected by Method 21. This is partly offset by the ability of OGI to identify leaks in inaccessible areas and by the undetected smaller leaks contributing lower proportions of the total emissions, so OGI can still detect similar proportions of the overall fugitive emissions at the surveyed sites.

5. SUMMARY OF THE FIRST CAMPAIGN

5.1 BACKGROUND INFORMATION

A pre-test visit to the decommissioned refinery in Southern France was carried out by all the participants in June 2016 and a suitable unit for the controlled releases identified. During this visit, locations for all the participant's meteorological stations was identified, a programme of work was also agreed to. Table Table 5.1 lists the organisations that took part at the first validation study and their responsibilities.

Table 5.1 List of participants at the first validation study and their responsibilities.

Participating Organisations	Responsibilities
Bureau Veritas	• Campaign coordinator • OGI technique operator
INERIS	• Meteorological sensors and wind LIDAR deployment • Controlled gas release system operator
NPL	• Supply the controlled gas release system • DIAL technique operator
FluxSense and Chalmers University of technology	• SOF technique operator • Tracer technique operator
Total	• RDM technique operator

The field validation programme, consisted of twenty controlled realises of about 90 minutes each with a typical interval between releases of about 30 minutes, was successfully carried out by all the participant in September 2016.

A total of nine meteorological stations were deployed to gather meteorological data for the different techniques as shown in Figure 3.1. The tracer gas (N_2O) release point for the tracer correlation method was situated in the centre of the release area.

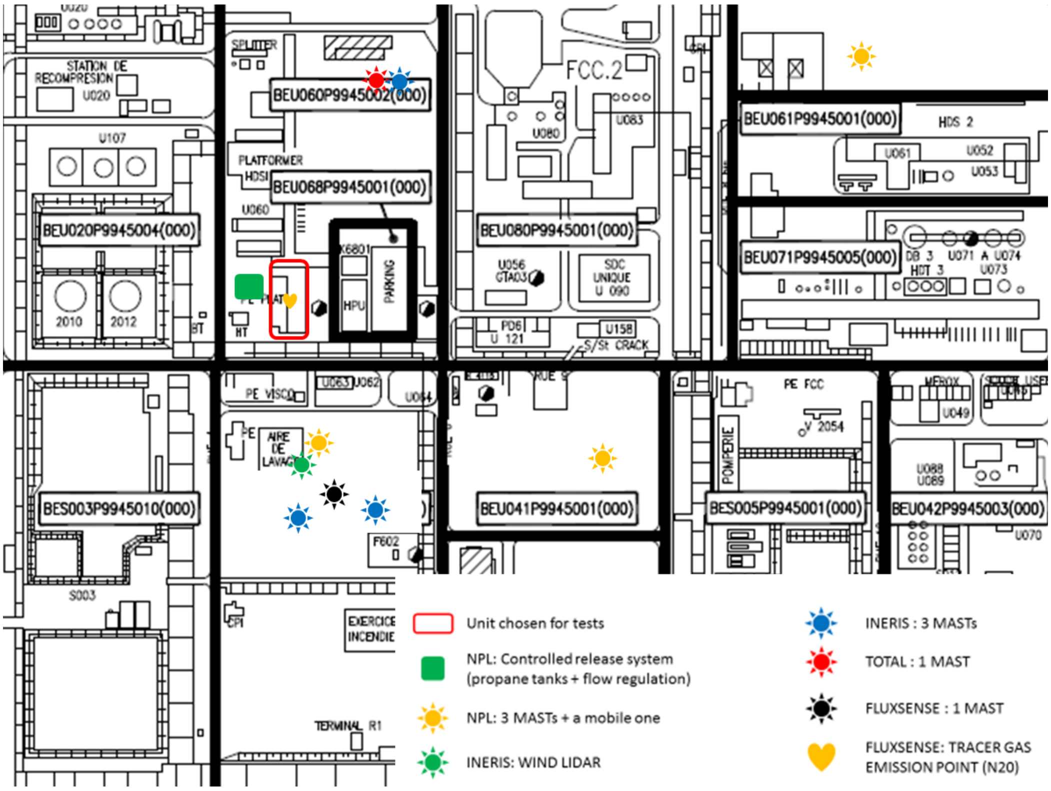


Figure 5.1 Locations of the meteorological stations

5.2 THE CONTROLLED RELEASE FACILITY (CRF)

NPL developed the Controlled Release Facility (CRF) to effectively simulate a broad range of real world gaseous emissions scenarios, with traceable defined fluxes, to challenge and validate new monitoring systems and methodologies. The CRF utilises a high flow gas blender, gases can be emitted from up to four independently controlled sources which can be spread over an area of up to one hectare.

The CRF was setup with five controlled release nodes inside the chosen decommissioned unit a diagram is shown in Figure 5.2 Locations of the five controlled release nodes and a photograph in Figure 5.3. The controlled CRF was operated by the Institut national de l'environnement industriel et des risques (INERIS) that was in charge of selecting for each test the release nodes and the amounts of gas, which were unknown to the participants.

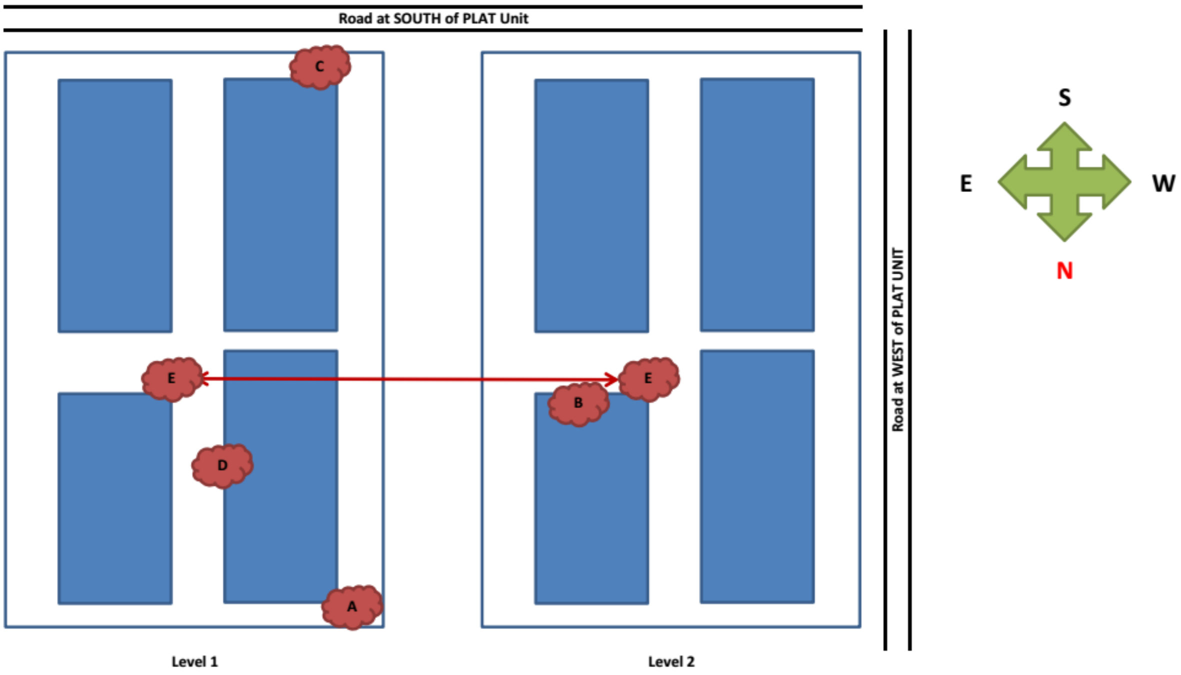
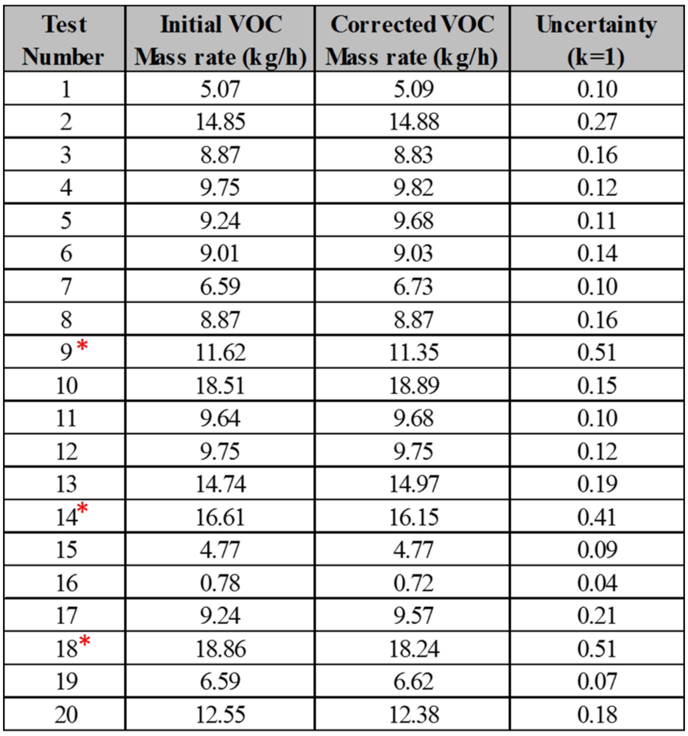


Figure 5.2 Locations of the five controlled release nodes

Figure 5.3. Photograph of controlled release arrangement with propane tanks and CRF trailer in foreground and unit where release nodes were positioned in background.

The released gas was mainly propane (about 93%) with a small percentage of propene, i-butane and n-butane. The controlled release facility was operated by INERIS who were in charge of selecting for each test, the release nodes and rates. The maximum achievable emission rate was about 30 kg/hr.

Table 5.2 Summary of CRF data from the different test releases.



Test Number	Initial VOC Mass rate (kg/h)	Corrected VOC Mass rate (kg/h)	Uncertainty (k=1)
1	5.07	5.09	0.10
2	14.85	14.88	0.27
3	8.87	8.83	0.16
4	9.75	9.82	0.12
5	9.24	9.68	0.11
6	9.01	9.03	0.14
7	6.59	6.73	0.10
8	8.87	8.87	0.16
9*	11.62	11.35	0.51
10	18.51	18.89	0.15
11	9.64	9.68	0.10
12	9.75	9.75	0.12
13	14.74	14.97	0.19
14*	16.61	16.15	0.41
15	4.77	4.77	0.09
16	0.78	0.72	0.04
17	9.24	9.57	0.21
18*	18.86	18.24	0.51
19	6.59	6.62	0.07
20	12.55	12.38	0.18

* *These releases were subject to unstable (decreasing) flows*

Table 5.2 above shows the initial VOC emission rates reported by INERIS to the field test participants based on the nominal flow rates and the corrected VOC emission rates based on the actual flow rates. As part of this work a full uncertainty analysis has also been completed and the uncertainty values are also shown in Table 5.2.

5.3 RESULTS OF FIRST CAMPAIGN

Table 5.3-5.6 highlight the quantified emission rates calculated using the four different techniques (DIAL, SOF, Tracer and RDM), these are then compared with the initial CRF data.

Table 5.3 Comparison of CRF and DIAL data for each test release.

Test	CRF emission rate (kg/h)	Number of Scans	Wind speed (m/s)	DIAL Emission Rate (kg/h)	Standard Deviation (kg/h)	Difference between Dial and Release (kg/h)	Relative difference (DIAL - CR)/CR
1	5.1	6	3	5.4	1.8	0.3	7%
2	14.9	6	3.1	16.1	2	1.2	8%
3	8.9	6	2.3	9.8	2.3	1	11%
4	9.8	5	3.7	8.4	2.6	-1.4	-14%
5	9.2	4	1.9	11.4	1.6	2.2	24%
6	9	4	2.4	9.2	1.4	0.2	2%
7	6.6						
8	8.9	5	2.5	9.6	1.1	0.7	8%
9	11.6	5	2.1	13.3	4.4	1.6	14%
10	18.5	6	1.7	18.5	5.6	0	0%
11	9.6	4	2.7	10.2	4.5	0.6	6%
12	9.8	6	2.8	8.5	4.5	-1.3	-13%
13	14.7						
14	16.6	6	1.9	15	3.7	-1.6	-10%
15	4.8	5	2.7	3.7	2.5	-1.1	-23%
16	0.8	4	2.9	1.2	3	0.4	56%
17	9.2	3	1.1	9.7	0.5	0.4	5%
18	18.9	5	2.1	14.9	8.3	-4	-21%
19	6.6	5	3.4	8.5	4.7	1.9	29%
20	12.6	4	2.8	11.5	5.3	-1.1	-8%

Table 5.4 Comparison of CRF and SOF data for each test release.

Test	CRF emission rate (kg/h)	Number of Scans	Wind speed (m/s)	SOF Emission Rate (kg/h)	Standard Deviation (kg/h)	Difference between SOF and Release (kg/h)	Relative difference (SOF - CR)/CR
1	5.1	8	4.2	5.3	0.8	0.3	5%
2	14.9	16	3.4	12.6	4	-2.3	-15%
3	8.9	8	2.7	12	1.5	3.2	36%
4	9.8	13	4.6	14.8	5.8	5	52%
5	9.2						
6	9	10	3	10.3	4.9	1.3	14%
7	6.6	6	3.5	8.6	2.2	2	
8	8.9						
9	11.6	4	2.4	26.8	2.8	15.2	131%
10	18.5						
11	9.6	14	3.5	10.1	2.9	0.5	5%
12	9.8	11	3.1	8.3	2.1	-1.5	-15%
13	14.7						
14	16.6	11	2.1	22.7	11.4	6.1	37%
15	4.8	13	3.7	6.2	2.3	1.4	29%
16	0.8						
17	9.2	11	1.5	11.4	5.7	2.2	24%
18	18.9	16	3.1	30.8	9.7	11.9	63%
19	6.6	12	3.8	11.3	4.5	4.7	71%
20	12.6	12.7	3.3	13.4	4	0.9	7%

Table 5.5 Comparison of CRF and time correlation tracer (TCT) data for each test release.

Test	CRF emission rate (kg/h)	Number of Scans	Wind speed (m/s)	TCT Emission Rate (kg/h)	Standard Deviation (kg/h)	Difference between TCT and Release (kg/h)	Relative difference (TCT - CR)/CR
1	5.1	10	4.2	4.1	2.2	-1	-19%
2	14.9	6	3.4	12.3	1.4	-2.6	-17%
3	8.9	7	2.7	11.8	1.3	2.9	33%
4	9.8	13	4.6	13.1	2	3.3	34%
5	9.2	4	1.5	11.7	2.4	2.5	27%
6	9	13	3	10.4	1.1	1.4	15%
7	6.6	12	3.5	9.1	2.4	2.5	0
8	8.9						
9	11.6	7	2.4	16.5	4.5	4.9	42%
10	18.5	12	1.8	21.1	4	2.6	14%
11	9.6	16	3.5	13.2	2.8	3.6	37%
12	9.8	19	3.1	12.8	2.8	3	31%
13	14.7						
14	16.6	10	2.1	19.6	4	3	18%
15	4.8	13	3.7	5.8	1.3	1	22%
16	0.8	7	4.6	1.5	0.6	0.7	91%
17	9.2	14	1.5	11.4	4.3	2.2	23%
18	18.9	12	3.1	27.1	7.8	8.2	44%
19	6.6	11	3.8	8.3	1.8	1.7	26%
20	12.6	18	3.3	17.4	6.1	4.8	39%

Table 5.6 Comparison of CRF and RDM data for each test release.

Test	CRF emission rate (kg/h)	Number of Scans	Wind speed (m/s)	TCT Emission Rate (kg/h)	Standard Deviation (kg/h)	Difference between TCT and Release (kg/h)	Relative difference (TCT - CR)/CR
1	5.1	16	2.4	7.2	n/a	2.1	42%
2	14.9	15	2.8	17.5	n/a	2.6	18%
3	8.9	24	1.4	3.1	n/a	-5.8	-65%
4	9.8	27	2.4	3	n/a	-6.8	-69%
5	9.2						
6	9	22	1.7	5.6	n/a	-3.4	-38%
7	6.6	32	1.9	26.8	n/a	20.2	306%
8	8.9	28	2	23.7	n/a	14.8	167%
9	11.6	32	2.4	9.9	n/a	-1.7	-15%
10	18.5	37	2	14.5	n/a	-4	-22%
11	9.6	33	2.6	8.7	n/a	-0.9	-10%
12	9.8	29	2	4.1	n/a	-5.7	-58%
13	14.7	32	0.9	3.3	n/a	-11.4	-78%
14	16.6	29	1.5	2.9	n/a	-13.7	-83%

One comment from the FluxSense/Chalmers team during the first validation study was that using the SOF and tracer correlation methods higher background levels were observed when the wind was in certain directions, due to several interfering sources of VOC upwind of the CRF release. The DIAL also measured background sources in most of the scans, but could generally isolate these plumes from the CRF releases.

The results as presented showed overall good agreement with the controlled release experiments. DIAL predicted fluxes were in-line with the release rates with uncertainty close or better than the proposed protocol value as shown in Figure 5.4.

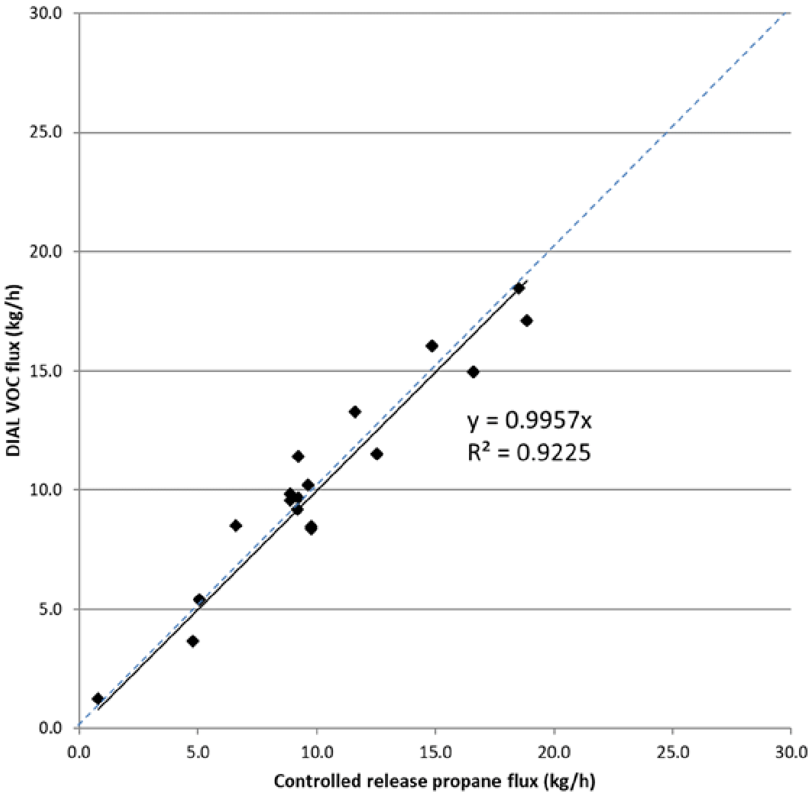


Figure 5.4. Correlation between DIAL and controlled release fluxes.

SOF predicted fluxes were proportional to the release rates with a positive bias, with much scatter in the individual results and the reported measurement uncertainty was greater than proposed in the protocol as shown in Figure 5.5. An example calculation to simulate the effect of increasing sample size suggested that increasing the number of scans to be averaged from 4 (or 6) to 16 would bring the difference between calculated flux and release rate at 10 kg/h within the 95% confidence limit on the sample mean.

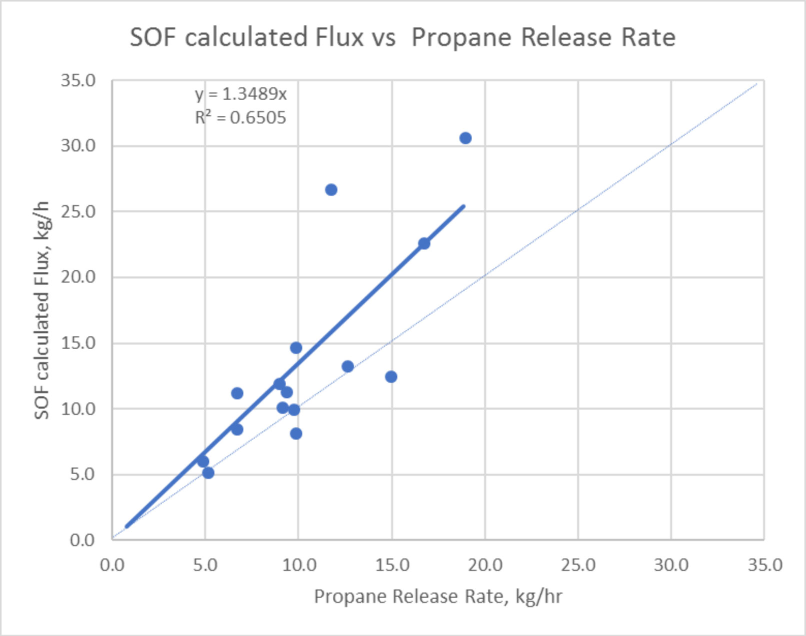


Figure 5.5. Correlation between controlled release and SOF.

The tracer correlation method with mobile sampling predicted fluxes proportional to the release rates and also with a positive bias as shown in Figure 5.6. The variability was less and the bias was less but analysis similar to that used for SOF showed that no increase in the number of samples taken would overcome the bias at 10 kg/h. These latter exercises do not address the possibility that a different treatment of the background would have produced a different outcome but do highlight a need to understand why the short time measurement (not given for the TC with MeFTIR) techniques produced positive bias (over prediction).

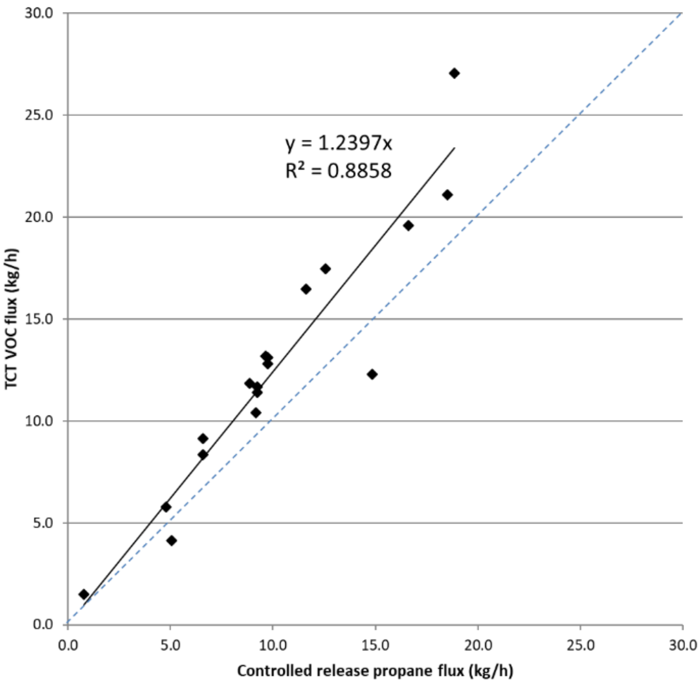


Figure 5.6. Correlation between controlled release and TC

The RDM method under predicted the release rates and this is likely due to the dispersion model over-predicting concentrations as shown in Figure 5.7. Again there was no discussion of the role of background concentrations on the results. Two tests where the RDM method gave far too high a flux could be eliminated on the grounds that the wind-speeds were too low. It seems more likely that these are outliers for unknown reasons. DIAL didn't report one of these and SOF didn't report the other.

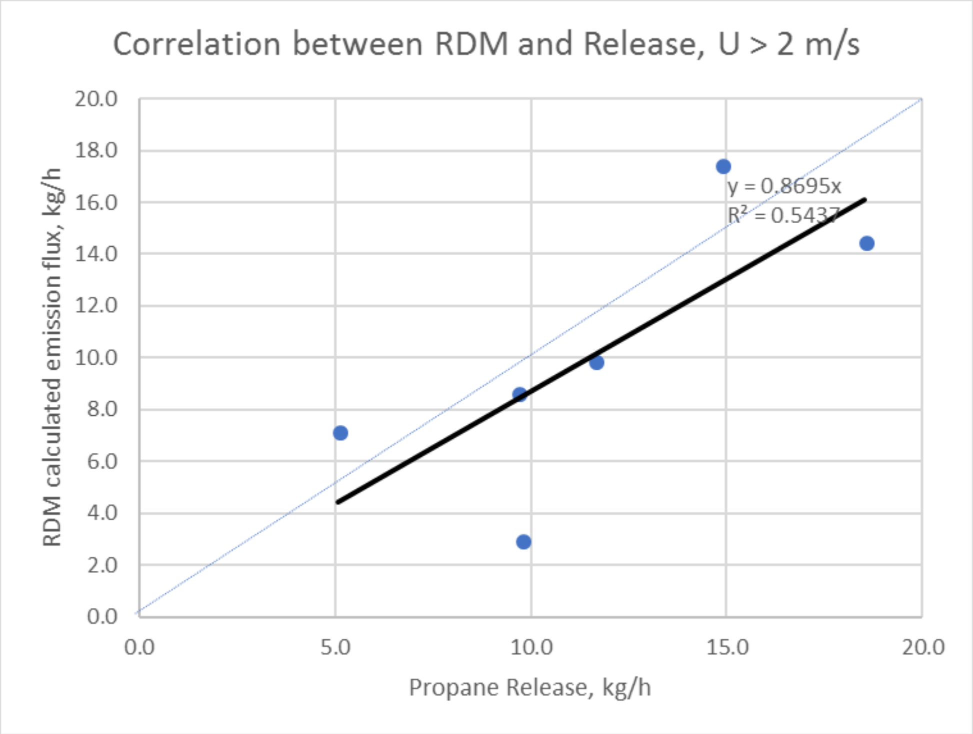


Figure 5.7. Correlation between controlled release and RDM (revised dataset).

The reports presenting the results from the individual techniques can be found in Annex E.

6. SUMMARY OF THE SECOND CAMPAIGN

6.1 BACKGROUND INFORMATION

A pre-test visit to the refinery in the Netherlands was carried out by all the participants in March 2017 to perform the pre-campaign activities identified in the protocol such as health and safety, campaign logistic and identification of suitable measurement locations. Suitable locations for the meteorological stations were also identified during the pre-test visit. INERIS were responsible for collecting the meteorological data. For this second validation study the configuration of met stations (supplied by INERIS) was used, which included: 3 ultrasonic fixed masts located within the pink areas 1, 2 and 3 and a Leosphere Windcube wind lidar positioned within area 1 (Figure 6.1). During the second campaign additional meteorological measurements were supplied by NPL (located in pink area 1) and Total (located in pink area 4).

Figure 6.1 Locations of the fixed meteorological stations

As part of the protocol the site (i.e. the customer) should identify all the areas to be measured. However, in this validation study all partners agreed to measure emissions from the whole site. Each technique would then carry out the measurements following its own protocol (outlined in Annex A). Table 6.1 lists the organisations that took part at the first validation study and their responsibilities.

Table 6.1 List of participants at the second validation study and their responsibilities.

Participating Organisations	Responsibilities
Bureau Veritas	• Campaign coordinator • OGI technique operator
INERIS	• Meteorological sensors and wind LIDAR deployment
NPL	• DIAL technique operator
FluxSense and Chalmers University of technology	• SOF technique operator • Tracer technique operator
Total	• RDM technique operator

6.2 RESULTS OF SECOND CAMPAIGN

All the techniques were successfully applied at a cooperating industrial site (refinery) according to a test plan prepared and executed according to the draft standard protocol.

A summary is given below of the results given by the techniques, rounded to the nearest whole number. The total for the chemical tank park for DIAL includes the dominating emission for the cyclo-hexane tank which, as is up-scaled by a large factor due to post measurement correction for speciation.

Table 6.2 Comparison of results for each technique from the second validation study.

Refinery Area	SOF		DIAL		TC (MeFTIR)		RDM	
	median	stdev	mean	stdev	mean	stdev	mean	stdev
	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h
1. East Tank Park	76	51	42					
2. West Tank park	30	11	10					
3. Middle Tank Park	316	296	150	60				
5. Petrochemical Tank park	61	30	108	80	43	23		
6. Main Process Area	40	24	55					
7. Petrochemical Process Area	37	25	48					
8. Waste Water Treatment	13	3	7		9	3	12	4
10. Vent Pipe	21	8	7	2	30	31		
11. Truck Loading Area	11	12	11					
Total (bottom up)	605		437					
Total (top down)	694							

The bottom up totals for SOF is greater than that for DIAL by 38% (which by numerical coincidence is close to the bias noted in the controlled release experiment) but the extent of the uncertainty on the flux estimates for the largest emitters is too great to draw conclusions on this difference. Sufficient to note that a wide range of emission values are assigned to the refinery areas.

The OGI campaign was very successful. Where the other techniques indicated the probability of an emission source an emission was nearly always found. Detection from a range of ≥50m was typical of the largest releases and emissions from tanks could be detected from both across the tank roof and from the ground. The combination of a rapid scouting for high concentrations using a mobile sensor (here SOF and MeFTIR) followed by OGI was felt to be very efficient. Follow up from DIAL scans, the majority of cases, was more thorough. The campaign supports the use of OGI for detecting diffuse as well as fugitive sources.

The reports presenting the results from the individual techniques can be found in Annex F.

7. DISCUSSION AND DATA ASSESSMENT

This section of the report gives an overview the output of work packages 7 and 8. It aims to provide a statistical evaluation of the monitoring data from the two field campaigns (Annex G), as well as providing some assessment of the protocols. Noted: finalised protocols can be found in Annex H.

The first field campaign involved the controlled release of propane gas in several different source arrangements within the process area of a disused refinery site. The releases were conducted "blind" and the remote sensing techniques used to identify the source location and estimate the release rates. Participating teams submitted their estimates before the release rates were published. The release rates used ranged from 0.8 to 18 kg/h. These values are representative of the smaller emission sources that the standard method should detect. Under the meteorological conditions of the campaign, and with the limitations on measurement access posed by a real site, the techniques DIAL, SOF and TCT were able to detect this full range and provide emission estimates that were consistent with the releases. Similarly the OGI operators were able to detect and make a qualitative assessment of each emission test. The technique RDM was not able to resolve emissions smaller than 5 kg/h.

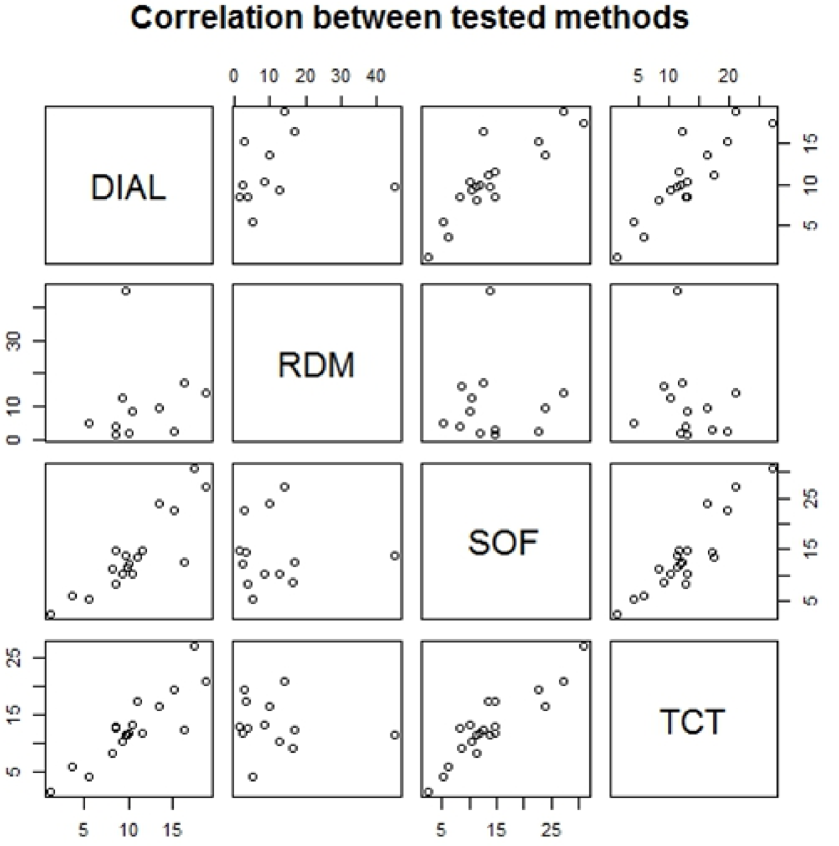


Figure 5.2 Controlled releases preliminary results correlation between DIAL, SOF, Tracer and RDM methods.

The first campaign demonstrated some inherent limitations in the planning of field measurements. The weather (wind direction and wind speed) was significantly different to the historic record for the location. The need for the standard to embrace flexibility in its requirements is thus underlined. Secondly the results of the field trial were obtained after correcting for external sources. A need to improve the protocols with respect to how such corrections are made and the contribution to uncertainty analysis was demonstrated.

The second field campaign was carried out on an operating refinery and timed to best fit the refinery operations. The aim of this campaign was to allow the draft standard to be applied, with each participant following their specific protocol. The individual techniques were applied independently and draft reports submitted to this assessment. Once all of the results were gathered they were shared between all the working groups for discussion and learning. This exchange led to only one significant adjustment in conclusions when the composition of one single VOC source was established as cyclo-hexane rather than a straight chain alkane requiring a significant adjustment of DIAL results. Although the second campaign did not include any reference sources, i.e. sources of known emission rate, there were emissions from two tanks that enabled a rate calculation methods to be compared. All techniques were deployed to good effect, with broad correspondence of the emission estimates for the quantitative techniques. The detection of sources by OGI mapped well to those found by other techniques. Generally missing from the reports is a quantitative discussion of how background concentrations were accounted for in determining emission fluxes. Qualitatively, the presence of background was described as significant and problematic.

The results of this second campaign has led to slight refinement of the individual protocols (WP8), which will be fed into the final standard.

The main learning points from the campaigns is that there should be some standardisation of reporting across the protocols to make the assumptions and uncertainty budgets more transparent. It was not possible to follow and assess the importance of background concentrations and how their correction affected the reported results. There is generally a high commentary that background correction is difficult and significant, but this needs to be quantified.

It is recommended that the observations made above are followed through, especially formalising the treatment of background concentrations and incorporation of sensitivity assessments into the uncertainty budget. The initial thoughts provided by Fluxsense on managing variability between individual flux measurements and developing robust sampling rules for SOF and TC+MeFTIR should be developed. A goal would be to understand why the methods should evidence positive bias.

8. CONCLUSIONS

Overall, the two validation studies were successfully executed. The first campaign was used to independently validate the different techniques ability to quantify VOC emissions. The second campaign was aimed to assess the test protocol for each technique. The combined outputs of the studies are being fed into the final standard.

1/ Identification	Wi number: 00264167
2/ Title	Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere
3/ Milestones so far	Validation work: • WP1: Research into performance of monitoring techniques see Annex A • WP2: First field test organised, planning of second field test • WP3: Specification of meteorological measurements see Annex C • WP4: Optical gas imaging camera see Annex D • WP5: field test controlled emissions of VOCs completed see Annex E • WP6: Implementation of monitoring methods the second industrial site. see Annex F • WP7: Statistical evaluation of all the results and conclusions to be carried out once the field trial data is analysed see Annex G Development of the standard: • WP8: The Working Group has recommended specifications / protocols for the techniques that have been incorporated into the most recent draft of the new standard. The protocols have been revised using the information from the validation studies completed. See Annex H. A separate summary report of WP8 has been written. • WP9: An interim report (assessing the progress of the project) and final report (covering the results of the two field validation programmes with conclusions) have been delivered.
4/ Remaining work	Validation studies and assessments completed. Outputs fed into standard. No remaining work outstanding.
5/ Documents	Annex A: Performance of monitoring techniques (WP1) Annex B: Planning information for the first field campaign Annex C: Meteorological measurements from test sites Annex D: Results of Optical gas imaging camera Surveys (WP4) Annex E: Results from First Validation Study (2016) Annex F: Results from Second Validation Study (2017) Annex G: Statistical Evaluation of Results Annex H: Finalised Protocols

9. ANNEXES

This section summarises the content of the individual annexes which are available as a separate document "*ANNEXES FOR: FINAL REPORT ON CEN/TC264/WG38 STATIONARY SOURCE EMISSIONS - STANDARD METHOD TO DETERMINE FUGITIVE AND DIFFUSE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE*"

ANNEX A: PERFORMANCE OF MONITORING TECHNIQUES (WP1)

ANNEX 1: TECHNIQUES REVIEW

See separate document for details: "Annex A - Techniques Review (WP1).pdf".

Overview:
This review looks at the available monitoring techniques for VOC emissions. Where available this includes examples of field measurement data and references for the published field work. In addition this report includes the method descriptions which have been used as the initial protocols of the techniques selected for the WG38 study. The report also includes recommendations for the best techniques to be used in future. Eight different techniques are covered, with varying suitability for particular applications. Sniffing, bagging and OGI are mainly used for leak detection and/or quantification. DIAL, SOF, tracer correlation and modelling techniques are mainly implemented for identifying and measuring plumes and fence line and/or whole site surveying. Flux chamber measurement is used for defined area source emissions such as water treatment ponds or landfill sites which can also be quantified by other techniques such as DIAL.

ANNEX B: PLANNING AND COORDINATION OF THE FIELD CAMPAIGNS

See separate documents for details: "Annex B – WP2 Site 1 Report.pdf" and "Annex B – WP2 Site 2 Report.pdf".

Overview:
The main objective of the Work Package 2 was to plan and coordinate the field measurement programme. The above reports outline the work done by Bureau Veritas to coordinate both of the WG38 field campaigns and ensure the projects was executed correctly.

ANNEX C: METEOROLOGICAL MEASUREMENTS FROM TEST SITES

See separate document for details: "Annex C – Wind Data Site 1.pdf" and "Annex C – Data Site 2.pdf".

Overview:
Work package 3 was primarily concerned with the collection of meteorological data during the field campaigns. The above reports list the equipment used during the campaigns and document the wind data recorded for respective campaigns.

ANNEX D: RESULTS OF OPTICAL GAS IMAGING CAMERA SURVEYS (WP4)

See separate documents for details: "Annex D – WP4 Site 1 Report.doc" and "Annex D – WP4 Site 2 Report.doc".

Overview:
The main objective of the Work Package 4 was to utilise optical gas imaging to assist remote monitoring methods during two field campaigns. A FLIR GF320 OGI camera was used to determine the exact location of the leaking sources of the main emissions highlighted by the remote monitoring methods. The reports above summarise the OGI work performed during the campaigns.

ANNEX E: RESULTS FROM FIRST CAMPAIGN (2016)

ANNEX E1: CRF RESULTS FROM FIRST CAMPAIGN

See separate document for details: “Annex E – CRF Report.pdf”

Overview:
This CRF report presents results of the quantified propane releases carried out using the National Physical laboratory (NPL) controlled release facility (CRF) in the South of France. This study was the first WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 22nd to the 29th of September 2016.

ANNEX E2: DIAL RESULTS FROM FIRST CAMPAIGN

See separate document for details: “Annex E – DIAL Report 2016.pdf”

Overview:
This report presents the results of propane emission measurements from controlled release experiments in the South of France, carried out using the NPL Differential Absorption Lidar (DIAL). This study was the first WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 22nd to the 29th of September 2016.

ANNEX E3: SOF RESULTS FROM FIRST CAMPAIGN

See separate document for details: “Annex E – SOF Report 2016.pdf”

Overview:
This report presents the results of propane emission measurements from controlled release experiments in the South of France, carried out using SOF. Solar Occultation Flux (SOF) method is based on using the sun as the light source and to detect gas species that absorb in the solar spectrum (Mellqvist, 2009). SOF measurements are carried out both in the infrared and UV visible regions using an infrared spectrometer and UV-spectrometer that is connected to a solar tracker. This study was the first WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 22nd to the 29th of September 2016.

ANNEX E4: TCT RESULTS FROM FIRST CAMPAIGN

See separate document for details: “Annex E – TCT Report 2016.pdf”

Overview:
This report presents the results of propane emission measurements from controlled release experiments in the South of France, carried out using Time correlation tracer (TCT). TCT uses an FTIR to detect plant emissions, scaled by the measured quantity of an inert tracer gas released at a known rate close to the leak location. These techniques are only used for quantification of existing identified emission sources. This study was the first WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions -

Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 22nd to the 29th of September 2016.

ANNEX E5: RDM RESULTS FROM FIRST CAMPAIGN

See separate document for details: “Annex E – RDM Report 2016.pdf”

Overview:
This report summarises the quantitative emissions assessment made by reverse dispersion modelling (RDM) technique during the first field campaign in the south of France (September 2016) for the WG38 standard. In addition to an initial emissions assessment the report documents the necessary modifications to original protocol to improve emission quantification. Finally, it includes the updated emissions acquired from these modifications.

ANNEX F: RESULTS FROM SECOND CAMPAIGN (2017)

ANNEX F1: DIAL RESULTS FROM SECOND CAMPAIGN

See separate document for details: “Annex F – DIAL Report 2017.pdf”

Overview:
This report presents the results of VOC emission measurements from a refinery site in the Netherlands, carried out using the NPL Differential Absorption Lidar (DIAL). This study was the second WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 8th to the 22nd June 2017.

ANNEX F2: SOF RESULTS FROM SECOND CAMPAIGN

See separate document for details: “Annex F – SOF Report 2017.pdf”

Overview:
This report describes a validation experiment in Rotterdam 2017 as part of standardizing methods to measure fugitive VOC emissions. The work has been carried out as part of CEN/WG38/TC264. The campaign was carried out from June 5 to June 22, at a refinery in Rotterdam. The main objective was to demonstrate different methods in a real facility and compare these if possible. The methods should follow their measurements protocol, as derived within the CEN project. This report describes measurements with the Solar Occultation Flux method which was carried out during 8 days. This mobile remote sensing method requires sunny conditions and the possibility of moving around the industrial site, inside and outside the site.

ANNEX F3: TCT RESULTS FROM SECOND CAMPAIGN

See separate document for details: “Annex F – TCT Report 2017.pdf”

Overview:
This report describes a validation experiment related to standardization of methods to measure fugitive VOC emissions (CEN WG 38 TC 264). A campaign was carried out from June 5 to June 22 2017 at a refinery in Rotterdam, denoted the Test Site in this report. The main objective was to demonstrate different methods in a real facility and compare these if possible. The methods follow their measurements protocol, as derived within the CEN project. This report describes measurements with the Tracer Correlation method based on Mobile extractive FTIR, MeFTIR.

ANNEX F4: RDM RESULTS FROM SECOND CAMPAIGN

See separate document for details: “Annex F – RDM Report 2017.pdf”

Overview:
This report summarises the quantitative emissions assessment made by reverse dispersion modelling (RDM) technique during the second field campaign in the Netherlands (June 2017) for the WG38 standard. During this campaign the RDM instrumentation was set-up in the waste water treatment (WWT) area of the selected oil refinery. The report summarises the emission estimates originally submitted using the RDM technique, modifications related to protocol adaptation, and a comparison with other techniques for the WWT area.

ANNEX G: STATISTICAL EVALUATION OF RESULTS

See separate document for details: “Annex G – Statistical Evaluation of Results.pdf”

Overview:
This report describes the output of work package (WP) 7 which provides a synthesis and statistical evaluation of the monitoring data from the two field campaigns.

ANNEX H: FINALISED PROTOCOLS FOR VOC MONITORING TECHNIQUES

See separate document for details: “Annex H – Protocols.pdf”

Overview:
This document contains the final test protocols for the all of the different VOC monitoring techniques selected as part of the WG38 standard. These techniques are: differential absorption lidar (DIAL), solar occultation flux (SOF), time correlation tracer (TCT) and reverse dispersion modelling (RDM). The protocols for each technique were tested during two field campaigns and revised according to the findings of these studies.

National Physical Laboratory

NPL REPORT ENV (RES) 038

ANNEXES FOR:
FINAL REPORT ON CEN/TC264/WG38 STATIONARY SOURCE EMISSIONS - STANDARD METHOD TO DETERMINE FUGITIVE AND DIFFUSE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE

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NPLML - COMMERCIAL

JULY 2018

ANNEXES
FOR
FINAL REPORT ON CEN/TC264/WG38 STATIONARY SOURCE EMISSIONS - STANDARD METHOD TO DETERMINE FUGITIVE AND DIFFUSE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS INTO THE ATMOSPHERE

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Approved on behalf of NPL by
Alan Brewin, Director, Operations Division.

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ANNEX B: PLANNING AND COORDINATION OF THE FIELD CAMPAIGNS

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NPL REPORT ENV (RES) 026

CEN/TC264/WG38 – WP 1 – TECHNIQUE REVIEW

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JUNE 2016

CEN/TC264/WG38 - WP 1 - TECHNIQUE REVIEW

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Approved on behalf of NPL by
Martyn Sene, Director, Operations Division.

CONTENTS

EXECUTIVE SUMMARY

1 INTRODUCTION

This review looks at the available monitoring techniques for VOC emissions. Where available this includes examples of field measurement data and references for the published field work. The report also includes recommendations for the best techniques to be used in future.

Eight different techniques are covered, with varying suitability for particular applications. Sniffing, bagging and OGI are mainly used for leak detection and/or quantification. DIAL, SOF, tracer correlation and modelling techniques are mainly implemented for identifying and measuring plumes and fence line and/or whole site surveying. Flux chamber measurement is used for defined area source emissions such as water treatment ponds or landfill sites which can also be quantified by other techniques such as DIAL.

2 DIAL

2.1 OVERVIEW

2.1.1 Scope

The Differential Absorption Lidar (DIAL) technique is a laser-based remote monitoring technique which enables range-resolved concentration measurements to be made of a wide range of atmospheric species. Mass emissions fluxes of various chemical species from a large area, such as an industrial site, can be obtained by combining DIAL and wind measurements.

2.1.2 Compounds measured

The DIAL is able to make measurements of a wide range of volatile organic compounds (VOC) (one or two at a time) in the UV (benzene, toluene) and in the IR (total VOC, methane, ethane, ethene, ethyne, methanol). Other additional compounds could be measured (nitric oxide, sulphur dioxide, ozone, hydrogen chloride, nitrous oxide).

2.1.3 Information provided

A scanner system directs the output beam and detection optics, giving almost full coverage in both the horizontal and vertical planes. From this data, concentration profiles and mass emission fluxes along defined vertical cross section can be produced.

2.1.4 Scale and limitations

The DIAL has a maximum working range of between 500 m to 2 km depending on atmospheric conditions, the pollutant being monitored and its concentration. The usual configuration to monitor an emissions flux is to measure in a scan which is close to normal to the pollutant plume. However, it should be noted that the DIAL does not provide data in the first 50 100 m from the DIAL.

2.2 DIAL MEASURING PRINCIPLE

2.2.1 Description of the technique

The DIAL technique uses pulsed tuneable laser radiation which is launched into the atmosphere over the paths to be monitored. The gas concentration can be measured as a function of range from the laser source by tuning the laser wavelength on and off the spectral absorption feature of the target gas. The DIAL technique operates using these principles in the infrared, visible and ultraviolet spectral regions. This enables a wide range of gases to be monitored specifically and sensitively.

The general hydrocarbon measurement uses an infrared absorption that is similar for all hydrocarbons with three or more carbon atoms, linked to the stretch frequency of the carbon-hydrogen bond. The line strengths for these species are proportional to the number of carbon-hydrogen bonds present and this enables a total mass emission to be determined. As such it provides a measure of the mixture of VOCs that are present. The pair of infrared wavelengths used for this DIAL measurement, at around 3 µm, can be selected so that the absorption per unit mass is relatively invariant with respect to the mix of different hydrocarbons that are present. The sensitivity of the DIAL is slightly different for different hydrocarbons, and for example an oxygenated hydrocarbon will give a different absorption per mass than a straight chain alkane. The differential absorption strength used in the DIAL measurements is calibrated to give a mass emission rate for gasoline vapour. A different ‘cocktail’ of hydrocarbons could give a slightly different response per unit mass. Although the general hydrocarbon measurement provides a good estimate of the overall amount of hydrocarbons present, the accuracy of this measurement can be improved, and the total VOC concentration calculated, by taking air samples at locations which would provide an indication of the actual speciation of the emission fluxes sampled by the DIAL. If the actual (relative) composition is known from the air sample analyses, then it is possible to check that the absorption coefficients used are appropriate for the actual hydrocarbon mixture present, and adjust the coefficients if necessary.

The DIAL measurement may be thought of as being comparable to a series of open-path measurements made with virtual retro reflectors at range, r, the spacing of which is defined by the range resolution of the DIAL system. The range-resolved concentration of the target species can then be derived by differentiating the path-integrated concentration.

Multiple range-resolved concentration measurements can be made along different lines-of-sight and combined to produce 2-D concentration distributions. These are typically made by scanning the line-of-sight in either azimuth or elevation, to produce horizontal or vertical scans. Horizontal scans are generally used to identify different sources across a sight. The typical DIAL measurement configuration is shown in Figure 1.1, with the mobile DIAL facility positioned downwind of the area being investigated. The DIAL laser beam is then scanned in a vertical plane and the distribution of the target gas in the measurement plane is mapped.

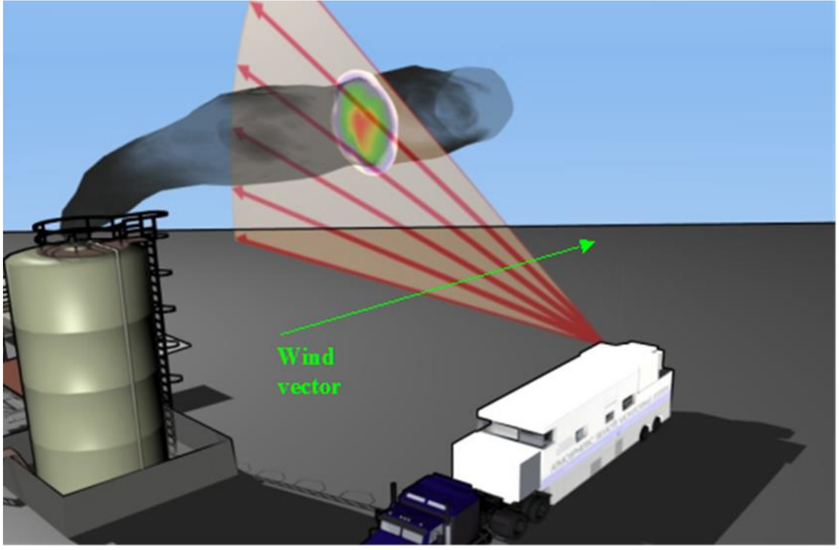

Figure 1.1 — DIAL Measurement Configuration

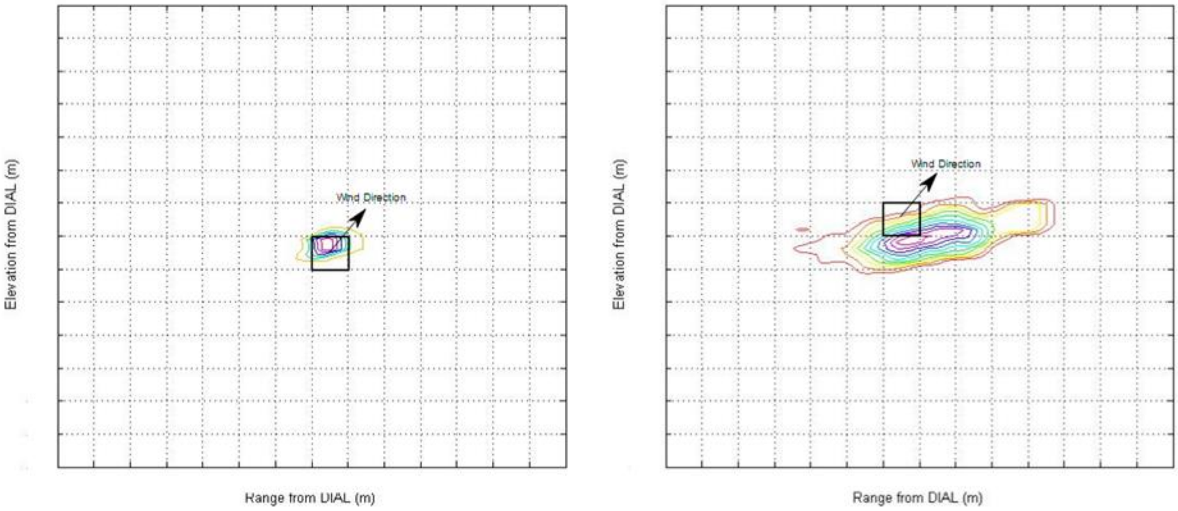

Figure 1.2 — Illustration of the emission rate calculation approach

Vertical scans are combined with wind information to derive the emission flux from the sources. This is done by determining a wind field, as a matrix of wind vectors, in the same plane as the vertical concentration data, and with the same spatial resolution. The flux in each cell is then determined by multiplying the wind vector for each cell with the average concentration in that cell. The plane of concentration fluxes is then integrated to determine the total flux for that measurement. Figure 1.2 shows an example of how plume size affects the emission rate that is calculated. This figure shows two example plumes (the cell grids are for indication and are not to scale), one which has a small plume, and therefore a small integrated emission rate, and the other which has a larger plume, and therefore represents a larger emissions rate, although the peak concentration in both is similar, and indeed may even be higher in the small plume than the large plume.

Figure 1.3 shows a schematic representation of two measurement plane configurations observing the same plume. One has a nearly perpendicular orientation to the plume, and the wind direction is therefore also perpendicular to the measurement plane. The other is at an angle through the plume, and therefore the wind is not perpendicular to the plane of the measurements. If only the concentration profile were observed the right hand measurement configuration would show a larger plume (as it cuts obliquely through the plume). However, when the wind direction is taken into account, the normal component of the wind vector is used, and this therefore reduces the emission rate determined from this scan, resulting in the same emission rate being determined for both measurement orientations.

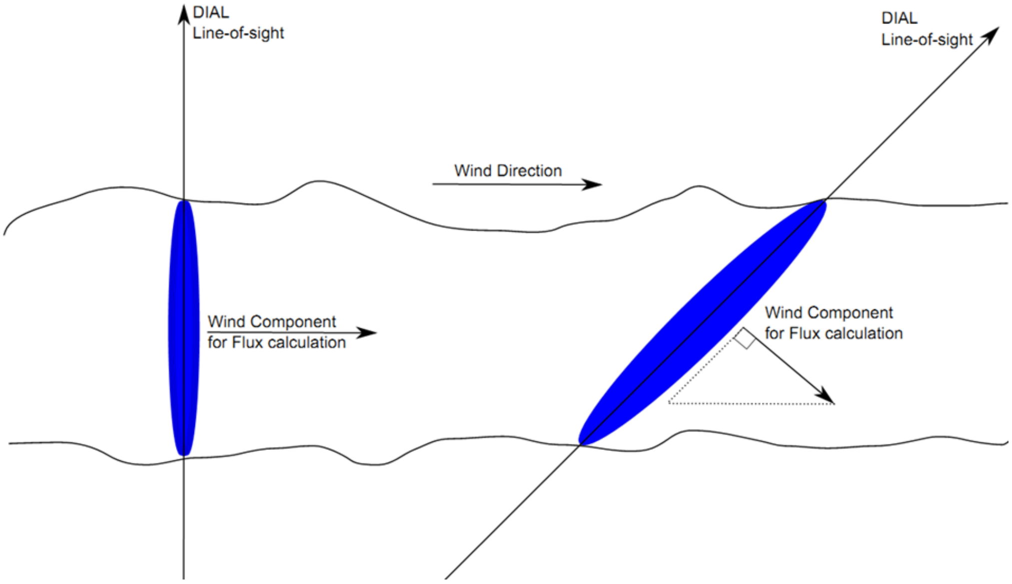

Figure 1.3 — Schematic showing relationship between emission rate and wind direction

Emissions from other areas of the site may have been upwind of the measured target area. These sources can be excluded in two ways. If the upwind sources to be excluded are close to the measured sources, and produce localised plumes, these can been discriminated spatially from the measured rates by selecting the regions of the scanned region to integrate, in order to calculate the emission rate only from the area of interest. Conversely, if the upwind sources are further away and the emissions from them have been measured in upwind scans then this can be subtracted from the downwind emission rate. In general the DIAL will be located so that a series of downwind scans can be obtained, and then moved to a position to be able to monitor the upwind flux, see Figure 1.4A. In many cases upwind and downwind fluxes can be obtained from a single location (Figure 1.4B).

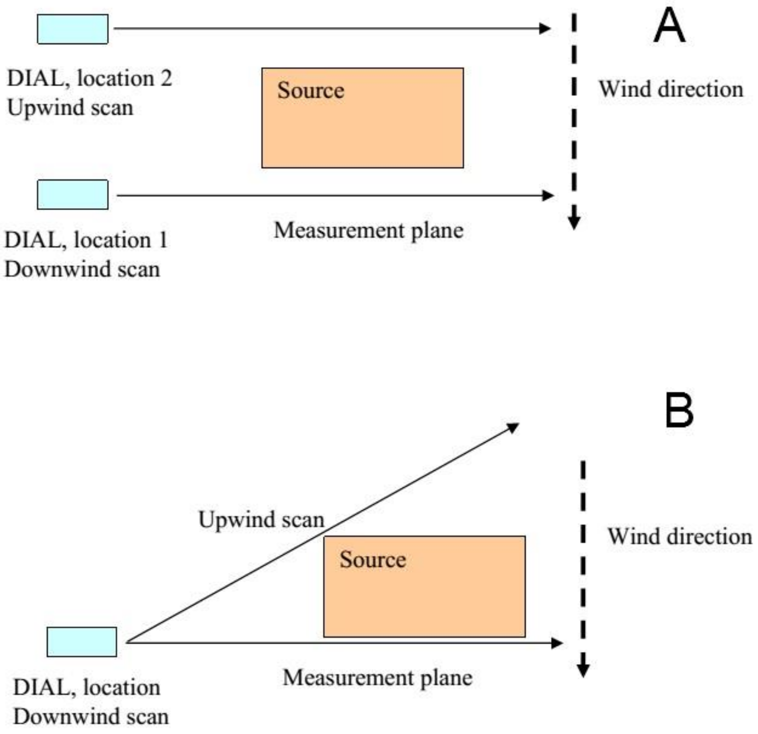

Figure 1.4 — Measurements of upwind and downwind emissions from one (B) or two (A) DIAL locations

Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large spatial variations since, for example, errors in the wind speed in regions where large concentrations are present will significantly affect the accuracy of the results. The wind over a flat surface shows an increase in wind speed with height. The vertical profile varies with atmospheric conditions but is typically taken to be logarithmic assuming that the wind does not change direction with height and a non-adiabatic process is verified. On such conditions the flow on the surface layer is defined by non-adiabatic wind and temperature profiles.

The wind profile is obtained by fitting to point measurements made using a tall mast, usually deploying two to four wind sensors at different heights up to 12 m to 15 m. Meteorological data is then processed to provide vector averaged wind data for the periods of each DIAL scan.

The meteorological station is typically deployed in a clear area giving an unperturbed wind field. This is a main uncertainty in the determination of the emitted flux and it can be reduced by deploying a portable wind sensor along the DIAL measuring line-of-sight to scale the wind profile derived from the fixed mast sensors to match the portable wind speed at the portable elevation.

Local terrain effect can be important and introduce systematic bias in flux determinations. The ground elevation where the wind measurement system is located needs to be checked to establish if it is similar to the ground level downwind of the source; if not, the ground elevation along the scan line where the plume is detected should be used as the reference point for establishing the wind profile.

2.2.2 Advantages and constraints

The DIAL system is typically mounted on a vehicle and it can only be parked on site’s road locations that don’t impact on site operations and safety. An advantage of the DIAL system is that the scanner unit can rotate 360° allowing different line-of-sight measurements to be taken from the same location.

All outdoor optical techniques like DIAL are affected by different atmospheric conditions although DIAL measurements are not restricted to weather conditions. Fog has an impact on DIAL measurements by reducing the maximum working range but enhancing the signal to noise ratio in the working range. Light rain and snow not only enhance the signal to noise ratio but also the maximum working range. Heavy rain and snow usually require stopping the measurements to avoid deterioration of the scanner mirrors. Clear atmospheric conditions with few particles would reduce the signal to noise ratio and the maximum working range.

The wind speed and direction are the major DIAL uncertainty sources and have an impact on planning DIAL measurements. With light wind speeds and variable wind directions it is difficult to determine the sources contributing to the emission along a measurement line-of-sight. The higher the wind speed and the faster the gas concentration is diluted possibly leading to under-estimation of the emission due to the concentration being below the detection limit of the DIAL. In this situation the DIAL scanner can be quickly reoriented in order to get closer to the emission area. If the wind direction varies significantly it might become impossible to measure the targeted area from where the DIAL is parked. An advantage of the DIAL compared to other optical techniques is that it can be quickly redeployed to a different location in order to carry out measurements of the targeted area.

Another DIAL constraint is that it does not provide data in the first 50 m – 100 m from the DIAL but this is also one of the main advantage of the technique as the DIAL doesn’t have to be located in the emissions source but it has to 'stand-off' by this much. This has the advantage that the DIAL usually doesn’t need to enter to restricted site areas (such as process units) and it doesn’t disrupt the site routine operations.

The DIAL is a complex technique and therefore it is relatively expensive. However, in only a few measurement days the DIAL is able to quantify the emissions from a site of about a kilometre square area and to separate the emission from each of the site’s several units. The DIAL also has a very short stand down time compared to other optical technique as it can quickly react to variable atmospheric conditions. Overall the quantity and quality of the data (e.g. direct emission mass measurements and 3D mapping of the emission) collected in few DIAL measurement days is cost effective when compared to other techniques.

2.2.3 Uncertainty

The DIAL flux is determined by multiplying the vertical concentration data with a matrix of wind vectors in the same plane as the vertical concentration data, and with the same spatial resolution. The wind profile across the measurement plane is the main uncertainty in the determination of the emitted flux and the uncertainty in concentration varies with range and atmospheric conditions. The flux accuracy can therefore vary from a fraction of kg/h for emissions close to the DIAL and in favourable atmospheric conditions to a few kg/h for emissions far away from the DIAL and in unfavourable atmospheric conditions.

A set of three or four DIAL scans should be made in order to minimise the uncertainty. The standard deviation of a set of measurements will include effects of the source variability, DIAL measurement uncertainty and the influence of other factors such as the wind speed and direction variability during the course of individual measurements. From various DIAL validation studies, the DIAL estimated uncertainty for a single flux measurement is about 20 % to 30 %, some of this uncertainty will be included in the standard deviation of a set of measurements.

The uncertainty associated with a set of measurements can be further decreased by randomising any systematic effect due to a particular measurement configuration. To achieve this, one or two extra sets of measurements should be made under different wind conditions or along different scan lines or from different locations.

DIAL VOC measurement is targeted on C3+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. For these measurements, when the absorption coefficient is adjusted using a correction factor, derived from air sample analyses, the scaling factor to go from the standard DIAL VOCs to the measured C3+ can increase the flux uncertainty of about 10 %. An additional scaling factor can be calculated to include the C2 contribution (dominated by ethane) – which the DIAL VOC measurements are not sensitive to – and the added uncertainty is minimal when the C2 contribution is small compare to C2+ but it is high when the C2 contribution is significant. In the latter case it is advisable to carry out separate DIAL measurements of ethane and VOCs.

2.3 PERFORMANCE CHARACTERISTICS

The detection limit values of a typical DIAL facility at industrial sites under typical conditions are about 0,1 kg/h in the ultraviolet and 0,3 kg/h in the infrared. These values are based on the actual levels of performance of existing DIAL systems obtained during field measurements and validation studies, rather than calculations based on theoretical noise performances. However, the actual sensitivity varies with atmospheric conditions, plume dimension and distance from the DIAL, wind speed and angle between the wind direction and DIAL measurement line-of-sight. The detailed performance behaviour of a DIAL system is therefore much more complex and there are a number of key points that should be noted:

- The DIAL measurement is of concentration per unit length rather than just concentration. Measurements over a shorter path would have a lower sensitivity, and would be more sensitive over a longer pathlength.
- For a fixed concentration sensitivity, the detection limit increases as the wind speed increases.
- Since the backscattered Lidar signal varies with range, generally following a (range)$^{-2}$ function, the sensitivity is also a function of range. The better sensitivity is obtained in the 100 m to 300 m region from the DIAL, and it will get poorer at longer ranges.
- The maximum range of the system is generally determined by the energy of the emitted pulse and the sensitivity of the detection system, the atmospheric conditions, the pollutant being monitoring and its concentration. It varies between 500 m to 2 km.
- In all cases the performance parameters are based on those obtained under typical meteorological conditions. For the ultraviolet measurements the meteorological conditions do not have a great effect on the measurements as the backscattered signal level is predominantly determined by molecular (Rayleigh) scattering, and this does not vary greatly. However, in the infrared the dominant scattering mechanism is from particulates (Mie scattering). So the signal level, and therefore the sensitivity, is dependent on the particular loading of the atmosphere, and this can vary dramatically over relatively short timescales.
- The optical configuration of the DIAL system means there is a minimum range between 50-100 m before measurements can be made.

The DIAL theoretical range resolution is determined by the detector bandwidth and the speed of the transient recorder used as data acquisition system. However, the actual range resolution is determined by the signal averaging used that depends on atmospheric conditions and the concentration of the measured pollutant, and may be of the order of 10-30 m.

2.4 QUALITY CONTROL

2.4.1 General

Quality assurance of the emission measurements is necessary. These procedures require detailed project planning and progress monitoring with project subject to regular internal reviews and quality audits at measurement institutions.

2.4.2 Spectroscopic calibration procedures

A crucial requirement for high quality DIAL measurements is accurate knowledge of the actual differential absorption coefficients that are appropriate for a particular measurement. The following calibration procedures should be employed to ensure the spectroscopic quality, and therefore the accuracy of the differential absorption measurement. The three key elements that need to be verified through these checks are that:

- A suitable calibration reference cell prepared with a known (concentration∗pathlength) parameter.
- The laser source is operating with a suitably narrow linewidth to properly resolve the spectral feature of interest.
- The wavelength of the laser source is fixed and stable on the appropriate on and off resonant wavelengths.

2.4.3 Calibration gases

A standard gas mixture of the target gas (or an appropriate proxy – e.g., propane or pentane for the total hydrocarbon measurements) should be used to provide the reference for the spectroscopic measurements. These standards should be, where possible, gravimetrically prepared, internationally-traceable reference gas mixtures with absolute volume mixing ratio (VMR) accuracies of 0,5 % or better.

2.4.4 Calibration cell

Direct measure of the transmission through a calibration cell filled to atmospheric pressure with the reference gas. This ensures that the pressure broadening, and therefore the linewidth, is the same for the calibration gas as in the ambient environment.

2.4.5 Spectral scans

A spectral scan of the relevant absorption feature should be carried out on a daily basis. The measured absorption feature is compared to the expected one. This provides confirmation that the cell has been filled correctly and that the laser source linewidth is correct. If the measured width of the absorption features differs significantly (typically by more than 0.2 cm^{-1}) from the expected widths then this indicates an issue with the laser source bandwidth and a number of laser checks should be carried out.

2.4.6 Continuous spectral monitoring

Having established that a suitable reference cell is available and the laser source linewidth is correct, the on- and off-resonant wavelengths are set to their chosen values for the DIAL measurements. A system to check the wavelengths do not drift from the expected value should be in place and logged continuously.

2.4.7 Detection and acquisition system checks

In addition to verifying the spectroscopic performance of the laser source, a check that the full detection and acquisition system is measuring correctly should be carried out at least once a day.

2.4.8 Meteorological sensor calibration

The meteorological sensor should be calibrated once a year by the manufacturer. The calibration certificates may provide a calibration factor for the wind speed and wind direction readings. If data loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.

In addition, the different sensors should be compared side-by-side in the field to provide a further check on their correct function.

2.5 DATA ANALYSIS

2.5.1 General

The data acquired has to be analysed to give the range-resolved concentration along each line-of-sight. The data analysis process consists of the following steps:

2.5.2 Background subtraction

Any DC background value is subtracted from the signals. This measured background takes account of any DC signal offset which may be present due to electronic offsets and from incident background radiation. The background level is derived from the average value of the far field of the returned Lidar signal where no significant levels of backscattered light is present

2.5.3 Normalisation for variation in transmitted energy

The two signal returns are normalized using the monitored values of the transmitted energy for the on and off resonant wavelength pulses. The mean transmitted energy is used to normalize the averaged return signal. For this application, this has been shown to be equivalent to normalizing individual shots against transmitted energy and then averaging the normalized values.

2.5.4 Calculation of path-integrated concentration

The path-integrated concentration of the target species, out to the range *r*, is calculated. The absorption coefficients used in this calculation are derived from high-resolution spectroscopy.

2.5.5 Derivation of range-resolved Concentrations

The integrated concentration profiles are piecewise differentiated with a selectable range resolution, to give the range-resolved concentration along the line-of-sight.

2.5.6 Calculation of emission fluxes

Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile. Care should be taken to reduce artefacts due to the difference in data density at different ranges, due to the polar scanning format of the data. The emission flux is then determined using the concentration profile together with meteorological data. The emitted flux is calculated using the following mathematical steps:

- The product is formed of the gas concentration measured with the DIAL technique at a given point in space and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.

- This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.

- This array of flux results is then integrated over the complete concentration profile to produce a value for the total emitted flux.

A logarithmic wind profile can be used to describe the vertical distribution of the wind by using at least two wind speed sensors at different heights. Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large spatial variations since, for example, errors in the wind speed in regions where large concentrations are present will significantly affect the accuracy of the results. In such cases, is advisable to use more wind speed sensors at different heights in order to calculates the variation of wind speed with height, as a function of various parameters (such as the roughness of the terrain). At close distance from the emission source the wind field could potentially have a complex behaviour due to the presence of buildings increasing the uncertainty in the determination of the emitted flux. This can be reduced by deploying a portable wind sensor along the DIAL measuring line-of-sight to either use the wind speed for the wind profile determination or to scale the wind profile derived from the fixed mast sensors to match the portable wind speed at the portable elevation. Local terrain effect can be important and introduce systematic bias in flux determinations. The ground elevation where the wind measurement system is located needs to be checked to establish if it is similar to the ground level downwind of the source; if not, the ground elevation along the scan line where the plume is detected should be used as the reference point for establishing the wind profile. The calculated wind field is then combined with the measured gas concentration profile using the procedure described above.

The spatial averaging applied to the DIAL data can be adjusted in post processing, to take account of low signals due to atmospheric backscatter. This primarily affects the production of concentration plots. These are a secondary data product used to provide visual indications of plume location and as an aid to source identification. The averaging used has minimal effect on calculation of the emission fluxes, which are the main data product.

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3 OGI

3.1 OVERVIEW

3.1.1 Scope

This document provides guidelines for the qualitative detection and location of certain hydrocarbon leaks by viewing them on a video screen (optical gas imaging, OGI).

The document focusses on portable, passive optical camera systems that enable certain volatile organic compounds to be made visible in real time under certain conditions.

The document lays down the requirements the IR camera shall meet and the method and strategy to be followed to enable reliable statements to be made.

OGI can be used as part of a LDAR (leak detection and repair) programme to:

- visualize diffuse VOC emissions of storage tanks
- visualize VOC released during loading operations
- visualize VOC emissions of sources not included in the SOW of a LDAR programme (inaccessible sources or irregular emission sources)
- For a qualitative inspection after maintenance actions

It can be used to validate repairs made on the faulty component by providing the operator with a means of direct inspection of the effectiveness of said maintenance.

In general, safety, the environment and loss of product are the drivers for applying OGI.

3.1.2 Detectable pollutants

Depending on the expected VOC to be detected, a suitable camera should be selected. A VOC plume can be made visible if at least three conditions are met:

The VOC plume shall absorb energy in the wavelength range that the filter allows to pass through

There shall be a difference between the background radiation emitted and the total radiation emitted by the VOC plume

Sufficient movement of the VOC plume

The IR camera detects compounds which absorb radiation in the IR range which the filter allows to pass through. Theoretical absorption spectra should be used to determine whether a gas absorbs radiation in the relevant wavelength range. Public and validated absorption spectra are available for most compounds.

The camera does not respond in the same way for every compound. Depending on its optical absorption properties in the IR, the response factor can vary by a factor of 10 or more from one compound to another.

If the absorption properties are not known (certain compounds or mixtures) a test should be performed to see if the camera is suited for the specific hydrocarbon.

The detection limit is higher for pure aromatics than for alkanes.

3.1.3 Information provided

An IR camera that is used for OGI shall at least provide the following information:

Visualisation of gases in real time

IR video recording of the leaking equipment, if necessary in high sensitivity mode

Optional:

Visible and IR picture of leaking equipment (recording or extraction)

the location of the leaking equipment (GPS coordinates)

detection time and date

In general, an IR camera has several displaying modes:

black and white (recommended)

different colour palette

high sensitivity (or equivalent)

3.1.4 Scale and limitations

Depending on the camera (lens), the studied VOC, the size of the leak and external factors, the detection range can vary between centimetres and tens of meters.

Detection limits for some commonly found VOC’s in petrochemical industry are established under laboratory conditions. For lower alkanes and some aromatics detection limits can range from less than one to a few grams per hour. From field studies it is concluded that in general detection limits will range from a few to tens of grams per hour. However depending on the many factors that influence visibility, detection limits in the field can vary a lot. If it is necessary to work with relatively low detection limits a camera with a high sensitivity mode should be used. However this is not a guarantee that small leaks will be seen. For that reason, OGI is more suited to detection of large emissions.

A high sensitivity is normally obtained when consecutive images are subtracted from each other in order to accentuate the movement of the VOC plumes even more.

An IR camera enables many potential emission sources to be viewed in a relatively short time.

For observing potential leak sources in a process unit from 3 meters distance and from more than one viewing angle, the survey speed is around 2000 components/day. This number can vary depending on the unit or site configuration, for example more components can be surveyed if they are located very close to one another as in the case of air-cooler plugs. .

OGI limitations are:

Not all VOCs are detectable or respond in the same way

Detection is influenced by many external factors

Unknown detection limits

Non-automatic detection (quality of the detection performed depends on training and experience of OGI operators)

no quantification of the emission

no distinction between different VOCs

Although it is not possible - yet - to quantify the VOC emissions that the IR camera can detect, it is possible to make a rough distinction between small, medium and large emissions on the basis of experience. Studies are being conducted into making more systematic estimates of the quantity of VOC emissions that are made visible using OGI. This quantitative OGI (QOGI) involves analysis of the pixel contrast intensity.

3.2 OGI DETECTION PRINCIPLE

Optical imaging can be split into two categories, active systems and passive systems:

Active optical imaging uses a laser to illuminate the observed scene. The wavelength used corresponds to the IR absorption spectrum of the VOCs. The radiation will be reflected by the objects in the background and will then pass through the VOC plume. Some of the IR radiation will be absorbed by it. The difference is measured to obtain an image of the plume.

Passive optical imaging uses the IR radiation emitted naturally by the objects in the background of the plume (background thermal emission, as well as the reflection by the background of the incident photonic radiation, thermal emission from the gas and absorption by the gas of the background compounds). Depending on the temperature of the objects, they emit IR radiation that will be absorbed by the VOC plume. By filtering only on the wavelengths on which the VOCs absorb IR, the camera can detect temperature gradients; when these are superimposed on the actual image of the scene, a real-time image of the plume is obtained.

3.2.1 Advantages and constraints

This method allows a precise location of each individual leaking source, so maintenance can be targeted in order to reduce emissions.

The optical imaging tools currently available are light instruments (passive detection). Their small size means that they can be used easily and quickly on a chemical or petrochemical site.

The instrument used is light, portable and has its own power supply (8 hrs). It can therefore be used easily without disrupting the organisation on site.

Operation test is easily performed using standard gases by the operator

Instrumentation cost is limited compared to other remote sensing techniques

Several instrument providers and service providers are available in Europe

An IR camera is immediately ready for use and suitable to be deployed. It is therefore suitable for “emergency” actions

However, these systems can also be used to detect from further away (with higher detection thresholds), which can be beneficial with regard to hard-to-reach areas (using different lenses).

As with all optical methods, the instruments can be limited in outdoor use by the presence of rain, snow, fog, water vapour, wind, etc.

It would be a plus for IR cameras to be equipped with specific protective devices to enable their use in an ATEX environment. Today the safer model is ATEX “Zone 2” only.

OGI is currently only recognised as a qualitative technique for identifying leaks. Since identifying leaks is the main challenge for fugitive emissions it has been widely adopted. OGI can be used to identify leaks that can then be assessed using quantitative techniques like bagging or have leak rates estimated using emission factors. QOGI is in development to add quantitative analysis for emission flux estimation, but has not yet been approved for use as an alternative method.

3.2.2 Uncertainty

OGI has been shown to be as efficient as the EPA Method 21 for detection of leaks from components above a 500ppm total hydrocarbon threshold, although it missed some smaller leaks detected by Method 21 (Robinson 2007). This is partly offset by the ability of OGI to identify leaks in inaccessible areas and by the undetected smaller leaks contributing lower proportions of the total emissions, so OGI still detected a similar proportion of the overall fugitive emissions at the surveyed sites.

3.3 QUALITY CONTROL

3.3.1 Test procedures

No calibration (from provider) is required for OGI used in "gas detection". On the other hand, a functional test is required. This functional test consists of validating the ability of the IR Camera to detect a certain determined flow rate of a certain substance, from a certain distance, under certain weather conditions.

3.3.2 Basic requirements

As weather conditions have an impact on OGI sensitivity, this test must be performed under real weather conditions (outside).

As substances have an impact on OGI sensitivity, this test must be performed using substances representative of the main streams to control.

As background has an impact on OGI sensitivity, this test must be performed using a heterogeneous background, representative to the background of the real place of work.

If the IR camera will be used in HSM mode (or equivalent) during the detection, the functional test can be performed using the IR camera in HSM mode (or equivalent).

3.3.3 Frequency

This functional test must be performed at least once per day, before starting the detection.

If major weather conditions change during a detection period, the test must be repeated (wind and humidity are known to be the most impacting factors).

3.3.4 Operating mode

An artificial leak, of two different representative VOC substances, with a determined constant flow rate is generated under real weather conditions (outside).

As far as possible, the background should be representative to the background of the real place of work.

After the IR camera's detector cooling period, the operator shall determine the maximum distance from which the IR Camera is able to detect the artificial leak. This maximum distance can be limited to the maximum necessary detection distance for the day work.

This distance shall not be exceeded during the detection period.

Record the test results for each substance:

Date and time of the test

Artificial leak flow rate (6 g/h is recommended)

Wind speeds

Maximum detection distance allowed

3.4 DATA ANALYSIS

All gathered pieces of information on site are recorded in a database.

3.4.1 Database Management

Information recorded during the identification allows:

Creation of a list of leaks with exact location

3.4.2 Mass flux calculation / quantification

The direct mass flow quantification using OGI technology is not - yet - possible.

In order to quantify leaks, several methods can be implemented:

FID measurement and quantification using specific correlations

Bagging

EPA emission factors (Lev-On et al., 2007)

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4 SOF

4.1 OVERVIEW

4.1.1 Scope

The Solar Occultation Flux (SOF) method is based on using the sun as the light source and to detect gas species that absorb in the solar spectrum (Mellqvist, 2009). SOF measurements are carried out both in the infrared and UV visible regions using an infrared spectrometer and UV-spectrometer that is connected to a solar tracker. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. Mass fluxes/emissions are obtained by combining SOF and wind measurements. The method is used to quantify and map the location of various gas emission sources with a spatial coverage going from industrial conglomerates down to sub-areas in individual plants.

4.1.2 Pollutants measured

The SOF method is able to make simultaneous measurements of a wide range of gas species in the infrared spectral region. Key pollutants that can be measured include alkanes (C2-C10), alkenes (ethene, propene, butadiene), alcohols (methanol, ethanol), alkynes (ethyne), ammonia, carbon-monoxide, formaldehyde, nitrous oxide and hydrogen chloride. Methane and Aromatic VOCs can be measured but with limited sensitivity due to the high atmospheric background levels in the former case and weak absorption properties and cross interference with CO_2 in the latter case. In the ultraviolet and visible wavelength region the species SO_2, NO_2 and formaldehyde can be measured.

The SOF method is usually combined with concentrations measurements on the ground level to measure the relative abundance of various pollutants (primarily aromatic VOC and methane) towards species that are measured by the SOF method, such as butane or ethane.

4.1.3 Information provided

A fast solar tracker is combined with an infrared or UV/visible spectrometer that is installed on a moving platform, such as van or boat. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. Measurements are usually carried out by moving and measuring in a circle around the leaking sources, then mapping the obtained column data. In this manner the influence of upwind sources can be excluded.

4.1.4 Scale and limitations

The SOF method is used to map and quantify gas emissions from industrial conglomerates (50 km by 50 km) down to sub-areas in individual plants (20*20 m). Flux measurements that are carried out at the fence line of the industries, or further away, have the smallest uncertainties (20-30 %). Measurements close to single tanks have larger uncertainties (~50%). The method only works in daylight at sunny conditions. The method has limited sensitivity for methane and aromatic VOCs. The emissions of these species are therefore assessed through complementary measurements.

4.2 SOF MEASURING PRINCIPLE

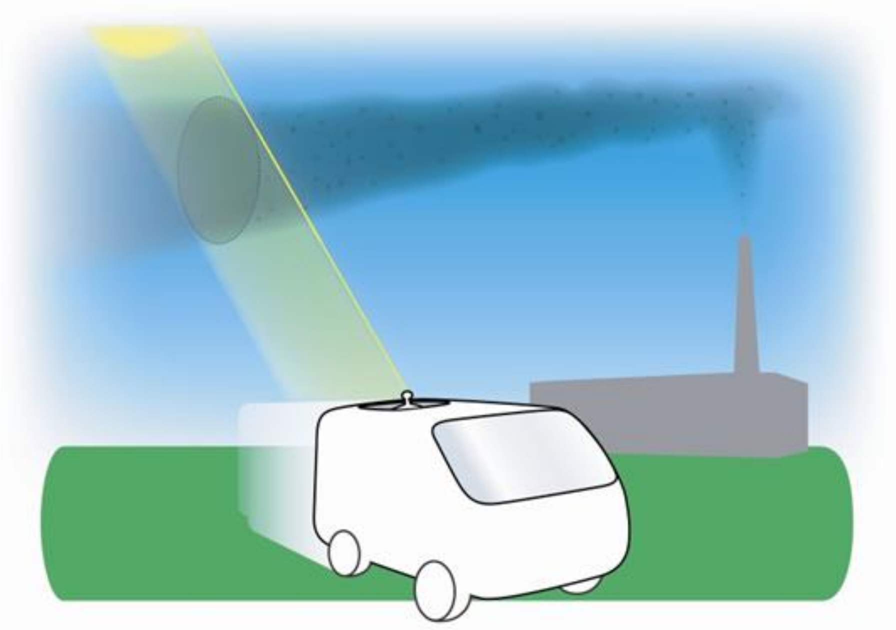

Figure 3.1 — In the Solar Occultation Flux method (SOF) gases are measured by observing solar light in the infrared portion of the solar spectrum. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of gas is obtained by multiplication with the wind speed.

4.2.1 Spectroscopy

4.2.1.1 Infrared measurements

The infrared part of the SOF method is based on the recording of broadband infrared spectra of the sun with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of its position. From the solar spectra it is possible to retrieve the path-integrated concentration (column, see Eq. 1) in the unit mg/m^2 of various species between the sun and the spectrometer. A system consists of a solar tracker, transfer optics and an FTIR spectrometer with a typical, variable, spectral resolution of 0.5 cm^{-1}, equipped with a combined MCT (mercury cadmium telluride) detector or an InSb (indium antimonide) detector. Optical filters are used to reduce the spectral bandwidth in order to improve the signal-to-noise ratio of the measurement.

The infrared SOF system is operated in two main spectral regions: i.e. the fingerprint and CH-stretch region. The fingerprint region corresponds to spectral measurements between 750 to 1000 cm^{-1} at 0.5 cm^{-1} spectral resolution. Typical measured species here includes alkenes, alkadienes and ammonia. In this spectral region warm objects radiate heat which creates a thermal background in the absorption spectrum. To correct for this a thermal background spectrum is recorded at regular intervals by measuring with the solar tracker pointed to the cold sky i.e., away from the sun. The background thermal spectrum is subtracted from each recorded solar spectrum. In the spectral retrieval interfering species such as water and CO_2 and others pollutants, are taken into account, depending on the key species.

The CH-stretch mode corresponds to measurements in the infrared region between 2700–3005 cm^{-1}, using the vibration transition in the carbon and hydrogen bond (CH-stretch). In this region most hydrocarbons absorb the infrared light such as alkanes, alcohols, alkenes and aldehydes. For refineries and tank storage areas the emissions of alkanes are dominant. The absorption features of the different alkanes are similar and interfere with each other, but since the number of absorbing C-H-bonds is directly related to the molecule mass, the total alkane mass can be retrieved despite the interference. In the spectral analysis, when measuring on refineries or similar, calibration spectra of propane, n-butane, and n-octane are fitted to the recorded spectra, using a resolution of 8 cm^{-1}. Aromatic VOCs, alcohols and alkenes also have absorption features in the CH-stretch region. Sensitivity studies of the

SOF alkane retrieval shows an uncertainty of around 6 % in the retrieved total VOC mass column (Mellqvist 2010b).

In the spectral retrieval, a reference spectrum is chosen from a region of the measurement transect where it can be assumed that the target gas concentration is near zero and which corresponds to the lowest column value measured, i.e. typically and upwind spectrum . Instead of calculating the transmittance by dividing all spectra with the reference, which is the common approach in long path FTIR, the logarithm of the reference spectrum is fitted to the measured spectrum together with cross sections of the gas species to be retrieved which are adapted to the instrumental parameters, as shown in equation (1) below, which simply is a rewriting of the Beer Lambert law. This approach makes it possible to account for wavelength shifts in the spectra and also to include several reference spectra in the fit, which results in efficient removal of the influence of the upper atmosphere.

The spectral retrieval is performed by spectral fitting of calibration spectra to measured ones using a nonlinear multivariate fitting routine. One of those schemes, working only for small absorbers is shown below.

$$\ln\left[I(\nu)\right] = \sum_j F_j \cdot \ln\left[I_{o,j}(\nu)\right] - \sum_i \sigma_i(\nu) \cdot \int conc_i(z) \cdot dz \qquad \text{(Eq.1)}$$

Here I(ν) corresponds to the measured light intensity as a function of frequency ν, $I_{0,j}$ corresponds to reference spectra with fitting factors f_j, σ_i corresponds to absorption cross sections for the fitted species and the last part of equation 1 is the vertically integrated concentration, i.e. column, to be determined.

For the spectral retrieval, high resolution spectra of the key pollutants (VOCs) and interfering species are obtained from databases such as the PNL (Pacific Northwest Laboratory) database [Sharpe 2004]. These are degraded to the spectral resolution of the instrument by convolution with the instrument lineshape. The uncertainty in the absorption strength of the calibration spectra is typically around 3 %.

Calibration data from the HITRAN database are used to simulate absorption spectra for atmospheric background species at the actual pressure, temperature and instrumental resolution of the measurements. The same approach is applied for several spectral retrieval codes for high resolution solar spectroscopy (Rinsland 1991; Griffith 1996) and the routine applied here has been tested against these with good results.

4.2.1.2 Ultraviolet measurements

The measurements in the ultraviolet (UV) spectral region are carried out in similar manner to the infrared region but with different hardware and spectral analysis. The path integrated concentration can be obtained by observing the direct solar light, as obtained from the solar tracker, or analysing the scattered solar light from a zenith viewing telescope. In the UV region, 300-380, the VOC species formaldehyde can be retrieved together with the pollutants SO_2 and NO_2 (Johansson 2014b).

The hardware consists of a grating spectrometer with a spectral resolution of around 0.5 nm equipped with a CCD detector. The spectrometer is connected to a solar tracker or a quartz telescope (typically 20 mrad field of view, diameter 7.5 cm) via an optical fibre. An optical band pass filter (Hoya) is used to prevent stray light in the spectrometer by blocking wavelengths longer than 380 nm. HCHO and NO_2 are retrieved between 324 to 350 nm, together with the interfering species O_3, O_4 and SO_2. SO_2 and O_3 is instead retrieved between 310 to 324 nm together with the NO_2 and HCHO columns obtained from the previous retrieval at 324–350 nm. In the spectral evaluation the recorded spectra along the measurement transect are first normalized against a reference spectrum recorded upwind of the industry of interest. In this way most of the absorption features of the atmospheric background and the inherent structure of the sun is eliminated. Ideally the reference spectrum is expected not to include any concentration above ambient of the trace species of interest, however in urban and industrial areas this is difficult to achieve, therefore our measurement in this case will produce the difference in vertical columns between the reference spectrum and all measured spectra across the plume for every measurement series. The normalized spectra are further high pass filtered and then calibration spectra obtained from the scientific literature are scaled to the measured ones by multivariate fitting (Johansson 2014b, Rivera 2010).

In addition to these calibration spectra it is also necessary to fit a so called Ring spectrum, correcting for spectral structures arising from inelastic atmospheric scattering. The Ring spectra can for instance be synthesized from a high resolution solar spectrum (Johansson 2014b).

4.3 FLUX MEASUREMENT

To obtain the gas emission from a source, the measurement vehicle (or boat) is driven in such way that the detected solar light cuts through the emission plume, as illustrated in Figure 3.1. To calculate the gas emission the wind direction and speed is also required and these parameters are usually measured from high masts and towers.

To obtain the gas emission from a target source, SOF transects, measuring vertically integrated species concentrations, are conducted along roads oriented crosswind and close downwind (0.5–3 km) of the target source so that the detected solar light cuts through the emission plume. The gas flux is obtained first by adding the column measurements and hence the integrated mass of the key species across the plume is obtained. To obtain the flux this value is then multiplied by the mass average wind speed of the plume, u'_{mw}. The flux calculation is shown in Eq. 2. Here, x corresponds to the travel direction, z to the height direction, u' to the wind speed orthogonal to the travel direction (x), u'_{mw} to the mass weighted average wind speed and H_{mix} to the mixing layer height. The slant angle of the sun is compensated for, by multiplying the concentration with the cosine factor of the solar zenith angle.

$$flux = \int_{x1}^{x2} \left(\int_{0}^{Hmix} conc(z) \cdot u'(z) \cdot dz \right) dx = u'_{mw} \int_{x1}^{x2} column(x)$$

(Eq.2)

Where: $u'_{mw} = \frac{\int^{Hmix} conc(z) u'(z) \cdot dz}{\int_{o}^{Hmix} conc(z) dz}$ and $column = \int_{0}^{Hmix} conc(z) \cdot dz$

The wind is not straightforward to obtain since it is usually complex close to the ground and increases with the height. The situation is helped by the fact that SOF measurements can only be done in sunny conditions. This is advantageous since it corresponds to unstable meteorological conditions for which wind gradients are smoothed out by convection. Over relatively flat terrain with turbulence inducing structures the mean wind varies less than 20 % between 20 and 100 m height as shown by meteorological models and height profile measurements of the wind using balloon soundings (Mellqvist 2010). In addition, for meteorological conditions with considerable convection, the emission plume from an industry mixes rather quickly vertically giving a more or less homogeneous distribution of the pollutant versus height through the mixing layer even a few kilometres downwind, as shown in airborne studies (Mellqvist 2010). In addition to the atmospheric mixing, the plumes from process industries exhibit an initial lift since they are usually hotter than the surrounding air.

The wind used when carrying out SOF measurements should be the non-obscured 10 minute wind above tank height level, i.e. 30-40 m altitude. In many cases this is obtained as a combination of wind measurements carried out on the ground combined with height profile measurements using wind balloons or remote sensing techniques such as Doppler LIDAR or radar.

4.4 MEASUREMENT METHODOLOGY

The SOF method is used to screen and quantify VOC emissions (alkanes, alkenes and alcohols) from industrial conglomerates down to sub-areas in individual plants, such as process areas, crude oil storage, product storage tanks, water treatment facilities, flares and loading operations. A typical survey of an industrial facility corresponds to 10 measurement days, often broken down into several periods over the different seasons to better represent mean annual conditions. The annual measurements makes it possible to establish a baseline emission for the facility and by comparison to previous years it is possible to keep track of the emissions, i.e. to understand whether some parts of the refinery are leaking more relative to last year and whether abatement measures are required. The measurements are also used to evaluate the efficiency of various abatement measures and for tuning flare combustion efficiency.

The SOF measurements have the smallest uncertainty when carrying out measurements outside the fenceline of the refineries, since the wind field is then less disturbed and most of the emissions plume has had time to distribute itself over considerable height (100-200 m). Box measurements on the fenceline, measuring in a circle around the refinery are therefore carried out for estimation of the total refinery emission. In this manner upwind emission can be subtracted from the downwind measurements. In addition, individual measurements are carried out inside the refinery on available roads, for estimation of emissions of subareas such as process areas, product tanks, crude oil tanks, water treatment facility, loading/unloading and flaring. The emission values obtained inside the refinery are therefore rescaled, if needed, so that their sum matches the emission value measured at the fence line. In this manner the uncertainty of the wind field close to tanks etc. is minimized.

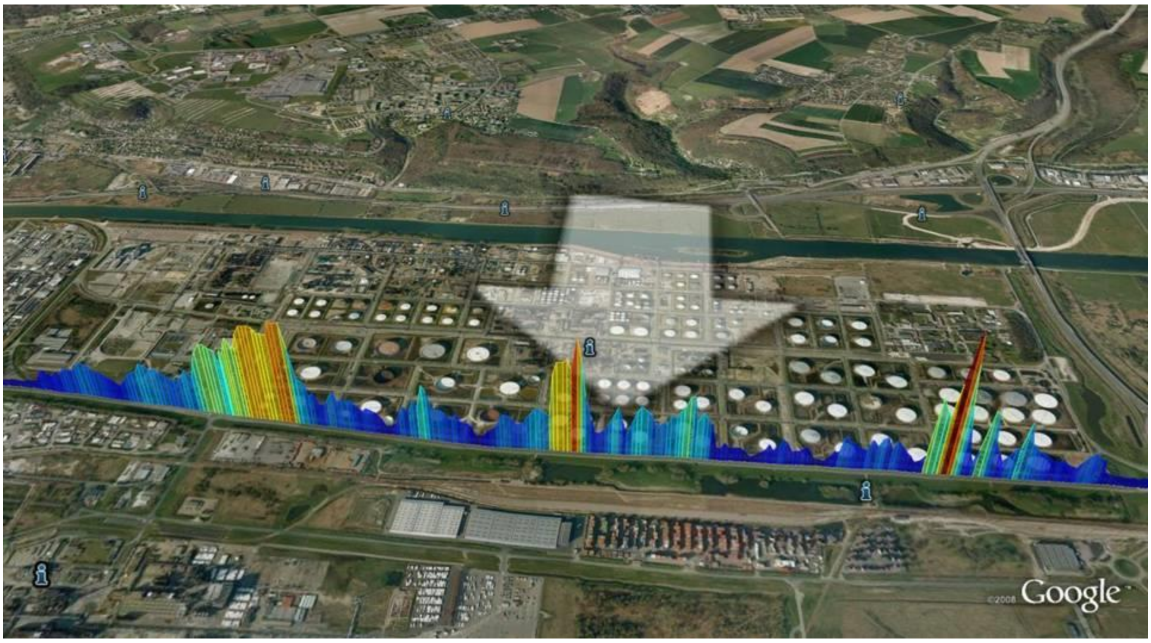

Figure 3.2 — A SOF transect past a refinery. The staples and colours shows the integrated amount of butane, as retrieved from the solar spectra. After multiplication with the wind velocity the mass flux is obtained.

The SOF measurements are influenced by turbulence in the wind field, causing horizontal shifts in the position of the plume, and it is therefore important to average over several measurements, to remove this effect. In Figure 3.3 annual emissions measurements obtained from the fenceline of a Swedish refinery are shown as a histogram, showing all emission measurements binned into different emission intervals. The wind variations normally causes an emission curve that follows a normal distribution while a skew shape of these curves is due to intermittent emissions due to tank cleaning etc. The refinery in Figure 3.3 has been measured 12 times since 1989 (DIAL four times and SOF nine times) and with exception for the first occasion the emission has varied within 30%. An issue with SOF measurements is the fact that measurements are only carried out at daytime and in sunny conditions. According to a recent study based on the conventional AP-42 model developed by the US EPA an upper estimate of the effects is 30-40 % maximum overestimation in the emissions for an external floating roof tank, compared to the annual average (Johansson 2014a).

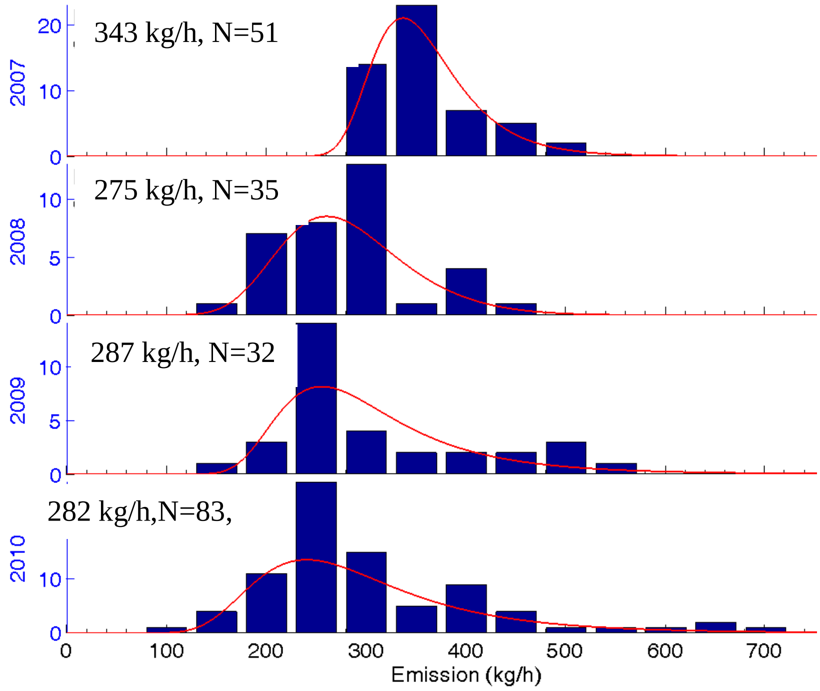

Figure 3.3 — Total VOC emission from a Swedish refinery over several years. The average emission is given, calculated as weighted average. Days with large variability are less weighted to minimize the influence of intermittent emissions, weight factor 1/standard deviation of daily emission values. The red curve is a skewed probability function that is fit to the data. The maximum is the most probable emission value.

4.5 ADVANTAGES AND CONSTRAINTS

SOF requires specific meteorological conditions, namely clear skies and sunshine. In some regions these conditions cannot be relied upon, making it difficult to plan measurement campaigns. Additionally this constraint will limit the plant conditions that can be monitored as no night measurements can be made and suitable conditions may not be expected in all seasons.

The system requires a means to traverse across the plume in a vehicle which will limit potential measurement locations. If traverse locations are not optimal it will reduce the ability of the system to pinpoint emission sources within complex sites. Even with ideal traverse location sites with many varied structures are likely to have turbulent wind fields that will reduce the ability of the technique to resolve different sources.

The technique requires measurements to be made up- and down-wind of the plume in order to remove background levels from the results, but to do this routes must be available for carrying out multiple parallel traverses in a vehicle, something that may well not be practical at some sites. In order to reduce the potential for homogenisation due to mixing in the air downwind, the traverses have to be made within a few kilometres (0.5-3km) of the source of the plume, further limiting potential routes.

Multiple traverses are required with the system in order to average out short-term features due to minor changes in plume position. On sites where the wind is likely to shift significantly this may limit the ability to get sufficient repeated measurements to average out these errors, requiring additional time on site to get sufficient measurements to provide reliable results.

Good for fenceline surveys with only limited access required to the site and the best uncertainties achieved when undertaking these types of measurements.

If conditions are suitable then SOF will be faster and more mobile than other potential quantifying techniques (e.g. DIAL).

Feature	Strength
Direct Measurement	Increases measurement accuracy by reducing uncertainty.
Passive Light Source	Decreases instrumental complexity for field operations and reduces amount of scattering errors in the UV.
Broadband Light Source	Multiple species detection over a wide range of wavelengths.
Better Mobility	More suitable for frequent field application.
Lower technical complexity	Decreased cost and easier field application.
FTIR Detection	Higher specificity and better signal-to-noise (relative to DIAL).
Measurements during Sunny conditions	Corresponds to unstable meteorological conditions where wind gradients due to convection are smoothed out.

Feature	Limitation
Interferogram Vibration Sensitivity	System requires vibration reduction platform and a smooth mobile path.
Wind Speed Error	Calculations based on wind speed measurements inherently add uncertainty due to the stochastic, uncontrollable, and highly variable nature of wind speed.
No Plume Height Measurement	Uncertainty of plume height increases measurement error from wind speed term.
Solar Light Source	Inappropriate to make measurements in the presence of clouds.
“Open Eye” Detection and Roadway Path Restriction	Difficulty in separating emissions sources that are close together.

Tables from EPA handbook

4.6 UNCERTAINTY

The overall uncertainty of SOF measurements is 20-30%, a value derived from error estimation, validation exercises and instrument comparisons. The highest proportion of the error comes from uncertainty related to the estimation of the mass weighted wind. This includes uncertainties from plume lift and in the wind profile. Wind speed measurements are normally within ±30%, while wind direction is typically recorded to within ±15°, which amounts to around 10% error on the wind flux [Mellqvist 2010].

4.7 PERFORMANCE CHARACTERISTICS

A summary of the performance capabilities of a typical SOF system under normal conditions are given in Table 3.1. The values provided are based on the actual levels of performance of existing SOF systems, determined from the typical absolute precision for column measurements in earlier studies when driving at 40 km/h downwind of industries in Houston. The numbers in table 3.1 are applicable given that there is enough solar radiation (relatively clear conditions and at least an hour away from sunset or sunrise. The numbers will be better for small sources and slower driving conditions.

The accuracy of the SOF and mobile DOAS systems is estimated as the square root sum of the precision and the systematic spectroscopic uncertainties. Accuracies of the instrumentations used in the project are listed in the following tables

Table 3.1 — Capability of a typical SOF measurement

Parameter	Precision/Detection Limit (1σ)	Detection Limit[1]	Accuracy
C2	TBC		10%
Alkanes (C3-C8) (IR)	3 mg/m^2/ 1.3 ppmm	26 ppb	10%
Ethene (IR)	1 mg/m^2/ 1.2 ppmm		10%
Propene (IR)	2 mg/m^2/1.2 ppmm		10%
NH3	0.5 mg/m^2/0.7 ppp		10%
SF6	0.2 mg/m^2		10%
SO2 (UV)	1 mg/m^2/0.4 ppmm		10%
NO2 (UV)	1 mg/m^2/ 0.5 ppmm	4	10%
HCHO (UV)	0.2 mg/m^2/0.15 ppmm		10%

(1) Precision in ppb, assuming 50 m path length and C4 mixture.

4.8 QUALITY CONTROL

Quality assurance of the emission measurements is necessary. These procedures require detailed project planning and progress monitoring with project subject to regular internal reviews and quality audits at measurement institutions.

4.8.1 Calibration

Instrument calibration and frequency

The SOF and mobile DOAS instruments are not calibrated prior to measurements but one instead relies on absorption fingerprints from the literature. This is appropriate as long as the instrument is well aligned, and whether the alignment has been sufficient can actually be checked, and corrected for, afterwards by investigating the widths and shape of the absorption lines in the measured spectra. An acceptable alignment is reached when the width of the measured absorption lines are smaller than a certain threshold, usually 0.6 cm^{-1} for the SOF and 0.4 nm for the DOAS, respectively. However the DOAS line-shape is measured by a mercury lamp and this is directly applied in the retrieval.

IR-SOF

The spectral retrieval code used in the SOF method, QESOF, relies on principles adopted by the NDACC community (Network for the detection of atmospheric composition change), which is a global scientific community in which precise solar FTIR measurements are conducted to investigate the gas composition changes of the atmosphere. Chalmers University is a partner of this community and has operated a solar FTIR in Norway since 1994.

The spectral retrieval for SOF is handled by custom software (QESOF), [Kihlman 2005] in which calibration spectra are fitted to the measured spectra using nonlinear multivariate analysis. Calibration data from the HITRAN database [Rothman 2003] are used to simulate absorption spectra for atmospheric background species at the actual pressure, temperature and instrumental resolution of the measurements. The same approach is applied for several retrieval codes for high resolution solar spectroscopy [Rinsland 1991; Griffith 1996] and QESOF has been tested against these with good results. For the retrievals high resolution spectra of ethene, propene, propane, n-butane and n-octane were obtained from the PNL (Pacific Northwest Laboratory) database [Sharpe 2004] and these are degraded to the spectral resolution of the instrument by convolution with the instrument line-shape. The uncertainty in the absorption strength of the calibration spectra is about 3.5% for all five species. The QESOF code has been evaluated against several published codes developed within NDACC with good agreement, better than 3%.

UV-SOF

The spectral retrieval for Mobile DOAS is done with the software package QDOAS (formerly WINDOAS) [Fayt & Van Roozendael 2001] developed at the Belgian Institute for Space Aeronomy (BIRA/IASB) in Brussels. The calibration spectra used here for the various gases are obtained from the following: HCHO [Cantrell 1990], NO_2 [Vandaele 1998], SO_2 [Bogumil 2003], O_3 [Burrows 1999] and O_4 [Hermans 1999]. In addition to the above mentioned calibration spectra, it is also necessary to fit so called "ring spectra", corresponding to spectral structures coming from inelastic atmospheric scattering [Fish 1995]. To do this we have used a software package denoted DOASIS [Kraus 2009] from the university of Heidelberg in which a ring spectrum is calculated from the Raman scattering processes of atmospheric nitrogen and oxygen applied on the intensities of the reference spectrum.

Meteorology

The meteorological sensor should be calibrated once a year by the manufacturer or by a reference wind meter.

The calibration certificates may provide a calibration factor for the wind speed and wind direction readings. If data loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.

In addition, the different sensors should be compared side-by-side in the field to provide a further check on their correct function. For instance, if anemometers are being used the ball bearing can be eared out which causes lower apparent wind speeds which is difficult to identify afterwards. This must therefore be checked by relatively short term comparisons in the field or lab to a reference wind meter once per year

4.9 DATA ANALYSIS

4.9.1 Spectroscopy

Spectral fitting is done by software packages, QESOF for IR and QDOAS for UV.

4.9.2 Wind field

Variations in the wind field causing shifts in the plume position are accounted for by averaging multiple measurements. The emission rates then show a bell curve around the centre of the plume.

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5 TRACER CORRELATION TECHNIQUES

5.1 OVERVIEW

5.1.1 Scope

Time correlation tracer (TCT) uses an FTIR to detect plant emissions, scaled by the measured quantity of an inert tracer gas released at a known rate close to the leak location. These techniques are only used for quantification of existing identified emission sources.

The SOF measurements are usually combined with extractive FTIR and UV measurement of VOCs in the same measurement vehicle, to investigate aromatic VOCs by measuring the ratio of all species against alkanes. The extractive measurements are also used to carry out complementary measurements by tracer correlation (Galle) for instance night time measurements of tanks and ship loading operations. Tracer gas is then positioned at the location of the leak and then the ratio of tracer gas and leaking VOC is measured by extracting the gas plume into a gas cell and then analysing the gas concentrations by infrared spectroscopy. The VOC flux measurements by SOF are also often combined with ultraviolet remote sensing measurements (mobile DOAS) of SO_2, NO_2 and formaldehyde.

5.1.2 Compounds measured

Different tracers and measurement techniques can be used to complement different combinations of methane or VOC.

5.1.3 Information provided

The measurement instrument should provide the analyte and tracer concentrations. When the analyser has been mobile the fluxes can be mapped with GPS locations for the measurements. Transects through the plume will show the level of correlation between the tracer and the analyte. With an analyser deployed at a fixed location down-wind from the tracer release point, the time taken for the tracer to reach the instrument can be used to calculate the flux of the analyte.

5.1.4 Scale and limitations

Whole site measurements are possible with a standoff distance for the instrument of several kilometres. By deploying the instrument closer it would be possible to resolve multiple sources from a smaller area, however multiple tracer releases would be required to cover larger sites.

The method works best when the tracer source is located as close to the analyte emission source as possible. The main source of uncertainty is then from any differences in behaviour of the analyte and tracer in the same atmospheric conditions.

5.2 MEASURING PRINCIPLE

5.2.1 Tracer correlation techniques

An inert gas, such as SF_6, is released at a known rate close to the suspected leak source. Gas samples are taken at a number of locations down-wind of the equipment and analysed. The ratio of the concentrations of the tracer gas to the process vapour is then determined permitting the leak rate to be calculated. If this method is used it is implicit that the potential emission source has already been identified.

From the known release rate and the measured concentration the dilution of the tracer emission between the point of release and the measurement location can be determined, and this can then be used to estimate the emission rate of VOCs that would be needed to result in the measured VOC concentration.

Tracer gas releases (SF_6) in combination with HC/SF_6 analysis with gas chromatography in a number of points downwind the plant (so called conventional SF_6 method).

Tracer gas studies can use different types of analyser including CRDS, FTIR (cell and open-path) and GC.

Static plume measurements can be made by setting up vacuum pumped gas bottles at locations down-wind from the tracer release site. A critical capillary fitted to the bottles will allow them to fill with air from the plume over a period of around four hours. The samples can then be analysed to reveal tracer and analyte concentrations. Deployment of a single bottle up-wind from the tracer release point is sufficient to provide a background for the remaining samples.

5.2.1.1 General description

Emission fuxes can be calculated from looking at changes in the vertical and horizontal components of the wind field, surface roughness and changes in the measured concentration of the tracer gas concentration, either in time or space. If the tracer measurement location is fixed the test will study changes over time. To investigate over space the analyser can be mounted in a vehicle and be transported while measuring the tracer release, or multiple instruments can be deployed in a range of locations down-wind of the tracer release point and measure the release concurrently.

The following equations determine how surface fluxes are quantified from the tracer concentration and meteorological parameters. Vertical fluxes of the tracer gas can be calculated from the changes in wind and tracer gas concentration over time or distance from release to detection (Equation 4.1).

Equation 4.1

$$F = \frac{1}{T(orS)} \int_0^{T(orS)} w'n'dt$$

Where: F is the flux, T is the time between release and detection, S is the distance between tracer release and measurement, w' is the changes in the wind field, n' is the changes in the detected tracer concentration.

Horizontal fluxes need to consider wind velocity near the surface, which can be calculated from Equation 4.2.

$$u(z) = \frac{u_*}{k} \ln\left[\frac{z-d}{z_0}\right]$$

Equation 4.2

Where: u(z) is the wind velocity, u_* is the friction velocity, k is the von Karman constant, d is the displacement height and z_0 is the surface roughness.

The emission rate can be calculated from simultaneous measurements of the target species and the tracer, as specified in Equation 4.3

Equation 4.3

$$Q_m = \frac{Q_t \Delta C_m}{\Delta C_t}$$

Where: Q_m is the analyte emission rate, Q_t is the tracer release rate, ΔC_m is concentration of the analyte above the background level and ΔC_t is the concentration of the tracer above the background level.

5.2.2 Advantages and constraints

Purely a quantification technique that requires emission source locations to be known so that tracer release points can be chosen that are close to the VOC leaks.

A key strength of using a tracer gas correlation technique is the ability to determine if varying weather conditions affect the calculation of emission rates, which is possible by knowing release rates and concentration. An additional strength is that emission rates are calculated within 15-30 percent precision.

However, stationary and mobile setups have their challenges in terms of logistics, location and whether available roads are near perpendicular to the flow of the plume. Other limitations are cost of tracer gases cylinders and transportation of these, as well as changing weather conditions affecting the calculation of emission rates.

Feature	Strength
Addresses Meteorology	Can determine if varying weather conditions affect the calculation of emission rates.
Relatively precise Method	Emission rates are calculated within 15 - 30 percent precision.
Portable instrumentation	Field units are lightweight, rugged, and relatively easy to transport and operate.

Feature	Limitation
Meteorological Concerns	Changing weather conditions affect the calculation of emission rates.
Logistical Concerns	Location and the availability of roads perpendicular to the plume create difficulties.
Related Expenses	Tracer Gas cylinders can be expensive to purchase and ship.

Tables from EPA handbook (2011)

5.2.3 Uncertainty

The method assumes that the tracer is subject to the same dilution and transport in the atmosphere as the VOC emissions, so any variation between their behaviours will be a major source of uncertainty.

Meteorological conditions (e.g. wind speed and direction) can vary over very short distances, so the tracer release point needs to be close to the emission point in order to minimise uncertainty.

The concentration and release rate of the trace gas have to be precise otherwise it will not be possible to calculate the flux of the analyte species. This can be controlled by using gas mixtures traceable to national standards and using calibrated mass flow controllers for the tracer release.

Instruments also need to be regularly checked and maintained to ensure they are able to achieve the required measurement uncertainty for both the analyte and the tracer. Using longer path lengths for optical instruments can improve their precision.

5.3 PERFORMANCE CHARACTERISTICS

Will vary depending on the instrument being used to measure the concentrations of the analyte and tracer.

5.4 QUALITY CONTROL

Standard instrument QA/QC needs to be followed.

When using the tracer gas approach, it is important to consider a gas that is stable and has low reactivity; thus, no significant sources and sinks that will alter the released concentration or, at least, good knowledge of the background concentrations. Spurious releases of tracer gases that reach 20 percent of the known concentration are easily identified CRDS, but anything below is probably not significant. Background levels of the analyte gas must be known to track the boundaries of the plume and to determine whether the measurements are in or out of the plume. The time delay between release and arrival at measurement site needs to be carefully determined before total methane emission results are considered acceptable. Flow rate of tracer gas released from all bottles be carefully monitored and recorded if total methane emissions from a landfill are to be accurately determined. A comparison (correlation plot) of analyte and tracer gas measurements taken close and far away from the source provide a correlation coefficient and the percentage difference or the total emission rate at close and far locations. Large percentage differences indicate insufficient overlap of the analyte plume and the tracer gas plume during stationary tracer-dilution measurements.

5.5 DATA ANALYSIS

Measured concentrations from up-wind of the release site are used as a background which is removed from the plume measurements.

The tracer concentration is modelled by calculating the atmospheric dispersion of the tracer sources over the area at constant rates (~1-2 g/s). This is compared to the measured tracer concentration, after background removal, to create a ratio for scaling the measured analyte concentrations.

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6 SNIFFING

6.1 OVERVIEW

6.1.1 Scope

“Sniffing method” is a standardised method in use since the early 1990s. This international approach is defined in the US through two standards, EPA-21 method & EPA-453/R-95-017, and in Europe through the EN 15446 standard. This method consists of detection, measurement, reduction and quantification of VOC emissions on all potential leaking components like flanges, valves, pumps, compressors, plugs, etc. The most common methodology using sniffing technology is Leak Detection And Repair Program (LDAR). This method is based on measuring concentration by “sniffing” using a portable instrument (currently an FID in accordance with EN 15446 & EPA-21). Mass emissions fluxes are quantified in accordance with the EN 15446 standard by using specific correlation curves.

6.1.2 Pollutants measured

TVOC - The detectors on the VOC analysers are sensitive to the different chemical species that make up the VOC family, including methane. FID has the same level of efficiency regardless of the type of VOC, including aromatics, methane, etc.

Response factors are used to correct each measurement value (for compounds and for mixtures).

6.1.3 Information provided

The implementation of a LDAR program provides:

List of leaking components with exact location

Possibility to repair leak (because precisely identified)

Maintenance quality control (Assistance during tightening actions)

Mass emission fluxes before maintenance

Mass emission fluxes after maintenance (allows quantifying of the gain)

Preparation of future maintenance actions on residual leaks (Repair folders)

Assistance to improve maintenance programs

6.1.4 Scale and limitations

LDAR program are implemented on all industrial sites, from remote areas (Tank farms, handlings,etc.) to process units, wherever potential leaking components may appear.

Thanks to the analyser’s portability, the measurements are performed by the operators on all the accessible components. For financial reasons, LDAR programmes are restricted to components that can be reached without scaffolding or specific safety equipment.

However:

An extension probe can be used

IR camera can be used for inaccessible components (out of range and under isolation)

The flow rate associated to the remaining inaccessible components can be quantified using specific average emission factors as described in the EN 15446 standard

6.2 MEASURING PRINCIPLE

6.2.1 Sniffing

The method is based on measuring concentration by sniffing using a portable instrument (currently a FID in accordance with EN 15446) at the various potential emission points.

The mass flow at each component is obtained using correlation curves specific to each type of component. These correlation curves link the leak concentration measured (in ppmv) to a leakage rate (in g/hr).

Initially, a review of the processes should be carried out in order to determine the lines to be inspected and their VOC compositions. A reference is given to each piece of equipment to be inspected.

The inspector then takes a measurement at each potential emission source listed, ensuring that an exhaustive inspection is carried out on all components requiring inspection.

6.2.2 Advantages and constraints

This method allows a precise location of each individual leaking component, so the exact point where to perform the maintenance in order to reduce emissions. The very low limit of detection allows repairing all leaks on accessible components.

Requires close proximity to each individual component. On a large site with thousands of components this is very time consuming, but all leaking components will be identified, precisely located and quantified. For inaccessible components complementary methods such as infra-red cameras are used, although this is less precise than the “sniffing” method. (Detection only / No measurement)

6.2.3 Uncertainty

The traceability of detection and the exhaustiveness of monitoring are set out in EN 15446.

Some validation work was performed in conjunction with the drafting of EN 15446.

Factors affecting the quality of the measurement are identified:

Training of the measurement operator (response factor knowledge...)

Environmental (wind, rain, extreme temperature...)

Quality of the methodology followed

Condition of the measurement devices (hydrophobic filter, calibration, general operating condition...)

Product measured

Corrective actions should be taken to minimize the effect of the wind when the wind speed exceeds 0,5 m/sec, particularly when working in elevation. Inspection routing can be adapted to weather conditions.

6.3 TECHNICAL PERFORMANCE/REQUIREMENTS

Performance requirements and characteristics of the equipment used are already described and set out in EN 15446.

The portable organic vapour analysers that currently comply with the standard are FIDs. This instrument can measure with the same level of efficiency all type of VOC (including aromatics, methane...).

According to EN 15446, the instrument should be intrinsically safe; it can therefore be used without any particular constraints.

It is important to note that the high sensitivity of detection and measurement of individual leaking component from 1 ppmv, which can be very interesting for the reduction of Carcinogenic, Mutagenic and Reprotoxic substance's emissions.

6.4 QUALITY CONTROL

6.4.1 Calibration procedures

Calibration procedures and gases used are described in the EN 15446 standard.

6.5 DATA ANALYSIS

All pieces of information gathered on site are recorded in a database.

6.5.1 Database management

Information recorded during the identification and measurement phase allow:

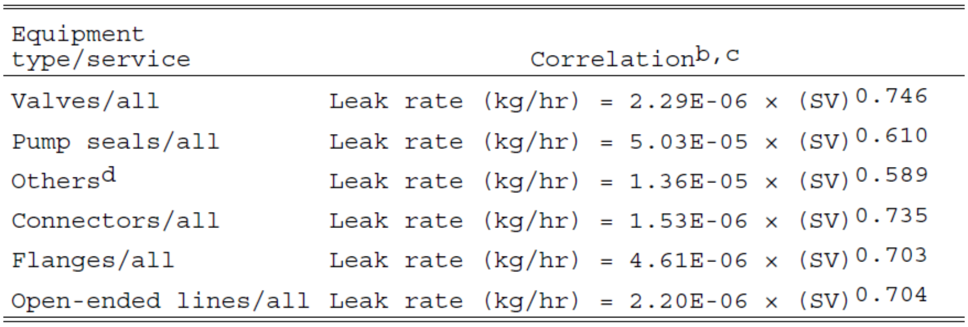
Creation of a list of leaks with exact location

Quantification of VOC's emissions

6.5.2 Mass fluxes calculation / quantification

The mass flow quantification method is clearly defined in the EN 15446 standard.

Table C.1 — Examples of correlation



Equipment type/service	Correlation[b,c]
Valves/all	Leak rate (kg/hr) = 2.29E-06 × $(SV)^{0.746}$
Pump seals/all	Leak rate (kg/hr) = 5.03E-05 × $(SV)^{0.610}$
Others[d]	Leak rate (kg/hr) = 1.36E-05 × $(SV)^{0.589}$
Connectors/all	Leak rate (kg/hr) = 1.53E-06 × $(SV)^{0.735}$
Flanges/all	Leak rate (kg/hr) = 4.61E-06 × $(SV)^{0.703}$
Open-ended lines/all	Leak rate (kg/hr) = 2.20E-06 × $(SV)^{0.704}$

In order to obtain mass flow quantification (kg/hr) you have to choose before:

Kind of component (valve, flange, etc.)

Phase (liquid, gas, all)

Measurement value (SV - after response factor correction)

The mass flow quantification on a specific period is also defined in the standard EN 15446.

6.5.3 Software validation

Due to a large number of data collected on site, software is required.

A specific procedure for the validation of the software is available at CEN.

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7 FLUX CHAMBER MEASUREMENTS

7.1 OVERVIEW

7.1.1 Scope

The flux chamber method allows quantification of VOC emissions through measurement. This method is not standardized. This method is used to detect and quantify VOC emissions from diffuse liquid or solid surface sources (water treatment ponds, settling basins, retention basins, biofilters, soil of waste and recycling collection centre, etc.).

7.1.2 Pollutants measured

TVOC, CH_4, or any specific VOC when connected to FID analyser. NH_3 or others gases, when connected to dedicated analysers.

7.1.3 Information provided

The implementation of Flux Chamber provides:

Concentration in ppmv of TVOC emissions

Flow rate of the surface fluxes emitted

Flow rate of specific VOC or Non VOC emissions (when sample analysed)

7.1.4 Scale and limitations

Flux Chambers are currently used to:

Quantify emissions from diffuse liquid or solid surfaces

Detect process dysfunction

Assess the surface fluxes emitted

Improve the operation process

7.2 DETECTION PRINCIPLE

7.2.1 Flux chamber detection

The fluxes are estimated by isolating a given surface from the external conditions (mainly wind speed) using a chamber made up of an enclosure open at the bottom, which is placed on the source. When the sources are large, a sampling plan can be implemented in order to find the spatial representativeness on the basis of a limited number of individual samples.

7.2.2 Advantages and constraints

Abnormal situation (unwanted product, abnormal flow rate) can be highlighted so actions can be taken to reduce emissions.

The weight and volume of some flux chambers impose two persons for the manipulation. Accessibility of surfaces for placing the flux chamber can be a constraint too.

7.2.3 Uncertainty

Factors affecting the quality of the quantification are identified:

Environmental: Wind speed, temperature, water, steam, emissions homogeneity

Type of chamber and methodology

Concentrations can be corrected by measuring temperature, data logging over long measurement periods, taking several measurements on the same surface and selection of more representative periods of the year for measurement.

7.3 TECHNICAL PERFORMANCE/REQUIREMENTS

Given the diversity of the surface sources (solid/liquid, ventilated/unventilated), different chambers and measurement strategies have been developed.

There are five types of chamber:

Chimney chambers;

Static and accumulation chambers;

Low flux (or renewal) chambers;

Dynamic flux chambers.

The CODIPESO study validated the inter-comparability of these types of chambers. The results will be used to produce a good practice guide. Detection takes place downstream of the sampling system using a specific analyser (FID, PID, etc.) to the compound to be monitored (TVOC, CH_4, etc.).

7.4 QUALITY CONTROL

7.4.1 Calibration procedures

Calibration procedures are required for the analyser in order to ensure it works properly.

7.5 DATA ANALYSIS

All pieces of information gathered on site are recorded in a database.

7.5.1 Database Management

Information recorded during the identification allows:

Quantification of surface emissions

7.5.2 Mass fluxes calculation / quantification

The mass flow quantification method is possible.

In order to quantify emissions several methods can be implemented:

Average of several measurements on different parts of the basin using one flux chamber

Average of several simultaneous measurements on different part of the basin using several flux chambers

Measuring over a long period in order to visualize emission variations

Extrapolation of the flux chamber surface emissions to the whole surface of the basin

Evaporative flux ratio correction factors can be used where flow rates are not ideal (Parker, 2013)

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8 MODELLING TOOLS TO QUANTIFY POLLUTING EMISSIONS ON A LOCAL SCALE

8.1 GENERAL

Modelling tools are at present widely used in environment for problems of chronic impact and for the evaluation of accidental impacts. Generally, the purpose of a model is to solve a "direct" problem, which is to obtain an estimate of concentrations of pollutants in the atmosphere from a set of input parameters that are mainly the weather conditions and the sources of emissions.

8.2 OVERVIEW

For reverse dispersion modelling (RDM), concentration measurements are carried out downwind of the source. Meteorological quantities are determined and conclusions are drawn, with the help of dispersion calculations, about the emission rate and, if necessary, the emission structure. The reverse dispersion modelling inverts the classical way of a dispersion calculation. Therefore, it is also termed inverse dispersion calculation.

8.2.1 Compounds measured

The RDM method is able to determine a wide range of VOC compounds, depending on the conventional ambient measurement methods available, which are carried out downwind of the source: total VOC, methane, ethane, ethene, ethyne, methanol, benzene, toluene, xylene and others.

From this data and meteorological quantities mass emission fluxes can be produced by reverse dispersion modelling.

8.2.2 Scale and limitations

The RDM method has been used for complex industrial sites in refineries.

8.3 RDM MEASURING AND MODELLING PRINCIPLE

In certain situations knowledge of emission data is weak (time variability, the multitude of potential point sources). The purpose of the inverse modelling is to solve the problem from the values of the parameters in the model and observations (measured concentrations). In practice, the purpose of the inverse modelling is to minimize the difference between the observations (measured concentration) and the result of the model (estimated concentration) to estimate better one or several input's parameters (on which it depends). This purpose is different from that of the assimilation of data which consists in integrating information such as observations to improve the evolution of the model.

The work in inverse modelling concerns mainly pollutant species on the global scale and mainly uses Kalman filtering (estimate of the emissions of CH_4, CO, CO_2) [1].The studies of inverse modelling on local scale and in the limit of industrial / urbanized area are less common [2; 3; 4].

The search for VOC diffuse emission sources in an industrial site requires the implementation of a methodology of inverse modelling on a local scale. The direct models used must manage the compromise of "calculation time" versus "performance" (by taking into account, for example, local effects of buildings).

The inverse modelling tools will have to raise 2 challenges: the localization of the sources (discrimination of the emitter among a large number of potential sources) and the flow of the source.

There are two surrounding areas of inverse methods:

The probability approach,

The non-probability approach which consists of defining a function cost representing the distance between the observations and the results of the model, expressed according to the parameter which we wish to determine, then to minimize it. To minimize this "distance" between the measurement and the model, two main approaches are used, the Kalman's filter and the method of adjoint model.

The adjoint model calculates the gradient of the function cost in a given point. The adjoint equations are obtained from model "tangent linear" which is the linearization of the direct model (non-linear) around the direct variables of input.

The main example of the use of simple adjoint is the Reverse Dispersion Modelling method to estimate the fugitive emission rates of diffuse fine and coarse dust sources from industrial plants or areas, which is standardized [5]. The application needs calculations using a dispersion model, and the definition of a sampling experimental set-up taking into account field data such as number, height and width of diffuse dust sources, sampling distances and meteorological information.

The above described RDM method does not allow quantification in absolute figures of the dust emission rates because of an undetermined accuracy depending on various site conditions, but it is a tool which enables each industrial plant to identify its highest emitting open dust sources, then implement actions reducing their importance by self-control and related improvement process as part of environmental management. In this framework, the RDM method shall not be used to control or verify any compliance with air quality threshold global values which might be contained in an operating permit, nor to carry out comparison between different plants belonging to the same industrial sector.

8.4 REVERSE DISPERSION MODELLING

8.4.1 General

Another approach which allows quantification is described in the Standard VDI 4285 [6].

For the reverse dispersion modelling, concentration measurements are to be carried out downwind of the source. Meteorological quantities are determined and conclusions are drawn, with the help of dispersion calculations, about the emission rate and, if necessary, the emission structure. The reverse dispersion modelling inverts the classical way of a dispersion calculation. Therefore, it is also termed inverse dispersion calculation.

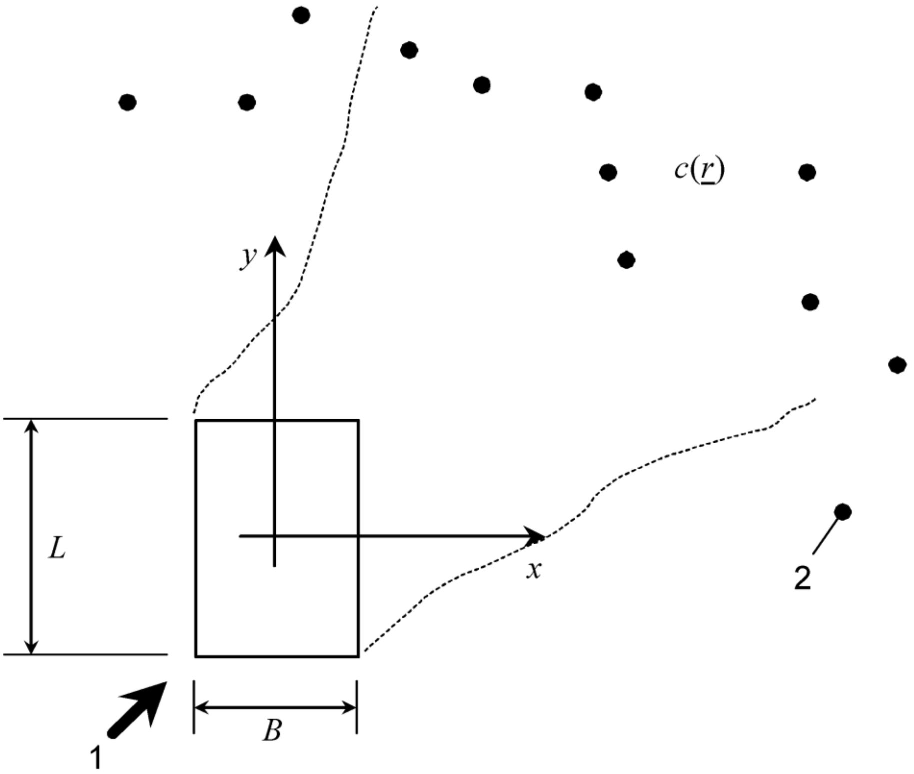
The methods to be used for the reverse dispersion modelling essentially depend on the fundamental properties of the source to be analysed. The respective procedure especially depends on the spatial structure of the source and the temporal emission behaviour over time. The development of a suitable source model has an essential effect on the diffuse source to be described. Diffuse sources mostly comprise space-like or volume-like source areas with a multitude of partial sources of different kinds and with different emission levels. If the total emission rate is the only critical factor, diffuse sources are preferably considered as homogeneous individual sources whose shapes and positions are known. In this case, it is assumed that the emission mass flow is evenly distributed over the whole source. The assumption that the source is homogeneous generally simplifies the real conditions considerably. If the emission rate distribution within the source area is important in addition to the total emission rate, additional requirements on the reverse dispersion modelling result from this.

Basically, the emission rate is only explicitly determined for the measurement period. If details of time periods deviating from this are of interest, an appropriate extrapolation of the results is only possible by having great knowledge of the temporal behaviour of the source. In most cases, a proper choice of the observation period ensures quasi-stationary conditions and a temporally constant and continuous release of emissions. This is a precondition. The modelling of non-stationary conditions is not dealt with.

The measurements required for the reverse dispersion modelling as well as the dispersion modelling shall be carried out in accordance with the requirements described in this standard.

8.4.2 Reverse dispersion modelling in the case of a homogeneous source structure

Assuming, for reasons of simplification, that the source is homogeneous and the emission rate is temporally constant, then the total emission rate can be determined as follows. Any emission rate distribution within the source is not taken into account. Only the sum of the emission components is considered. These are homogeneously distributed over the source (see Figure 7.1). Neglecting significant inhomogeneities often results in an overestimate of the total emission rate.



1	wind direction
2	concentration measuring points

Figure E.1 — Modelling of a heterogeneous source area of length L and width B as a homogeneous individual source

The geometry of the source is transferred to the calculation model and spatially defined in a way that the emission-relevant areas are considered. In this case, simple and regular geometries are advantageous. The centre of gravity of the emission source is described by the position vector $\vec{q} = (x_q, y_q, z_q)$. The starting point of the reverse dispersion modelling is the concentration $c(\vec{r})$ to be measured at the point $\vec{r} = (x_c, y_c, z_c)$. In principle, the concentration consists of the source-specific part $c_\mathrm{Q}(\vec{r})$ and the background pollution c_∞:

$$c(\vec{r}) = c_\mathrm{Q}(\vec{r}) + c_\infty \tag{4}$$

In the case of temporally constant emission conditions and under invariable dispersion conditions, where the dispersion factor is $f(\vec{r} - \vec{q}, \alpha)$, the part $c_\mathrm{Q}(\vec{r})$ is proportional to the emission rate $Q(\beta)$. The dispersion factor describes the dilution of the source-specific emissions that is dependent on the source distance $(\vec{r} - \vec{q})$ and other influencing factors α (e.g. meteorological parameters, type of source). The variable β describes the factors that influence the emission rate, such as the operating conditions, and is constant in this case.

The background pollution comprises the concentrations of adjacent emission sources, which are present during the measurements. It is assumed to be independent of the location in the area of the sources to be analysed. Comparative concentration measurements made downwind and upwind of the source can provide temporally and spatially representative information about the background pollution of the respective series of measurements. In total, the following results from this:

$$c(\vec{r}) = f(\vec{r} - \vec{q}, \alpha)\, Q(\beta) + c_\infty \tag{5}$$

where

$c(\vec{r})$	is the concentration measured at reference point $\vec{r}$
$c_\mathrm{Q}(\vec{r})$	is the source-specific part of the concentration measured at reference point $\vec{r}$
c_∞	is the local background pollution present during the measurement
$f(\vec{r}-\vec{q},\alpha)$	is the dispersion factor
$\vec{r}$	is the vector to the point of the concentration measurement
$\vec{q}$	is the vector to the centre of the source
$Q(\beta)$	is the emission rate
α	is the sum of the factors influencing the dispersion of air pollutants (e.g. meteorological parameters, type of source)
β	is the sum of the factors influencing the emission rate (e.g. operating conditions)

NOTE For reasons of formal simplification, the influencing factors α and β are no longer quoted in the following.

To calculate the dispersion factor, the following procedure is applied. In a first step, the concentration c_1 is calculated at point $\vec{r}$ by means of dispersion modelling and the given unit emission rate Q_1. The dispersion conditions at the time of the measurements have to be taken into account. The dispersion factor is then given by the following:

$$f(\vec{r}-\vec{q}) = c_1(\vec{r})/Q_1 \tag{6}$$

Since the dispersion factor has an effect on the following calculations, the dispersion model is to be chosen carefully. It should depict the real dispersion conditions as accurately as possible. Then the emission rate in question can be calculated in accordance with Equation (7):

$$Q = \frac{c(\vec{r})-c_\infty}{f(\vec{r}-\vec{q})} = \frac{c(\vec{r})-c_\infty}{c_1(\vec{r})}\, Q_1 \tag{7}$$

If measurements that integrate the path length are carried out instead of point-related measurements, the following equation for the emission rate results analogously to Equation (7):

$$\begin{aligned} Q &= \frac{C}{F} \\ &= \frac{\int_L \left(c(\vec{r})-c_\infty\right) \mathrm{d}\xi}{\int_L f(\vec{r}-\vec{q})\, \mathrm{d}\xi} \\ &= \frac{\int_L \left(c(\vec{r})-c_\infty\right) \mathrm{d}\xi}{\int_L c_1(\vec{r})\, \mathrm{d}\xi}\, Q_1 \end{aligned} \tag{8}$$

where

C is the integral value of the concentration distribution

F is the integral value of the dispersion factors

L is the length of the monitoring path

ξ is the integration variable

The required integration of the dispersion factor f along the monitoring path L has to be adequately considered for the dispersion calculation (see Example).

In Equations (7) and (8), the emission rate Q is clearly related to the measured concentration value. Under the mentioned ideal conditions, the reverse dispersion modelling only requires one individual point or integral concentration measurement. However, this procedure is connected with some uncertainties. In practice, errors in measurement as well as model deficiencies result in deviations with respect to the emission rate.

In most cases, it will not be sufficient to use only one individual measured value to reliably determine the source term. Results can be improved by an adequate number of suitable repeat measurements if the emission rate $Q(\beta)$ can be simultaneously assumed to be constant over the period of additional measurements. Measurements that are carried out under different dispersion conditions, each at the same position, or measurements that are carried out at different positions are possible alternatives.

Using such an extended database, the emission rate can be determined with the help of statistical methods. The purpose of this is to reach an optimum agreement between the different concentration measurements and the corresponding dispersion calculations, in order to compensate for non-negligible stochastic errors. Due to the demonstrated proportionality between the emission rate and the downwind concentration value, linear statistical methods are generally sufficient.

In the simplest case, the emission rate can be determined from the arithmetic mean of the N measured concentration values and the assigned dispersion factors. In the case of integral measurements, the estimated emission rate is to be determined in accordance with Equation (9):

$$\tilde{Q} = \frac{1}{N} \sum_{i=1}^{N} \frac{C_i}{F_i} \tag{9}$$

NOTE The superscript „~" denotes the statistical estimate of the emission rate.

Among other factors, the site and the period of time of the concentration measurements are of great importance to the accuracy with which the source term is determined. The emission plume should be continuously determined over the entire measurement period, and it should be as representative as possible. For this purpose, path length-averaging measurements can be better used than spatially resolving concentration measurements, because the influence of the wind direction on the measurement result is decreased. Moreover, the integration compensates for possible deficiencies with respect to the geometry and the spatial structure of the source model.

The results can be further improved by a specific adaption of the flow and dispersion models to each individual case. Particularly under complex boundary conditions with respect to buildings or topography this can become necessary and necessitate additional studies, for example in the boundary layer channel or tracer gas field measurements.

8.4.3 Reverse dispersion modelling in the case of an inhomogeneous source structure

If the emission distribution within a source area is of importance to a diffuse source, adequate spatially resolving measurements and calculations have to be carried out.

For the reverse dispersion modelling, the source area is to be separated into M homogeneous individual sources. If no specific previous information about the structure of the source is available, the source area expediently undergoes discretization by means of a regular grid of geometrically unique (e.g. cubic) sources. Each individual source is characterized by its centre of gravity $\vec{q}_j$ = $(x_q, y_q, z_q)_j$ and its spatial dimensions.

All defined sources are given an emission rate $Q_j > 0$ ($j = 1$ to M), which leads to a contribution $c_j(\vec{r})$ at the site of the concentration measurement $\vec{r} = (x_c, y_c, z_c)$. The sum of all parts of the source is, superposing with the background concentration, the measurable quantity:

$$\begin{aligned} c(\vec{r}) &= \sum_{j=1}^{M} c_j(\vec{r}) + c_\infty \\ &= \sum_{j=1}^{M} f_j(\vec{r} - \vec{q}_j, \alpha_j)\, Q_j(\beta_j) + c_\infty \end{aligned} \tag{10}$$

NOTE 1 For reasons of formal simplification, the influencing factors α_j and β_j are no longer quoted in the following.

NOTE 2 The described methods can also be used for integral concentration measurement values if the respective defining equations take account of the spatial averaging along the monitoring path in accordance with Equation (8).

f_j is the participating dispersion factor for the measuring point $\vec{r}$ with respect to source j at the position $\vec{q}_j$. The purpose of the reverse dispersion modelling is to determine the individual emission rates Q_j and the total emission rate Q:

$$Q = \sum_{i=1}^{M} Q_j \tag{11}$$

To completely determine the emission rates of all individual sources, several concentration measurements, which are independent of one another, are basically required.

The repeated measurements are to be carried out, if possible, at different measuring sites with predominantly constant emission levels. If the local conditions allow such a procedure, the measuring sites should be determined in a way that each of the concentrations occurring there is dominated by one individual partial source. Under such conditions, the emission rate distribution can be iteratively derived from the measurements. Simplified estimates of the source structure are not required then.

Each repeated measurement $i = 1$ to N results in a new, statistically independent concentration measurement value $c_i(\vec{r})$ for the measuring point $\vec{r}$:

$$c_i(\vec{r}) = \sum_{j=1}^{M} c_{ij}(\vec{r}) + c_{i,\infty} \tag{12a}$$

$$c_i(\vec{r}) = \sum_{j=1}^{M} f_{ij}(\vec{r} - \vec{q}_j)\, Q_j + c_{i,\infty} \tag{12b}$$

Each measured value is composed of the actual contribution of the participating M sources and the background pollution of the respective series of measurements. f_{ij} denotes the dispersion factor for the measuring point $\vec{r}$ with respect to the source j at the position $\vec{q}_j$ for the measurement i. For the totality of all measurements, the following results:

$$\vec{c} = \mathbf{F} \cdot \vec{q} + \vec{c}_\infty \tag{13}$$

where

$\mathbf{F}$ is the matrix of the dispersion factors $f_{ij}(\vec{x})$ having the dimension $M \times N$

$\vec{c}$ is the vector of the concentration measurement values $c_i(\vec{r})$ having the dimension N

$\vec{c}_\infty$ is the vector of the local background pollution present during the measurement

$\vec{q}$ is the vector of the emission rate distribution Q_j having the dimension M

The equation system set up by Equation (13) is linear and can be inverted with restrictions. Minor errors in the input variables (for example, due to errors in measurement) give considerable deviations in the results. In the case of the reverse dispersion modelling, the equation system will remain underdetermined because the number of concentration measurements is generally smaller than the number of the individual sources ($M < N$). Then the emission rate distribution can only be determined using additional assumptions.

8.4.4 Practical procedure

In practice, the determination of the emission rate is simplified by less complex source modelling. There are the following possibilities:

a) Due to the local conditions, the whole source area can be divided into individual, homogeneous sources that are independent of one another. Under favourable meteorological conditions, the emission dispersion of each individual source is spatially separate, and there is no significant overlap with the emission flows of adjacent sources. Each source is surveyed separately. The contributions of the adjacent sources to the concentration measurement value are lumped together as prior pollution of the area. The reverse dispersion modelling for the individual sources is carried out in accordance with the Section above. The total emissions are calculated from the individual values according to Equation (9).

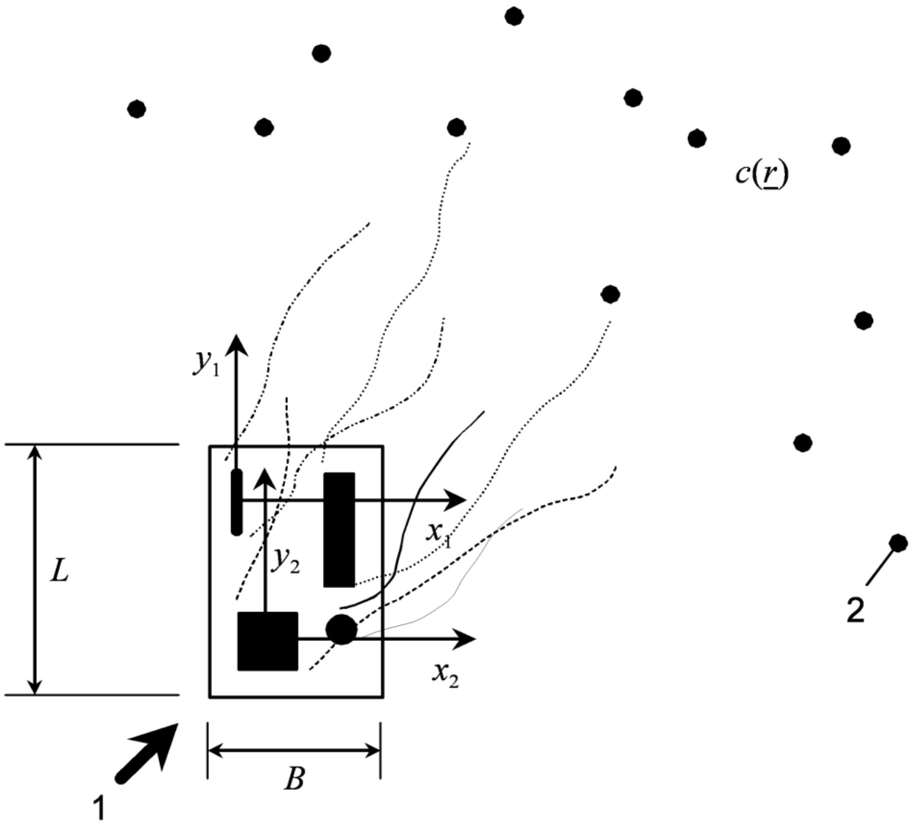
b) If the emission rates Q_j of all individual sources are of a comparable order of magnitude ($\hat{Q} = Q_j$), Equation (12) is simplified as follows:

$$c(\vec{r}) = \hat{Q} \sum_{j=1}^{M} f_j(\vec{r} - \vec{q}_j) + c_\infty \tag{14}$$

For the total emission rate the following applies:

$$Q = \frac{c(\vec{r}) - c_\infty}{\frac{1}{N} \sum_{j=1}^{M} f_j(\vec{r} - \vec{q}_j)} = M\ \hat{Q} \tag{15}$$

The advantage of this procedure over the one described above is the explicit depiction of the geometrical source conditions. Each partial source is considered, in accordance with its distance to the measuring site and its individual dimensions, by a source-specific dispersion factor f_j (see Figure 7.2).



1 wind direction
2 concentration measuring points

Figure E.2 — Modelling of heterogeneous source areas of length L and width B by four individual sources

The influence of the source structure and the source geometry declines with increasing distance to the source. The results of the calculations with Equations (15) and (7) are almost the same then. If measurements carried out at a greater distance to the source can be taken as a basis because of the local conditions and the concentration level to be expected, a procedure according the homogenous case is recommended. This means that it is sufficient to carry out measurements at a point that is far away from the diffuse source. This conflicts with practical reasons such as the measurement method, the overlap by other sources, transformation processes in the atmosphere and dispersion conditions. In the measurement planning, this shall be taken into account accordingly.

c) The source modelling described in case b) can be easily transferred to source areas with differing levels of emission. In this case, however, additional assumptions or details concerning the relative proportions of the individual sources Q_j in the total emission rates Q are required. Using Equations (16) and (17),

$$c(\vec{r}) = Q\sum_{j=1}^{M}\lambda_j \; f_j(\vec{r}-\vec{q}_j)+c_\infty \tag{16}$$

$$\lambda_j = Q_j/Q \tag{17}$$

the total emission rate can be estimated in accordance with Equation (18):

$$Q = \frac{c(\vec{r}) - c_\infty}{\sum_{j=1}^{M} \lambda_j \ f_j(\vec{r} - \vec{q}_j)} \tag{18}$$

For example, in the case of area sources at ground level, the proportion λ_j can be determined by field measurements on a grid.

d) The emission distribution in the area of a source is considerably determined by the emission mass flow and the characteristical dimensions of the source. Using the mass flow density $\dot{m}_{\mathrm{d},j}$, the emission rate Q_j is related to the size of the transitional area A_j of the emissions, $\dot{m}_{\mathrm{d},j} = Q_j / A_j$. The lower the mass flow density, the lower the concentrations, in the case of a constant emission rate, at the place of transition to the atmosphere (see also Example E1). In large source areas (e.g. leakages at chemical plants), it is sometimes possible to determine the real conditions more exactly by assuming a constant mass flow density than according to Equation (5). If this is the case, the concentration at the point $\vec{r}$ is given by:

$$c(\vec{r}) = \hat{\dot{m}}_\mathrm{d} \sum_{j=1}^{M} A_j \ f_j(\vec{r} - \vec{q}_j) + c_\infty \tag{19}$$

where $\hat{\dot{m}}_\mathrm{d} = \dot{m}_{\mathrm{d},j}$. The distribution of the emission rate is determined in accordance with Equation (20):

$$Q_j = A_j \frac{c(\vec{r}) - c_\infty}{\sum_{j=1}^{M} A_j \ f_j(\vec{r} - \vec{q}_j)} \tag{20}$$

The total emission rate is determined in accordance with Equation (21):

$$Q = Q_j \sum_{k=1}^{N} \frac{A_k}{A_j} \tag{21}$$

8.5 EXAMPLE OF RDM APPLICATION IN QUANTIFICATION OF VOC IN REFINERY

Based on the European Standard, and in agreement with VDI description, this chapter describes field experiments conducted by the French Petroleum company (TOTAL) in a refinery in order to adjust the RDM methodology to VOC quantification.

The scope of the application is to improve the quantification of global VOC emission in the waste water treatment sector. As a reminder, other main VOC sources are quantified either by the application of the standardised method of sniffing for the units, or by the use of emission’s model for tanks (e.g. TANKS® model based on API equation [7]).

For water treatment, classical approaches [8] consist in using either emissions models (like Lichfield equation or RWET from EPA [9]), or measurements with flux chambers. Unfortunately, obtaining all parameters for model's calculations can be difficult, and flux chambers give an emission factor that only represents quiet parts of the pond.

This approach aims to assess the VOC’s emission from the measurement of concentration in air. The concentration of VOC in the atmosphere could be monitored by several techniques, but for the calculation of emission flux the effects of wind and dispersion must be taken into account as well.

Pollutant Measurements

Pollutant Measurements need to have a lot of data to correctly describe the inhomogeneous area (several ponds, water elevators, tanks, etc.). Uses of a multitude of analysers or optical techniques were judged too expensive or not useful. So, the choice has been made to use a combination of mobile and fixed analysers:

One mobile analyser (portable FID / PID) is used to quantify specific points in the perimeter of the sources ($\vec{c}$ in equation (13)). The objective is to cover a representative part of the space to identify the heterogeneity of emission sources. For each point, the record time is one minute. A background correction of concentrations is done with upstream wind concentration ($\vec{c}_\infty$ in equation (13)).

A limited number of fixed analysers (in our case 3 FID or PID) record the concentration during a representative period of 2 weeks with a frequency of 15 minutes. Their localisations are chosen around the area to cover the main wind directions and at a minimum distance of ~10 meters from sources to avoid very local influence.

Effects of wind and dispersion

A meteorological station installed in an undisturbed place near the emitting area, monitors wind and stability changes at high frequency (30 s). But, the use of a single meteorological station cannot be representative of all wind fields in complex, cluttered industrial site like a refinery. So, a description of winds affecting each concentration measurement point needs to be simulated by 3D fluid models with the single meteorological measurement as input.

As there are several nearby sources, treatment of the results must be done with a direct dispersion model and a reverse model. For direct dispersion model specification, a 3D Lagrangian model is able to represent short-term changes (concentration and meteorology) and keeps pollutant mass during transport with some meteorological variation.

Figure 7.3 presents an example of tracks with a mobile FID/PID detector in a water treatment area and the simulated dispersion with a Lagrangian model.

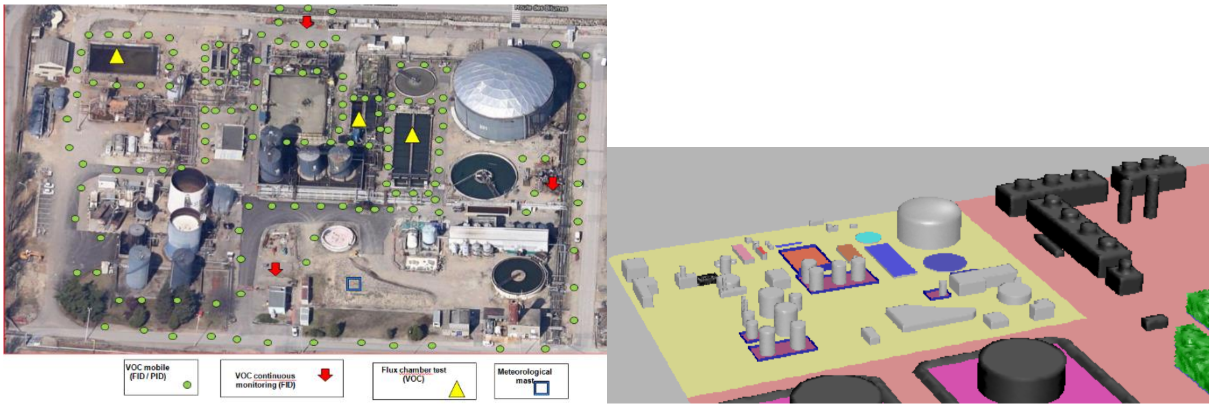


Figure E.3 : example of tracks with mobile detector and the model area use for dispersion

A classical RDM is realised to combine model results and measurements:

Classical direct dispersion is done with a theoretical emission flux set at 1 g/s for each source, to obtain the matrices' of dispersion factor ($\mathbf{F}$ in equation (13)).

Concentrations simulated in each point are adjusted to mobile measured concentrations at the same time using the "reverse model", i.e. a linear regression. Thus conducting to the emission flux estimates for each source ($\vec{q}$ in equation (13)).

To improve and validate the flux estimation, a new final step is done by comparing a direct dispersion scenario with the emission flux estimated and the set of fixed monitors, not used in the initial RDM. This last test confirms or not if the emission estimation is representative for a larger period.

Examples of emission quantification obtained with several measurement campaigns (Figure 7.4) illustrate:

the repartition of VOC emission from the different ponds.

the progress done by the refinery to reduce VOC in water and VOC emissions.

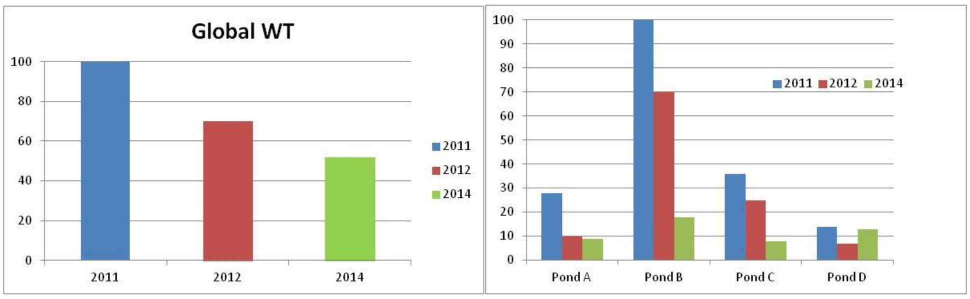


Figure E.4 : Emissions estimated with RDM for the water treatment area and for each pond (normalized to 100 for the highest) from 2011 to 2014

8.6 TECHNICAL PERFORMANCE

8.6.1 Performance characteristics

In principle, the RDM approach can be used for each industrial sites and type of emission. The only limiting parameter is only depending on the possibility to detect the pollutant in several localizations around the emission area.

In practice, it can be applied for each type of pollutants if there is an adapted analyser.

The detection limits is function of the sensibility of ambient analyser used downwind of the source and correction of concentrations which is done with upstream wind concentration (in equation (13)).

8.6.2 Advantages and constrains

The RDM is a complex technique and therefore it is relatively expensive. However, cost effective when using it for a long term site specific monitoring, using data from fixed VOC analysers in the process area or with moving monitoring techniques and data from a meteorological station installed in an undisturbed place near the emitting area, monitoring wind and stability changes at high frequency.

The effort to establish a 3D fluid model with the single meteorological measurement as input and the dispersion model (3D Lagrangian) is only necessary once. It could be reused for the same site in the following years.

8.6.3 Uncertainty

The RDM flux is determined by modelling on the basis of VOC measurements, the effects of wind field and dispersion must be taken into account as well.

So, uncertainty depends on measurement uncertainty of downwind/upwind VOC-measurements, on the complexity of the industrial site, which means complexity of wind field modelling and dispersion modelling.

8.7 QUALITY CONTROL

Quality assurance of the emission measurements is necessary. These procedures require detailed project planning and progress monitoring with project subject, in addition to regular internal reviews and quality audits at measurement institutions.

It is also possible to validate the quality of the RDM result by comparing dispersion of emission determined by RDM with a specific analyser not used as input of the RDM.

8.7.1 Calibration procedures

8.7.2 Calibration gases

A standard gas mixture of the target gas (or an appropriate proxy – e.g., propane or pentane for the total hydrocarbon measurements) should be used to provide the reference for the measurements. These standards should be, where possible, gravimetrically prepared, internationally-traceable reference gas mixtures with absolute volume mixing ratio (VMR) accuracies of 0,5 % or better.

8.7.3 Meteorological sensors calibration

The meteorological sensor should be calibrated once a year. The calibration certificates may provide a calibration factor for the wind speed and wind direction readings. If data loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.

In addition, the different sensors should be compared side-by-side in the field to provide a further check on their correct function.

8.8 DATA ANALYSIS

The data analysis process consists of the following steps:

8.8.1 Background subtraction

Any background value is subtracted from the signals.

8.8.2 Calculation of emission fluxes

As describe in the RDM Standard, the calculation of the flux is the result of an adjustment of direct dispersion with a theoretical emission and the real monitoring data.

8.9 REFERENCES

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9 BAGGING METHOD

9.1 OVERVIEW

9.1.1 Scope

“Bagging method” is a standardised method used since the early 1990s. This international approach is defined in the US through a standard, EPA-453/R-95-017.

This method consists of enclosing (“bagging”) a leaking component like flanges, valves, pumps, compressors, plugs, to measure mass emissions of organic compounds (VOC).

Measured emission rates from bagged equipment coupled with screening values can be used to develop unit-specific screening value/mass emission rate correlation equations.

Correlation equations detailed in US EPA-453/R-95-017 or EN 15446 standards come from bagging compliant with this method.

9.1.2 Pollutants measured

TVOC - The detectors on the VOC analysers are sensitive to the different chemical species that make up the VOC family, including methane. FID has the same level of efficiency regardless of the type of VOC, including aromatics, methane, etc.

Response factors are used to correct each measurement value (For compounds and for mixtures).

9.1.3 Information provided

The implementation of a bagging provides mass emission fluxes of VOCs on a leaking source.

This leaking source can be detected using an FID analyser (in the case of leaking threshold defined in ppmv) or using OGI technology.

9.1.4 Scale and limitations

Bagging can be performed on small individual potential leaking equipment of industrial sites, from remote areas (Tank farms, handlings, etc.) to process units.

Thanks to the analyser’s portability and the limitation of the necessary equipment to use, bagging can be performed by the operators on all the accessible components.

9.2 MEASURING PRINCIPLE

9.2.1 Bagging technical description

Three methods are employed to perform a bagging:

The vacuum method.

The blow through method.

The high flow sampling method

All methods involve enclosing individual equipment part with a bag and a known rate of a carrier gas is induced through this bag.

The flow rate through the bag has to be adjusted to find a good balance between reaching equilibrium conditions and having a high enough concentration of VOCs in the bag for accurate results.

A measurement with an appropriate (e.g. FID, PID) analyser of the diluted concentration of VOCs is performed.

If possible a data logging of VOC concentration during a period is preferable to a single measurement in order to:

Adjust the dilution flow rate to achieve a stable VOC concentration.

Calculate the average concentration during this period.

Mass emissions are calculated based on the measured concentration and the flow rate of carrier gas through the bag.

The methods differ in the ways in which the carrier gas is conveyed through the bag.

In vacuum and high flow sampling methods, a vacuum pump is used to pull air through the bag.

In blow-through method, a carrier gas is blow into the bag.

In general, the blow-through method has advantages over the vacuum method, these advantages are as follows:

Better mixing in the bag in blow through method

No correction for background VOC concentrations in the blow through method

The blow through method does require a carrier gas (free of VOCs), and the vacuum method does not, but in the vacuum method, the residual risk to add background concentration to the leaking concentration is significant.

- The high flow sampling method allows for more rapid bagging of the component. Care must be taken with the calibration of the induced flow through the bag and for correction for the background concentration.

In case of liquid loss from the equipment, this part of emissions must be collected for quantification.

9.2.2 Advantages and Constraints

These methods allow a precise mass flow quantification of individual leaking component, however leaking components must be identified by an alternative method.

It is not recommended that the vacuum method be used to measure the leak rate from equipment that has low screening values (approximately 10 ppmv or less), because considerable error can be introduced due to the background organic concentration in the ambient air that is pulled through the bag.

9.2.3 Uncertainty

Uncertainty factors must be mastered for both methods.

Pressure and temperature must be checked for the correction of:

The VOC concentration

The flow rate of carrier gas through the bag

Instrument precision must be known before:

Linearity (0-> 10 000 ppmv)

Linearity (10 000 ppmv -> x%) using dilution probe

Precision on the range (+ dilution probe)

Response factors between calibration gas and the measured compounds

Operation **/** background precision must be known before:

Background concentration (For vacuum method and HFS methods)

VOC concentration in the carrier gas (cylinder)

VOC concentration in the fuel gas of the analyser (H2)

VOC concentration in case of liquid leak in the bag

9.3 TECHNICAL PERFORMANCE/REQUIREMENTS

Performance requirements and characteristics of the equipment used for the measurement of VOCs concentration are already described and set out in EN 15446. The portable organic vapour analysers that currently comply with the standard are FIDs, although in future alternative detectors could be approved for this application. This instrument can measure with the same level of efficiency all types of VOC (including aromatics, methane, etc.).

9.3.1 Blow through method requirements

The carrier gas should be inert and free of any organic compounds and mixtures.

The flow rate of the carrier gas is monitored in a gas flow regulator calibrated to the gas. Typical flow rates are approximately 60 l/min or less.

9.3.2 Vacuum method requirements

At least a 135 LPM vacuum pump is used, driven by an electric or air motor.

An American manufacturer proposes a sampling flow rate near 300 LPM in their equipment.

The concentration in the background bag is subtracted from the average concentration in the sample bags when calculating the leak rate.

9.3.3 Common requirements

The bag used to enclose individual equipment parts and all accessories must not emit VOCs.

9.4 QUALITY CONTROL

9.4.1 Calibration procedures

Calibration procedures and gases used are described in the EPA standard (EPA-453/R-95-017).

9.5 DATA ANALYSIS

9.5.1 Mass flux calculation / Quantification

The mass flow quantification method is clearly defined in the EPA standard (EPA-453/R-95-017).

In case of liquid loss, the associated flow must be included into the overall quantification.

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10 RPM

10.1 OVERVIEW

Radial plume mapping (RPM) uses open-path optical techniques to measure an area using multiple, non-overlapping beam paths. It can be deployed in two configurations, horizontal RPM (HRPM) to locate surface emission points, or vertical RPM (VRPM) to quantify downwind emission fluxes. This is similar to the capabilities of DIAL, but due to the equipment used for RPM it is a far more limited approach.

10.1.1 Scope

As an optical technique it requires line of site so is best suited to flat sites (e.g. landfill sites) or fence line surveys for refinery sites. The open path measurements can be made over distances of up to 250 metres.

RPM normally uses FTIR systems, but other path integrated optical remote sensing techniques like UV-DOAS or TDLAS can also be used.

10.1.2 Compounds measured

If FTIR is used it will detect VOC with the benefit that it can also identify the species that are present.

10.1.3 Information provided

Average concentration of the different detected species over the distance measured.

10.1.4 Scale and limitations

The limited effective range of open-path techniques (<250m) will require repeated measurements to cover larger sites, with each additional set requiring the redeployment of the equipment. For VRPM mirrors are mounted on a mast, but this will limit the maximum measurement height to ~10 metres making the technique unsuitable for measuring plumes from stacks and elevated flares, especially since these sources are typically at high temperatures so emissions will quickly rise out of range.

The resolution of RPM is limited by the number of paths used and by the fact that each path is an average concentration. Low resolution will limit the ability to identify individual sources and prevent the attribution of emissions where leaks are close together.

Mirrors to reflect light back to the instrument have to be kept clean and properly aligned with the instrument, with realignment required for each redeployment of the equipment making surveys of large sites slow and therefore expensive.

10.2 MEASURING PRINCIPLE OF RPM

10.2.1 Description of technique

A number of mirrors are deployed across the site to be measured at distances of between 100 and 250 metres. For HRPM these will be at different angles and distances to measure over a specified area (Figure 9.1). With VRPM most of the mirrors are mounted on a mast in order to generate a vertical profile, with the remaining mirrors at ground level along the line from the instrument to the mast to identify the distance at which the plume is located (Figure 9.2). Light from the instrument will be influenced by the molecules present in the path causing them to scatter. Light returning to the instrument is analysed to produce spectra that indicate which molecules are present and at what quantity, providing average concentrations of the detected species along each path.

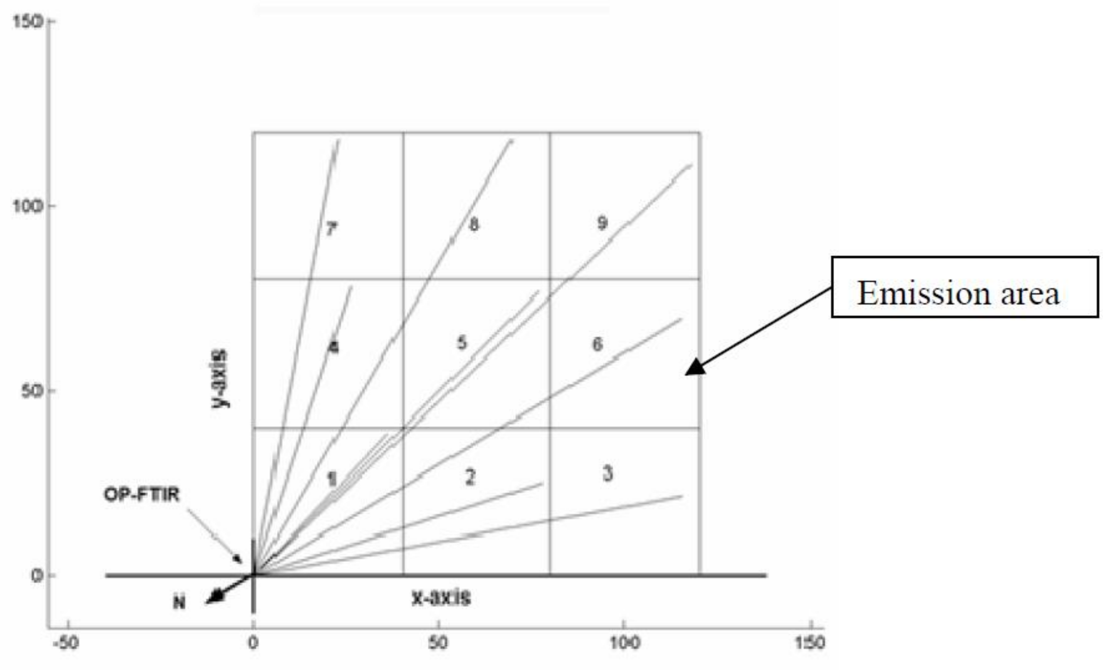

Figure 9.1: Typical HRPM measurement configuration (Modrak 2006)

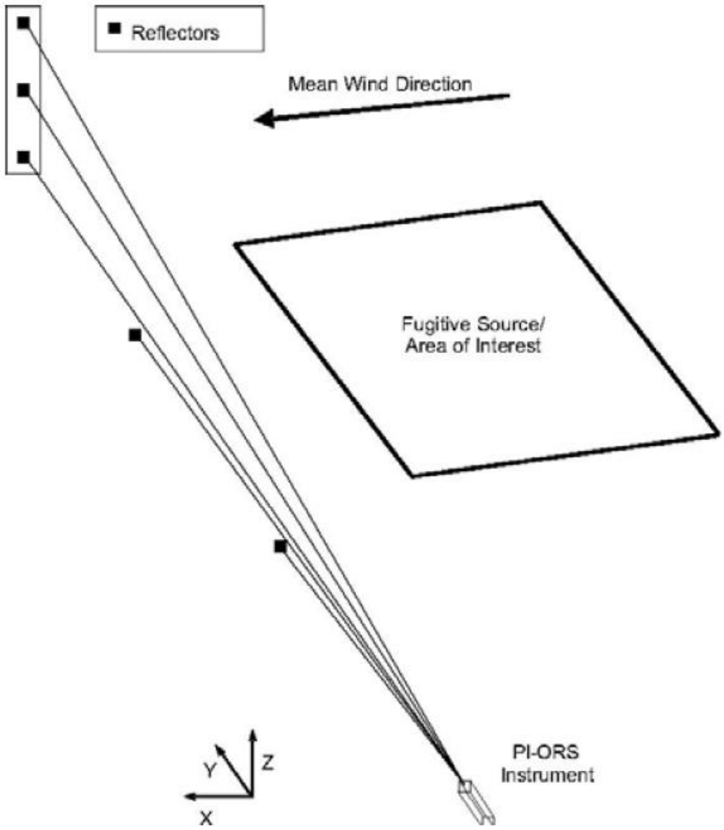

Figure 9.2: Typical VRPM measurement configuration (Modrak 2006)

10.2.2 Advantages and constraints

The main advantage of using an open-path FTIR is the ability to provide a breakdown of the concentration of each species present in the path. However it will only provide the average concentration along the whole length of the path.

Limited range on open-path instruments will make surveying large sites time consuming and impractical. Repeatedly moving and redeploying equipment, including the realignment of mirrors, is unlikely to be a realistic proposal on large industrial sites like refineries.

For VRPM mirrors have to be mounted on a mast, but this will limit the maximum measurement height to ~10 metres making the technique unsuitable for measuring plumes from stacks and elevated flares, especially since these sources are typically at high temperatures so emissions will quickly rise out of range.

RPM has limited resolution so will be unable to resolve the exact sources of emissions and will fail to detect if the source is multiple small emissions or one larger source. This is mainly down to each path being an average concentration so there is no spatial resolution along each path. Making this worse is the limited number of paths surveyed at each location so while emissions can be detected they have to be assigned to a relatively large area. The technique is best for diffuse emissions on flat featureless sites (e.g. sealed landfill sites or lagoons).

Any disruption to the beam, for example by people, vehicles or topography, will interfere with the results. Weather conditions including rain, fog or snow will also disrupt the beam. Wind conditions will also influence the quality of results from RPM measurements.

10.2.3 Uncertainty

The level of acceptable uncertainty is dependent on the application of the reported data. The user must tailor their choice of measurement system, configuration and tolerance parameters to meet their needs. Table 9.1 lists typical sensitivity that is achievable the main potential instruments for RPM.

Table 9.1 Typical sensitivity ranges for some suitable RPM instruments

Instrument	Formaldehyde	1,3-Butadiene	Acrolein	Benzene	Ammonia	Total VOC
Scanning OP-FTIR (for >100m path-length)	2 - 10 ppb	2 – 10 ppb	8 – 30 ppb	15 – 50 ppb	0.5 – 4 ppb	1 – 5 ppb
UV-DOAS (for >250m path-length)	0.5 ppb	NA	NA	0.1 ppb	1 ppb	NA
TDLAS (for >250m path-length)	NA	NA	NA	NA	20 – 50 ppb	NA
PI-DIAL (1000m path-length)	*	*	*	10 µg/m^3	*	*

NA This compound cannot currently be measured by this instrument
* Typically a custom built instrument and sensitivity ranges are instrument-specific.

10.3 PERFORMANCE CHARACTERISTICS

Performance is closely tied to the instrument being used. Table 9.1 gives some typical instrument sensitivity levels and the required path lengths for these techniques.

10.4 QUALITY CONTROL

The level of acceptable uncertainty is dependent on the application of the reported data – whether for hot spot determination (HRPM), measurement of emissions flux (VRPM), or line-of-sight profile concentrations (1D-RPM). The user must tailor their choice of PI-ORS system, configuration, and tolerance parameters to meet their end needs.

Instrument QA/QC procedures should be followed to ensure suitable data is recorded. Similarly any instrumentation for recording meteorological conditions should be operated following appropriate QA/QC procedures.

Controlled releases can be made to verify the performance of RPM techniques, with targets set for the required levels of accuracy (i.e. hot spot detected within specified acceptance limits of actual release point for HRPM or measured emission rate within acceptance levels for VRPM).

10.5 DATA ANALYSIS

10.5.1 Overview

Prior to analysis, determine the moving averaging scheme for generation of the plume maps for any methodologies used in this protocol. Because data is acquired sequentially, a moving average is required to reduce errors that originate from temporal variability. Typically, a moving average with a grouping of three cycles is sufficient to provide stable results with a CCF larger than 0.8.

10.5.2 HRPM Methodology

10.5.3 HRPM Theory

Once the PIC for all beam paths are averaged with the predetermined grouping of cycles for the gas species of interest, the HRPM calculations make use of the information to reconstruct a plume map over the area of interest. An example emission source location map is shown in Figure 9.3. The cross shows the location of the plume centre from a study where propane gas was released at the location shown by the open circle.

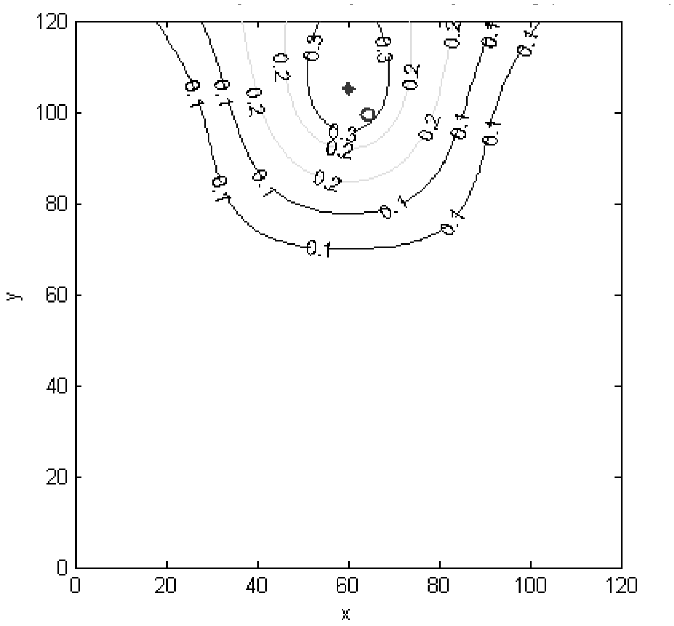

Figure 9.3: Example emission source location map, with the circle representing the controlled release point and the cross representing the detected centre of the plume.

10.5.4 HRPM Algorithm

Average concentrations for each pixel are obtained by applying an iterative algebraic deconvolution algorithm. The measured PIC, as a function of the field of concentration, is given by equation 9.1

Equation 9.1

$$PIC_k = \sum_m K_{km} c_m$$

Where:

K = a kernel matrix that incorporates the specific beam geometry with the pixel dimensions

k = the number index for the beam paths

m = the number index for the pixels

c = the average concentration in the mth pixel

Each value in the kernel matrix *K* is the length of the k^{th} beam within the m^{th} pixel; therefore, the matrix is specific to the beam geometry. The HRPM procedure solves for the average concentrations (one for each pixel) by applying non-negative least squares (NNLS).

The HRPM procedure multiplies the resulting vertical vector of averaged concentration by the matrix *K* to yield the end vector of predicted PIC data. The second stage of the plume reconstruction involves interpolation among the reconstructed pixel's average concentration, providing a peak concentration not limited to the center of the pixels. A triangle-based cubic interpolation procedure (in Cartesian coordinates) is currently used in the HRPM procedure.

10.5.5 Check for Reasonableness of Surface Concentration Plot Results

Evaluate the data for reasonableness with the following qualitative (9.5.2.3.1) and quantitative (9.5.2.3.2) checks.

10.5.6 Qualitative check

If the order in which the beam paths were scanned (and the corresponding pixel numbering convention inside the HRPM program) are different than the order of PIC data input, the reconstructed plume centre could fall in an incorrect pixel. Verify that the generated result is reasonable based on the raw PIC data.

10.5.7 Quantitative checks

To determine the quality of the reconstructed plume maps against the measured PIC data, the Concordance Correlation Factor (CCF) is used to represent the level of fit between measured PIC and predicted PIC. A CCF greater than 0.8 verifies that the surface concentration plot is a reasonable fit with the raw data. If the CCF is less than 0.8, the Check for Reasonableness procedures should be performed a second time to confirm the input data. The analysis may repeated with a longer average scheme, which typically increases the CCF value.

10.5.8 Hot spot location determination

The HRPM procedure provides a plume map and calculates the location of the peak concentrations. It is for the user to interpret this information and site constraints, such as obstructions or terrain complexities, for the determination of the actual location of the hot spot.

10.5.9 VRPM Methodology

10.5.10 VPRM Theory and Algorithms

Once the PIC for all beam paths are averaged with the predetermined grouping of cycles for the gas species of interest, the VRPM calculations make use of the information to reconstruct a plume map in the vertical downwind plane. Two different beam configurations of the VRPM methodology are recommended: the five-beam (or more) and the three-beam VRPM configuration. Figure 9.2 illustrates the setup for these two VRPM beam configurations. In the five-beam (or more) configuration, the ORS instrument sequentially scans over five PDCs. Three PDCs are along the ground-level crosswind direction (beams a, b, and c in Figure 9.2), and the other two are elevated on a vertical structure (beams e and f in Figure 9.2). The additional beam (d) in Figure 9.2 is for 6-beam configuration, which provides better spatial definition of the plume in the crosswind direction. In the three-beam configuration, the ORS instrument sequentially scans over three PDCs. Only one beam is along the ground level (beam c or d in Figure 9.2) and the other two are elevated on a vertical structure (beams e and f in Figure 9.2). PIC data are collected over time, completing many cycles through the defined beams of each configuration.

$$G(r,\theta) = \frac{A}{2\pi\sigma_y\sigma_z\sqrt{1-\rho_{12}^2}} \exp\left\{-\frac{1}{2\left(1-\rho_{12}^2\right)}\left[\frac{(r\cdot\cos\theta - m_y)^2}{\sigma_y^2} - \frac{2\rho_{12}\left(r\cdot\cos\theta - m_y\right)\left(r\cdot\sin\theta - m_z\right)}{\sigma_y\sigma_z} + \frac{\left(r\cdot\sin\theta - m_z\right)^2}{\sigma_z^2}\right]\right\}$$

A two-phase smooth basis function minimization (SBFM) approach is applied where there are three or more beams along the ground level (5-beam or more configuration). In the two-phase SBFM approach, a one-dimensional SBFM reconstruction procedure is first applied in order to reconstruct the smoothed ground level and crosswind concentration profile. The reconstructed parameters are then substituted into the bivariate Gaussian function when applying a two-dimensional SBFM procedure.

A one-dimensional SBFM reconstruction is applied to the ground level segmented beam paths (Figure 9.2) of the same beam geometry to find the cross wind concentration profile. A univariate Gaussian function is fitted to measured PIC ground level values.

The error function for the minimization procedure is the Sum of Squared Errors (SSE) function and is defined in the one-dimensional SBFM approach as Equation 9.2.

Equation 9.2

$$SSE(B_j, m_{y_j}, \sigma_{y_j}) = \sum_i \left(PIC_i - \sum_j \frac{B_j}{\sqrt{2\pi}\sigma_{y_j}} \int_0^{r_i} \exp\left[-\frac{1}{2}\left(\frac{m_{y_j} - r}{\sigma_{y_j}}\right)^2\right] dr \right)^2$$

Where:

B = equal to the area under the one-dimensional Gaussian distribution (integrated concentration)

r_i = the path length of the ith beam

my = the mean (peak location)

σ_y = the standard deviation of the jth Gaussian function

PIC_i = the measured PIC value of the ith path

The SSE function is minimized using the Simplex minimization procedure to solve for the unknown parameters (i.e., B, m_y, σ_y).

When there are more than three beams at the ground level, two Gaussian functions are fitted to retrieve skewed and sometimes bi-modal concentration profiles. This is the reason for the index *j* in Equation 9.2.

Once the one-dimensional phase is completed, the two-dimensional phase of the two-phase process is applied. To derive the bivariate Gaussian function used in the second phase, it is convenient to express the generic bivariate function *G* in polar coordinates *r* and θ:

Equation 9.3

The bivariate Gaussian has six unknown independent parameters:

A = normalising coefficient which adjusts for the peak value of the bivariate surface

ρ_{12} = correlation coefficient which defines the direction of the distribution-independent variations in relation to the Cartesian directions *y* and *z* (ρ_{12}=0 means that the distribution variations overlap the Cartesian coordinates)

m_y and m_z = peak locations in Cartesian coordinates

σ_y and σ_z = standard deviations in Cartesian coordinates

Six independent beam paths are sufficient to determine one bivariate Gaussian that has six independent unknown parameters.

Some reasonable assumptions are made when applying the VRPM methodology to this problem, to reduce the number of unknown parameters. The first is setting the correlation parameter ρ_{12} equal to zero. This assumes that the reconstructed bivariate Gaussian is limited only to changes in the vertical and crosswind directions. Secondly, when ground level emissions are known to exist, the ground level PIC is expected to be the largest of the vertical beams. Therefore, the peak location in the vertical direction can be fixed to the ground level.

In the above ground-level scenario, Equation 9.3 reduces into Equation 9.4:

Equation 9.4

The standard deviation and peak location retrieved in the one-dimensional SBFM procedure are substituted in equation 9.3 to yield:

Equation 9.5

$$G(r,\theta) = \frac{A}{2\pi\sigma_y\sigma_z}\exp\left\{-\frac{1}{2}\left[\frac{(r\cdot\cos\theta - m_y)^2}{\sigma_y^2} + \frac{(r\cdot\sin\theta)^2}{\sigma_z^2}\right]\right\}$$

Where:

$\sigma_{y\text{-}1D}$ = standard deviation along the crosswind direction (found in the one-dimensional SBFM procedure)

$m_{y\text{-}1D}$ = peak location along the crosswind direction (found in the one-dimensional SBFM procedure)

A and σ_z are unknown parameters to be retrieved in the second phase of the fitting procedure.

$$G(A,\sigma_z) = \frac{A}{2\pi\sigma_{y-1D}\sigma_z}\exp\left\{-\frac{1}{2}\left[\frac{(r\cdot\cos\theta - m_{y-1D})^2}{\sigma_{y-1D}^2} + \frac{(r\cdot\sin\theta)^2}{\sigma_z^2}\right]\right\}$$

An error function (SSE) for minimization is defined for this phase in a similar manner. The SSE function for the second phase is defined as:

Equation 9.6

Where:

PIC$_i$ = the measured path-integrated concentration of the *i*th path

The SSE function is minimised using the Simplex method to solve for the two unknown parameters.

$$SSE(A,\sigma_z) = \sum_i \left(PIC_i - \int_0^{r_i} G(r_i,\theta_i,A,\sigma_z)\,dr \right)^2$$

When the VRPM configuration consists only of three beam paths—one at the ground level and the other two elevated—the one-dimensional phase can be skipped, assuming that the plume is very wide. In this scenario, peak location can be arbitrarily assigned to be in the middle of the configuration. Therefore, the three-beam VRPM configuration is most suitable for area sources (where no localized hot spot is expected) or for sources with a series of point and fugitive sources that are known to be distributed across the upwind area. In this case, the bivariate Gaussian has the same two unknown parameters as in the second phase (Equations 9-5 and 9-6), but information about the plume width or location is not known. The standard deviation in the crosswind direction is typically assumed to be about 10 times that of the ground level beam path (length of vertical plane). If r_1 represents the length of the vertical plane, the bivariate Gaussian would be as follows:

Equation 9.7

This process is for determining the vertical gradient in concentration. It allows an accurate integration of concentrations across the vertical plane as the long-beam ground-level PIC provides a direct integration of concentration at the lowest level.

$$G(A,\sigma_z) = \frac{A}{2\pi(10r_1)\sigma_z}\exp\left\{-\frac{1}{2}\left[\frac{(r\cdot\cos\theta - \frac{1}{2}r_1)^2}{(10r_1)^2} + \frac{(r\cdot\sin\theta)^2}{\sigma_z^2}\right]\right\}$$

Once the parameters of the function are found for a specific run, the VRPM procedure calculates the concentration values for every square elementary unit in a vertical plane. Then, the VRPM procedure integrates the values, incorporating wind speed data at each height level to compute the flux. The concentration values are converted from parts per million by volume (ppmv) to grams per cubic meter (g/m^3), taking into consideration the molecular weight of the target gas. This enables the direct calculation of the flux in grams per second (g/s), using wind speed data in meters per second (m/s).

10.5.11 Check for reasonableness of the calculated flux

Evaluate the data for reasonableness with the following qualitative and quantitative checks.

Verify that the generated result is reasonable based on the raw PIC data.

To determine the quality of the reconstructed plume maps against the measured PIC data, the Concordance Correlation Factor (CCF) is used to fit between measured PIC and predicted PIC.

As described in earlier studies, CCF was used to represent the level of fit for the reconstruction in the path-integrated domain (predicted versus measured PIC).

CCF is defined as the product of two components:

CCF = rA

Equation 9.8

Where:

r = the Pearson correlation coefficient

A = a correction factor for the shift in population and location

This shift is a function of the relationship between the averages and standard deviations of the measured and predicted PIC vectors:

Equation 9.9

Where:

σ_{PIC_P} = standard deviation of the predicted PIC vector

σ_{PIC_M} = standard deviation of the measured PIC vector

$$SSE(B_j, m_{y_j}, \sigma_{y_j}) = \sum_i \left(PIC_i - \sum_j \frac{B_j}{\sqrt{2\pi}\sigma_{y_j}} \int_0^{r_i} \exp\left[-\frac{1}{2} \left(\frac{m_{y_j} - r}{\sigma_{y_j}} \right)^2 \right] dr \right)^2$$

= mean of the predicted PIC vector

= mean of the measured PIC vector

The Pearson correlation coefficient is a good indicator of the quality of fit to the Gaussian mathematical function. In this procedure, typically an *r* close to 1 will be followed by an *A* very close to 1. This means that the averages and standard deviations in the two concentration vectors are very similar and the mass is conserved (good flux value). However, when a poor CCF is reported (CCF<0.80) at the end of the fitting procedure it does not directly mean that the mass is not conserved. It could be a case where only a poor fit to the Gaussian function occurred if the correction factor *A* was still very close to 1 (*A*>0.90). However, when both *r* and *A* are low one can assume that the flux calculation is inaccurate.

A CCF greater than 0.80 indicates that the surface concentration plot is a reasonable fit with the measured PIC. If the CCF is less than 0.80, but *A*>0.90, this is still a reasonable indication of a good mass equivalent surface concentration plot. If the CCF is less than 0.80, but *A*<0.90, then the Check for reasonableness procedures should be performed a second time to confirm the input data. The analysis may be repeated with a longer average scheme, which typically increases the CCF value.

10.5.12 1D-RPM Methodology

10.5.13 1D-RPM Theory and Algorithms

Once the PIC for all beam paths are averaged with the predetermined grouping of cycles for the gas species of interest, the 1D-RPM calculations make use of the information to reconstruct a plume concentration profile along the measurement line-of-sight. Similar to the case of VRPM (which assumes a bivariate Gaussian plume mass in two dimensions), the 1D-RPM calculations utilize the one-dimensional (1D) SBFM to reconstruct a mass-equivalent plume concentration profile along the line-of-sight measurement. The plume crosswind peak location, coupled with the average wind direction data, can provide an idea of the emission source location and configuration.

The 1D-RPM procedure fits a univariate Gaussian function to measured PIC ground-level values. The error function for the minimization procedure is the SSE function, and is defined in the 1D-SBFM approach as follows:

Equation 9.10

The unknown independent parameters for the 1D-SPFM Gaussian are:

B = area under the Gaussian distribution

r_i = path length of the *i*th beam

$$A = \left[\frac{1}{2} \left(\frac{\sigma_{PIC_P}}{\sigma_{PIC_M}} + \frac{\sigma_{PIC_M}}{\sigma_{PIC_P}} + \left(\frac{\overline{PIC_P} - \overline{PIC_M}}{\sqrt{\sigma_{PIC_P} \sigma_{PIC_M}}} \right)^2 \right) \right]^{-1}$$

m_y = the mean (peak location)

σ_y = standard deviation of the *j*th Gaussian function

PIC_i = measured path-integrated concentration value of the *i*th path

10.5.14 Check for reasonableness of the concentration profile

Evaluate the data for reasonableness with the following qualitative (9.5.4.2.1) and quantitative (9.5.4.2.2) checks.

10.5.15 Qualitative checks

Verify that the generated result is reasonable based on the raw PIC data.

10.5.16 Quantitative checks

To determine the quality of the reconstructed plume maps against the measured PIC data, the CCF is used to represent the level of fit between measured PIC and predicted PIC (see Note 10). A CCF greater than 0.8 verifies that the surface concentration plot is a reasonable fit with the raw data (Table 2, Section 9.2).25 If the CCF is less than 0.8, the Check for Reasonableness procedures should be performed a second time to confirm the input data. The analysis may be repeated with a longer average scheme, which typically increases the CCF value.

1D-RPM source triangulation

The 1D-RPM procedure reconstructs the plume profile along the measurement line-of-site and notes the peak location. Over time, as the wind direction fluctuates, different peak locations are reconstructed from the PIC measurements as illustrated in Figure 9.4. Each time a peak location is noted, a source projection line is drawn for each peak location. This is done by calculating a line equation through the peak location, with the same orientation as the averaged wind direction for the same measurement time interval. Ideally, for a stationary point source, all source projection lines drawn over time should intersect at a point upwind of the measurement line in the vicinity of the real emission source location. Calculating the density of lines per unit area upwind from the measurement plane, the most likely location of the source can be estimated as the region of the maximal line density.

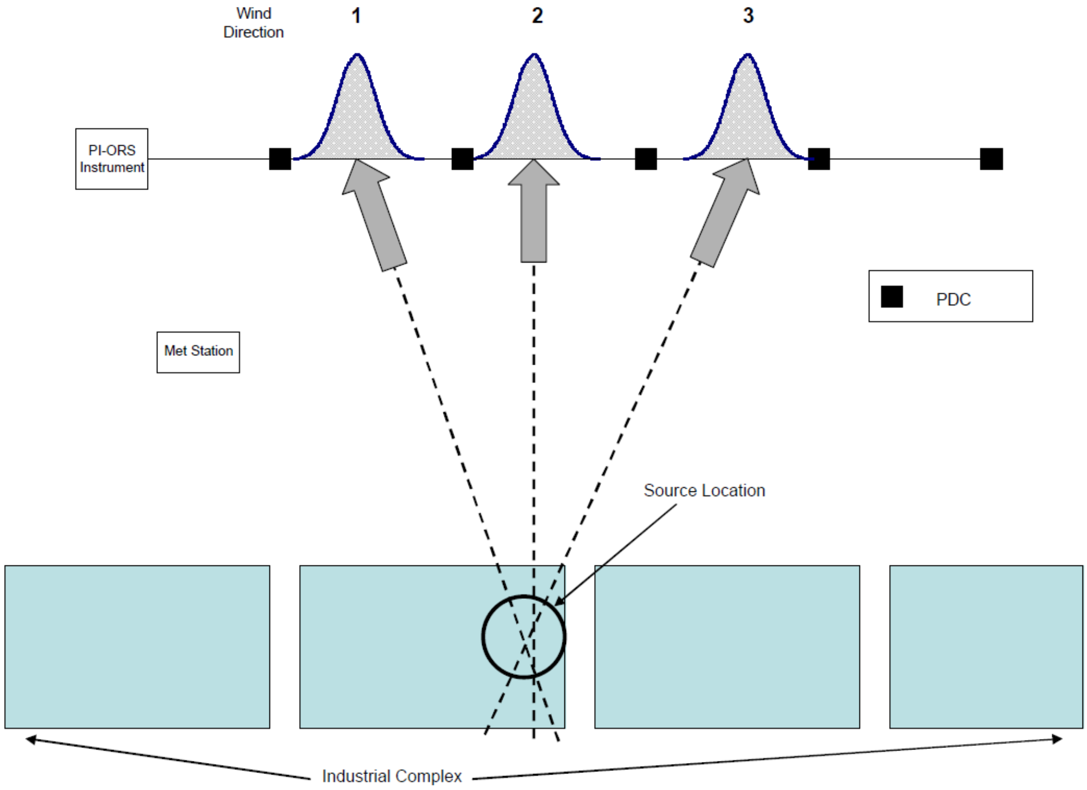

Figure 9.4: 1D-RPM set up with multiple peaks recordered over time due to shifting winds used to triangulate the source of the detected plume

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WG38 – Site test #1 – September 2016

Work Package 2 - Report

Writer: Jonathan Martinez

BUREAU VERITAS
Revision 0 – June 2018

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E C S
Move Forward with Confidence*

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✓ OBJECTIVES

The main objective of the Work Package 2 was to plan and coordinate the field measurement programme.
The coordinator's role was to oversee the mission. He was the guarantor of the good execution of the project.

✓ SCOPE OF WORK

The coordinator's first attribution was to submit to CEN/TC 264/WG 38, a short list of candidate site(s) for the two validation studies identified.

The coordinator was then in charge of establishing the work plans for the two validation studies.

During the field measurements the coordinator provided guidance and inputs to the field measurements.

SUMMARY

I - Phases description and methodology

The performed tasks included the following phases:

1/ - Initial consultation and planning

1A - Candidate sites selection
1B - Test scheduling and coordination with all players for the two sites

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2/ - Support for validation programme at site 1

2A - Preparation: Logistic organisation - Coordination
2B - Existing data recovering and reviewing of LDAR programmes in place
2C - Drawing up of a tests plan
2D - Site visit
2E - Presence at site 1 during trials
2F - Collection of observations during the trials

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1) - INITIAL CONSULTATION AND PLANNING

PHASE 1A - Candidate sites selection

The very first step of this phase was to appoint from our resources, the coordinator for the field measurement programme. The selected expert was Jonathan MARTINEZ.

The second step of this phase was to generate selection criteria for sites for the 2 campaigns (taking into account results from WP1). This work was performed in collaboration with WG38 taking into account criteria listed in the tender.

Assisted by our European Centre of Expertise (Fugitive Emissions Management **CoE**) and thanks to our clients' network and reputation, we have then presented the project to potential candidate sites, corresponding to defined criteria.

The expected weather conditions into the pre-selected plants were taken into account during the selection process.

Upon completion of this step, a short list of candidate sites for the 1st validation study has been issued and then submitted to CEN/TC 264/WG 38.

List of potential
candidates sites rev0

During a subsequent meeting with all players of the WG38, a non-active plant (stopped refinery) located in France, has been selected.

The next phase has been to present the project to the plant and to convince them to allow us to implement this study on their plant. For this reason, an "Introductory letter" has been written.

Introductory Letter rev3 180416 - (Français) - Final (autres sites français).pdf

PHASE 1B - Test scheduling and coordination with all players for the two sites

During this phase, the site coordinator drafted the schedule of all sub-phases of the 1st field validation test.
To perform this task, he has collected the needs of each player (involved in the execution of WP3, WP4, WP5 and WP6) and ensured their coordination in line with the constraints of the site hosting the test.

He also took care of driving everyone to meet the established deadline.

Mission preparation -
Rev4 (130716).xlsx

2) - SUPPORT FOR VALIDATION PROGRAMME AT SITE 1

PHASE 2A - Preparation: Logistic organisation - Coordination

Coordinator provided assistance to coordinate contracts signing between CEN and site.

Together with the site representative, the coordinator was in charge of the delimitation of the "testing area" on the first selected industrial site (where the controlled release will be generated).

The coordinator then communicated to all involved players through a report, the validated/adjusted schedule and all decisions taken and their reasons. This, among others things, covered the selection of the representative VOC.

Planning tentatif.pdf

The coordinator played the role of "focal point" between each actor and the site for all logistic aspects of the project, such as applicable procedures to enter the site (personal, vehicles and tools) or necessary safety trainings…

Bilan des pièces attendues rev0.xlsx

PHASE 2B - Existing data recovering and reviewing of LDAR programmes in place

As test #1 was performed on a non-active plant, existing data recovering of LDAR programme in place was not required.

PHASE 2C - Drawing up of a tests plan

Together with WG 38, the selected site, and the selected providers of the controlled release and measurement techniques, the coordinator drew up a test plan for the first validation study.

This, among others things, defined the number and range of the controlled releases, the location of the control release source(s) in order to be accessible for all techniques.

The test plan took care about requirements of all techniques, especially spatial constraints.

This test plan took into account the defined duration of the tests.

It was anticipated that the measurement of the controlled release will take place over a period of 3 – 4 days with a number of controlled releases each day (at least 5 per day).
It was anticipated that the complete field campaign will have a duration of one to two weeks.

Test plan - Rev0 (150616).pdf

Work plan situation - Rev0 (170616).pdf

Effective work plan situation - Rev1 (120117).pdf

PHASE 2D - Site visit

Coordinator organised and led a pre-study visit to the industrial site.

This visit notably permitted discussions with the plant owners, to ensure that the defined validation work programme is practical and achievable during the selected times and within the allocated time scale.
Qualified scientists participated to this visit.

PHASE 2E - Presence at site 1 during trials

Coordinator led the opening of the project with the site representative and provided assistance for logistic aspects regarding all players.

The first role of the coordinator during the trials was to guide all players into the site for each step of the trial (safety procedures, work permits establishment, installation at site, field measurements…).

The coordinator was the permanent focal point for exchanges with the site representative.

Coordinator was also charged of providing inputs to the field measurements, taking care of the respect of the test plan and the schedule.

He also checked if every expected raw data was recorded, and ensured a backup of these.

Coordinator managed the closing of the project with the site representative and provided assistance for logistic aspects regarding all players.

PHASE 2F - Collection of observations during the trials

Coordinator collected observations from all experts participating to the site study.

Observations during
study rev0.xlsx

Report reference: 389923/7000379-2

To the attention of: CEN WG38

Project followed by: MARTINEZ Jonathan
Operations Manager
Phone: +33 6 17 57 76 79
E-mail: jonathan.martinez@fr.bureauveritas.com

WG38 – Site test #2 – June 2017

Work Package 2 - Report

Writer: Jonathan Martinez

BUREAU VERITAS
Revision 0 – June 2018

Environnement Contrôle Service

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✓ OBJECTIVES

The main objective of the Work Package 2 was to plan and coordinate the field measurement programme.
The coordinator's role was to oversee the mission. He was the guarantor of the good execution of the project.

✓ SCOPE OF WORK

The coordinator's first attribution was to submit to CEN/TC 264/WG 38, a short list of candidate site(s) for the two validation studies identified.

The coordinator was then in charge of establishing the work plans for the two validation studies.

During the field measurements the coordinator provided guidance and inputs to the field measurements.

SUMMARY

I - Phases description and methodology

The performed tasks included the following phases:

1/ - Initial consultation and planning

1A - Candidate sites selection
1B - Test scheduling and coordination with all players for the two sites

---

2/ - Support for validation programme at site 2

2A - Preparation: Logistic organisation - Coordination
2B - Existing data recovering and reviewing of LDAR programmes in place
2C - Drawing up of a tests plan
2D - Site visit
2E - Presence at site 1 during trials
2F - Collection of observations during the trials

---

1) - INITIAL CONSULTATION AND PLANNING

PHASE 1A - Candidate sites selection

The very first step of this phase was to appoint from our resources, the coordinator for the field measurement programme. The selected expert was Jonathan MARTINEZ.

The second step of this phase was to generate selection criteria for sites for the 2 campaigns (taking into account results from WP1). This work was performed in collaboration with WG38 taking into account criteria listed in the tender.

Assisted by our European Centre of Expertise (Fugitive Emissions Management **CoE**) and thanks to our clients' network and reputation, we have then presented the project to a single potential candidate site, corresponding to defined criteria.

The expected weather conditions into the pre-selected plants were taken into account during the selection process.

Upon completion of this step, a short list of candidate sites for the 2nd validation study has been issued and then submitted to CEN/TC 264/WG 38.

List of potential
candidates sites rev0

During a subsequent meeting with all players of the WG38, an active plant (refinery + chemical plant) located in The Netherlands, has been selected.

The next phase has been to present the project to the plant and to convince them to allow us to implement this study on their plant. For this reason, an "Introductory letter" has been written.

Introductory Letter - Rev3.pdf

PHASE 1B - Test scheduling and coordination with all players for the two sites

During this phase, the site coordinator drafted the schedule of all sub-phases of the 2nd field validation test.
To perform this task, he has collected the needs of each player (involved in the execution of WP3, WP4, WP5 and WP6) and ensured their coordination in line with the constraints of the site hosting the test.

He also took care of driving everyone to meet the established deadline.

Requirements from
experts - Rev7 - 170

2) - SUPPORT FOR VALIDATION PROGRAMME AT SITE 1

PHASE 2A - Preparation: Logistic organisation - Coordination

Coordinator provided assistance to coordinate contracts signing between CEN and site.

Together with the site representative, the coordinator was in charge of the delimitation of the "testing area" on the 2nd selected industrial site.

The coordinator then communicated to all involved players through a report, the validated/adjusted schedule and all decisions taken and their reasons.

Scheduled activity
per firm - Rev1 - 250

The coordinator played the role of "focal point" between each actor and the site for all logistic aspects of the project, such as applicable procedures to enter the site (personal, vehicles and tools) or necessary safety trainings…

Document and
information collection

PHASE 2B - Existing data recovering and reviewing of LDAR programmes in place

The coordinator was in charge of "data recovering" regarding LDAR programmes in place on the site. The collected pieces of information were provided to the WG38.

PHASE 2C - Drawing up of a tests plan

Together with WG 38, the selected site, and the selected providers of measurement techniques, the coordinator drew up a test plan for the first validation study.

The test plan took care about requirements of all techniques, especially spatial constraints.

This test plan took into account the defined duration of the tests.

It was anticipated that the complete field campaign will have a duration of approximately three weeks.

Measurement Plan (Basic) - Rev0 - 300317.pdf
Measurement strategy.pdf
Instruments location on site rev2 - Final and real.pdf

In order to ensure the confidentiality between all techniques, the communication of detected emissions location has never been done on the radio without preliminary information coding.
For this reason, some maps with different grids have been provided to each technique representatives and only the OGI operator and the field tests coordinator had access to the key maps.

Fluxsense.pdf
Npl.pdf
Total.pdf

PHASE 2D - Site visit

Coordinator organised and led 2 pre-study visits to the industrial site (one in February and one in March).

This visit notably permitted discussions with the plant owners, to ensure that the defined validation work programme is practical and achievable during the selected times and within the allocated time scale.
Qualified scientists participated to this visit.

PHASE 2E - Presence at site 1 during trials

Coordinator led the opening of the project with the site representative and provided assistance for logistic aspects regarding all players.

The first role of the coordinator during the trials was to guide all players into the site for each step of the trial (safety procedures, work permits establishment, installation at site, field measurements…).

The coordinator was the permanent focal point for exchanges with the site representative.

Coordinator was also charged of providing inputs to the field measurements, taking care of the respect of the test plan and the schedule.

He also checked if every expected raw data was recorded, and ensured a backup of these.

Coordinator managed the closing of the project with the site representative and provided assistance for logistic aspects regarding all players.

PHASE 2F - Collection of observations during the trials

Coordinator collected observations from all experts participating to the site study.

Observations during
study rev0.xlsx

METEOROLOGICAL DATA FROM THE SECOND WG38 FIELD CAMPAIGN

INTRODUCTION

The European Commission has requested the development and validation of a European Standard that can be used for the determination of fugitive and diffuse emissions of VOCs to the atmosphere from certain industrial sectors.

The European Commission's standardisation mandate M/514 under the Directive 2010/75/EU on industrial emissions has been accepted by CEN/BT and a decision has been taken to establish this standardisation work with CEN/TC 264/WG 38.

VDI issued a call for tender for field validation tests, controlled release, for data evaluation and for a project coordinator for the development of standardized method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere.

METHODOLOGY

Meteorological measurements have been carried out during the first field trial to derive wind speed and direction profiles in a vertical plane.
INERIS has assisted the contractor of WP2 "Planning and coordination of the field measurement programme" in order to determine the suitable locations to deploy the meteorological sensors around the selected site for controlled releases. After the site visit (May 2016), a consensus between all partners has decided that the set of stations to be deployed would be:

- Three identical met stations, placed around the unit. Each of these stations has been equipped with the same sensors (VAISALA WXT520), fixed on top of a 10 meters mast.
- A wind LIDAR (LEOSPHERE WindCube), placed in the expected dispersion area, i.e. south from the unit.

EQUIPMENT

INERIS has deployed the following equipment:

METEOROLOGICAL SENSORS

INERIS has deployed three Vaisala WXT 520 sensors that measure wind speed and direction as well as temperature, barometric pressure, humidity and precipitation. Vaisala Ultrasonic Wind Sensor uses ultrasound to determine wind speed and direction. The sensor has no moving parts, which makes it independent of the limitations of mechanical wind sensors such as friction, inertia, time constant, over-speeding, and starting threshold. Every sensor is regularly controlled and certified by the manufacturer:

Wind Speed Accuracy +/- 3% at 10 m/s
Wind Direction accuracy +/- 3°

Every sensor has been fixed on a 10 m telescopic mast.

WIND LIDAR

INERIS has deployed a mobile Doppler LIDAR vertical profiler from LEOSPHERE that continuously measures wind data at twelve different heights, mapping wind speed and direction, turbulence and wind shear with the following performance criteria:

Speed accuracy: 0,1 to 0,5 m/s (from 0 to 60 m/s)

Direction accuracy: 2

SENSORS LOCATION

Each station has been deployed at a location around the unit with the most open area. For precise location of the stations, please refer to the Figure 3.1

INERIS_S

INERIS_SE

INERIS_N

Wind LIDAR

DATA ACQUISITION AND PROCESSING

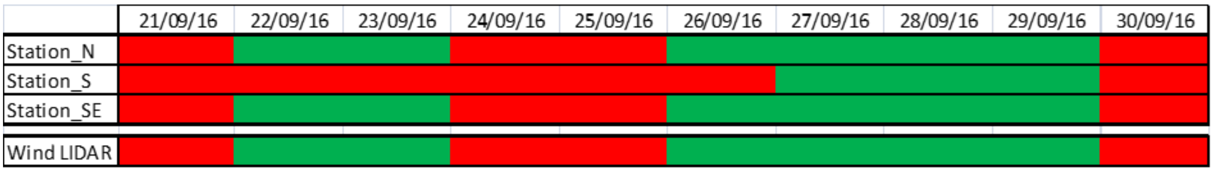
Specifications for data acquisition and processing as well as data base format has been defined in consultation with WG 38.

Met stations: measurement at 10 m, 1-minute averaging, local time.

Wind LIDAR: measurement at 12 different heights (40 m, 50 m, 60 m, 70 m, 80 m, 90 m, 100 m, 120 m, 140, 160, 180, 200 m), 1-minute averaging, local time.

RESULTS

All instruments except the met station “Station S” have been running without any problem during the test releases. Only the station “Station S” has faced some acquisition problems, causing the loss of three days of data, out of six.



	21/09/16	22/09/16	23/09/16	24/09/16	25/09/16	26/09/16	27/09/16	28/09/16	29/09/16	30/09/16
Station_N	🟥	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥
Station_S	🟥	🟥	🟥	🟥	🟥	🟥	🟩	🟩	🟩	🟥
Station_SE	🟥	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥
Wind LIDAR	🟥	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥

Figure 1 Gantt diagram – met data acquisition

ANNEX A: WIND ROSES FOR COMPARISON OF THE INERIS WIND DATA

Wind roses have been prepared by INERIS to compare the wind data from each of their instruments on a daily basis for the duration of measurement at Test Site 1.

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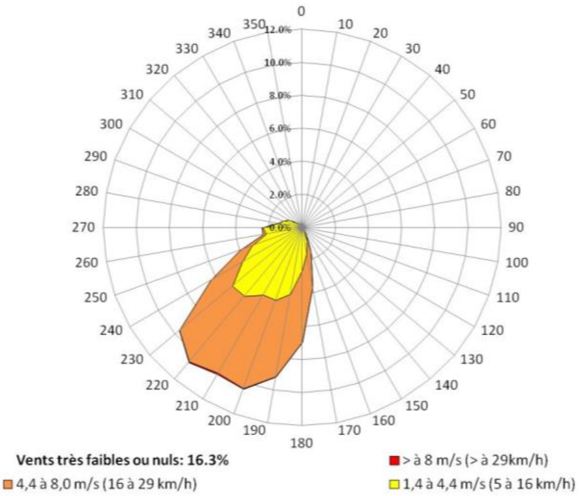
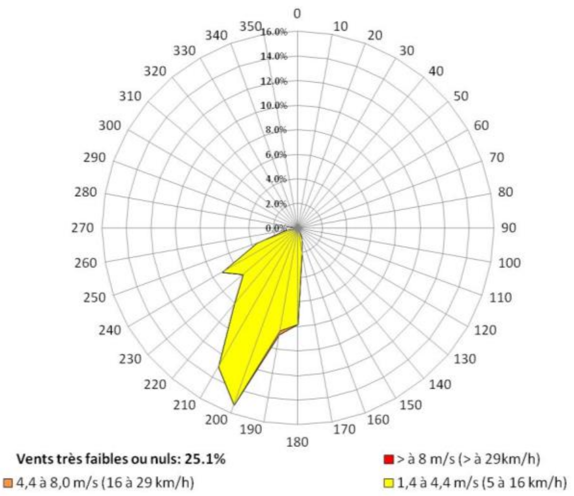
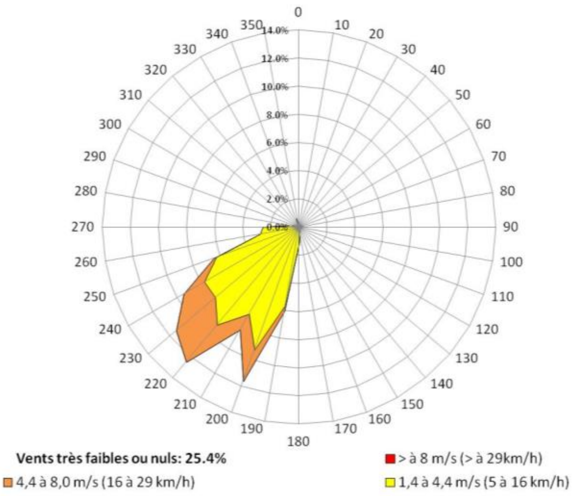
<tr><td> </td><td> </td></tr>
<tr><td>Wind LIDAR 40 m</td><td>Station N 10 m</td></tr>
<tr><td>-</td><td> </td></tr>
<tr><td>Station S 10 m</td><td>Station SE 10 m</td></tr>
</table>

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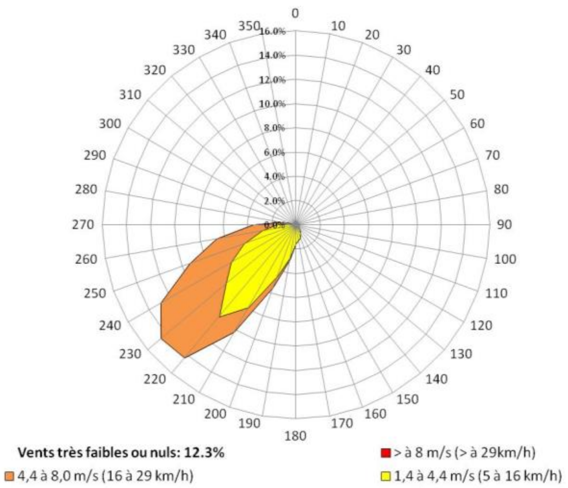
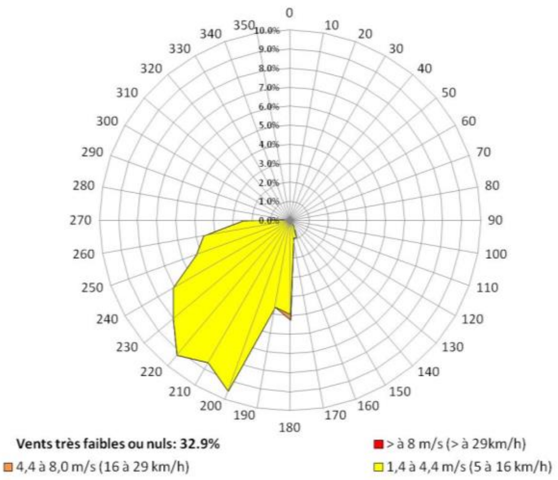
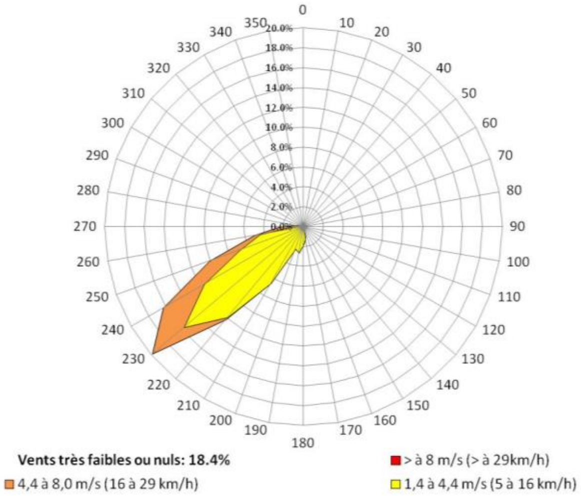
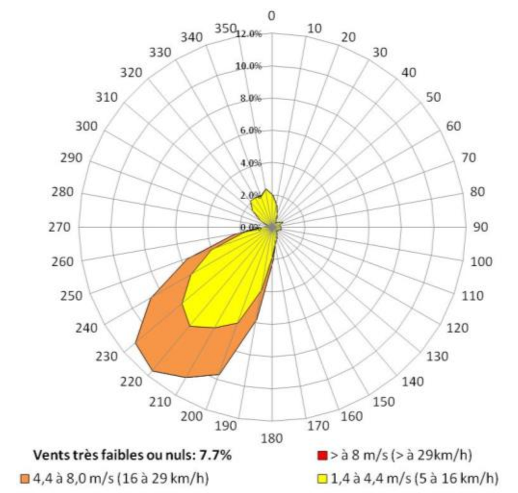
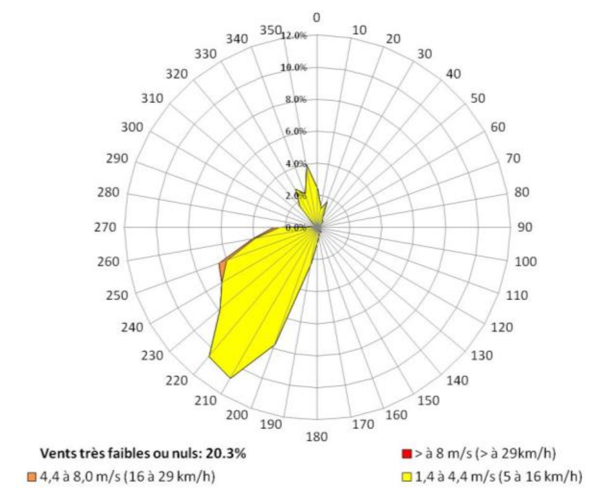
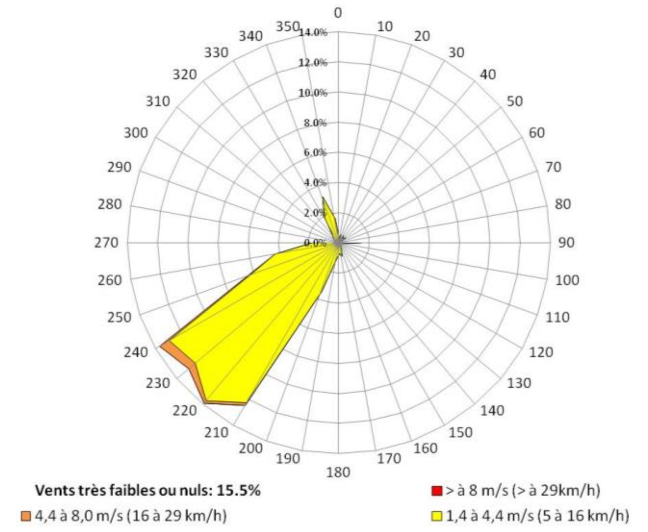
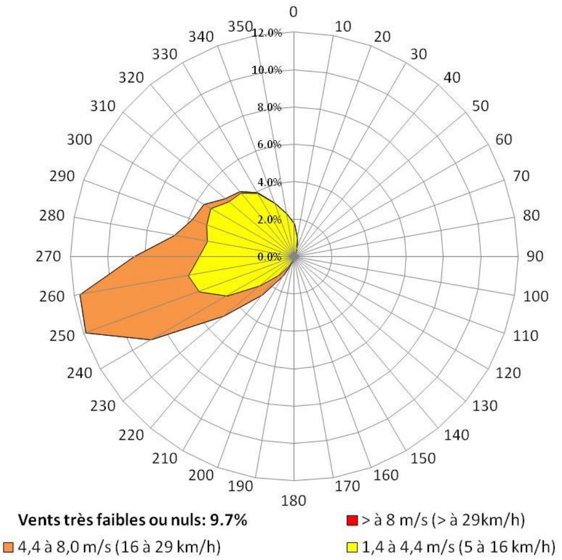
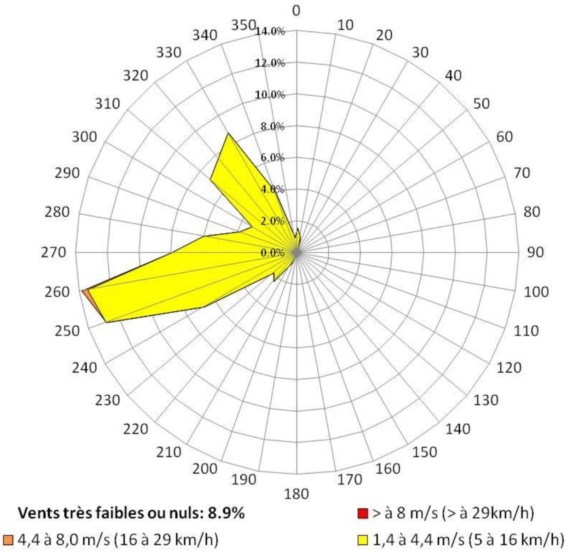
	
Wind LIDAR 40 m	Station N 10 m
-	
Station S 10 m	Station SE 10 m

26/09/2016	
	
Wind LIDAR 40 m	Station N 10 m
-	
Station S 10 m	Station SE 10 m

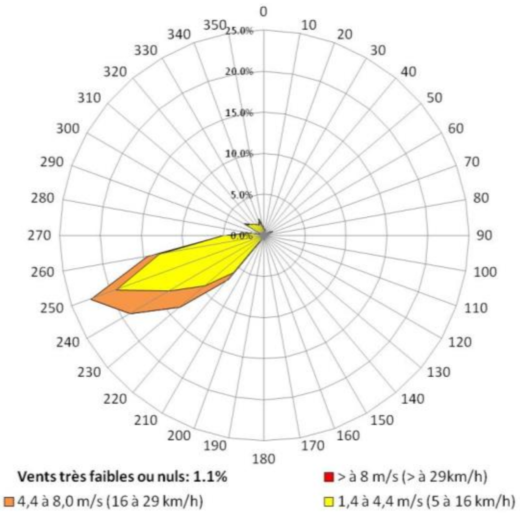
27/09/2016



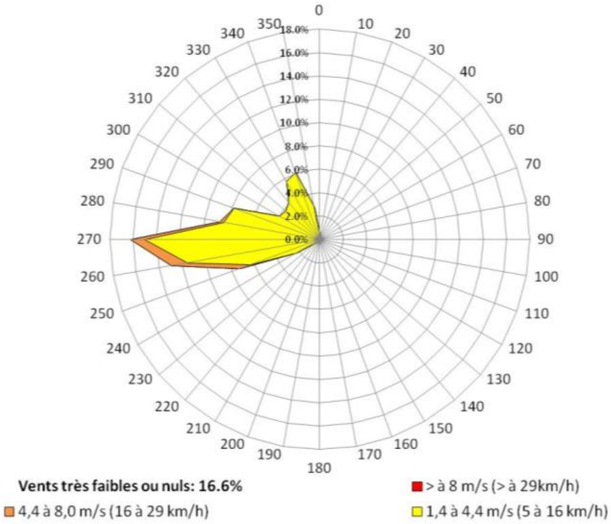
Wind LIDAR 40 m



Station N 10 m

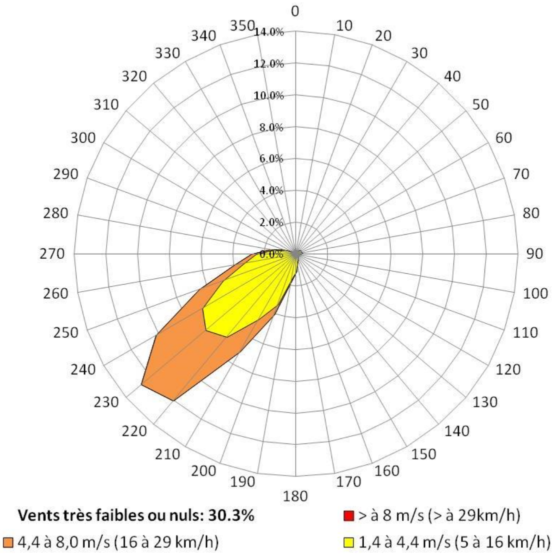


Station S 10 m

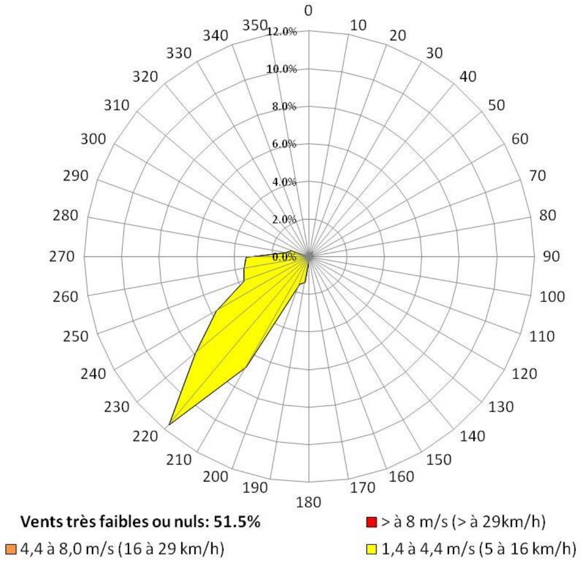


Station SE 10 m

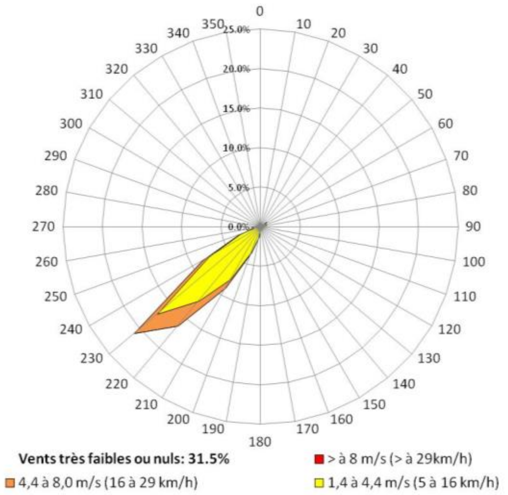
28/09/2016



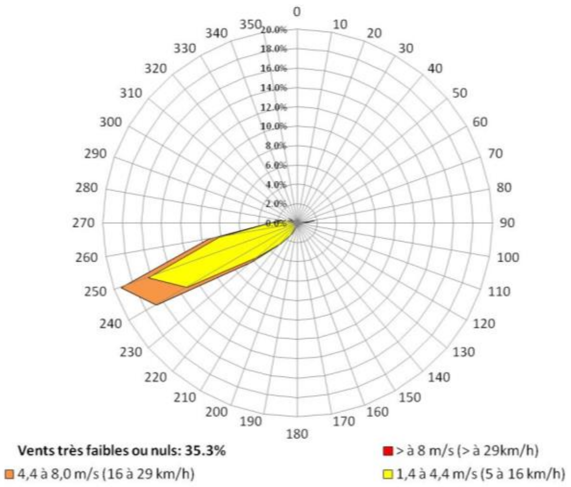
Wind LIDAR 40 m



Station N 10 m

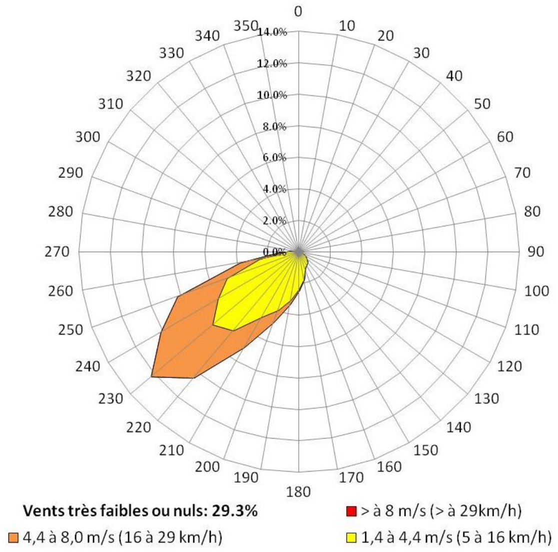


Station S 10 m

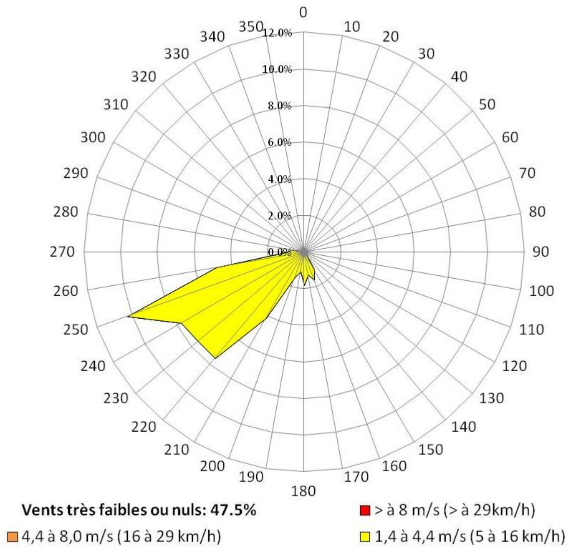


Station SE 10 m

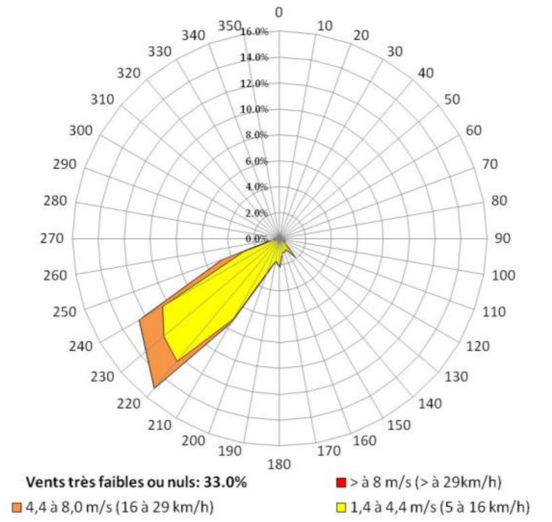
29/09/2016



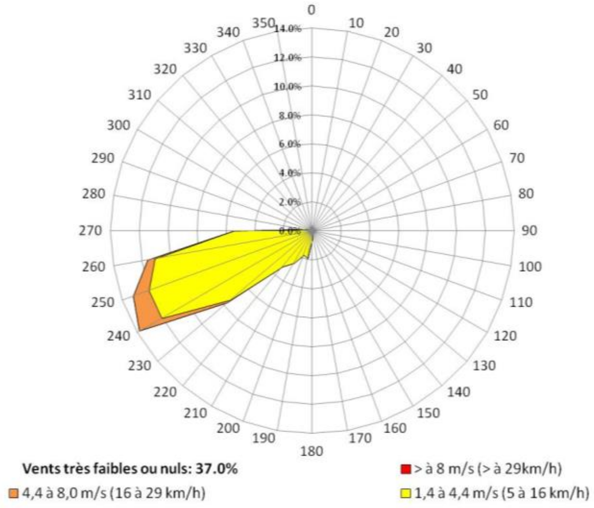
Wind LIDAR 40 m



Station N 10 m



Station S 10 m

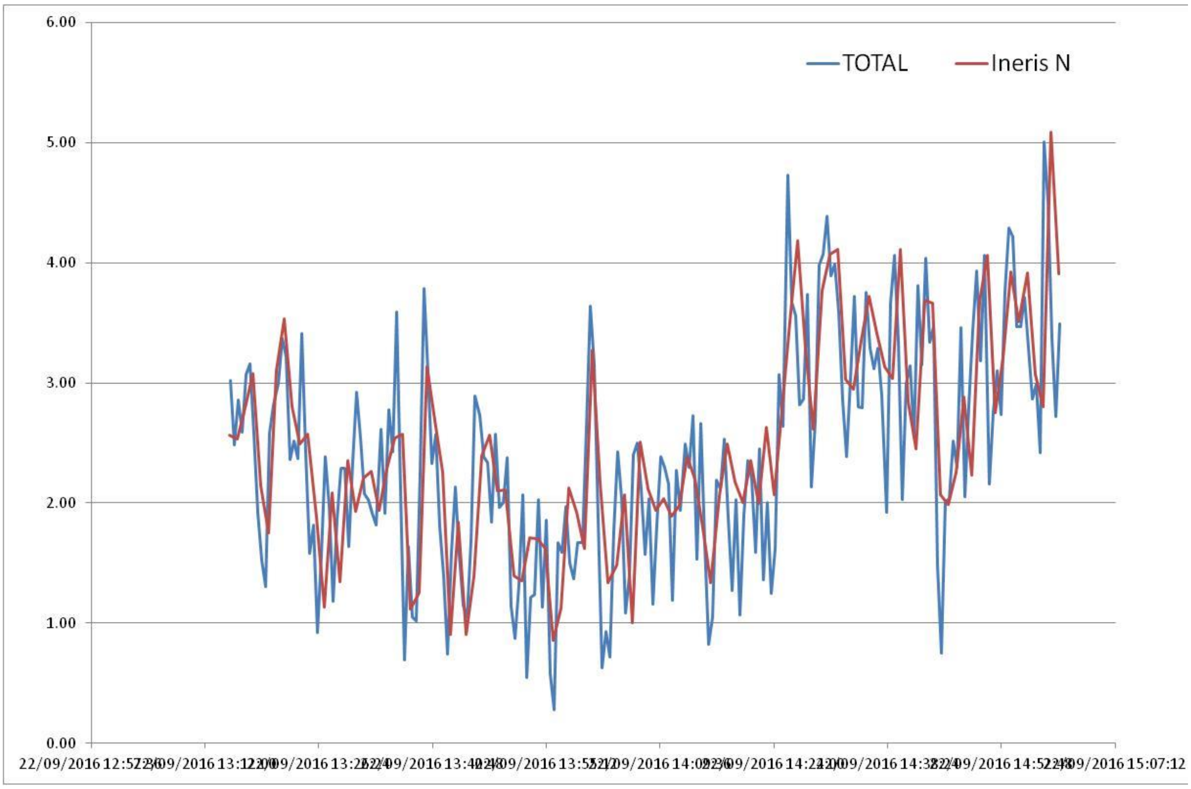


Station SE 10 m

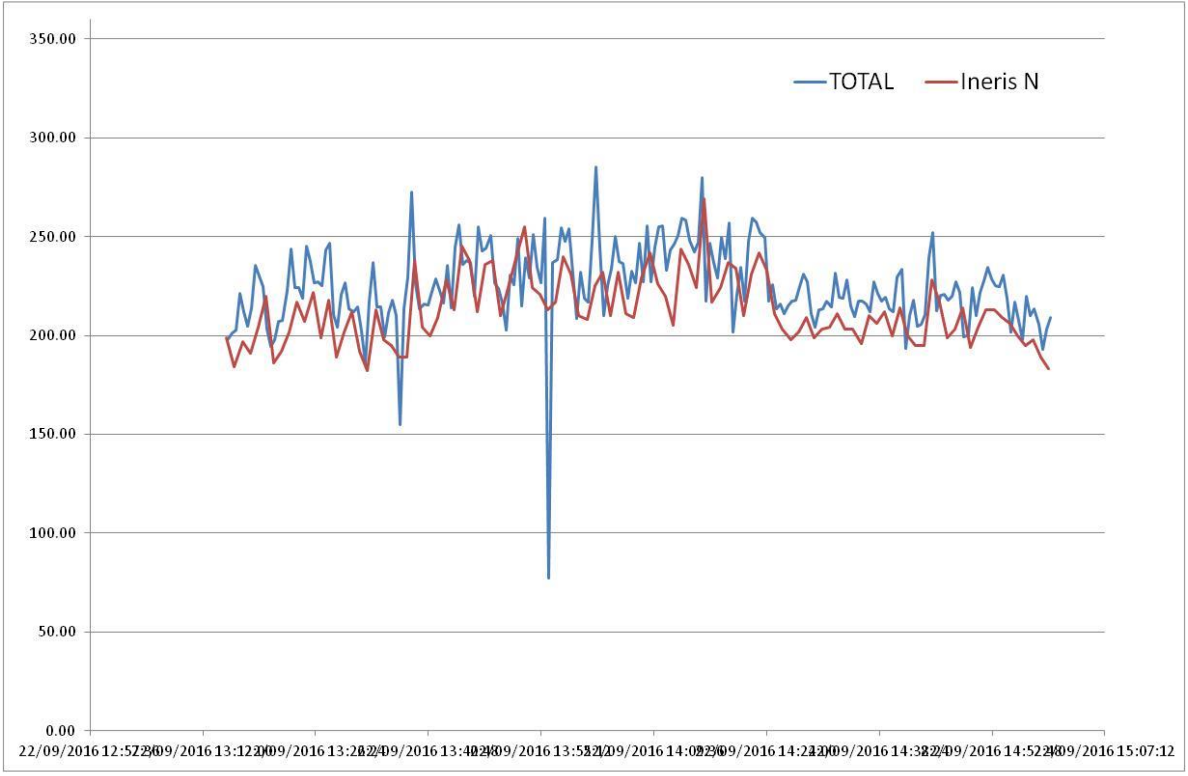
C.8 COMPARISON OF TOTAL AND INERIS NORTH MET STATIONS

The INERIS North met station was collocated with the Total met mast. The following plots illustrate the degree of alignment achieved by the two met stations.

Test # 1 – 22/09 13h15 15h00

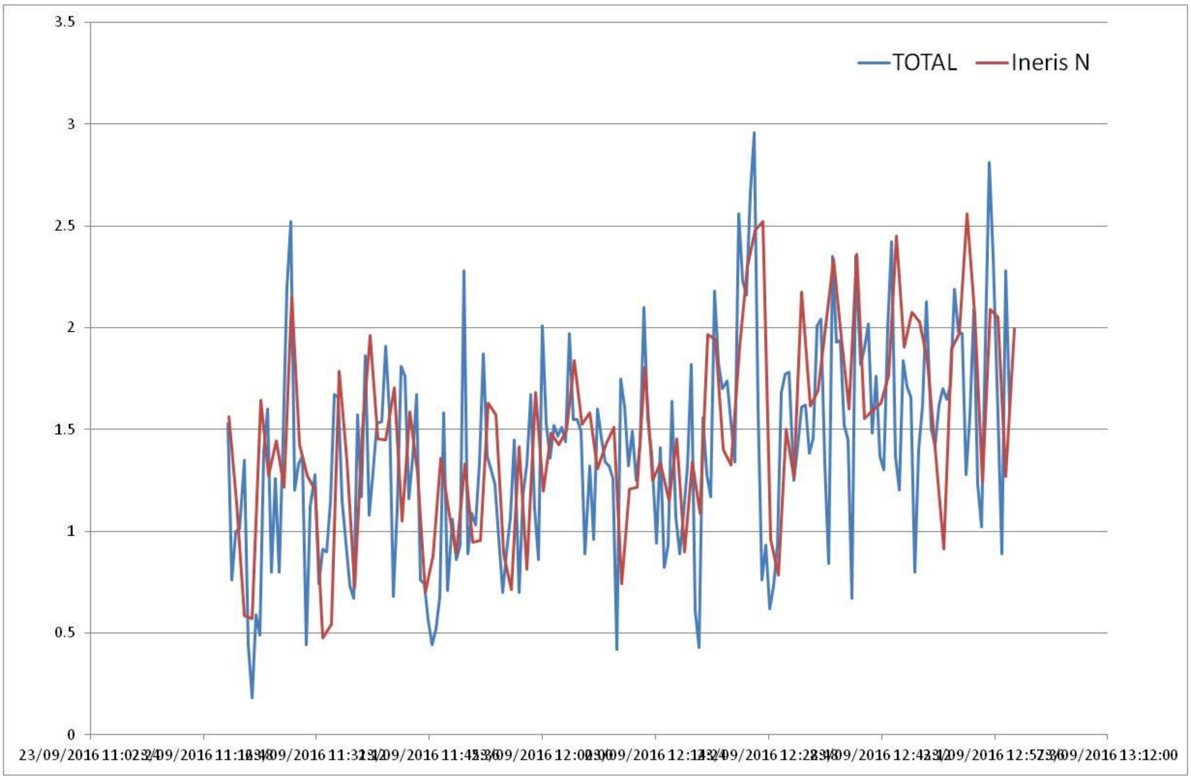


Wind speed

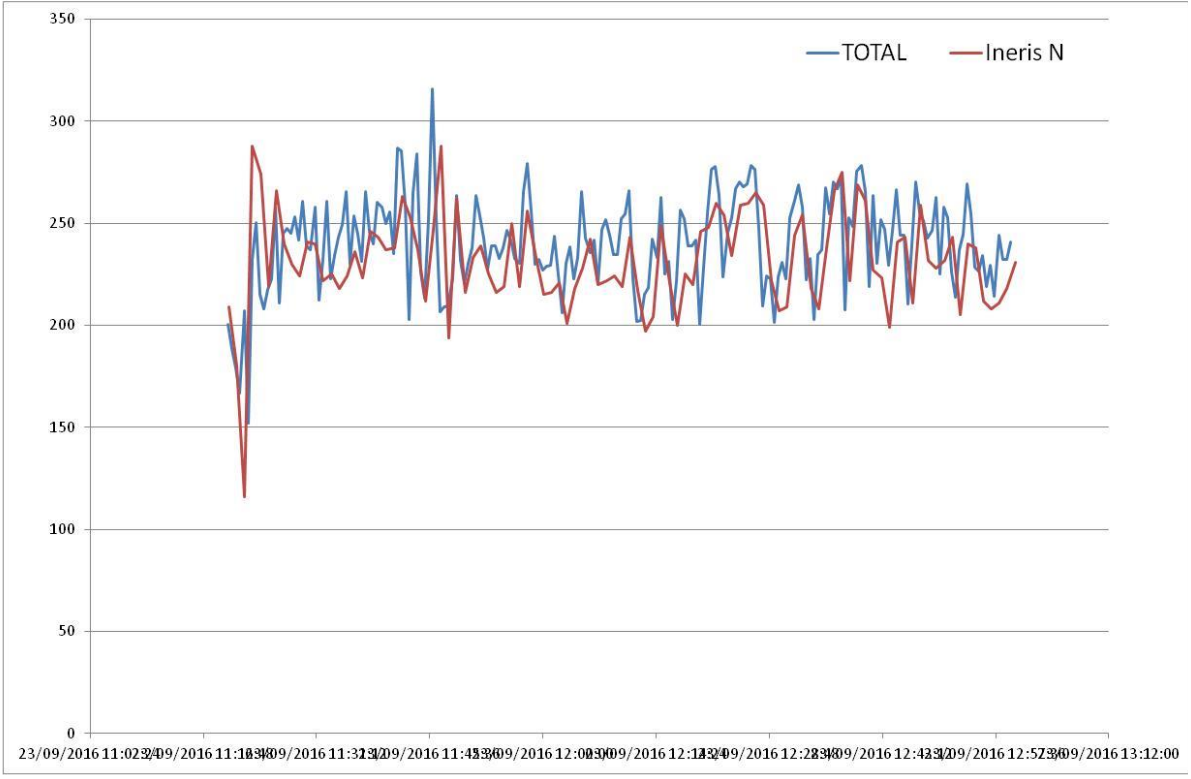


Wind direction

Test # 3 – 23/09 11h20 13h00

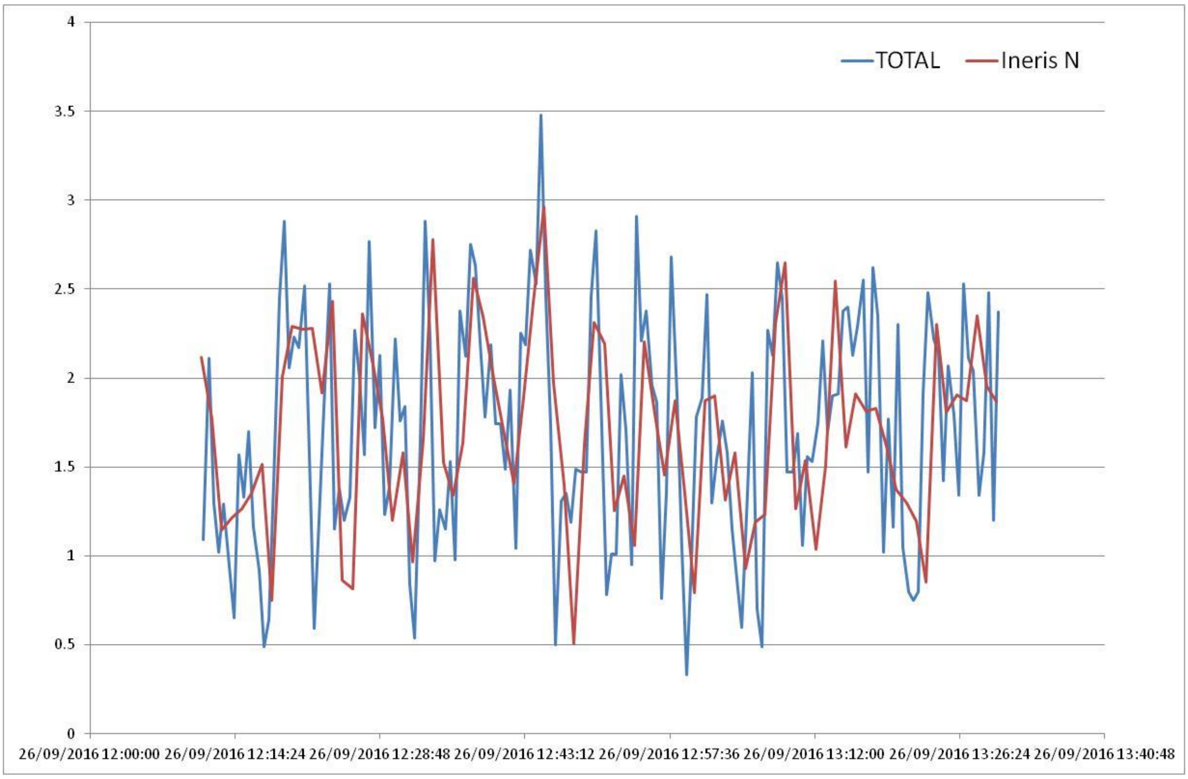


Wind speed

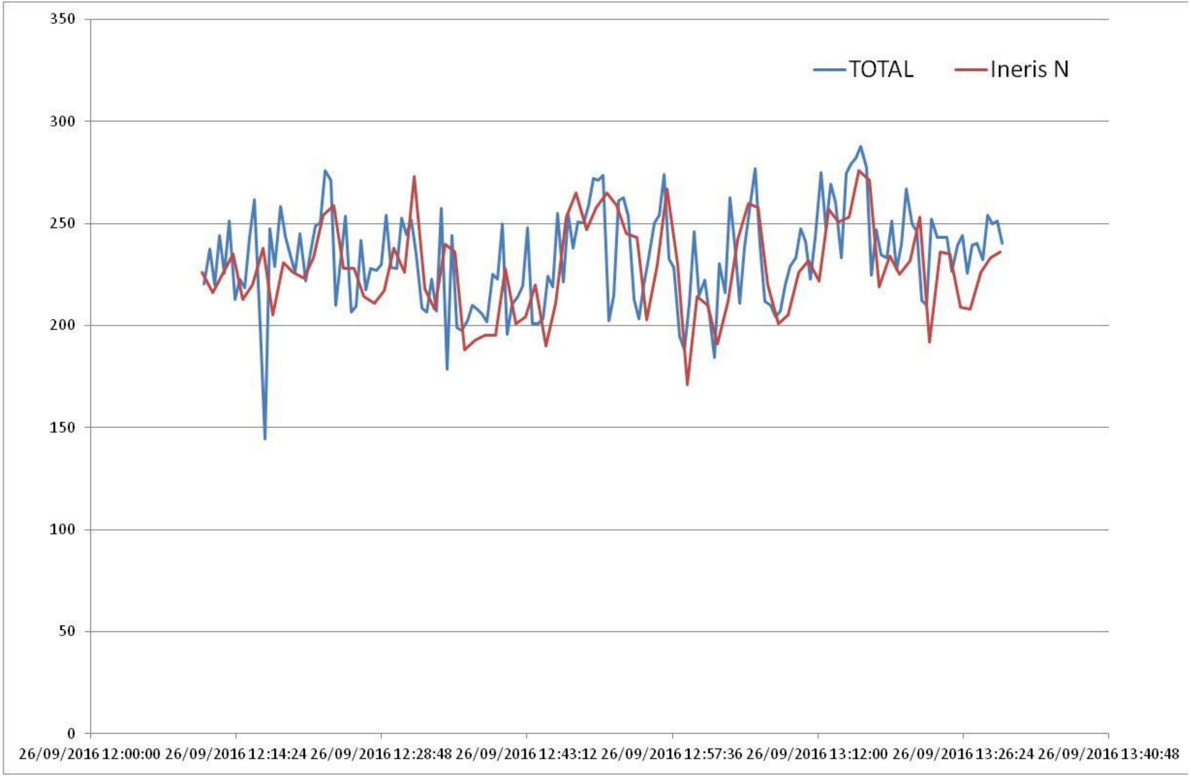


Wind direction

Test # 6 – 26/09 12h11 13h30

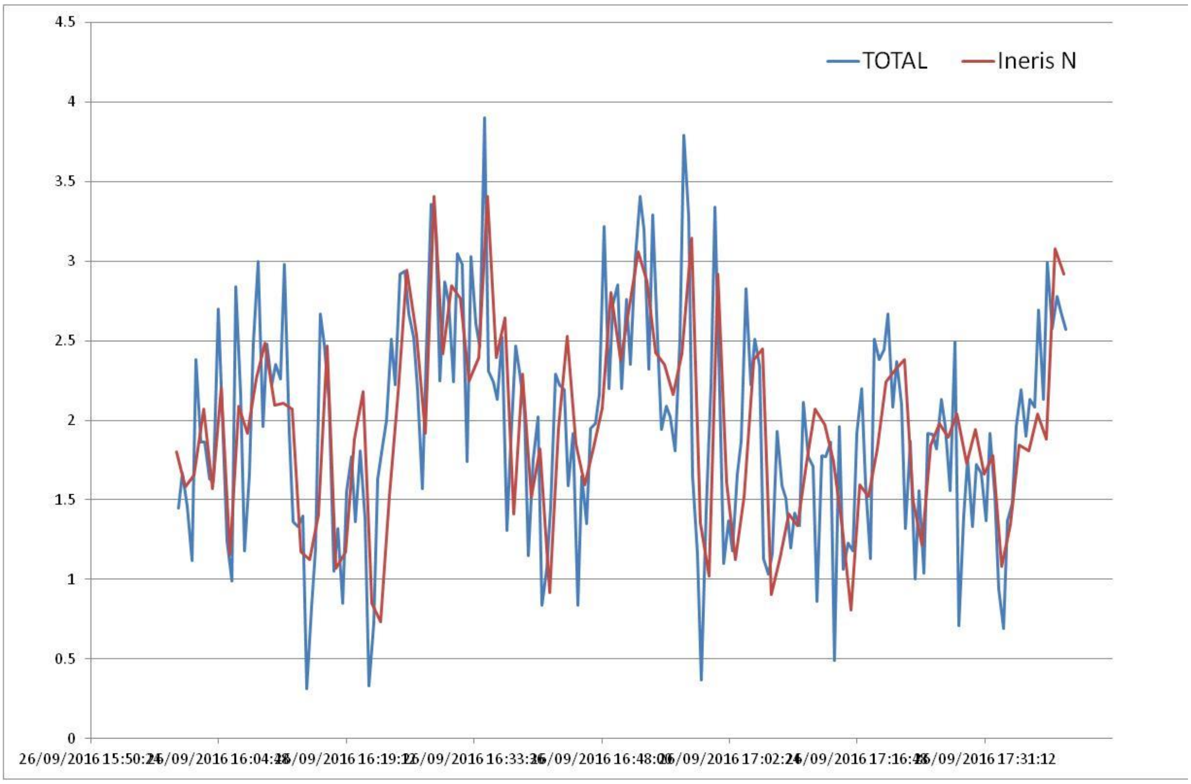


Wind speed

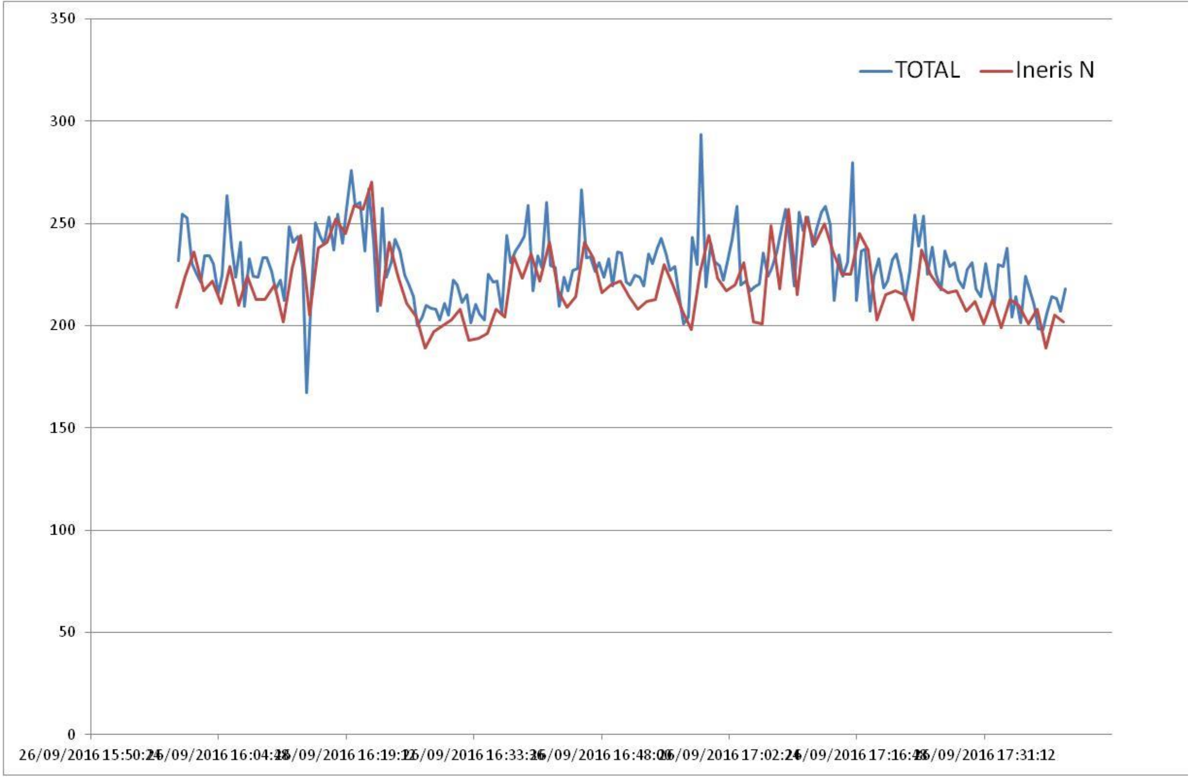


Wind direction

Test # 8 – 26/09 16h00 17h40

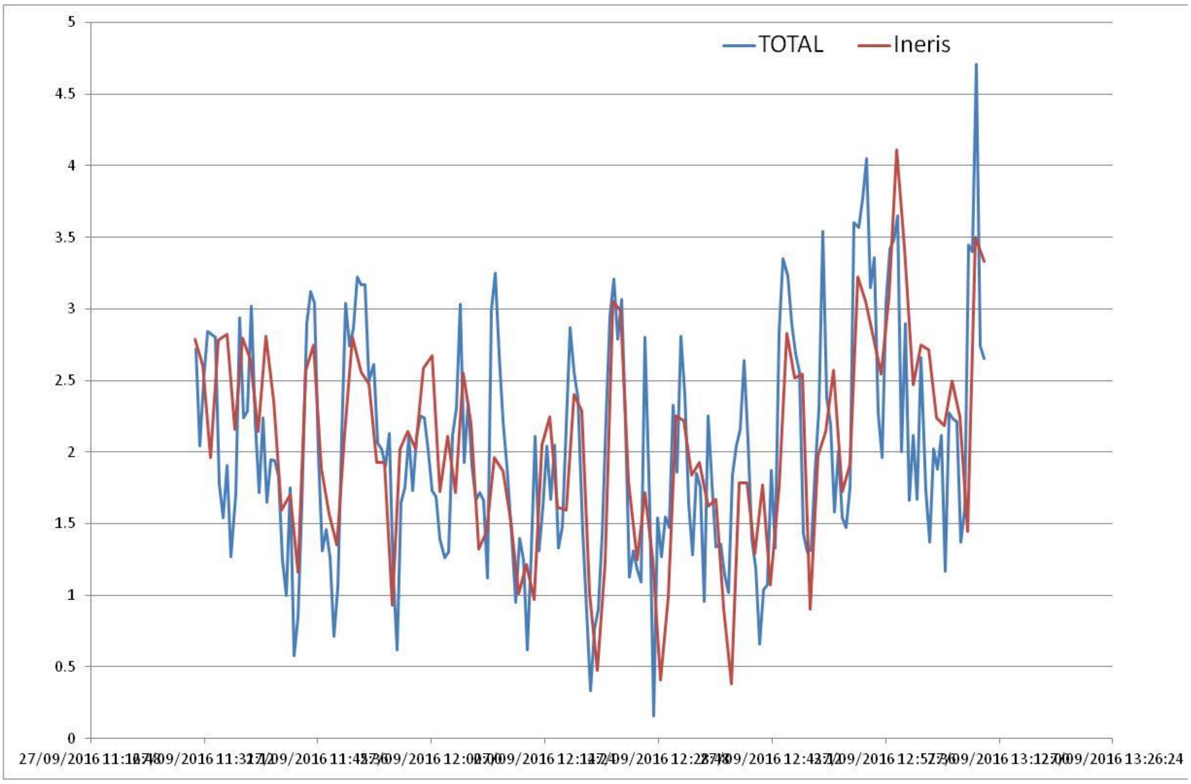


Wind speed

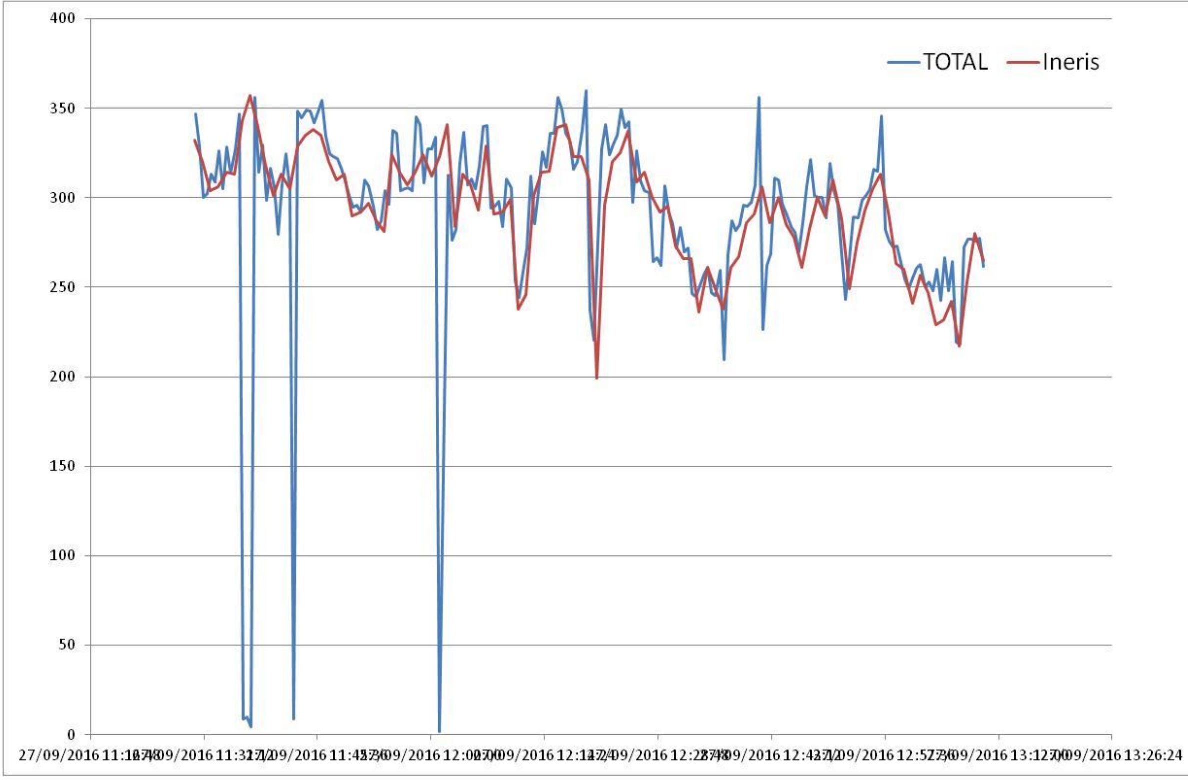


Wind direction

Test # 10 – 27/09 11h30 13h10

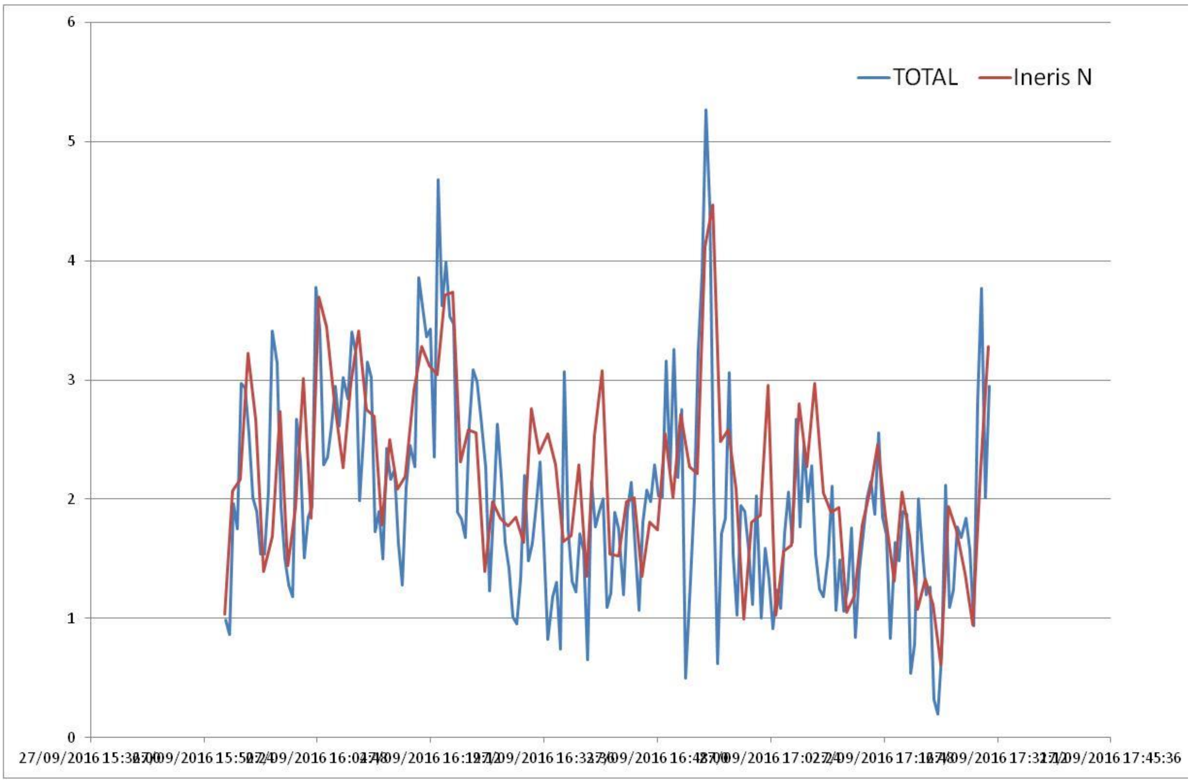


Wind speed

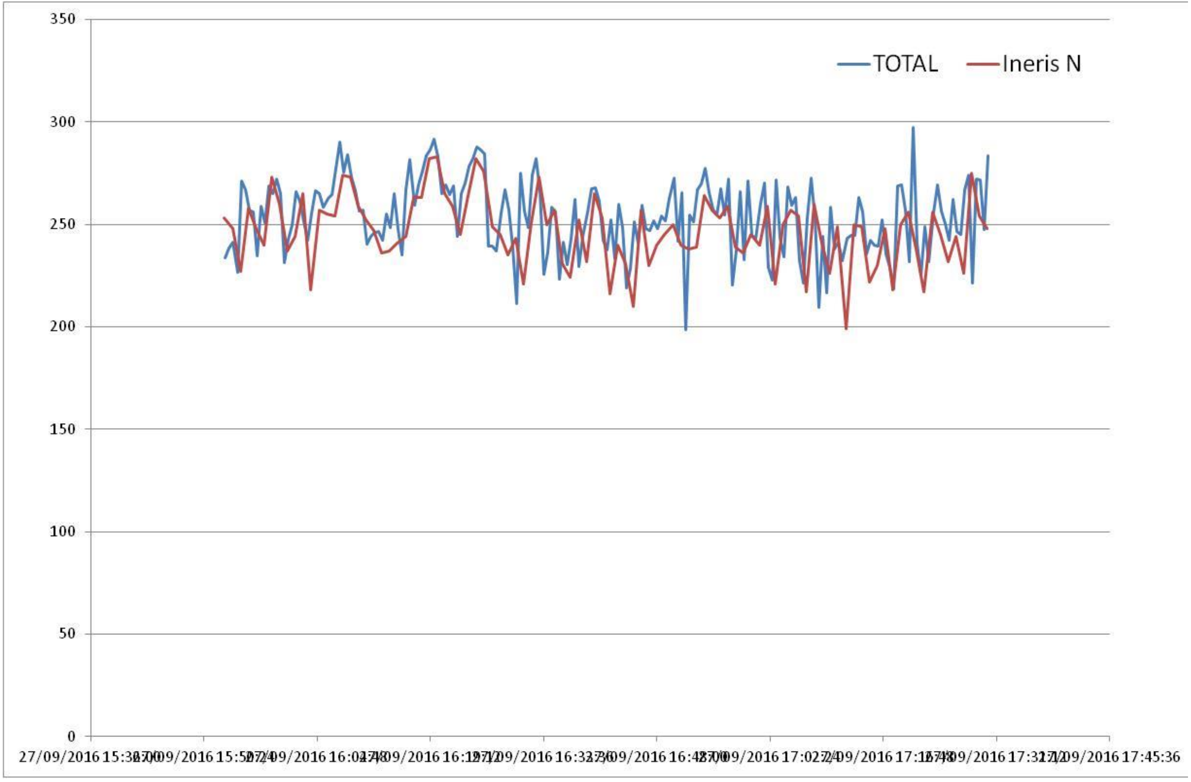


Wind direction

Test # 12 – 27/09 15h53 17h30

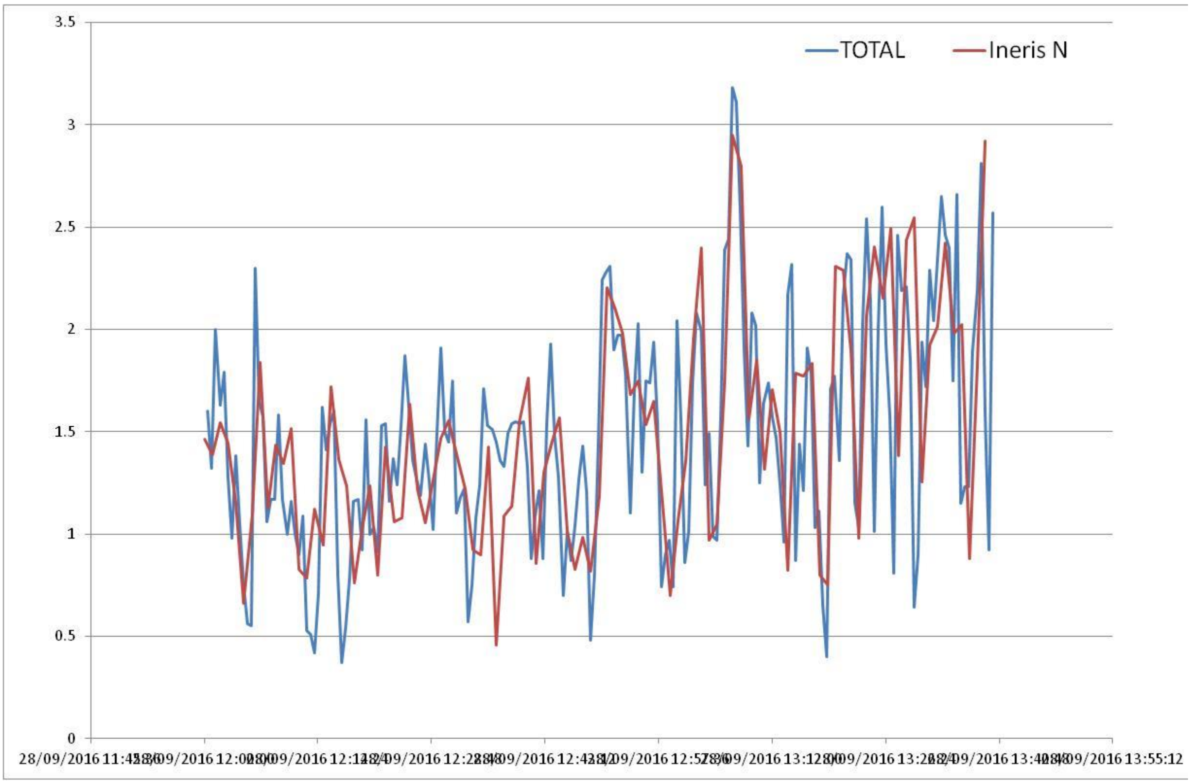


Wind speed

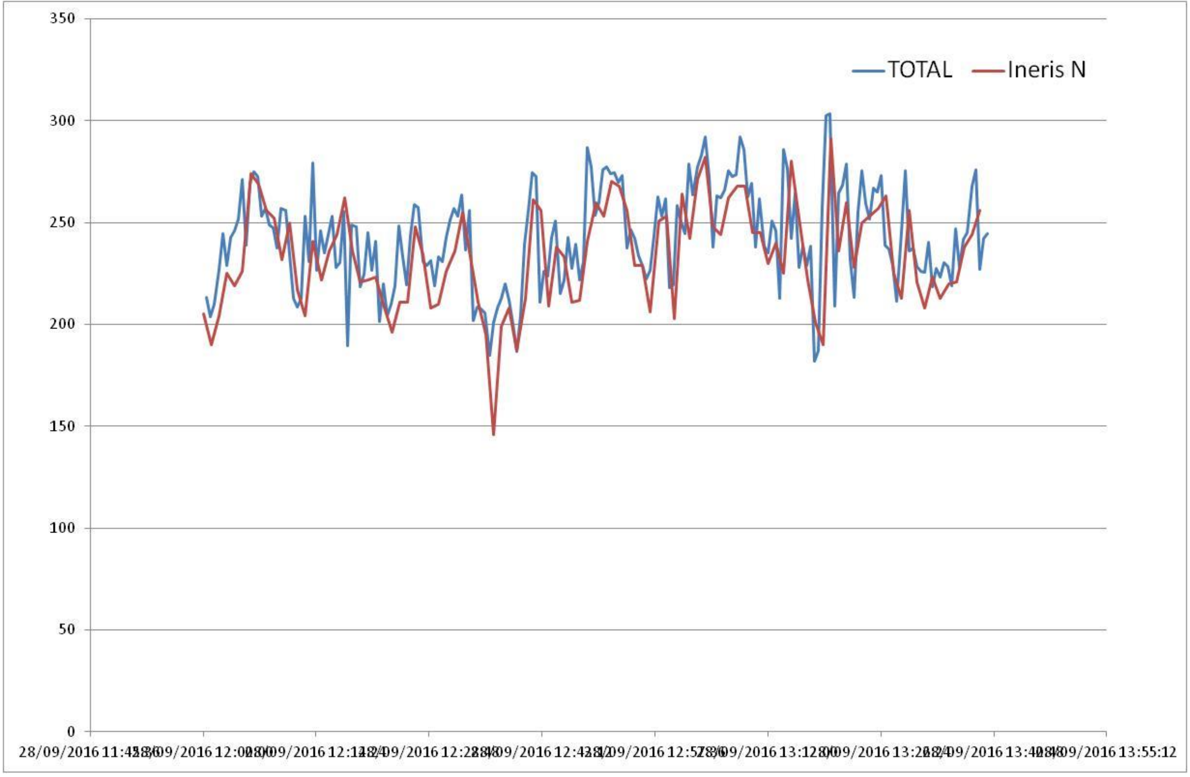


Wind direction

Test # 14 – 28/09 12h15 13h39



Wind speed



Wind direction

METEOROLOGICAL DATA FROM THE SECOND WG38 FIELD CAMPAIGN

INTRODUCTION

This note is a short description of the wind data from the fixed monitoring stations from CEN WG38 Phase II project together with the wind-lidar.

SUMMARY AND CONCLUSIONS

A comparison of day time wind measurements at three refinery locations supported by upper air measurements at intervals up to 200 m show some important features. The measurements use anemometers on 10 m masts.

There is a significant turbulence and data have been smoothed using a ten-minute moving average. There remains variability on time-scales less than an hour. It can be generally said that wind-speeds may vary by +/- 1 m/s and directions by +/- 20^o at times within an hour. At any one moment it is possible for different stations to give (smoothed) wind-direction differences of 40^o. These two observations are for periods where the general wind behaviour logged at the stations is similar. Variability does appear often appear periodic with a cycle taking ~1hr. A spectral analysis of the data would be needed to be more precise and establish correlations in time between the stations that would test the time-of-flight of turbulence of refinery scale.

There are some periods where consistent differences between stations is apparent. These take two main forms:

- Sheltering. One station is measuring a wind-speed that is less than the other two stations.
- Diversion. One station is measuring a wind-direction that is different to the other two stations.

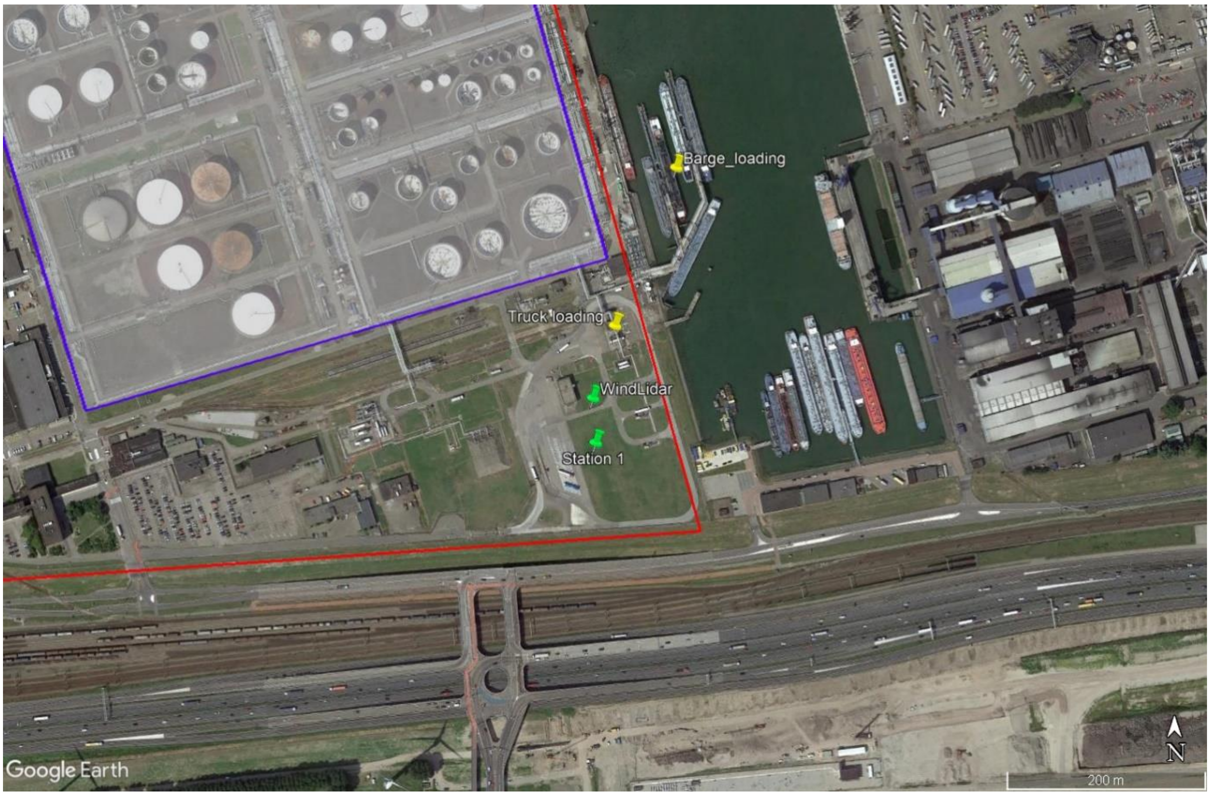
Surprisingly there seem to be few instances where both wind-direction and wind-speed are obviously different at one station compared to the others. There are occasions when all three are different.

Of the three stations the one at the Truck-Loading are in the SE of the refinery is most often similar to one or other of the other two stations. This station is collocated with the wind LIDAR that gives upper air data. The upper air data for wind-direction, which should be less influenced by the refinery structures appears consistent with the collocated mast measurements. Therefore, the discussion will mainly concern how measurements at the other two stations differ either from each other or from the ensemble of the other two where these are similar.

- On one occasion measurements at the station at the truck loading (SE) appeared different to the other two
- On five occasions measurements at the station at the North West tanks (NW) appeared different to the others.
- On nine occasions measurements at the South West units (SW) appeared different to the others.

Here occasion means a day or part of a day. A day is taken to be 08:00 to 20:00.

The difference at the truck loading occurred with a falling wind-speed and after a shift in wind-direction from SSE to W. As the figure below shows it is credible that with the wind due Westerly and reducing wind speed the wind direction at Station1 (the tanker loading) should bias to the SW due to the blocking of the wind by the tank farm and the factory buildings East of Station 1.

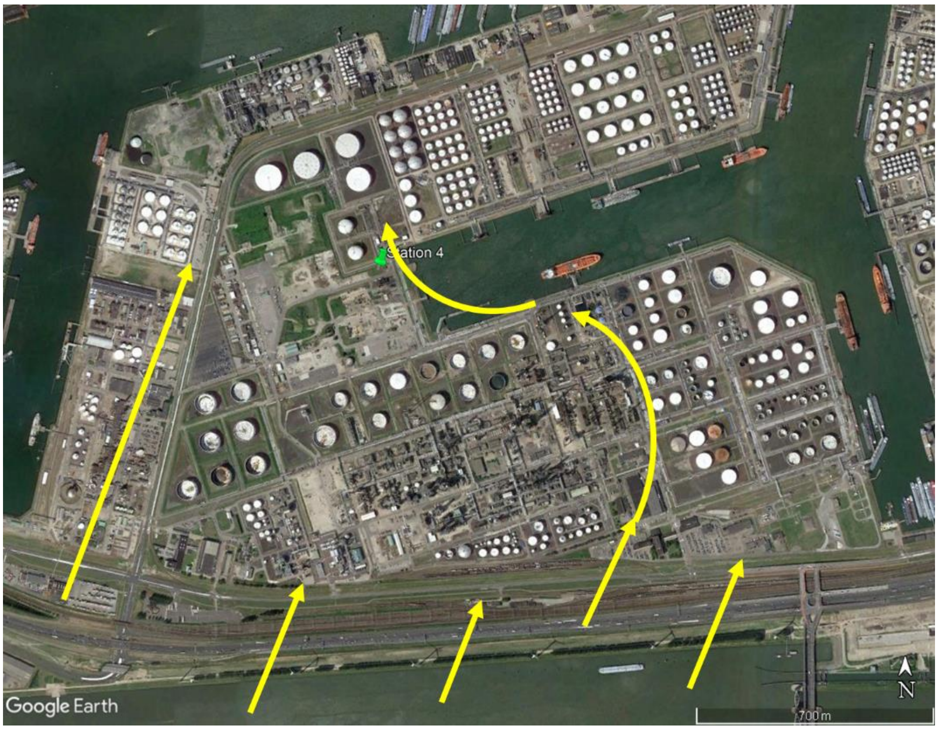


The five period differences observed at the North Tanks Station were:

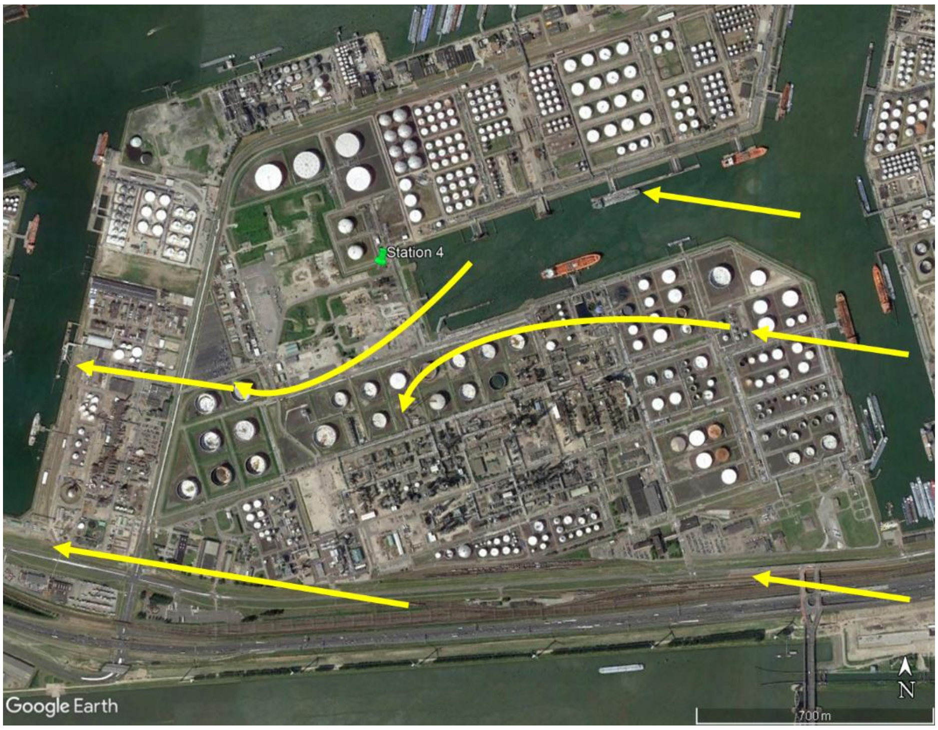
- Station measures SSE when the other stations measure SWS or S.
- Station measures S when others measure SE.
- Station measures ENE when other stations measure ESE and wind speed is low.
- Station measures E to ENE when others measure E turning ESE.
- Station measures variable E to ENE when others measure E to ESE and wind speed lower.

As the figure below shows, the North Tanks station (Station 4) lies at the West end of a canal oriented ENE. From the other side the ground is fairly clear for wind-directions that are WSW to WNW. There are several tanks between NW and N and dense arrays of storage tanks between N and almost ENE. Tanks and the main body of the refinery block other wind-directions.

It seems possible that there can be a complex flow in the canal area with features of the wake behind the main refinery process being reinforced by blockage by the Northern Tanks. Two suggestions are sketched in the figures below. No explanation comes to mind as to why the wind-speed on one occasion was less than at the other two stations with the wind in the East, unless the wind speed is augmented in some way at the other stations for this direction.



Wind turning slightly East for slightly west of south or south winds



Wind turning slightly north of east for slightly south of east winds

The South Tanks station shows the greatest number of differences from the other two stations and a greater disparity in wind-speed. The nine period differences were:

- Lower wind speed when wind is in the WSW

- Direction SSW when others are SW
- Lower wind speed when wind is just S of W
- Lower wind speed when wind is in the WSW
- Direction tends to W when others are NW
- Lower wind speed when wind is WSW
- Lower wind speed when wind is SW
- Direction tends to W when others are NW
- Direction tends to NNW when others are NNE and lower wind speed

The South West station (Station 2) location is partially enclosed with buildings to the SW and SE, a process unit to the E and a process area to the North. It is relatively open to the South.

The majority of the cases of lower recorded wind speed are when the Wind is WSW and SW. This places the Station behind the building and the presumption is that it is sheltered to an extent. It is a bit surprising that the wind is not consistently different during these periods but all the stations show considerable variation in time.

With the wind in the North West the station registers a more westerly wind. This could be a local deflection of the wind around the north bounding process area and around the process unit to the East of the station. There are roads heading ENE that would encourage such a flow.

With the wind in the NNE the likely flow out of the area where the station is to the South and the incoming flow has to pass through the process area. It is credible then that the Station indicates NNW.

THE IMPLICATIONS FOR THE STANDARD ARE:

Reference Stations at three corners of the refinery are capable time, to time, to measure different wind speeds and directions. On a 10-minute smoothed average basis the difference between stations in direction can be taken to be 20^{o} attributable to turbulence.

For particular wind directions there can be systematic differences in wind-direction of 45^{0}. Heuristic reasons for these can be found by looking at the stations in respect of the site. The key point is that local topography can affect the measurements.

A relatively confined station showed the most effect of interference of the wind by structures. This has implications both that reference stations should be clearly situated and that measurements made during remote sensing will also be affected by the effect of structures on local wind-flow.

Lidar provided a useful view of the upper wind. This could help resolve ambiguity about which of the 10 m mast measures were most representative of the incoming wind.

Lidar showed that vertical wind shear (velocity gradient) was relatively shallow up to 200m for the daytime duration of this study. Strong stratification, associated with stable atmospheric conditions, persisted past 08:00 on one day. The night-time record has not been inspected because only day-time concentration measurements were made.

There is periodicity apparent in all the horizontal wind measurements, both for the ground stations and for the LIDAR. There is also regular evidence of periods of alternate up and down flow at the LIDAR station. There is not much scope to identify convective conditions but it would be worth conducing some spectral analysis of the data to identify frequencies as this may have implications for measurement strategy.

Description

The three stations were located on the refinery as shown in the following figure. In the bottom right hand corner the wind LIDAR system is next to Station 1 (truck loading). Station 4 is called North West tanks in this report and Station 2 is called South West tanks.

Data was logged as 1 minute averages and reported in a spread-sheet.

Method

For the purposes of this note the 1 minute data was smoothed using a 10-minute moving average centred on the current time. This is the procedure used by FluxSense as reported at the WG 38 meeting in December. For example, in the table below the reported moving averages for minute 5 (red text) are based on the shaded text. Minute 0 is the start of <u>output</u> for the moving average and requires 4 minutes of preceding 1 minute data for the calculation.

	10 minute moving average				One minute	
time from start	Scalar Speed	Vector Speed	Wind-Direction	persistence	Scalar speed	Direction
0	*4.509*	*4.458*	*218.5*	*0.989*	3.752	216
1	*4.442*	*4.429*	*220.3*	*0.997*	4.416	224
2	*4.378*	*4.365*	*220.6*	*0.997*	5.042	224
3	*4.296*	*4.266*	*218.1*	*0.993*	3.895	222
4	*4.149*	*4.121*	*217.3*	*0.993*	3.857	220
5	4.299	4.267	218.4	0.992	3.085	214
6	4.37	4.336	216.8	0.992	4.158	211

7	4.476	4.424	213.6	0.988	4.371	223
8	4.577	4.528	213.1	0.989	4.829	203
9	4.674	4.62	213.7	0.988	4.087	216
10	4.87	4.814	214.2	0.988	5.254	225

Calculated were the average scalar wind speed (U), the modulus of the 10-minute wind vector (V) and the average wind direction (θ). The persistence $P = \frac{V}{U}$ indicates the variability of the wind-direction over the interval. A value P=1 denotes a constant wind-direction over the averaging period. A value close to zero indicates there was no preferred wind direction.

Daytime measurements are reported here for brevity as the accompanying remote sensing tasks were not conducted at night. Daytime is taken to be 08:00 – 20:00. The first day of data collection was June 08th 2017 and data was processed from 13:00.

The same averaging procedure was applied to the 1-minute resolution wind LIDAR data at each of the reported data heights. These are 40, 50, 60, 70 ,80,90,100, 120, 140, 160, 180 and 200m. The wind lidar measurements are taken to be spatial averages over +/- 5 m height from the reported datums.

Wind Lidar data at 1-min frequency was reported for the 14th-20th June inclusive. Between 9 and 13th June data was logged at 10 minute intervals only. This is not reported here.

Results are summarised below and each day data is plotted on the following pages.

Narrative

Day	Description
June 8th 2017	All three anemometers were logging to a common time-base by 13:00 and data is given from 13:00 to 20:00. Wind direction was steady from the SSW until ~17:30 when it changed to westerly. The change was seen first by the North Tanks site, then the South-West site and then the Truck loading. With the wind in the SSW the direction measured at the South west units was generally most S and that at the North Tanks most SW. After the direction shift the direction at the truck loading moved back toward the SW whereas the wind continued W at the other stations. After ~19:00 the direction at the truck-loading was a consistently different, by 45 degrees at 20:00, to the other stations. Wind vector speeds (average speed in the average direction) were broadly similar at the three stations. Each station shows variability in time and, as would be expected on a common time basis, the wind speeds illustrate phase differences between stations. The wind speed is about 5 +/- 1 m/s until the direction shift at ~17:30 when it reduces to ~3 m/s. The smoothed wind reported by the stations may differ by up to 2 m/s at a given time. Persistence was near 1 for the whole period, dropping only slightly during the wind direction shift.
June 9th 2017	24 hour data is available on all stations and described here between 08:00 and 20:00. Wind direction was between S and SSW at 08:00 turning over a period of 2 hours to WSW for the rest of the day. Variations were generally within 20^o and between W and SW. The variability was similar for all stations, slightly greater at the South West station. Difference between stations can be 20 degrees at any time. Vector wind speed was variable. It dropped at all stations between 08:00 and 10:00 and then picked up at all stations between 10:00 and 12:00. After 12:00 the record at the South West units (~ 5 m/s) was significant different to that at the other two stations (~ 7 m/s) with the wind-speed less, often by more than 2 m/s. Periodicity in the wind-speed was apparent at all stations with wind speed varying by up to 2 m/s over periods of an hour. Persistence was high. It was lower for the South West trucks station indicating more variability. The data suggests that there is significant sheltering (reduced wind speed, unchanged wind direction) of the South West station for wind direction WSW.
June 10th 2017	Data is described between 08:00 and 20:00. Wind direction was consistently SW until 19:00 when it turned W. The direction at the South West station was consistently different and SSW. The difference between the North Tank and South West station directions was occasionally more than 45 degrees. The direction at the Truck Loading was generally between the two but more aligned with the North West station.

	Vector wind speed increased steadily during the day from just over 2 m/s at 08:00 to 4 m/s at the close of day. It became more variable after 19:00. Some periodicity in the wind speed is seen, again on a time-scale of about an hour. At any time the station signals could differ by up to 1 m/s. Persistence was high but less than on the preceding days indicating that the time averaging is covering up more short-term variability in wind-direction. Data showed consistent difference in direction between North Tank and South West units of up to 45 degrees with overall wind SW. The SW units more SSW.
June 11th 2017	Data is described between 08:00 and 20:00. Wind direction changed considerably through the day starting in the SE and ending in the WSW. A distinct change from SSW to WSW occurred at ~17:30. Between 08:00 and 11:30 the wind-direction at the North Tanks was significantly different to the other two stations and more W. Vector wind speed was consistent at ~ 2 m/s until 11:00 and then built to 4 m/s at 14:00 then remained steady until 17:00 before building again and becoming variable. During this period the wind speed at the South West units was less than at the other stations by up to 4 m/s. Persistence shows short term variability at all stations between 9:30 and 12:30 with this variability decreasing until the wind-direction change at ~17:30. The data suggests that there is some sheltering of the South West station for wind direction WSW and deviation in wind flow at the North Tanks station for wind direction SSE.
June 12th 2017	Data is described between 08:00 and 20:00. Wind direction very consistent at all stations and from the WSW. Wind speed at the South West units (~5 m/s) consistently less than at the other two stations (~ 7 m/s), often by more than 2-3 m/s. Wind speeds are quite high compared to preceding days. All stations show variability in wind-speed and differences that are not in phase. Persistence is high in-line with the consistent wind direction. The data suggests that there is significant sheltering of the South West station for wind direction WSW
June 13th 2017	Data is described between 08:00 and 20:00 Wind-direction is variable through the day. Between 08:00 and 11:00 there is difference between the measurement stations with the South West units station reporting more W/SW directions than the other stations which report more W/NW directions. Between 11:00 and 15:00 wind direction is more steady and W before changing NW @ 15:00 and then steadily changing toward N at 19:00.

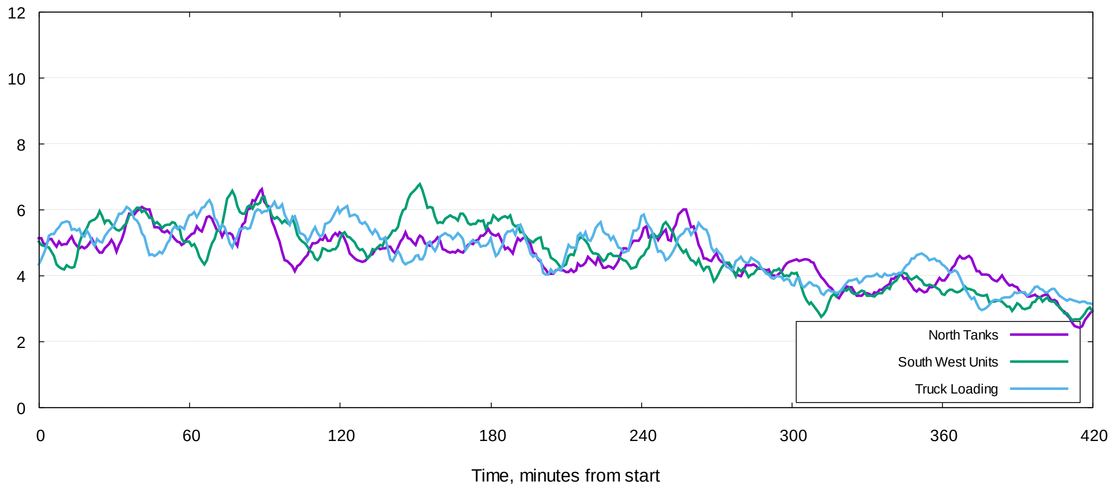
	Wind vector speed is relatively low starting at ~ 2 m/s for all stations until 11:00 and strengthening to 4m/s over a period of an hour then falling back to ~ 3 m/s. All stations show similar variability. Persistence shows a short term direction variability throughout the day. The data show that the wind direction at the South West Units tends to be W when the wind direction at the other stations is NW.
June 14th 2017	Data is described between 08:00 and 20:00. One minute LIDAR data is available. Wind direction has changed overnight. There is a consistent difference between the direction measured at the North tanks station (E) than at the other stations (ESE). Upper wind direction supports ESE as the morning wind direction turning E after 13:00. Vector wind speed is consistent between all stations (~ 3 m/s) throughout the day, building after 19:00. Upper air data shows only a small variation in wind speed with height. Speed becomes more variable after 16:00. Persistence is initially high but decreases steadily after 10:00 showing increasing short-term variability in wind-direction. The North tanks station is most affected. The data suggests a deviation in wind flow at the North tanks station for wind in the ESE.
June 15th 2017	Data is described between 08:00 and 20:00. One minute LIDAR data is available. Wind direction changes significantly through the day from SE at 08:00 to WSW after ~ 11:30. This is consistent with upper air data from LIDAR. Wind speed builds from ~ 2 m/s at 08:00 to ~ 7 m/s at 14:00 when it remains fairly steady with some periodic variation about the mean. The wind-speed at the SW units is significantly less, by 2 m/s or more than at the other stations from 11:00 onwards. Lidar shows strong wind-shear at 08:00 dissipating by 11:00. LIDAR data. The wind speed is variable at all heights showing periodicity. After 13:00 the vertical wind speed shows periodic (hourly) up and down drafts. Persistence is high over the day except for the North Tanks between 08:00 and 09:00 The data suggests that there is some sheltering of the South West station for wind direction WSW. The North tanks station responds differently to the other stations during the early wind-change from SE to S.

June 16th 2017	Data is described between 08:00 and 20:00. One minute LIDAR data is available. Wind direction is consistently between WNW and NNW with a ~ 20° variation about NW. Upper air data from LIDAR is NW. All three stations show similar variability in wind-speed (+/- 1 m/s) during the day about an average of 5 m/s. The station South-West units consistently reports the lowest wind-speed of the group. Upper air data shows an increase in wind-speed with height and significant periodic variation at all heights that appears decoupled from the ground. Lidar shows 2 episodes of downdraught. At ~12:45 and ~14.45 and general alternating up and down motion through the day. Persistence is high but indicates wind-direction variability throughout the day. The data suggest a lower wind speed at the South West station.
June 17th 2017	Data is described between 08:00 and 20:00. One minute LIDAR data is available. Wind direction is in the NW. There is growing difference between the stations throughout the day, starting at 10:00 with the South West tanks station but more generally after 12:00. The South West Tanks station registers more E winds and the Truck loading more N winds and the differences are significant at times (> 45°). The upper air data is more consistently between NW and WNW. Wind speed is consistent (~ 3 m/s) through the day and similar for all stations. The upper air data shows wind shear eroding between 8:00 and 10:00 with a decrease in speed by about 2 m/s. Thereafter it is more steady. Vertical wind speed shows extended period of downflow between 09:00 and 12:00 and upflow between 12:00 and 15:00. Persistence shows that the wind-direction variability is greatest at the South West Units station. Data suggests the wind direction at the South West station can be up to 45 degree different (W cf NW) to the other stations.
June 18th 2017	Data is described between 08:00 and 20:00. One minute LIDAR data is available. Wind direction is highly variable throughout the day which is consistent with low wind speeds. During the morning the wind direction is SE reversing to NNW at ~12:30 with multiple crossings to NNE. After 17:00 the picture becomes confused. Upper wind data shows a SE wind until 12:30 then turning back through N to NNW until 14:30 when it moves N with several crossings between NNE and NNW. At 16:45 it moves from NNE to SE to SW, then reversing through S to North and back to ESE. then back through N to NW at 19:00.

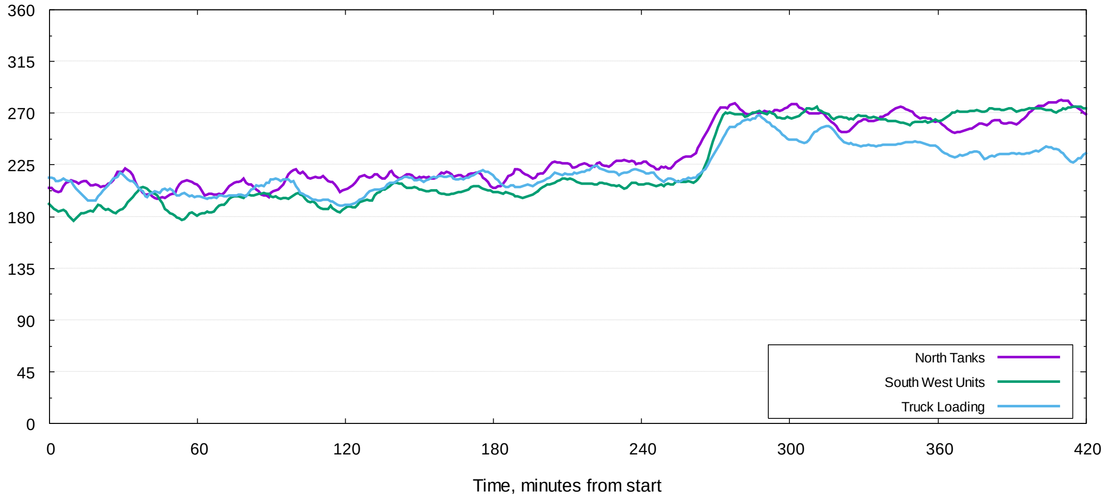
	Wind speed is low, 2-3 m/s with the North Tanks station registering winds below 1 m/s before 11:00. The wind speed is also low in the upper air, ~3 m/s in the afternoon. Persistence shows extreme variability in wind-direction throughout the day, and this extends up to 200m. Between 13:00 and 16:30 there appears to be a net upflow at the lidar station.
June 19th 2017	Data is described between 08:00 and 20:00. One minute LIDAR data is available. Wind direction is originally in the SE. The North tanks station record significantly different direction ENE to NW until 16:00 when all stations show a shift to NNW. This is mirrored in the LIDAR data. Wind speeds are low initially picking up to ~3 m/s at 12:00 then falling steadily to below 1 m/s at 15:00. At 16:00 coincident with the wind-direction change, the wind picks up to ~ 4 m/s at all stations. The lidar data also show low wind speeds. Early stratification is gone by 08:30 and thereafter mean wind-speed is very similar at all heights slowly building from 2 to 3 m/s at 12 before reducing and becoming variable. There is a loss of LIDAR data between 14:30 and ~16:30 when the wind picks up again and a vertical velocity profile re-establishes. The persistence shows high variability through the low wind speed periods for all the stations, decreasing to show steady conditions after 16:00. This is reflected in the upper air data after 12:30. The results suggest the flow at the North Tanks station is significantly affected when the wind is SE and wind speed is low. With wind-speed less than 1 m/s the direction is probably unreliable but shows a shift to N and NNW.
June 20th 2017	Data is described between 08:00 and 20:00. One minute LIDAR data is available. Wind direction is in the NNE with different between stations. Upper air data from the LIDAR is consistent with a NNE direction. The South West Units station measures NNW with occasional crossings of North, marked after 16:00. The NT station is more often NE. Wind speed is consistent at all stations (~ 4 m/s) until 16:00 when the South West Units station shows a drop in wind speed whereas the other stations show an increase. The upper air data show wind speed variable about 5 m/s with little change in height from 08:00 to 14:00 then building to 18:00 then dropping again. Persistence shows that variability lies mainly with the South West units station being most marked after 16:00. The LIDAR data show marked instances of downdraft at ~12:00, at ~14:15 and at ~16:30.

	The results suggest deviation in flow at the South West unit station when the wind is in the NNE. The period of sheltering, with significantly lower winds is not associated with an obvious wind direction change but coincides with the South West station recording North.
June 21st 2017	Data is described between 08:00 and 20:00 All three stations show differences in wind-direction before 15:00. The direction recorded at the North Tanks station is remarkably steady. After 15:00 the direction shown at the Southwest units and Truck loading converge to show ESE. The North Tanks station reports winds that change from NE to E during the day. Apart from 4 short periods of less than an hour the station maintains a different direction reading of ~ 45 degree to the South West units. Wind speed decreases slightly during the day with differences between the stations that become less marked after 13:00. The wind speed at the North Tanks station changes least. In the morning it is less (~4 m/s) than at the other stations (~ 5.5 m/s). After 15:30 the lowest wind speed is seen at the Truck Loading station(~ 2 m/s). Persistence is high all day showing steady conditions over the averaging period. The data suggest a consistent difference between the North Tanks and South West Unit stations for wind in the E with both sheltering and change in flow direction.
June 22nd 2017	Data is described between 08:00 and 20:00 Wind direction is in the SW turning slightly W over the length of the day. All three stations record similar directions with the South-West units slightly more S of SW then the other two. There are some fluctuations in wind-direction between 15:00 and 16:00. Wind speeds increases through the day from 3 to 6 m/s. There are differences between stations outside the time window 15:00 to 16:00 when the wind measured at the North Tanks and Truck Loading drops. Wind recorded at the South West units is consistently lower than at the other two stations. Wind speed is quite variable at all stations on an hourly cycle. Persistence is high. The wind direction at the South West units is more variable over the averaging time than at the other stations. The results suggest sheltering at the South West units when the wind is in the SE .

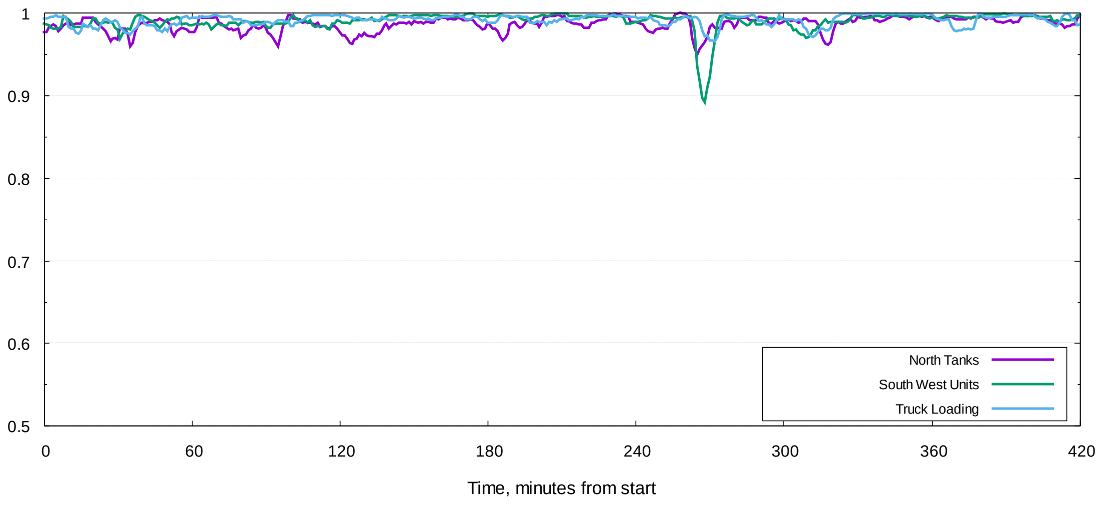
Vector Wind Speed, m/s



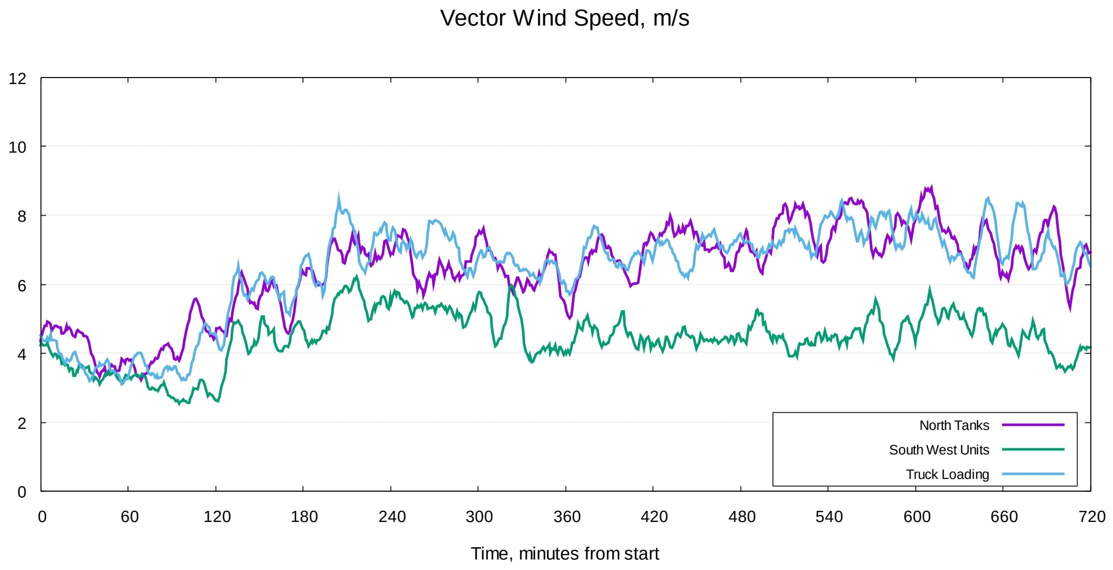
Vector Wind Direction, degrees

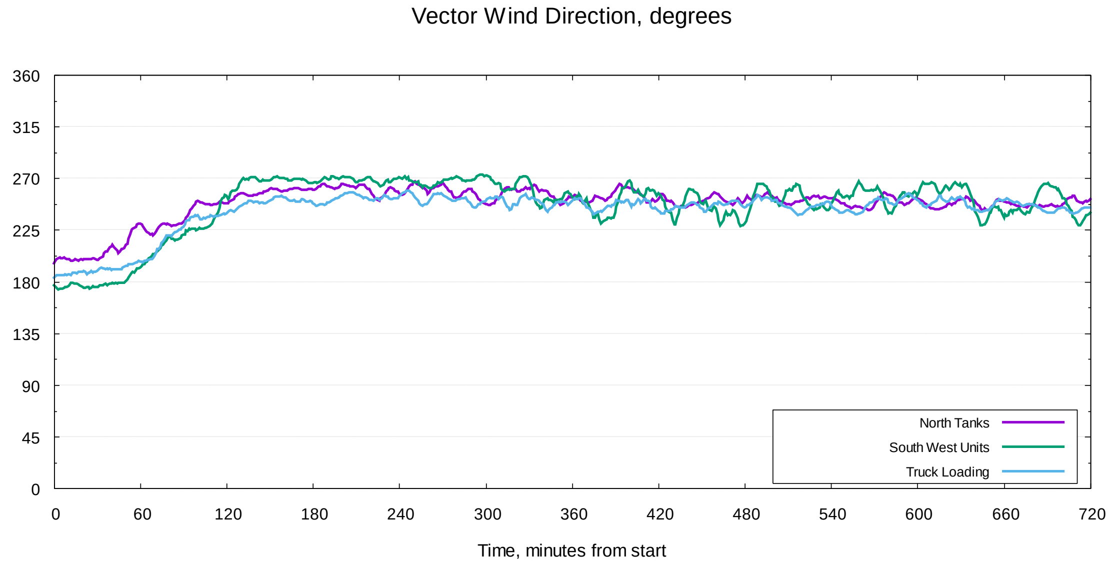


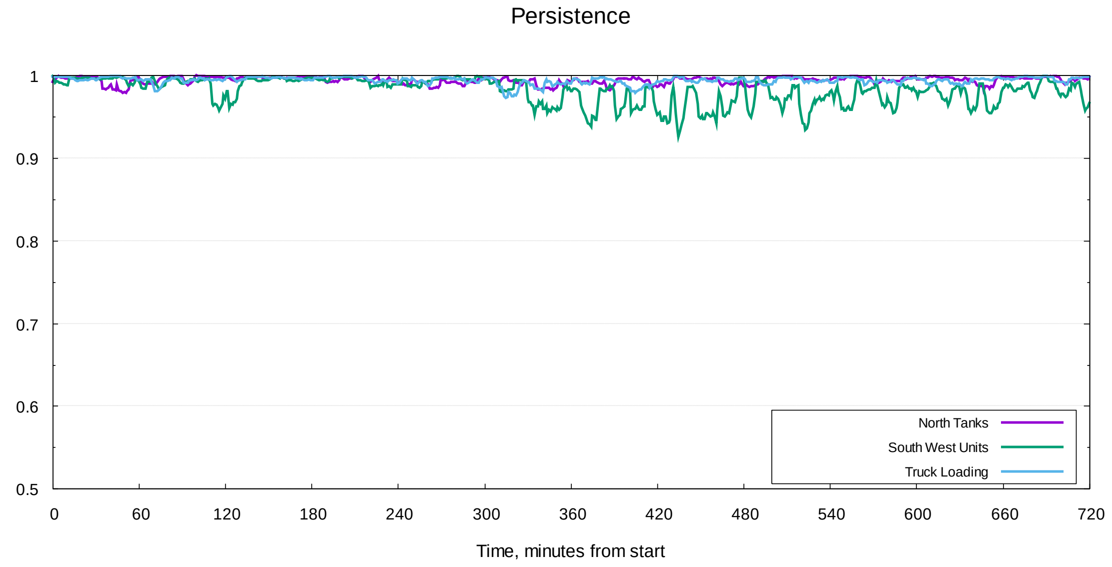
Persistence



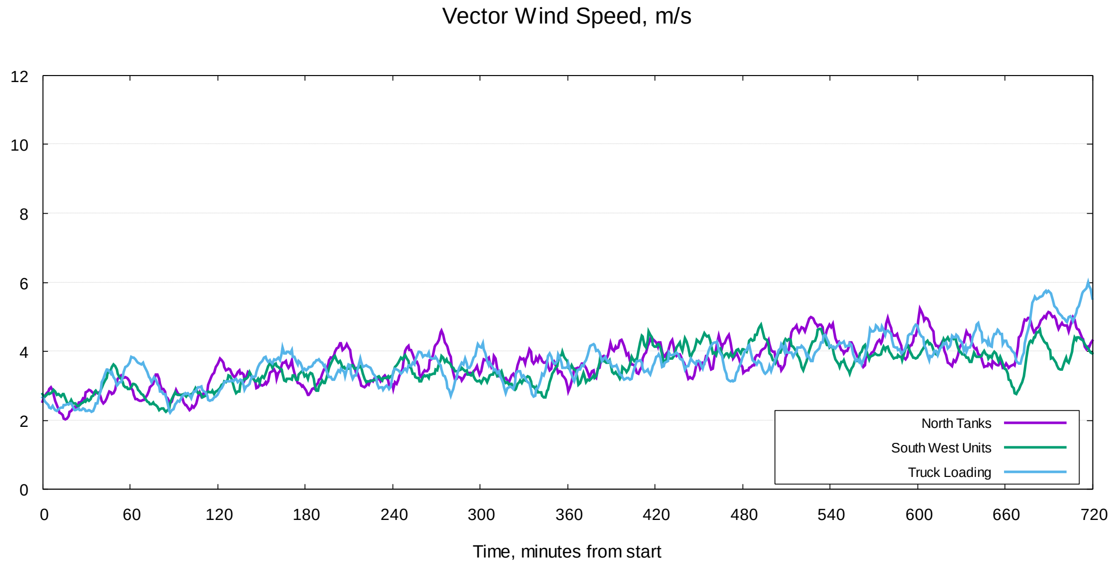
Day 8th June 13:00 – 20:00

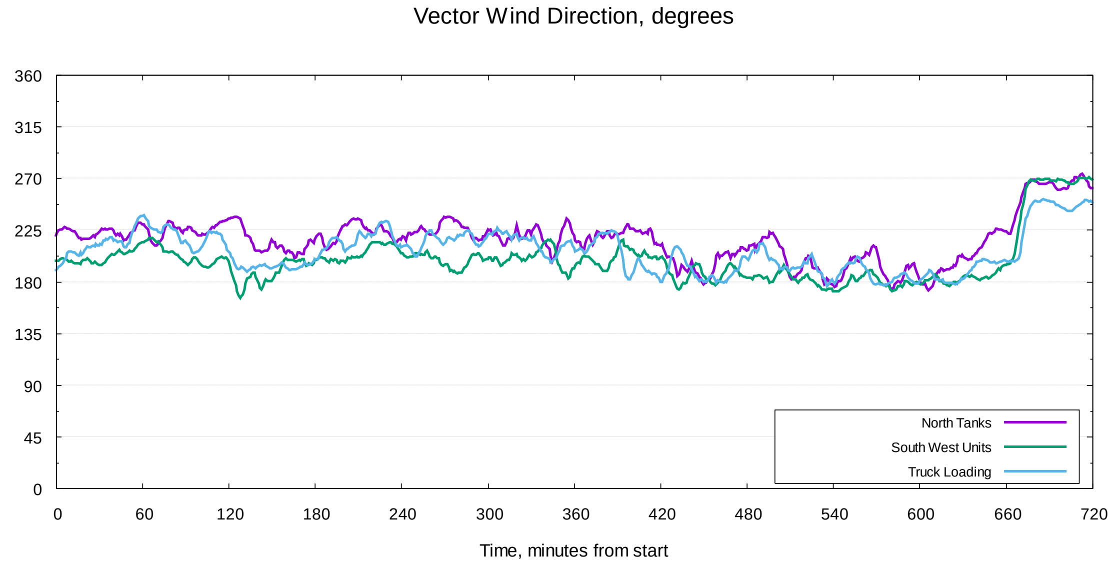


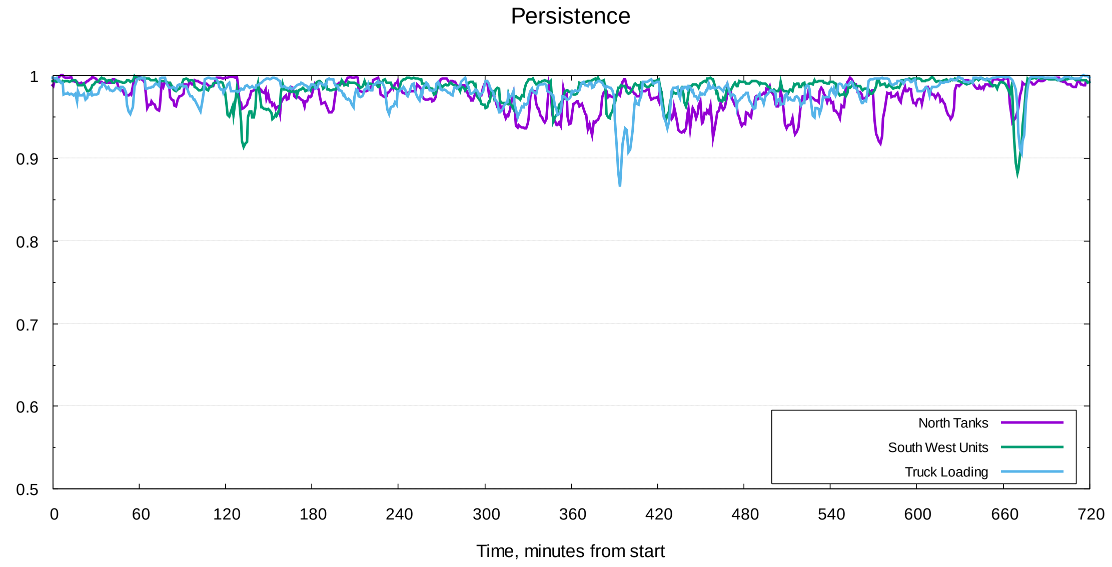




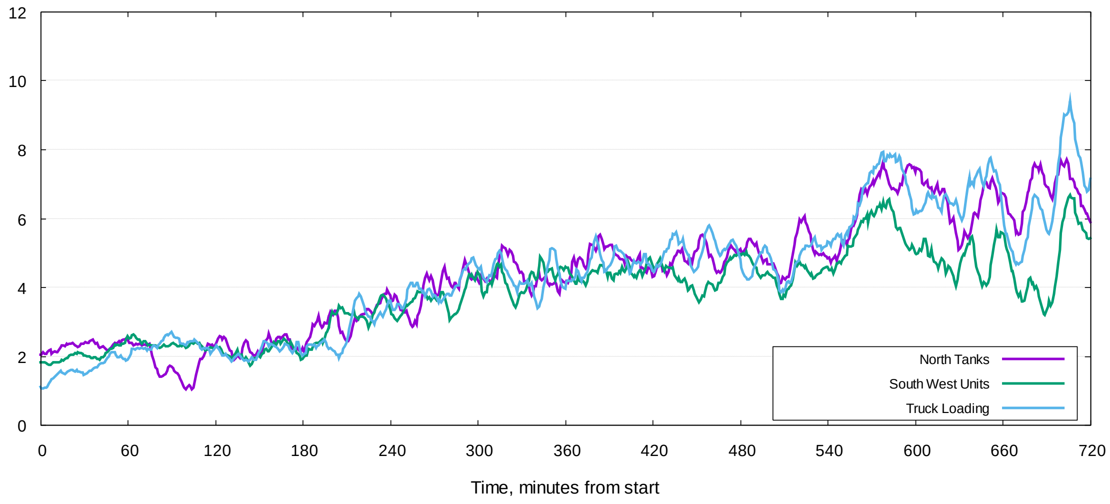
Day 9th June 08:00 – 20:00

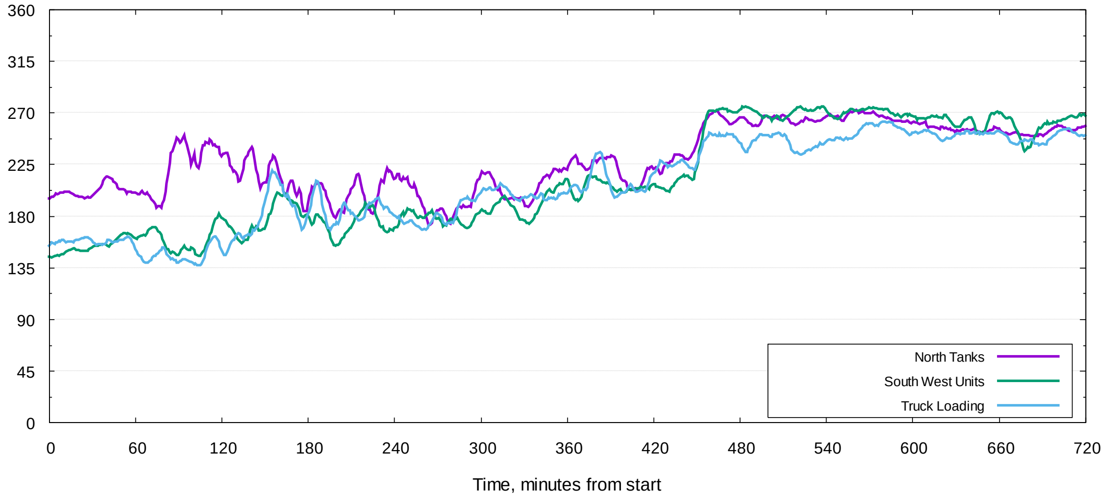


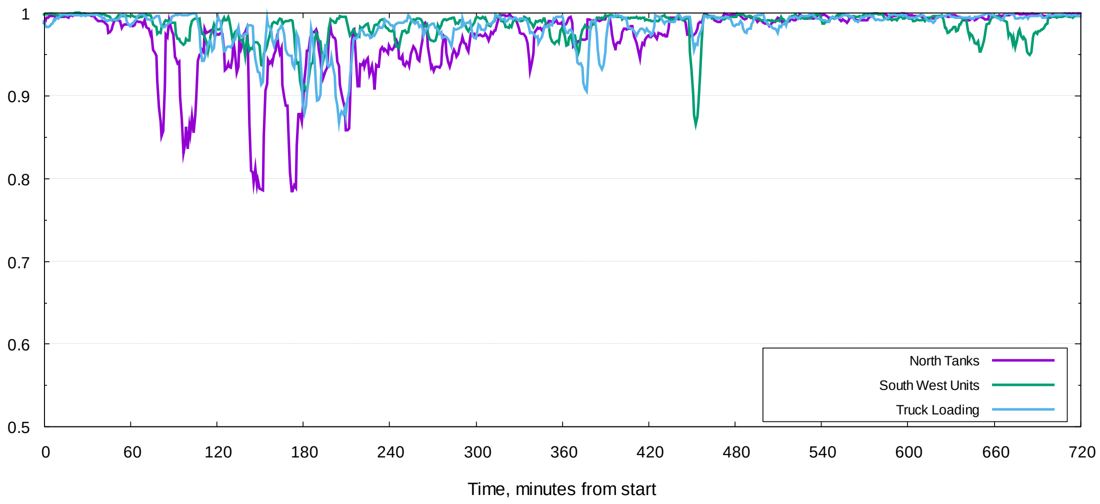




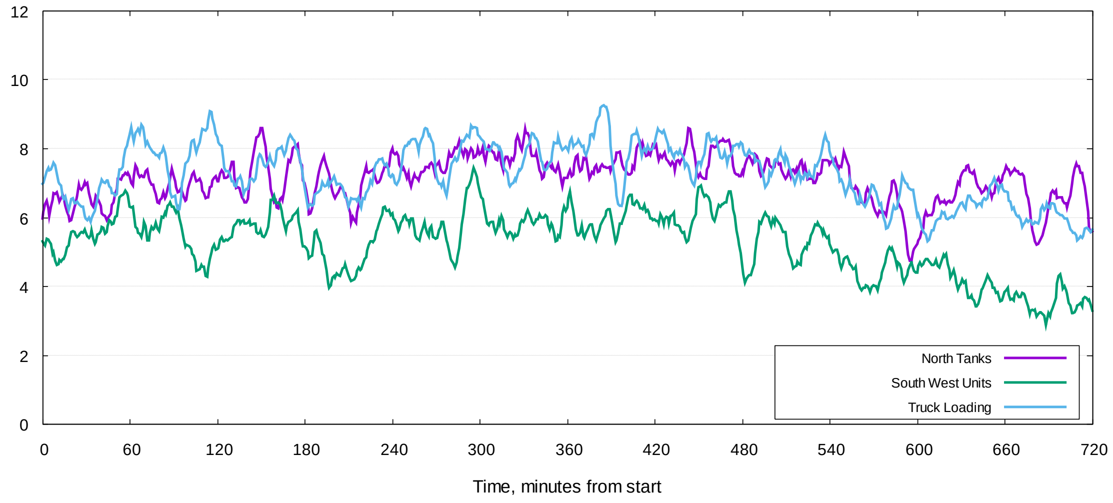
Day 10th June 08:00 – 20:00


Vector Wind Speed, m/s

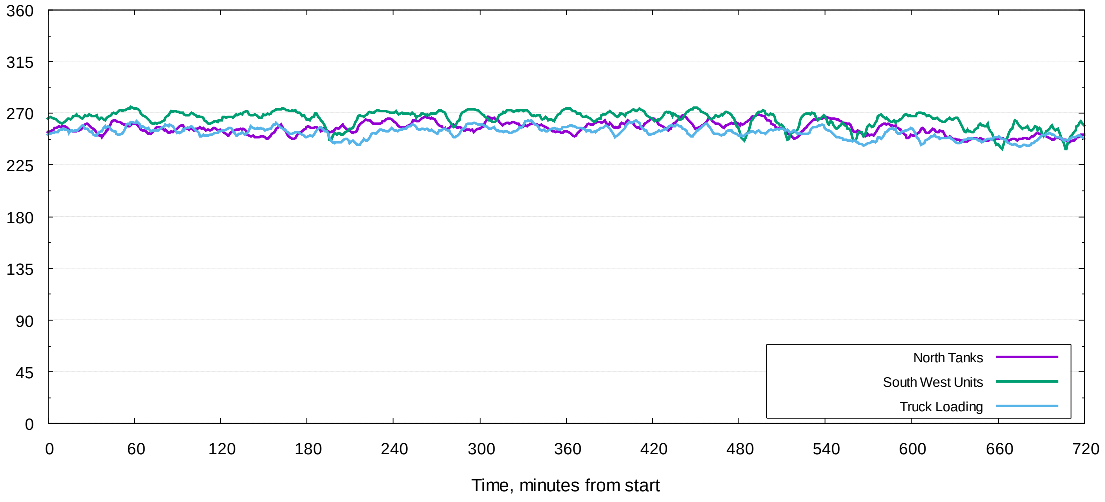

Vector Wind Direction, degrees


Persistence

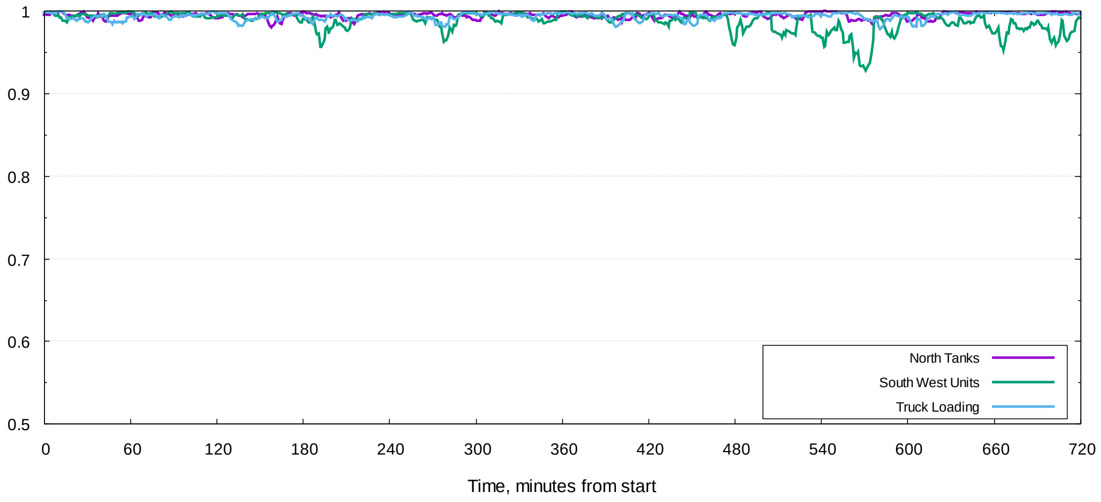
Day 11th June 08:00 – 20:00



Vector Wind Speed, m/s



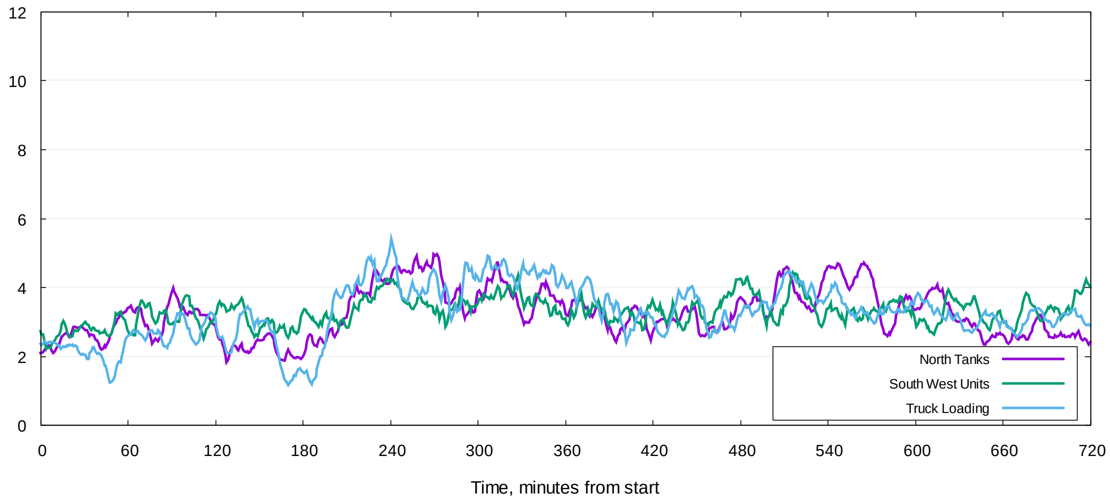
Vector Wind Direction, degrees



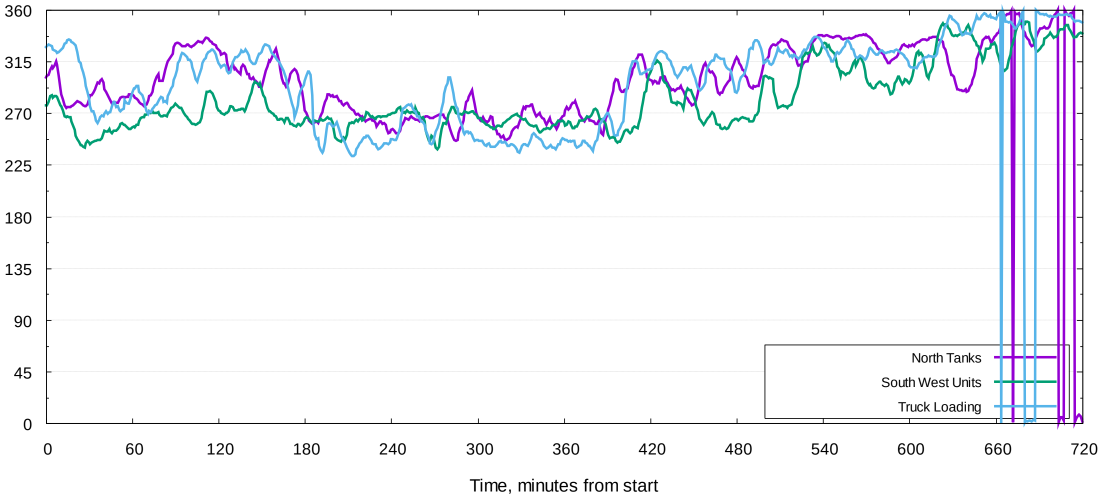
Persistence

Day 12th June 08:00 – 20:00

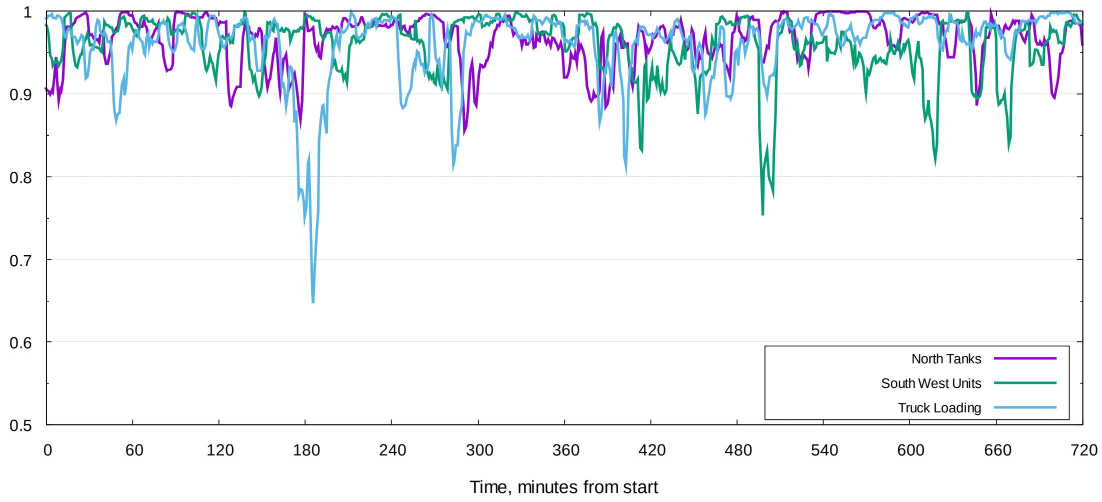
Vector Wind Speed, m/s



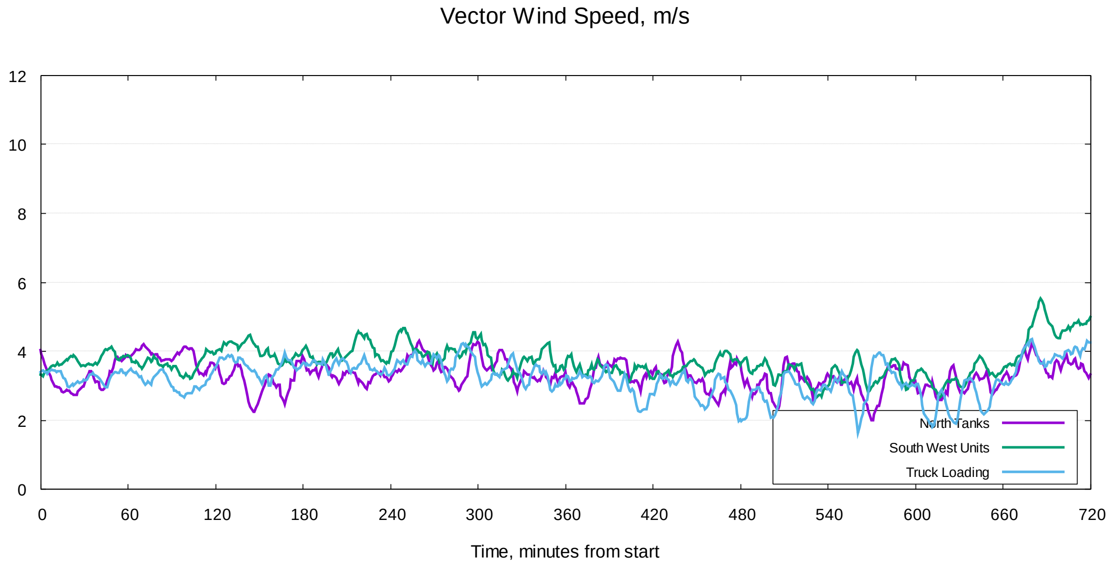
Vector Wind Direction, degrees

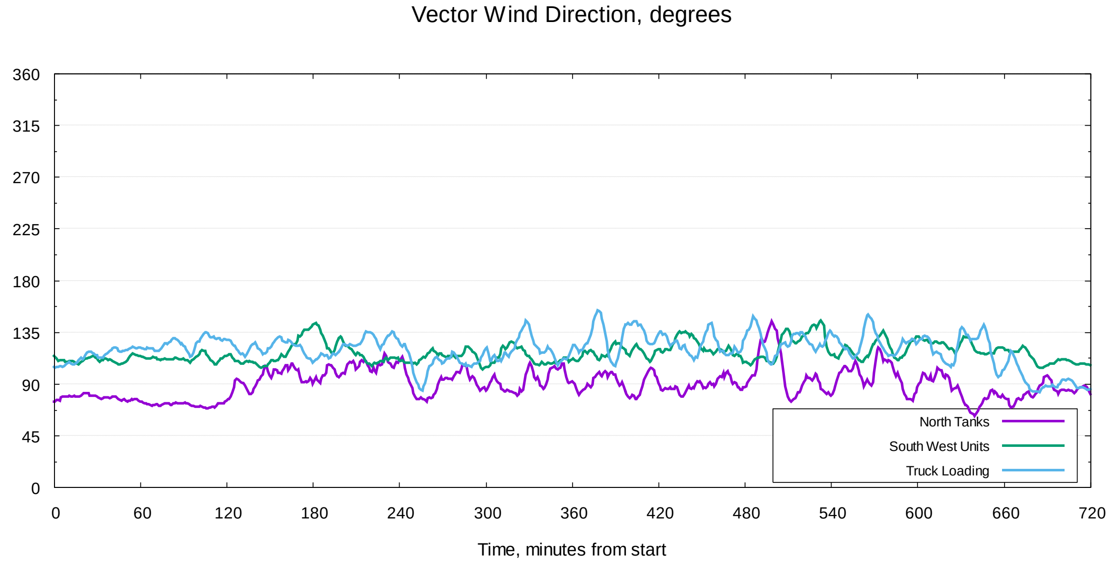


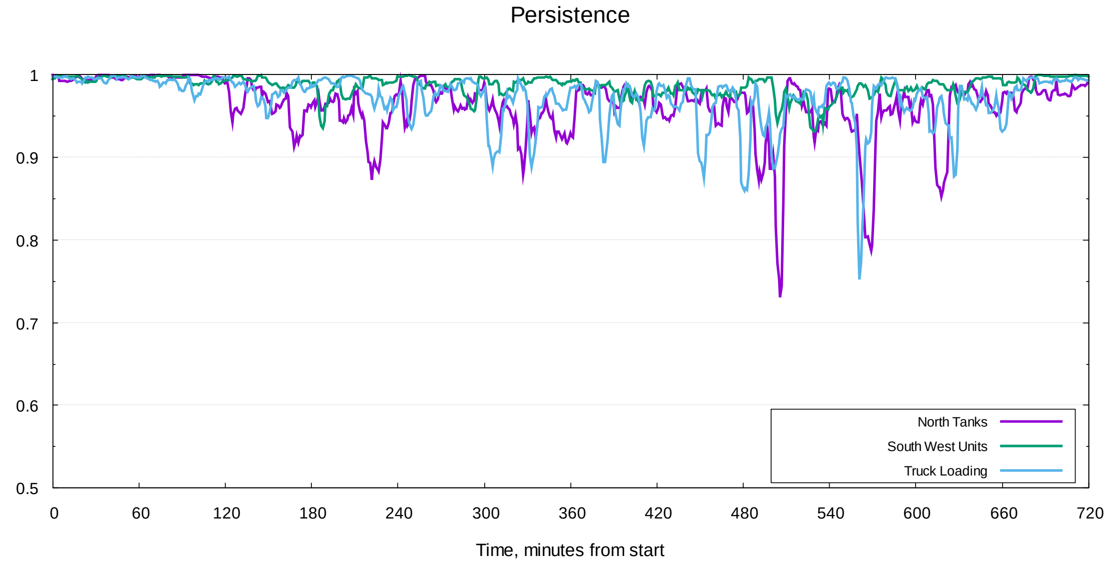
Persistence



Day 13th June 08:00 – 20:00



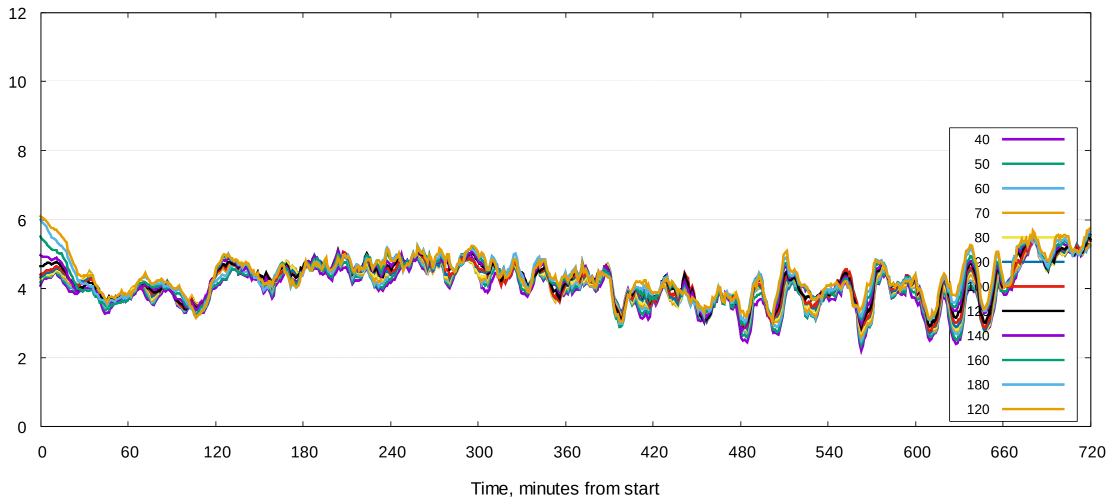




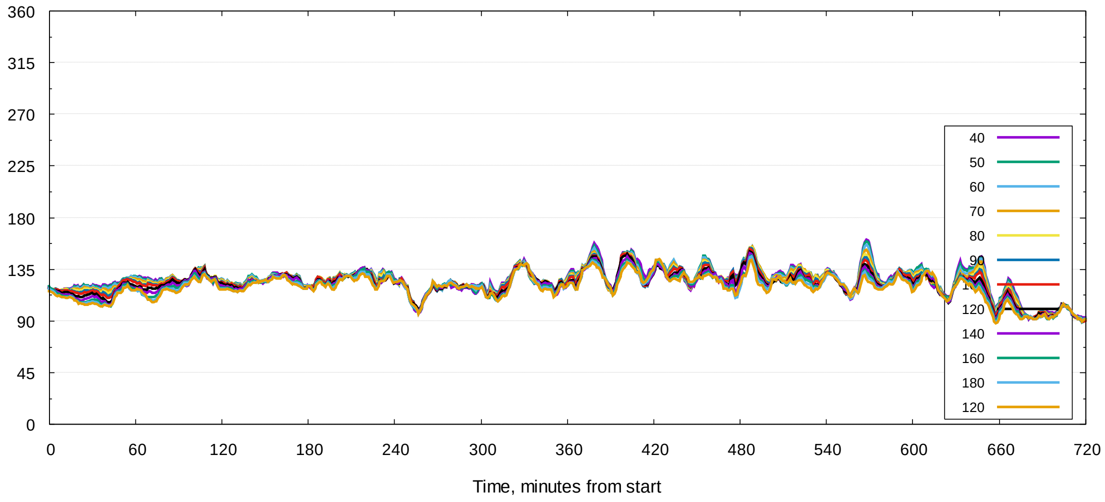
Day 14th June 08:00 – 20:00

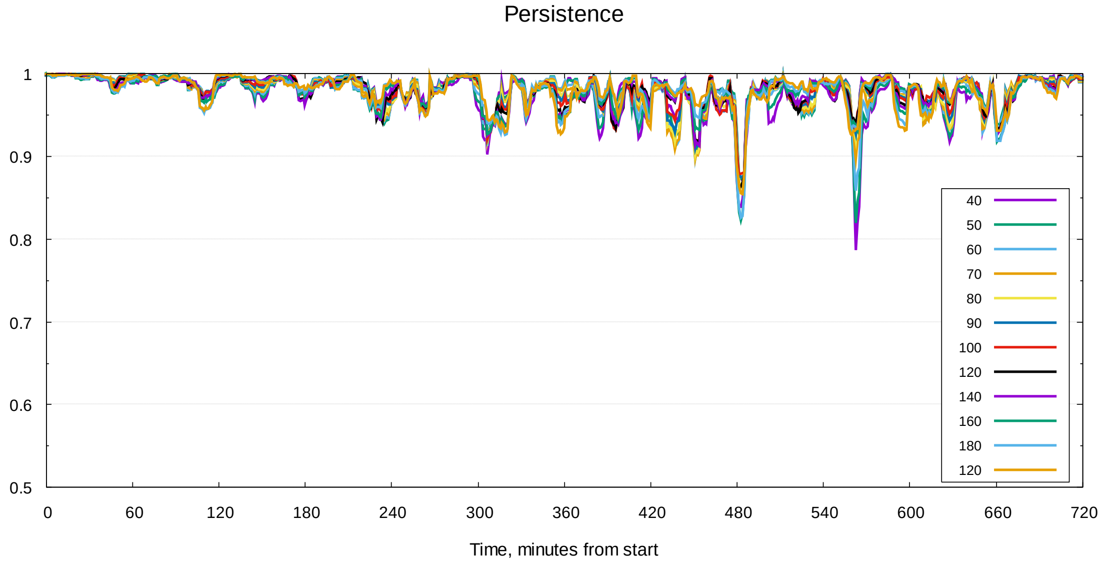
LIDAR data for 14th June:

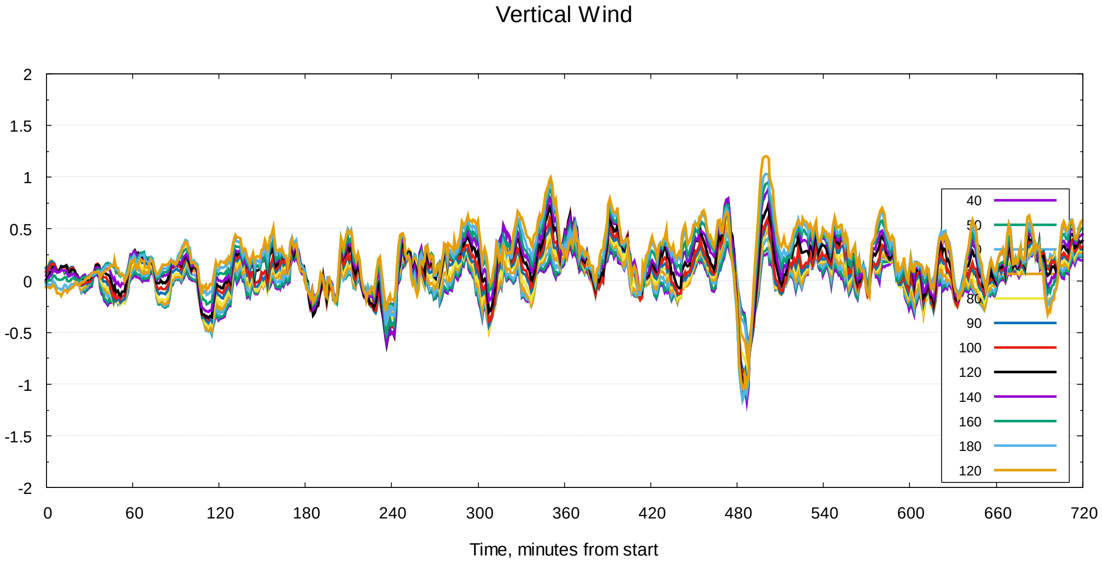
Vector Wind Speed, m/s

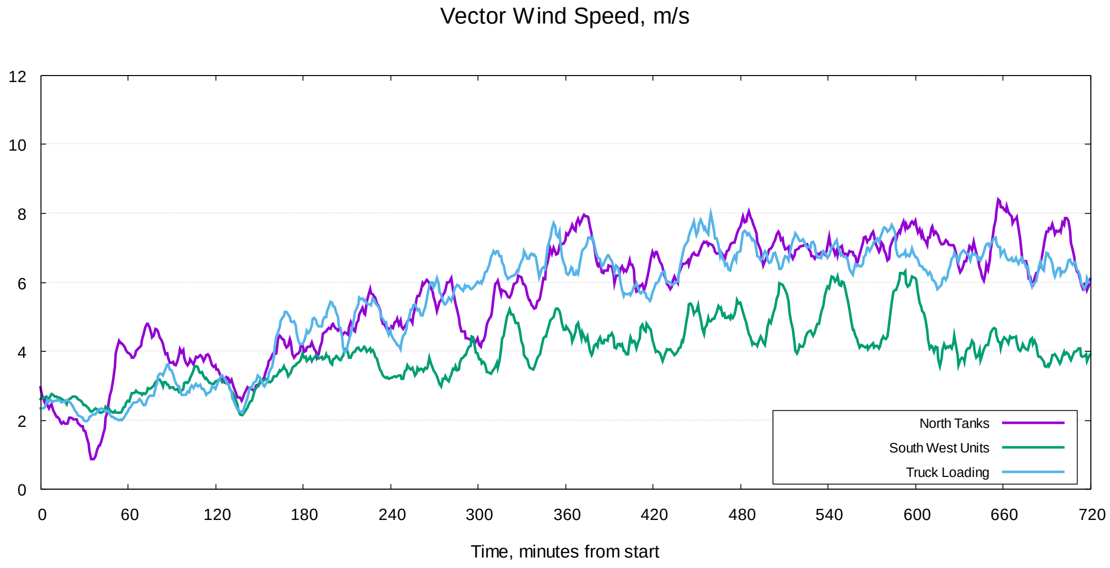


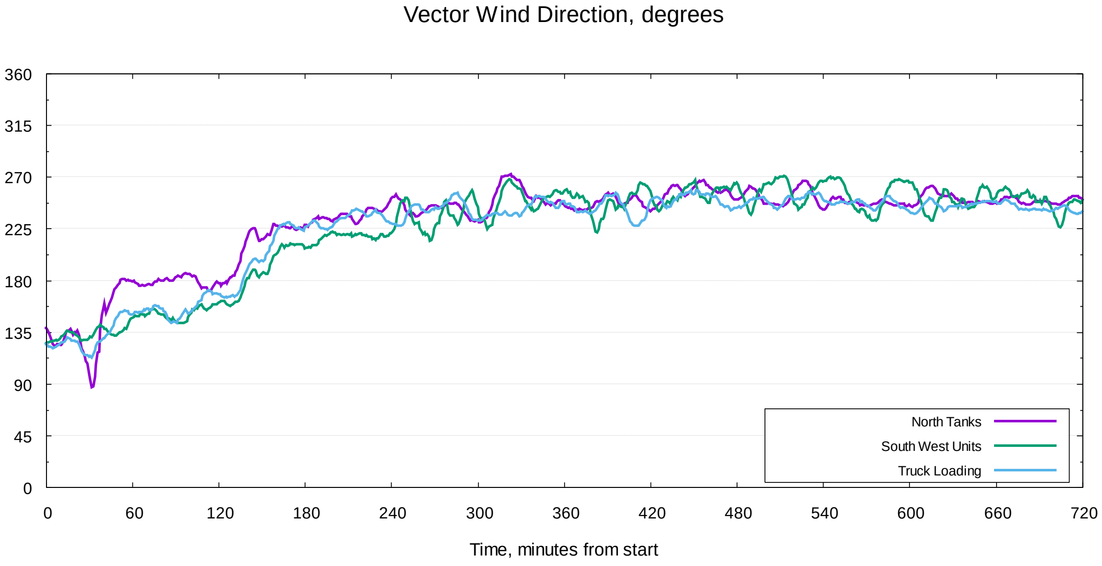
Vector Wind Direction, degrees

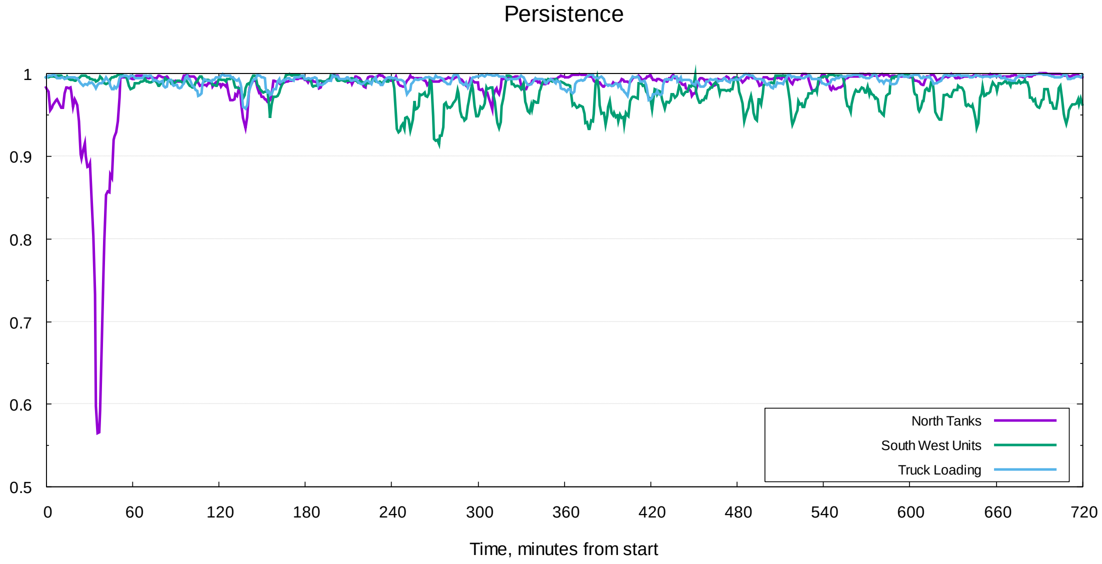



Persistence


Vertical Wind



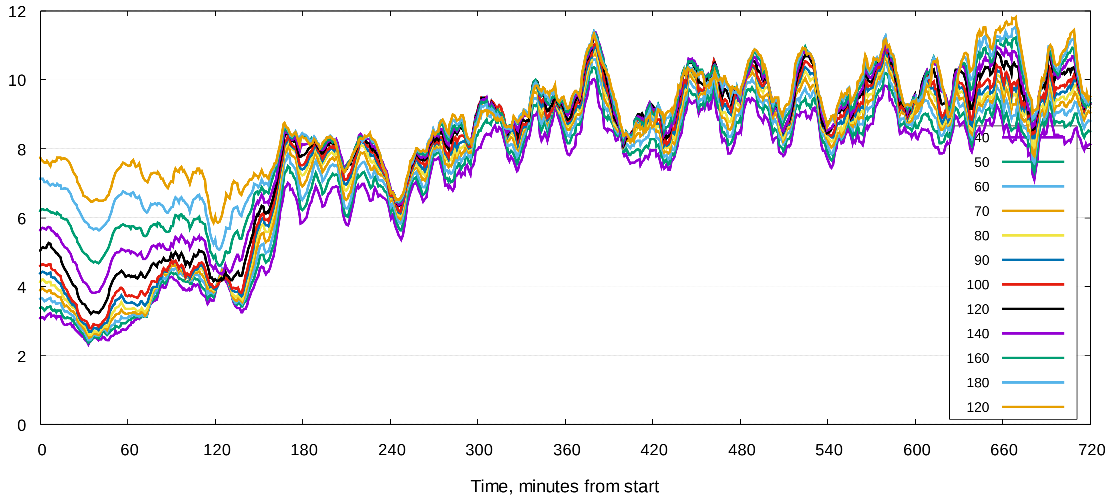




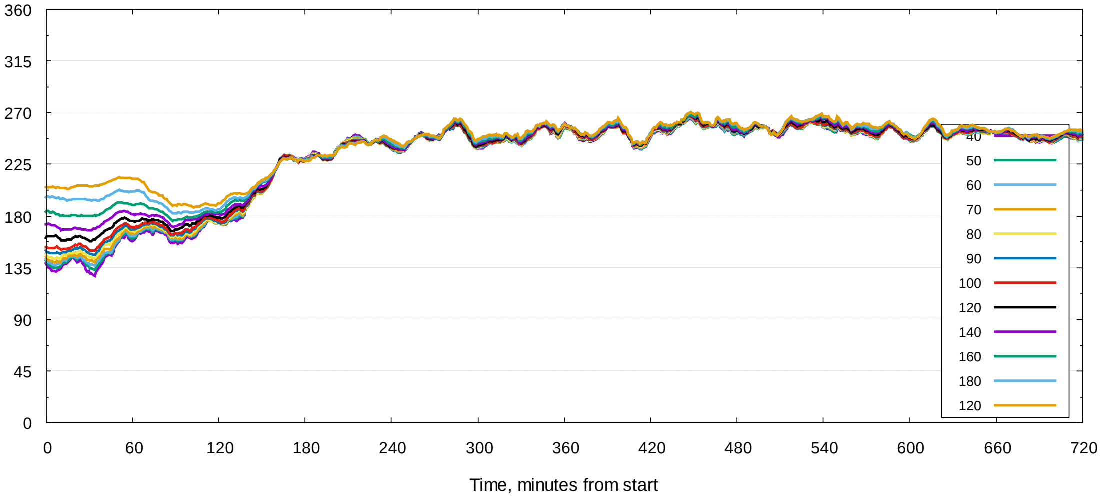
Day 15th June 08:00 – 20:00

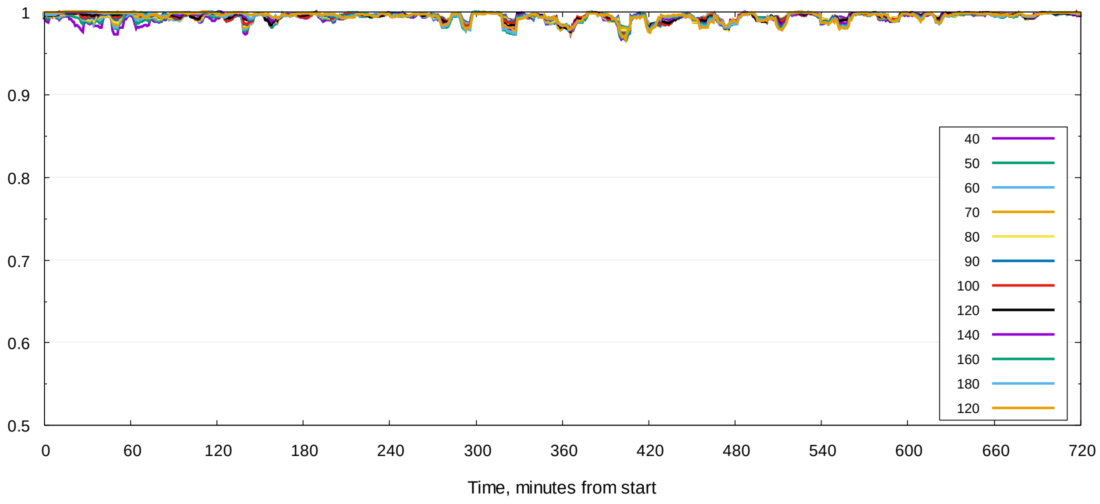
Lidar Data for the 15th of June.

Vector Wind Speed, m/s

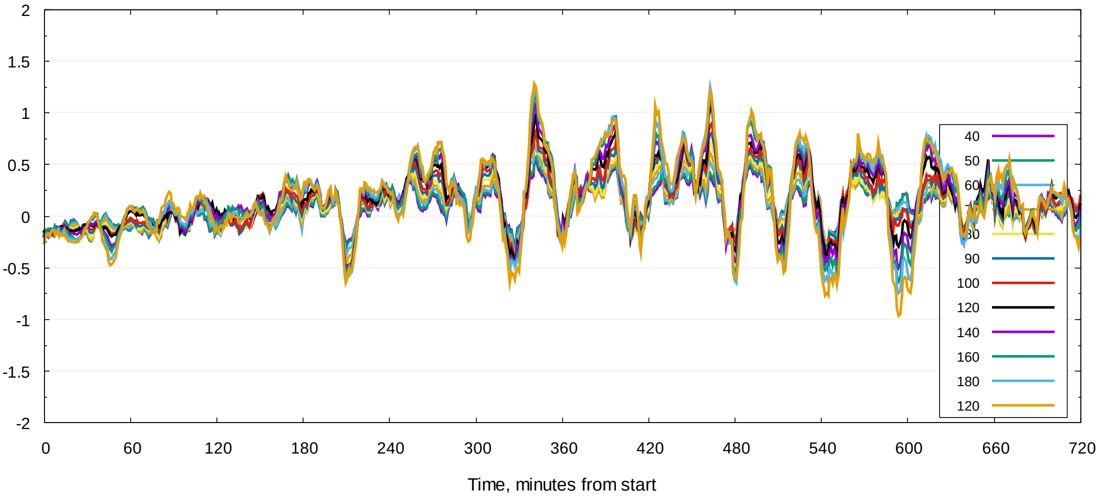


Vector Wind Direction, degrees



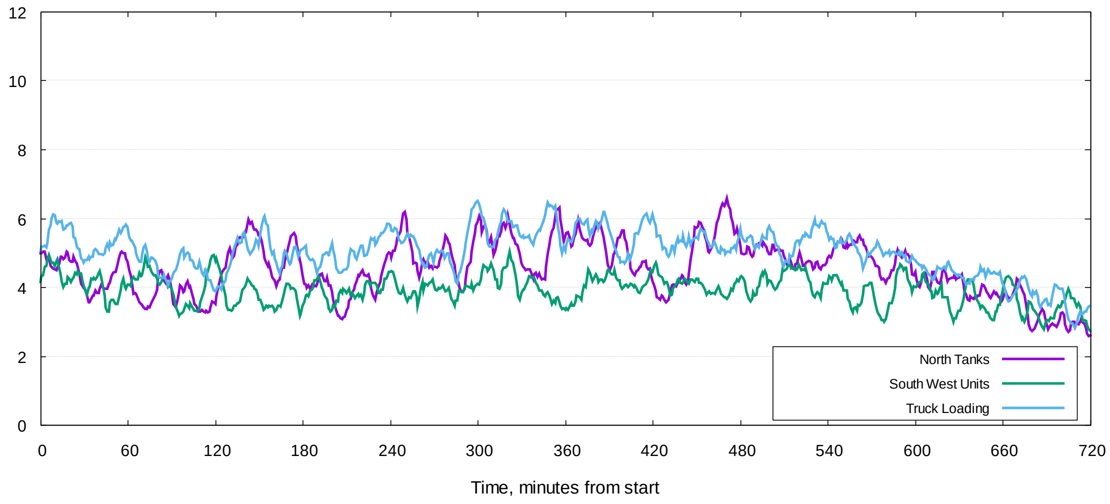


Persistence

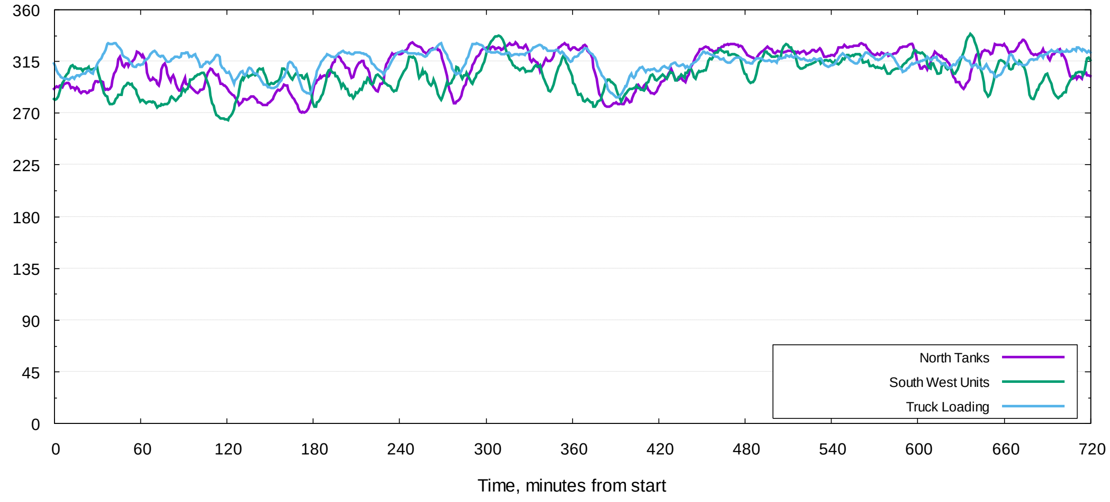


Vertical Wind

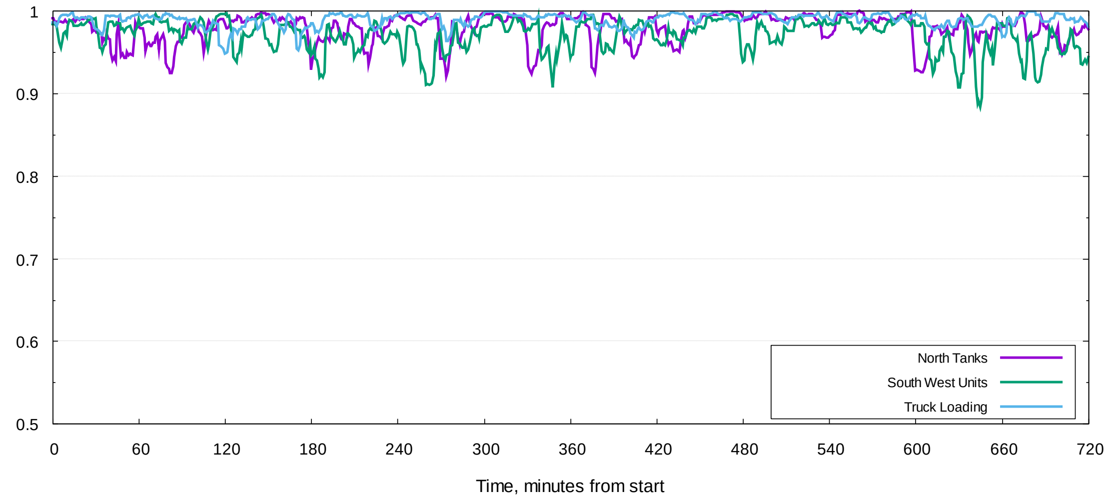
Vector Wind Speed, m/s



Vector Wind Direction, degrees

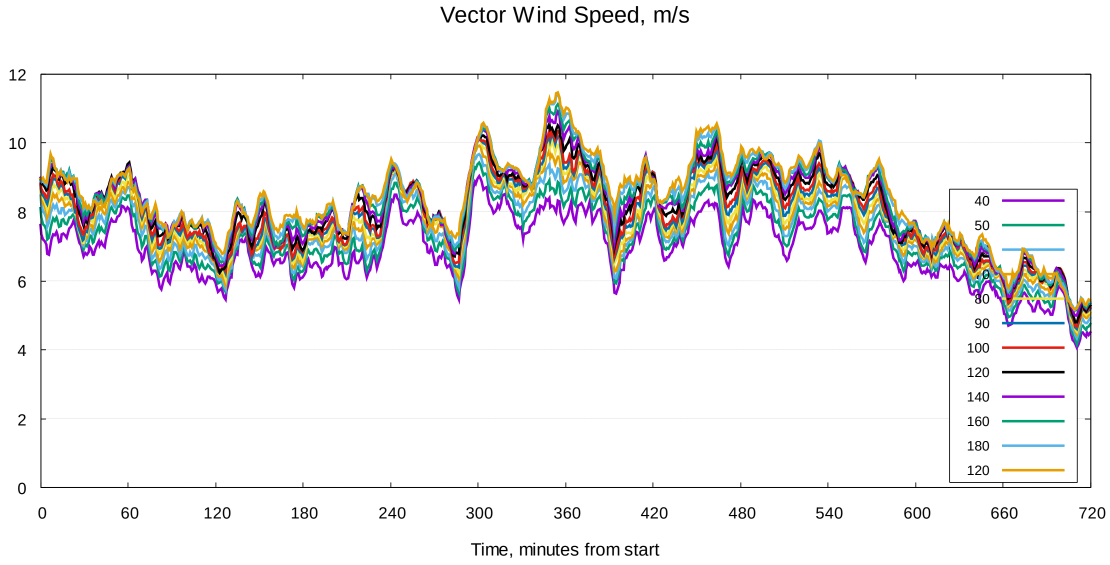


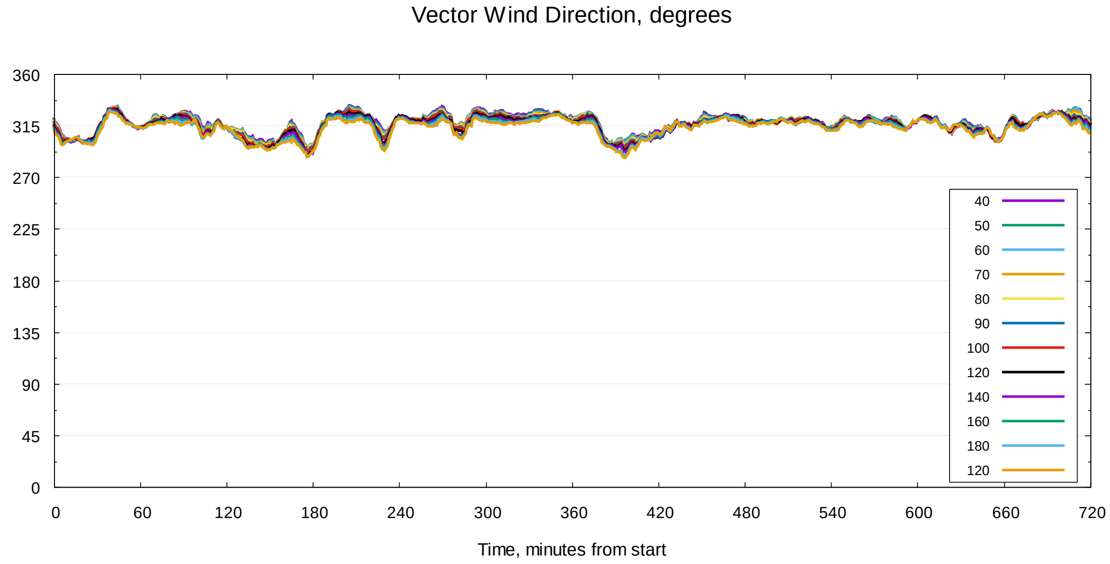
Persistence

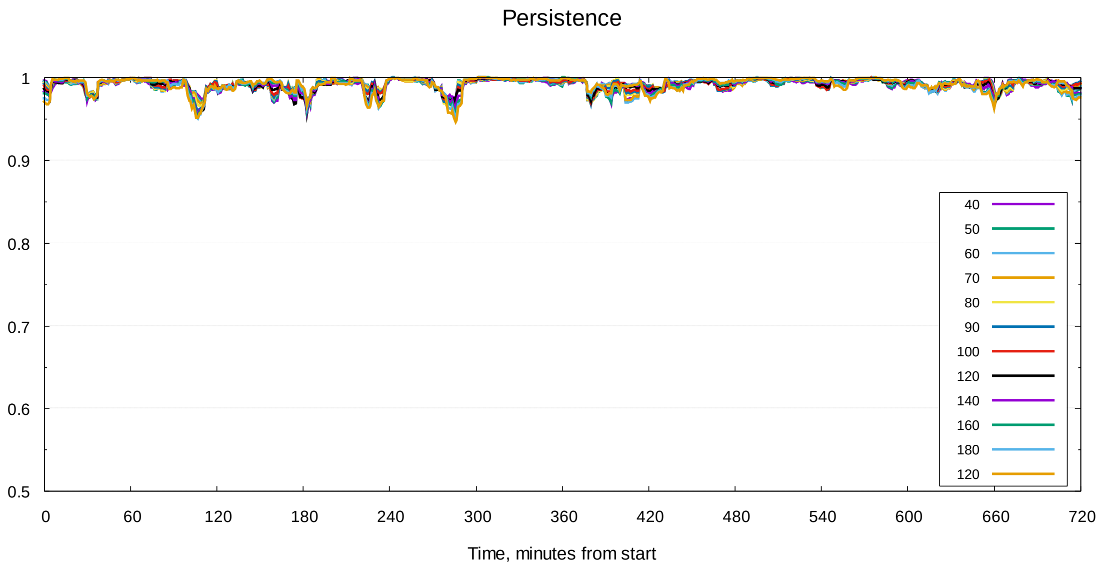


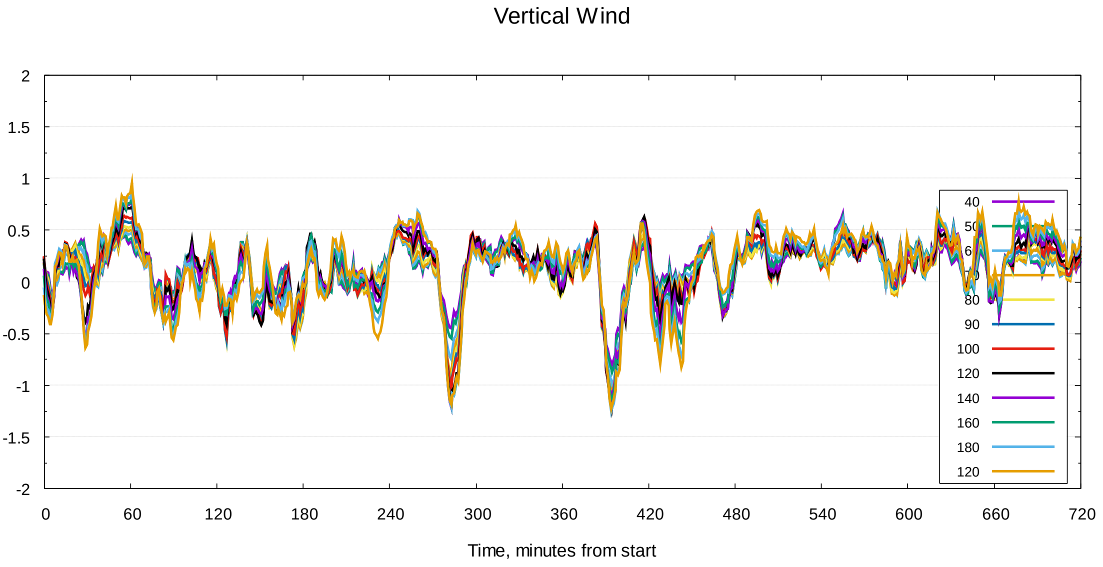
Day: 16th June 08:00 – 20:00

Lidar Data for the 16th of June:

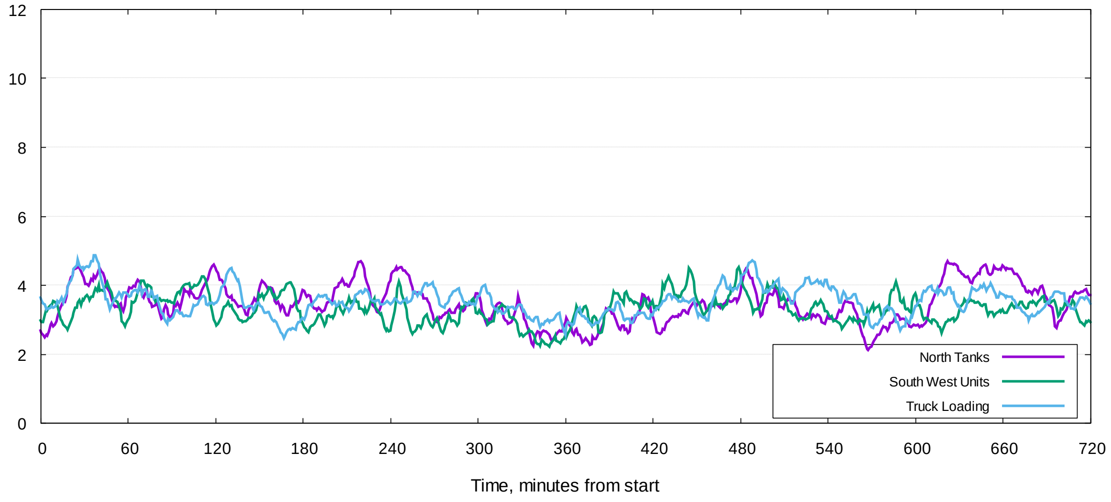

Vector Wind Speed, m/s


Vector Wind Direction, degrees

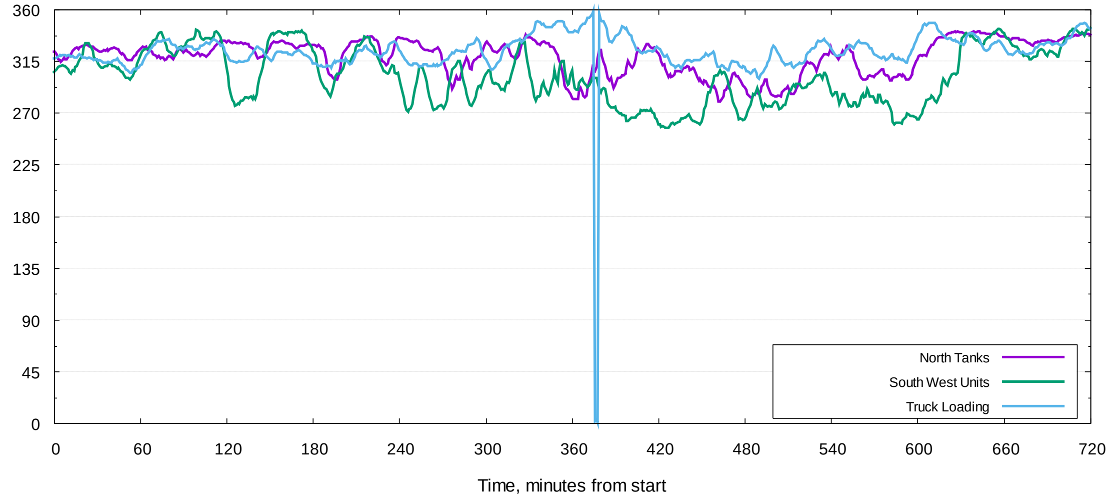

Persistence
1
0.9
0.8
0.7
0.6
0.5
0
60
120
180
240
300
360
420
480
540
600
660
720
Time, minutes from start
40
50
60
70
80
90
100
120
140
160
180
120


Vertical Wind
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0
60
120
180
240
300
360
420
480
540
600
660
720
Time, minutes from start
40
50
80
90
100
120
140
160
180
120

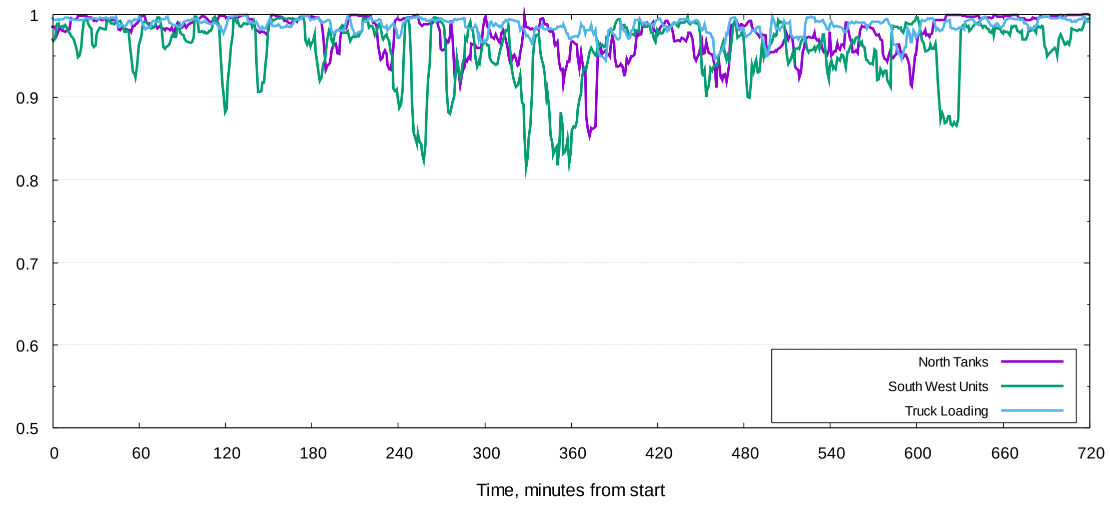
Vector Wind Speed, m/s



Vector Wind Direction, degrees



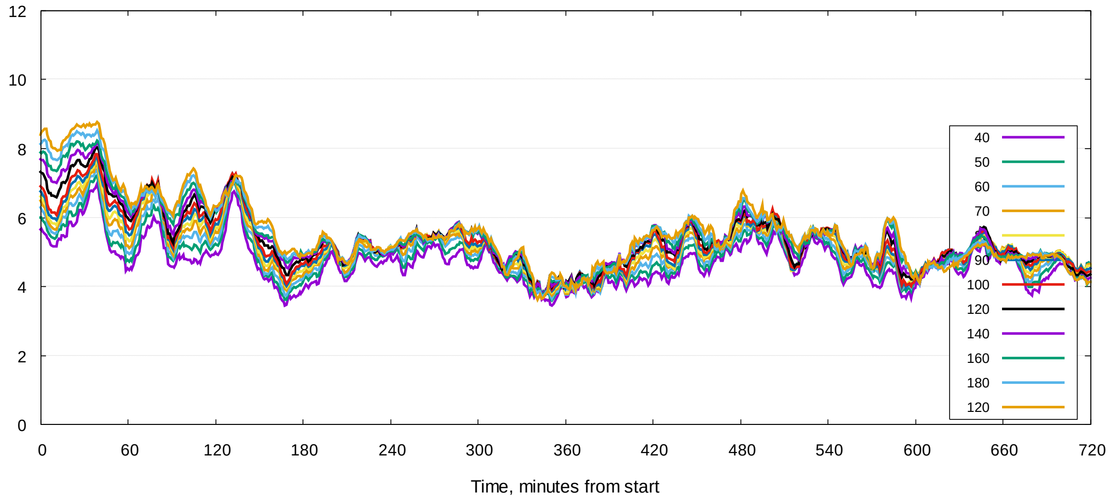
Persistence



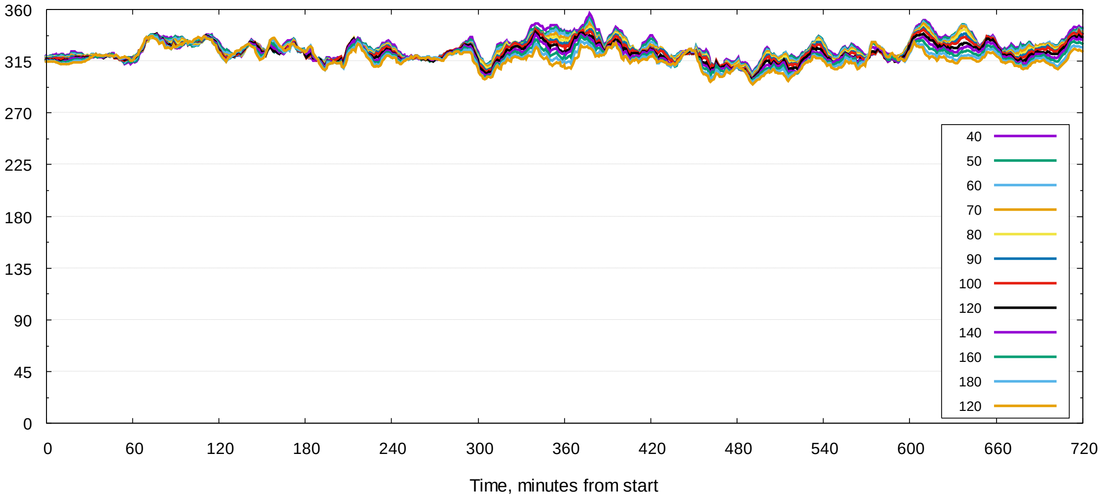
Day: 17th June 08:00 – 20:00

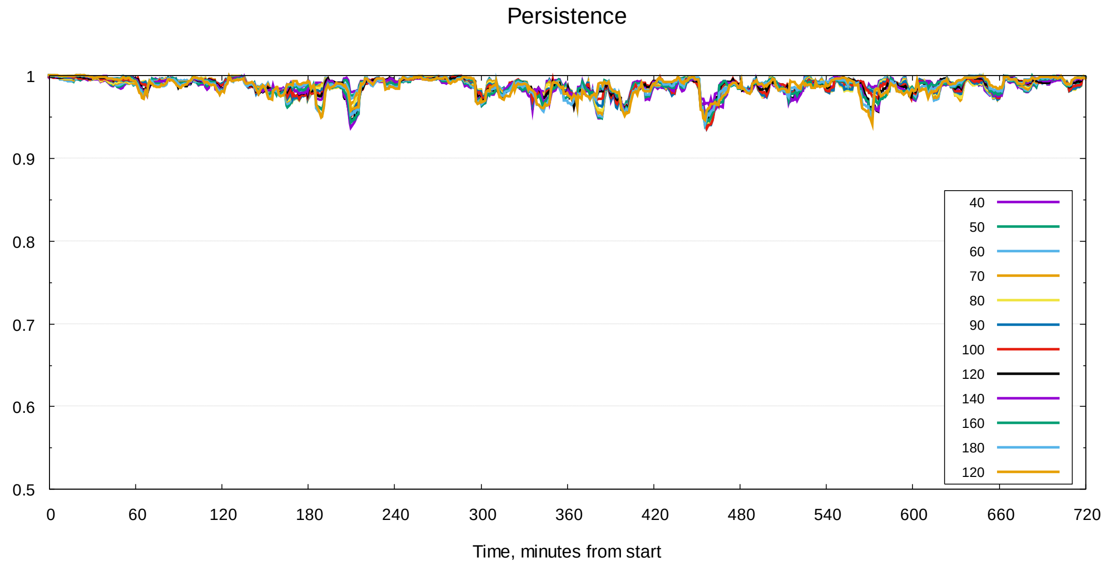
Lidar data for the 17th of June.

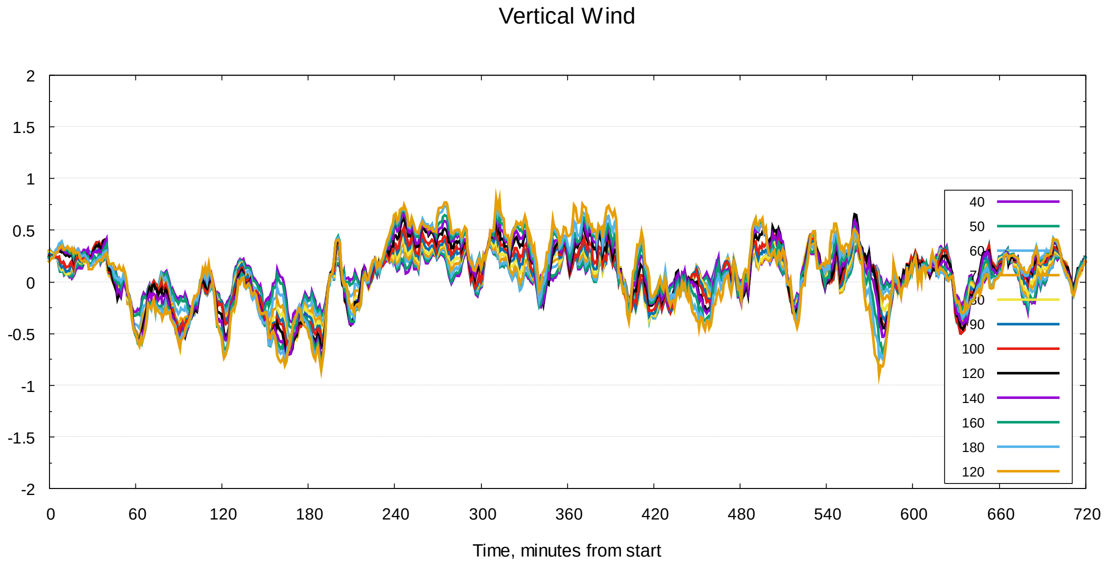
Vector Wind Speed, m/s

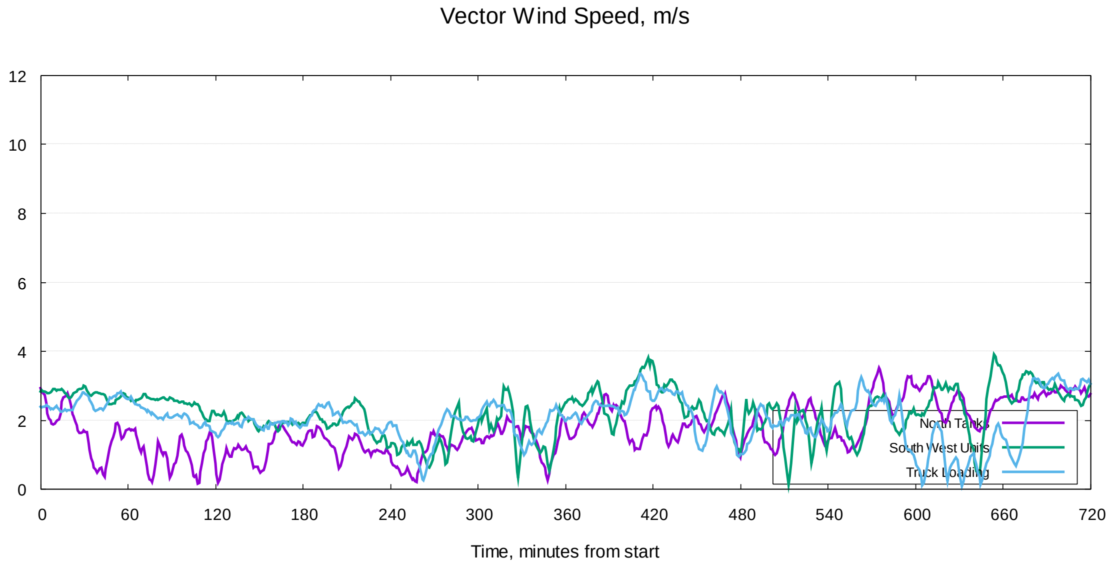


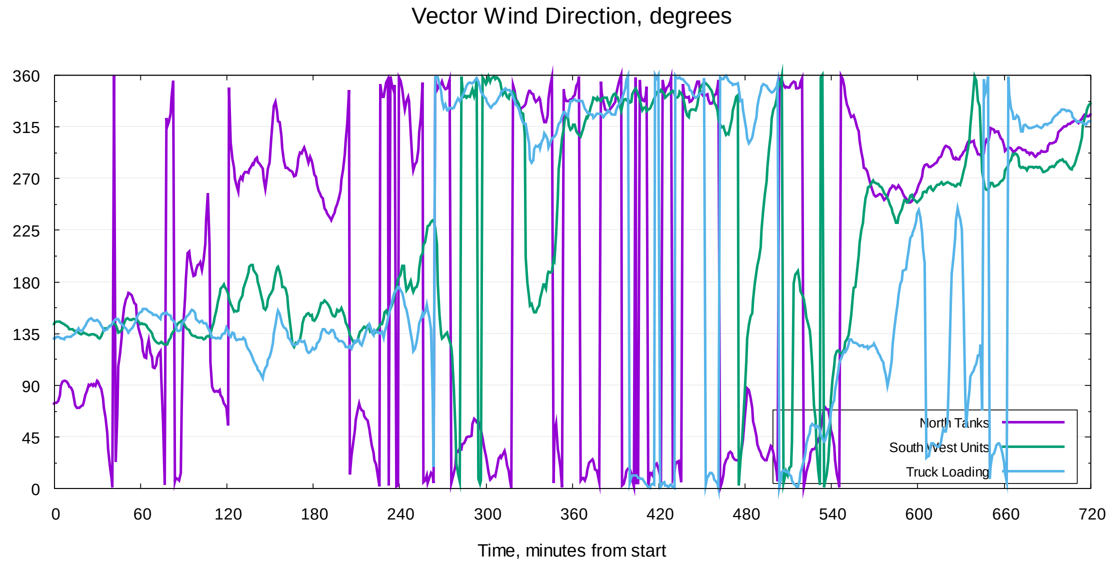
Vector Wind Direction, degrees

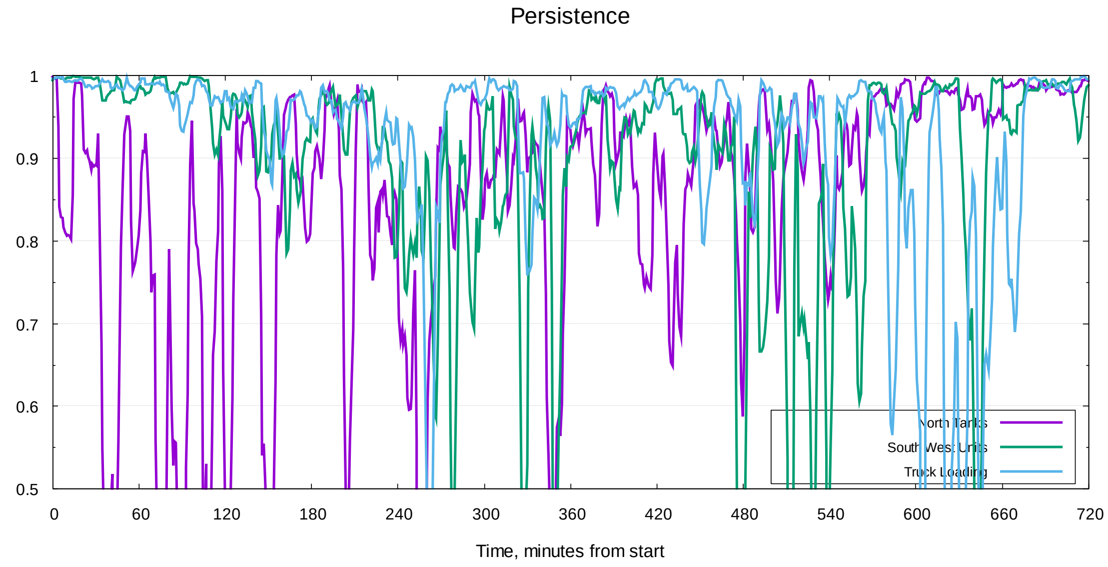



Persistence


Vertical Wind

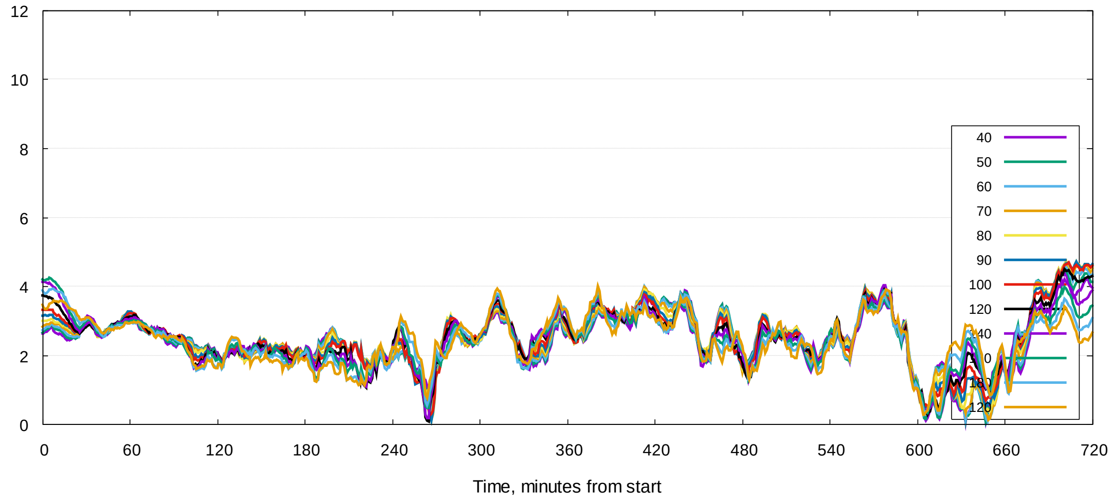


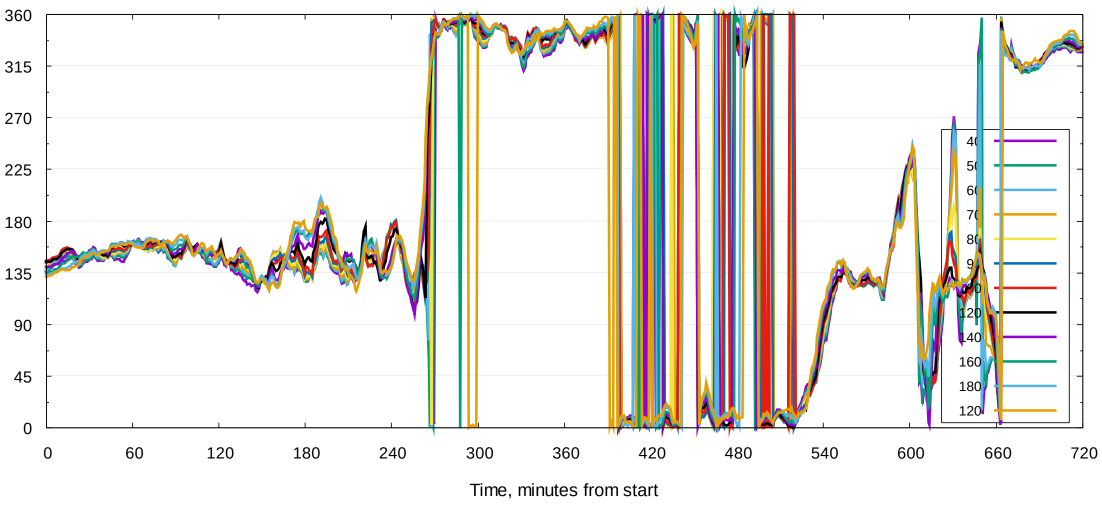




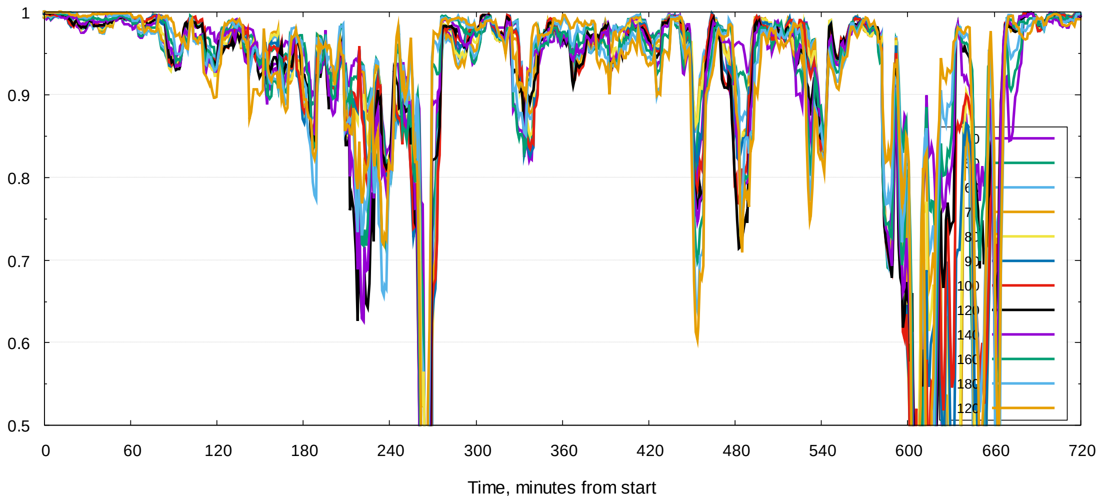
Day: 18th June 08:00 – 20:00

Lidar Data for the 18th June.

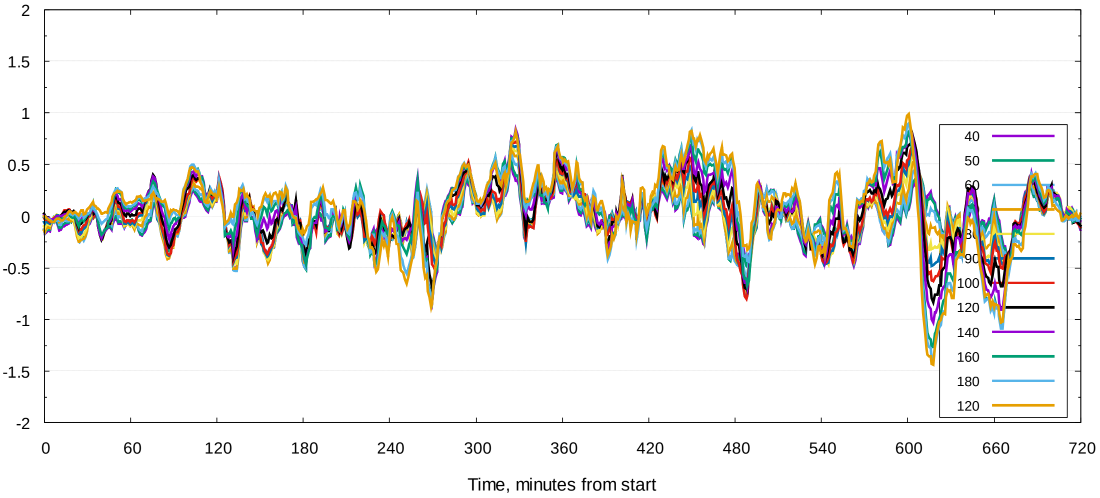

Vector Wind Speed, m/s


Vector Wind Direction, degrees

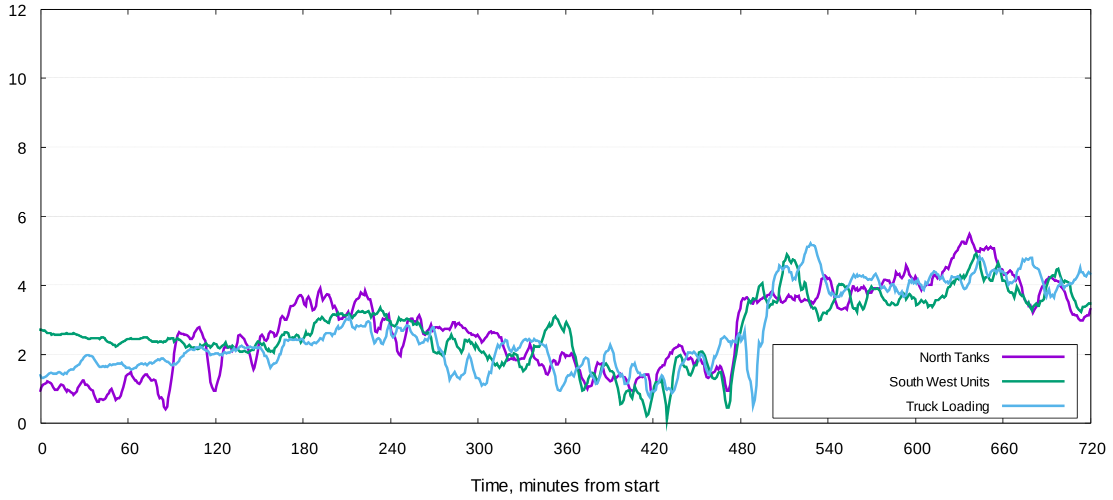
Persistence



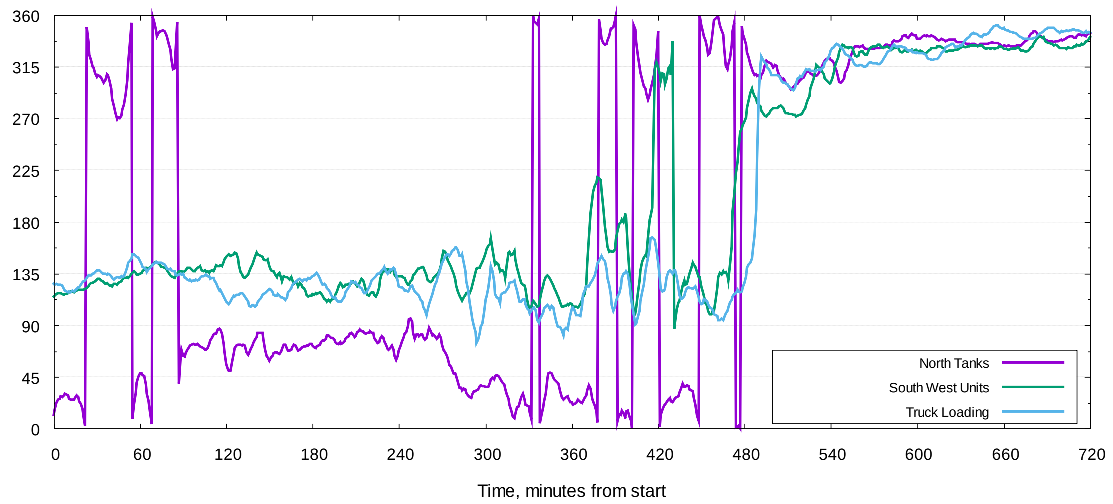
Vertical Wind



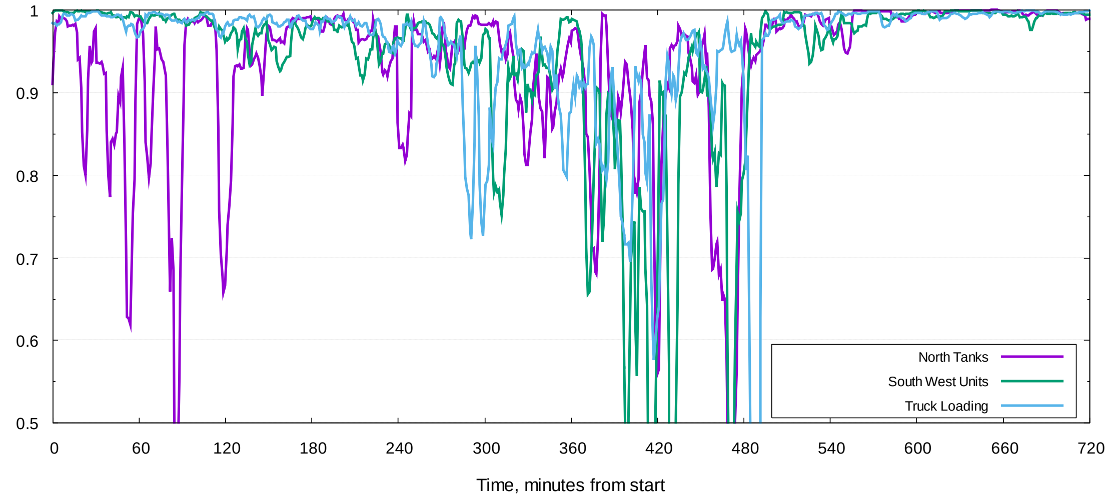
Vector Wind Speed, m/s



Vector Wind Direction, degrees

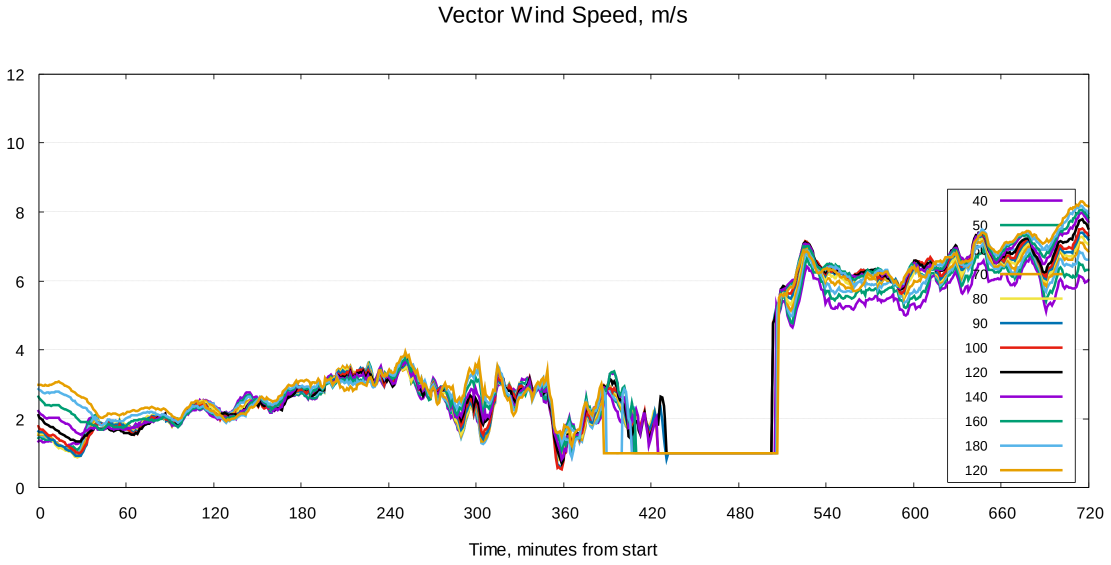


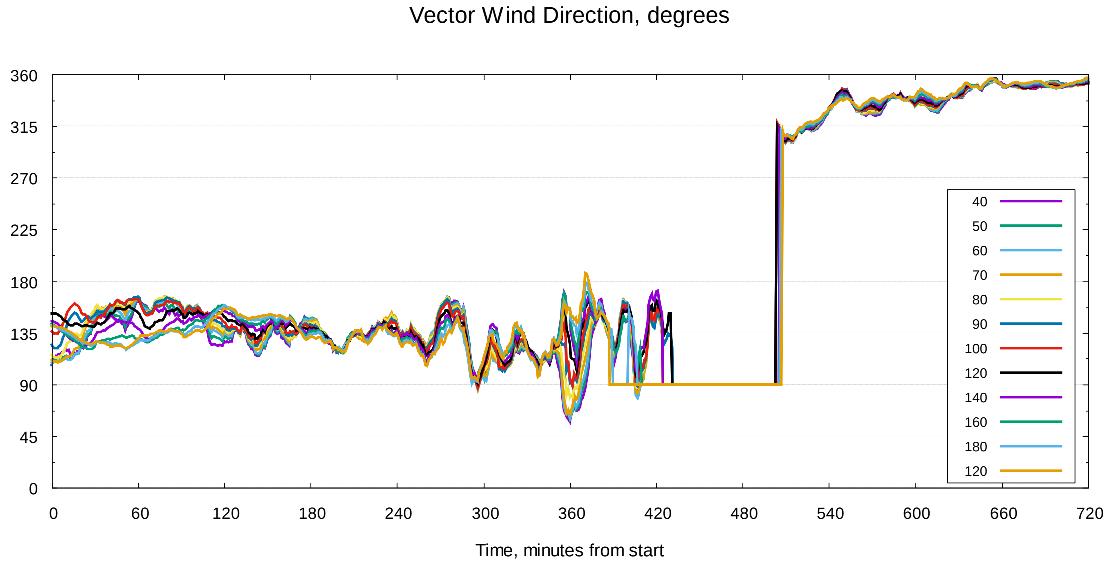
Persistence

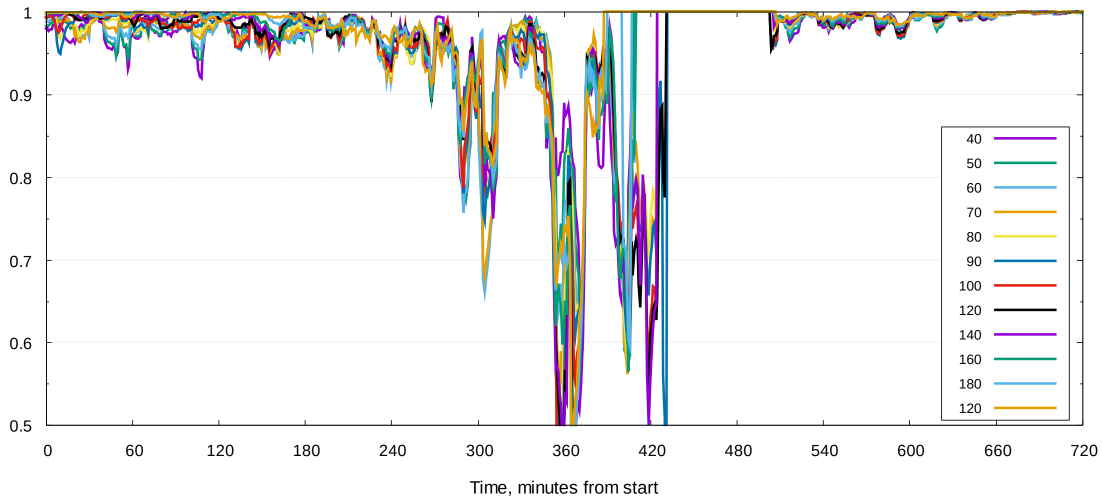


Day 19th June 08:00-20:00

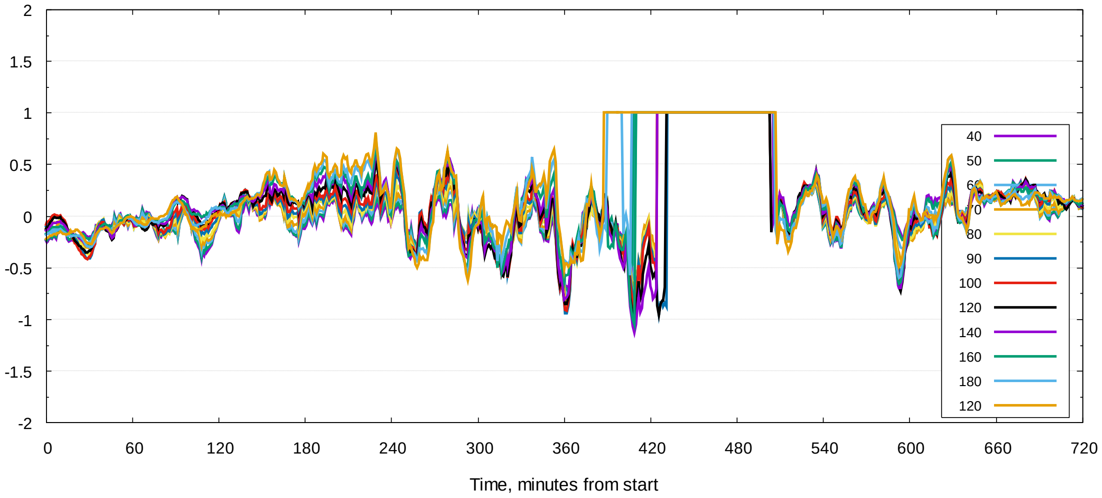
Lidar Data for June 19th


Vector Wind Speed, m/s

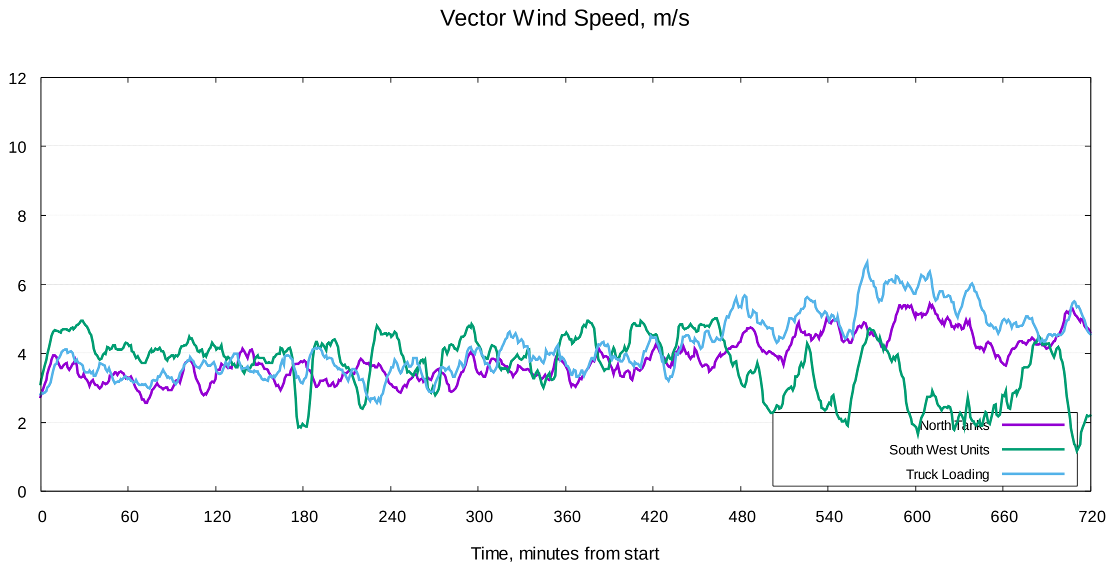

Vector Wind Direction, degrees

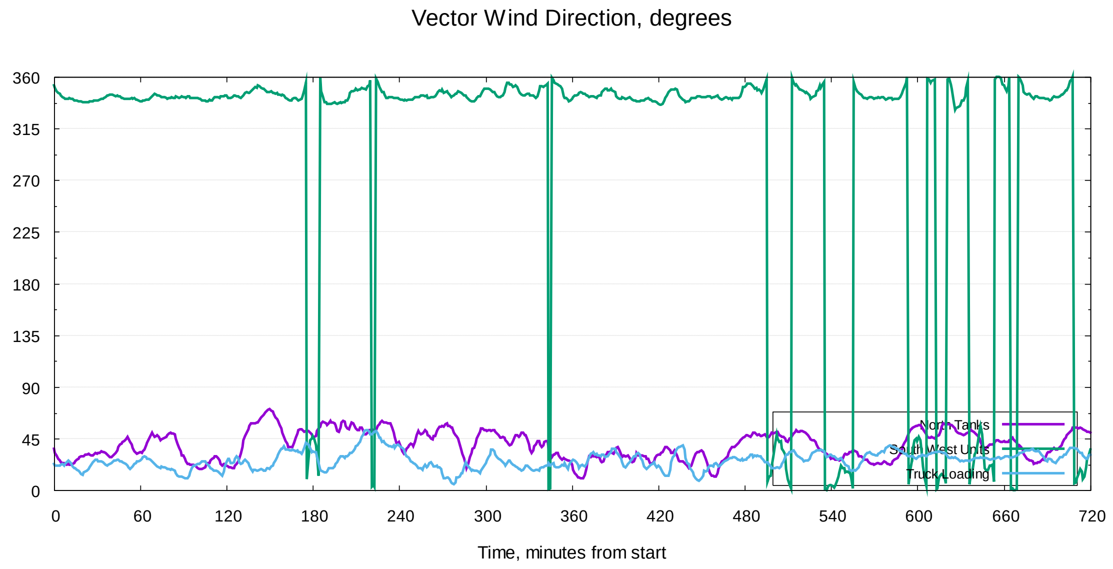


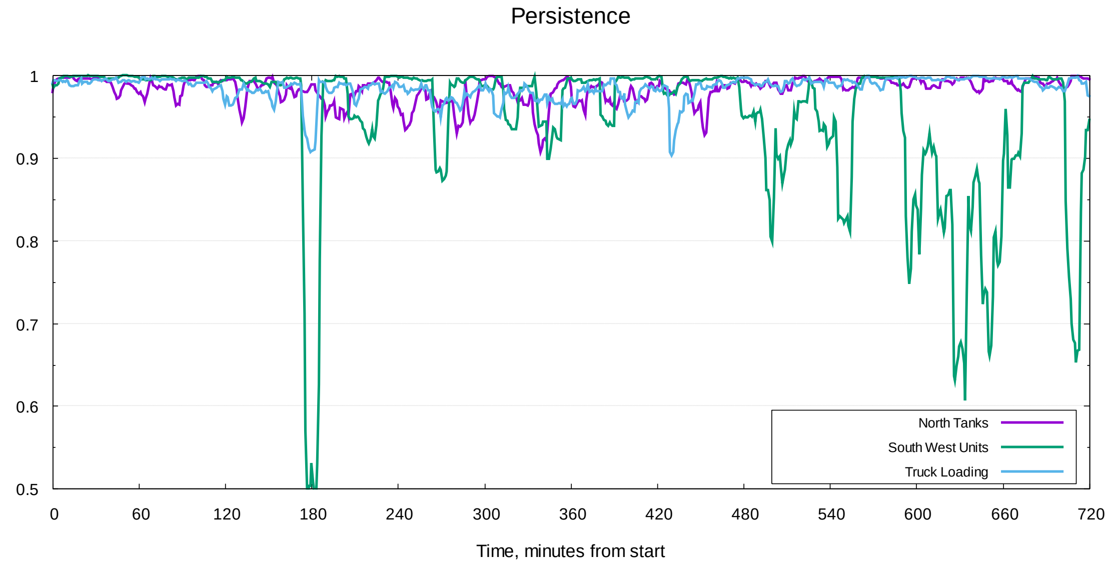
Persistence



Vertical Wind

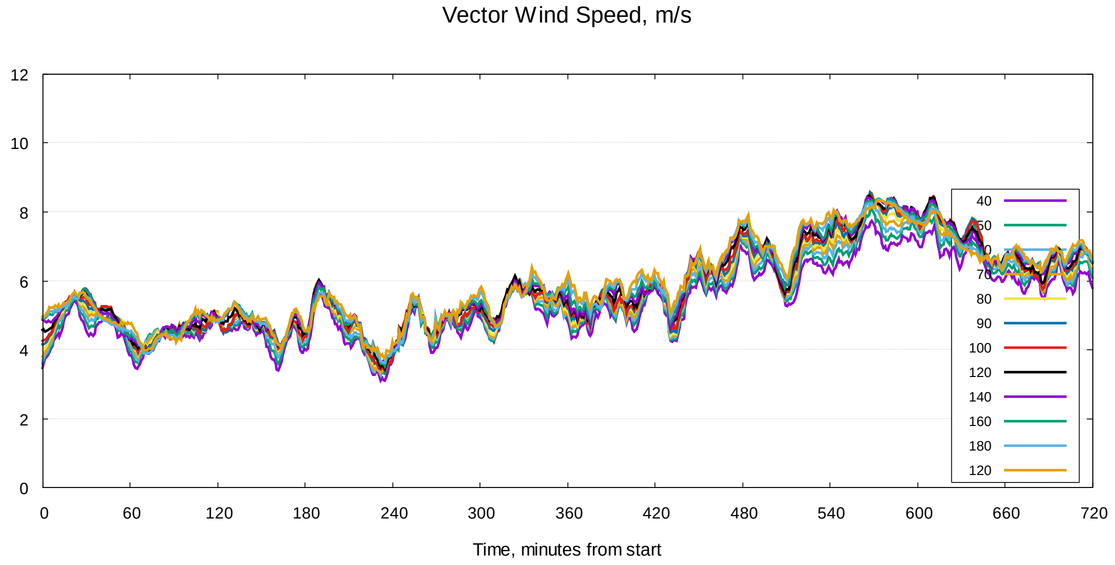


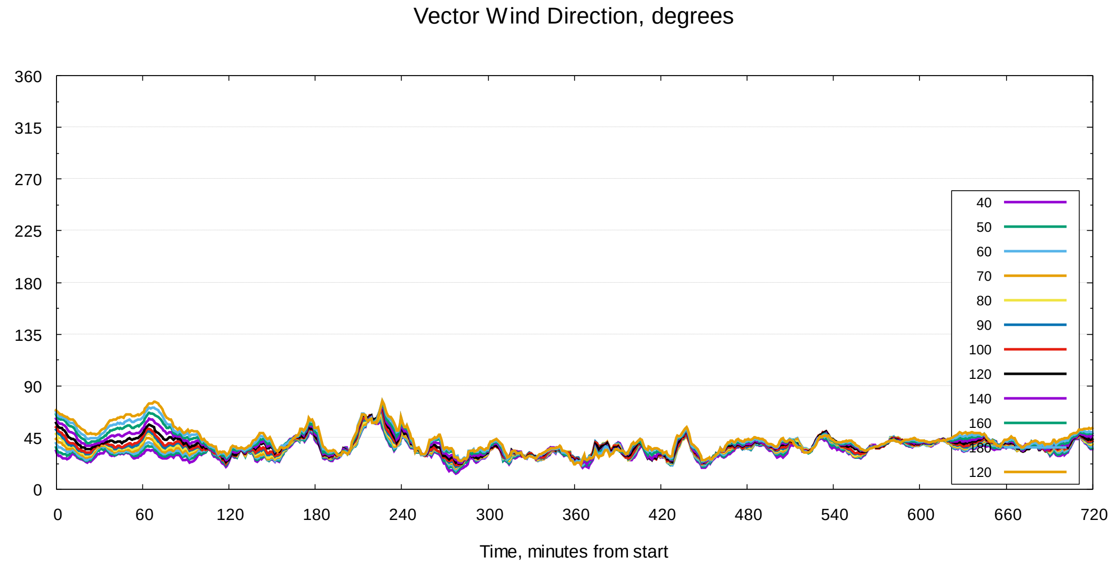


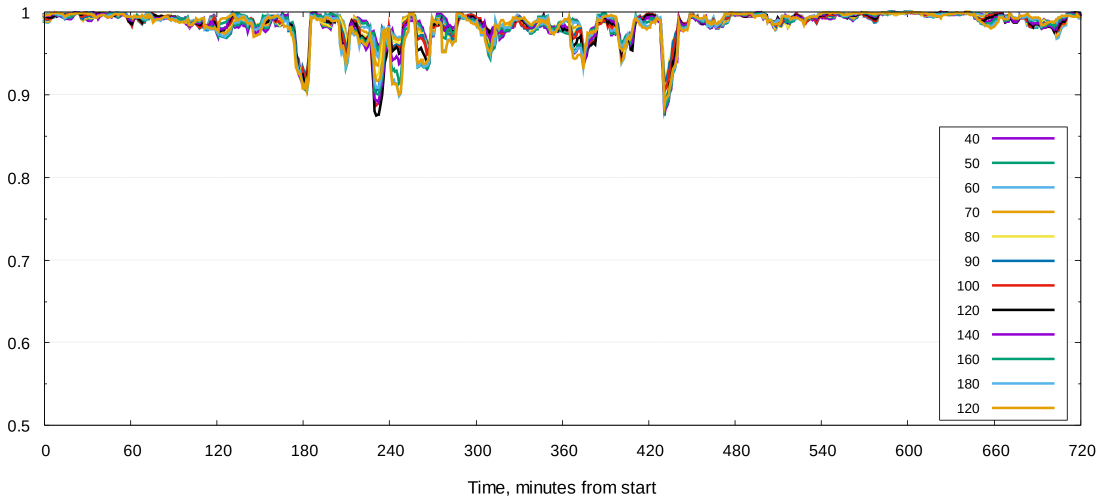


Day 20th June 08:00 – 20:00

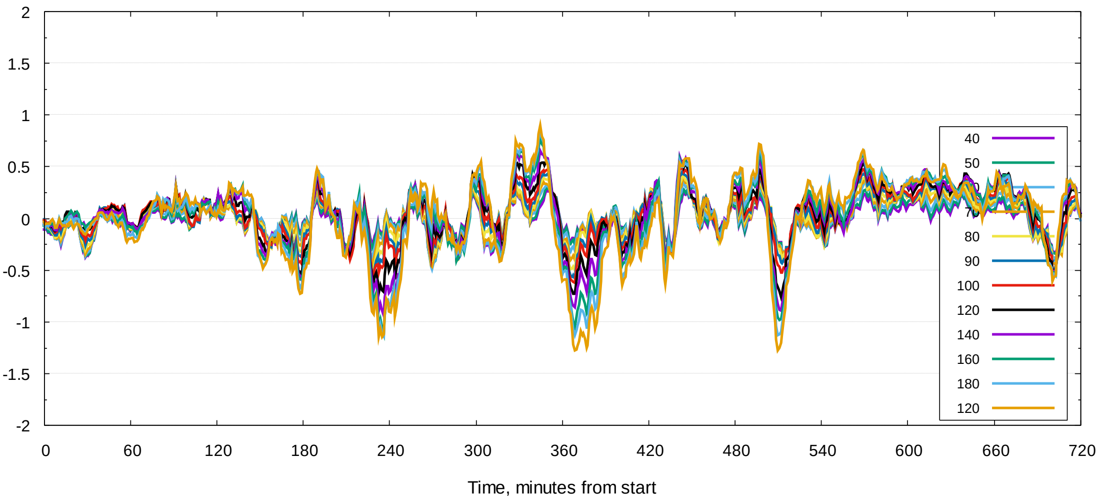
Lidar Data for June 20th


Vector Wind Speed, m/s

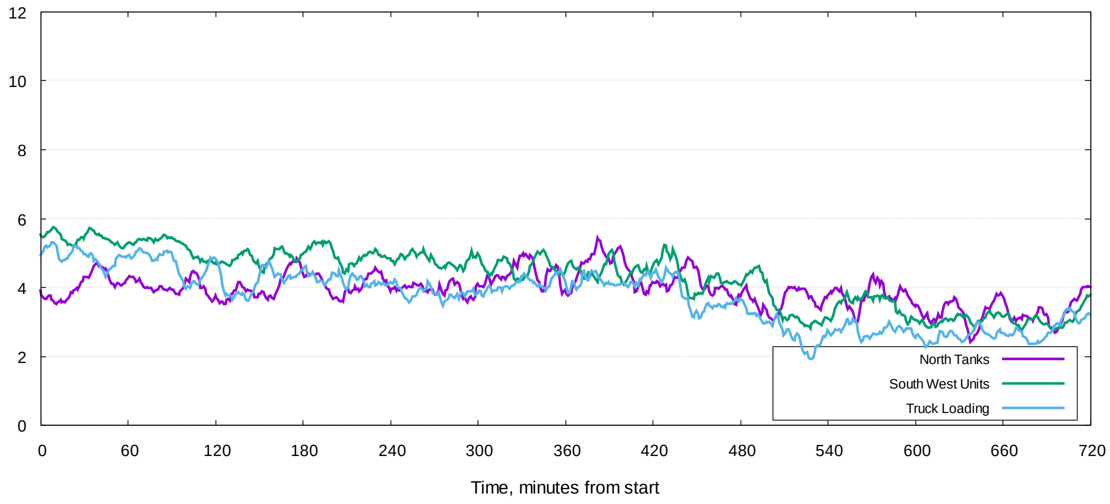

Vector Wind Direction, degrees



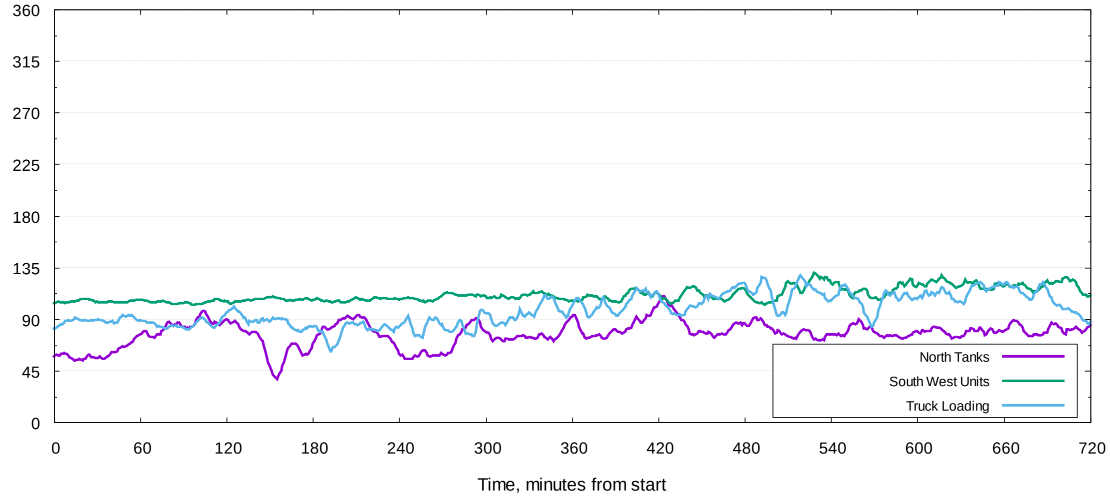
Persistence



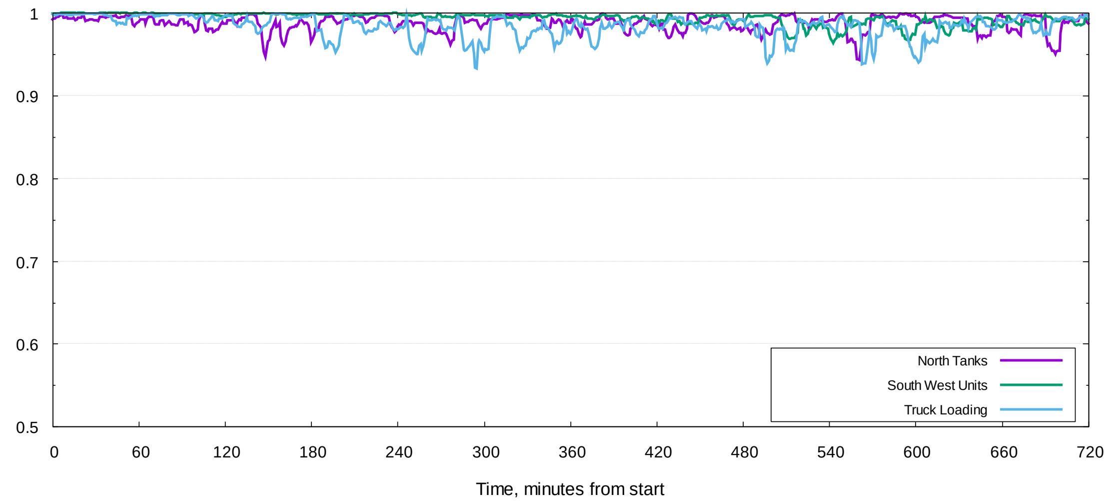
Vertical Wind



Vector Wind Speed, m/s

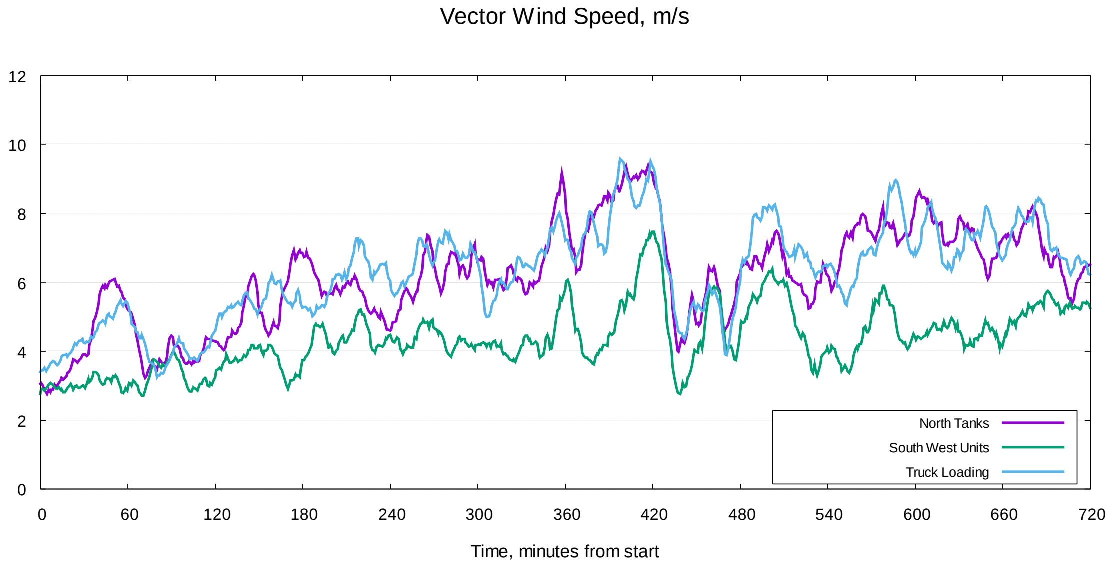


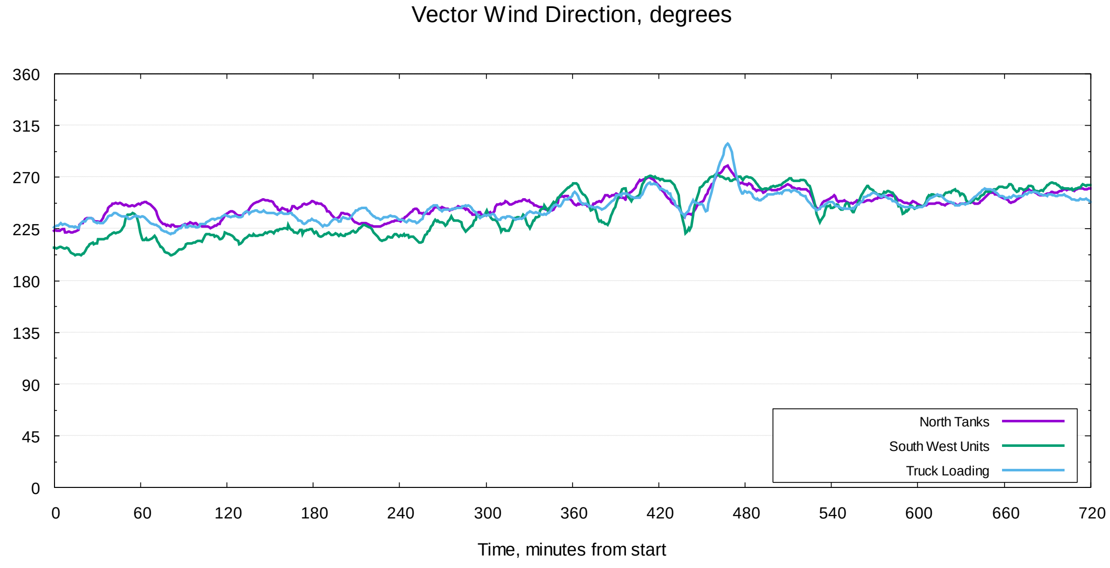
Vector Wind Direction, degrees

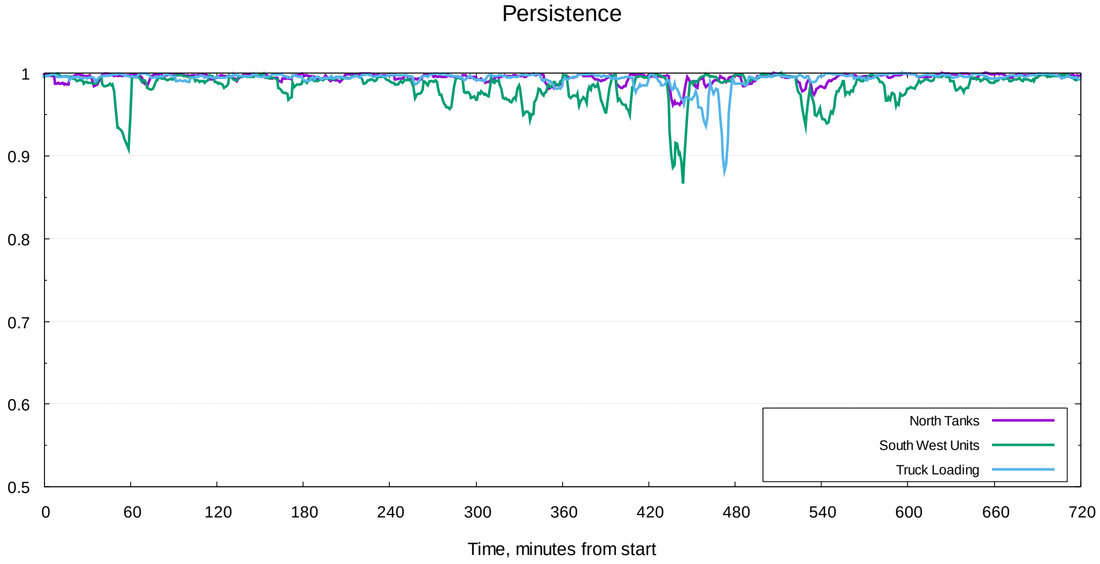


Persistence

Day 21st June 08:00-20:00


Vector Wind Speed, m/s


Vector Wind Direction, degrees


Persistence

Day: 22nd June 08:00 – 20:00

Report reference: **389923/7000393-1**

To the attention of: CEN WG38

Project followed by: MARTINEZ Jonathan
Operations Manager
Phone: +33 6 17 57 76 79
E-mail: jonathan.martinez@fr.bureauveritas.com

WG38 – Site test #1 – September 2016

Work Package 4 - Report

Writer: Jonathan Martinez

BUREAU VERITAS
Revision 0 – June 2018

✓ OBJECTIVES

The main objective of the Work Package 4 was to use the OGI as a linked technology to assist remote monitoring methods during two field validation exercises.
The OGI was used to determine the exact location of the leaking sources of the main emissions highlighted by the remote monitoring methods.

✓ SCOPE OF WORK

At Site 1 (Relatively simple site with controlled releases), the OGI was mainly used to confirm its ability to highlight known emission sources with different emission levels.

SUMMARY

I - Phases description and methodology

The performed tasks included the following phases:

1/ - Theoretical study

1A - OGI selection
1B - Specifications of the OGI completed
1C - OGI validation requirements

2/ - Actions to be performed during execution of WP5 (Site 1)

2A - Preparation
2B - Presence at site 1 during trials
2C - Reporting

1) - THEORETICAL STUDY

PHASE 1A - OGI selection

Assisted by our European Centre of Expertise (Fugitive Emissions Management **CoE**) and thanks to our providers' network and experience, we have selected an OGI from those available.

The selected OGI was obviously the most commonly used in Europe and around the world.
In addition to meeting all requested criteria for ensuring the best possible leak detection, the use of this OGI allows reflecting the best practices of the leak detection activity.

The model used during the 1st site test was the GF320 from FLIR System.

PHASE 1B - Specifications of the OGI completed

After completion of the previous phase, we have collected the specifications of the selected OGI.

PDF

GF320_US.pdf

PHASE 1C - OGI validation requirements

In order to ensure the proper execution of the OGI validation task during the field trials, we have detailed the requirements for the implementation of the selected OGI.

OGI - Method Statement.pdf

2) - ACTIONS TO BE PERFORMED DURING EXECUTION OF WP5 (SITE 1)

PHASE 2A - Preparation

Prior to using the OGI for this study, we have proceeded to the following steps:
- Checking and revisions of the OGI
- Creation of a dedicated data recording support (for data collection on site)
- Logistic organisation (people and tools)

PHASE 2B - Presence at site 1 during trials

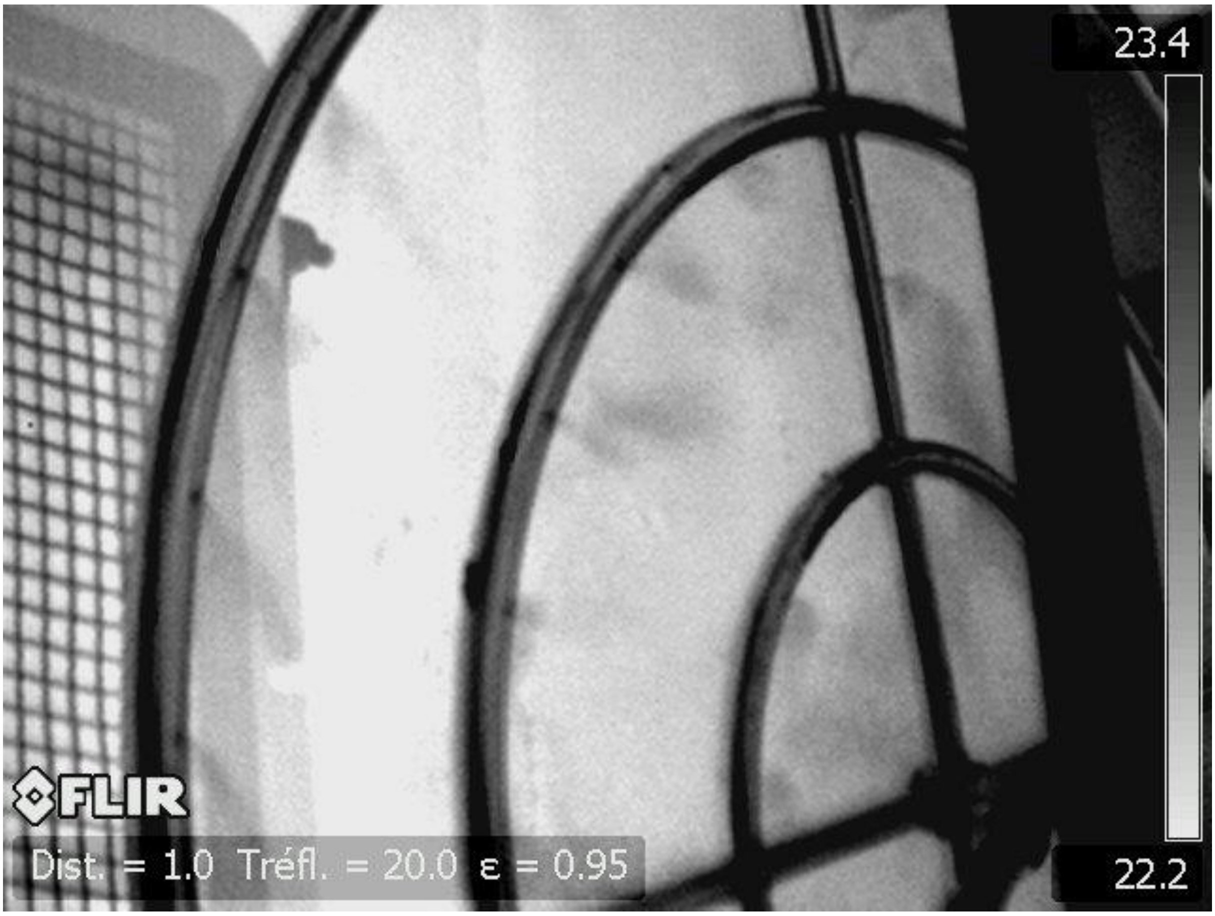
From our operational team we have selected 1 inspector (plus one in spare) qualified in the use of OGI with extensive experience in O&G leak detection. He was equipped with all necessary PPEs and an OGI "GF320" (plus a spare).

During each one of the 20 controlled releases that occurred at site 1 trials, our inspector respected the following operating procedure:

- Prior daily check of the OGI's ability to detect a liberated emission from a certain distance
- Leak detection starting from far away of the plant (for safety reasons)
- Leak detection performed in HSM mode
- Setting of all necessary OGI parameters such as:
    - Temperature range
    - Polarity
    - Histogram detection mode
    - Focus
    - Distance of detection (according to daily check results)
- Research of the most adapted background (to allow easy leak detection)
- IR video recording
- Collection of information into the "data recording support"

During each release, each one of the 5 potential emission sources (controlled release sources) of VOCs has been screened using the OGI.

Even if the OGI cannot estimate emission rates, our inspector recorded into our "data recording support" his estimation of emissions rate in comparing the current emission to the previous ones observed.


23.4
22.2
FLIR
Dist. = 1.0 Tréfl. = 20.0 ε = 0.95

PHASE 2C - Reporting

A "data recording support" has been utilised for each one of the 20 releases.

Collected data rev0
(translated to English

For each detected emission, at least one IR video has been recorded.

Report reference: **389923/7000393-2**

To the attention of: CEN WG38

Project followed by: MARTINEZ Jonathan
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E-mail: jonathan.martinez@fr.bureauveritas.com

WG38 – Site test #2 – June 2017

Work Package 4 - Report

Writer: Jonathan Martinez

BUREAU VERITAS
Revision 0 – June 2018

*Avançons en confiance

BUREAU VERITAS 1828
E C S
Move Forward with Confidence*

✓ OBJECTIVES

The main objective of the Work Package 4 was to use the OGI as a linked technology to assist remote monitoring methods during two field validation exercises.
The OGI was used to determine the exact location of the leaking sources of the main emissions highlighted by the remote monitoring methods.

✓ SCOPE OF WORK

At Site 2 (Complex operating site), the OGI was mainly used to confirm its ability to locate precisely emission sources within areas described as "main emitters" by the remote monitoring methods.

SUMMARY

I - Phases description and methodology

The performed tasks included the following phases:

1/ - Theoretical study

1A - OGI selection
1B - Specifications of the OGI completed
1C - OGI validation requirements

2/ - Actions to be performed during execution of WP6 (Site 2)

2A - Preparation
2B - Presence at site 2 during trials
2C - Reporting

1) - THEORETICAL STUDY

PHASE 1A - OGI selection

Assisted by our European Centre of Expertise (Fugitive Emissions Management **CoE**) and thanks to our providers' network and experience, we have selected an OGI from those available.

The selected OGI was obviously the most commonly used in Europe and around the world.
In addition to meeting all requested criteria for ensuring the best possible leak detection, the use of this OGI allows reflecting the best practices of the leak detection activity.

The model used during the 2nd site test was the GFX320 from FLIR System.
It has the same capabilities as the GF320, but this one is also ATEX rated (for Zone 2).

PHASE 1B - Specifications of the OGI completed

After completion of the previous phase, we have collected the specifications of the selected OGI.

FLIR-GFx320-Datasheet-EN.pdf

PHASE 1C - OGI validation requirements

In order to ensure the proper execution of the OGI validation task during the field trials, we have detailed the requirements for the implementation of the selected OGI.

OGI - Method Statement.pdf

2) - ACTIONS TO BE PERFORMED DURING EXECUTION OF WP6 (SITE 2)

PHASE 2A - Preparation

Prior to using the OGI for this study, we have proceeded to the following steps:
- Checking and revisions of the OGI
- Creation of a dedicated data recording support (for data collection on site)
- Logistic organisation (people and tools)

PHASE 2B - Presence at site 2 during trials

From our operational team we have selected 1 inspector (plus one in spare) qualified in the use of OGI with extensive experience in O&G leak detection. He was equipped with all necessary PPEs and an OGI "GFX320" (plus a spare).

Every time an emission area was detected by a major technique, our inspector was called to try to locate the emission source(s) responsible of the detected emission.

The leak detection occurred respecting the following operating procedure:

- Prior daily check of the OGI's ability to detect a liberated emission from a certain distance
- Leak detection starting from far away of the plant (for safety reasons)
- Leak detection performed in HSM mode
- Setting of all necessary OGI parameters such as:
    - Temperature range
    - Polarity
    - Histogram detection mode
    - Focus
    - Distance of detection (according to daily check results)
- Research of the most adapted background (to allow easy leak detection)
- IR video recording
- Collection of information into the "data recording support"

During each requested leak research, our inspector controlled (using the OGI) all potential emission sources present into the area delimited by the major technique.

He also delimited each "suspected emitting areas" on a plant map and estimated the associated surface, in order to collect information about the ability of each major technique to locate emissions sources.


Fluxense
TOTAL
NPL
B8
B5
A3
B3
B2
C1
B4
B7
A4
A1
B11
B9
B10
A2
B1
B6

PHASE 2C - Reporting

A "data recording support" has been utilised for each one of the 42 requests of leak detection.

Collected data rev1.xlsx

115591-115591 (Simplified plot plan).pdf

For each detected (or undetected) emission, at least one IR video and one picture (in visible light) has been recorded.

Observations:

Most of the leaks detected during this survey (42/43) are out of the LMDAR scope as they are channelled emissions, surface emissions or tanks roofs emissions.

Based on observation of the leaks, in terms of emission rate, all detected emissions seem to be bigger than the emissions usually observed during LDAR surveys. 100% of them can be detected from more than 20 meters distance, when classic LDAR emissions are usually detectable from < 5 meters.

In terms of delimitation of areas emitting VOCs, the SOF has shown more efficiency than the DIAL.
The areas delimited by SOF were much more precise than the ones collected from DIAL technique. So the time spent using OGI to localise the emission source(s) was more important in those cases.

The "combination of major techniques + OGI" gave successful results in storages areas, where a low density of potential emitters was observed.

The "combination of major techniques + OGI" didn't give successful results in process areas, where a high density of potential emitters was observed.

NPL REPORT CMES (RES) 035

CONTROLLED RELEASE FACILITY (CRF) RESULTS FOR THE FIRST WG38 FIELD VALIDATION STUDY IN SOUTH OF FRANCE, SEPTEMBER 2016

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NPLML - COMMERCIAL

JUNE 2018

Controlled Release Facility (CRF) Results for the First WG38 Field Validation Study in South of France, September 2016

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Chemical, Medical & Environmental Science Division

ABSTRACT

This report presents results of the quantified propane releases carried out using the National Physical laboratory (NPL) controlled release facility (CRF) in the South of France. This study was the first WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 22nd to the 29th of September 2016.

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Approved on behalf of NPL by
Alan Brewin, Director, Operations Division.

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EXECUTIVE SUMMARY

Background

The European Commission's standardisation mandate M/514 under the Directive 2010/75/EU on industrial emissions, was accepted by CEN/BT, and a decision was taken to establish this standardisation work within CEN/TC264/WG38.

The control of the emissions of VOCs to atmosphere due to their losses during storage or transport is covered by both EU legislation and international protocols. The legislation on industrial emissions (Directive 2010/75/EU) is supported by the Best Available Techniques Reference documents (BREFs), which set out at an EU level the best available techniques for defined industrial activities and/or across these activities. Several BREFs also cover the prevention and control of fugitive and diffuse emissions of VOCs from industrial storage and transfer activities, in particular the BREFs concerned with mineral oil and gas refineries, large volume organic chemicals, and the "horizontal" BREF on the emissions from storage. The mandate for this work requests the European standardisation organisations to develop a European Standard that can be used in the determination of VOC emissions to be regulated within permits that are issued according to the Directive.

Total VOC emissions are also regulated at the EU and Member States levels under the National Emission Ceilings Directive (2001/81/EC) which sets total emission ceilings for such emissions at specific levels to be met from 2010 onwards.

VOCs are emitted by a wide range of sources including transport and industrial processes, as well as biogenic and other natural sources, and also by associated storage and handling activities, and the industrial and domestic use of VOC containing products.

VOCs are emitted to a significant extent by fugitive and diffuse sources (including non-point sources), although this is difficult to quantify accurately. This requirement for more accurate determination of these important VOC emissions creates a challenge because of their area emissions, and they require specific measurement and estimation methods that are currently not standardised. However, improving the accuracy of determining these VOC emissions should enable an improved assessment of these losses, and may provide an incentive to reduce such losses, as well as the benefits to their effects on the environment and human health. This should also contribute to the more uniform application of EU regulations and EU guidance documents.

Objectives

Mandate M/514 requires CEN to prepare and validate a standard for the determination of diffuse and fugitive emissions from oil and gas facilities. It should be complementary to the existing standard for the determination of leaks from piping and equipment EN 15446:2008.

This European Standard specifies the framework for determining emissions to the atmosphere of Volatile Organic Compounds (VOCs). It defines a system of methods to detect and/or identify and/or quantify diffuse/fugitive emissions from industrial sources. These methods include Optical Gas Imaging (OGI), Differential Absorption Lidar (DIAL), Solar Occultation Flux (SOF), tracer correlation, flux chamber measurement techniques, calculation and estimation methods.

Two validation studies will be undertaken. The first will use a controlled release, able to replicate typical industrial emission levels, at an industrial location to challenge the remote sensing techniques with a known release of VOC under typical industrial conditions. A second validation study will deploy the suite of techniques at an industrial facility to validate the combined framework of techniques defined in the standard and demonstrate their operation at a typical site.

A decommissioned area of a refinery in Southern France was selected as the location for the first validation study, taking place from 22nd - 29th September 2016. Testing used a controlled release facility (CRF) provided by the National Physical laboratory (NPL) to measure a known quantity of VOC. Four participants participated in the tests, running a total of five instruments, covering five of the proposed techniques. The results obtained with the DIAL method are described in this report.

Method

The CRF was setup with five controlled release nodes inside the chosen decommissioned unit. The controlled CRF was operated by the Institut national de l'environnement industriel et des risques (Ineris) that was in charge of selecting, for each test, the release nodes and the amounts of gas, unknown to the participants. The field validation programme, consisted of twenty controlled releases of about 90 minutes each with a typical interval between releases of about 30 minutes.

Results

The table below shows the VOC emission rates reported by Ineris to the field test participants based on the nominal flow rates and the correct VOC emission rates based on the actual flow rates. The reasons for these minor differences are explained in this report. As part of this work a full uncertainty analysis has also been completed and the uncertainty values are shown in table below.

Test Number	Initial VOC Mass rate (kg/h)	Corrected VOC Mass rate (kg/h)	Uncertainty (k=1)	Percentage Uncertainty
1	5.07	5.09	0.10	1.9%
2	14.85	14.88	0.27	1.8%
3	8.87	8.83	0.16	1.8%
4	9.75	9.82	0.12	1.2%
5	9.24	9.68	0.11	1.1%
6	9.01	9.03	0.14	1.5%
7	6.59	6.73	0.10	1.5%
8	8.87	8.87	0.16	1.8%
9*	11.62	11.35	0.51	4.5%
10	18.51	18.89	0.15	0.8%
11	9.64	9.68	0.10	1.1%
12	9.75	9.75	0.12	1.2%
13	14.74	14.97	0.19	1.3%
14*	16.61	16.15	0.41	2.5%
15	4.77	4.77	0.09	1.9%
16	0.78	0.72	0.04	5.2%
17	9.24	9.57	0.21	2.2%
18*	18.86	18.24	0.51	2.8%
19	6.59	6.62	0.07	1.1%
20	12.55	12.38	0.18	1.4%

** These releases were subject to unstable (decreasing) flows*

1 INTRODUCTION

This report presents the results carried out using the National Physical Laboratory's (NPL) controlled release facility (CRF) system (shown in Figure 1.1) to produce controlled emission rates of VOC gas from a decommissioned area of a refinery in southern France, in September 2016. This was part of the first validation study to prepare and validate the standard for the determination of diffuse and fugitive emissions from oil and gas facilities within CEN/TC264/WG38, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere" for which NPL was selected to provide the CRF system to conduct validation and inter-comparison work using the selected remote sensing techniques. In order to obtain critically important quality assurance information on emission rate measurements and compare the performance of all participating optical remote sensing methods controlled released experiments were carried out using NPL CRF system by the Institut national de l'environnement industriel et des risques (Ineris) from 22nd to 29th September 2016 from inside a decommissioned unit of a refinery in Southern France. Significantly, although the location of all release nodes was known by the participating teams the actual releasing nodes during each test were not shared. Also, the mass emission rates of the test releases were not shared, as these were to be quantified by the different measurement techniques.


Figure 1.1 NPL CRF facility.

This report will feature information on the calibration of the mass flow controllers (MFCs), and the final VOC emission rates for each of the test releases. In the following section (Section 2), a description of the site and controlled release facility is provided. Details of the calibrations conducted for each of the flow controllers is given in Section 3. Section 4 presents the quantified gas release rates and concludes with a discussion of the results.

2 BACKGROUND INFORMATION

2.1 SITE DESCRIPTION

A pre-test visit to the decommissioned refinery in southern France was carried out by all the participants in June 2016 and the location of the controlled release nodes identified inside a unit circled in the red in Figure 2.1. The locations where all the participant's meteorological stations would be deployed were also identified. A total of nine meteorological stations were deployed to gather meteorological data for the different techniques as shown in Figure 2.1.

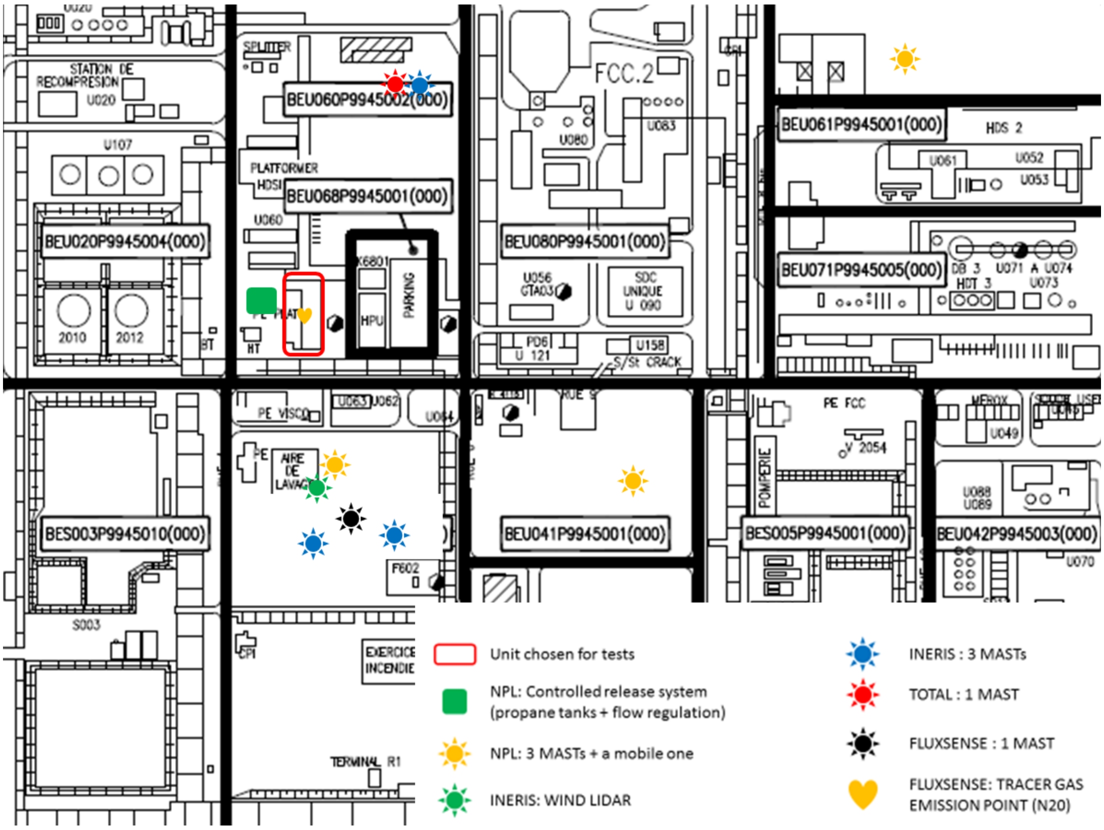


Figure 2.1 Locations of the meteorological stations

2.2 DESCRIPTION OF THE CONTROLLED RELEASE FACILITY

NPL has developed the Controlled Release Facility (CRF) to effectively simulate a broad range of real world gaseous emissions scenarios, with traceable defined fluxes, to challenge and validate new monitoring systems and methodologies. Gases can be emitted from up to four independently controlled sources which can be spread over an area of up to one hectare. A wide range of pure or mixed ratio gaseous species can be emitted, including propane up to 40 kg/h per channel. Repeatability of flow output from each primary channel is typically less than 1% of the rate.

The CRF consists of high flow gas blender controlled by custom-made software and distribution and emission system comprised of the release nodes and distribution hoses to connect nodes to the blender.

The high flow blender consists of four main gas channels, each with a MFC with full scale flow equivalent to 500 l/min propane, and two smaller channels (100 l/min nitrogen), which can be blended into each of the four main channels by the control of appropriate valves. These smaller channels are intended to be used for introducing interfering or tracer gases and also for purge gas. Figure 2.2 shows a schematic and photograph of the high flow blender system. The blender unit measures approx. 1.2 x 1.1 x 0.4 m, weighs about 100 kg and is enclosed within a housing similar to a flight case.

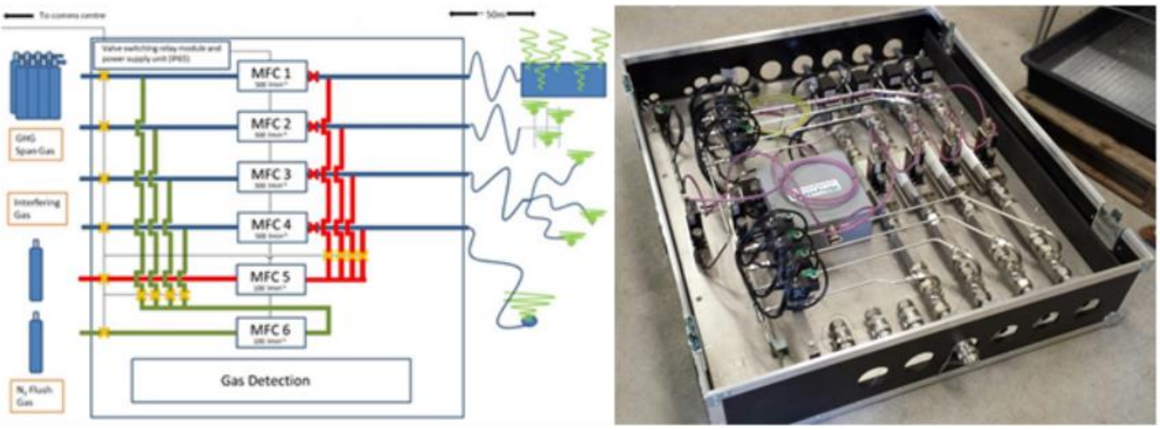


Figure 2.2 Schematic (left) and photograph (right) of the high flow gas blender

The system is controlled through customized software utilizing the Brooks SMART Interface. The software allows direct control of the MFCs and valves. Execution of a pre-programmed routine is also possible.

The CRF has four primary distribution hoses to connect the high flow blender to the release nodes. The hoses are Swagelok 1’’ PB rubber hoses that are chemically compatible with most inorganic and non-aromatic organic gases and fluids.

The CRF has been deployed successfully on a number of UK and international campaigns to validate and compare emission flux identifying and quantifying instruments and methods, including differential absorption Lidar, open-path Fourier infrared spectroscopy and optical gas imaging.

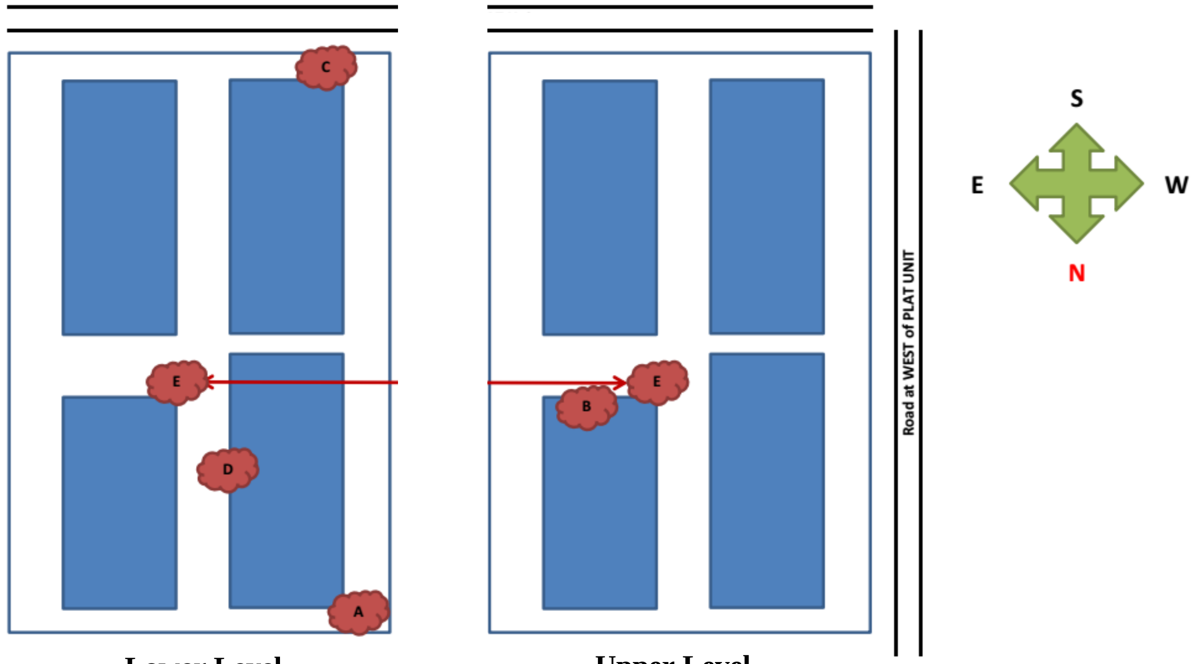
2.3 TEST RELEASES

The control system for the CRF was setup by NPL outside the selected decommissioned unit and then independently operated by the Ineris staff during the experiments. Twenty controlled release tests were performed from the 22nd to 29th September as reported in Table 2.1. Each release lasted for about 90 minutes with an interval between releases of about 30 minutes. During these tests various amounts of gas from a combination of different release nodes was emitted using the CRF, both the release rates and combination of nodes used were kept from the participating teams. The composition of released gas was mainly propane (~ 93%) with about 3% of i-butane, 2% of propane and n-butane and a very small fraction of ethane, 1-butene, 1,3 butadiene, i-pentane and n-pentane.

Table 2.1 Details all 20 test releases completed during campaign

Test #	Date	Start Time	End Time
1	22/09/2016	13:17	14:48
2	22/09/2016	15:10	16:46
3	23/09/2016	11:27	12:57
4	23/09/2016	14:00	15:30
5	26/09/2016	09:41	11:11
6	26/09/2016	12:00	13:30
7	26/09/2016	14:30	16:00
8	26/09/2016	16:05	17:30
9	27/09/2016	09:35	11:04
10	27/09/2016	11:26	13:05
11	27/09/2016	14:00	15:33
12	27/09/2016	15:55	17:25
13	28/09/2016	10:07	11:37
14	28/09/2016	12:05	13:35
15	28/09/2016	14:37	16:03
16	28/09/2016	16:45	17:50
17	29/09/2016	10:50	12:15
18	29/09/2016	12:38	13:51
19	29/09/2016	14:10	15:10
20	29/09/2016	15:30	17:00

The configuration and locations of the controlled release nodes were agreed by all project partners. Figure 2.3 shows the locations inside the selected decommissioned unit, where the five controlled release nodes (A to E) were deployed, see Figure 2.4. Note that as the CRF has only 4 MFCs, only 4 nodes could be used simultaneously.



Lower Level **Upper Level**

Figure 2.3 Locations of the five controlled release nodes

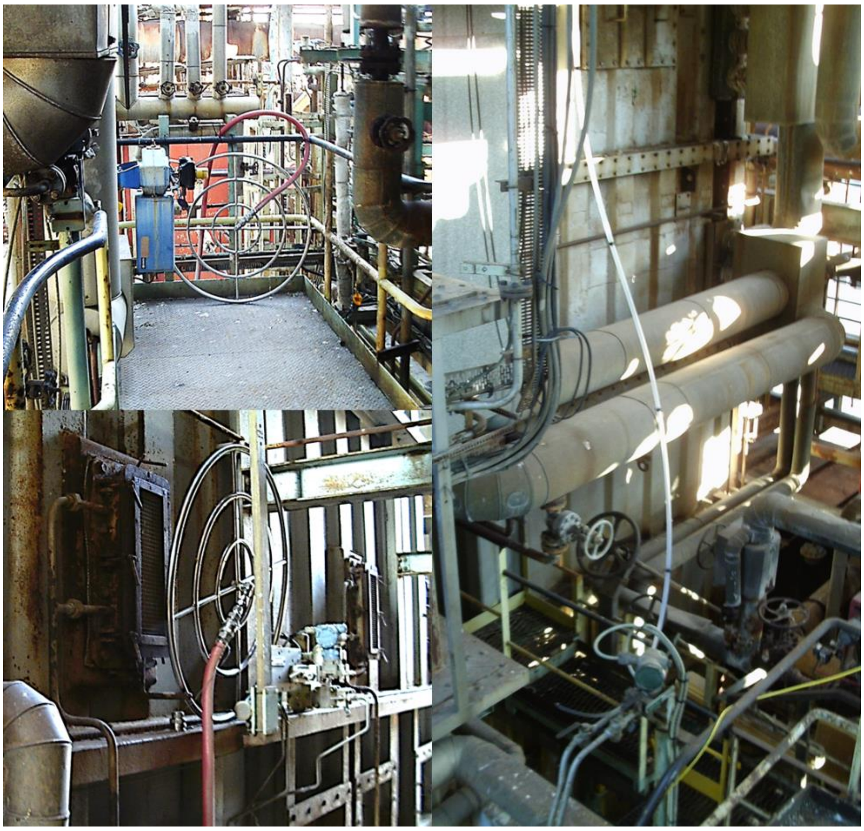


Figure 2.4 Photographs of some of the different release nodes used throughout the campaign

3 CALIBRATION OF CRF MASS FLOW CONTROLLERS

To ensure the accuracy of the CRF release rates all the MFCs were individually calibrated, using a MesaLab BIOS primary flow calibrator, during the campaign. For each MFC the gas flow was standardised to 0°C (273.15 K). The calibration plots for each MFC are shown below in Figures 3.1 to 3.4. Details of the linear fittings for each plot are found in Table 3.1.

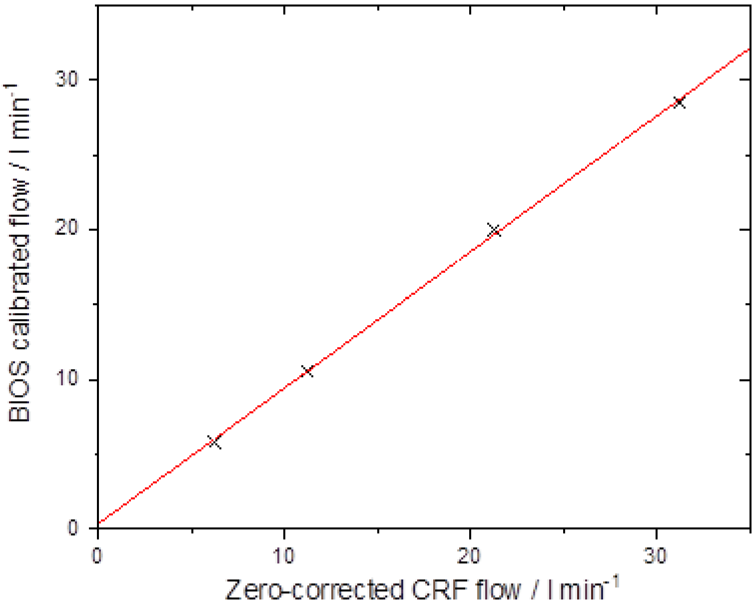


Figure 3.1 Calibration plot for MFC 1

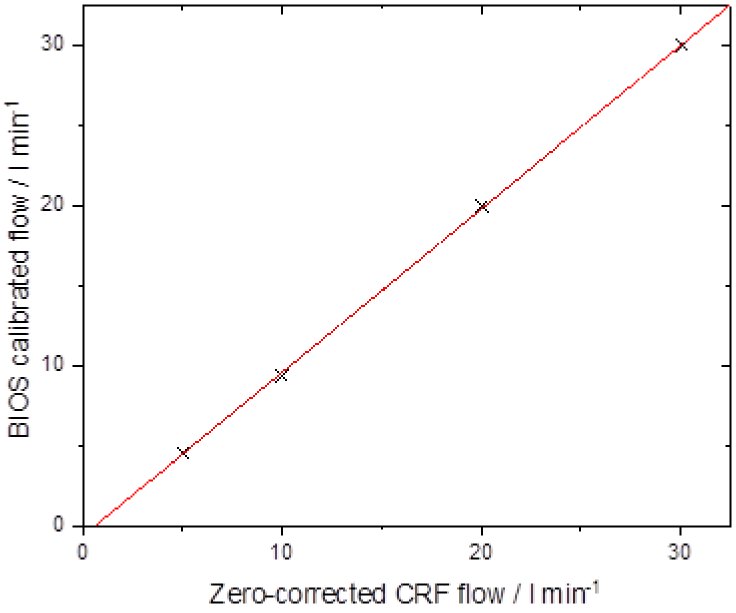


Figure 3.2 Calibration plot for MFC 2

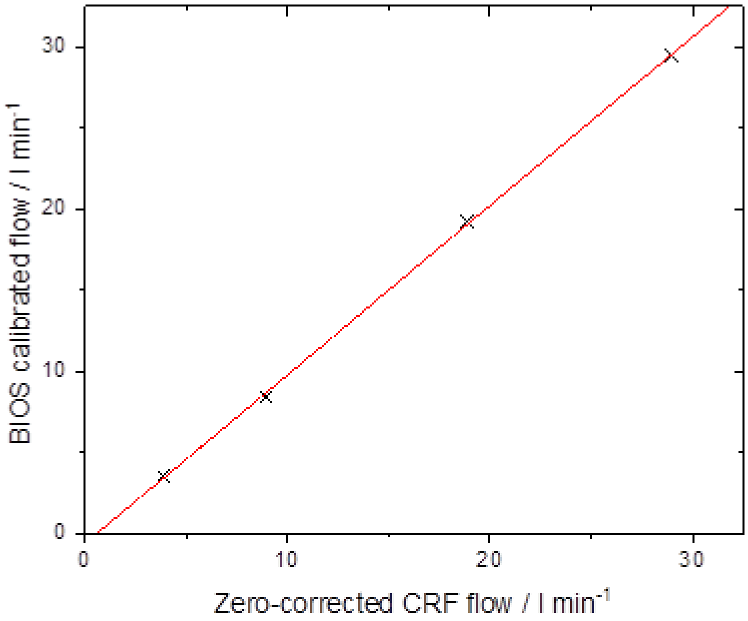


Figure 3.3 Calibration plot for MFC 3

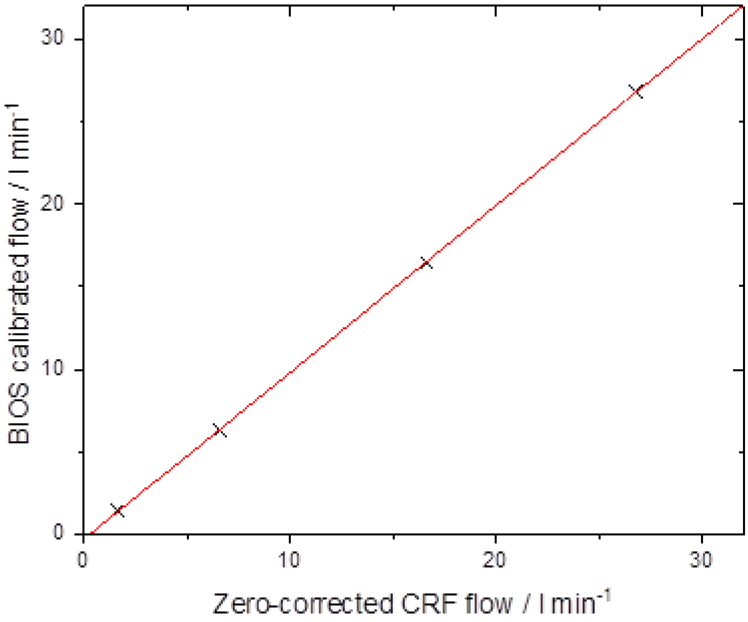


Figure 3.4 Calibration plot for MFC 4

Table 3.1 Data from analysis of MFC calibrations. The uncertainties reported are calculated from a linear regression analysis.

MFC	gradient	uncertainty in gradient	y-intercept	uncertainty in y-intercept
1	0.9085	0.0161	0.3672	0.3203
2	1.0208	0.0090	-0.6291	0.1695
3	1.0412	0.0123	-0.6092	0.2201
4	1.0116	0.0059	-0.3006	0.0950

Although it was Ineris staff in charge of operating the CRF throughout the campaign, the calibrations data was collected and analysed by NPL. The original calibration factors reported to Ineris did not include a zero-offset correction to the MFC flow data, even though the CRF flow controllers were known to have a zero-offset. Previously it has been assumed that the MFC zero offsets remained constant, meaning a reasonably accurate evaluation of the mass emission rate can be obtained, as the y-intercept of the calibration fitting should account for any offset. However, recent work has confirmed that the zero offsets of each MFC drift slightly with time, with conditions such as large changes in ambient temperature thought to worsen this effect. Therefore, to accurately determine the gas emission rates during the releases, the zero offsets should be considered in both the analysis of the calibration flow data and the individual test release flow data (see Section 4).

4 ANALYSIS OF TEST RELEASE RATES

4.1 INITIAL FLOW DATA REPORTED BY INERIS

After the submission of the results from each method provider, a WG38 meeting was held to discuss the results and the controlled release emission rates were made available by Ineris as shown in Table 4.1. These emission rates were calculated using the MFC nominal set-points as flow outputs and no zero-offset correction was applied to the MFC flows. This was the correct method handling of the data as no zero offset was applied to the initial calibration flow data originally supplied by NPL.

Table 4.1 Ineris reported total calibrated flows and mass emission rates calculated using the MFC nominal set-points as flow outputs.

	MFC#1 Output (lpm)	MFC#2 Output (lpm)	MFC#3 Output (lpm)	MFC#4 Output (lpm)	Real total flow (lpm)	VOC Mass rate (kg/h)
Test 1	45				42.35	5.07
Test 2	135				124.11	14.85
Test 3	80				74.15	8.87
Test 4			80		81.52	9.75
Test 5		64		16	77.21	9.24
Test 6	64	16			75.34	9.01
Test 7	15	15	15	15	55.11	6.59
Test 8	80				74.15	8.87
Test 9			95		97.14	11.62
Test 10	40	40	40	40	154.67	18.51
Test 11		16	64		80.60	9.64
Test 12			80		81.52	9.75
Test 13			120		123.17	14.74
Test 14			135		138.79	16.61
Test 15			40		39.88	4.77
Test 16			8		6.56	0.78
Test 17		64		16	77.21	9.24
Test 18		155			157.62	18.86
Test 19	15	15	15	15	55.11	6.59
Test 20	27.5	27.5	27.5	27.5	104.89	12.55

4.2 CORRECTED CRF FLOW DATA

The total calibrated flow data shown in Table 4.2 varies slightly from those released by Ineris using the initial flow data (see Table 4.1), although these flow rates should be same if each MFC zero offset was constant during all the test releases. However, as the zero offset is known to drift with time, it is integral that this is considered, and it cannot be assumed that the zero-offset measured during the MFC calibrations are valid for all the test releases. For the zero-corrected flow data shown in Table 4.2, a 10-minute average (where possible) of the zero-offset data before and after each test is calculated then subtracted from the total flow output, yielding the total zero-corrected flow.

Furthermore, the data reported by Ineris uses the MFC nominal set-point values as flow outputs to calculate the total calibrated flows and mass emission rates, this does not take into account the actual flow recorded or the variation in flow through the MFC during each release. For the most part this is not an issue as the set-point data is usually similar to average flow output from each of the MFCs as can be seen by comparing the values reported in Tables 4.1 and 4.2. Also, the flow variation during each 90-minute release was typically very low with the standard deviation for each of the MFCs smaller than

0.25 l min^{-1} as shown in Figure 4.1. However, during test releases 9, 14 and 18 the MFC flow was not stable (decreasing) and the MFC nominal set-point value was significantly different from the average flow output with the variation in flow output greater than 2.5 l min^{-1}.

Table 4.2 Total flow outputs, total zero-corrected flows outputs and total calibrated flow outputs calculated using the recorded average flow output from each MFC. The '*' highlights that releases 9, 14, 18 were all subject to unstable (decreasing) MFC flows.

Test Number	MFC1 Flow Output (l min^{-1})	MFC2 Flow Output (l min^{-1})	MFC3 Flow Output (l min^{-1})	MFC4 Flow Output (l min^{-1})	Total Flow Output (l min^{-1})	Total Zero-Corrected Flow (l min^{-1})	Total Calibrated Flow (l min^{-1})
1	44.99				44.99	46.40	42.52
2	135.00				135.00	136.49	124.37
3	80.00				80.00	80.86	73.82
4			80.01		80.01	79.37	82.03
5		63.99		16.00	79.99	80.28	80.88
6	63.99	15.99			79.98	81.36	75.49
7	15.00	14.99	14.99	14.99	59.97	57.85	56.27
8	80.00				80.00	81.15	74.09
9 *			90.75		90.75	91.72	94.90
10	39.99	40.00	39.99	39.99	159.97	159.84	157.85
11		16.00	63.99		79.99	79.23	80.93
12			80.00		80.00	78.84	81.49
13			119.99		119.99	120.72	125.09
14 *			130.88		130.88	130.20	134.96
15			39.99		39.99	38.87	39.87
16			7.99		7.99	6.36	6.01
17		63.99		15.99	79.98	79.35	79.94
18 *		149.88			149.88	149.97	152.47
19	15.00	14.99	14.95	14.97	59.91	56.90	55.29
20	27.50	27.49	27.44	27.44	109.87	105.32	103.43

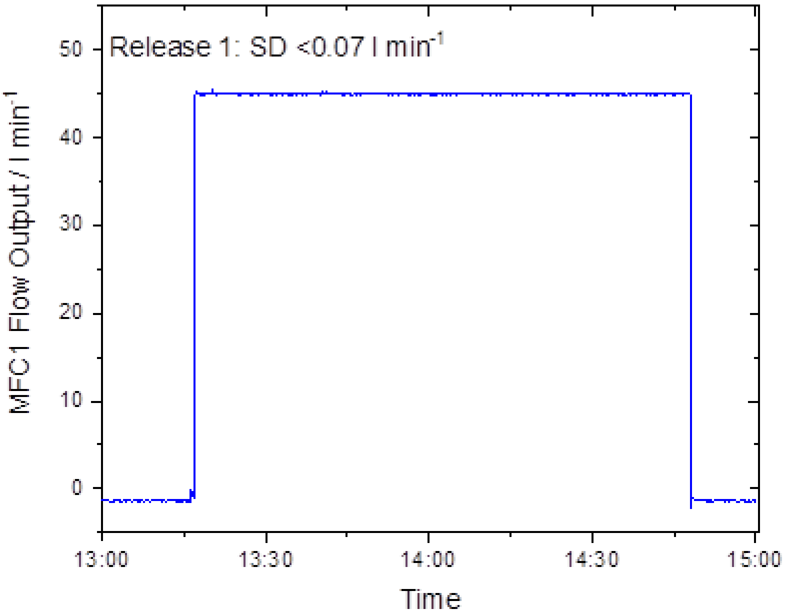


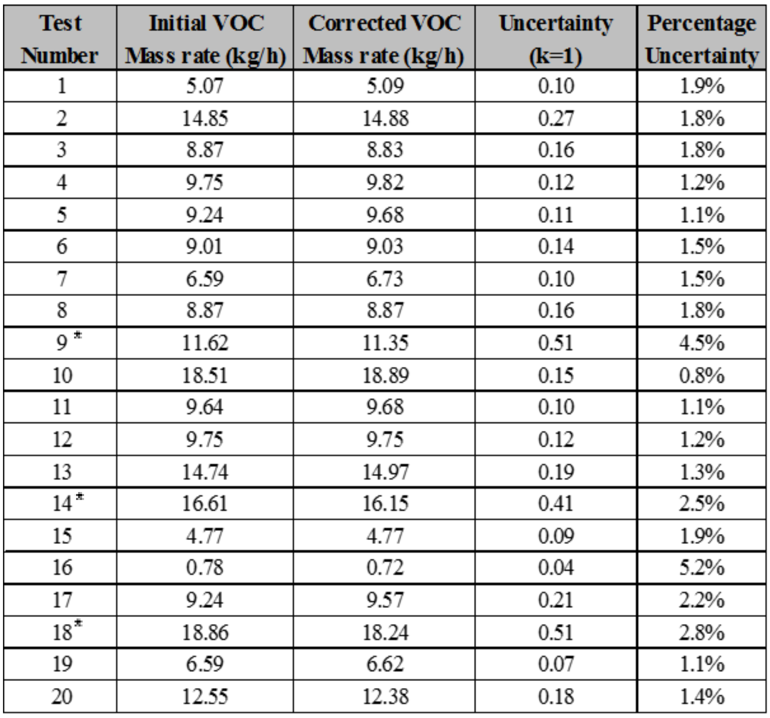
Figure 4.1 Plot of MFC1 Flow Output during Release 1 of campaign. The standard deviation (SD) of the flow during this release was <0.07 l min^{-1}

4.3 UPDATED MASS EMISSION RATES

The modifications in the handling of the flow data highlighted in Sections 4.1 and 4.2 lead to slight differences in the corrected VOC mass emission rates when compared to the VOC mass emission rates reported by Ineris as displayed in Table 4.3. The uncertainty in the mass emission rates shown have been propagated using the estimated standard error of the mean determined from the regression analysis, the standard deviation of the mean in the MFC flow during the releases and the uncertainty of the zero-offset data, which was calculated using a rectangular distribution. It should be noted that the uncertainty for the molecular mass of the gas used (calculated from the composition of the propane cylinders determined from GC-FID gas analysis) was also included in the uncertainty propagation.

From the data shown in Table 4.3 it can be seen that the differences between the two sets of mass emission rates are generally small. In fact, if it is assumed that both initial and corrected emission rates for each test have the same measurement uncertainty (i.e. the k=1 uncertainty listed), then in 18 out of 20 of the test releases the mass emission rates reported are not significantly different from each other. However, for releases 5 and 10 the mass emission rates calculated are not within the combined uncertainty of the measurements. That being said, it can be seen that for both releases the difference is only about 0.4 kg/h and the percentage uncertainty calculated for these two releases is among the lowest observed. Notably, if these were increased to 2.5% and 1.0% for releases 5 and 10 respectively, there would no longer be a significant difference between the reported measurements.

Table 4.3 Comparison of the mass emission rates reported by Ineris and those calculated using the updated flow data presented above. The '*' highlights that releases 9, 14, 18 were all subject to unstable (decreasing) MFC flows.



Test Number	Initial VOC Mass rate (kg/h)	Corrected VOC Mass rate (kg/h)	Uncertainty (k=1)	Percentage Uncertainty
1	5.07	5.09	0.10	1.9%
2	14.85	14.88	0.27	1.8%
3	8.87	8.83	0.16	1.8%
4	9.75	9.82	0.12	1.2%
5	9.24	9.68	0.11	1.1%
6	9.01	9.03	0.14	1.5%
7	6.59	6.73	0.10	1.5%
8	8.87	8.87	0.16	1.8%
9 *	11.62	11.35	0.51	4.5%
10	18.51	18.89	0.15	0.8%
11	9.64	9.68	0.10	1.1%
12	9.75	9.75	0.12	1.2%
13	14.74	14.97	0.19	1.3%
14*	16.61	16.15	0.41	2.5%
15	4.77	4.77	0.09	1.9%
16	0.78	0.72	0.04	5.2%
17	9.24	9.57	0.21	2.2%
18*	18.86	18.24	0.51	2.8%
19	6.59	6.62	0.07	1.1%
20	12.55	12.38	0.18	1.4%

Table 4.3 also includes the percentage uncertainty of the corrected mass emission rates. This typically is between 1 - 2% of the VOC emission rate. However, for release 9, 14 and 18 the associated uncertainties (and hence percentage uncertainties) are greater. This was due to the unstable nature of the MFC flow during these releases, because of this it was not valid to use the standard deviation of the mean for the uncertainty in the test flow data, as the average flow itself could not be considered constant. Therefore, rather than using this parameter, for these unstable releases the standard deviation of the test flow data was used instead. Finally, it is observed that the percentage uncertainty is also much greater for release 16. This measurement has a significantly lower flow rate than all the other releases and

therefore the associated uncertainties from the calibration plot and zero offsets are proportionally larger, hence when propagated lead to greater percentage uncertainty, even though the absolute uncertainty calculated is small, ~0.04 kg/h.

5 CONCLUSION

In conclusion, the initial VOC emission rates reported by Ineris are of sufficient quality for the working group discussion. However, the corrected VOC emission rates presented in this report are thought to be more accurate and include an associated uncertainty. It is therefore recommended that any future assessments should be carry out using these corrected emission rates.

NPL REPORT CMES (RES) 023

DIFFERENTIAL ABSORPTION LIDAR (DIAL) RESULTS FOR THE FIRST WG38 FIELD VALIDATION STUDY IN SOUTH OF FRANCE, SEPTEMBER 2016

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JUNE 2018

Differential Absorption Lidar (DIAL) Results for the First WG38 Field Validation Study in South of France, September 2016

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Environment Division

ABSTRACT

This report presents the results of propane emission measurements from controlled release experiments in the South of France, carried out using the NPL Differential Absorption Lidar (DIAL). This study was the first WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 22nd to the 29th of September 2016.

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Approved on behalf of NPL by
Alan Brewin, Director, Operations Division.

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EXECUTIVE SUMMARY

Background

The European Commission's standardisation mandate M/514 under the Directive 2010/75/EU on industrial emissions, was accepted by CEN/BT, and a decision has been taken to establish this standardisation work within CEN/TC264/WG38.

The control of the emissions of volatile organic compounds (VOCs) to atmosphere due to their losses during storage or transport is covered by both EU legislation and international protocols. The legislation on industrial emissions (Directive 2010/75/EU) is supported by the Best Available Techniques Reference documents (BREFs), which set out at an EU level the best available techniques for defined industrial activities and/or across these activities. Several BREFs also cover the prevention and control of fugitive and diffuse emissions of VOCs from industrial storage and transfer activities, in particular the BREFs concerned with mineral oil and gas refineries, large volume organic chemicals, and the "horizontal" BREF on the emissions from storage. The mandate for this work requests the European standardisation organisations to develop a European Standard that can be used in the determination of VOC emissions to be regulated within permits that are issued according to the Directive.

Total VOC emissions are also regulated at the EU and Member States levels under the National Emission Ceilings Directive (2001/81/EC) which sets total emission ceilings for such emissions at specific levels to be met from 2010 onwards.

VOCs are emitted by a wide range of sources including transport and industrial processes, as well as biogenic and other natural sources, and also by associated storage and handling activities, and the industrial and domestic use of VOC containing products.

VOCs are emitted to a significant extent by fugitive and diffuse sources (including non-point sources), although this is difficult to quantify accurately. This requirement for more accurate determination of these important VOC emissions creates a challenge because of their area emissions, and they require specific measurement and estimation methods that are currently not standardised. However, improving the accuracy of determining these VOC emissions should enable an improved assessment of these losses, and may provide an incentive to reduce such losses, as well as the benefits to their effects on the environment and human health. This should also contribute to the more uniform application of EU regulations and EU guidance documents.

Objectives

Mandate M/514 requires CEN to prepare and validate a standard for the determination of diffuse and fugitive emissions from oil and gas facilities. It should be complementary to the existing standard for the determination of leaks from piping and equipment EN 15446:2008.

This European Standard specifies the framework for determining emissions to the atmosphere of VOCs. It defines a system of methods to detect and/or identify and/or quantify diffuse/fugitive emissions from industrial sources. These methods include Optical Gas Imaging (OGI), Differential Absorption Lidar (DIAL), Solar Occultation Flux (SOF), tracer correlation, flux chamber measurement techniques, calculation and estimation methods.

Two validation studies will be undertaken. The first will use a controlled release, able to replicate typical industrial emission levels, at an industrial location to challenge the remote sensing techniques with a known release of VOC under typical industrial conditions. A second validation study will deploy the suite of techniques at an industrial facility to validate the combined framework of techniques defined in the standard and demonstrate their operation at a typical site.

A decommissioned area of a refinery in Southern France was selected as the location for the first validation study, taking place from 22nd - 29th September 2016. Testing used a controlled area release facility (ASF) provided by NPL to measure a known quantity of VOC. Four participants took part in the tests, running a total of five instruments, covering five of the proposed techniques. The results obtained with the DIAL method are described in this report.

Method

DIAL is a well-established and proven optical remote sensing technique that has been used by NPL in numerous emission surveys around the globe. The DIAL method provides spatially resolved concentration measurements of a target gas along the path of an eye-safe laser beam transmitted into the atmosphere. During the measurement, the laser is operated alternately at two adjacent carefully chosen wavelengths. One, called the ‘on-resonant wavelength’, is a wavelength which is absorbed by the target species. The other, the ‘off-resonant wavelength’, is a wavelength which is not absorbed significantly by the target species. The difference in the absorption of the two wavelengths is related to the concentration of the gas. Spatial resolution is obtained by pulsing the laser beam. Emissions rates are determined by scanning the laser beam through the atmosphere to build up a concentration map, and combining this with measurements of the wind speed and direction.

Results and Discussion

The CRF was set up with five controlled release nodes inside the chosen decommissioned unit. The controlled CRF was operated by the Institut national de l'environnement industriel et des risques (Ineris) that was in charge of selecting, for each test, the release nodes and the variable amounts of VOC, unknown to the participants. The field validation programme, consisted of twenty controlled releases of about 90 minutes each with a typical interval between releases of about 30 minutes.

DIAL measurements were made by determining the concentration of VOC in vertical measurement planes downwind and upwind of the area being measured, and combining these concentrations with wind measurements to determine the emission rate. DIAL measurements were challenging because of fairly low wind speed conditions, relatively high background sources and very clear atmospheric conditions with low aerosol concentration and therefore low DIAL return signals. Tests 7 and 13 were not measured as the DIAL was parked in non-ideal locations as a consequence of the low wind speed and variable wind direction. However, the two tests would have not fulfilled the DIAL validation criteria of average wind speed from the top meteorological sensor being in the 1 - 15 m/s range and would therefore have been excluded in any case. The other 18 experiments fulfilled all the DIAL QA/QC criteria.

The DIAL measured relatively high background sources in most of the scans, but generally these plumes could be isolated from the plume of the intended release. Nonetheless, background scans were usually carried before and after each test and analysed in the same region as the test scans showing some contribution from upwind sources. The values reported in the table are after the subtraction of the background contribution from the test scans and the standard deviation (stdev) is the sum in quadrature of the two sets of measurements. For this reason, the reported standard deviations are relatively high, particularly when the test emission rates are low.

During Test 5 it was not possible to carry out background scans since the wind direction changed after the test release stopped, therefore Test 5 emission rate probably overestimate the actual controlled release rate.

After the submission of the results from each method provider, a WG38 meeting was held to discuss the results and the controlled release emission rates were made available. In the table below 18 of the 20 controlled releases measured by the DIAL are compared to the actual release rates. According to the DIAL protocol, the stdev of a set of at least four DIAL scans should be representative of the measurement uncertainty. This has been validated since the measured stdev for each test is higher than the actual error calculated by subtracting from the average DIAL emission rate the controlled release emission rate. The only exception was Test 5, most likely because of the contribution of a small unknown background value.

Controlled Release Runs	CR Emission Rate	DIAL Average Emission Rate	DIAL Standard Deviation	Error: DIAL-CR	(DIAL-CR)/CR
	kg/h	kg/h	kg/h	kg/h	%
Test 1	5.1	5.4	1.8	0.3	6.8%
Test 2	14.9	16.1	2.0	1.2	8.2%
Test 3	8.9	9.8	2.3	1.0	10.8%
Test 4	9.8	8.4	2.6	-1.4	-14.3%
Test 5 *	9.2	11.4	1.6	2.2	23.6%
Test 6	9.0	9.2	1.4	0.2	1.8%
Test 8	8.9	9.6	1.1	0.7	7.8%
Test 9	11.6	13.3	4.4	1.6	14.2%
Test 10	18.5	18.5	5.6	0.0	-0.2%
Test 11	9.6	10.2	4.5	0.6	6.0%
Test 12	9.8	8.5	4.5	-1.3	-13.2%
Test 14	16.6	15.0	3.7	-1.6	-9.9%
Test 15	4.8	3.7	2.5	-1.1	-23.0%
Test 16	0.8	1.2	3.0	0.4	56.0%
Test 17 **	9.2	9.7	0.5	0.4	4.8%
Test 18	18.9	14.9	8.3	-4.0	-21.1%
Test 19	6.6	8.5	4.7	1.9	28.9%
Test 20	12.6	11.5	5.3	-1.1	-8.4%

* DIAL emission rate includes small unknown background emission

** Wind from the south, no background expected

The total DIAL measured emission rate for the 18 tests was 184.7 kg/h while the total controlled release emission rate was 184.6 kg/h. This shows that the dominant DIAL uncertainties sources during this field validation campaign had a random behaviour and therefore by increasing the number of DIAL scans the uncertainty can be expected to decrease accordingly. This also simulates DIAL measurements of different areas on a site that are then summed together to obtain an estimate of the total emission rate. Therefore, since typically the dominant DIAL uncertainties sources have a random behaviour the reported total emission rate as a sum of several sets of at least four DIAL scans can be expected to have significantly lower associated uncertainty in comparison to each independent set of measurement.

The DIAL protocol states that since typically the dominant DIAL uncertainties sources have a random behaviour, the DIAL uncertainty for a set of at least 4 scans, and for emission rates above the detection limit, is expected to be about 10% - 30%. During this field campaign each set of DIAL measurements has shown a behaviour consistent with a standard uncertainty of 5% - 10% of the measured emission rate, lower than the expected uncertainty reported in the protocol, and with no significant systematic bias. The overall uncertainty budget that has been validated during this specific field validation campaign is as reported in the following table.

Uncertainty Sources	Standard Uncertainty
Random, including wind and concentration	< 10%
VOC gas composition analysis	< 0.1 %
Bias	< 0.1 %

1 INTRODUCTION

This report presents the results carried out using the National Physical Laboratory's (NPL) differential absorption lidar (DIAL) system (shown in Figure 1.1) to measure emission rates of VOC gas from several controlled releases from a decommissioned area of a refinery in southern France, in September 2016. This was part of the first validation study to prepare and validate a standard for the determination of diffuse and fugitive emissions from oil and gas facilities within CEN/TC264/WG38, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere" for which NPL was selected to conduct validation and inter-comparison work using the DIAL method. In order to obtain critically important quality assurance information on emission rate measurements and compare the performance of all participating optical remote sensing methods controlled released experiments using the NPL Controlled Release Facility (CRF) were carried out by the Institut national de l'environnement industriel et des risques (Ineris) from 22nd to 29th September 2016 from inside a decommissioned unit of a refinery in Southern France.

Figure 1.1 NPL DIAL facility.

In the following Section 2 a description of the site and controlled release set-up is provided. An overview of the DIAL technique is given in Section 3. A brief overview of the measurement approach and the DIAL measurement locations used during the campaign is given in Section 4. Section 5 presents the summary tables and figures for each day of measurement, Section 6 presents a discussion of the results of the VOC emission rate measurements and Section 7 analyses the DIAL measurements in comparison to the actual release emission rates. The conclusions are presented in Section 8. Technical details for the DIAL technique are presented in Appendix A, including a discussion of the calibration and validation procedures. Annex B presents a series of wind roses to provide a summary of the wind conditions present during the campaign.

2 SITE DESCRIPTION

2.1 OVERVIEW

A pre-test visit to the decommissioned refinery in southern France was carried out by all the participants in June 2016 and the location of the controlled release nodes identified inside a unit circled in the red in Figure 2.1. The locations where all the participant's meteorological stations would be deployed were also identified. A total of nine meteorological stations were deployed to gather meteorological data for the different techniques as shown in Figure 2.1

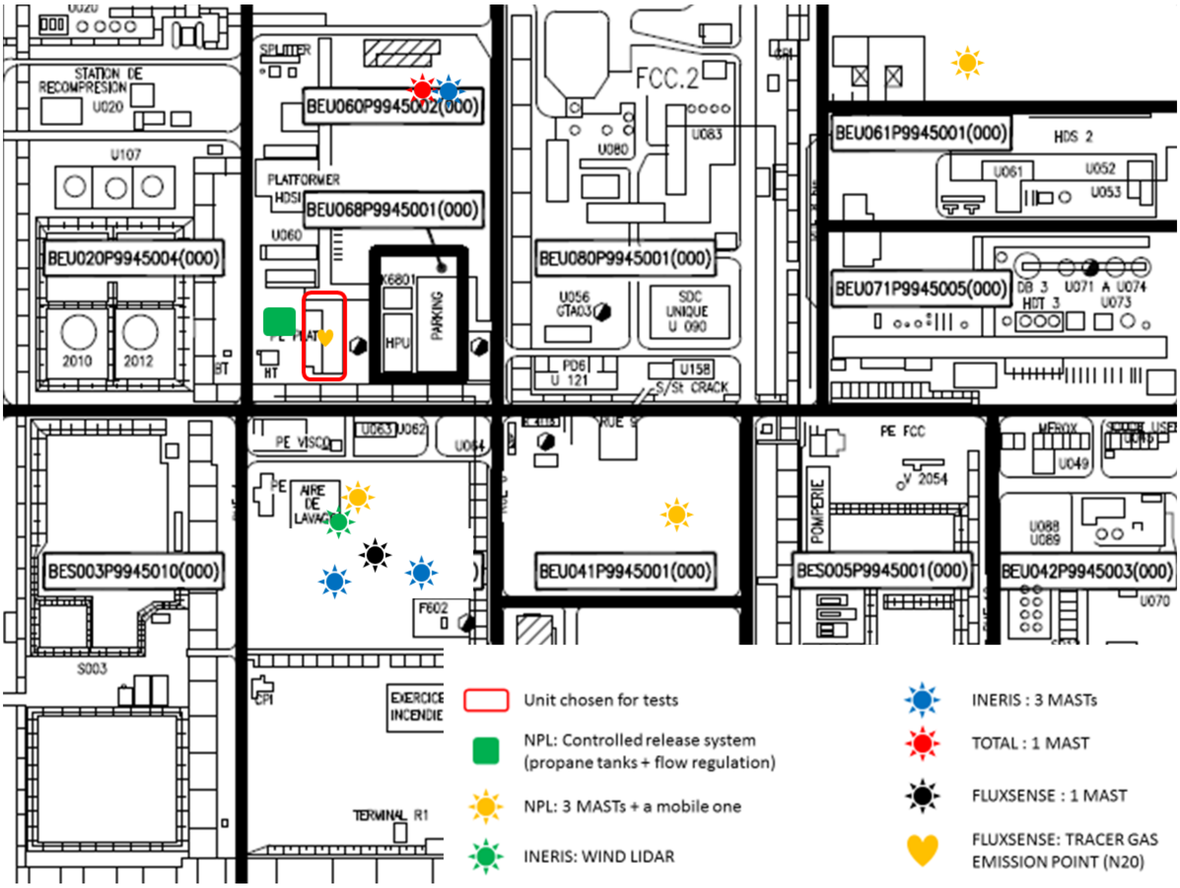

Figure 2.1 Locations of the meteorological stations

2.2 CONTROLLED RELEASE SETUP

The control system for the CRF was setup by NPL outside the selected decommissioned unit and then operated by the Ineris staff during the experiment when variable amounts of VOC and different release nodes, unknown to the participants, were released using the CRF.

The configuration and locations of the controlled release nodes were agreed by all project partners. Figure 2.2 shows the locations inside the selected decommissioned united where the five controlled release nodes were deployed. The released gas was mainly propane (about 93.5%) with a small percentage of propene, i-butane and n-butane. The maximum achievable emission rate was about 30 kg/hr. The field validation programme consisted of twenty controlled realises of about 90 minutes each with a typical interval between releases of about 30 minutes.

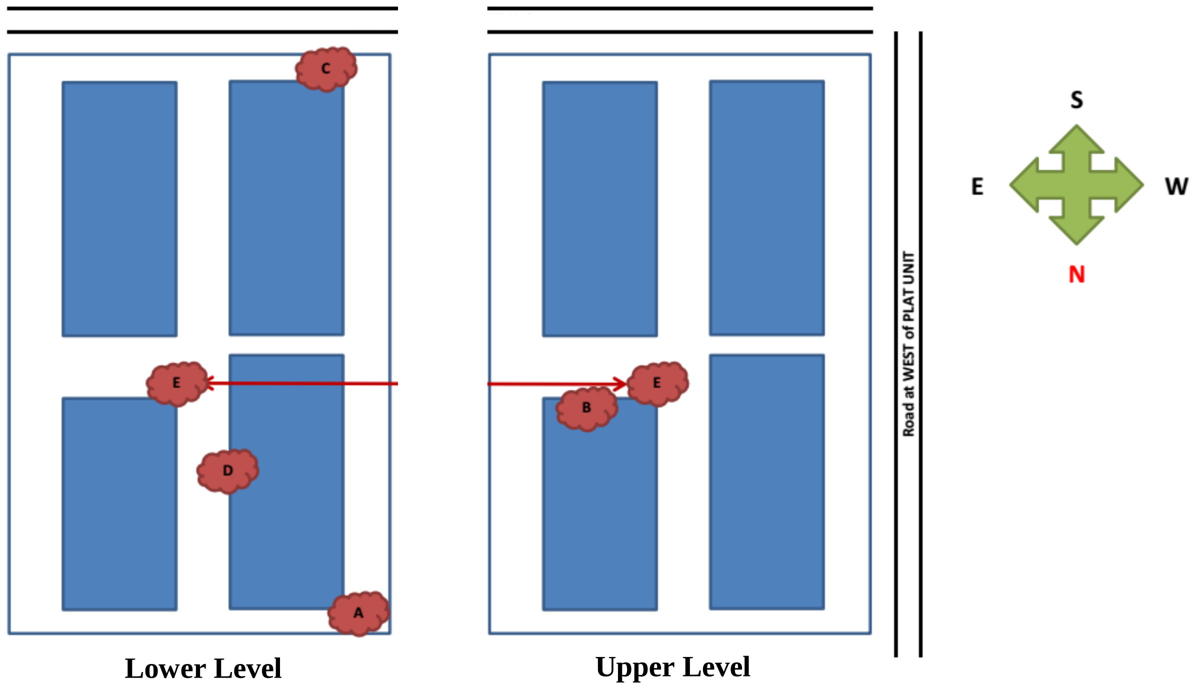

Figure 2.2 Locations of the five controlled release nodes

3 DIAL MEASUREMENT TECHNIQUE

This section describes the principles for applying the DIAL technique, a more detailed description of the DIAL methodology can be found in Appendix 1.

3.1 THE DIAL TECHNIQUE

The DIAL technique is a remote sensing method capable of making spatially resolved measurements of concentrations of a target gas (in this case methane) along the path of an eye-safe laser beam transmitted into the atmosphere.

In the DIAL technique, the laser is operated alternately at two adjacent wavelengths (in the 3.3 µm region for VOC). One of these, the 'on-resonant wavelength', is chosen to be at a wavelength which is absorbed by the target species. The other, the 'off-resonant wavelength', is chosen to be a wavelength which is not absorbed significantly by the target species. The difference in the absorption of the two wavelengths allows the concentration of the gas to be calculated. Spatial resolution is obtained by pulsing the laser beam. DIAL VOC measurement is targeted on C2+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. A scaling factor to go from the standard DIAL VOC mass to the measured C2+ VOC mass (mainly propane in this controlled release study) is then applied.

Emissions rates are determined by scanning the laser beam through the atmosphere to build up a concentration map, and combining this with measurements of the wind speed and direction as shown in Figure 3.1. Range-resolved remote DIAL measurements enable total site emissions and area-specific emissions to be measured, with no disruption to normal operational activities. The DIAL data quantify emission rates in kg/hr and provide 2D/3D mapping of emission concentrations in ppm.

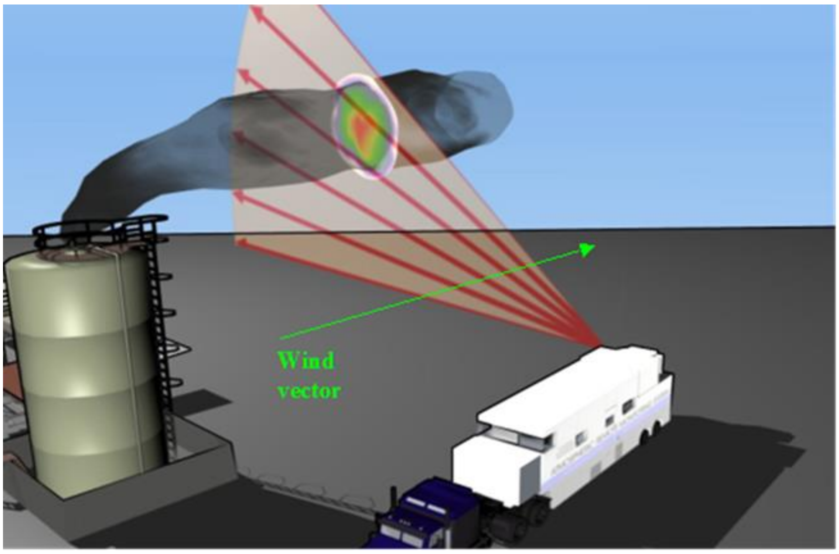

Figure 3.1 DIAL Measurement Configuration

3.2 DIAL TRAILER LOCATION

To measure the emission rate from identified target source, the DIAL is first placed so that a series of downwind scans can be obtained, and then, if possible, DIAL is moved to another position to monitor the upwind emission rate (Figure 3.2a). In some cases upwind and downwind emission rates can be obtained from a single location (Figure 3.2b). In order to perform measurements, the DIAL has to 'stand-off' by a minimum measurement distance of 50m (that is measurements cannot be undertaken in the first 50m from the Trailer) so the DIAL does not have to be located in the emission plume.

For each source, the DIAL placement location is chosen by taking into consideration the availability of unobstructed view of the different areas of the site and the current wind direction. The DIAL can be moved during the day if the wind direction changes and if different areas of the site can be measured from other locations.

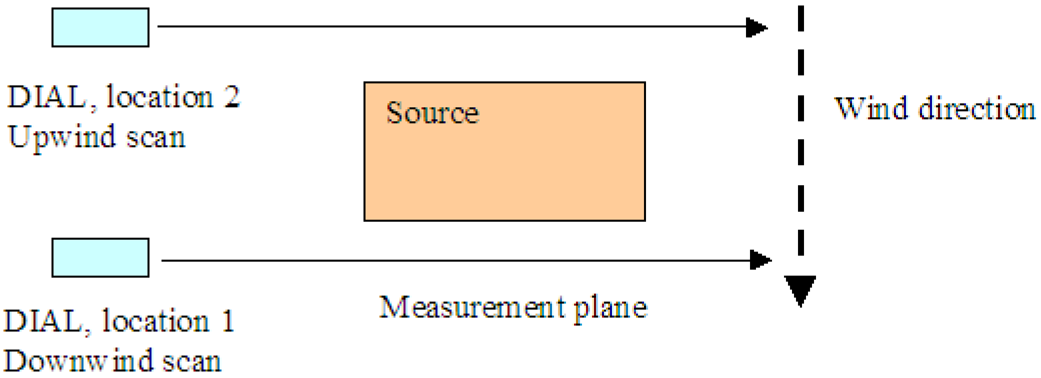

Figure 3.2a Measurement of emissions from two DIAL locations

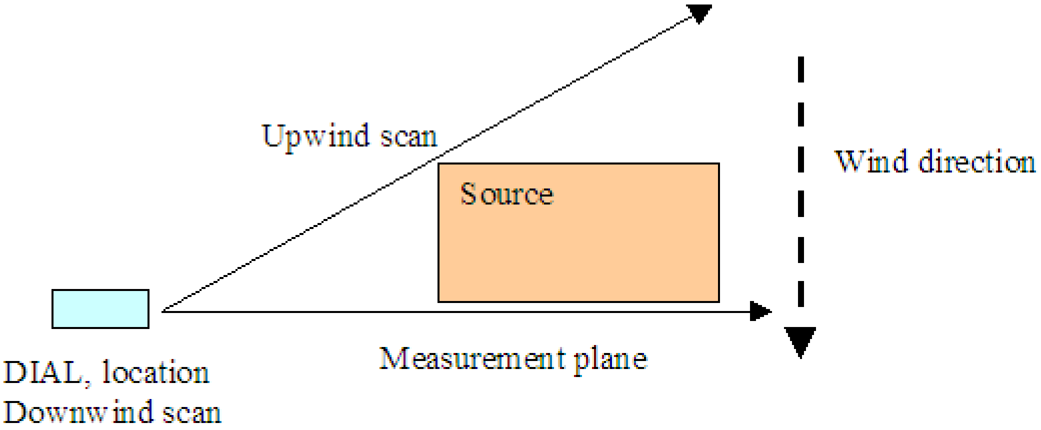

Figure 3.2b Measurement of emissions from one DIAL locations

For this study each controlled release was about 90 minutes long with a typical interval between releases of about 30 minutes. For this reason, background scans were recorded during the 30 minutes' interval between releases from the same location and line-of-sight where the controlled release measurements were carried out.

The strength of the returning DIAL radiation depends on atmospheric conditions as the transmitted infrared radiation is returned by scattering from aerosol/dust particles in the atmosphere. Therefore, the maximum scan range of the DIAL system depends on the atmospheric conditions, and varies from day to day and can also change throughout the day. For VOC the range is typically between 300 m and 600 m. During the two weeks study the weather was dry with long spells of sunshine and clear view, therefore not many aerosol/dust particles were present in the atmosphere resulting in a very low strength DIAL return signal.

As the suitability of a measurement location is dependent on wind direction, the choice of measurement locations was made on a daily basis. Most of the morning the wind speed was very low and the wind direction variable, as consequence it was not possible to find an ideal parking location to measure the release gas for a couple of controlled release tests.

3.3 LINES-OF-SIGHT AND NUMBER OF SCANS

From each location, DIAL scans are normally carried out using different lines-of-sight (LOS) in order to perform downwind and upwind measurements when necessary and to have different cuts through the area of interest. In general approximately four scans (individual emission measurements) are made along each LOS. The majority of the scans recorded during a DIAL campaign are downwind of different areas of the site. The rest of the scans are upwind or background measurements.

For this study because of the short interval between two controlled release tests, only one or two background scans were recorded after each test when the wind direction was stable and the DIAL didn’t need to be moved at a different location.

3.4 EMISSIONS FROM DIFFERENT AREAS OF THE SITE

Emissions from other areas of the site or other upwind sources may have been upwind of the measured sources and therefore contributing to the measured emission rates. However, generally upwind sources can be excluded in three ways:

1) If the upwind sources to be excluded were close to the measured sources and produced localised plumes, these were discriminated spatially from the measured rates by selecting the regions of the scanned region to integrate, in order to calculate the emission rate only from the area of interest.
2) Conversely, if the upwind sources could not be spatially discriminated and the emissions from them have been measured separately in upwind scans then these values were subtracted from the downwind emission rate.
3) If the upwind sources were further away (typically more than ~300m - 500 m) and relatively low, they normally would be diffuse and below the measurement noise or detection limit or subtracted as a fixed background slope.

This study was more complicated than expected since several background sources have been measured by all the participants from the north-east to the west of the decommissioned unit where the controlled release nodes were deployed. The DIAL could generally isolate the upwind plumes from the plume of the intended release using the first technique. Nonetheless, background scans were carried before and after each test and analysed in the same region as the test scans showing still some contribution from upwind sources. Therefore, the second technique was also used and the reported values for each test are after the subtraction of the background contribution from the test scans and the standard deviation (stdev) is the sum in quadrature of the two sets of measurements. One specific factor of these tests was that due to time constrains between tests, typically less than 30 minutes, it was not possible to carry out the usual upwind scan approach with a set of at least four scans. Therefore, it was only possible to carry out fewer background scans between tests from the same DIAL location where the controlled release measurements were made.

3.5 METEOROLOGICAL MEASUREMENT

The location of meteorological monitoring stations is usually determined in advance of arriving at the site by examining the local historical meteorology data. For this campaign, the fixed mast, located east of the controlled release unit, supported four wind sensor packages at 11.9 m, 9.0 m, 6.2 m and 3.4 m elevation from the ground. A second fixed mast, located north-east of the controlled release unit, supported two wind sensor packages at 11.9 m and 3.4 m elevation from the ground. A 3 m meteorological station was also deployed south of the controlled release unit. Additionally, a portable mast that operates at about 2.3 m height was also deployed near the DIAL truck or along the measurement line-of-sight. The DIAL truck was equipped with a met mast that operated at a height of 10.5 m. The fixed mast’s wind sensors were calibrated Vector Instrument wind vanes and cup anemometers. These instruments were also checked prior to deployment. Wind data were recorded using battery powered loggers, with two second sampling. The meteorological data were then processed to provide vector averaged wind data for the periods of each DIAL scan. The wind speed data is used to construct a logarithmic vertical wind profile as described in Appendix 1 (Section 3).

3.6 CALIBRATION PROCEDURE

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. The gas cells were filled with known concentrations of the target species, from NPL standard gas mixtures, which are directly traceable to national standards. A fraction of the transmitted beam was split off and half was directed straight to a detector, the other half was directed through the gas cell and then onto a detector. This provided a direct measurement of the differential absorption at the operating wavelengths. The ratio between the energy on each detector was continuously monitored during the operation of the system to detect any possible drift in the laser wavelengths. Additionally, once a day the wavelength was scanned through the absorption peak of methane and then tuned to appropriate wavelengths for DIAL measurements. The calibration cells were also periodically placed in the output beam to check that the concentration response of the whole system was as expected.

3.7 MEASUREMENT UNCERTAINTY

In previous NPL validation studies, DIAL measurements of total emission rate have shown agreement with known emission sources of between 5-20% as described in Appendix 1 (Section 7). The uncertainty of the measurements in this study was estimated based on the stdev of the individual emission rate measurements from which each mean emission rate value has been determined.

The DIAL estimated uncertainty for a single measurement is about 30-40%, and some of this uncertainty will be included in the reported stdev. A set of at least four measurements is usually made which reduces the uncertainty typically below 30%. The reported uncertainty is the variability of the measured results. As such it encapsulates variability occurring during the measurements which will include the measurement itself (random DIAL measurement uncertainty), variability in the source emissions, and variability in the wind direction and speed used since for each scan a different wind profile is calculated from the wind mast data.

In this study the reported average emission rate for each test is obtained after the subtraction of the background contribution from the average test scans emission and the stdev is the sum in quadrature of the two sets of measurements. For this reason, the reported standard deviations are relatively high, particularly when the test emission rates are low.

4 OVERVIEW OF MEASUREMENT APPROACH

The NPL DIAL measurements were conducted from a series of locations around selected decommissioned unit in order to determine VOC emission rates from all the five release nodes. These locations and the locations of the fixed meteorological stations are shown in Figure 4.1.

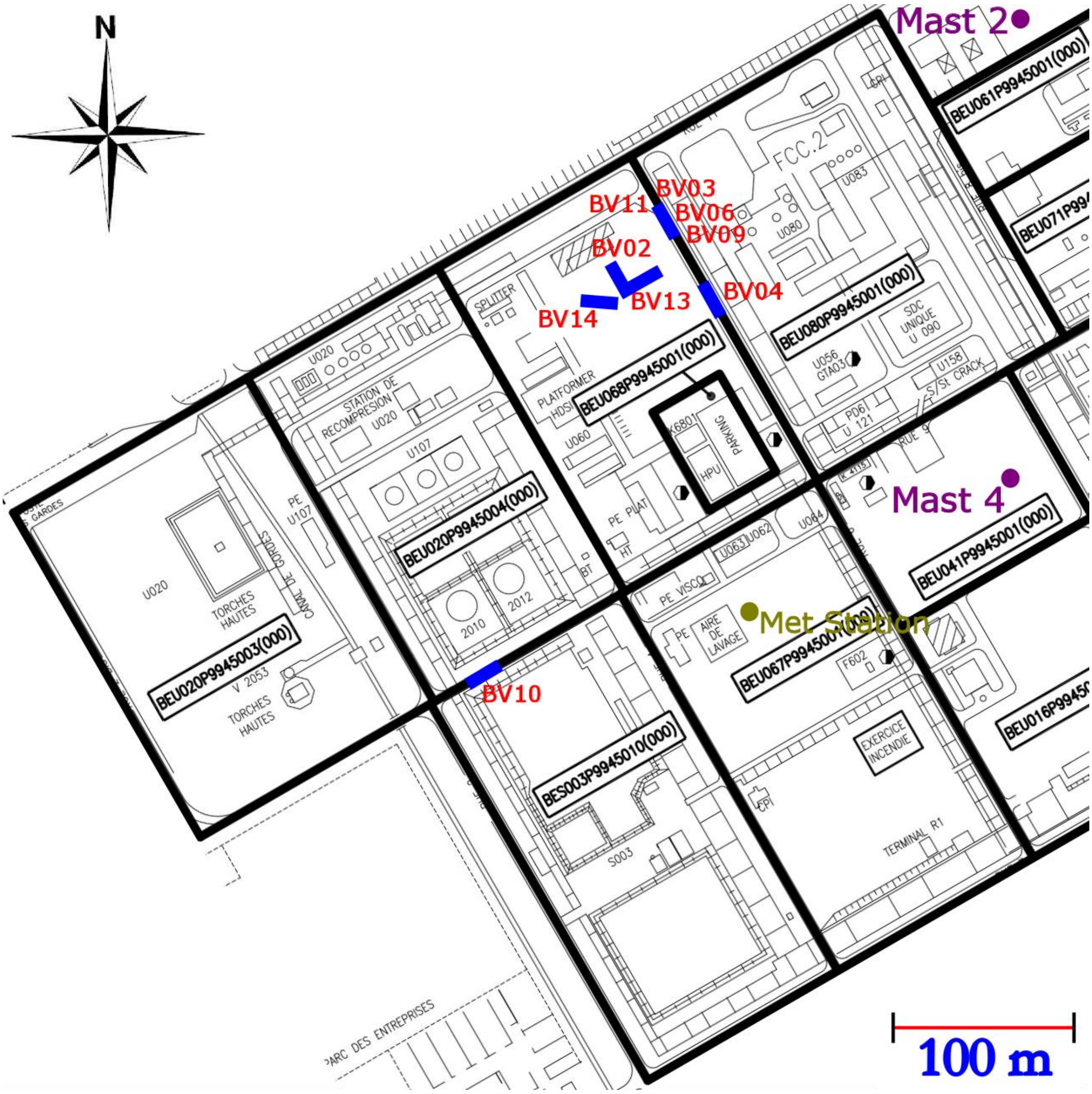

Figure 4.1 DIAL measurement locations and location of fixed meteorological masts

Emission rates were determined using the procedure described in Sections 3.2 - 3.3 and Appendix 1, by scanning the DIAL measurement beam in a vertical plane downwind of the target sources, and measuring the total concentration of methane in that plane.

The logarithmic wind field profile used for the emission rate calculations (see Appendix 1) was determined either from the speeds on the fixed mast sensors located east of the controlled release area (indicated by ‘Mast 4’ in Figure 4.1) or from the speeds on the fixed mast sensors located north-east of the controlled release area (indicated by ‘Mast 2’ in Figure 4.1). The wind sensor used to define the wind direction for the emission rate calculation was typically the top sensor from Mast 4 apart from

Test 17 with light and variable wind, therefore quite different from sensor to sensor and Mast 2 wind direction was the only one that could explain the location of the measured plume for each scan.

During the two weeks study the weather was dry with long spells of sunshine and clear views. For most of the mornings the wind speed was very low and the wind direction variable. Overall, the main wind direction experienced during this period was from the west and occasionally from the N/NW and S/SW. The wind directions over the course of each measurement during the campaign are summarized in Annex 2. The wind roses reported in Annex 2 for each location are from the wind sensor used to define the wind direction for the emission rate calculations.

4.1 CONTROLLED GAS RELEASE

Twenty controlled release tests were performed from the 22nd to 29th September as reported in Table 4.1. Each release lasted for about 90 minutes with a typical interval between releases of about 30 minutes. The released gas was mainly propane (about 93.5%) with about 2.3% of i-butane, 1.8% of propane, 1.4% of n-butane and a very small fraction of ethane, 1-butene, i-pentane, n-pentane, t-2-butene, iso-butene and c-2-butene. Two different gas composition analysis were carried out for the two propane tanks that were used for the tests. The average gas composition was then used to calculate a scaling factor to go from the standard DIAL VOC mass to the measured C2+ mass. All the DIAL VOC emission rates shown in this report have already been corrected using this scaling factor of 1.277 ± 0.001, with an associated uncertainty of 0.09%.

Table 4.1 Controlled test releases

Test #	Date	Start Time	End Time
1	22/09/2016	13:17	14:48
2	22/09/2016	15:10	16:46
3	23/09/2016	11:27	12:57
4	23/09/2016	14:00	15:30
5	26/09/2016	09:41	11:11
6	26/09/2016	12:00	13:30
7	26/09/2016	14:30	16:00
8	26/09/2016	16:05	17:30
9	27/09/2016	09:35	11:04
10	27/09/2016	11:26	13:05
11	27/09/2016	14:00	15:33
12	27/09/2016	15:55	17:25
13	28/09/2016	10:07	11:37
14	28/09/2016	12:05	13:35
15	28/09/2016	14:37	16:03
16	28/09/2016	16:45	17:50
17	29/09/2016	10:50	12:15
18	29/09/2016	12:38	13:51
19	29/09/2016	14:10	15:10
20	29/09/2016	15:30	17:00

4.2 EMISSION RATE SUMMARY TABLES

Table 6.1 presents the mean and stdev of the VOC emission rates determined from each location for each LOS. The stdev values include the effects of the source variability, DIAL measurement uncertainty and the influence of other factors such as the wind speed and direction variability during the course of individual measurements.

Because the DIAL emission rate measurement depends on several different experimental conditions, the detection limit can be experimentally estimated when the measured stdev is similar to the measured value. The stdev therefore defines the detection limit for a given set of measurements.

5 SUMMARY TABLES AND FIGURES

5.1 EMISSION RATE RESULTS

The LOS used at each measurement location are shown in Figures 5.1 through 5.9. The figures also show the average wind direction measured over the full time frame during which the measurements from a given location took place.

Figures designated a1, b1, c1, d1, a2, b2, c2 and d2 are exemplar contour plots and visualizations of the emissions observed in the downwind DIAL measurements. The contour plots (a1, b1, c1, d1 figures) are scaled to the maximum concentration value in each plot while all the 3D visualizations (a2, b2, c2, d2 figures) use a common colour scale which was 7.0 ppm. Therefore, the colour scale of the contour plot is different with respect to the colour scale of the 3D visualization. In some cases this difference in scaling leads to a slight difference in apparent plume shapes between a contour plot and the 3D visualization.

Tables 5.1 to 5.9 report the emission rates determined for each scan made during the measurement campaign. The scan numbers are not necessarily sequential because they exclude scans recorded for data quality checks and scans aborted by the operator. No valid scan has been eliminated from the report. The tables also list the locations and the LOS used for each measurement. The wind directions reported in the tables are from the sensor used for the emission rate calculations. The wind speeds reported in the tables are from the higher of the sensors used to determine the wind profile. The notes in each table are only indicative of the area measured in a specific LOS to aid the reader in visualising the general location from where the emissions are coming. Reference should be made to the results discussion (Section 6) for more detailed explanations.

Table 5.1 VOC emission rates determined from BV02 on 22nd September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
6	BV02/LOS1	13:17	13:29	2.7	240.5	6.92	Downwind Test 1
7	BV02/LOS1	13:35	13:47	1.9	211.1	9.56	Downwind Test 1
8	BV02/LOS1	13:48	14:04	2.8	223.9	6.63	Downwind Test 1
9	BV02/LOS1	14:08	14:23	3.9	220.9	6.69	Downwind Test 1
10	BV02/LOS1	14:24	14:40	3.4	230.1	9.54	Downwind Test 1
11	BV02/LOS1	14:40	14:56	3.2	223.9	7.01	Downwind Test 1
13	BV02/LOS1	15:11	15:26	3.6	185.9	18.58	Downwind Test 2
15	BV02/LOS2	15:36	15:47	2.6	193.8	17.89	Downwind Test 2
16	BV02/LOS2	15:48	16:01	2.4	192.3	21.39	Downwind Test 2
17	BV02/LOS2	16:04	16:19	2.9	216.6	17.03	Downwind Test 2
18	BV02/LOS2	16:19	16:35	3.3	198.1	18.03	Downwind Test 2
19	BV02/LOS2	16:35	16:50	3.9	195.4	17.34	Downwind Test 2
20	BV02/LOS2	16:51	17:06	4.0	196.6	1.50	Background
21	BV02/LOS2	17:06	17:22	3.8	198.3	3.13	Background

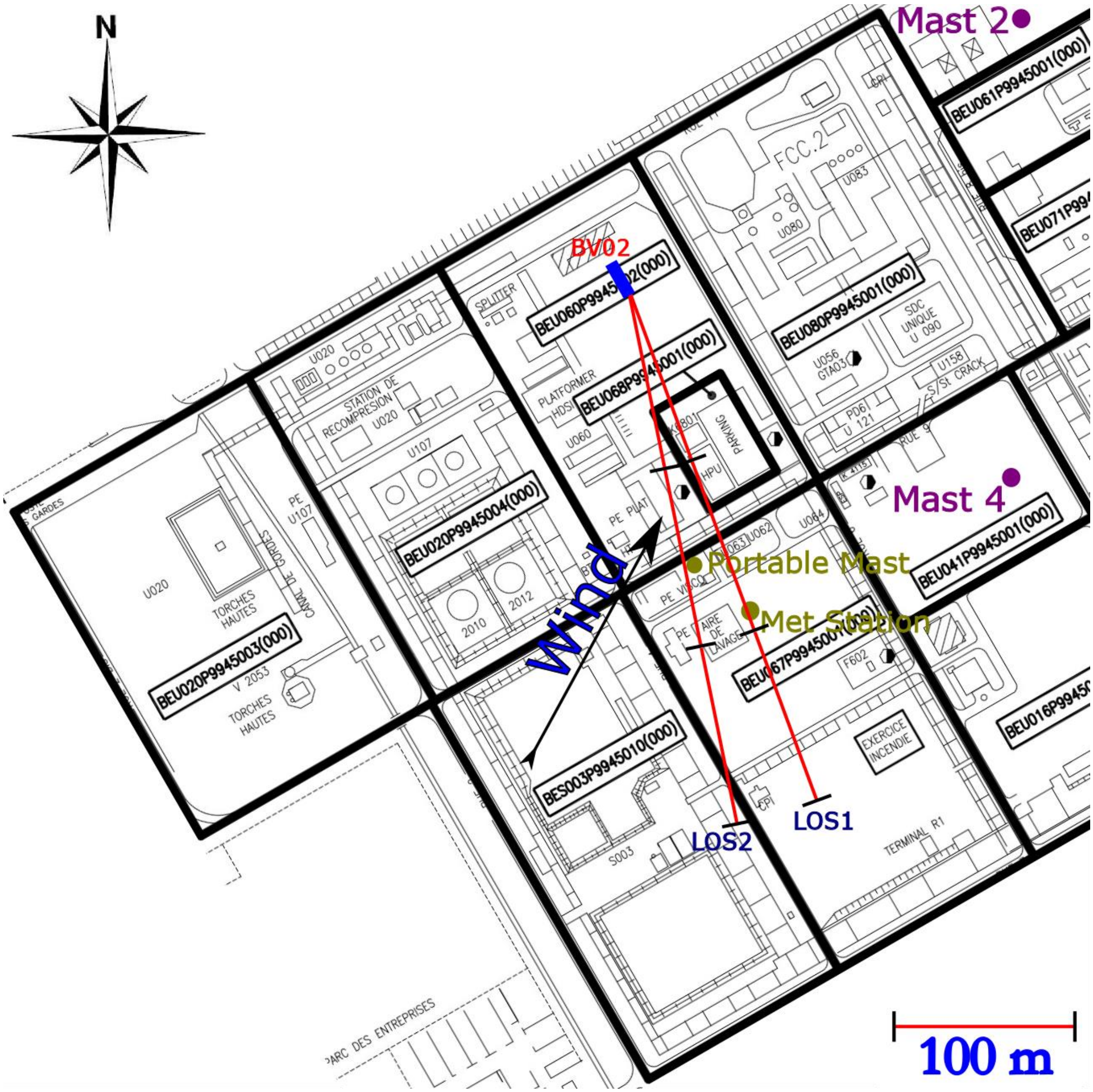

Figure 5.1 Measurement configuration for location BV02 on 22nd September.

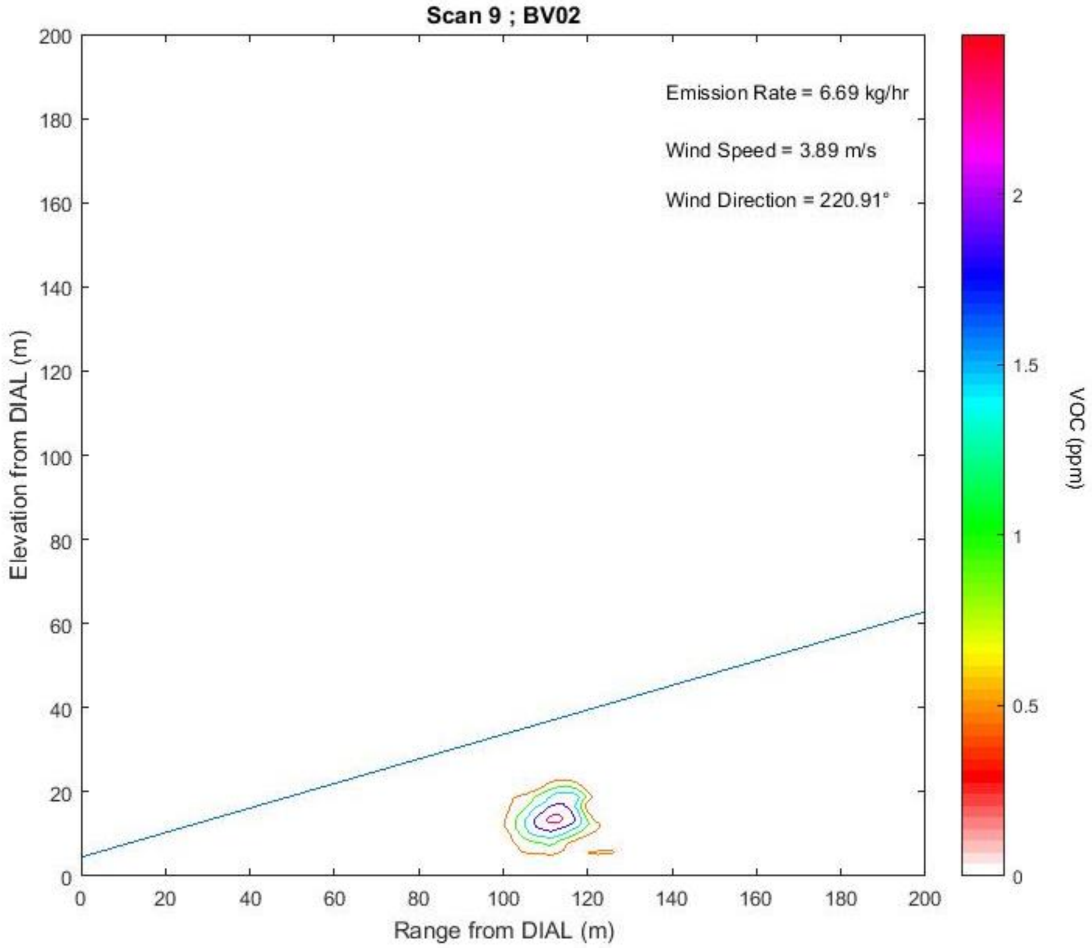

Figure 5.1a1 Observed VOC concentration for Scan 9 representing BV02/LOS1.

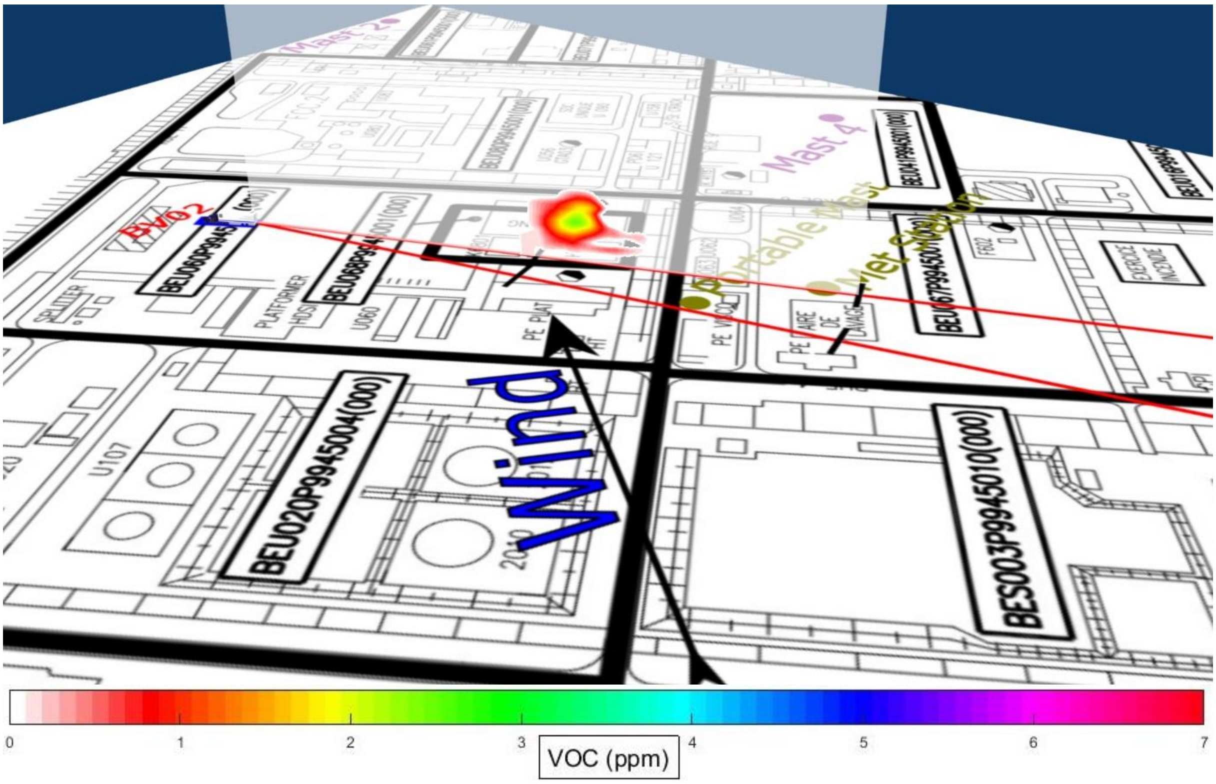

Figure 5.1a2 Visualisation of emission rate for Scan 9 representing BV02/LOS1.

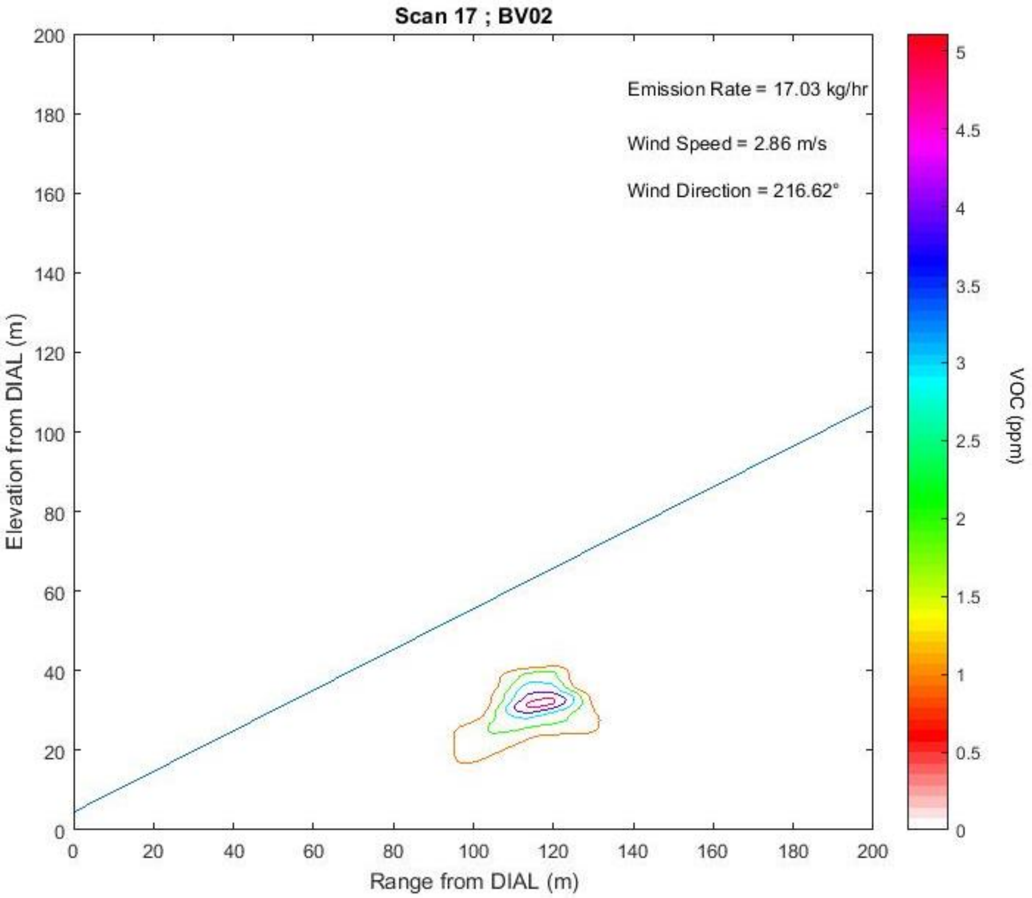

Figure 5.1b1 Observed VOC concentration for Scan 17 representing BV02/LOS2.

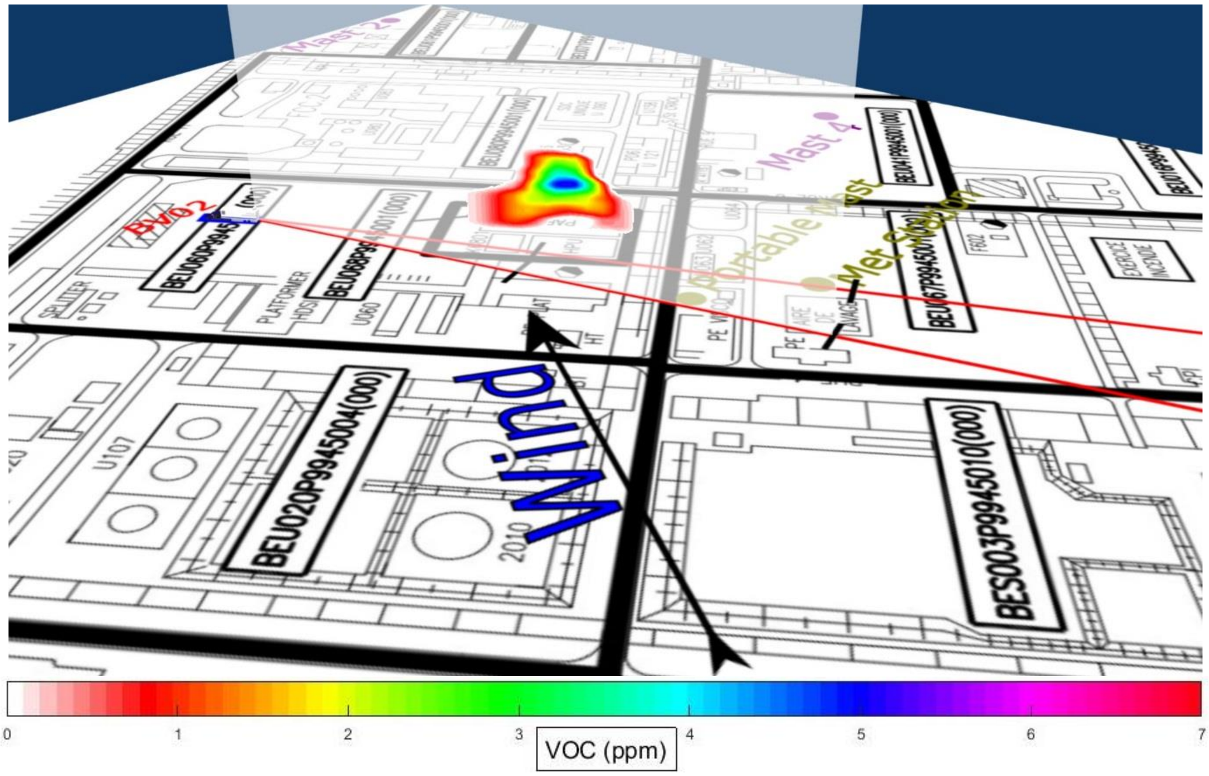

Figure 5.1b2 Visualisation of emission rate for Scan 17 representing BV02/LOS2.

Table 5.2 VOC emission rates determined from BV03 on 23rd September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
25	BV03/LOS1	11:42	11:58	2.4	225.6	13.16	Downwind Test 3
26	BV03/LOS1	11:58	12:13	2.0	226.6	11.96	Downwind Test 3
27	BV03/LOS1	12:14	12:28	1.7	212.2	14.47	Downwind Test 3
28	BV03/LOS1	12:29	12:42	2.1	231.2	15.51	Downwind Test 3
29	BV03/LOS2	12:43	12:54	2.9	227.8	11.67	Downwind Test 3
30	BV03/LOS2	12:54	13:04	3.0	227.5	15.49	Downwind Test 3
32	BV03/LOS2	13:48	13:58	3.0	224.8	2.76	Background
33	BV03/LOS2	14:02	14:12	3.8	237.9	9.16	Downwind Test 4
35	BV03/LOS1	14:15	14:30	3.1	248.7	13.99	Downwind Test 4
37	BV03/LOS2	14:45	15:03	4.6	231.7	13.71	Downwind Test 4
38	BV03/LOS2	15:04	15:21	3.5	255.1	11.08	Downwind Test 4
39	BV03/LOS2	15:22	15:31	3.7	248.2	13.27	Downwind Test 4
40	BV03/LOS2	15:31	15:40	3.5	251.4	5.01	Background

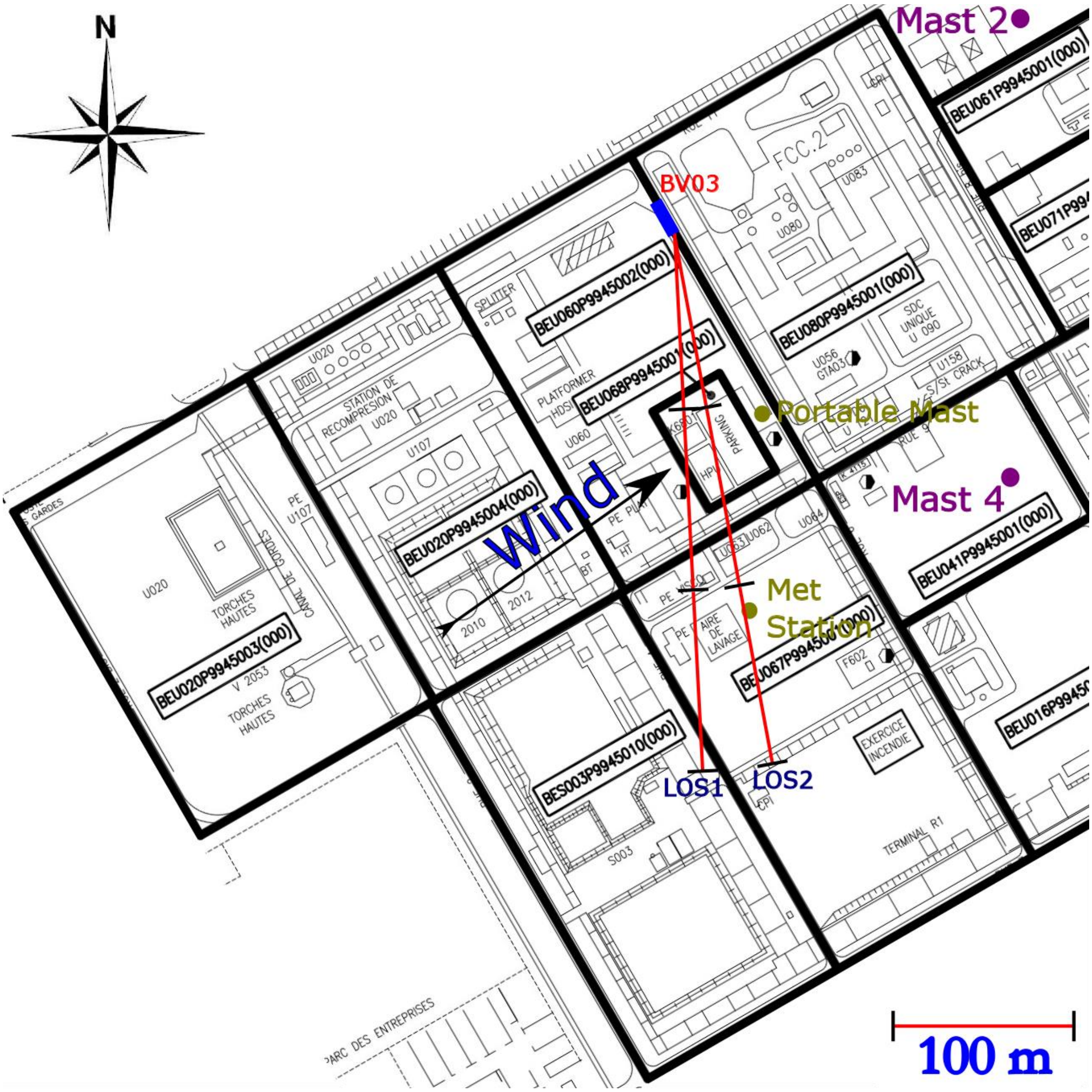

Figure 5.2 Measurement configuration for location BV03 on 23rd September.

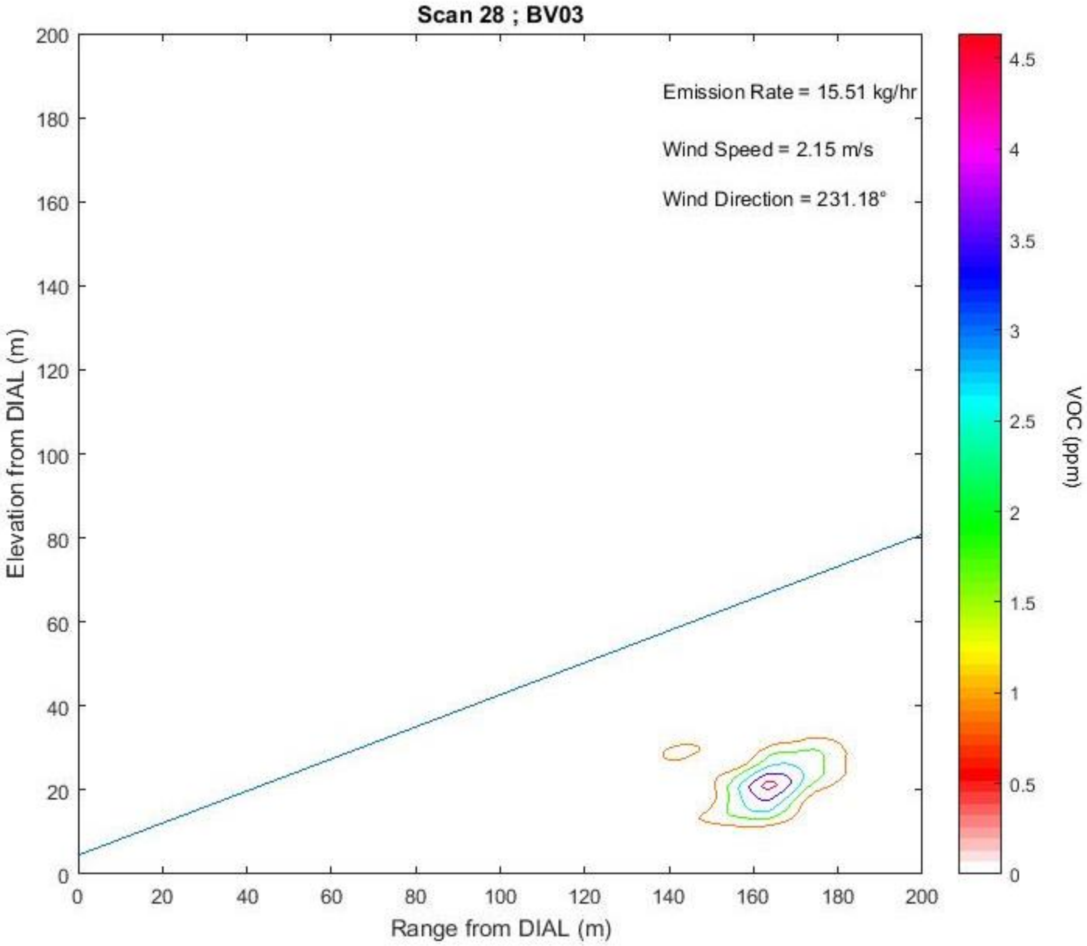

Figure 5.2a1 Observed VOC concentration for Scan 28 representing BV03/LOS1.

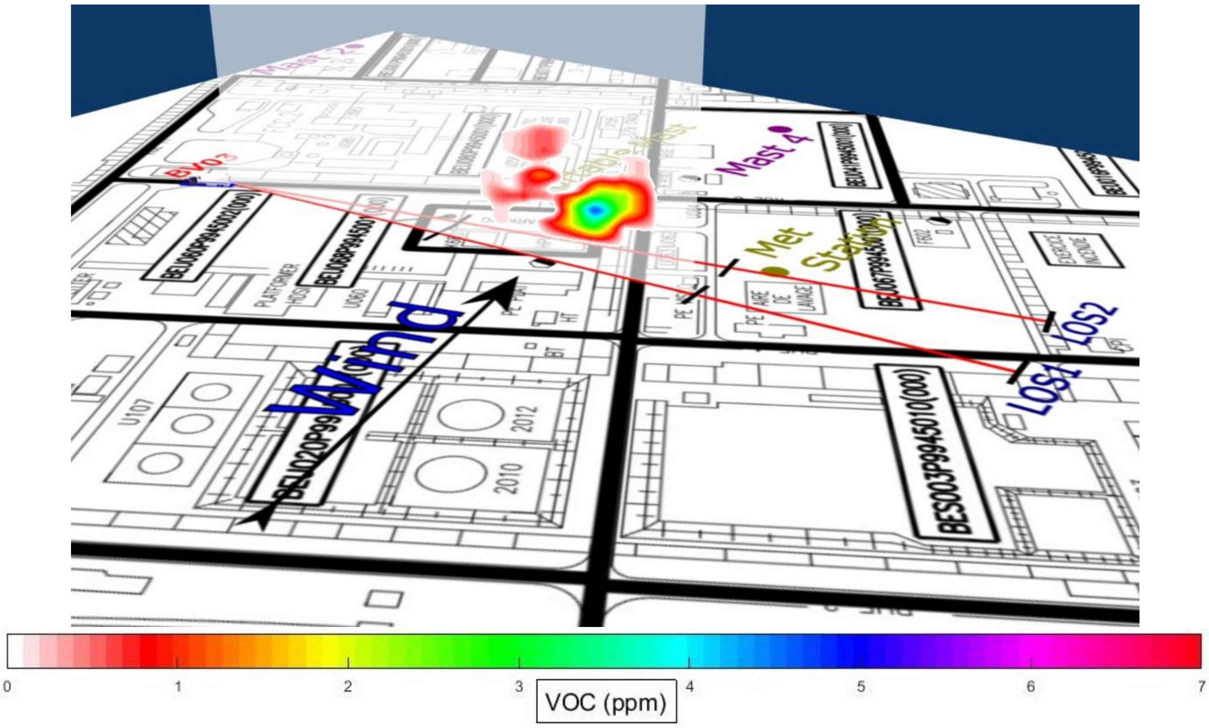

Figure 5.2a2 Visualisation of emission rate for Scan 28 representing BV03/LOS1.

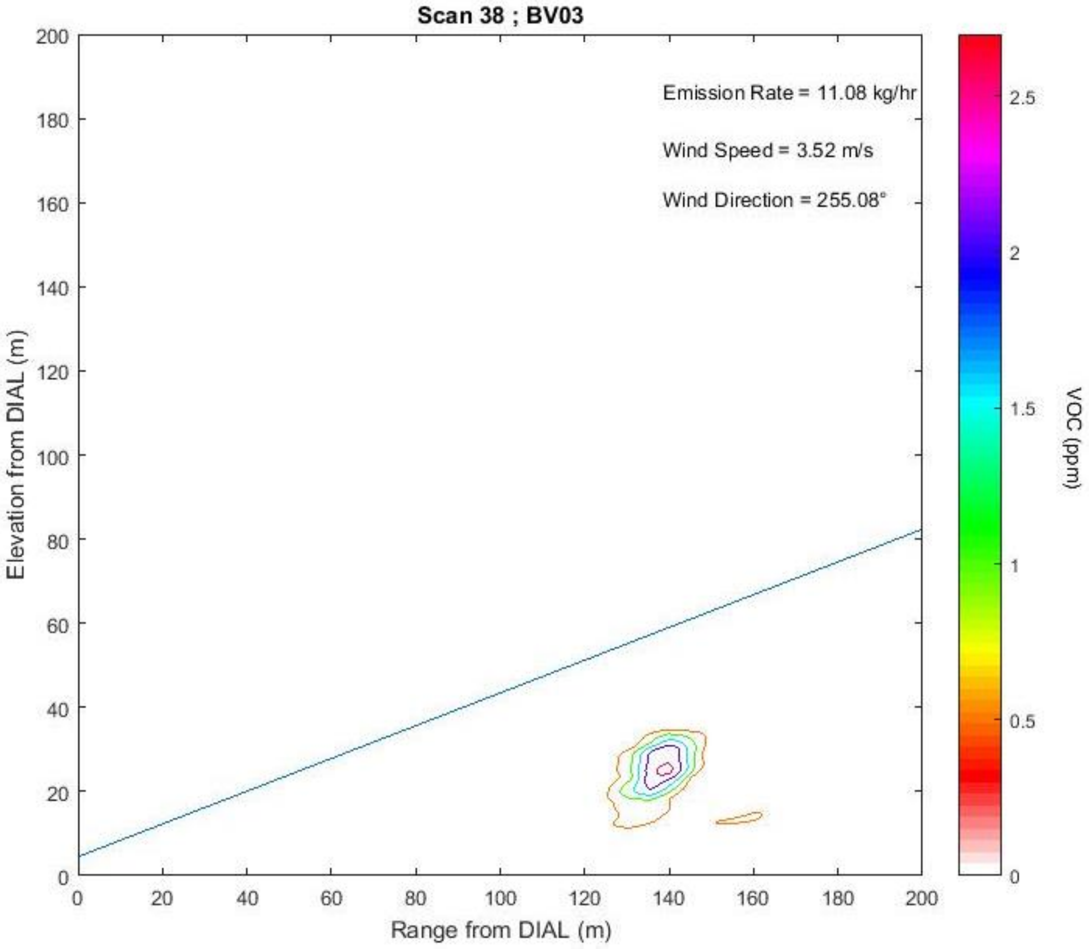

Figure 5.2b1 Observed VOC concentration for Scan 38 representing BV03/LOS2.

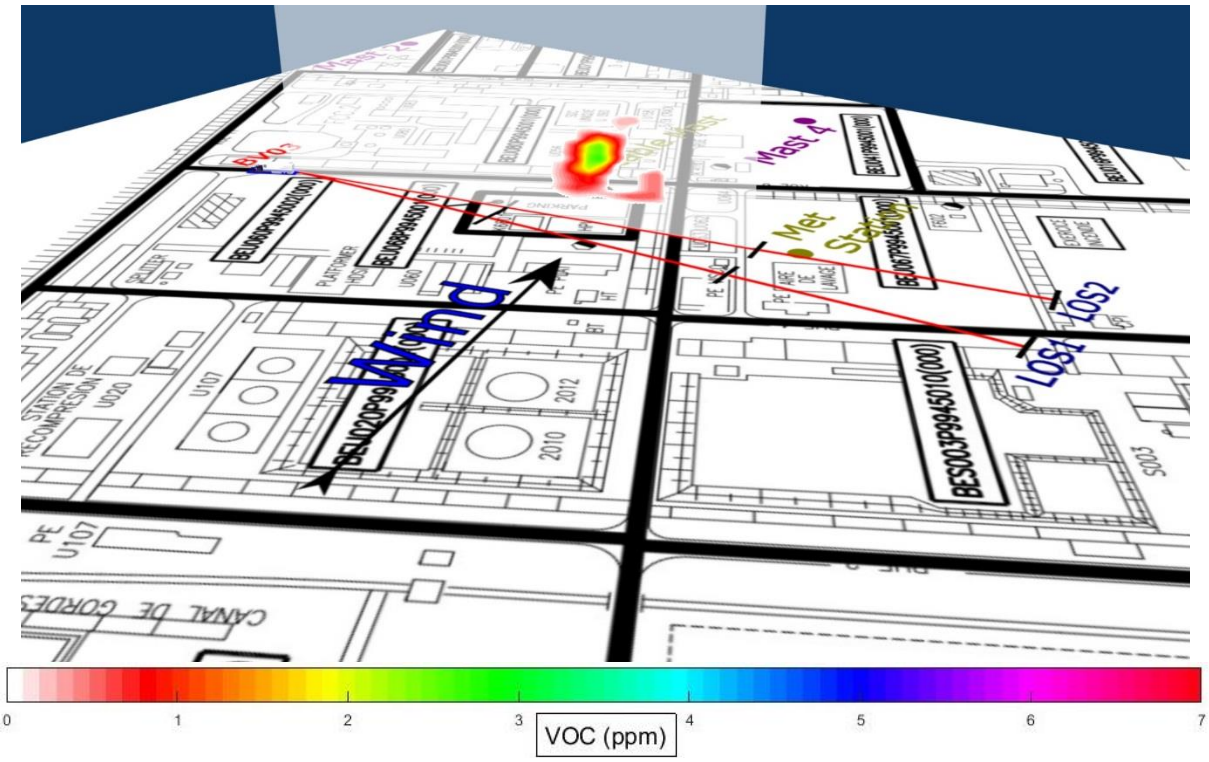

Figure 5.2b2 Visualisation of emission rate for Scan 38 representing BV03/LOS2.

Table 5.3 VOC emission rates determined from BV04 on 26th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
41	BV04/LOS1	09:41	09:58	2.2	333.5	13.61	Downwind Test 5
42	BV04/LOS1	09:58	10:14	2.1	335.3	11.49	Downwind Test 5
43	BV04/LOS1	10:15	10:31	1.8	341.9	10.44	Downwind Test 5
44	BV04/LOS1	10:32	10:48	1.7	353.6	10.14	Downwind Test 5
45	BV04/LOS1	10:49	11:06	0.8	118.6	-	Variable Wind Direction

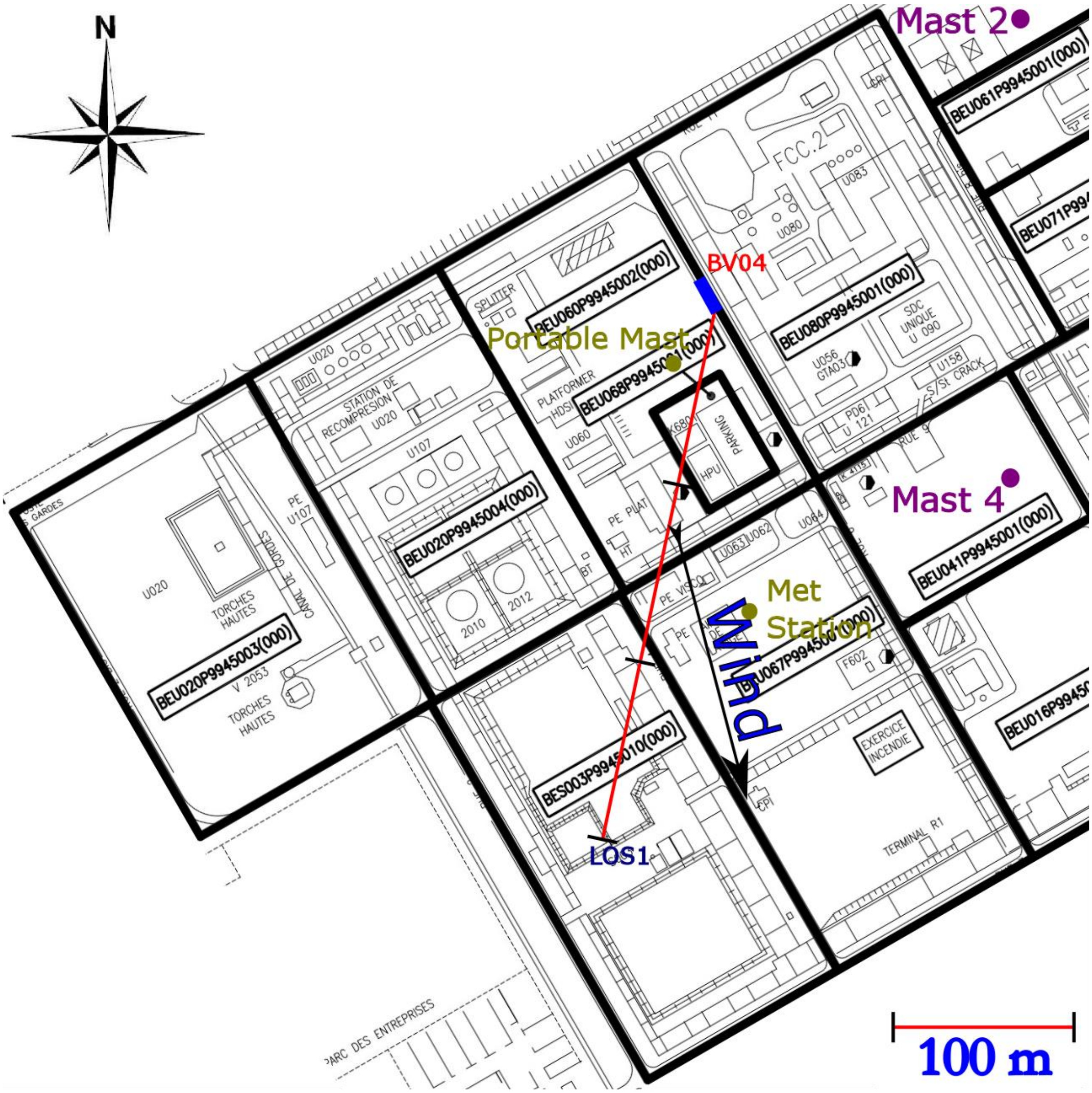

Figure 5.3 Measurement configuration for location BV04 on 26th September.

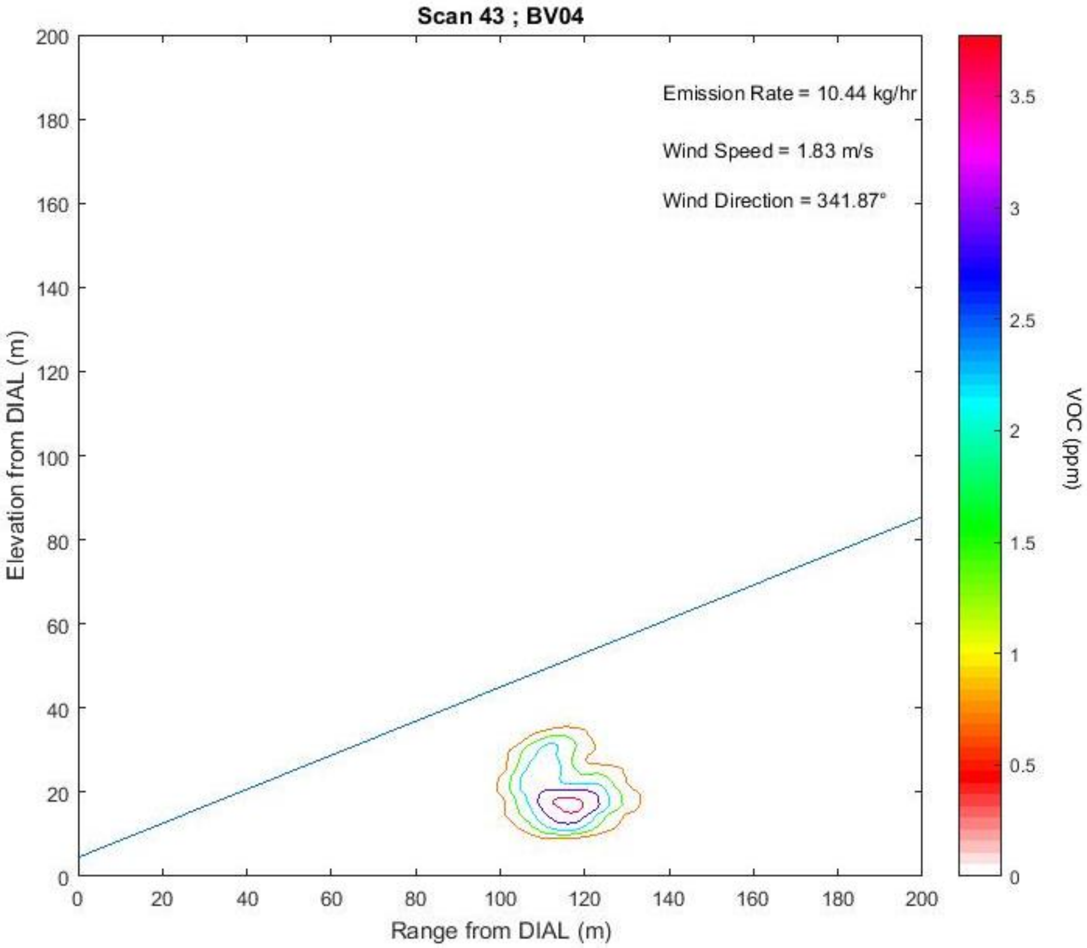

Figure 5.3a1 Observed VOC concentration for Scan 43 representing BV04/LOS1.

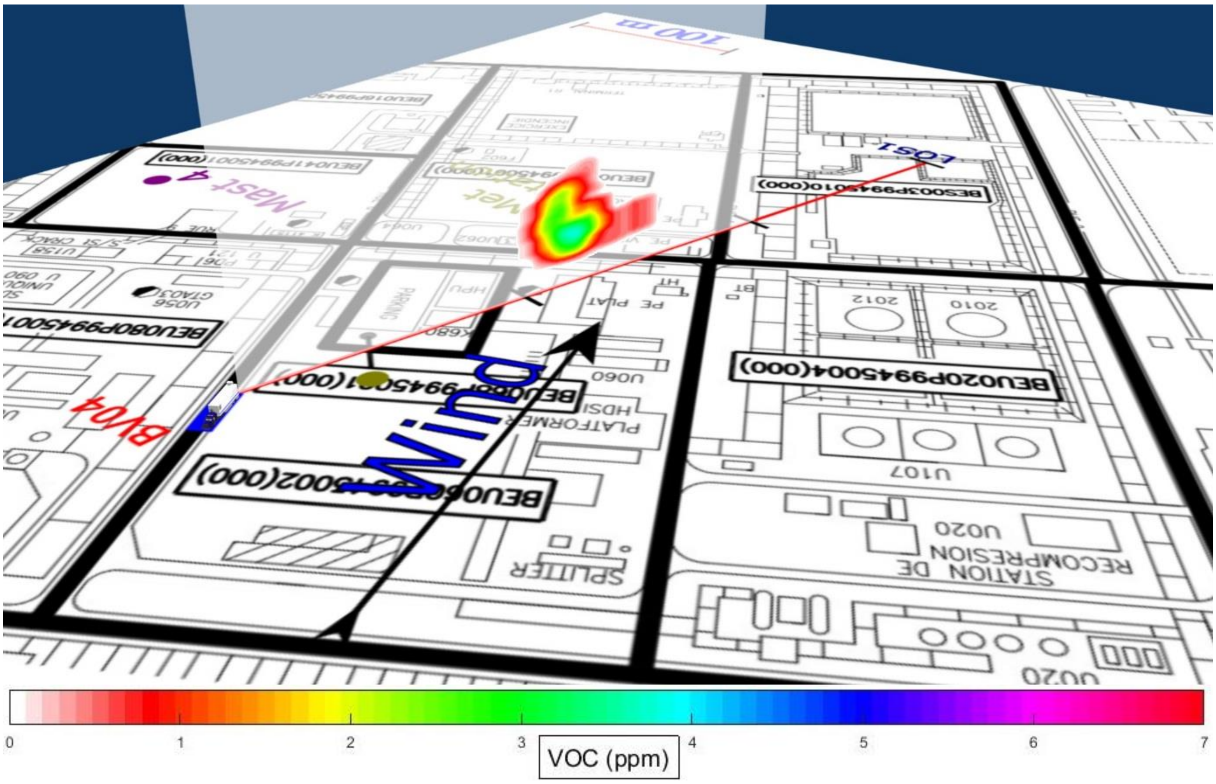

Figure 5.3a2 Visualisation of emission rate for Scan 43 representing BV04/LOS1.

Table 5.4 VOC emission rates determined from BV06 on 26th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
47	BV06/LOS1	12:22	12:44	2.1	230.8	9.15	Downwind Test 6
48	BV06/LOS2	12:49	13:05	1.9	210.5	8.68	Downwind Test 6
49	BV06/LOS2	13:05	13:21	2.5	240.3	11.04	Downwind Test 6
50	BV06/LOS2	13:21	13:37	2.8	245.3	9.64	Downwind Test 6
52	BV06/LOS2	14:24	14:35	2.4	226.2	0.45	Background

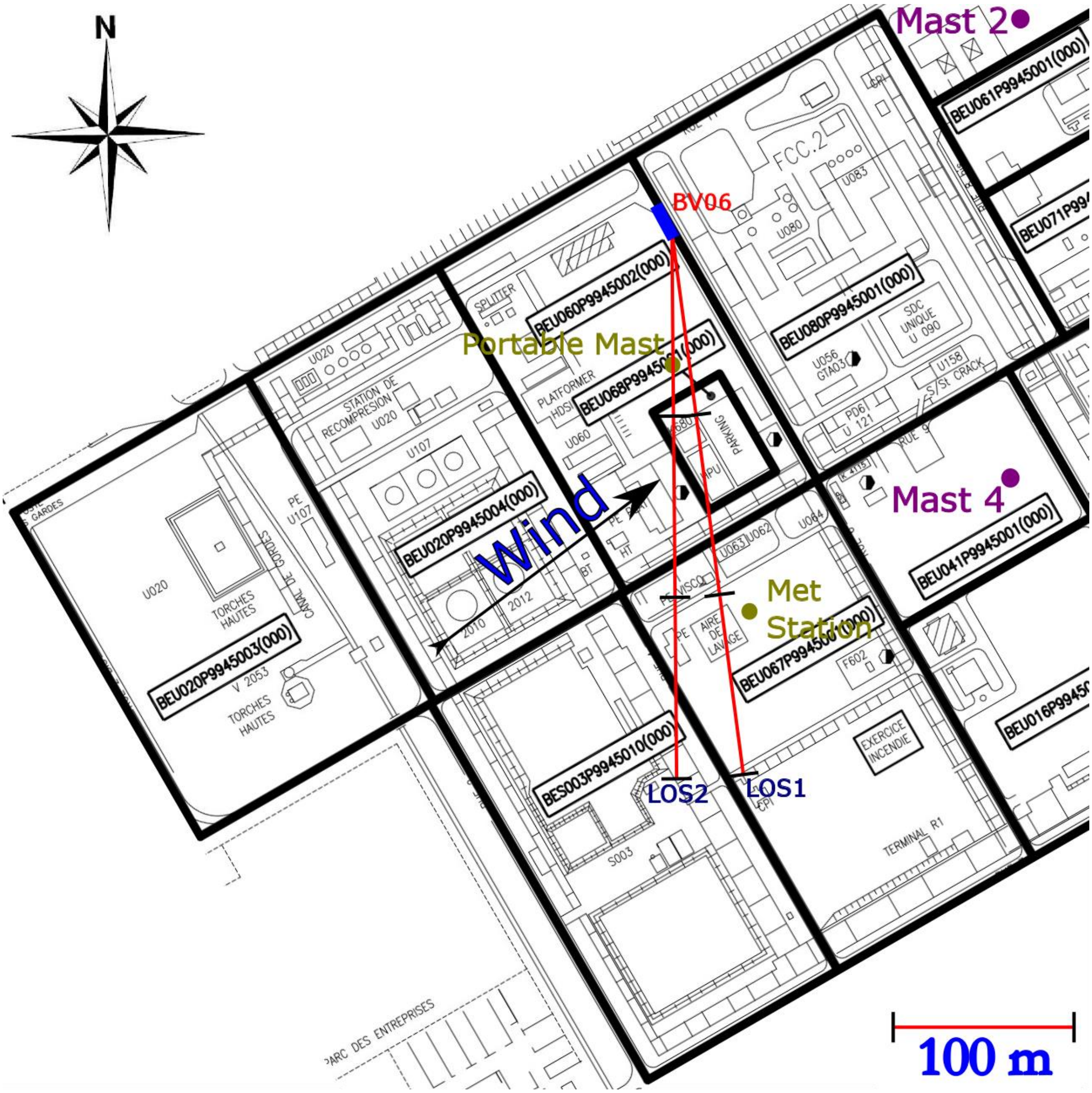

Figure 5.4 Measurement configuration for location BV06 on 26th September.

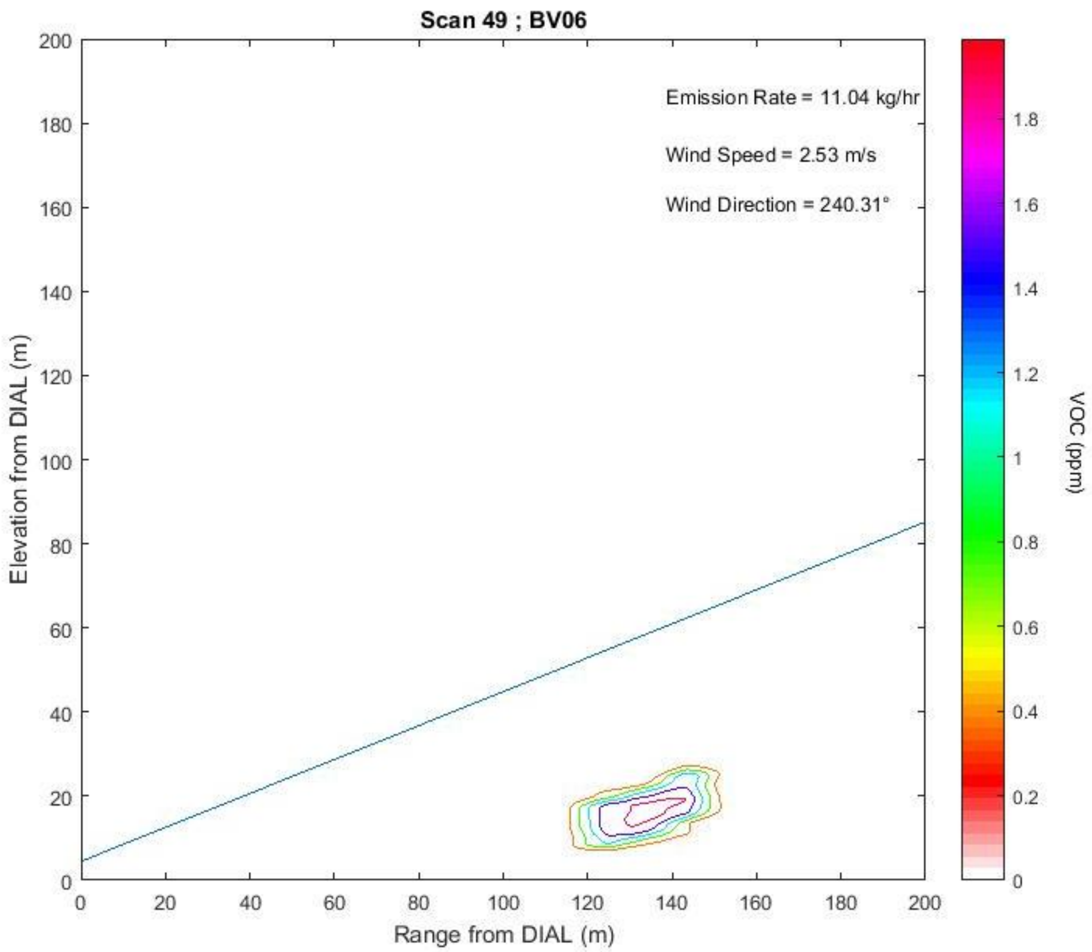

Figure 5.4a1 Observed VOC concentration for Scan 49 representing BV06/LOS2.

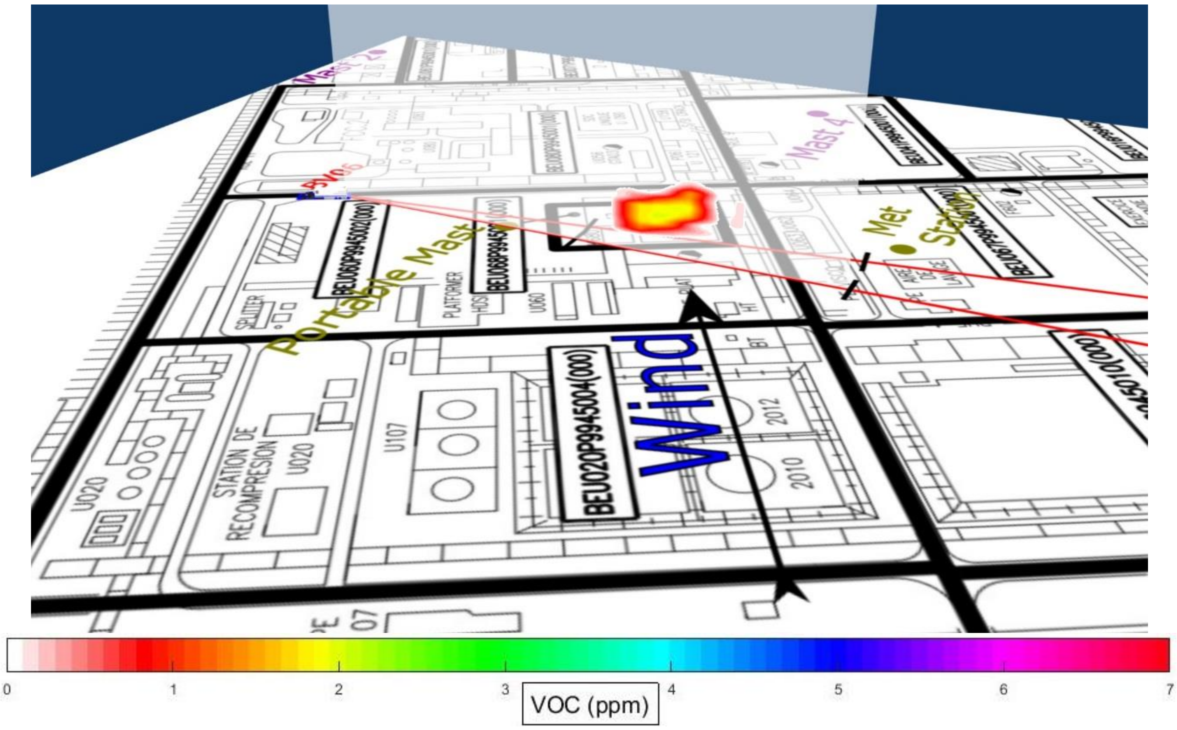

Figure 5.4a2 Visualisation of emission rate for Scan 49 representing BV06/LOS2.

Table 5.5 VOC emission rates determined from BV09 on 26th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
57	BV09/LOS1	16:05	16:21	2.9	223.5	13.58	Downwind Test 8
58	BV09/LOS1	16:22	16:38	2.3	224.5	13.41	Downwind Test 8
59	BV09/LOS2	16:39	16:56	2.5	215.4	13.04	Downwind Test 8
60	BV09/LOS2	16:56	17:12	2.4	222.5	12.67	Downwind Test 8
61	BV09/LOS2	17:14	17:29	2.5	224.3	12.32	Downwind Test 8
62	BV09/LOS2	17:36	17:50	2.2	206.8	3.44	Background

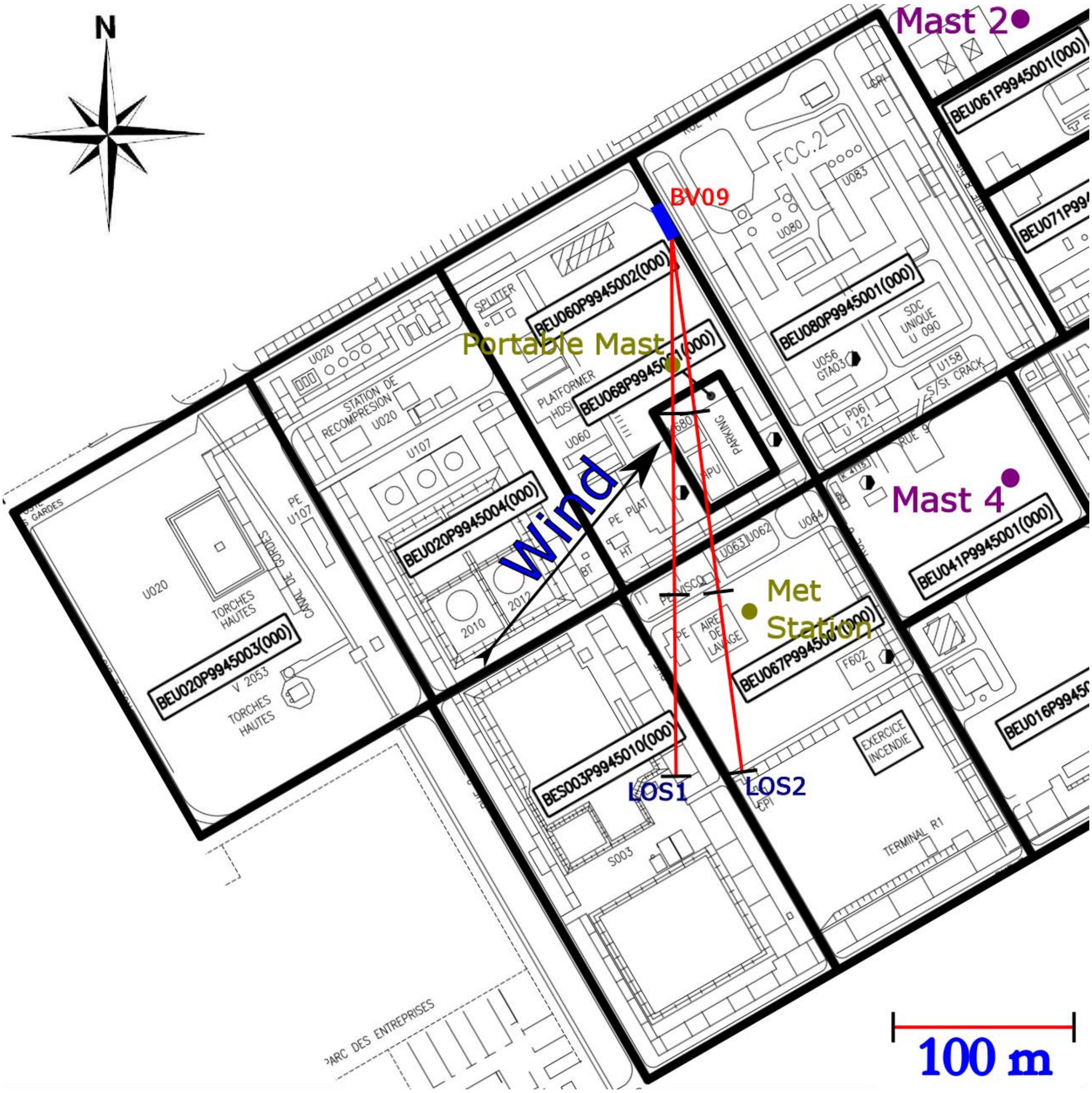

Figure 5.5 Measurement configuration for location BV09 on 26th September.

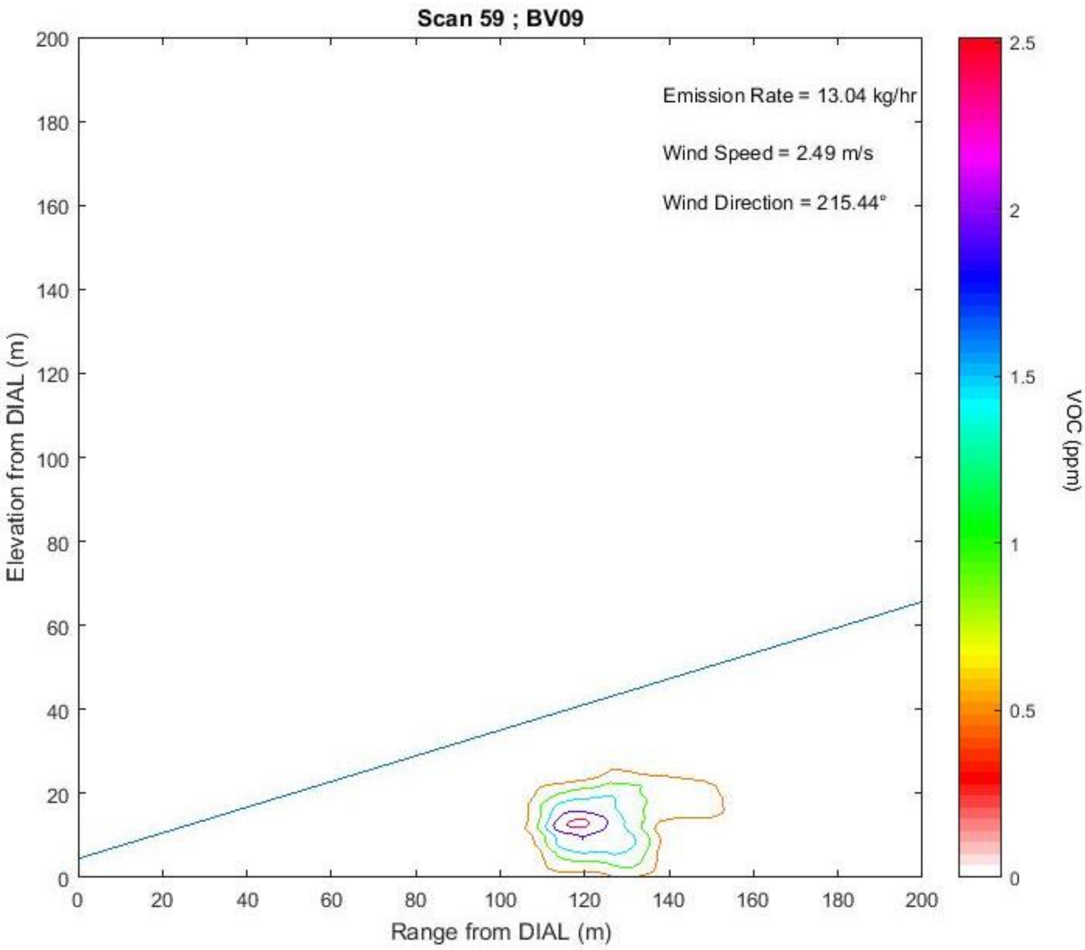

Figure 5.5a1 Observed VOC concentration for Scan 59 representing BV09/LOS2.

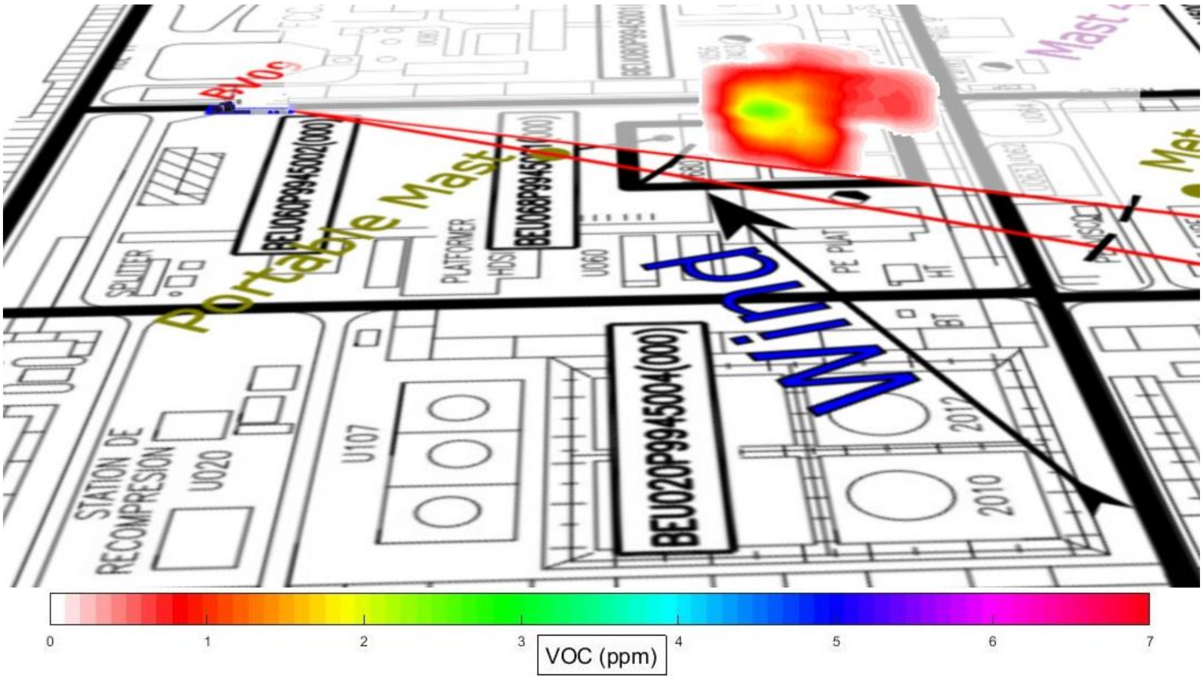

Figure 5.5a2 Visualisation of emission rate for Scan 59 representing BV09/LOS2.

Table 5.6 VOC emission rates determined from BV10 on 27th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
63	BV10/LOS1	09:14	09:31	1.5	322.0	22.28	Background
64	BV10/LOS1	09:37	09:52	2.3	338.4	37.89	Downwind Test 9
65	BV10/LOS1	09:53	10:08	2.2	335.9	33.70	Downwind Test 9
66	BV10/LOS1	10:09	10:24	2.2	330.0	38.14	Downwind Test 9
67	BV10/LOS1	10:26	10:41	2.1	318.3	41.76	Downwind Test 9
68	BV10/LOS1	10:42	11:06	1.8	310.1	37.95	Downwind Test 9
69	BV10/LOS1	11:07	11:23	2.0	320.5	26.96	Background
70	BV10/LOS1	11:28	11:45	2.3	333.4	43.34	Downwind Test 10
71	BV10/LOS1	11:45	12:01	1.8	301.4	50.91	Downwind Test 10
72	BV10/LOS1	12:02	12:18	1.5	296.0	39.42	Downwind Test 10
73	BV10/LOS1	12:20	12:38	1.5	288.4	38.03	Downwind Test 10
74	BV10/LOS1	12:38	12:56	1.7	267.9	20.36	Downwind Test 10
75	BV10/LOS2	12:59	13:07	1.7	279.8	18.62	Downwind Test 10
76	BV10/LOS1	13:08	13:26	2.8	250.0	0.69	Background

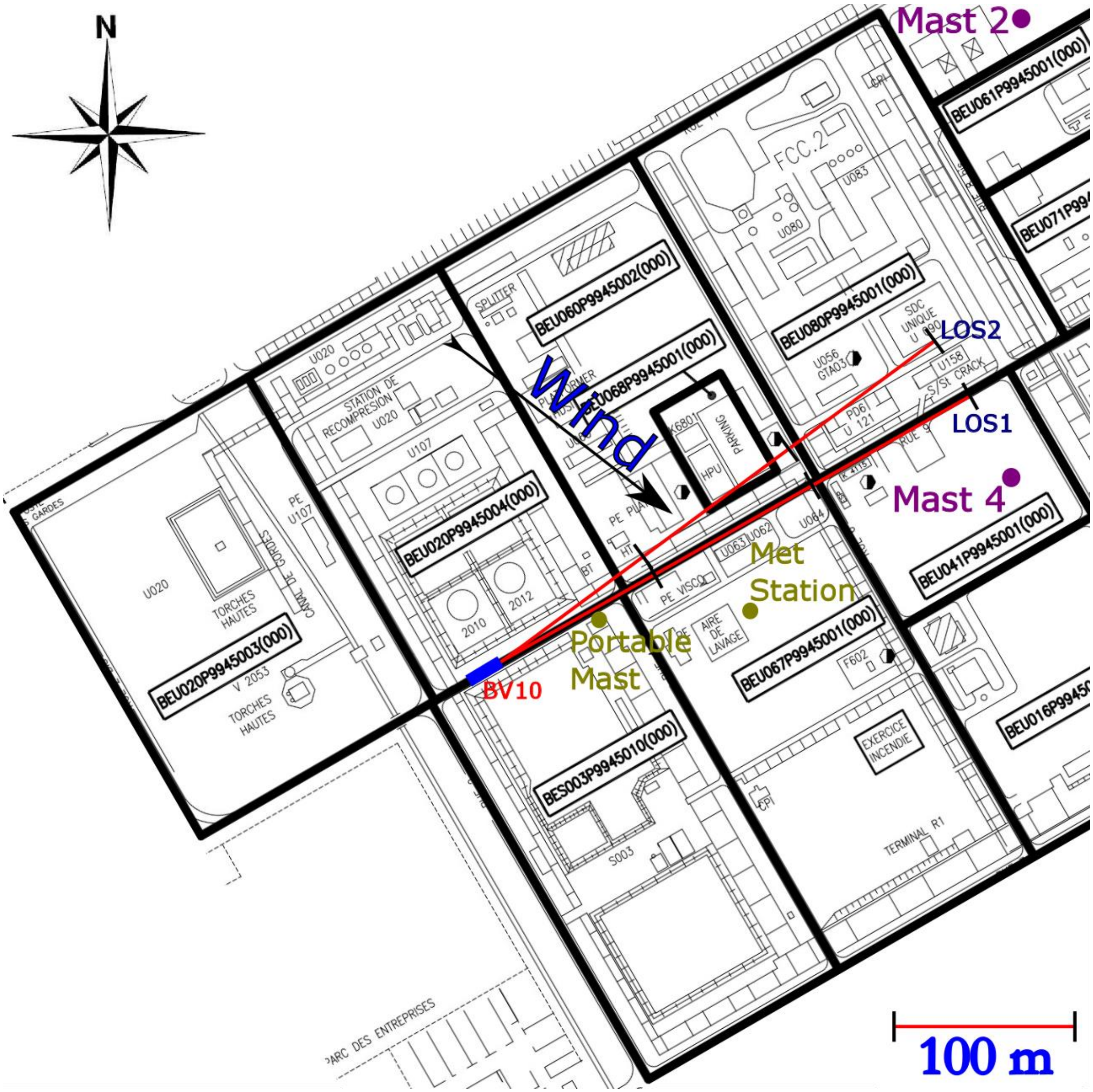

Figure 5.6 Measurement configuration for location BV10 on 27th September.

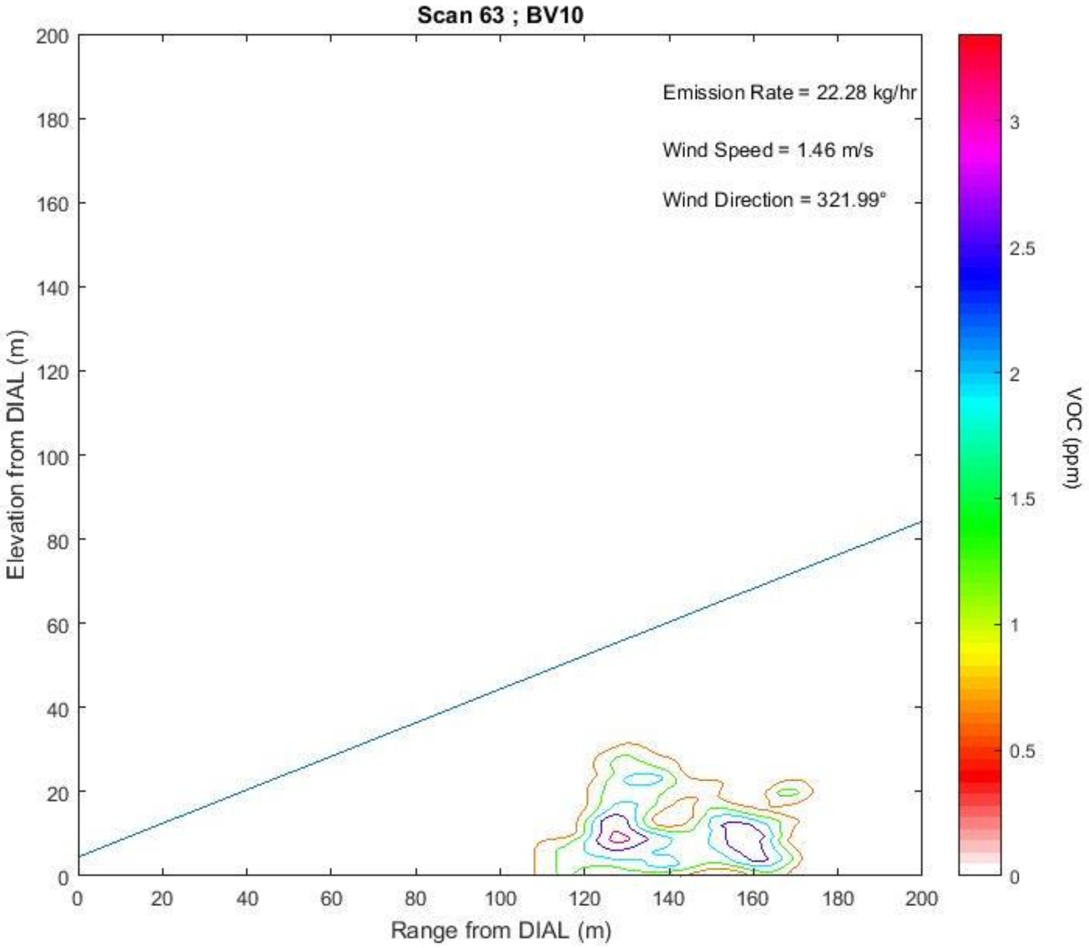

Figure 5.6a1 Observed background VOC concentration for Scan 63 representing BV10/LOS1.

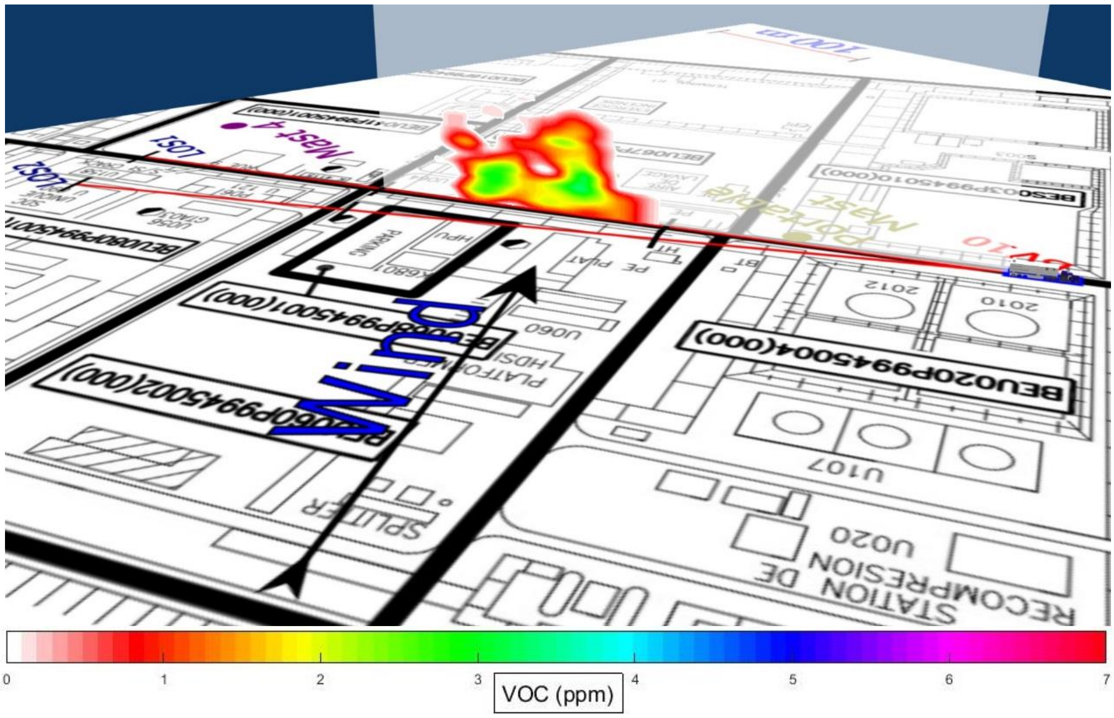

Figure 5.6a2 Visualisation of background emission rate for Scan 63 representing BV10/LOS1.

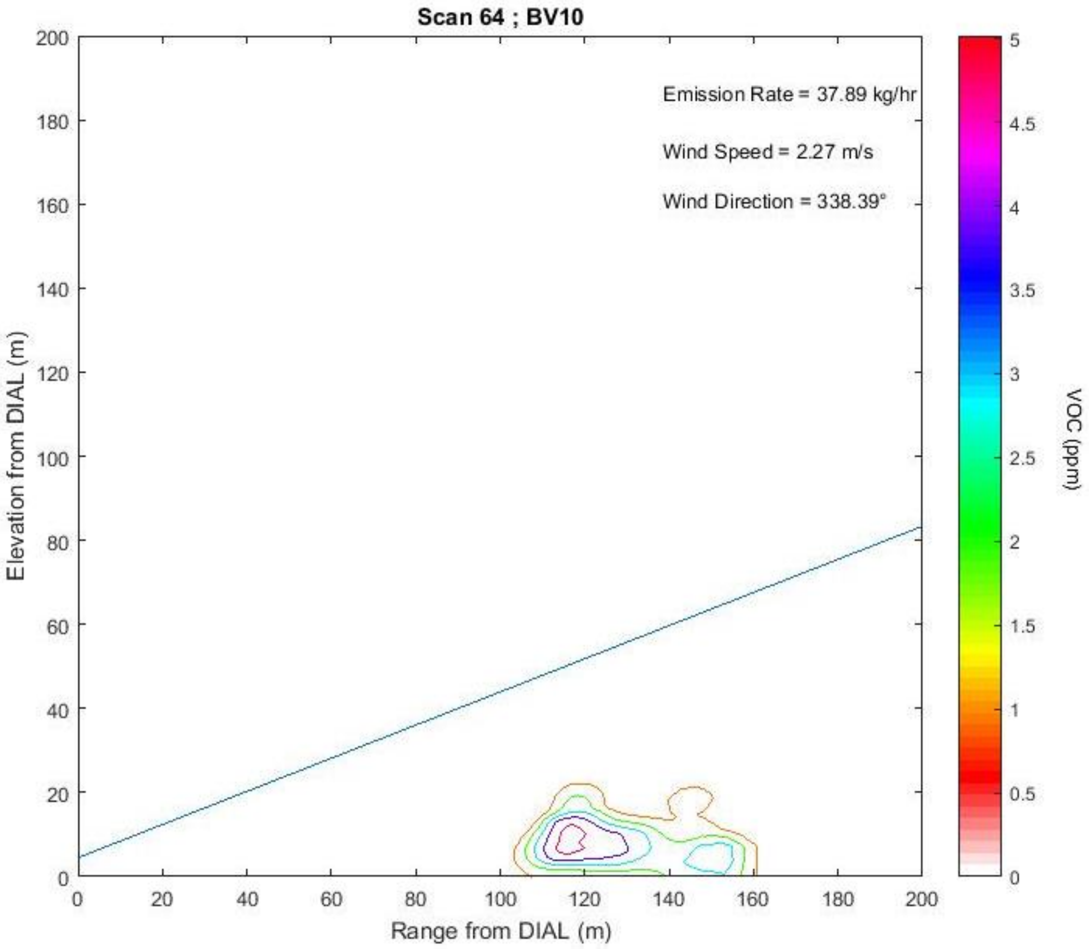

Figure 5.6b1 Observed VOC concentration for Scan 64 representing BV10/LOS1.

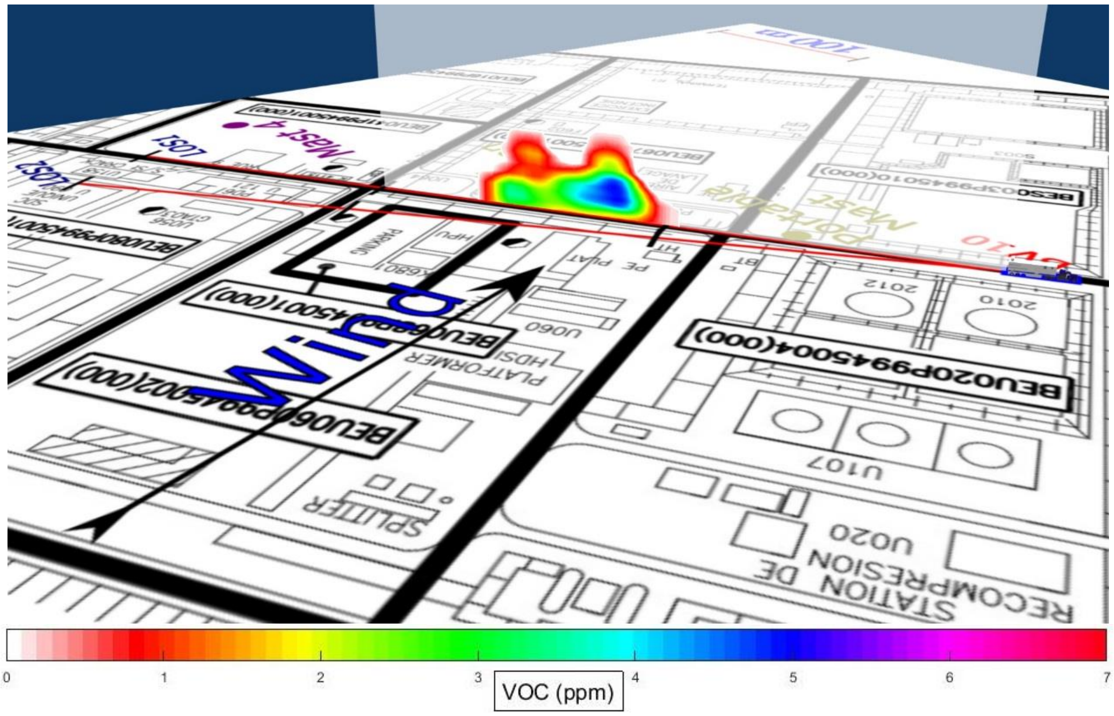

Figure 5.6b2 Visualisation of emission rate for Scan 64 representing BV10/LOS1.

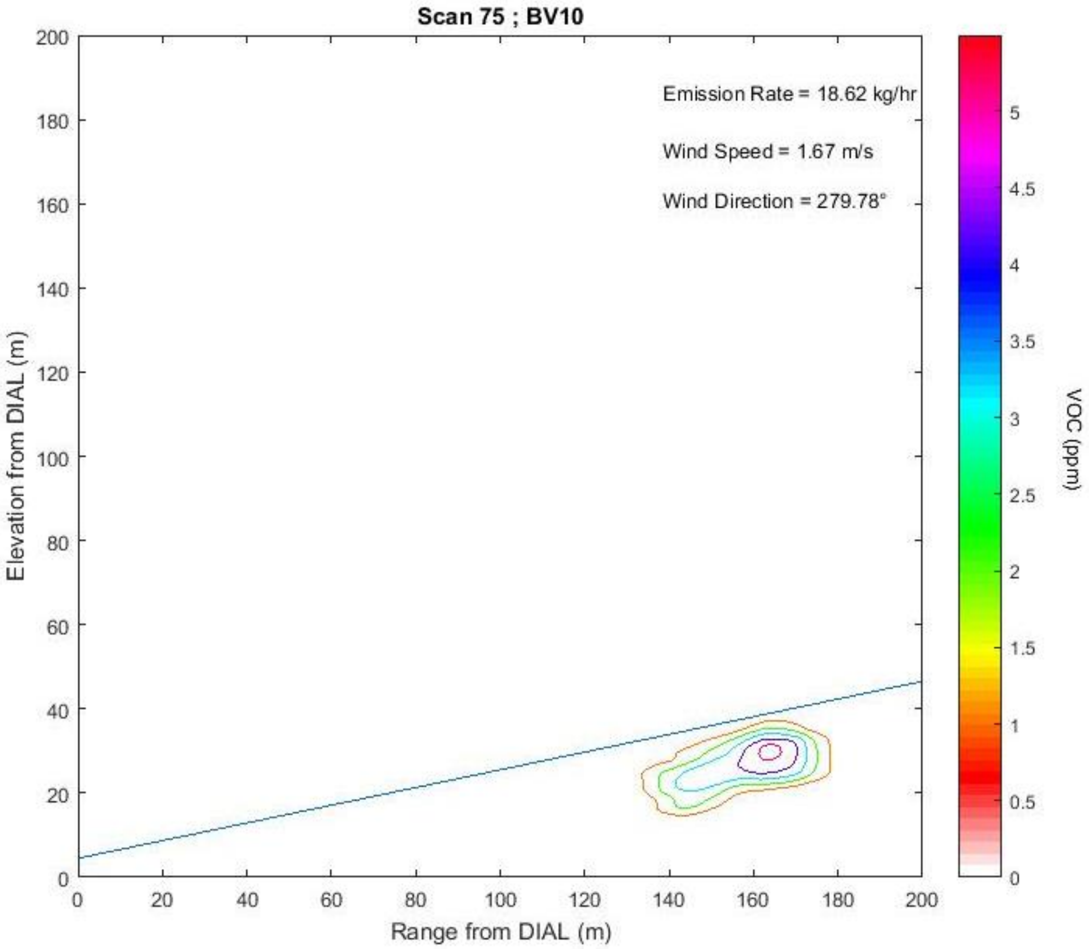

Figure 5.6c1 Observed VOC concentration for Scan 75 representing BV10/LOS2.

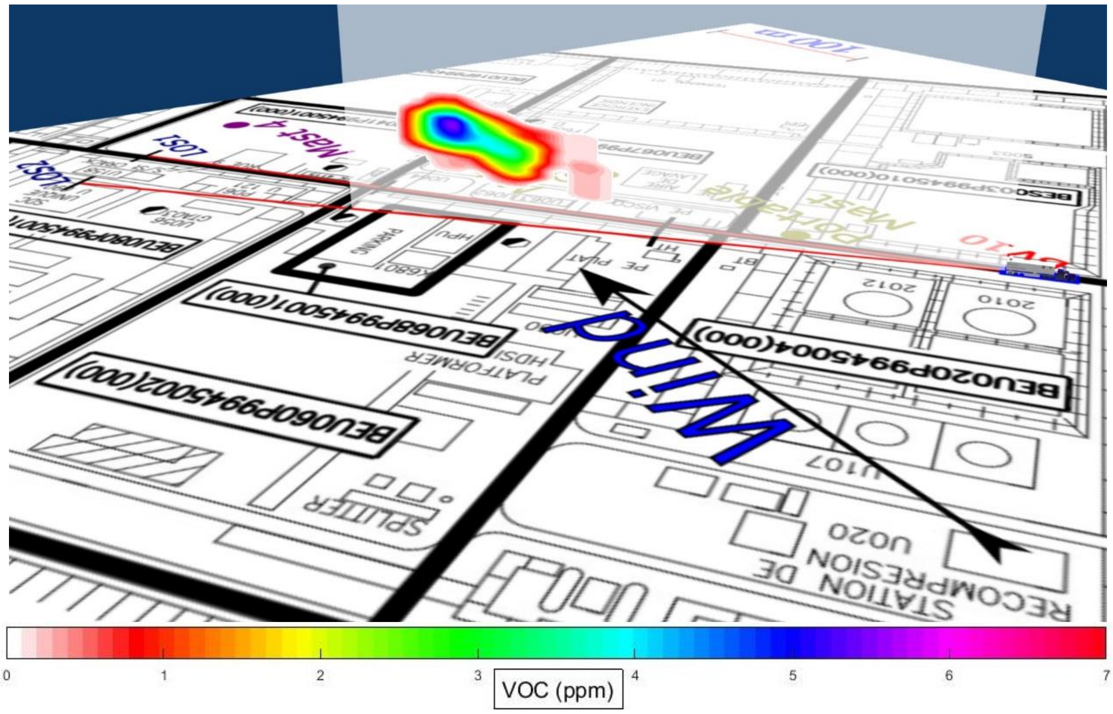

Figure 5.6c2 Visualisation of emission rate for Scan 75 representing BV10/LOS2.

Table 5.7 VOC emission rates determined from BV11 on 27th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
77	BV11/LOS1	14:20	14:35	2.7	260.3	25.41	Downwind Test 11
78	BV11/LOS2	14:37	14:53	2.6	255.2	20.13	Downwind Test 11
79	BV11/LOS1	14:55	15:09	3.0	254.7	17.42	Downwind Test 11
80	BV11/LOS1	15:10	15:24	2.4	266.3	15.06	Downwind Test 11
82	BV11/LOS1	15:35	15:49	3.5	242.5	9.47	Background
83	BV11/LOS1	15:55	16:09	2.5	261.8	14.07	Downwind Test 12
84	BV11/LOS1	16:10	16:24	2.5	261.6	21.91	Downwind Test 12
85	BV11/LOS1	16:24	16:39	2.6	249.2	16.08	Downwind Test 12
86	BV11/LOS1	16:39	16:53	2.7	246.6	15.18	Downwind Test 12
87	BV11/LOS1	16:56	17:10	2.9	246.7	24.73	Downwind Test 12
88	BV11/LOS1	17:11	17:24	3.4	244.6	14.50	Downwind Test 12
89	BV11/LOS1	17:30	17:44	2.3	259.8	9.09	Background

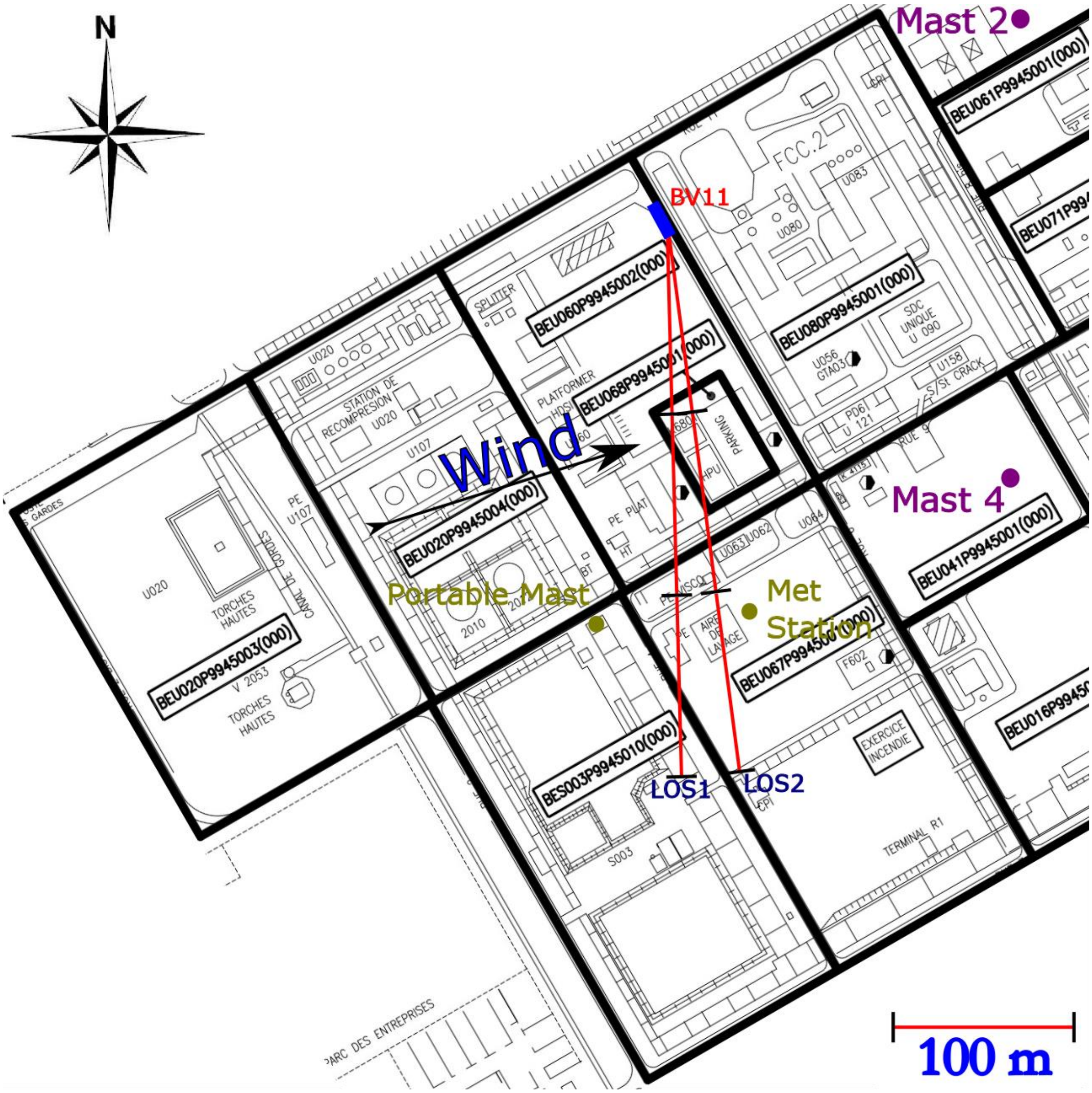

Figure 5.7 Measurement configuration for location BV11 on 27th September.

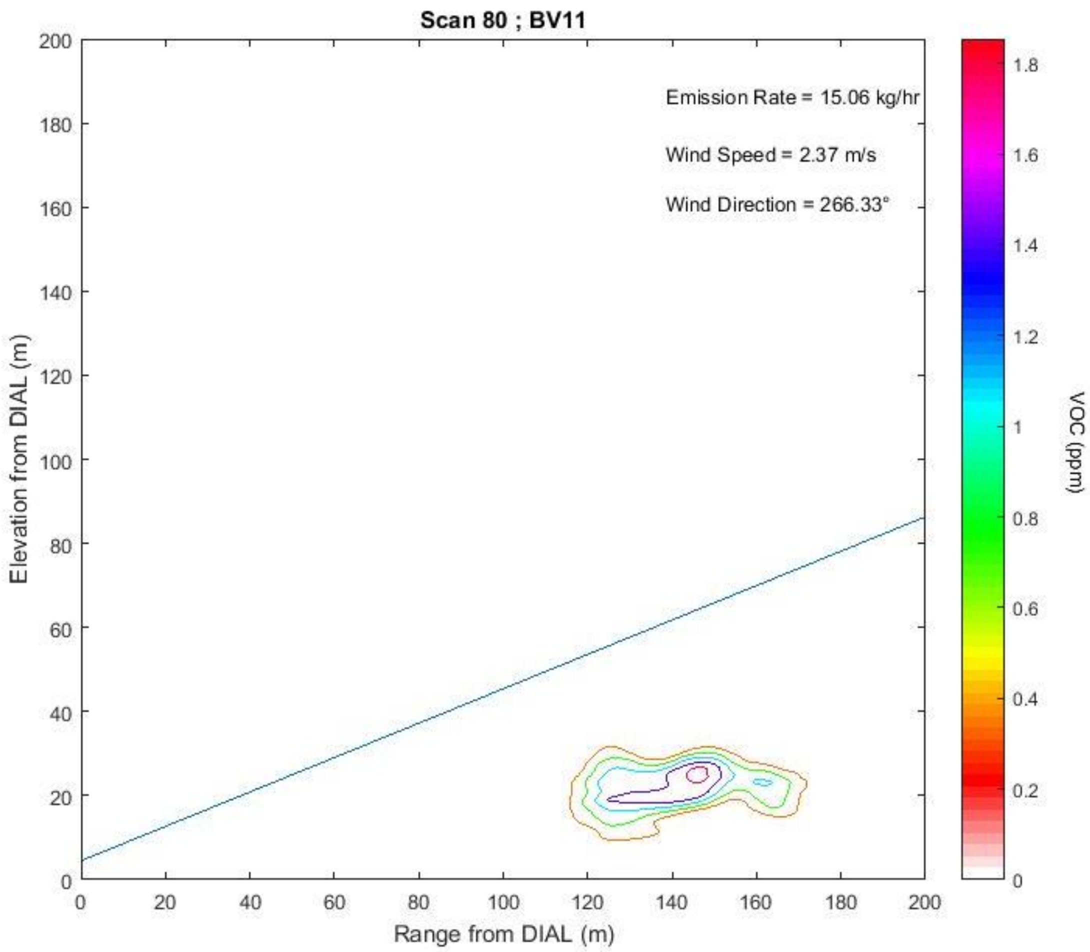

Figure 5.7a1 Observed VOC concentration for Scan 80 representing BV11/LOS1.

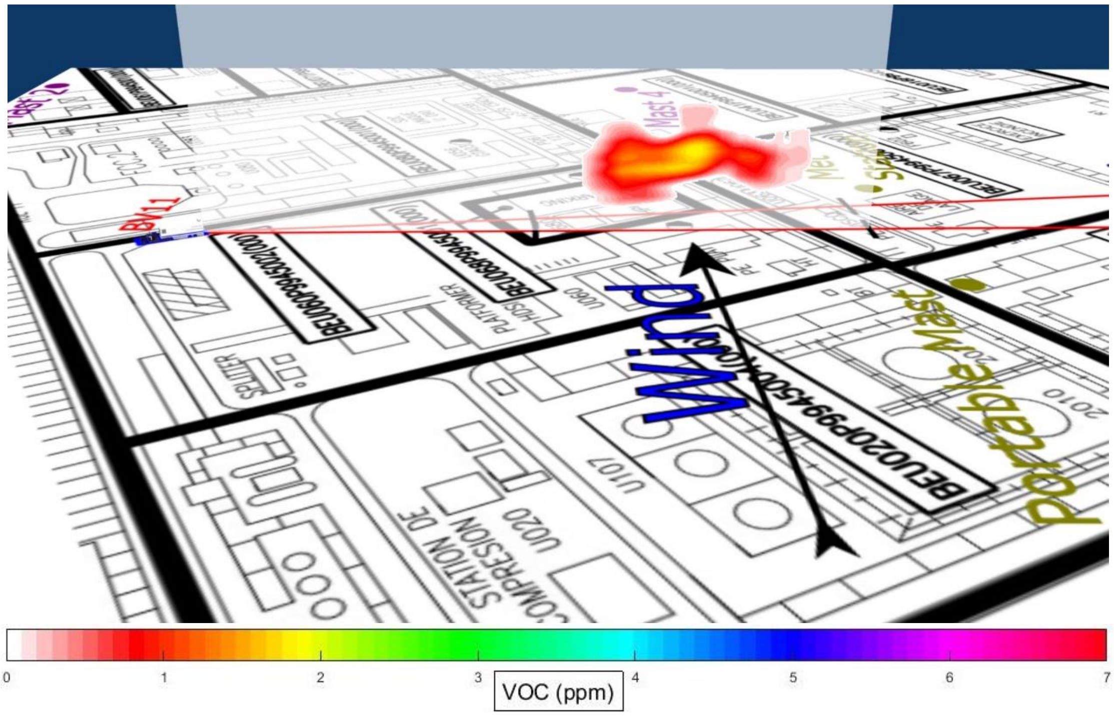

Figure 5.7a2 Visualisation of emission rate for Scan 80 representing BV11/LOS1.

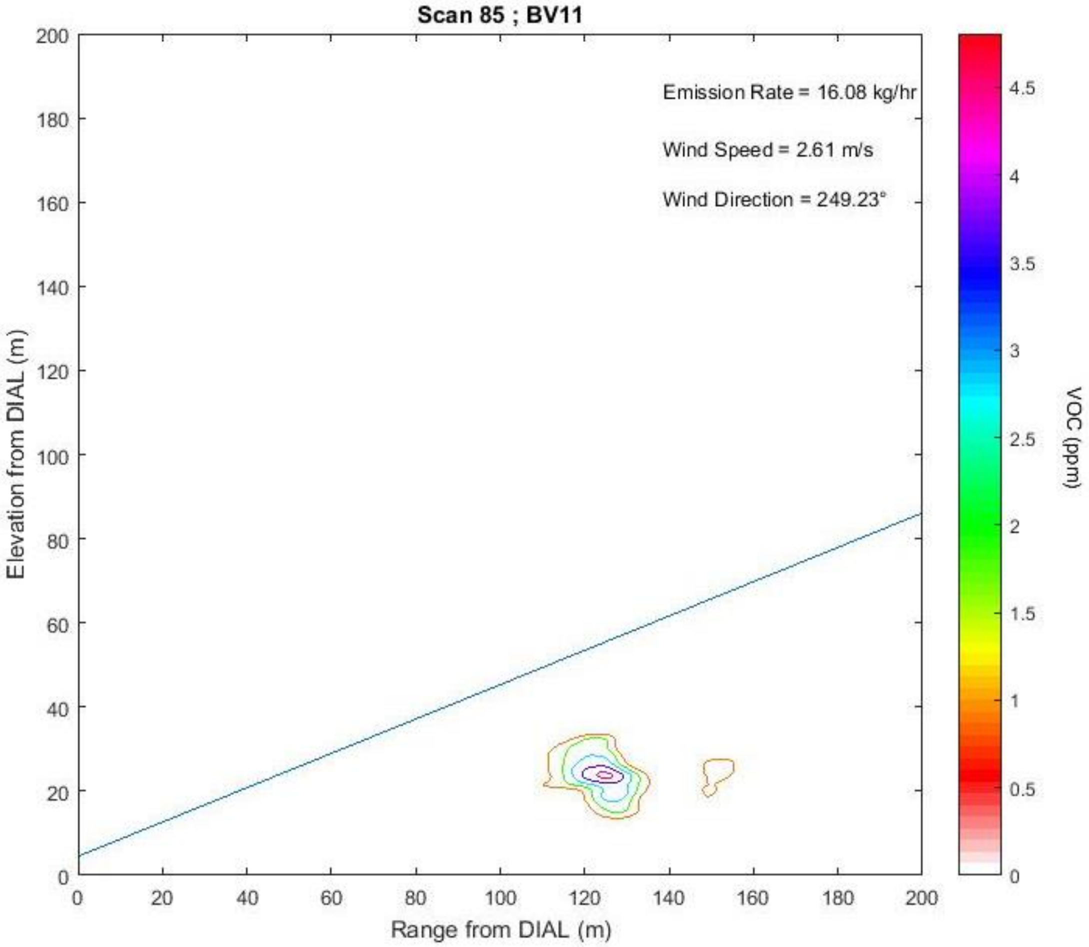

Figure 5.7b1 Observed VOC concentration for Scan 85 representing BV11/LOS1.

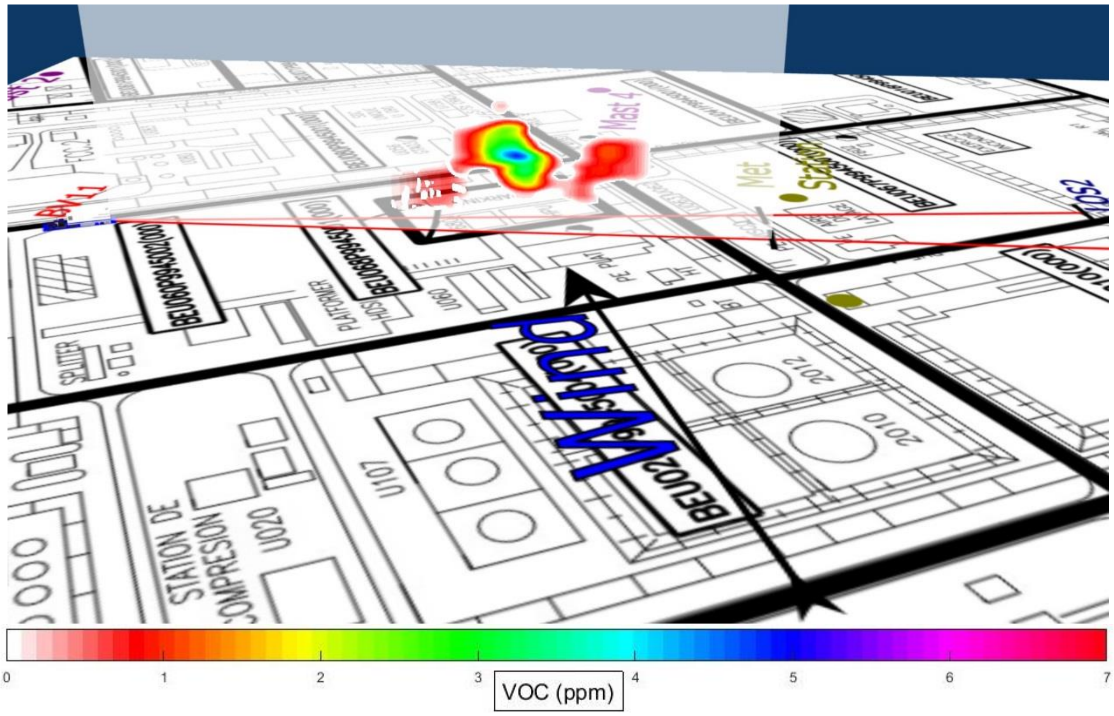

Figure 5.7b2 Visualisation of emission rate for Scan 85 representing BV11/LOS1.

Table 5.8 VOC emission rates determined from BV13 on 28th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
95	BV13/LOS1	12:05	12:20	1.9	235.9	30.26	Downwind Test 14
96	BV13/LOS1	12:21	12:36	1.7	232.8	26.25	Downwind Test 14
97	BV13/LOS1	12:37	12:52	1.4	230.6	28.16	Downwind Test 14
98	BV13/LOS1	12:52	13:08	2.0	242.2	32.72	Downwind Test 14
99	BV13/LOS1	13:08	13:23	2.2	241.7	24.67	Downwind Test 14
100	BV13/LOS1	13:24	13:39	2.2	231.3	24.95	Downwind Test 14
101	BV13/LOS1	13:40	13:55	2.5	265.1	12.58	Background
102	BV13/LOS1	14:37	14:52	2.6	228.5	14.77	Downwind Test 15
103	BV13/LOS1	14:55	15:11	2.8	237.8	16.21	Downwind Test 15
104	BV13/LOS1	15:12	15:30	3.0	237.9	17.31	Downwind Test 15
105	BV13/LOS1	15:30	15:47	2.7	231.0	15.30	Downwind Test 15
106	BV13/LOS1	15:48	16:06	2.7	233.4	19.17	Downwind Test 15
107	BV13/LOS1	16:06	16:24	2.4	239.9	11.23	Background
108	BV13/LOS1	16:24	16:39	4.0	232.3	14.81	Background
110	BV13/LOS1	16:45	17:00	2.8	236.1	17.43	Downwind Test 16
111	BV13/LOS1	17:01	17:16	3.1	234.5	12.77	Downwind Test 16
112	BV13/LOS1	17:17	17:32	2.8	232.8	14.36	Downwind Test 16
113	BV13/LOS1	17:32	17:48	2.9	235.1	11.82	Downwind Test 16

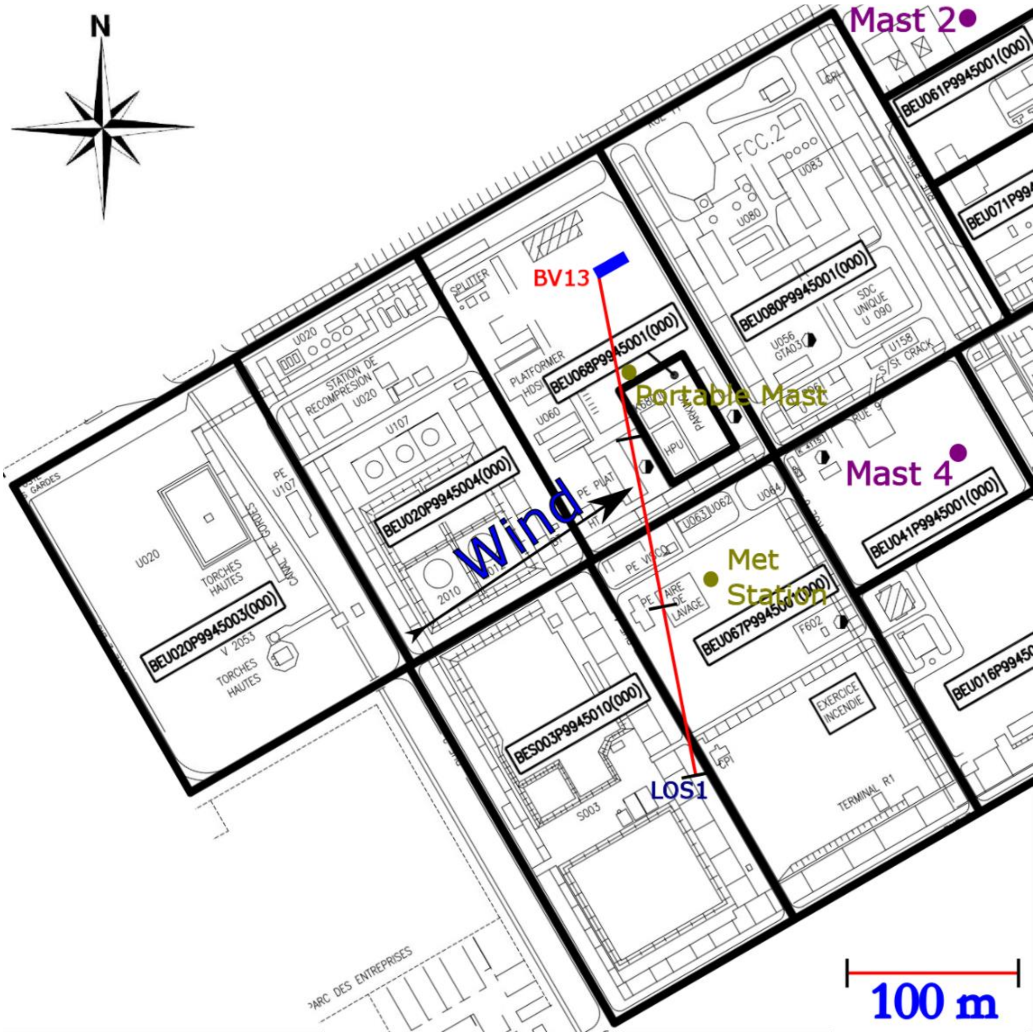

Figure 5.8 Measurement configuration for location BV13 on 28th September.

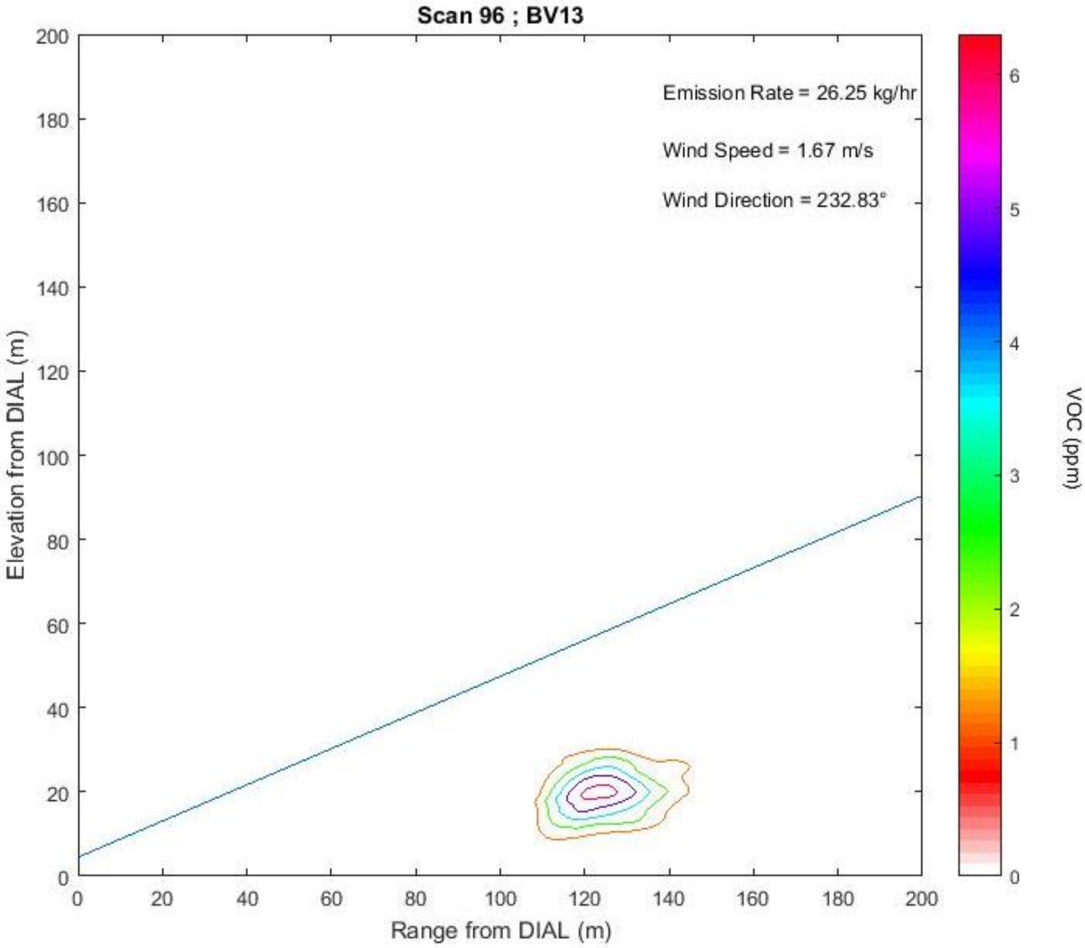

Figure 5.8a1 Observed VOC concentration for Scan 96 representing BV13/LOS1.

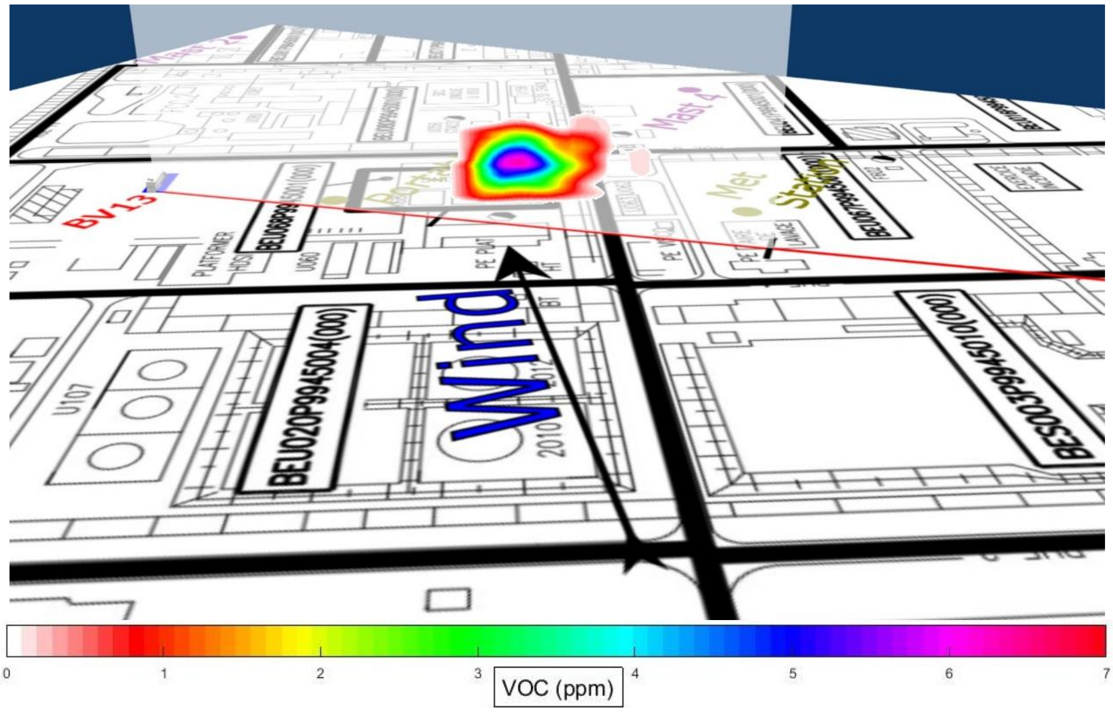

Figure 5.8a2 Visualisation of emission rate for 96 representing BV13/LOS1.

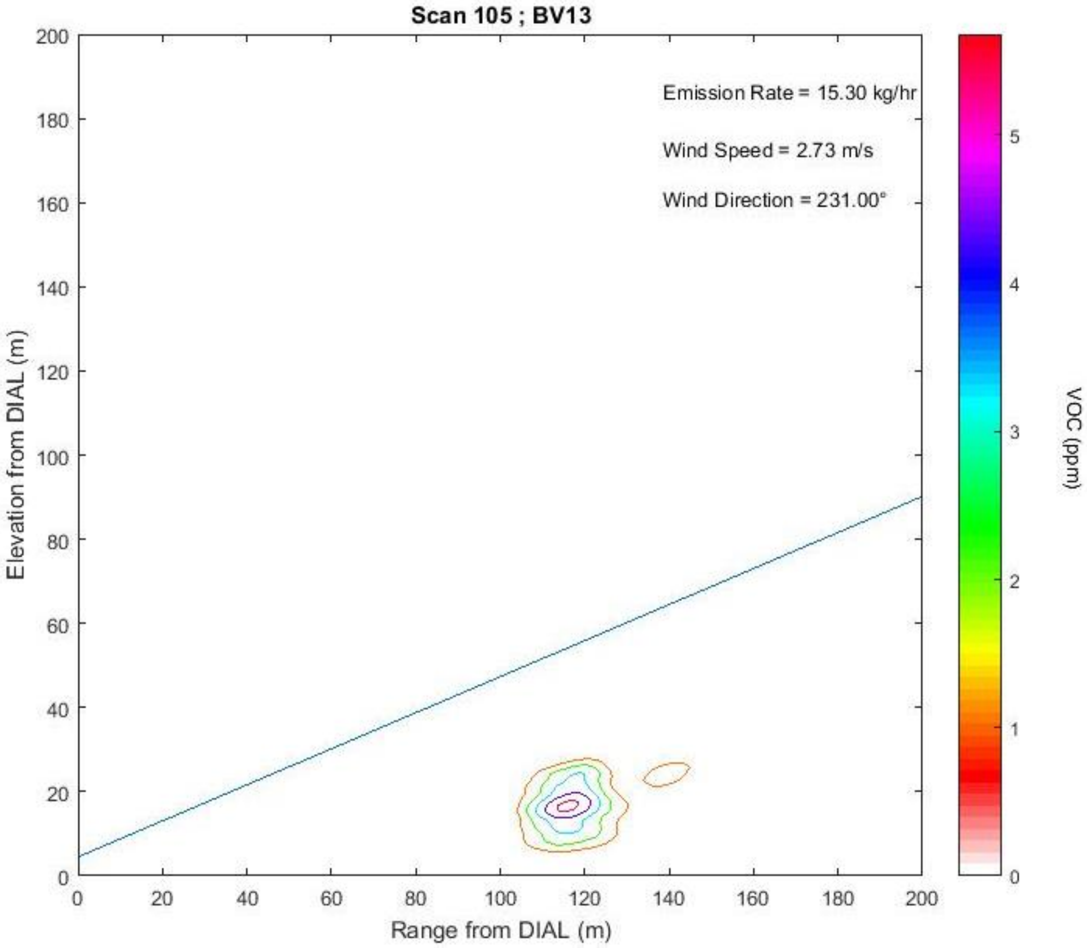

Figure 5.8b1 Observed VOC concentration for Scan 105 representing BV13/LOS1.

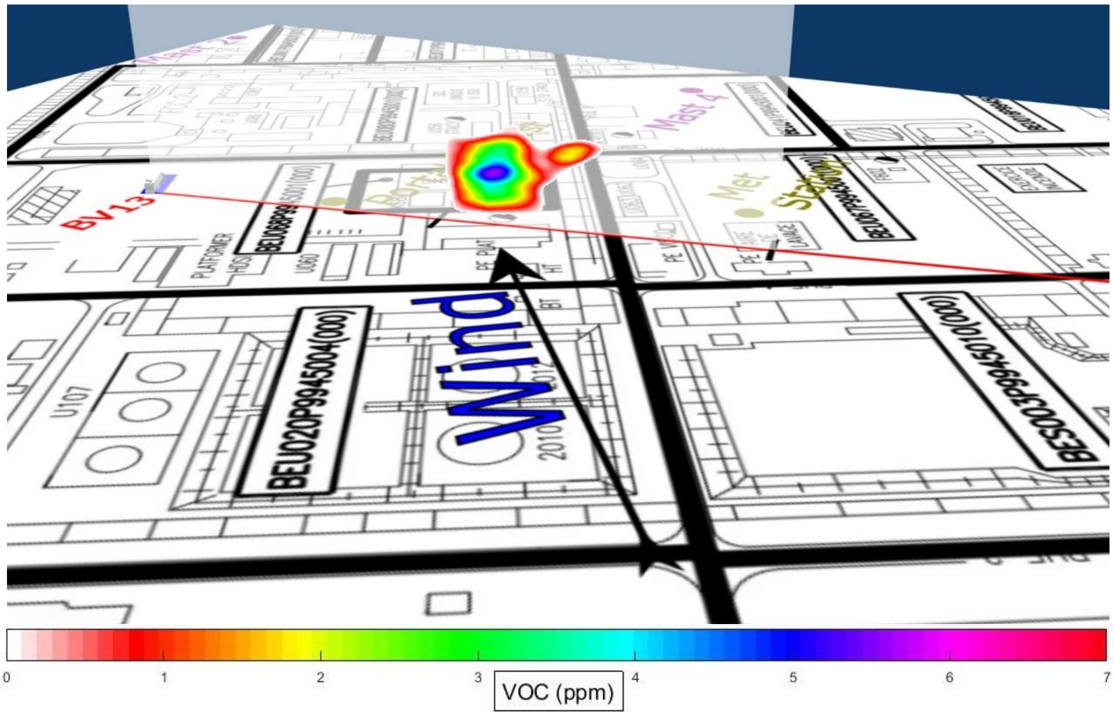

Figure 5.8b2 Visualisation of emission rate for Scan 105 representing BV13/LOS1.

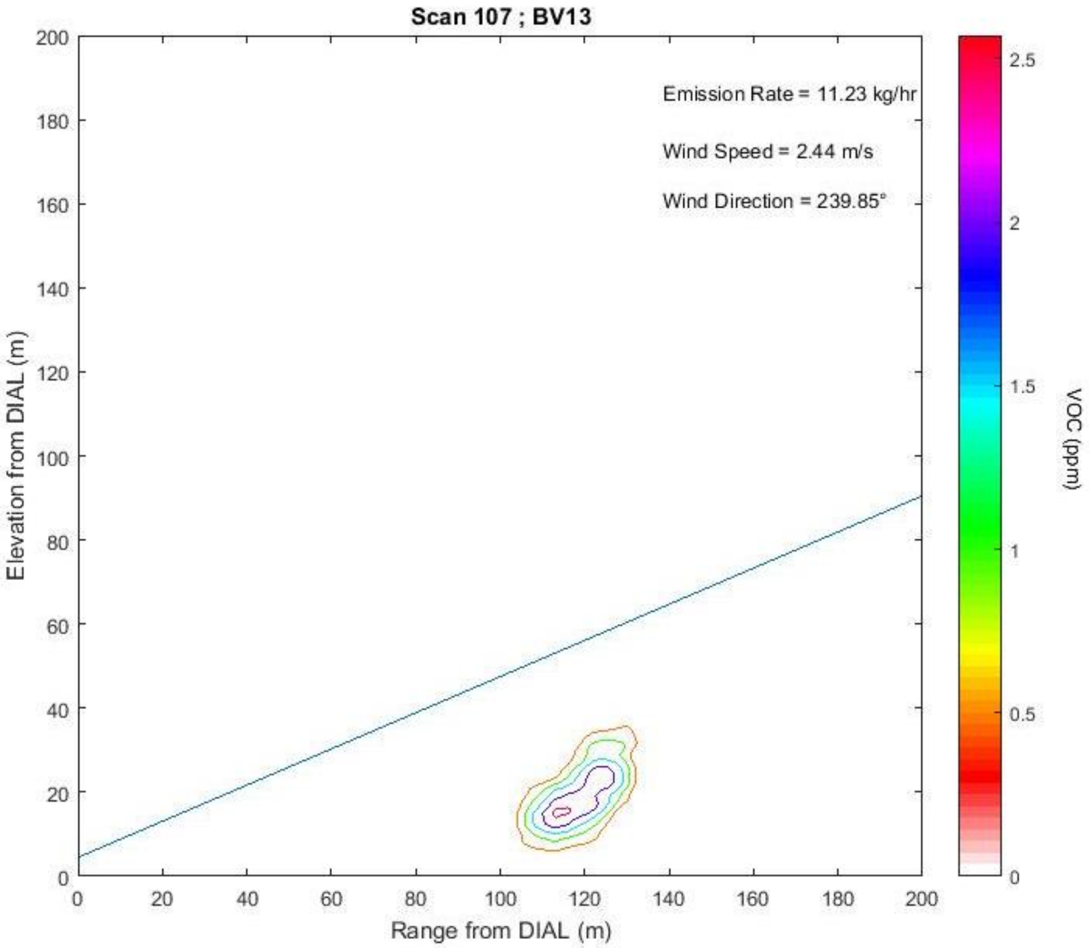

Figure 5.8c1 Observed background VOC concentration for Scan 107 representing BV13/LOS1.

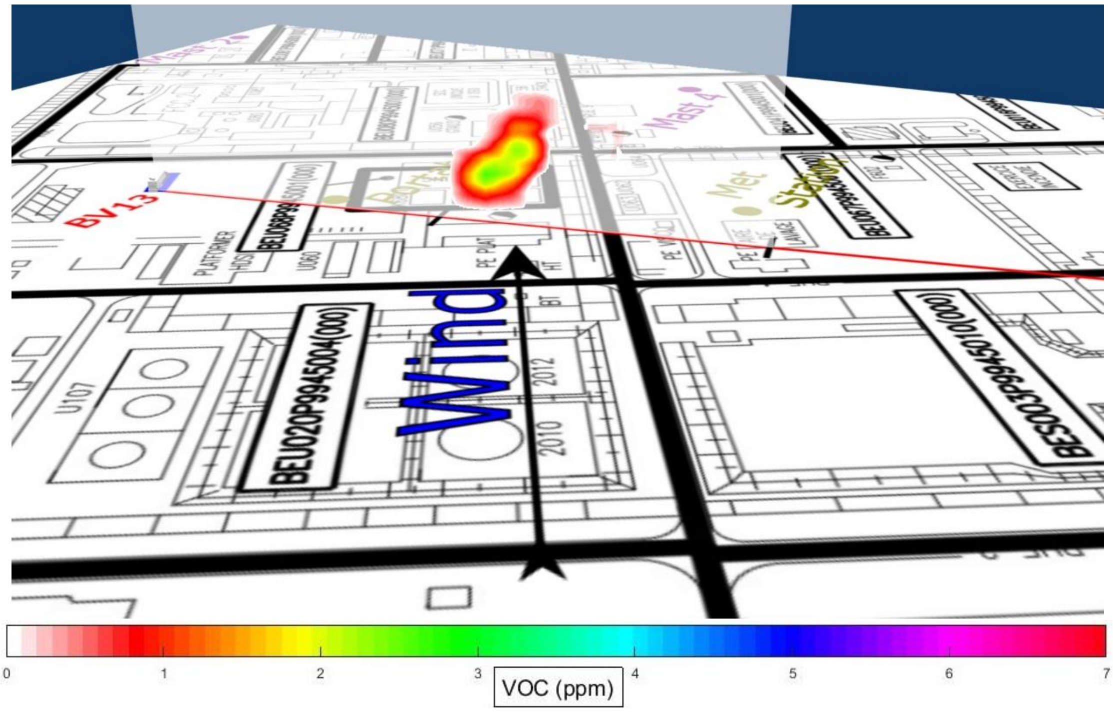

Figure 5.8c2 Visualisation of background emission rate for Scan 107 representing BV13/LOS1.

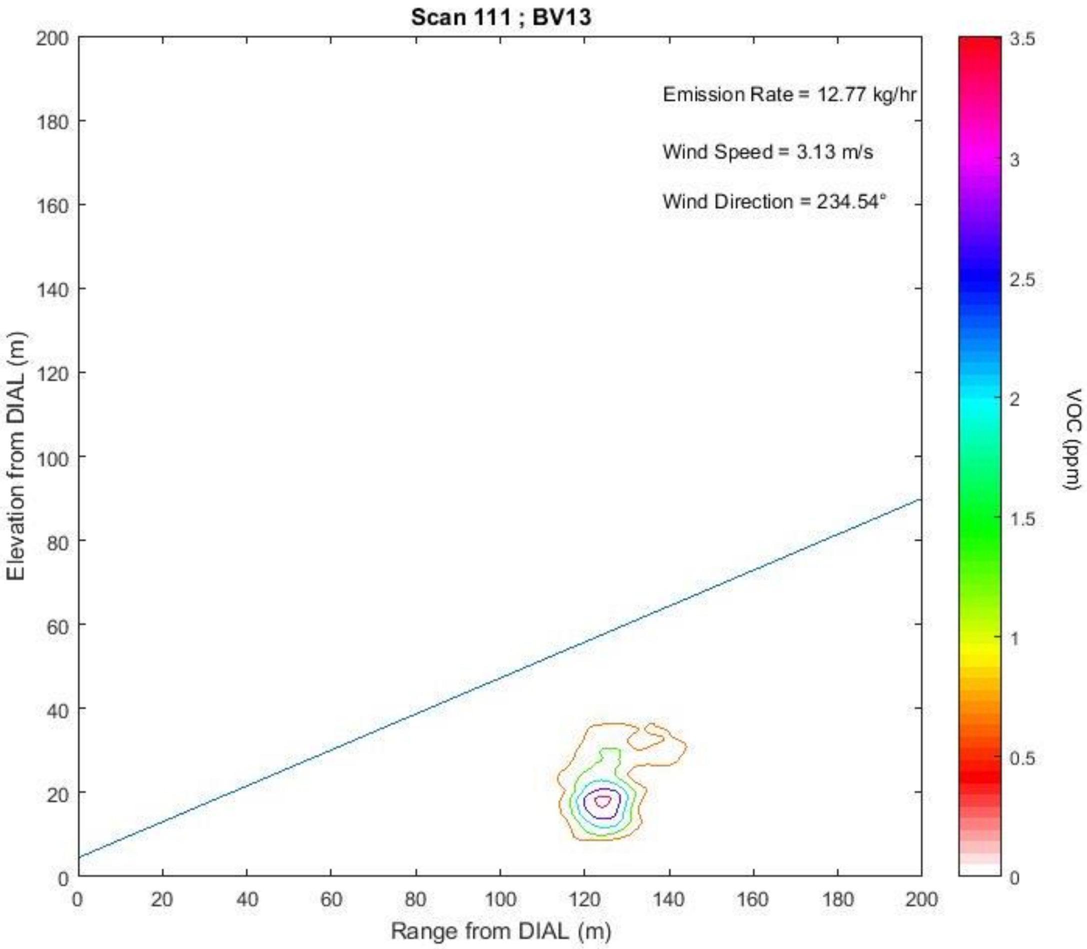

Figure 5.8d1 Observed VOC concentration for Scan 111 representing BV13/LOS1.

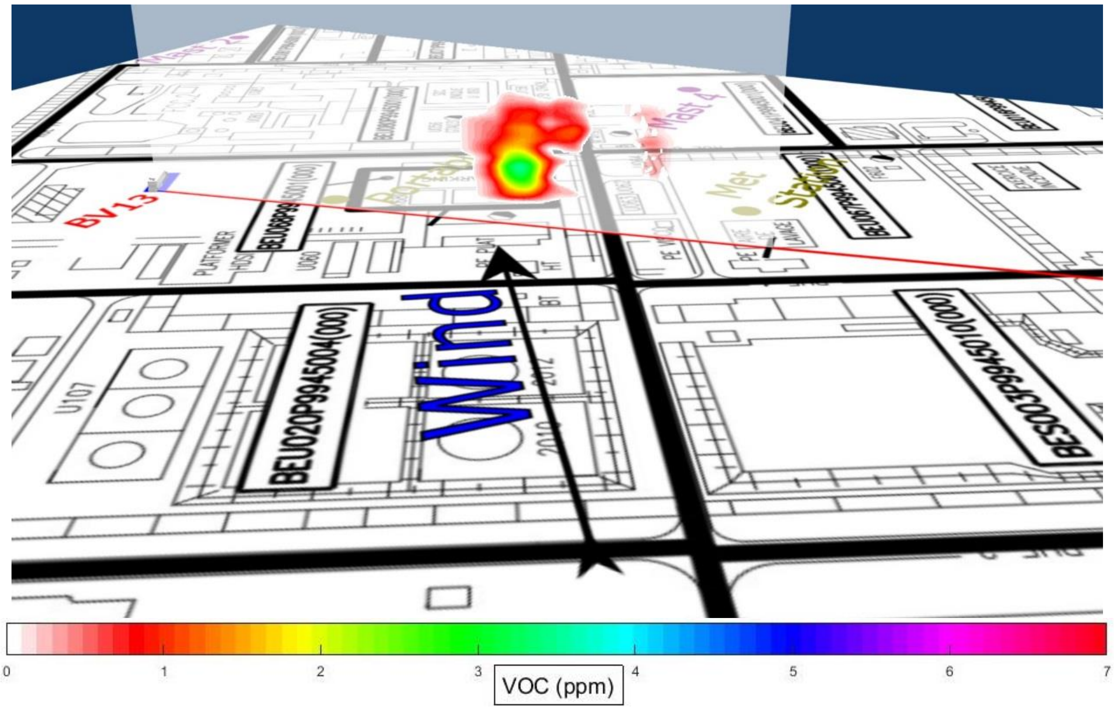

Figure 5.8d2 Visualisation of emission rate for Scan 111 representing BV13/LOS1.

Table 5.9 VOC emission rates determined from BV14 on 29th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
115	BV14/LOS1	10:51	11:08	1.3	184.1	9.11	Downwind Test 17
116	BV14/LOS1	11:09	11:26	1.0	197.7	9.75	Downwind Test 17
117	BV14/LOS1	11:31	11:46	1.0	208.5	10.18	Downwind Test 17
118	BV14/LOS1	11:47	12:00	1.1	162.8	-	Wind Direction \\ to LOS
119	BV14/LOS1	12:00	12:14	1.1	152.7	-	Wind Direction \\ to LOS
120	BV14/LOS1	12:14	12:27	1.0	186.9	5.08	Partial Plume
121	BV14/LOS1	12:28	12:36	2.0	228.6	35.91	Background
122	BV14/LOS2	12:40	12:56	2.3	238.8	61.08	Downwind Test 18
123	BV14/LOS1	12:57	13:09	2.2	234.3	53.36	Downwind Test 18
124	BV14/LOS2	13:11	13:24	2.3	226.2	58.43	Downwind Test 18
125	BV14/LOS1	13:25	13:37	1.9	210.2	47.16	Downwind Test 18
126	BV14/LOS1	13:38	13:50	1.8	214.5	44.16	Downwind Test 18
128	BV14/LOS1	13:56	14:10	2.7	233.3	33.59	Background
129	BV14/LOS1	14:11	14:24	3.4	233.6	43.97	Downwind Test 19
130	BV14/LOS1	14:25	14:38	3.7	233.3	48.96	Downwind Test 19
131	BV14/LOS1	14:38	14:52	3.1	235.4	45.68	Downwind Test 19
132	BV14/LOS1	14:52	15:05	3.2	240.4	48.83	Downwind Test 19
133	BV14/LOS1	15:06	15:13	3.3	251.3	44.84	Downwind Test 19
134	BV14/LOS1	15:13	15:27	3.1	235.7	39.51	Background
135	BV14/LOS1	15:33	15:46	3.1	235.9	51.47	Downwind Test 20
136	BV14/LOS1	15:47	16:02	2.8	237.7	54.16	Downwind Test 20
137	BV14/LOS1	16:03	16:18	2.8	230.8	49.64	Downwind Test 20
138	BV14/LOS1	16:18	16:34	2.5	242.0	48.52	Downwind Test 20
139	BV14/LOS1	16:34	16:49	2.8	231.1	43.70	Downwind Test 20
140	BV14/LOS1	16:50	17:05	2.8	238.5	49.24	Downwind Test 20
141	BV14/LOS1	17:05	17:21	2.7	238.5	42.82	Background

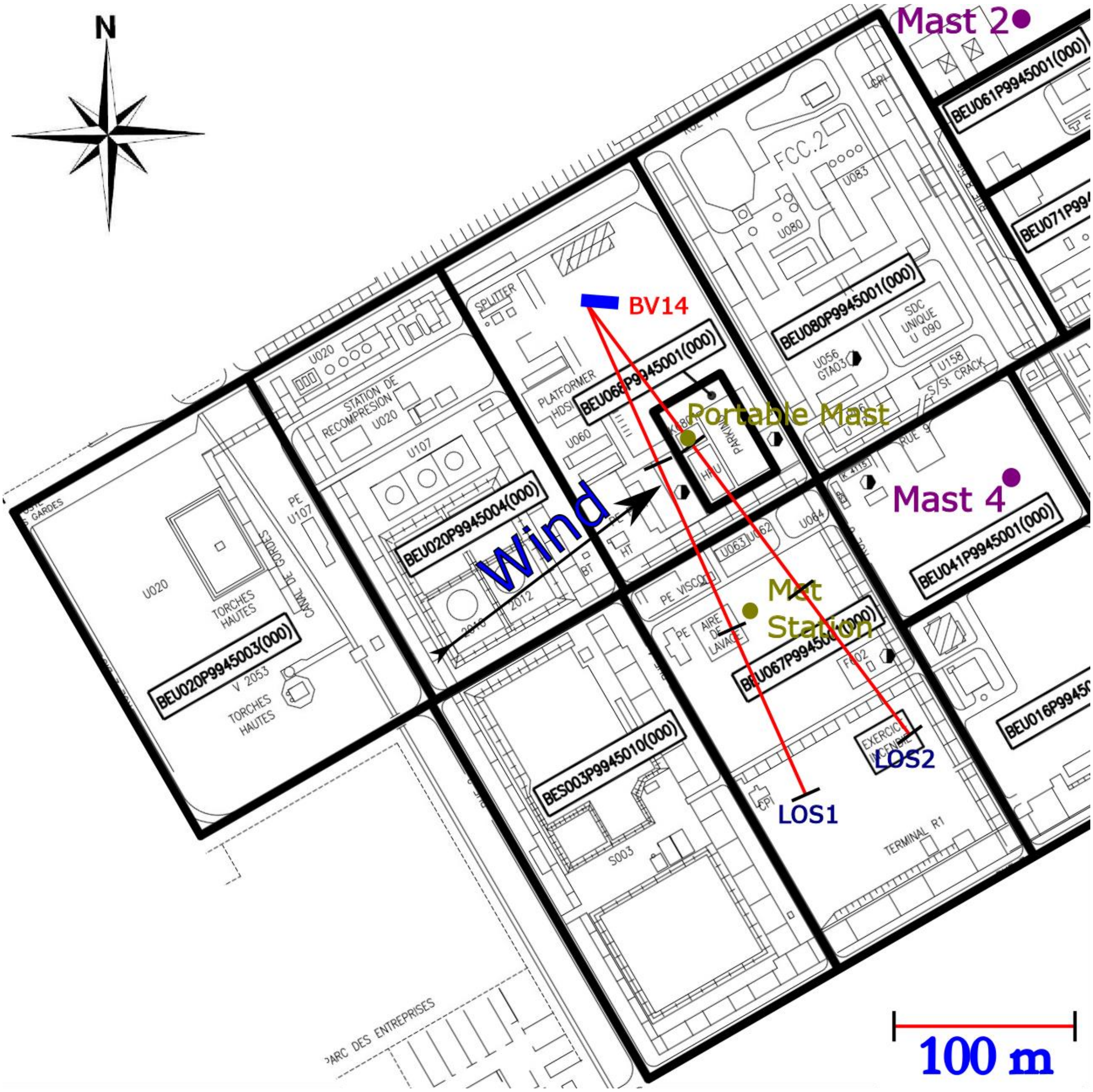

Figure 5.9 Measurement configuration for location BV14 on 29th September.

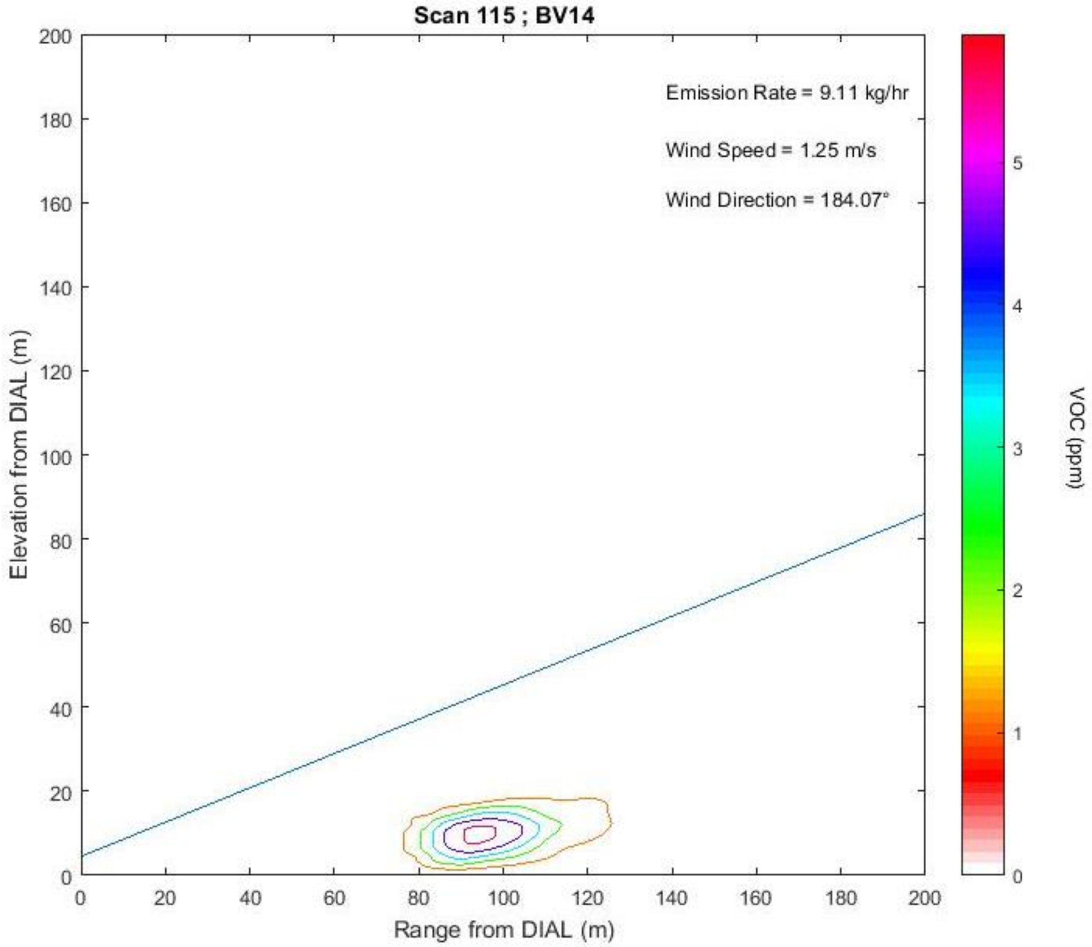

Figure 5.9a1 Observed VOC concentration for Scan 115 representing BV14/LOS1.

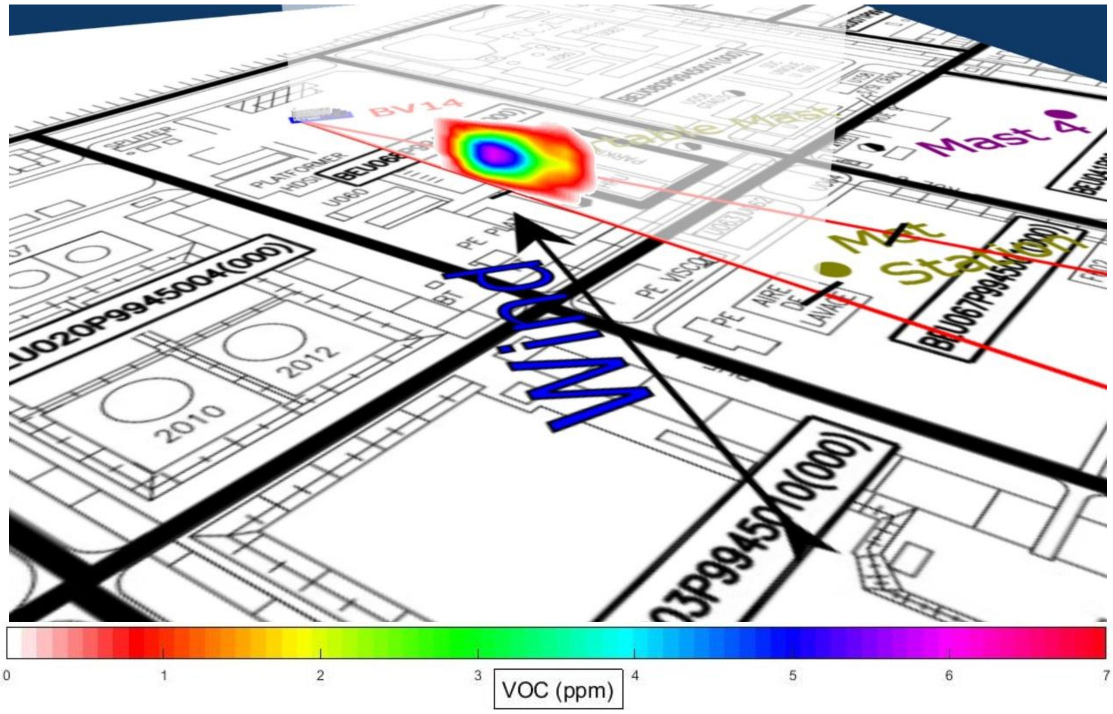

Figure 5.9a2 Visualisation of emission rate for Scan 115 representing BV14/LOS1.

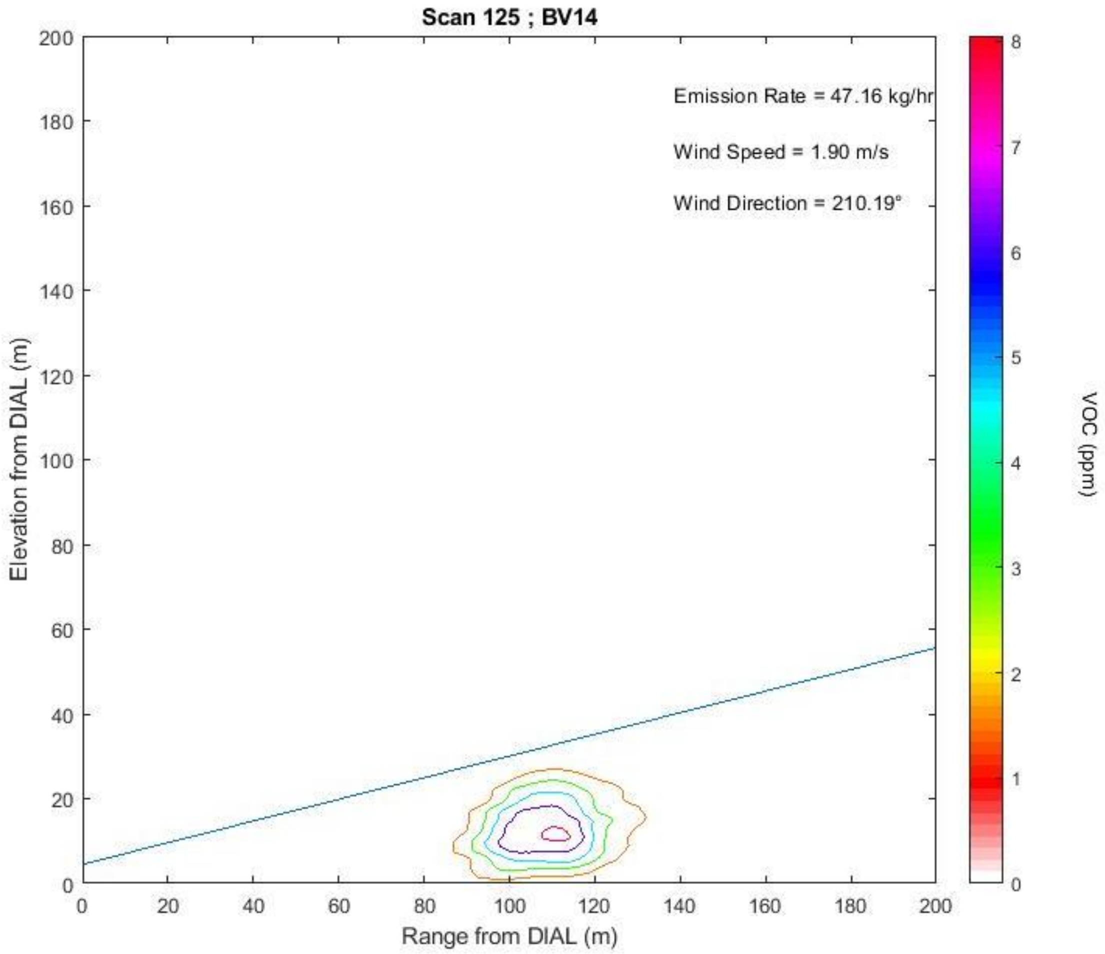

Figure 5.9b1 Observed VOC concentration for Scan 125 representing BV14/LOS1.

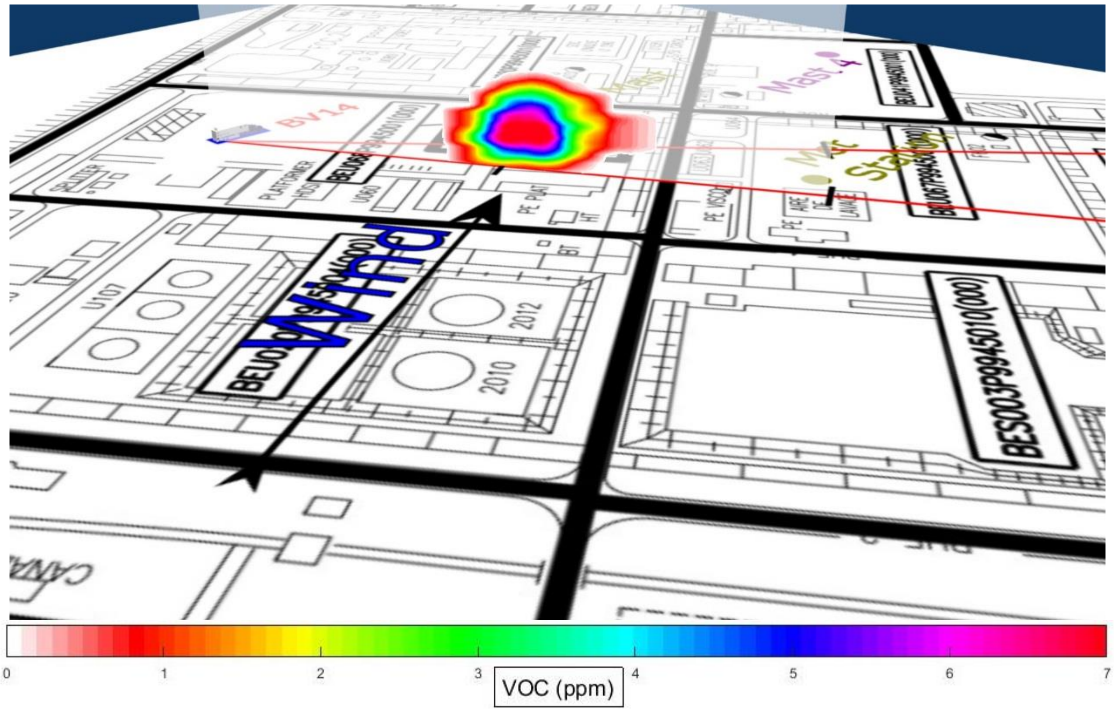

Figure 5.9b2 Visualisation of emission rate for Scan 125 representing BV14/LOS1.

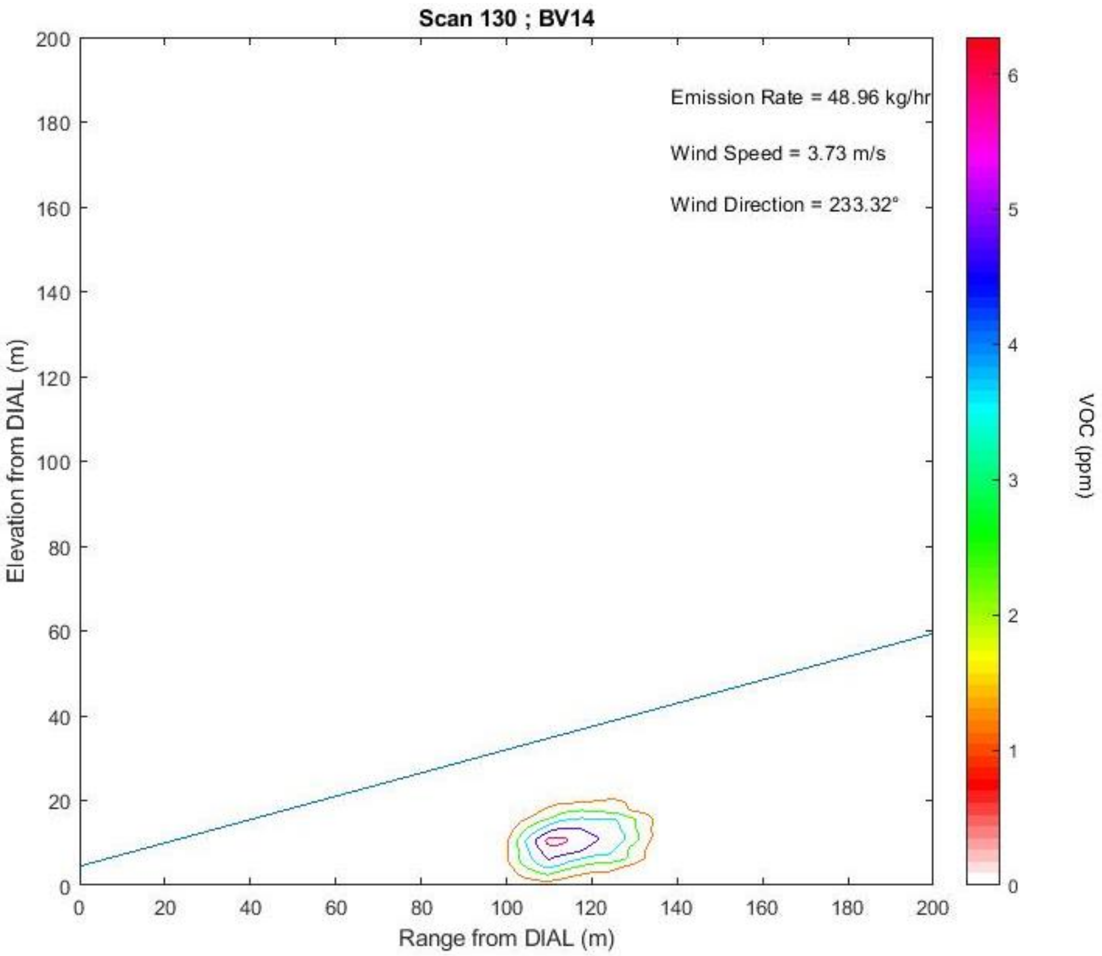

Figure 5.9c1 Observed VOC concentration for Scan 130 representing BV14/LOS1.

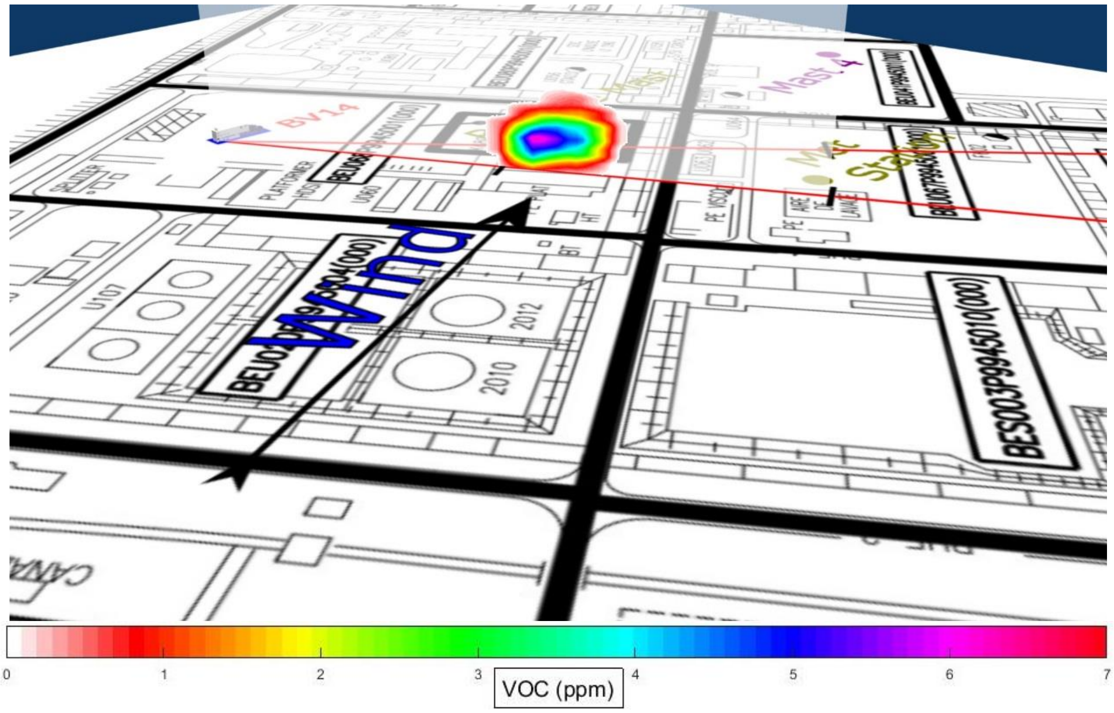

Figure 5.9c2 Visualisation of emission rate for Scan 130 representing BV14/LOS1.

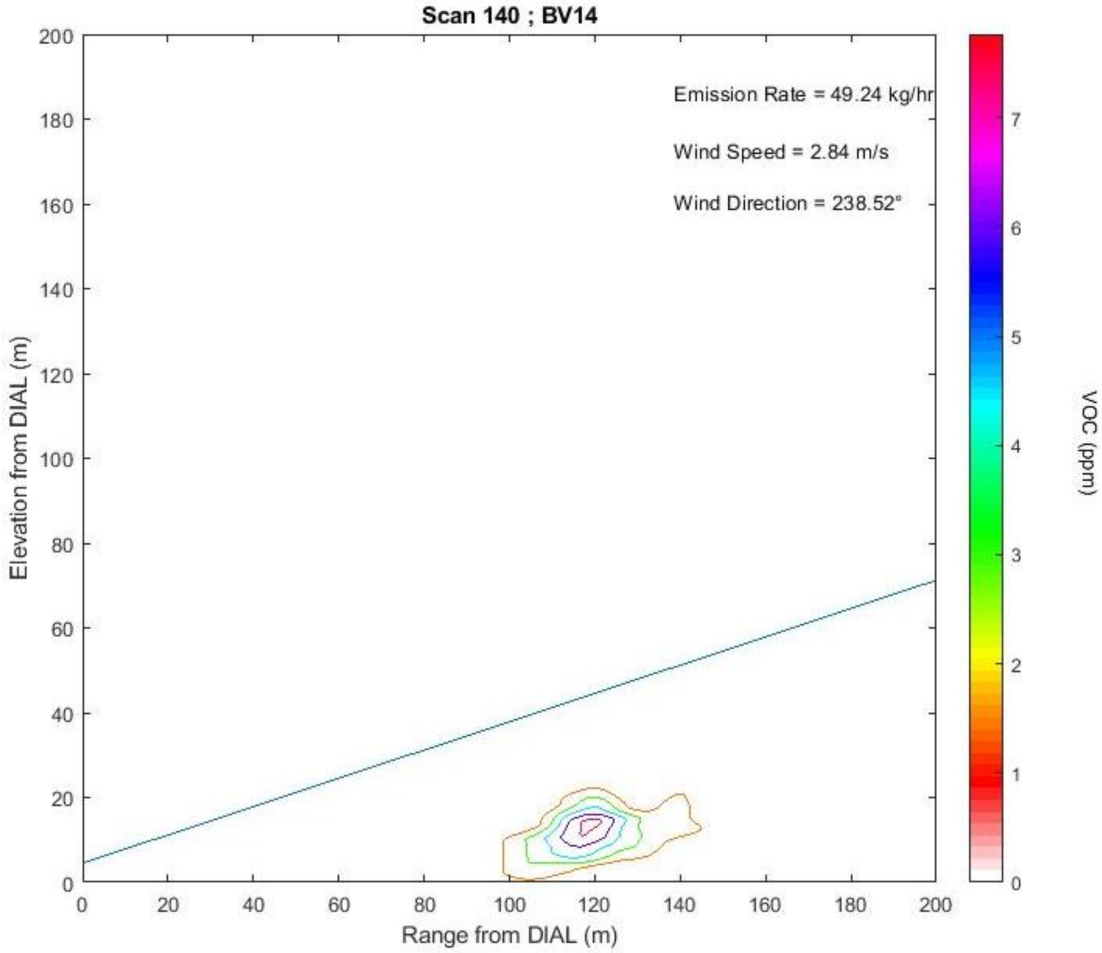

Figure 5.9d1 Observed VOC concentration for Scan 140 representing BV14/LOS1.

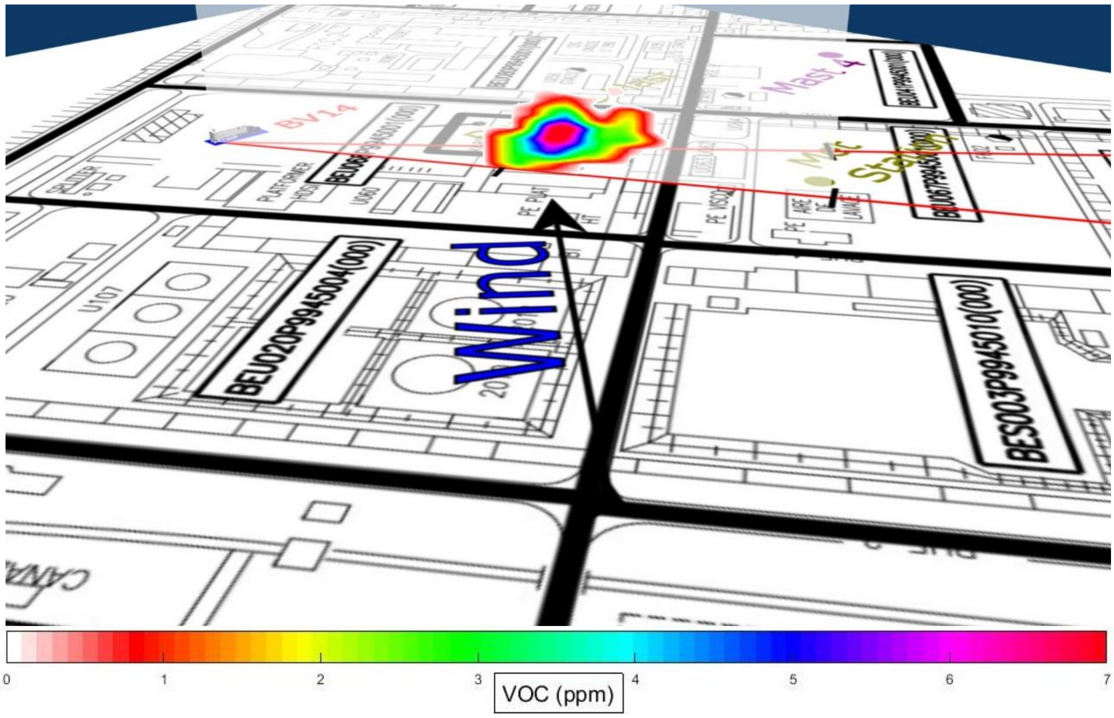

Figure 5.9d2 Visualisation of emission rate for Scan 140 representing BV14/LOS1.

6 RESULTS DISCUSSION

The calculations of the VOC emission rates from the different locations from the 22nd to 29th September are described in the following sections. Table 6.1 provides overview of measured VOC emission rates, stdev and standard uncertainty. The background data reported in Table 6.1 are the averages from different background scans carried out between tests releases measured at the same location. Therefore, the same background value applies to all the tests carried out at the same location unless specified differently as for Test 10.

Table 6.1 Summary of determined VOC emission rates. For each location and LOS the average emission rate and stdev (when more than one scan is available) are reported.

Date	Location/	Notes	Average Emission Rate	Standard Deviation	Standard Uuncertainty	Scans
			kg/h	kg/h	kg/h	#
22-Sep	BV02/LOS1	Downwind Test 1	7.7	1.4	0.6	6
22-Sep	BV02/LOS1,2	Downwind Test 2	18.4	1.6	0.6	6
22-Sep	BV02/LOS2	Background	2.3	1.2	0.8	2
23-Sep	BV03/LOS1,2	Downwind Test 3	13.7	1.7	0.7	6
23-Sep	BV03/LOS1,2	Downwind Test 4	12.2	2.1	0.9	5
23-Sep	BV03/LOS2	Background	3.9	1.6	1.1	2
26-Sep	BV04/LOS1	Downwind Test 5	11.4	1.6	0.8	4
26-Sep	BV06/LOS1,2	Downwind Test 6	9.6	1.0	0.5	4
26-Sep	BV06/LOS2	Background	0.4	1.0	1.0	1
26-Sep	BV09/LOS1,2	Downwind Test 8	13.0	0.5	0.2	5
26-Sep	BV09/LOS2	Background	3.4	1.0	1.0	1
27-Sep	BV10/LOS1	Downwind Test 9	37.9	2.9	1.3	5
27-Sep	BV10/LOS1	Downwind Test 10 a	42.9	5.8	2.9	4
27-Sep	BV10/LOS1,2	Downwind Test 10 b	19.5	1.2	0.9	2
27-Sep	BV10/LOS1	Background a	24.6	3.3	2.3	2
27-Sep	BV10/LOS1	Background b	0.7	1.0	1.0	1
27-Sep	BV11/LOS1,2	Downwind Test 11	19.5	4.4	2.2	4
27-Sep	BV11/LOS1	Downwind Test 12	17.7	4.5	1.8	6
27-Sep	BV11/LOS1	Background	9.3	0.3	0.2	2
28-Sep	BV13/LOS1	Downwind Test 14	27.8	3.2	1.3	6
28-Sep	BV13/LOS1	Downwind Test 15	16.5	1.8	0.8	5
28-Sep	BV13/LOS1	Downwind Test 16	14.1	2.5	1.2	4
28-Sep	BV13/LOS1	Background	12.9	1.8	1.0	3
29-Sep	BV14/LOS1	Downwind Test 17	9.7	0.5	0.3	3
29-Sep	BV14/LOS1,2	Downwind Test 18	52.8	7.2	3.2	5
29-Sep	BV14/LOS1	Downwind Test 19	46.5	2.3	1.0	5
29-Sep	BV14/LOS1	Downwind Test 20	49.5	3.5	1.4	6
29-Sep	BV14/LOS1	Background	38.0	4.1	2.0	4

Note: Where a background emission rate is based on 1 scan a stdev of 1.0 has been quoted as a typical value for this measurement.

6.1 MEASUREMENTS OF TEST 1

Test 1 took place on the 22nd September from 13:17 to 14:48. DIAL measurements were taken from location BV02 with a south westerly wind along LOS1 downwind of the unit where the release was taking place as shown in Figure 5.1. The average emission rate measured over 6 scans was 7.7 ± 1.4 kg/h. A contour plot of the VOC concentration from scan 9 is shown in Figure 5.1a1 and a 3D visualisation of the plume is shown in Figure 5.1a2. The position of the plume and the wind direction indicates that the emission may have originated at the southern end of the unit. To investigate the possibility of upwind

VOC emissions two background scans were carried out after Test 2 controlled release had been stopped. The background emission rate measured to be 2.3 ± 1.2 kg/hr.

6.2 MEASUREMENTS OF TEST 2

Test 2 took place on the 22nd September from 15:10 to 16:46. The DIAL system remained in location BV02 for this test as the wind initially continued to be from the southwest. The first measurement was made along LOS1 but the wind turned more southerly and the LOS was moved closer to the unit, LOS2, so that the emission was not blown too close to the DIAL as shown in Figure 5.1. The average emission rate measured over 6 scans was 18.4 ± 1.6 kg/h. A contour plot of the VOC concentration from scan 17 is shown in Figure 5.1b1 and a 3D visualisation of the plume is shown in Figure 5.1b2. The position of the plume and the wind direction indicates that the emission may have originated at the southern end of the unit however the wind direction was not ideal. The background emission rate measured for this location was 2.3 ± 1.2 kg/hr.

6.3 MEASUREMENTS OF TEST 3

Test 3 took place on the 23rd September between 11:27 and 12:57. DIAL measurements were made from location BV03 to the north of the unit. The wind was W/SW as shown in Figure 5.2. Of the 6 scans carried out the first 4 were along LOS1 and the last two along LOS2. The average emission rate measured over the 6 scans was 13.7 ± 1.7 kg/h. Figure 5.2a1 shows the VOC concentration measured during scan 28 along LOS1 and a 3D visualisation of the plume is shown in Figure 5.2a2. The plume location and wind direction would indicate that the emission originated from the south to middle of the unit. The background emission rate measured for this location was 3.9 ± 1.6 kg/h.

6.4 MEASUREMENTS OF TEST 4

Test 4 was carried out on the 23rd September between 14:00 and 15:30. DIAL measurements were made from location BV03 with a W/SW wind as shown in Figure 5.2. One scan was carried out along LOS1 and 4 scans along LOS2. The average emission rate over the 5 scans was 12.2 ± 2.1 kg/h. A plot of the VOC concentration from scan 38 along LOS2 is shown in Figure 5.2b1 and a 3D visualisation of this scan is shown in Figure 5.2b2. From the location of the plume the source is likely to have been more to the centre of the unit. The background emission rate measured for the BV03 location was 3.9 ± 1.6 kg/h.

6.5 MEASUREMENTS OF TEST 5

Test 5 took place on the 26th September from 09:41 to 11:11. The wind was from a northerly direction and the DIAL was positioned at location BV04 as shown in Figure 5.3. Five scans were carried out over the duration of the test and the average emission rate was measured to be 11.4 ± 1.6 kg/h. The last scan didn't fulfil the validation criteria since the wind direction was variable and the speed low, therefore it was not used for the quantification of the emission rate. A contour plot of the VOC concentration from scan 43 is shown in Figure 5.3a1 and a 3D visualisation of this scan is shown in Figure 5.3a2. Because of the wind direction it was not possible to isolate the location of the source of the emission within the unit. During this test it was also not possible to carry out background scans since the wind direction changed after the test release stopped, therefore Test 5 emission rate probably overestimate the actual controlled release rate.

6.6 MEASUREMENTS OF TEST 6

Test 6 took place on the 26th of September between 12:00 to 13:30. The DIAL was positioned at location BV06 to the north of the unit and the wind was from the W/SW. Four scans were carried out over the duration of the test, the first of which was along LOS1 and the others along LOS2. The average VOC emission rate measured during the test was 9.6 ± 1.0 kg/h. A contour plot of the VOC concentration measured on scan 49 along LOS2 is shown in Figure 5.4a1 and a 3D representation of this scan is shown in Figure 5.4a2. The plume appears quite wide and its position may indicate more than one release position with the centre of the plume approximately in the middle of the unit. The background emission rate measured for this location was 0.4 kg/h.

6.7 MEASUREMENTS OF TEST 8

Test 8 took place on the 26th September from 16:05 to 17:30. The DIAL was positioned at location BV09 to the north of the unit and the wind was from the southwest as shown in Figure 5.5. Five scans were completed during the test the first two of which were along LOS1 and the remainder along LOS2. The average VOC emission rate measured was 13.0 ± 0.5 kg/h. A contour map of the VOC concentration measured on scan 59 along LOS2 is shown in Figure 5.5a1 and a 3D representation of this scan is shown in Figure 5.5a2. The shape of the plume suggests that it may originate from the south or middle of the unit. A scan was carried out after the test was completed to measure the background upwind emission which was 3.4 kg/h.

6.8 MEASUREMENTS OF TEST 9

Test 9 took place on the 27th September between 09:35 and 11:04. The DIAL was positioned to the southwest of the unit and the wind was from the northwest as shown in Figure 5.6. Five scans were carried out during the test along the road, LOS1, to the south of the unit. The average VOC emission measured during the test was 37.9 ± 2.9 kg/h. The VOC concentration measured on scan 64 is shown in a contour plot in Figure 5.6b1 and a 3D representation of this scan is shown in Figure 5.6b2. As the wind direction was along the unit it wasn’t possible to identify the exact source of the emission. Background scans were carried out before and after the test release with emissions measured to be 24.6 ± 3.3 kg/h, this is the background referred to as background ‘a’ in Table 6.1. A contour plot of the VOC concentration for background scan 63 is shown in Figure 5.6a1 and a 3D visualisation of this scan is shown in Figure 5.6a2. This is a significant proportion of the test emissions measured and owing to the variable wind direction could affect the measured emission on a scan to scan basis.

6.9 MEASUREMENTS OF TEST 10

Test 10 was carried out on the 27th September from 11:26 to 13:05. The DIAL remained at location BV10 to the southwest of the unit as shown in Figure 5.6 with a northwest wind. Six scans were carried out during the test, the first five of which were along LOS1 and the last scan along LOS2. The VOC concentration measured on scan 75 is shown in a contour plot in Figure 5.6c1 and a 3D representation of this scan is shown in Figure 5.6c2. As the wind direction was along the unit it wasn’t possible to identify the exact source of the emission. During the test after the first four scans the wind changed to a more westerly direction for the last two scans. This is significant as the upwind emission sources changed which can be seen from the background measurements for the different wind directions. For this reason the emission rates are reported separately for the different wind directions. Test 10a is for the first four scans and the average emission rate was 42.9 ± 5.8 kg/h and the background ‘a’ emission rate for this wind direction was 24.6 ± 3.3 kg/h. For the last two scans, Test 10b the emission rate was measured to be 19.5 ± 1.2 kg/h with an upwind background ‘b’ emission rate of 0.7 kg/h.

6.10 MEASUREMENTS OF TEST 11

Test 11 took place on the 27th September between 14:00 and 15:33. The DIAL was positioned to the north of the unit at location BV11 with the wind from the W/SW as shown in Figure 5.7. Four scans were completed during the test, three of which were along LOS1 with the second along LOS2. The average VOC emission rate measured during the test was 19.5 ± 4.4 kg/h. A contour plot of the VOC concentration measured on scan 80 is shown in Figure 5.7a1 and a 3D representation of this scan is shown in Figure 5.7a2. The plume appears to be elongated suggesting that there were emissions from north to south ends of the unit, therefore at least two release nodes were used. Background scans were made from this location after this and the following test with an emission rate of 9.3 ± 0.3 kg/h.

6.11 MEASUREMENTS OF TEST 12

Test 12 was carried out on the 27th September from 15:55 to 17:25. The DIAL remained in location BV11 with a S/WS wind as shown in Figure 5.7. Six scans were completed during the test, all along LOS1 and the average emission rate was measured to be 17.7 ± 4.5 kg/h. The measured VOC concentration of scan 85 is shown as a contour plot in Figure 5.7b1 and a 3D representation of this scan is shown in 5.7b2. The plume position and wind direction would indicate that the emission release point was in the centre or north of the unit. The dimension of this plume is smaller when compared to the plume observed from Test 11, suggesting that only one node was used during Test 12. Background measurements showed an emission rate of 9.3 ± 0.3 kg/h.

6.12 MEASUREMENTS OF TEST 14

Test 14 took place on the 28th September from 10:07 to 11:37. The DIAL was positioned to the north of the unit in location BV13 with a W/SW wind as shown in Figure 5.8. Six scans were carried out during the release along LOS1 and the average measured VOC emission rate was 27.8 ± 3.2 kg/h. A contour plot of the observed VOC concentration for scan 96 is shown in Figure 5.8a1 and a 3D visualisation of this scan is shown in Figure 5.8a2. The position and shape of the plume would suggest a single emission point possibly to the middle of the unit. The measured background VOC emission rate for this location and wind direction was relatively high at 12.9 ± 1.8 kg/h.

6.13 MEASUREMENTS OF TEST 15

Test 15 was carried out on the 28th September between 14:37 and 16:03. The DIAL remained in location BV13 as the wind continued to be from the WSW as shown in Figure 5.8. Fives scans were carried out during the test release and the average VOC emission rate was measured to be 16.5 ± 1.8 kg/h. The VOC concentration measured in scan 105 is shown as a contour plot in Figure 5.8b1 and a 3D representation of this scan is shown in Figure 5.8b2. The position and shape of the plume would suggest a single emission point possibly to the middle of the unit. The measured background VOC emission rate for this location and wind direction was relatively high at 12.9 ± 1.8 kg/h. A contour plot of the background VOC concentration in the region of the unit used for the release is shown in Figure 5.8c1 and a 3D representation is shown in Figure 5.8c2.

6.14 MEASUREMENTS OF TEST 16

Test 16 took place on the 28th September from 16:45 to 17:50. Four scans were taken during the test, all along LOS1. The average VOC emission rate was measured to be 14.1 ± 2.5 kg/h. A contour plot of the VOC concentration from scan 111 is shown in Figure 5.8d1 and a 3D visualisation of this scan is shown in Figure 5.8d2. The plume size is small and would indicate a single emission point to the middle or south of the unit. The measured background VOC emission rate for this location and wind direction was relatively high at 12.9 ± 1.8 kg/h.

6.15 MEASUREMENTS OF TEST 17

Test 17 took place on the 29th September between 10:50 and 12:15. The DIAL was positioned to the north of the unit at location BV14 with the wind from the S/SW. Six scans were carried out along LOS1 during the test release however the wind moved to the S/SE on the last three scans, almost parallel to LOS1, therefore they didn’t fulfil the validation criteria and they were not used for the quantification of the emission rate. From the three valid scans the average emission rate was measured to be 9.7 ± 0.5 kg/h. A contour plot of the VOC concentration measured on scan 115 is shown in Figure 5.9a1 and a 3D representation of this scan is shown in Figure 5.9a2. The plume position suggests that the release may have been from the north but with low confidence because of the wind direction. No background measurements were made with the southerly wind present during these measurements but the area south of the unit was expected to have no emission sources.

6.16 MEASUREMENTS OF TEST 18

Test 18 was carried out on the 29th September from 12:38 to 13:51. The DIAL was positioned at location BV14 with the wind from W/SW as shown in Figure 5.9. Five scans were taken during the test release with the 1st and 3rd scans taken along LOS2 the others along LOS1. The average VOC emission rate measured was 52.8 ± 7.2 kg/h. A contour plot of the VOC concentration measured from scan 125 is shown in Figure 5.9b1 and a 3D representation of this scan is shown in Figure 5.9b2. The plume position and wind direction suggests that the emission was in the north of the unit but is large in cross section and could have a contribution from the middle. The background VOC emission rate was measured over 4 scans and the average was 38.0 ± 4.1 kg/h which is very high in relation to the emissions from the test.

6.17 MEASUREMENTS OF TEST 19

Test 19 took place on the 29th September from 14:10 to 15:10. The DIAL remained in location BV14 with a W/SW wind as shown in Figure 5.9. Five scans along LOS1 were taken during the test and the average emission rate was measured to be 46.5 ± 2.3 kg/h. The VOC concentration measured on scan 130 is shown in a contour plot in Figure 5.9c1 and a 3D representation is shown in Figure 5.9c2. The plume appears to be elongated suggesting that there were emissions from north to south ends of the unit and that several nodes were used. The background VOC emission rate was measured over 4 scans and the average was 38.0 ± 4.1 kg/h which is very high in relation to the emissions from the test.

6.18 MEASUREMENTS OF TEST 20

Test 20 took place on the 29th September between 15:30 and 17:00. The DIAL was at location BV14 as before with a W/SW wind as shown in Figure 5.9. Six scans along LOS1 were completed during the test and the average VOC emission rate was measured to be 49.5 ± 3.5 kg/h. A contour plot of the VOC concentration measured on scan 140 is shown in Figure 5.9d1 and a 3D visualisation of the plume is shown in Figure 5.9d2. The plume appears to be elongated suggesting that there were emissions from north to south ends of the unit and that several nodes were used. The background VOC emission rate was measured over 4 scans and the average was 38.0 ± 4.1 kg/h which is very high in relation to the emissions from the test.

6.19 SUMMARY OF THE RESULTS

DIAL measurements were challenging because of fairly low wind speed conditions, relatively high background sources and very clear atmospheric conditions with low aerosol concentration and therefore low DIAL return signals. Two controlled release experiments were not measured as the DIAL was parked in non-ideal locations as a consequence of the low wind speed and variable wind direction. However, the two tests would have not fulfilled the DIAL validation criteria of average wind speed from the top meteorological sensor being in the 1 - 15 m/s range. The other 18 experiments fulfilled all the DIAL QA/QC criteria.

The DIAL measured relatively high background sources in most of the scans, but it could generally isolate their plumes from the plume of the intended release. Nonetheless, background scans were usually carried out before and after each test and analyzed in the same region as the test scans showing some contribution from upwind sources. The reported controlled release values were calculated by subtracting the background contribution from the test measurements and the reported stdev is the sum in quadrature of these two sets of measurements (controlled release and background). Due to time constrains between tests, fewer background scans were available compared to the usual approach with a set of at least four scans. This may have slightly increased the uncertainties reported in these tests.

A summary of the emission rates measured during the test releases are shown below in Table 6.2. These figures have had any upwind background VOC emissions measured at the time subtracted and are therefore the net emission from the test releases from the unit.

Table 6.2 Summary of the net VOC emission rate measurements from the test releases.

Emission Area	Average Emission Rate	Standard Deviation	Standard Uuncertainty
	kg/h	kg/h	kg/h
Test 1	5.4	1.8	1.0
Test 2	16.1	2.0	1.0
Test 3	9.8	2.3	1.3
Test 4	8.4	2.6	1.5
Test 5 *	11.4	1.9	1.3
Test 6	9.2	1.4	1.1
Test 8	9.6	1.1	1.0
Test 9	13.3	4.4	2.7
Test 10	18.5	5.6	3.0
Test 11	10.2	4.5	2.2
Test 12	8.5	4.5	1.8
Test 14	15.0	3.7	1.7
Test 15	3.7	2.5	1.3
Test 16	1.2	3.0	1.6
Test 17 **	9.7	1.1	1.0
Test 18	14.9	8.3	3.8
Test 19	8.5	4.7	2.3
Test 20	11.5	5.3	2.5

* DIAL emission rate includes small unknown background emission

** Wind from the south, no background expected

7 ANALYSIS OF RESULTS IN COMPARISON TO ACTUAL RELEASE RATES

After the submission of the results from each method provider, a WG38 meeting was held to discuss the results and the nominal controlled release emission rates were made available by Ineris. It was then possible to carry out the following additional assessments.

The results of the DIAL measurements compared to the controlled release rates are shown below in Table 7.1. The overall error measured as the difference between the DIAL average emission rate and the controlled release emission rate was less than 30% apart from Test 16 which had an emission rate close to the DIAL detection limit. Typically the dominant DIAL uncertainties sources have a random behavior then the uncertainty for a set of at least four DIAL scans above the detection limit is expected to be below 30% as reported in the protocol. The total DIAL measured emission rate for the 18 tests was 184.7 kg/h while the total controlled release emission rate was 184.6 kg/h with a difference of only 0.03%. This confirms that the dominant DIAL uncertainties sources during this field validation campaign had a random behaviour and therefore by increasing the number of DIAL scans the uncertainty decrease accordingly. This also simulates DIAL measurements of different areas on a site that are then summed together to obtain an estimate of the total emission rate. Therefore, since typically the dominant DIAL uncertainties sources have a random behaviour, see Annex A6, the reported total emission rate as a sum of several sets of at least four DIAL scans can be expected to have significantly lower associated uncertainty in comparison to each independent set of measurement.

Table 7.1 Results of the DIAL measurements compared to the controlled release rates

Controlled Release Runs	CR Emission Rate	DIAL Average Emission Rate	DIAL Standard Deviation	Error: DIAL-CR	(DIAL-CR)/CR
	kg/h	kg/h	kg/h	kg/h	%
Test 1	5.1	5.4	1.8	0.3	6.8%
Test 2	14.9	16.1	2.0	1.2	8.2%
Test 3	8.9	9.8	2.3	1.0	10.8%
Test 4	9.8	8.4	2.6	-1.4	-14.3%
Test 5 *	9.2	11.4	1.6	2.2	23.6%
Test 6	9.0	9.2	1.4	0.2	1.8%
Test 8	8.9	9.6	1.1	0.7	7.8%
Test 9	11.6	13.3	4.4	1.6	14.2%
Test 10	18.5	18.5	5.6	0.0	-0.2%
Test 11	9.6	10.2	4.5	0.6	6.0%
Test 12	9.8	8.5	4.5	-1.3	-13.2%
Test 14	16.6	15.0	3.7	-1.6	-9.9%
Test 15	4.8	3.7	2.5	-1.1	-23.0%
Test 16	0.8	1.2	3.0	0.4	56.0%
Test 17 **	9.2	9.7	0.5	0.4	4.8%
Test 18	18.9	14.9	8.3	-4.0	-21.1%
Test 19	6.6	8.5	4.7	1.9	28.9%
Test 20	12.6	11.5	5.3	-1.1	-8.4%

* DIAL emission rate includes small unknown background emission

** Wind from the south, no background expected

7.1 ACTUAL UNCERTAINTY/ STANDARD UNCERTAINTY ESTIMATION

According to the DIAL protocol, the stdev of a set of at least four DIAL scans should be representative of the measurement uncertainty. This has been validated as shown in Table 7.1 with the measured stdev for each test higher than the actual error calculated by subtracting from the controlled release emission rate the average DIAL emission rate. The only exception was Test 5, most likely because of the contribution of a small unknown background value.

Since typically the dominant DIAL uncertainties sources have a random behavior as demonstrated for these tests, the DIAL uncertainty for a set of at least 4 scans, and for emission rates above the detection limit, is expected to be about 10%-30%. This is also validated as shown in Table 7.1 where all the values in the column (DIAL-CR)/CR are below 30% apart for Test 16 that is close to the detection limit, although in absolute terms this uncertainty is small, about 0.4 kg/h. Most of the DIAL emission rates (16 of the 18 tests) are derived from differences of two sets of measurements, therefore the actual DIAL uncertainty for a single set of DIAL measurements can be expected to be lower.

The standard uncertainty (u) for a set of DIAL measurements can be estimated dividing the stdev by the square root of the number of scans. For two sets of DIAL measurements, m_1 (CR emission rate + background) and m_2 (background), the estimated CR emission rate is m_1-m_2 and the combined standard uncertainty is:

$$u = \sqrt{u_1^2 + u_2^2}.$$

In Table 7.12 the estimated standard uncertainty and the expanded (k = 2) uncertainty representing the 95% level of confidence are reported for each controlled release test. As already shown for the stdev, the expanded (k = 2) uncertainty for each test is higher than the actual uncertainty except for Test 5 (17 out of 18 tests, i.e. 94.4% of the tests), most likely because of the contribution of a small unknown background value.

Table 7.2 Results of the DIAL measurements compared to the controlled release rates

Controlled Release Runs	Estimated Stand. Unc.	95% Level of Confidence	Error: DIAL-CR	Target 30% Stand. Unc.	Target 20% Stand. Unc.	Target 10% Stand. Unc.	Target 5% Stand. Unc.
	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h
Test 1	1.0	2.0	0.3	2.4	1.6	0.8	0.4
Test 2	1.0	2.1	1.2	5.6	3.7	1.9	0.9
Test 3	1.3	2.6	1.0	4.3	2.9	1.4	0.7
Test 4	1.5	2.9	-1.4	3.9	2.6	1.3	0.6
Test 5 *	0.8	1.6	2.2	3.4	2.3	1.1	0.6
Test 6	1.1	2.2	0.2	2.9	1.9	1.0	0.5
Test 8	1.0	2.1	0.7	4.0	2.7	1.3	0.7
Test 9	2.7	5.3	1.6	13.6	9.0	4.5	2.3
Test 10	3.0	6.0	0.0	9.2	6.2	3.1	1.5
Test 11	2.2	4.5	0.6	6.5	4.3	2.2	1.1
Test 12	1.8	3.7	-1.3	6.0	4.0	2.0	1.0
Test 14	1.7	3.3	-1.6	9.2	6.1	3.1	1.5
Test 15	1.3	2.6	-1.1	6.3	4.2	2.1	1.0
Test 16	1.6	3.2	0.4	5.7	3.8	1.9	1.0
Test 17 **	0.3	0.6	0.4	2.9	1.9	1.0	0.5
Test 18	3.8	7.6	-4.0	19.5	13.0	6.5	3.3
Test 19	2.3	4.5	1.9	18.0	12.0	6.0	3.0
Test 20	2.5	4.9	-1.1	18.7	12.5	6.2	3.1

* DIAL emission rate includes small unknown background emission

** Wind from the south, no background expected

If a target uncertainty of X percentage of the average emission rate is defined for each set of DIAL measurements m_1 and m_2, then the target combined uncertainty would be

$$u = X\sqrt{m_1^2 + m_2^2}.$$

The last four columns in the Table 7.1 are calculated in this way for X = 30%, 20%, 10%, and 5% excluding Tests 5 and 17 that only have one set of measurements m_1. By comparing these values with the error (DIAL-CR) it is possible to derive that:

- Test 5, even if a small background value is probably missing, has an uncertainty (2.2 kg/h) which is lower than 20% of the measured value (2.3 kg/h).
- All the other tests show that a combined uncertainty of 10% for each set of DIAL measurements m_1 and m_2 is better than the observed uncertainties. The only exception is Test 4 with an uncertainty of 1.4 kg/h slightly higher than the 10% combined uncertainty of 1.3 kg/h.
- The expanded (k = 2) uncertainty representing the 95% level of confidence for the target 10% combined uncertainty would be the same as the target 20% combined uncertainty and therefore well represents the uncertainty for all the 18 tests.
- Most of the tests show that a combined uncertainty of 5% for each set of DIAL measurements m_1 and m_2 is better than the observed uncertainties. The expanded (k = 2) uncertainty representing the 95% level of confidence for the target 5% combined uncertainty would be the same as the target 10% combined uncertainty and therefore well representing the uncertainty of all the tests but tests 4 and 5 (89% of the tests).

In conclusion, each set of DIAL measurements has shown a behavior during this field campaign consistent with a standard uncertainty of between 5% - 10% of the measured emission rate. This is lower than the 10% - 30%, expected uncertainty reported in the protocol, and with no significant systematic bias. Therefore, for this specific field validation campaign, the uncertainty budget reported in Table 7.3 has been determined.

Table 7.3 DIAL uncertainty budget for the controlled release tests

Uncertainty Sources	Standard Uncertainty
Random, including wind and concentration	< 10%
VOC gas composition analysis	< 0.1 %
Bias	< 0.1 %

7.2 REPRODUCIBILITY/PRECISION

Eight different controlled releases at about 9.3 kg/h have been performed over five different days using different node configurations and under different meteorological conditions. Table 7.4 shows that the DIAL average emission rate was very close to the controlled releases average emission rate (~3%), while the stdev indicates that dispersion of single result is very low. This confirms good reproducibility of the DIAL method under different wind conditions and source configurations.

Table 7.4 Mean and stdev for the release rates and DIAL measurements

	Controlled Release	DIAL
Mean (kg/h)	9.3	9.6
Stdev (kg/h)	0.4	1.0

7.3 QUANTIFICATION RANGE & LINEARITY

As presented in Figure 7.1, the full range of emitted fluxes, i.e. 0.8 - 18.9 kg/h has been successfully detected and quantified by the DIAL. Correlation between DIAL results and controlled release rates is good with a linear coefficient of 0.996 and an R^2 value of 0.922. The overall spread of each DIAL data point from the linear fit is relatively high, mainly due to the subtraction for each test of a relatively high background value that has been measured from fewer scans when compared to the typical approach of a set of at least four scans. However, since the dominant DIAL uncertainties sources during this field validation campaign had a random behaviour, the total number of background scans performed during the 18 tests was relatively high. This decreases the overall uncertainty due to the background sources, hence the good correlation between DIAL results and controlled release rates shown in Figure 7.1.

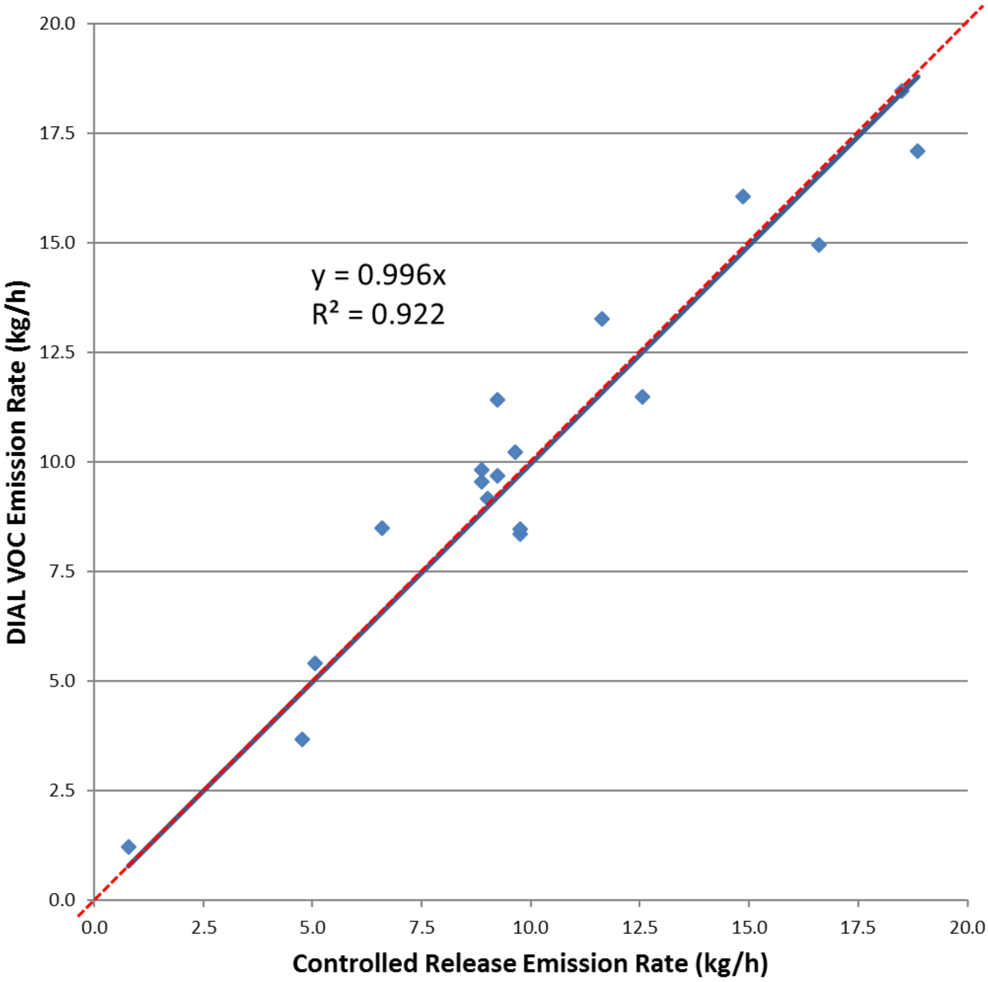

Figure 7.1. Comparison of DIAL measured emission rate to the controlled release rate.

7.4 EMISSION SOURCE LOCALISATION

The capability of DIAL to produce 2-D concentration distributions enables discrimination of two or more plumes and to distinguish between broad and diffused emission that could originate from a distant source from concentrated and narrow plume that could originate from a closer source. This allows the users to understand plumes pattern, elevation, dimension but also to estimate the source location, the number of sources and/or to isolate background sources from the plume of the source under investigation, as has been demonstrated during these tests.

During the controlled release tests some observations have been made regarding the location of the sources according to the dimension and location of the measured plume. Most of these observations have been confirmed from data analysis results as reported in Section 6 and summarized in the Table 7.5. For tests 5, 9 and 10 it was not possible to infer the node(s) used since the wind direction was along the unit (north/south). For the other tests it was indicated if the emission was likely to be in north, middle or south end of the unit and if it was from one or more nodes. Most of the observation are correct, confirming DIAL can provide spatial information on the plume location in the 20 m - 30 m resolution range.

Table 7.5 Sources location estimation based on the dimension and location of the measured plume

Test	Nodes Used	DIAL Observations	Real Configuration
1	D	Plume probably from the south end of the unit rather than the north end.	Plume located in the south end of the unit, but source located in the middle of the unit
2	B	Similar to Test 1.	Similar to Test 1.
3	A	Plume probably from the south end of the unit rather than the north end.	Plume located in the south end of the unit, but source located in the north of the unit
4	E	Compared to Test 3 the plume seems to be more northerly. Probably north or middle node or combination of the two.	Source located in the middle of the unit (diffusion tube)
5	D	Because of the wind direction is not possible to say from which node the release was from.	
6	A+C	Relatively wide plume indicating more than one release centred on the South end of the unit. South-Middle nodes.	Two sources located at both north and South side of the unit
8	C	Relatively wide plume because of wind direction, probably south or middle node or combination of the two.	One source on South side of the unit
9	E	Because of the wind direction is not possible to say from which node the release was from.	
10	A+B+C+D	Same as Test 9	
11	A+B	Elongated plume indicating emission sources from both south and north end of the unit. At least two release nodes used.	Two sources, on south side and middle
12	B	Smaller plume compared to Test 11, emission probably from middle-north of unit. Possibly just one node used.	One source, in the middle of the unit
14	E	Relatively wide plume centred about middle of the unit. Likely to be from one node, it could be from any node apart from the north node	One source but diffused in the middle of the unit
15	E	Same as test 14.	One source but diffused in the middle of the unit
16	E	Same as tests 14 and 15.	One source but diffused in the middle of the unit
17	A+D	Plume position suggests the release may have been from the north, it is difficult to tell because of the southerly wind direction.	Two sources, more on the North side of the unit
18	A	Plume position suggests the release may have been from the north, it is wide and it could have a contribution from the middle node.	One source on the North side of the unit
19	A+B+C+D	Complex broad plume indicating more nodes were used from at least both south and north end of the unit.	All sources on
20	A+B+C+D	Similar to Test 19 even if the plume seems slightly smaller. Difficult to tell if only south and middle nodes used or also the north node	All sources on

7.5 WIND DIRECTION

The wind sensor used to define the wind direction for the reported emission rates was the top sensor from Mast 4 apart from Test 17 when the wind was light and variable, therefore the wind direction was quite different from sensor to sensor. In this case, Mast 2 wind direction was used since it was the only one that could explain the location of the measured plume for each scan.

The portable sensor wind direction can also be used to calculate mass emission rates when it is deployed in a suitable location. This is typically downwind of the measured unit along the scanning LOS and it may be used when it is believed to better represent the local wind direction, particularly when the main emission plume is at low elevation, affected by the local terrain and buildings. Another reason to choose the emission rate calculated using the portable sensor rather than the mast sensor is when the emission rate stdev obtained using the portable sensor is significantly lower than the stdev obtained using the mast sensor. This would imply that the portable sensor wind direction variability between different

DIAL scans better represents the measured DIAL concentration matrix variability since the difference between the two sets of measurements and standard deviations is only due to the wind direction. Therefore, the set of measurements with significantly smaller stdev would potentially be a better choice.

During the measurements carried out from DIAL locations BV02, BV04 and BV11 the portable wind sensor was not deployed at an ideal location. For all the tests carried out from the other DIAL locations emission rates were recalculated using the wind direction from the portable sensors. These emission rates and standard deviations are reported in Table 7.6 and compared to the results obtained using the mast sensor. It is worth noting that all these tests results are obtained by subtracting background values increasing stdev values and therefore adding complexity to the data comparison. Consequently, in all the tests the difference between the emission rates calculated using the mast and portable sensors are comparable or lower than the associated stdev.

Table 7.6 Average emission rates and standard deviations calculated using the wind direction measured by the mast and portable wind sensors

Emission Area	CR Emission Rate	Mast Emission Rate	Standard Deviation	Portable Emission Rate	Standard Deviation	Mast - Portable	Comments
	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	
Test 3	8.9	9.8	2.3	12.7	2.8	-2.9	Elevated Plume, centre > 10 m
Test 4	9.8	8.4	2.6	8.5	2.8	-0.2	Elevated Plume, centre ~ 20 m
Test 6	9.0	9.2	1.4	10.2	1.7	-1.0	Elevated Plume, centre > 10 m
Test 8	8.9	9.6	1.1	11.7	2.3	-2.2	Plume from ground to 20 m, centre ~ 10 m
Test 9	11.6	13.3	4.4	13.1	2.9	0.2	Plume from ground to 20 m, centre < 10m
Test 10	18.5	18.5	5.6	16.4	9.5	2.1	Elevated Plume, centre > 20 m
Test 14	16.6	15.0	3.7	16.9	4.9	-2.0	Elevated Plume, centre > 10 m
Test 15	4.8	3.7	2.5	4.5	3.7	-0.9	Elevated Plume, centre > 10 m
Test 16	0.8	1.2	3.0	1.9	4.2	-0.7	Elevated Plume, centre > 10 m
Test 18	18.9	14.9	8.3	17.1	5.5	-2.2	Plume from ground to 20 m, centre ~ 10 m
Test 19	6.6	8.5	4.7	8.0	4.6	0.5	Plume from ground to 20 m, centre ~ 10 m
Test 20	12.6	11.5	5.3	10.9	5.1	0.6	Elevated Plume, centre ~ 10 m

The wind direction from the mast sensor was chosen mainly because most of the plumes were elevated and in an area where there was not much obstruction from the unit itself. The results in Table 7.6 confirms this assumption was appropriate since for most tests the emission rates calculated using the mast sensor are closer to the release emission rates than the emission rates calculated using the portable sensor. Also, in most cases the stdev obtained using the portable sensor was higher or similar to the stdev obtained using the mast sensor. The following are interesting exceptions to analyze:

- DIAL location BV10: the portable is not in an ideal location but during Test 9 with NW wind it is downwind of the tanks that could mimic the release unit. The stdev obtained using the portable sensor is lower than the stdev obtained using the mast sensor and the centre of the plume is relatively low. This would confirm that for low elevation plumes the effect of a building is important and the use of the wind direction from a local sensor maybe preferable. Nonetheless in this specific case the emission rates obtained using the mast and portable sensors are almost identical. During Test 10 the wind was more westerly and the portable location was probably no longer representative of the measured area, this is confirmed by the very high stdev value obtained using the portable sensor wind direction.
- DIAL location BV13: the centre of the release plume during tests 14, 15 and 16 was on average just above 10 m. The standard deviations obtained using the portable sensor during the test releases are similar to the standard deviations obtained using the mast sensor but during the background scans the stdev obtained using the portable sensor was higher. Therefore, the combined stdev calculated using the portable sensor was higher than the stdev calculated using the mast sensor. The emission rates calculated using the portable wind sensor were closer to the controlled release emission rates for test 14 and 15 but not for Test 16. While the measured plumes are probably not completely in free air, they are also not so affected by the unit to fully justify the use of the portable sensor rather than the mast sensor.

- DIAL location BV14: Test 18 is the only test where the stdev obtained using the portable sensor is significantly smaller than the stdev obtained using the mast sensor. The emission rate calculated using the portable wind sensor is also significantly closer to the controlled release emission value than the emission rate calculated using the mast sensor. The plume in the measured plane is probably affected by the unit as it extends from ground to about 20 m, confirming that for this test the portable sensor wind direction should be used instead of the mast sensor.

Overall these data confirm the assumptions made in the DIAL protocol when selecting the wind sensor to be used for the wind direction measurement, i.e. that a local wind sensor may be used when it better represents the local wind direction, particularly when the main emission plume is at low elevation, affected by the local terrain and buildings. Also, when two sets of wind directions from different sensors are used to calculate the average emission rate, the set of data with significantly lower stdev should be preferably used.

It should be noted that the data and observations reported in this Section, in particular the fact that following the DIAL protocol the wind direction from the portable sensor would have been chosen for Test 18, was submitted to Ineris before they made the controlled release emission rates available.

8 CONCLUSIONS

DIAL measurements were made by determining the concentration of VOC in vertical measurement planes downwind and upwind of the area being measured, and combining these concentrations with wind measurements to determine the emission rate. DIAL measurements were challenging because of fairly low wind speed conditions, relatively high background sources and very clear atmospheric conditions with low aerosol concentration and therefore low DIAL return signals. Tests 7 and 13 were not measured as the DIAL was parked in non-ideal locations as a consequence of the low wind speed and variable wind direction. However, the two tests would have not fulfilled the DIAL validation criteria of average wind speed from the top meteorological sensor being in the 1 - 15 m/s range and would therefore have been excluded in any case. The other 18 experiments fulfilled all the DIAL QA/QC criteria.

The DIAL measured relatively high background sources in most of the scans, but generally these plumes could be isolated from the plume of the intended release. Nonetheless, background scans were usually carried before and after each test and analysed in the same region as the test scans showing some contribution from upwind sources. The values reported for each controlled release are after the subtraction of the background contribution from the test scans and the stdev is the sum in quadrature of the two sets of measurements. For this reason, the reported standard deviations are relatively high, particularly when the test emission rates are low.

During Test 5 it was not possible to carry out background scans since the wind direction changed after the test release stopped, therefore Test 5 emission rate probably overestimate the actual controlled release rate.

According to the DIAL protocol, the stdev of a set of at least four DIAL scans should be representative of the measurement uncertainty. This has been validated since the measured stdev for each test is higher than the actual error calculated by subtracting from the average DIAL emission rate the controlled release emission rate. The only exception was Test 5, most likely because of the contribution of a small unknown background value.

The total DIAL measured emission rate for the 18 tests was 184.7 kg/h while the total controlled release emission rate was 184.6 kg/h. This shows that the dominant DIAL uncertainties sources during this field validation campaign had a random behaviour and therefore by increasing the number of DIAL scans the uncertainty can be expected to decrease accordingly. This also simulates DIAL measurements of different areas on a site that are then summed together to obtain an estimate of the total emission rate. Therefore, since typically the dominant DIAL uncertainties sources have a random behaviour the reported total emission rate as a sum of several sets of at least four DIAL scans can be expected to have significantly lower associated uncertainty in comparison to each independent set of measurement.

The DIAL protocol states that since typically the dominant DIAL uncertainties sources have a random behaviour, the DIAL uncertainty for a set of at least 4 scans, and for emission rates above the detection limit, is expected to be about 10% - 30%. During this field campaign each set of DIAL measurements has shown a behaviour consistent with a standard uncertainty of 5% - 10% of the measured emission rate, lower than the expected uncertainty reported in the protocol, and with no significant systematic bias. The overall uncertainty budget that has been validated during this specific field validation campaign is as reported in the following table.

Uncertainty Sources	Standard Uncertainty
Random, including wind and concentration	< 10%
VOC gas composition analysis	< 0.1 %
Bias	< 0.1 %

ANNEX A: DESCRIPTION OF THE DIAL TECHNIQUE

A.1 OVERVIEW OF THE DIAL TECHNIQUE

The Differential Absorption Lidar (DIAL) technique is a laser-based remote monitoring technique which enables range-resolved concentration measurements to be made of a wide range of atmospheric species. This section explains the theory of the DIAL technique and describes the NPL system in detail.

A.2 DESCRIPTION OF THE THEORY OF DIAL MEASUREMENTS

The atmospheric return signal, P, measured by a DIAL system from range r and at wavelength x is given by the Light Detection and Ranging (Lidar) equation, a simplified form of which is given in Equation 1.

$$P_x(r) = E_x \frac{D_x}{r^2} B_x(r) \exp\{-2\int_0^r [A_x(r') + \alpha_x C(r')]dr'\} \qquad \textbf{(1)}$$

where Dx is a range independent constant, C(r) is the concentration of an absorber with absorption coefficient αx and Ax(r) is the absorption coefficient due to all other atmospheric absorption, Ex is the transmitted energy and Bx is the backscatter coefficient for the atmosphere.

The equation has three basic components:

- a backscatter term based on the strength of the signal scattering medium
- parameters associated with the DIAL system
- a term which is a measure of the amount of absorption of the signal which has occurred due to the presence of the target species.

In the DIAL technique, the laser is operated alternately at two adjacent wavelengths. One of these, the "on-resonant wavelength", is chosen to be at a wavelength which is absorbed by the target species. The other, the "off-resonant wavelength", is chosen to be at a wavelength which is not absorbed significantly by the target species, and is not interfered with by other atmospheric constituents.

Pairs of on- and off-resonant signals are then acquired and averaged separately until the required signal to noise ratio is achieved.

The two wavelengths used are close together, hence the atmospheric terms Ax(r) and Bx(r) in the lidar equation can be assumed to be the same for both wavelengths. These terms are then cancelled by taking the ratio of the two returned signals.

The path-integrated concentration (CL) may be derived (Equation 2) by multiplying the logarithm of the ratio of the signals by the ratio of the absorption of the two wavelengths by the target species.

$$CL(r) = \frac{1}{2\Delta\alpha} \frac{1}{N} \sum_{i=1}^{N} \log \frac{S_{ON,i}(r)}{S_{OFF,i}(r)} \qquad \textbf{(2)}$$

where N is the number of pulse pairs averaged, Δα = αOFF-αON is the differential absorption coefficient and S represents the received power after energy normalisation of the on- and off-resonant signals respectively.

This path-integrated concentration represents the total concentration of the target species in the atmosphere along the measured line-of-sight out to the range r.

The range-resolved concentration can then be derived by differentiating the path-integrated concentration (Equation 3).

$$C(r) = \frac{dCL(r)}{dr} \qquad \textbf{(3)}$$

where C(r) is the concentration at range r along the line-of-sight averaged over the spatial resolution of the DIAL along its line-of-sight (typically 3.75 m).

A.3 DESCRIPTION OF FACILITY OPERATED BY NPL

The DIAL system operated by NPL is housed in a mobile laboratory. It can operate in the infrared and ultraviolet spectral regions allowing coverage of a large number of atmospheric species. A scanner system directs the output beam and detection optics, giving almost full coverage in both the horizontal and vertical planes.

The system also contains ancillary equipment for meteorological measurements, including an integral 10 m meteorological mast with wind speed, direction, temperature and humidity measurements.

The system is fully self-contained, with power provided by an on board generator, and has full air conditioning to allow operation in a range of ambient conditions.

The following sections describe the DIAL system in more detail.

Source

The source employs a combination of Nd-YAG and dye lasers together with various non-linear optical stages to generate the tuneable infrared and ultraviolet wavelengths. The source has a pulse repletion rate of 10 Hz and an output laser pulse duration of ~10 ns. A small fraction of the output beam in each channel is split off by a beam splitter and measured by a pyroelectric detector (PED) to provide a value for the transmitted energy with which to normalise the measured backscatter return.

Detection

The returned atmospheric backscatter signal is collected by the scanning telescope. This directs the collected light into separate paths for the infrared and ultraviolet channels. The returned light passes through band pass filters relevant to each detection channel and is then focused onto the detection elements. Solid-state cryogenically-cooled detectors are used in the infrared channel and low-noise photomultipliers in the ultraviolet.

After amplification the signals from these detectors are digitised using a high speed digitiser. The digitiser is clocked using a clock generator triggered by the same trigger used to fire the lasers. This ensures the range gating is correctly synchronised to the laser pulse transmission. The signals from the PED monitoring the transmitted energy are also digitised and stored.

Data Analysis

The data acquired are analysed, using the DIAL techniques described below, to give the range-resolved concentration along each line-of-sight.

The data analysis process consists of the following steps:

i) Background subtraction

Any DC background value is subtracted from the signals. This measured background takes account of any DC signal offset which may be present due to electronic offsets and from incident background radiation. The background level is derived from the average value of the far field of the returned lidar signal where no significant levels of backscattered light is present.

ii) Normalisation for variation in transmitted energy
The two signal returns are normalised using the monitored values of the transmitted energy for the on and off resonant wavelength pulses. The mean transmitted energy is used to normalise the averaged return signal. For this application, this has been shown to be equivalent to normalising individual shots against transmitted energy and then averaging the normalised values.

iii) Calculation of path-integrated concentration
The path-integrated concentration of the target species, out to the range r, is calculated using equation 2.

The absorption coefficients used in this calculation are derived from high-resolution spectroscopy carried out using reference gas mixtures at NPL.

iv) Derivation of range-resolved concentrations.
The integrated concentration profiles are piecewise differentiated with a selectable range resolution, to give the range-resolved concentration along the line-of-sight, as in equation 3.

v) Calculation of emission rates
Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile. This is carried out using algorithms developed at NPL which reduce artefacts due to the difference in data density at different ranges, due to the polar scanning format of the data. The emission rate is then determined using the concentration profile together with meteorological data.

The emitted rate is calculated using the following mathematical steps:
(a) The product is formed of the gas concentration measured with the DIAL technique at a given point in space, and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.
(b) This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.
(c) This array of results is then integrated over the complete concentration profile to produce a value for the total emitted rate.

Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large spatial variations since, for example, errors in the wind speed in regions where large concentrations are present will significantly affect the accuracy of the results. A logarithmic wind profile is used to describe the vertical distribution of the wind. Two wind speeds at different heights, usually from the fix mast sensors, are used to calculate the wind profile. The calculated wind field is then combined with the measured gas concentration profile using the procedure described above.

A summary of the ultraviolet and infrared performance capabilities of the NPL DIAL facility are given in Tables A.1 and A.2. The values given in these tables are based on the actual levels of performance of the system obtained during field measurements, rather than calculations based on theoretical noise performances. For simplicity the numbers are presented as a single concentration sensitivity and maximum range values. However, the detailed performance behaviour of a DIAL system is much more complex and there are a number of key points that should be noted:

- The DIAL measurement is of concentration per unit length rather than just concentration. So the sensitivity applies for a specified pathlength – 50 metres in this case. Measurements over a shorter path would have a lower sensitivity, and would be more sensitive over a longer path length.
- Since the backscattered lidar signal varies with range, generally following a (range)$^{-2}$ function, the sensitivity is also a function of range. The sensitivity values given in the tables apply at a range of 200 metres, and these will get poorer at longer ranges.

- The maximum range of the system is generally determined by the energy of the emitted pulse and the sensitivity of the detection system, except in the case of nitric oxide where range is limited by oxygen absorption at the short ultraviolet wavelengths required for this species.
- In all cases the performance parameters are based on those obtained under typical meteorological conditions. For the ultraviolet measurements the meteorological conditions do not have a great effect on the measurements as the backscattered signal level is predominantly determined by molecular (Rayleigh) scattering, and this does not vary greatly. However, in the infrared the dominant scattering mechanism is from particulates (Mie scattering). So the signal level, and therefore the sensitivity, is dependent on the particular loading of the atmosphere, and this can vary dramatically over relatively short timescales.
- The optical configuration of the DIAL system means there is a minimum range between 40-100 m before measurements can be made.

The NPL DIAL has a theoretical range resolution of 3.75 metres along the measurement beam, and a vertical and horizontal scan resolution which can be less than 1 metre at 100 metres. However, the actual range resolution determined by the signal averaging used, will depend on atmospheric conditions and the concentration of the measured pollutant, and may be of the order of 20-30 m.

Table A.1 Ultraviolet capability of NPL DIAL Facility

Species	Concentration sensitivity (ppb km) (1)	Max Range (m) (2)
NO	1	500
N_2O	10	500
SO_2	3	1000
O_3	1.5	1000
Xylene	1	500
Toluene	0.5	600
Benzene	0.5	600

Table A.2 Infrared capability of NPL DIAL Facility

Species	Concentration Sensitivity (ppb km) (1)	Max Range (m) (2)
CH_4	20	600
VOCs	3	600
C_2H_6	3	600
C_2H_4	15	600
C_2H_2	3	600
HCl	2	800
N_2O	25	600
CH_3OH	45	500

(1) The concentration sensitivities apply for measurements of a 50 metre wide plume at a range of 100m to 200m from the DIAL, under typical meteorological conditions.

(2) The range value represents the typical working maximum range for the NPL DIAL system.

A.4 GENERAL HYDROCARBON SCALING FACTOR

The DIAL is able to make measurements of a wide range of compounds, including benzene and other aromatics, individual VOCs and total VOCs, see Tables A.1 and A.2. The methodology for obtaining measurements of the total VOC content from C3 to C15 is provided below. It consists of the combination of DIAL measurements with air sampling and GC analysis. The system is able to monitor individual aromatic compounds and VOC species, which have absorption features in the IR and UV spectral regions covered by the DIAL system. NPL has the spectral expertise, access to spectral libraries and an in-house spectroscopic capability to assess the DIAL sensitivity for additional individual species.

The general hydrocarbon measurement listed in Table A1.2 uses an infrared absorption that is similar for all hydrocarbons with three or more carbon atoms, linked to the stretch frequency of the carbon-hydrogen bond. The line strengths for these species are proportional to the number of carbon-hydrogen bonds present and this enables a total mass emission to be determined. As such it provides a measure of the mixture of volatile organic compounds (VOCs) that are present at an oil or petrochemical site. The pair of infrared wavelengths used for this DIAL measurement are selected so that the absorption per unit mass is relatively invariant with respect to the mix of different hydrocarbons that are present. However, the sensitivity of this measurement in terms of ppb of hydrocarbon depends on the mixture of species present, and the value given in the table reflects the typical mix of hydrocarbons found at oil refineries.

Although the general hydrocarbon measurement provides a good estimate of the overall amount of hydrocarbons present, the accuracy of this measurement can be improved, and the total VOC concentration calculated, by combining the DIAL measurements with the results of gas chromatography (GC) analysis of the emitted gases. The standard procedure for this involves taking whole air samples around the site in locations where the DIAL measurements show the emitted plumes are present. The VOCs present in these samples are identified and quantified by GC analysis. The results provide the relative levels of all the VOCs present with a concentration of 0.1 ppb or higher. The results of this analysis are combined with NPL's unique spectral library of quantified infrared absorptions of an extensive set of VOCs to calculate the combined absorption coefficient for the actual VOC mixture present at the site. Appling this absorption coefficient to the DIAL results enables the total VOC emission rates to be calculated.

A.5 RELATIONSHIP BETWEEN EMISSION RATE AND CONCENTRATIONS

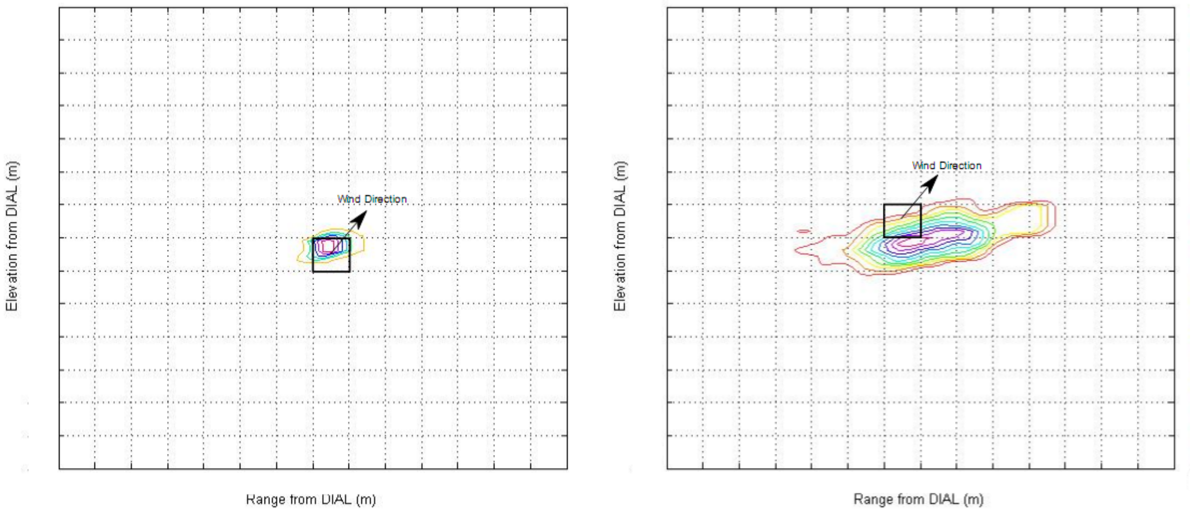

Figure A.1 Illustration of the emission rate calculation approach

Where concentrations are provided as an indication of the levels observed in a measurement scan, the reported concentration in the measurement plane is the maximum concentration seen in a cell in the measurement plane. The resolution of the planes used is equal to the DIAL system resolution and is 3.75 m, so each cell is 3.75 m square. Figure A.1 shows how plume size affects the emission rate that is calculated. The concentration assigned to each cell is multiplied by the perpendicular wind field determined for that cell, and then the individual cell emission rates are summed to give the total emission rate through the plane. This figure shows two example plumes (the cell grids are for indication and are not to scale), one which has a small plume, and therefore a small integrated emission rate, and the other which has a larger plume, and therefore represents a larger emissions rate, although the peak concentration in both is similar, and indeed may even be higher in the small plume than the large plume.

Figure A.2 shows a schematic representation of two measurement plane configurations observing the same plume. One has a nearly perpendicular orientation to the plume, and the wind direction is therefore also perpendicular to the measurement plane. The other is at an angle through the plume, and therefore the wind is not perpendicular to the plane of the measurements. If only the concentration profile were observed the right hand measurement configuration would show a larger plume (as it cuts obliquely through the plume). However, when the wind direction is taken into account, the normal component of the wind vector is used, and this therefore reduces the emission rate determined from this scan, resulting in the same emission rate being determined for both measurement orientations.

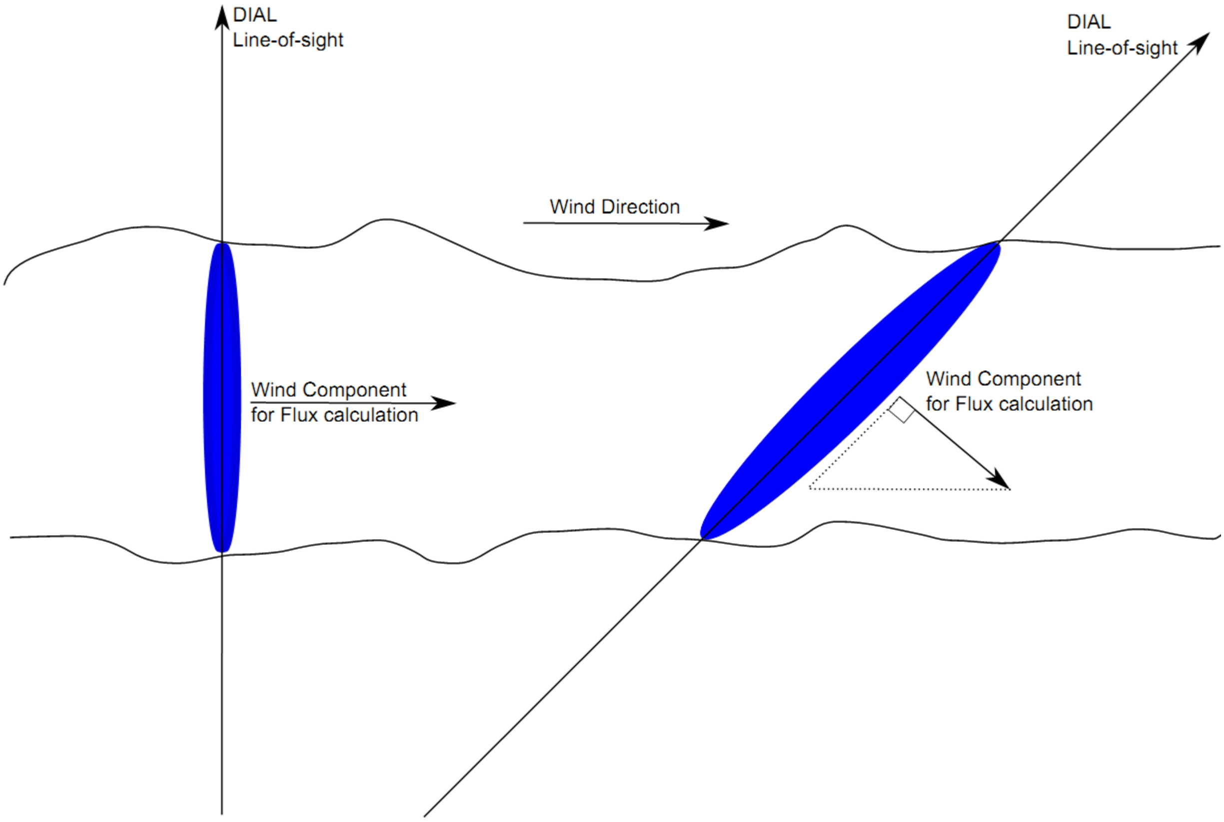

Figure A.2 Schematic showing relationship between emission rate and wind direction

A.6 CALIBRATION AND VALIDATION

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. The gas cells are filled with known concentrations of the target species, obtained from NPL standard gas mixtures, which are directly traceable to national standards. A fraction of the transmitted beam is split off and directed through a gas cell to a PED, in the same way as with the beam for the transmitted energy monitors. This provides a direct measurement of the differential absorption at the operating wavelengths by the target gas. The transmission through the gas cells is continuously monitored during the operation of the system to detect any possible drift in the laser wavelengths. The calibration cells are also periodically placed in the output beam to show the concentration response of the whole system is as expected.

A number of field comparisons have been undertaken to demonstrate the accuracy of the measurements obtained with DIAL. Examples of these carried out by NPL are summarized below:

i) Intercomparisons have been carried out on chemical and petrochemical plants where a large number of different volatile organic species are present. In these intercomparisons, the DIAL beam was directed along the same line-of-sight as a line of point samplers. The point samplers were operated either by drawing air into internally-passivated, evacuated gas cylinders or by pumping air at a known rate, for a specified time, through a series of absorption tubes which efficiently absorb all hydrocarbon species in the range C_2 - C_8. The results obtained for the total concentrations of VOCs measured by the point samplers and those measured by the infrared DIAL technique agreed within ± 15%. The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within ± 20%.

ii) The ultraviolet DIAL system was used to monitor the emission rates and concentrations of sulphur dioxide produced from combustion and emitted by industrial stacks. These stacks were instrumented with calibrated in-stack sampling instruments. The results of the two sets of measurements agreed to within ± 12%.

iii) DIAL Measurements of controlled releases of methane from a stack agreed with the known emission rates to within ± 15%.

iv) The California Air Quality Regulator (SCAQMD) commissioned in 2015 a series of field tests at refineries and small retail petrol stations as part of a larger research programme. The NPL area source facility was used to separately validate several standard methods to determine fugitive and diffuse emissions at these sites. The following techniques were validated NPL IR DIAL, Open-Path FTIR (OP-FTIR) Spectroscopy, Tunable Diode Laser Absorption (TDL) Spectroscopy, and Solar Occultation Flux (SOF). During the SCAQMD blind controlled release study the DIAL demonstrated to be very accurate. The DIAL method was not affected by meteorological conditions and it was able to report emissions from all the test releases. For each release the difference between the released and DIAL rates was less than the stdev of the DIAL measurements, see Table A.3. This includes Release 7 that was quite low and close to the DIAL detection limit that during this experiment can be estimated to be between 0.5 kg/hr and 1 kg/hr. The emission rates measured by the DIAL were also linear as shown in Figure A.3 with an excellent R2 value.

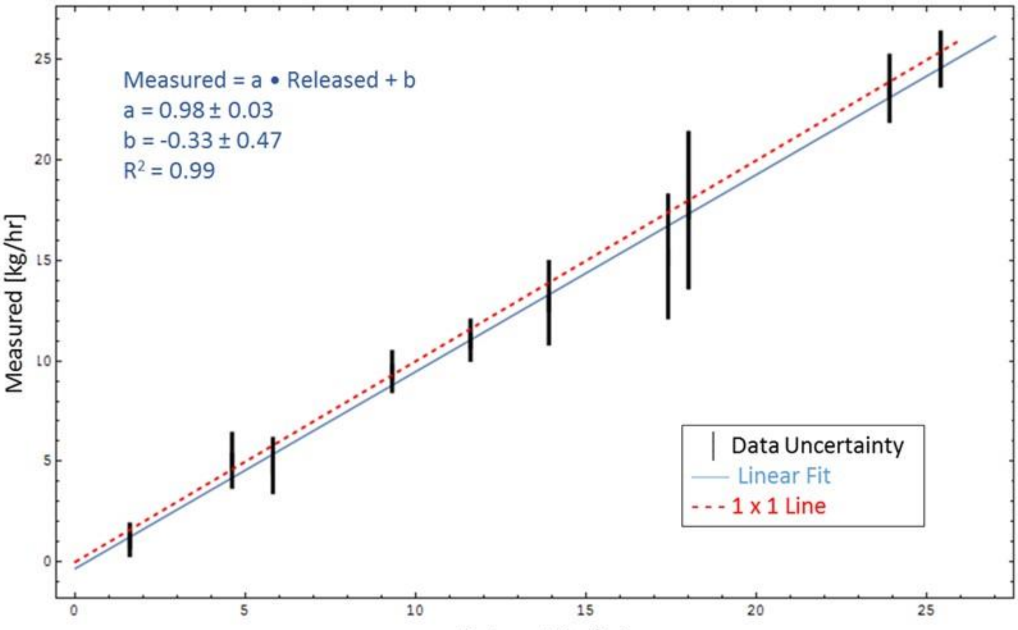

Figure A.3 Comparison of actual propane release rates with DIAL measurements

Table A.3 Summary of determined propane emission rates, for each controlled release the average emission and stdev are reported. Positive and negative % difference between measured and released rates corresponds to overestimation and underestimation of emissions respectively

Notes	Average Flux	Standard Deviation	Scans	Controlled Release	Difference DIAL-Release	
	kg/hr	kg/hr	#	kg/hr	Kg/hr	%
Release 1 13:02-13:56 - 3m	4.8	1.3	6	5.8	-1.0	-17.3
Release 2 14:00-14:55 - 3m	11.0	1.0	4	11.6	-0.6	-4.8
Release 3 15:00-15:58 - 3m	15.2	3.0	3	17.4	-2.2	-12.6
Release 5 10:44-11:43 - 3m	12.9	2.0	4	13.9	-1.0	-7.2
Release 6 11:47-12:40 - 6.4m	5.1	1.3	4	4.6	0.5	10.0
Release 7 12:48-13:41 - 7.9m	17.5	3.9	4	18.0	-0.5	-2.8
Release 8 13:43-14:38 - 7.9m	1.1	0.8	3	1.6	-0.5	-31.1
Release 9 14:44-15:39 - 7.9m	9.5	1.0	3	9.3	0.2	1.9
Release 10 15:44-16:29 - 7.9m	25.0	1.3	3	25.4	-0.4	-1.5
Release 11 16:34-17:16 - 3m	23.6	1.6	3	23.9	-0.3	-1.4

The sum of all the DIAL emission rates and the release rates are 125.7 kg/hr and 131.5 kg/hr respectively, with a difference of only -4.4%. This is equivalent to an approximately ten hour long controlled release experiment but also it simulates DIAL measurements of different areas on a site that are then summed together to obtain an estimate of the total emission rate. This also shows that the dominant DIAL uncertainties sources during this field validation campaign had a random behaviour and therefore by increasing the number of DIAL scans the uncertainty can be expected to decrease accordingly.

v) Validation of the DIAL against controlled releases at NPL. As a part of research and development programmes NPL have a continuous development programme for the DIAL technology and have conducted a number of validation studies using the NPL controlled release facility (CRF). The results of a series of these have been assessed and published in the peer review literature. These results confirm that the DIAL provides measurements of mass emission rates which are linear with release rate, fall within the stated variability for the measurements, and most critically, that the systematic biases in the DIAL measured emission estimates are less than 4% as illustrated in Figure A.4.

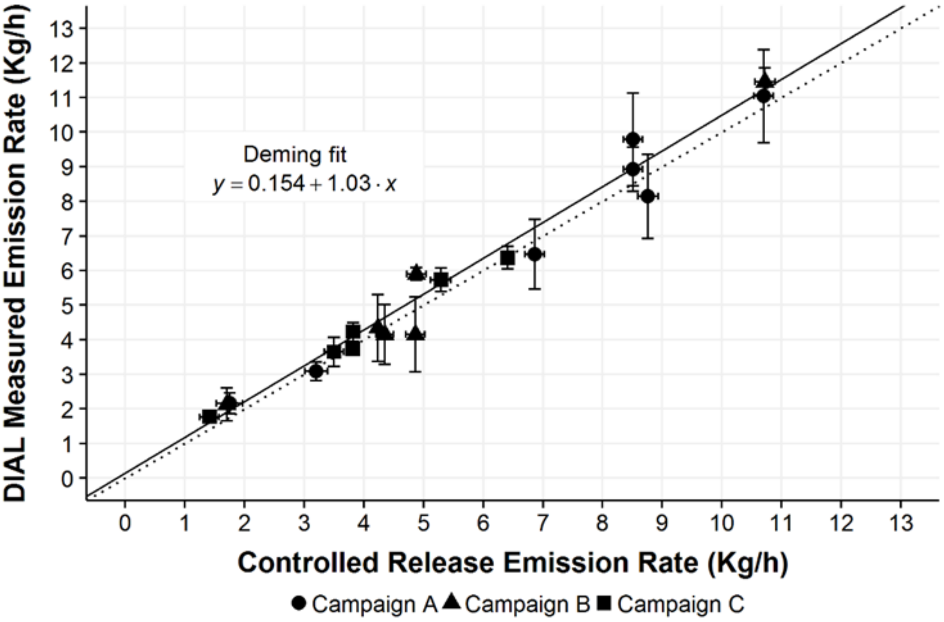

Figure A.4 Results of three validation campaigns comparing the NPL DIAL emission rate measurements to 20 CRF release rates (solid line: Deming regression fit; dotted line: 1:1 fit)

ANNEX B: METEOROLOGICAL MEASUREMENTS

Wind data were collected from two fixed mast. The 4 channel fixed mast (located at the position ‘Mast 4’ identified in Figure 4.1) supported four wind sensor packages, at 11.9 m, 9.0 m, 6.2 m and 3.4 m local elevation. The 2 channel fixed mast (located at the position ‘Mast 2’ identified in Figure 4.1) supported two wind sensor packages, at 11.9 and 3.4 m local elevation. Figure A2.1 shows an example of the meteorological mast. The DIAL (10.5 m), meteorological station (3 m) and portable (2.3 m) wind sensors were also deployed.

Figure B.1 Example NPL meteorological mast.

The following figures present the average wind roses for the measurement periods on each location from the 21st to the 29th of September.

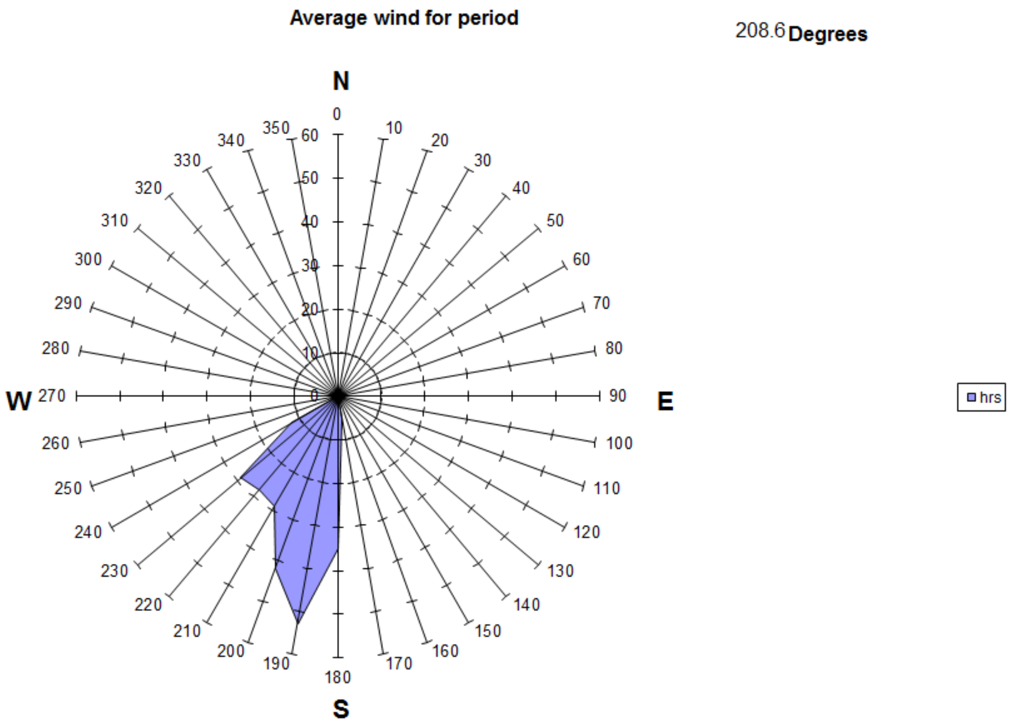

Figure B.2 Wind rose for 22nd September during measurements from BV02, 13:17 - 17:22

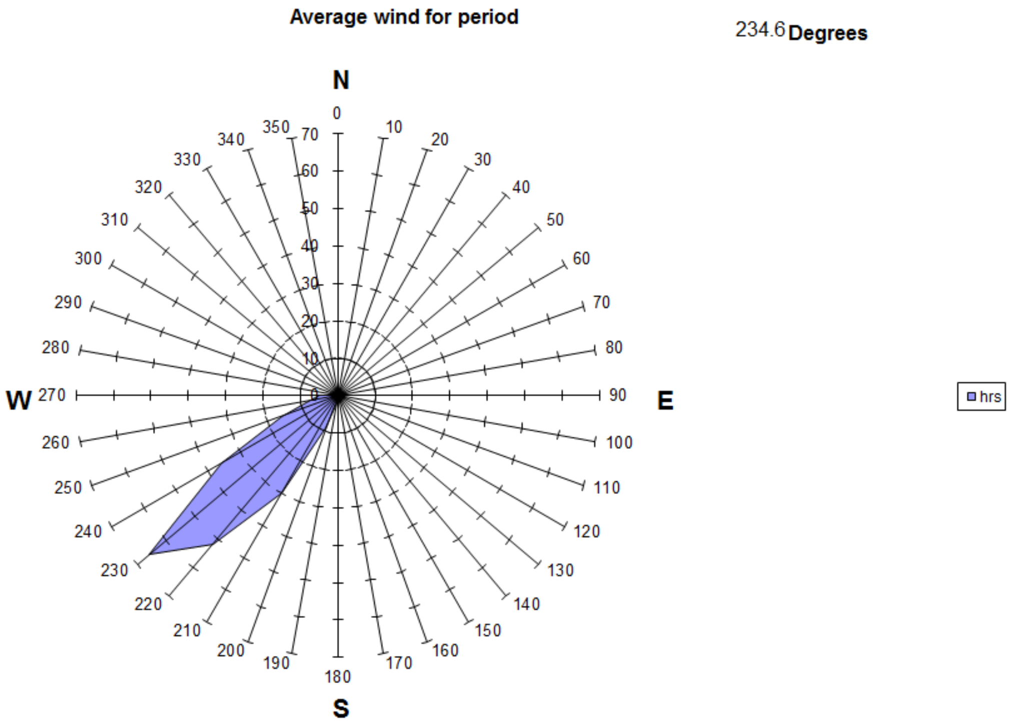

Figure B.3 Wind rose for 23rd September during measurements from BV03, 11:29 - 15:40

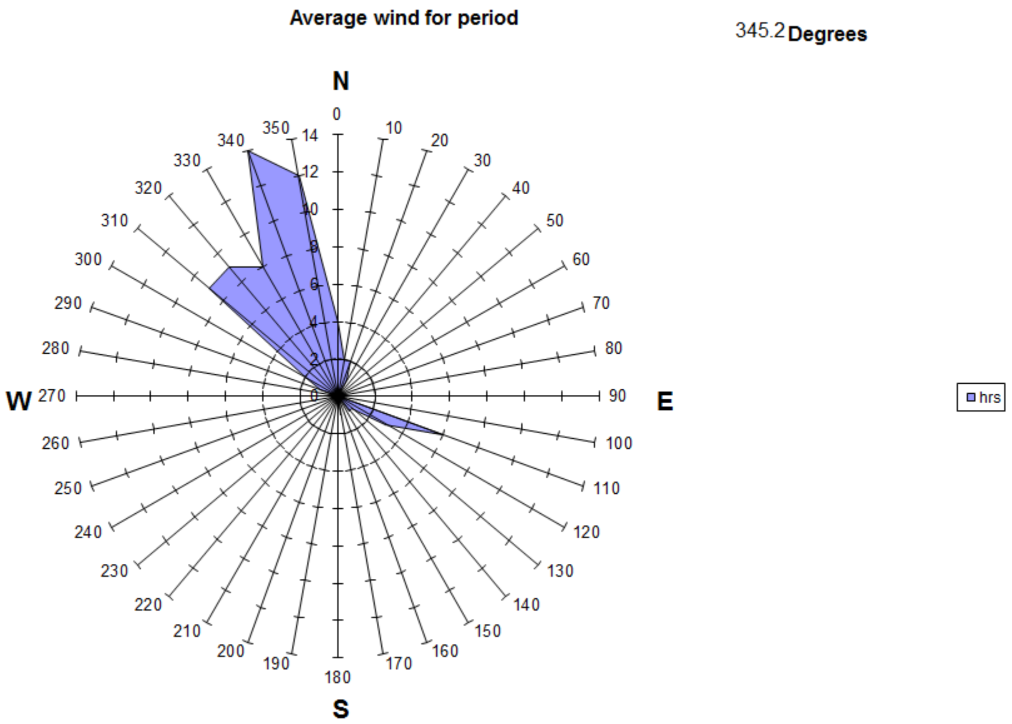

Figure B.4 Wind rose for 26th September during measurements from BV04, 9:41 - 11:06

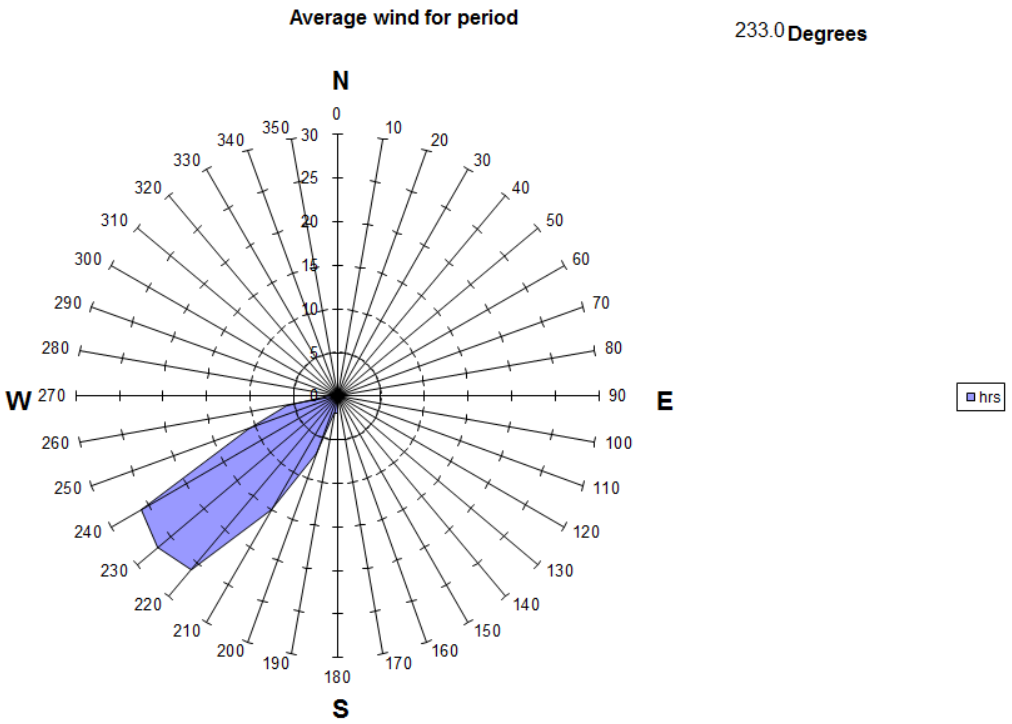

Figure B.5 Wind rose for 26th September during measurements from BV06, 12:22 - 14:35

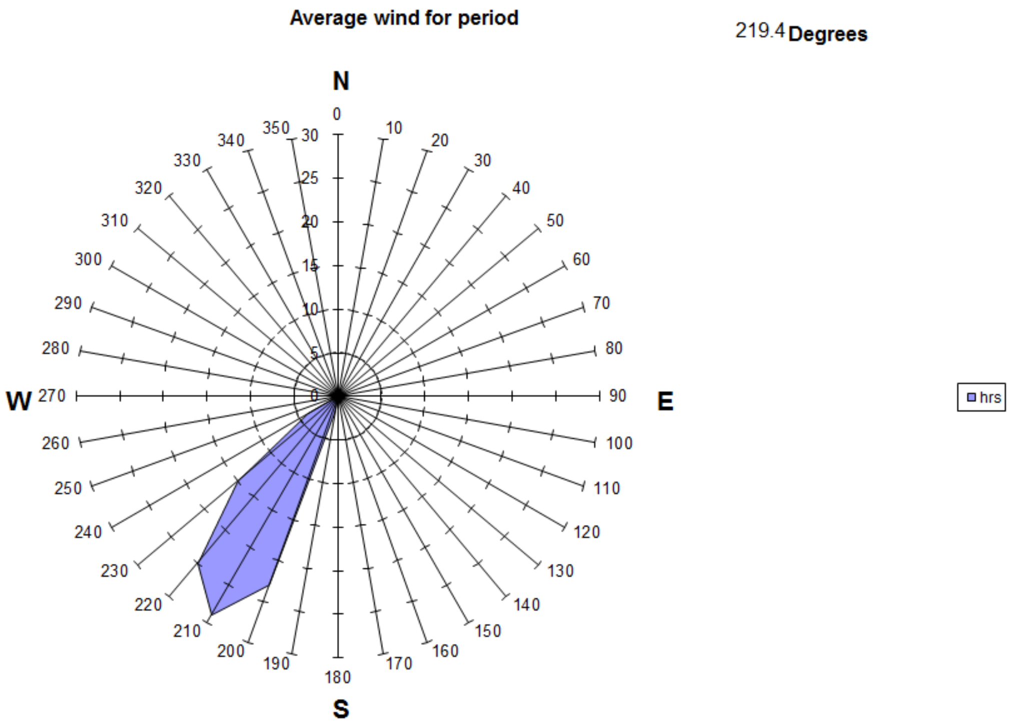

Figure B.6 Wind rose for 26th September during measurements from BV09, 16:05 - 17:50

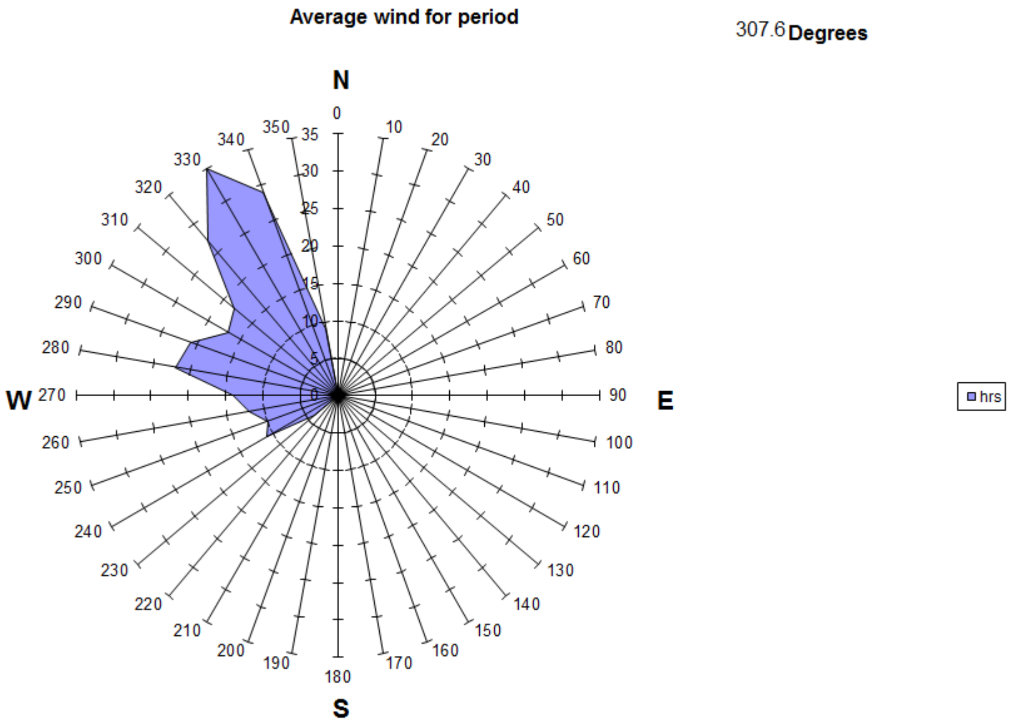

Figure B.7 Wind rose for 27th September during measurements from BV10, 9:14 - 13:26

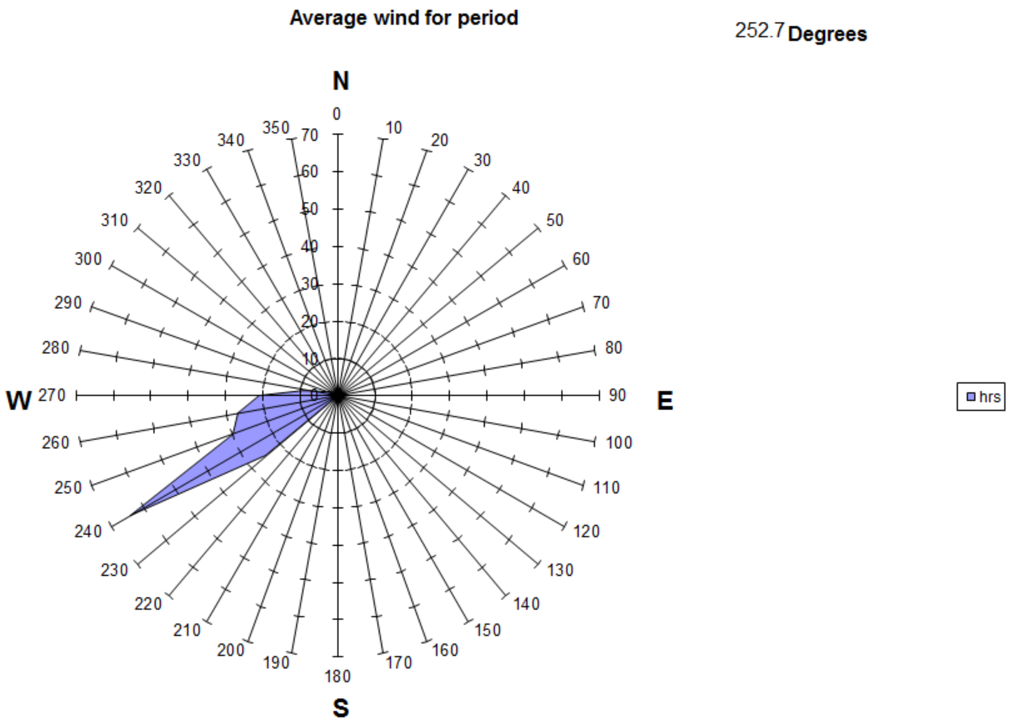

Figure B.8 Wind rose for 27th September during measurements from BV11, 14:20 - 17:44

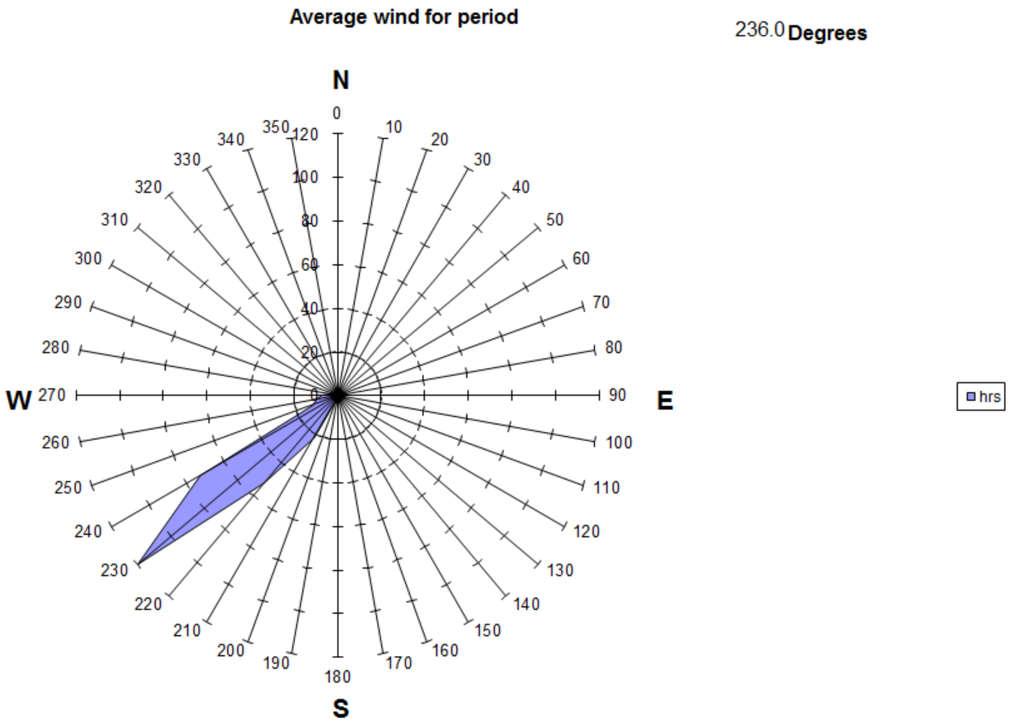

Figure B.9 Wind rose for 28th September during measurements from BV13, 12:05 - 17:48

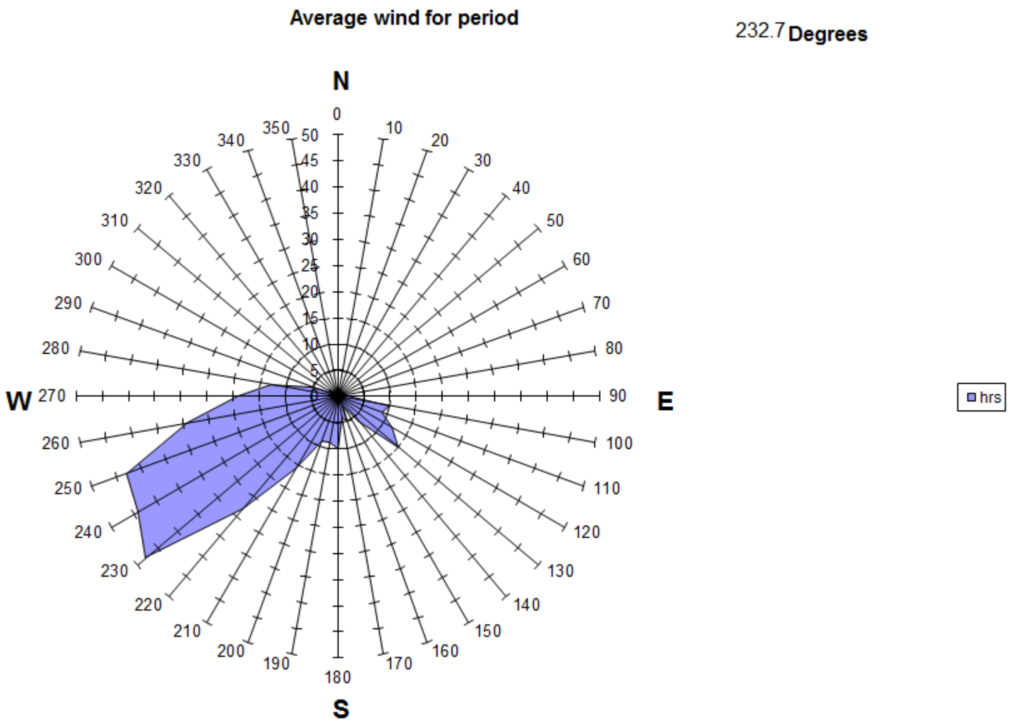

Figure B.10 Wind rose for 27th September during measurements from BV14, 10:51 - 17:21

2018

CEN / TC 264 / WG38 – WP5
Controlled release validation - SOF

Final report – ver. 1

FluxSense AB

1 July 2018

Date: 1 July 2018

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[Cover: VOC measurement transect by Solar Occultation Flux (SOF) at the Berre l'Étange test site area. The wind was coming from west-south-west, as indicated by the white arrow. The measurements were done September 28, 2016, 12:54. The red-black curve shows measured vertical column of propane, where 1 m height above ground corresponds to 1 mg/m^2. Image overlay on GoogleEarth 2018.]

Summary

This report describes Solar Occultation Flux (SOF) results from a validation experiment related to standardization of methods to measure fugitive volatile organic carbon (VOC) emissions within CEN / TC 264 / WG 38. The work was carried out by FluxSense AB and funded by the European Commission.

A validation campaign was carried out from September 19 to September 30, 2016, at a decommissioned refinery site in southern France. The main objective was to demonstrate and validate different methods by controlled releases of VOCs in a real facility environment, where the various methods were operated according to protocol.

The experiment was run in a very realistic and quite complex environment, with large structures and obstacles surrounding the release unit. VOC, consisting primarily of propane, could be released from up to five different nodes located in a process type unit of size 25 by 25 m and three floors height. Four of the nodes were of point type (1 m dispenser diameter) and one was of line dispenser type, extending in the vertical from ground to second floor.

The experiment was run "blind" so that the remote sensing operators did not know the released rates or which node configurations were active. The release experiment was planned and governed by INERIS, France, using a gas release system supplied by National Physical Laboratory (NPL), UK.

Overall the total amount of VOC reported by SOF was within 25% of the released amount, 178 kg/h versus 142 kg/h, based on 14 out of 20 test which fulfilled the quality criteria of the SOF measurement protocol. Overall the measurements showed good response over the covered release rate range of 5-19 kg/h.

For individual test configurations, the measured emission rate ranged -15% to +72% compared to the released rate. For the three tests that deviated the most (no. 4, 18 and 19) winds were south-westerly, and in this case the release plume passed a unit in the north eastern part of the measurements area in which a pipeline was being cleaned and this potentially interfered with our measurements. The interference was observed during the measurements and post-analysis and measurements with large interference from other sources were discarded based on composition analysis.

Six of the controlled release tests were run at almost the same emission rate, 9.4±0.4 kg/h but utilizing different release nodes, including one or two point-nodes at a time or the linear node alone. On average, the measured emission rate was 11.2 kg/h, and this is 19% higher than the average release rate, covering effects of release location/distribution as well as inherent measurement variabilities.

Compared to a normal SOF survey, the controlled release experiment was run under more complex and complicating conditions. The duration of every experiment was very short (1.5 h), limiting the number of plume and upwind background transects. In a normal SOF survey the measurements are planned according to conditions, to allow for measurements during different wind directions and optimize the measurements for the site. Bumpy, confined roads with shadow patches and disturbed wind fields added uncertainty as well as significant background sources in the area.

The stated uncertainty range of 20-35% for SOF measurements is in line with the validation results of the controlled release experiment described in this report, considering that the measurements were complex.

Acronyms, Units and Definitions

Acronyms used in this report

FTIR	Fourier Transform InfraRed
MeFTIR	Mobile extractive FTIR
SOF	Solar Occultation Flux
SNR	Signal-to-Noise Ratio
QA	Quality Assessment
QC	Quality Control

Commonly used Gas Molecules

CH_4	Methane
NMVOC	Non-methane VOC
VOC	Volatile organic compound, used interchangeably for non-methane VOC (NMVOC)

Units

Wind direction	degrees North
Length	m
Weight	kg
Wind speed	m/s
Column	mg/m^2
Concentration	mg/m^3, 1 mg/m^3 = 1000 $\mu g/m^3$
Flux	kg/h

Table of Contents

1 Introduction

1.1 Background and objective

This report describes Solar Occultation Flux (SOF) measurement results from a validation experiment related to standardization of methods to measure fugitive VOC emissions (CEN / TC 264 / WG 38). A campaign was carried out from September 19 to September 30, 2016, at a decommissioned refinery site in southern France. The main objective was to demonstrate and validate different methods by controlled release experiments (of Volatile Organic Carbons, VOCs) in a real facility environment, where the various methods were operated according to their measurement protocols.

1.2 Project overview

Emission measurements and concentration mapping was done using the SOF method for two weeks at the end of September 2016. Following initial setup and planning, 20 controlled release experiments were run during the period September 22 – 29, each release having a duration of about 1.5 hour.

The release unit was located inside a refinery site which was being decommissioned at the time of measurements and there was therefore only minor gas handling present in the area, including a few process areas which still contained pressurized gas, a few tanks which contained VOCs and occasional cleaning activities of pipeline. North of the area there were several active chemical plants with distinct VOC emissions that could be observed in northerly wind. This area also had an active flare which was situated 200 m west of the controlled source release points. In Figure 1 the position of the controlled source releases is shown together with the refinery and surrounding chemical industries

Wind measurements were governed by INERIS (French National Institute for Industrial Environment and Risks), providing three 10 m wind towers and one wind LIDAR (Leosphere WindCube v2) that measured vertical wind profiles in the 40-200 m range. In addition, several of the participants in the campaign also brought wind towers in the 2-10 m range for supporting wind information. Figure 2 shows the location of the INERIS wind stations that were used for the emission assessments.

The experiment was run in a very realistic and quite complex environment, with large structures and obstacles surrounding the release unit, Figure 3. VOC could be released from up to five different nodes located in a process type unit of size 25 by 25 m and three floors height. Four of the nodes were of point type (1 m dispenser diameter) and distributed on floors 1 and 2 of the unit, both centrally and close to the building edges. One release node was of line dispenser type, extending in the vertical from ground to second floor.

The experiment was run “blind” so that the ORS operators did not know the released rates or which node configurations were active. The release experiment was planned and governed by INERIS, France, using a gas release system supplied by National Physical Laboratory (NPL), UK.

Alkanes was measured using Solar Occultation Flux (SOF), which is a method based on infrared absorption of direct sun light. Ground level concentrations of alkanes were measured by mobile extractive Fourier Transform Infrared spectroscopy (MeFTIR) for tracer correlation (TC) purposes but reported separately.

Figure 1. Map showing the locations of the Controlled Release site during the 2016 survey. Map from Google Earth © 2018.

Figure 2. Site overview showing the locations of the Controlled Release unit and installed wind data monitors during the 2016 survey. Map from Google Earth © 2018.

Figure 3. Site 3D-overview showing the locations of the Controlled Release unit. Map from Google Earth © 2018.

2 Instrumentation and Methods

The FluxSense mobile laboratory had two optical remote gas sensing instrumental setups for gas monitoring during this survey; SOF (Solar Occultation Flux) (this report) and MeFTIR (Mobile extractive FTIR, separate Tracer Correlation report) (Figure 4 and Table 1). The SOF method is only described briefly here, and a more comprehensive description is given in section 8 (Annex A and B). SOF measures gas columns through the atmosphere by means of infrared light absorption, utilizing direct infrared light from the sun. Figure 4 gives a general overview of the measurement setup (the figure also includes some other techniques normally present in the FluxSense mobile lab).

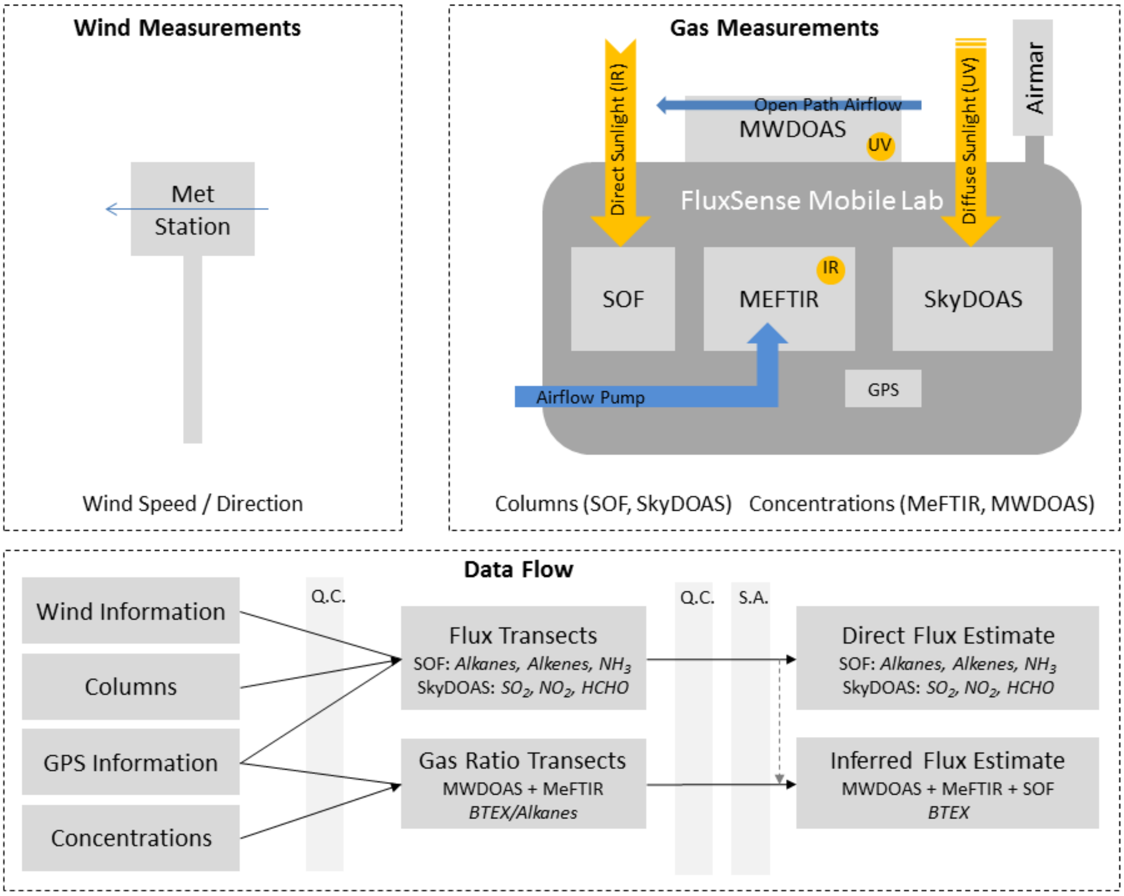

Figure 4. Overview of the FluxSense mobile lab and its main instruments: **SOF**, MeFTIR, MWDOAS and SkyDOAS (upper right panel) and wind measurements (upper left panel) and simplified data flow diagram (lower panel). The data flow describes what information that goes into the flux emission estimates. Direct flux emissions are produced from measured columns (SOF). Q.C. = Quality Control, S.A. = Statistical Analysis.

To derive final emission flux estimates, the GPS-tagged gas column measurements by SOF are combined with wind data and integrated across the plume transects at the various source locations. A table summarizing the main features and characteristics is found in Table 1.

Table 1. Summary of FluxSense gas measurement techniques used in this measurement campaign. *For typical wind conditions at an optimal distance from the source.

Method	**SOF**
Compounds	**Alkanes**: (C_nH_{2n+2}) **Alkenes:** C_2H_4, C_3H_6 **Other:** NH_3
Detection limit, column	0.1-5 mg/m^2
Detection limit, flux*	0.2-1 kg/h
Wind Speed Tolerance	1.5-12 m/s
Sampling Time Resolution	1-5 s
Measured Quantity [unit]	Integrated vertical column mass [mg/m^2]
Complementary data	Vehicle GPS-coordinates, plume wind speed and direction

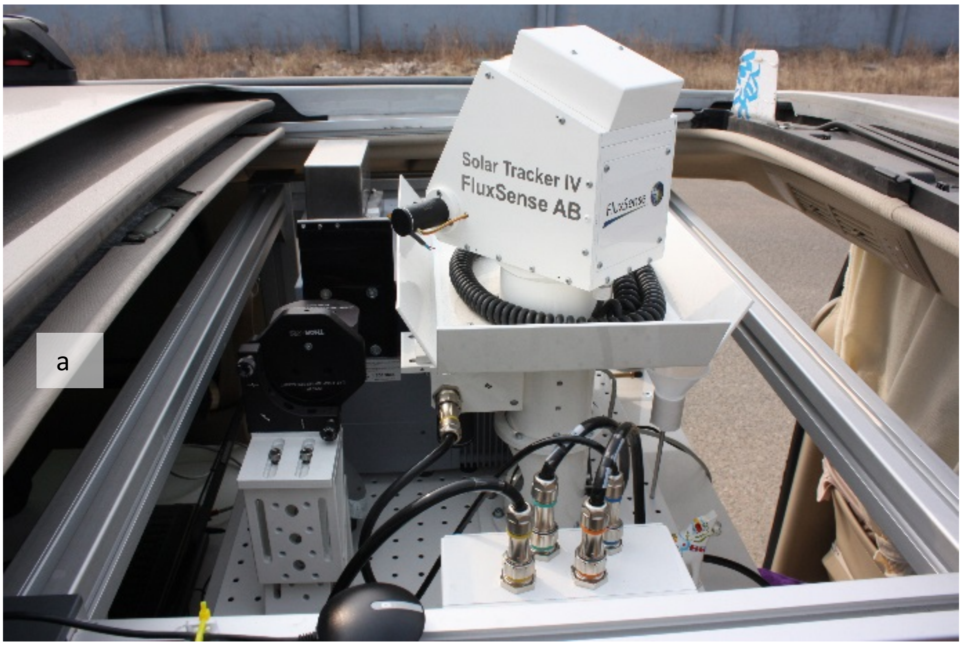

Figure 5. FluxSense mobile lab SOF system.

The SOF system is installed in a measurement vehicle (Figure 5) which allows consecutive column concentration measurements to be performed while driving. The flux of a species in a plume from an industry is measured by collecting spectra while driving the vehicle so that the light path from the sun to the instrument gradually cuts through the whole plume, preferably as orthogonally as possible to the wind direction, see Figure 6.

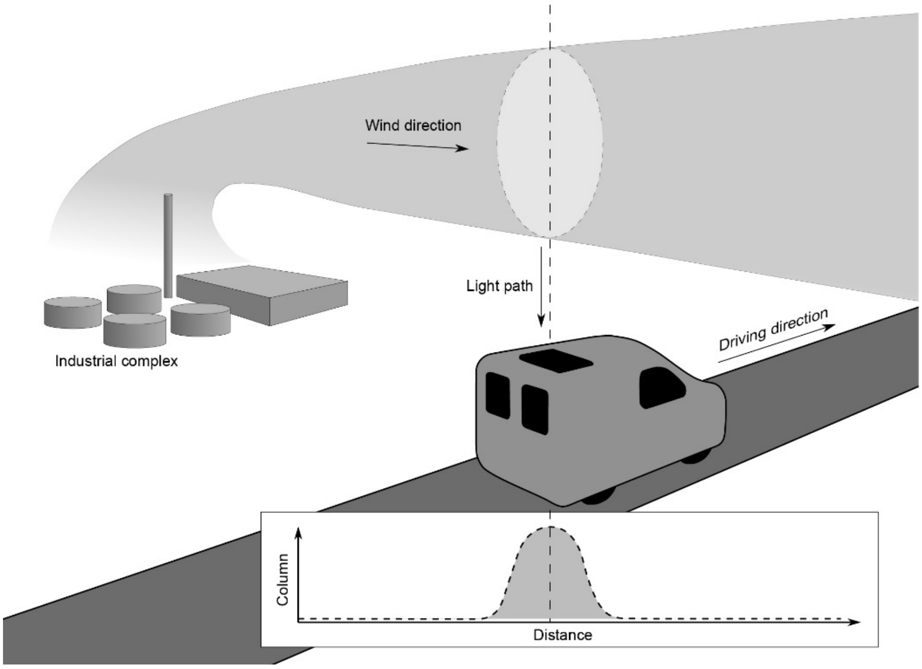

Figure 6. Schematic of the SOF measurement where the vehicle is driven across the prevailing wind so that the solar beam cuts through the emission plume while the sun is locked into the FTIR spectrometer by the solar tracking device on the roof. The VOC mass (or other compound of interest) is integrated through the plume cross section.

2.1 Principal Equations

Direct flux measurements:

Direct flux is measured by SOF. The emission mass flux (Q) of species (j) for a single transect (T) across the plume (P) along path (l), can be expressed by the following integral (Si-units in grey brackets):

$$Q_T^j[\mathrm{g/s}] = \bar{v}_T[\mathrm{m/s}] \cdot \int_P C_l^j[\mathrm{mg/m^2}] \cdot \cos(\theta_l) \cdot \sin(\alpha_l)\, dl\, [\mathrm{m}],$$

where

$\bar{v}_T$ = the average wind speed of the mass plume for the transect T,
C_l^j = the measured slant column densities for the species j as measured by SOF,
θ_l = the angles of the light path from zenith ($\cos(\theta_l)$ gives vertical column),
α_l = the angle between the wind direction and driving direction
dl = the driving distance across the plume

The measured SOF slant column orientation and length vary with latitude, season and time of day following the associated changes in solar elevation.

To isolate emissions from a specific source, the incoming/upwind background flux must be either insignificant or subtracted. If the source is encircled, the integral along l is a closed loop and the flux calculation is done with sign, and the emission emerging from within the closed loop is obtained.

3 Performance characteristics and measurement protocol

A summary of the performance capabilities of a typical SOF system under normal conditions are given in Table 2. The values provided are based on the actual levels of performance of existing SOF systems, determined from the typical absolute precision for column measurements in earlier studies when driving 40 km/h downwind of industries in Houston. The numbers in Table 2 are applicable given that there is enough solar radiation (relatively clear conditions and at least an hour away from sunset or sunrise). The performance will improve for small sources and slower measurement speed. The column accuracy is the combined effect of instrument and retrieval stability on the total columns for a plume transect in real conditions. The flux is determined by multiplying the column across the gas plume with the orthogonal wind speed. The main uncertainty of the flux measurements of diffuse emission sources comes from the uncertainty in the wind field in relation to the emission plume.
Table 3 shows the estimated uncertainty for flux measurements in various field conditions when measuring alkane emission from refineries and petrochemical industries. This estimate is obtained as the root-sum-square of various error sources estimated from a one month campaign in Texas, but the numbers are representative for other campaigns as well

The infrared cross sections for alkane have an uncertainty of 3–3.5 % and retrieval errors of 10 % have been estimated for the different species. This is the combined effect of instrument and retrieval stability on the total columns for a plume transect. For the alkane retrieval this also includes a 6 % mass retrieval uncertainty due to limited specificity. All these uncertainty sources have been combined by root-sum-square to a composite flux measurement uncertainty range for each species and study. The maximum and minimum for each range was calculated using the maximum and minimum uncertainties of both wind speed and wind direction. In most cases, the composite uncertainty is approximately 20-35 %.

Table 2— Capability of a typical SOF column measurement based on direct solar measurements in the IR region and zenith scattered light in the UV

Parameter	Precision/Detection (1σ)	Accuracy
Alkanes (C2-C8) (IR)	3 mg/m^2	10%

(1) Precision in ppb, assuming 50 m path length and C4 mixture.

Table 3. Typical uncertainty estimation of alkane flux measurements for diffuse emission sources (the variability of the sources not taken into account).

	Wind Speed [a)]	**Wind direct** [b)]	**Spectroscopy (cross sections)** [c)]	**Retrieval error** [d)]	**Composite flux measurement uncertainty** [e)]
Alkanes	15–30 %	5–10 %	3.5 %	10 %	20–35 %

[a)] Comparing mast wind averages with the 0–500 m GPS sonde averages, the max data spreads 16–30 % (1σ, 30 %)

[b)] The 1σ deviation among the wind data compared to the 0–500 m sonde is 18º. For a plume transect orthogonal to the wind direction, which is always the aim, this would give a 6 % error. For a measurement in 75º angle the error is 9 %.

[c)] Includes systematic and random errors in the cross section database.

[d)] The combined effects of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect and error of the SOF alkane mass retrieval. Estimated for SOF.

[e)] The composite square root sum of squares uncertainty

The main objective of this study was to demonstrate the SOF technique for measurements of fugitive VOC emissions in a real measurement situation. The measurements were based on a measurements protocol developed as part of the CEN WG 38 TC 264 work, see Annex. .

The general methodology followed, as given in the SOF CEN-protocol, is:

- Carry out the SOF measurements in a box around the area investigated, subtracting the measured VOC inflow from the outflow. Both inside and outside of the plant.
- The wind is obtained from an upwind mast of approximately 10 m, corresponding to a relatively undisturbed flow at 10 m. .
- The alkane composition for the background sources and source was evaluated by comparing to propane, hexane and cyclohexane The cyclo-hexane and hexane could be identified from the measured background spectra and or other sources inside the measurement area.
- For valid data is required a solar angle above 20^{o}, average wind speed above 1.5 m/s and below 12 m/s and at least 4 measurement transect per day downwind of each reported source. Additional criteria are found in the annex B.

4 Controlled VOC release setup

Twenty controlled release tests were made at a decommissioned refinery site. VOC (mainly propane) was released from different nodes planted at different heights and positions within a process unit. The release was run “blind”, e.g. the SOF and other remote sensing operators did not know which nodes were active and at what rate for respectively for the various test configurations. Each release test had duration of about 90 minutes.

The controlled release setup and operation was managed by INERIS, and actual configurations run were revealed after emission results were reported by the various instrument operators taking part in the validation. Figure 7 shows a view from the north of the release unit area, and Figure 8 describes the location of the release nodes within the unit. Table 4 summarizes the applied release node configurations for the 20 release experiments run in the validation survey.

Figure 7. Overview of the controlled release unit seen from the north. Map from Google Earth © 2018.

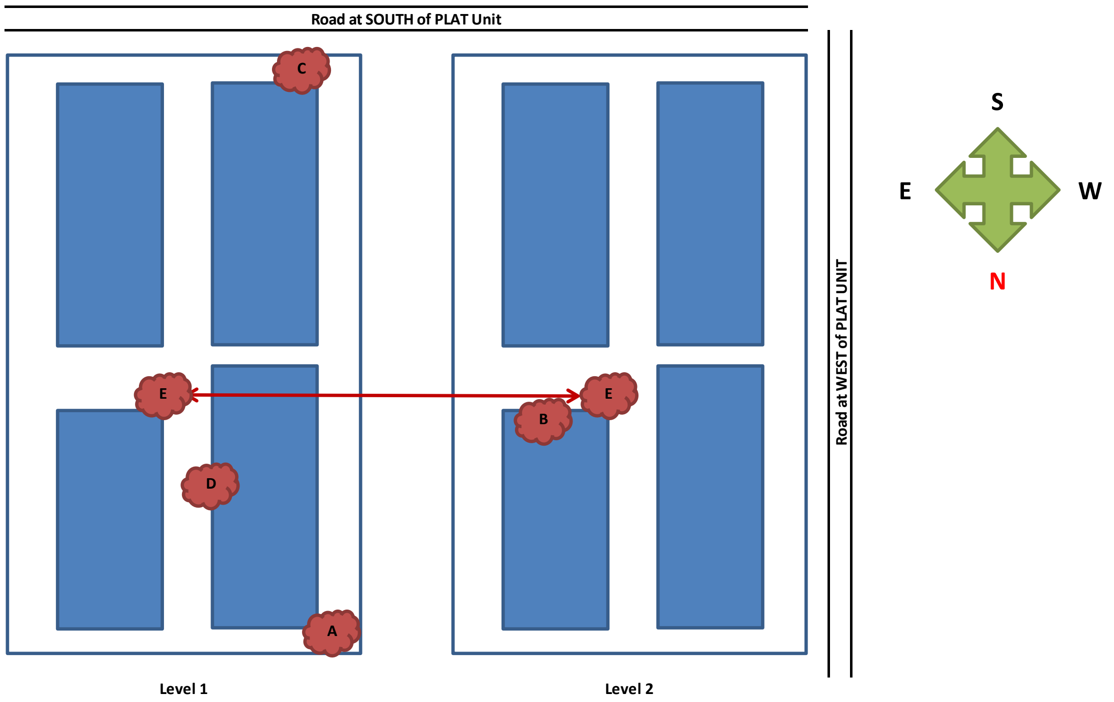

Figure 8. Overview of the location of the controlled release nodes (used with courtesy to INERIS from their report to WP7 of the CEN validation work). A, B, C and D correspond to point release nodes (1 m dispenser diameter) whereas node E is a line dispenser node extending from floor level 1 to level 2.

Table 4. Controlled release node configurations applied for the different release experiments, as operated and given by INERIS report to WP7 of this project. Released amounts in kg/h.

	Test 1	**Test 2**	**Test 3**	**Test 4**	**Test 5**	**Test 6**	**Test 7**	**Test 8**	**Test 9**	**Test 10**
A			8.87		7.39	1.80	1.65			4.63
B		14.85					1.65			4.63
C						7.21	1.65	8.87		4.63
D	5.07				1.85		1.65			4.63
E				9.75					11.62	
Total: (kg/h)	***5.07***	***14.85***	***8.87***	***9.75***	***9.24***	***9.01***	***6.59***	***8.87***	***11.62***	***18.51***
	Test 11	**Test 12**	**Test 13**	**Test 14**	**Test 15**	**Test 16**	**Test 17**	**Test 18**	**Test 19**	**Test 20**
A	1.93						7.39	18.86	1.65	3.14
B	7.71	9.75							1.65	3.14
C									1.65	3.14
D							1.85		1.65	3.14
E			14.74	16.61	4.77	0.78				
Total: (kg/h)	***9.64***	***9.75***	***14.74***	***16.61***	***4.77***	***0.78***	***9.24***	***18.86***	***6.59***	***12.55***

Table 5. Composition of the controlled release gas. Average molecular weight of the gas: 45.08 g/mol. Average carbon number: 3.07.

Compound	Composition (%)	Molar mass (g/mol)	Carbon number
ethane	0.05	30.07	2
propane	91.17	44.1	3
propene	2.05	42.08	3
i-butane	3.32	58.12	4
n-butane	2.20	58.12	4
1-butene	0.25	56.11	4
1,3-butadiene	0.27	54.09	4
i-pentane	0.48	72.15	5
n-pentane	0.21	72.15	5

The main constituent of the gas released during the tests were propane, but also some other alkanes and alkenes were present, see Table 5. The released gas had a composite molecular weight of 45.1 g/mol and an average carbon number of 3.1.

5 Results

In Table 6 the main SOF measurement results are summarized. Fourteen out of twenty release tests fulfilled the quality control criteria and these data were compared to the actual release rates. For the other 6 release tests the SOF quality criteria were not met, either since the wind was too low (<1.5 m/s) or the number of valid SOF plume transects was too few (<4). In the latter case, the reasons limiting the number of useable SOF transects were too low wind speed, too high and variable background plumes or instrument/vehicle issues. The elimination of the background sources and the SOF measurements for each controlled release experiment is described in further detail in the section below and the differences are further discussed in section 6.

Table 6. Summary of results from the 20 controlled release tests, September 22-29, 2016. N denotes number of valid SOF transects during the release test. A-E denotes which source release nodes that were active. SD = standard deviation of the N transects. Valid SOF tests are marked green, and non-valid ones are marked light red with the cause for non-validity indicated (N<4 or wind speed <1.5 m/s).

Release Test no.	**Source config.**	**Controlled Release rate (CR) (kg/h)**	**N**	**Wind speed (m/s)**	**Wind direction degree**	**Average measured emission SOF (kg/h)**	**SD SOF (kg/h)**	**Diff. SOF - CR (kg/h)**	**Relative difference (SOF-CR) /CR (%)**
1	D	5.07	8	4.2	203	5.3	0.8	0.23	4.5
2	B	14.85	16	3.4	181	12.6	4	-2.25	-15.2
3	A	8.87	8	2.7	211	12	1.5	3.13	35.3
4	E	9.75	13	4.6	225	14.8	5.8	5.05	51.8
5	*A+D*	*9.24*	*3(<4)*	*<1.5*	338	*N.A.*	*N.A.*	*N.A.*	*N.A.*
6	A+C	9.01	10	3	204	10.3	4.9	1.29	14.3
7	A+B+C+D	6.59	6	3.5	214	8.6	2.2	2.01	30.5
8	*C*	*8.87*	*3(<4)*	*3.6*	215	*N.A.*	*N.A.*	*N.A.*	*N.A.*
9	*E*	*11.62*	*3(<4)*	*2.4*	293	*N.A.*	*2.8*	*N.A.*	*N.A.*
10	*A+B+C+D*	*18.51*	*3(<4)*	*1.8*	296	*N.A.*	*N.A.*	*N.A.*	*N.A.*
11	A+B	9.64	14	3.5	248	10.1	2.9	0.46	4.8
12	B	9.75	11	3.1	247	8.3	2.1	-1.45	-14.9
13	*E*	*14.74*	*8*	*<1.5*	182	*N.A.*	*N.A.*	*N.A.*	*N.A.*
14	E	16.61	11	2.1	239	22.7	11.4	6.09	36.7
15	E	4.77	13	3.7	227	6.2	2.3	1.43	30.0
16	*E*	*0.78*	*3(<4)*	*4.6*	222	*N.A.*	*N.A.*	*N.A.*	*N.A.*
17	A+D	9.24	11	1.5	103	11.4	5.7	2.16	23.4
18	A	18.86	16	3.1	186	30.8	9.7	11.94	63.3
19	A+B+C+D	6.59	12	3.8	233	11.3	4.5	4.71	71.5
20	A+B+C+D	12.55	14	3.3	218	13.4	4	0.85	6.8
Total:		**142.2**				**177.8**		35.7	**25.1**

Elimination of interfering sources

In a standard SOF survey, measurements should ideally be carried out in a circle (or “box”) around the emission source, to be able to subtract the upwind gas flux (background) from the downwind one, on a continuous basis. Measurements are generally conducted over a longer time frame than in this experiment and planned according to favourable wind directions so that enough transects of source plumes and background is obtained. In the present controlled release survey each release was limited to 1.5 hours, and in order to obtain enough measurements of the source emission plume, emphasis was given to the downwind measurements, whereas background influence was judged by observing any baseline offset at plume edges, plume composition and by occasional upwind transects.

During the measurement survey several other sources of VOCs were observed, both sources inside the measurements area and background sources. Dependent on wind direction, sources were occasionally blowing into the site from adjacent plants in the north, or from a non-controlled active source inside the actual measurements area. The northern background source had an average emission of 121±41 kg/h, based on eight measurements from September 23, 26 and 27. The western background source was measured on six different days with an average emission of 4.1±3.9 kg/h. The northeast background source had an average emission of 5.9±2.0 kg/h, based on 20 measurements on 5 different days. The emission on September 28 stood out with 13.8±2.1 kg/h for this source, whereas the other days had emissions in the range 2-6 kg/h. Figure 9 shows an overview of observed background source areas adjacent to the controlled release site. Figure 10 shows an upwind background measurement during Release 7, September 26, 14:35.

The interfering source plumes could be identified from a different VOC composition than the controlled released plume (mainly propane), with a large fraction of heavier hydrocarbons (C_{6+} alkanes and cyclohexane). The main approach used in the data retrieval was therefore to discard the downwind SOF measurements with significant amounts of C_{6+} alkanes, i.e. when the corresponding flux of these were larger than 10 % of the total flux. However since the reported flux measurements are based on a combined retrieval of propane, hexane and cyclohexane, there is a positive influence in the measurements used to calculate the average emission. In Table 5 the fluxes of the C_{6+} alkane species in the different controlled gas releases is shown together with the fraction of this number compared to the total reported gas flux. As can be seen the background C_{6+} alkane emissions contribute to 3-15% of the total reported emissions, hence explaining part of the positive biases in the SOF measurements.

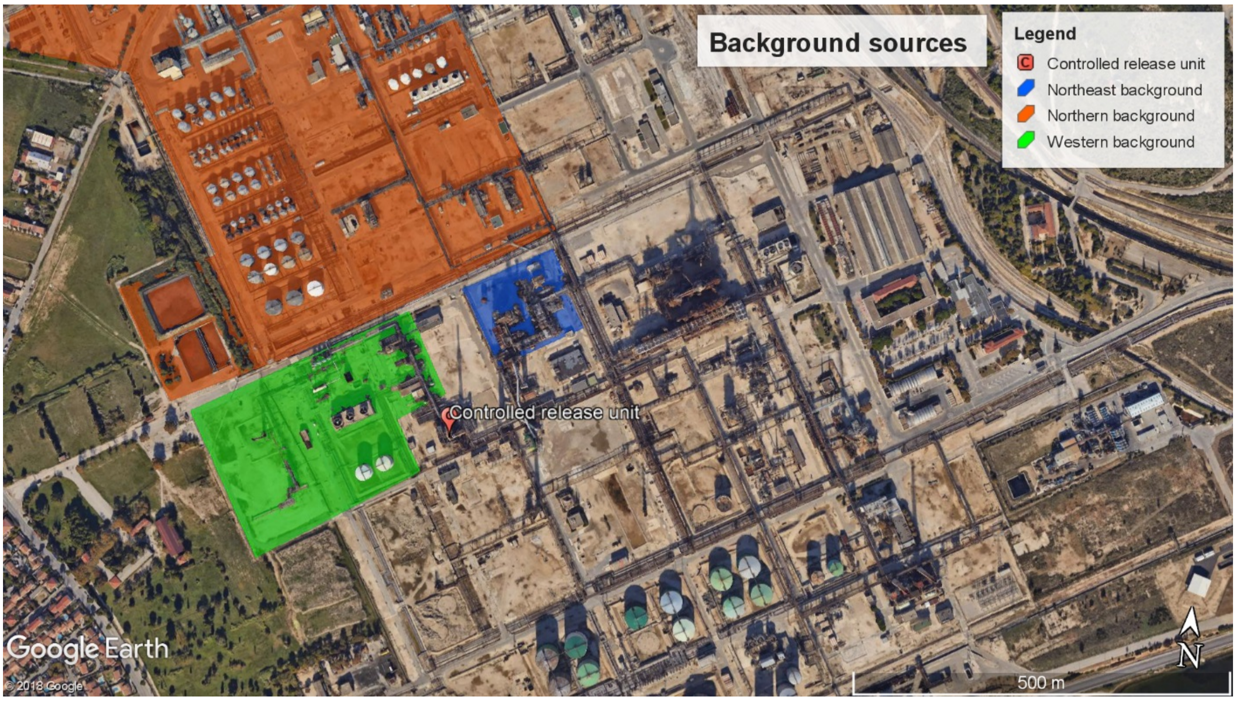

Figure 9. Identified background source areas adjacent to the controlled release site.

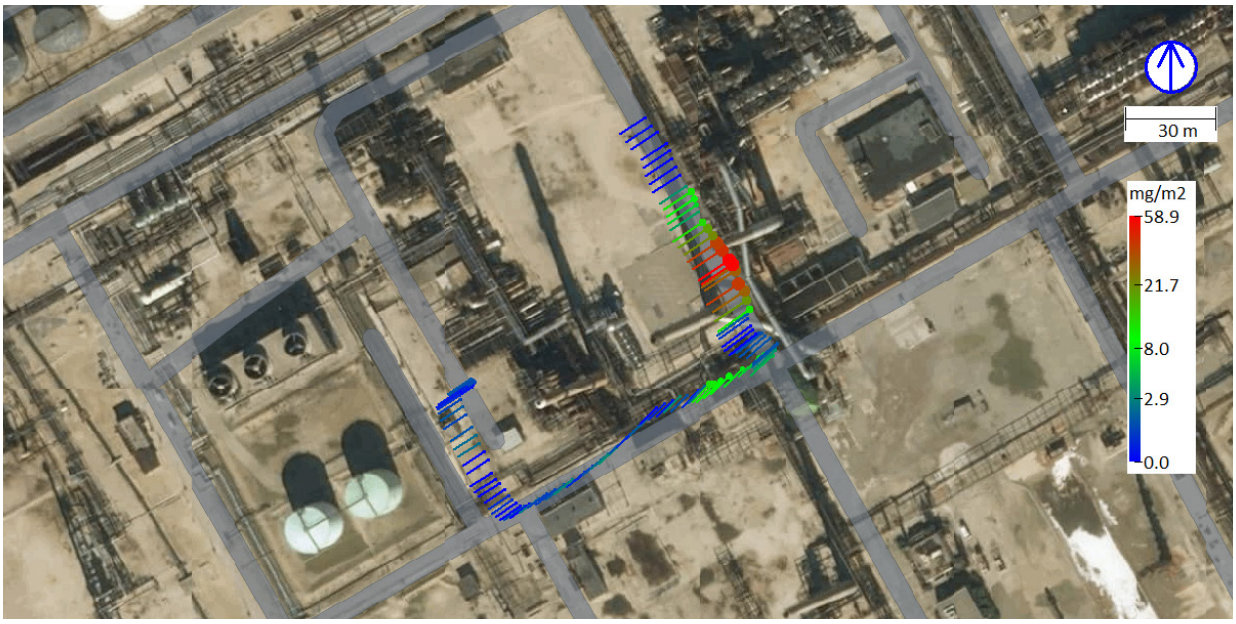

Figure 10. SOF measurements upwind and downwind of Release # 7 on September 26, 14:35. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m^2. North is upwards, as indicated by the blue arrow.

Table 7. Background observations during the various release tests, obtained as the combined hexane and cyclo-hexane mass in the reported SOF measurements. The fraction compared to the total reported flux is also given.

Controlled release number	**Background observations** [a)] **Average ± SD (kg/h)**	**Fraction of reported total emission**	**Wind speed m/s**	**Wind direction degree**
1	0.51±0.39	9.6%	4.2	203
2	0.69±0.58	5.5%	3.4	181
3	1.8±1.0	15.0%	2.7	211
4	2.4±2.4	16.2%	4.6	225
5	N.A. (not valid)	NA	*<1.5*	338
6	0.59±0.47	5.7%	3	204
7	1.1±0.8	12.8%	3.5	214
8	N.A. (not valid)	NA	*3.6*	215
9	14±5	NA	*2.4*	293
10	82±55	NA	*1.8*	296
11	0.4±0.5	4.0%	3.5	248
12	0.57±0.38	6.9%	3.1	247
13	N.A. (not valid)	NA	*<1.5*	182
14	1.3±0.6	5.7%	2.1	239
15	0.78±0.46	12.6%	3.7	227
16	N.A. (not valid)	NA	*4.6*	222
17	1.4±1.5	12.3%	1.5	103
18	3.9±3.1	12.7%	3.1	186
19	1.3±1.6	11.5%	3.8	233
20	0.38±0.48	2.8%	3.3	218

5.1 Controlled release 1

Release number 1 was run on September 22, 13:18-14:48. Release node D (on first level) was the only active node, with a release rate of 5.07 kg/h. Winds were south-westerly in the 3-5 m/s range. An emission of on average 5.3±0.6 kg/h was measured, based on eight SOF transects (Table 1). Figure 11 shows a plume transect example during controlled release 1. The SOF measurement route was blocked by a service truck for a few minutes during the experiment.

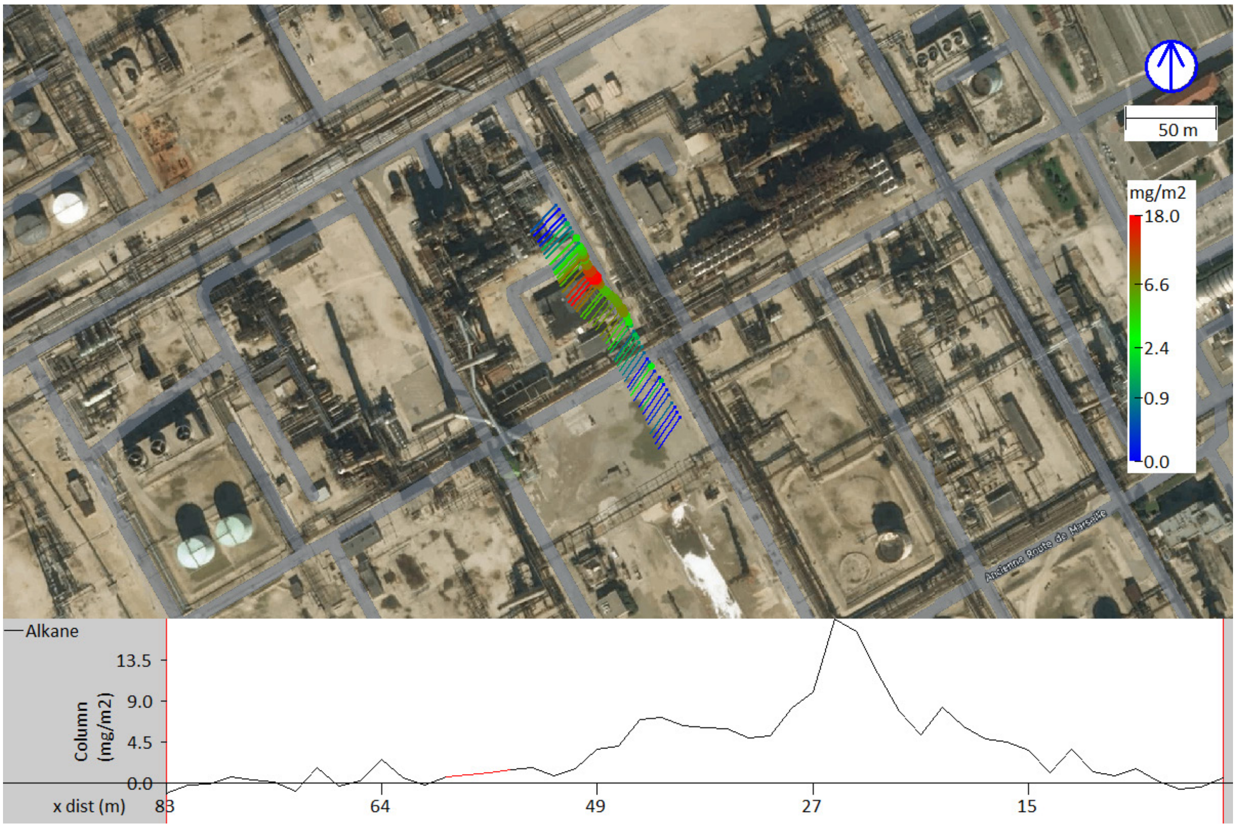

Figure 11. SOF measurement of the emission plume east of the release unit on September 22, 14:00. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m^2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m^2) as a function of the distance travelled through the plume cross section.

Table 8. Summary of SOF measurement results for Controlled Release 1.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160922	132744-144747	8	5.3	0.8	3.1-5.3	203-248
Average			**5.3**	**0.8**		
Median			**5.4**			

5.2 Controlled release 2

Release number 2 was run on September 22, 15:10-16:46. Release node B was the only active node, with a release rate of 14.85 kg/h. Winds were south-south-westerly in the 2.5-4 m/s range. An emission of on average 12.6±4.0 kg/h was measured, based on 16 SOF transects (Table 9). Figure 12 shows a plume transect example during controlled release 2.

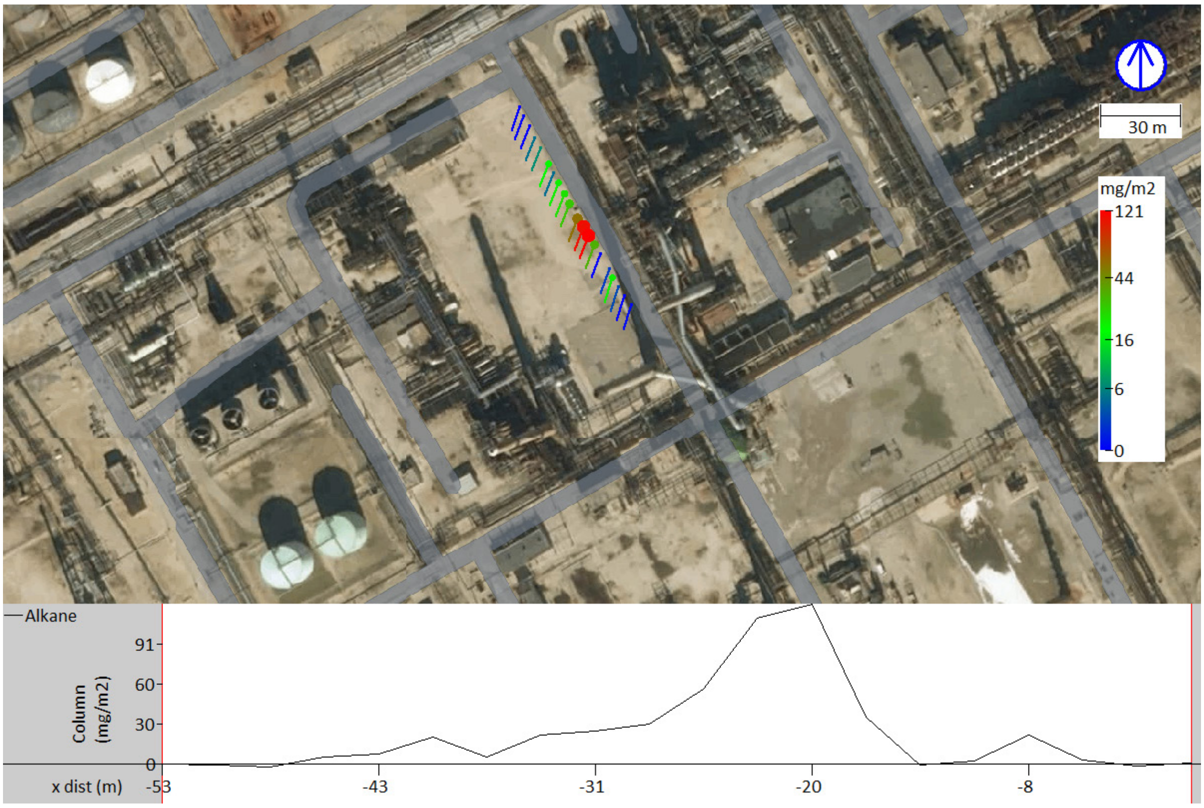

Figure 12. SOF measurement of the emission plume during Release 2 on September 22, 15:58. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m^2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m^2) as a function of the distance travelled through the plume cross section.

Table 9. Summary of SOF measurement results for Controlled Release 2.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160922	151725-164246	16	12.6	4.0	2.6-4.0	181-224
Average			**12.6**	**4.0**		
Median			**11.7**			

5.3 Controlled release 3

Release number 3 was run on September 23, 11:27-12:57. Release node A was the only active node, with a release rate of 8.87 kg/h. Winds were south-westerly in the 1.5-3 m/s range. An emission of on average 12.0±1.5 kg/h was measured, based on 8 SOF transects (Table 10). Figure 13 shows a plume transect example during controlled release 3. The VOC background during this experiment was often stronger than usual and interfering plumes were observed limiting the number of useful transects, see example in Figure 14.

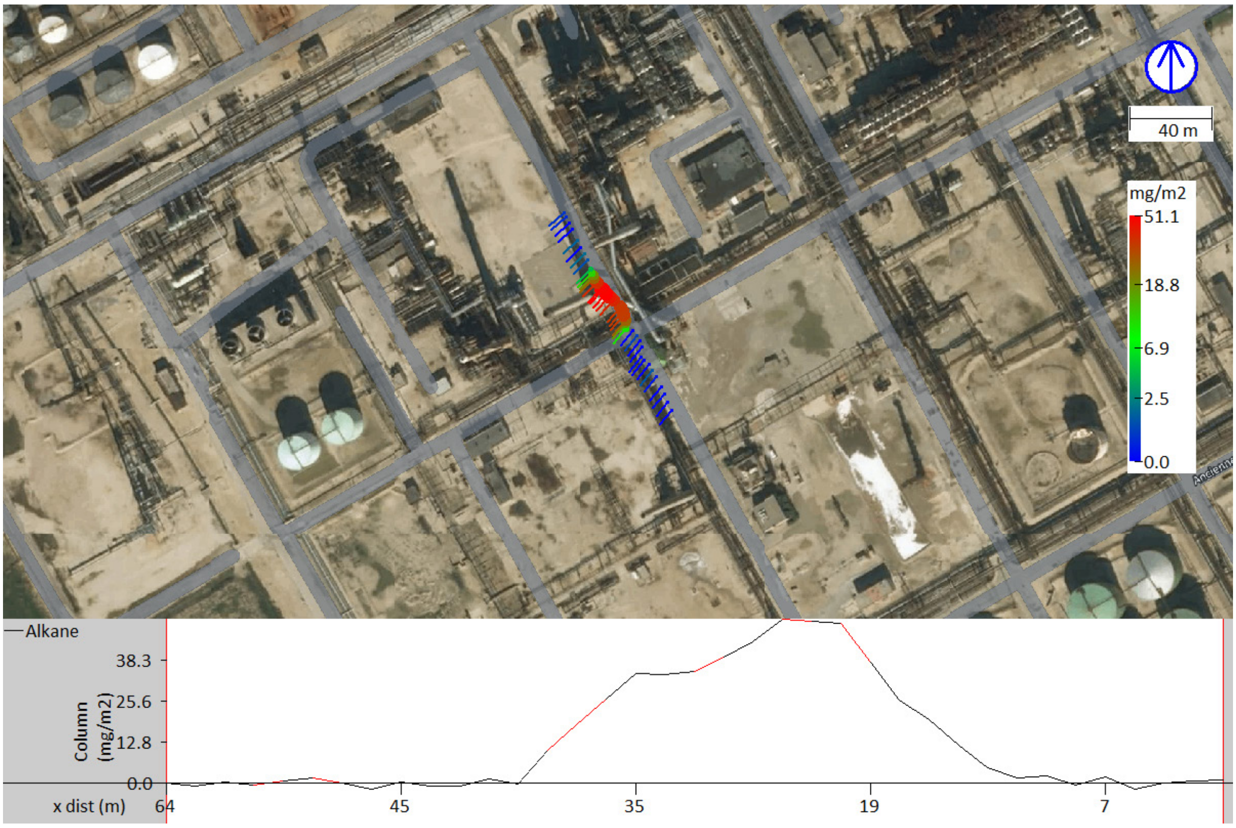

Figure 13. SOF measurement of the emission plume during Release 3 on September 23, 12:34. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

Table 10. Summary of SOF measurement results for Controlled Release 3.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160923	113954-125602	8	12.0	1.5	1.6-3.2	211-241
Average			**12.0**	**1.5**		
Median			**11.7**			

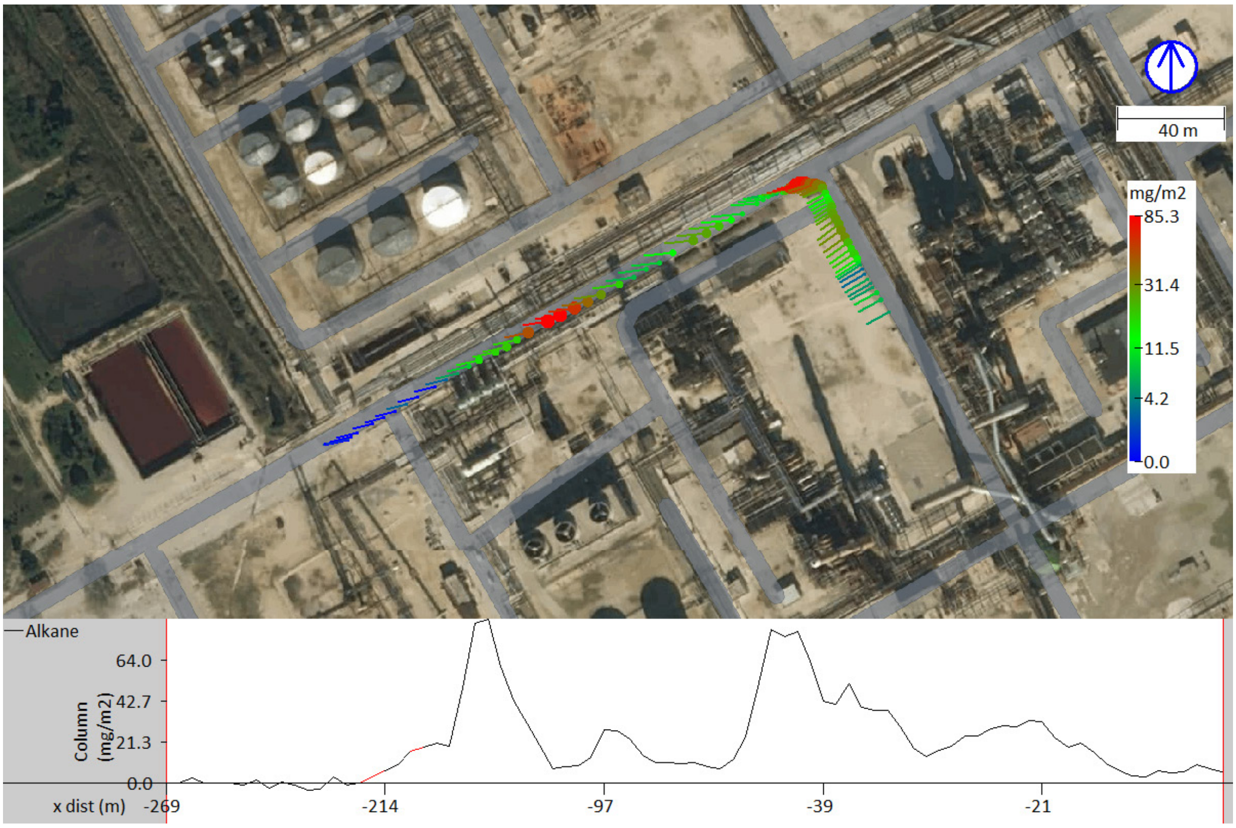

Figure 14. SOF measurement of the adjacent background plume during Release 3 on September 23, 12:26. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.4 Controlled release 4

Release number 4 was run on September 23, 14:00-15:30. Release node E was the only active node, with a release rate of 9.75 kg/h. Winds were south-westerly in the 3.5-5.5 m/s range. An emission of on average 14.8±5.8 kg/h was measured, based on 13 SOF transects (Table 11). Figure 15 shows a plume transect example during controlled release 4. Frequent comparably stronger adjacent background plumes were observed during this experiment increasing uncertainties.

Table 11. Summary of SOF measurement results for Controlled Release 4.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160923	141549-152554	13	14.8	5.8	3.6-5.4	225-257
Average			**14.8**	**5.8**		
Median			**14.5**			

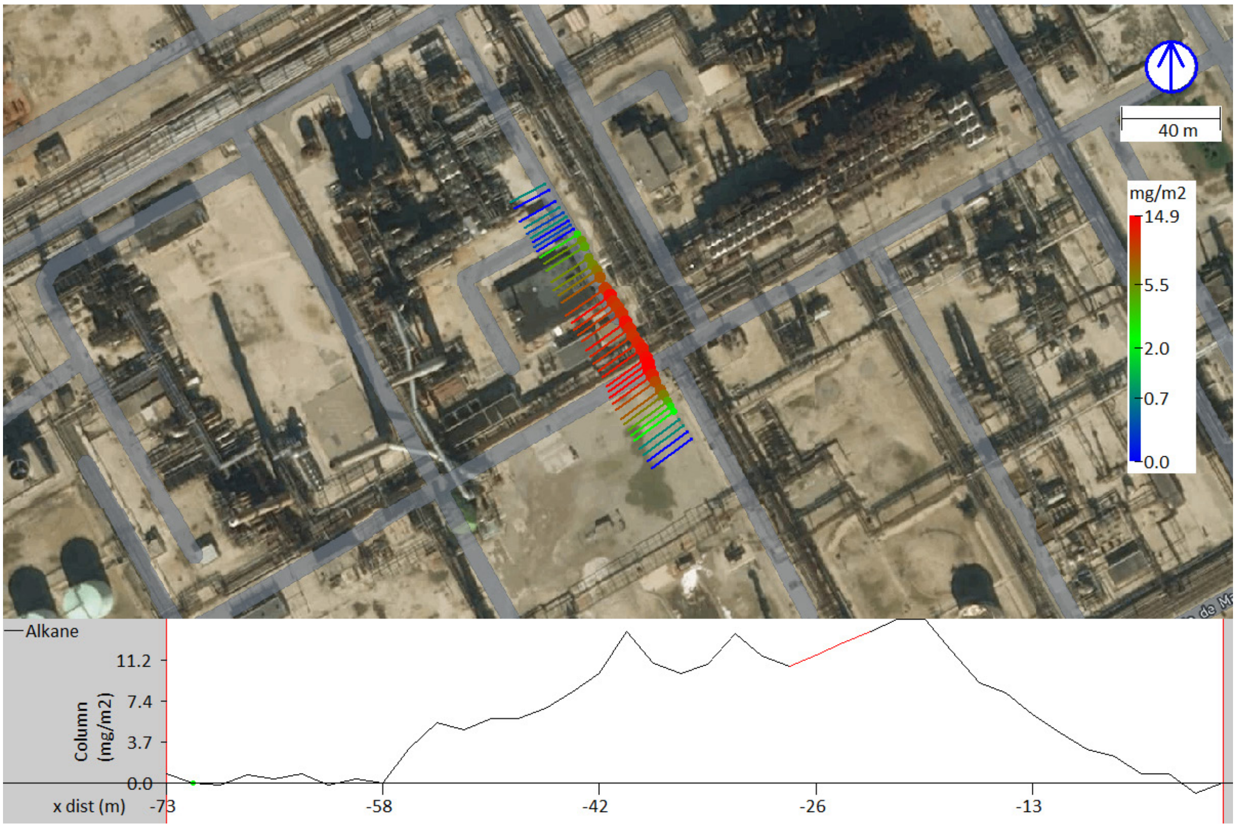

Figure 15. SOF measurement of the emission plume during Release 4 on September 23, 14:30. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.5 Controlled release 5

Release number 5 was run on September 26, 09:41-11:11. Release nodes A and D were active, with a total release rate of 9.24 kg/h, where node A released 7.39 kg/h and node D 1.85 kg/h. Winds were weak north-north-westerly in the 1-2 m/s range. This experiment suffered from too weak winds and very strong background plumes from the north, which led to less than four acceptable SOF transects during this configuration, and no acceptable data according to protocol is reported for Release 5. Figure 16 shows a plume transect of the northerly background plume during controlled release 5. The VOC background in this transect was about 80 kg/h.

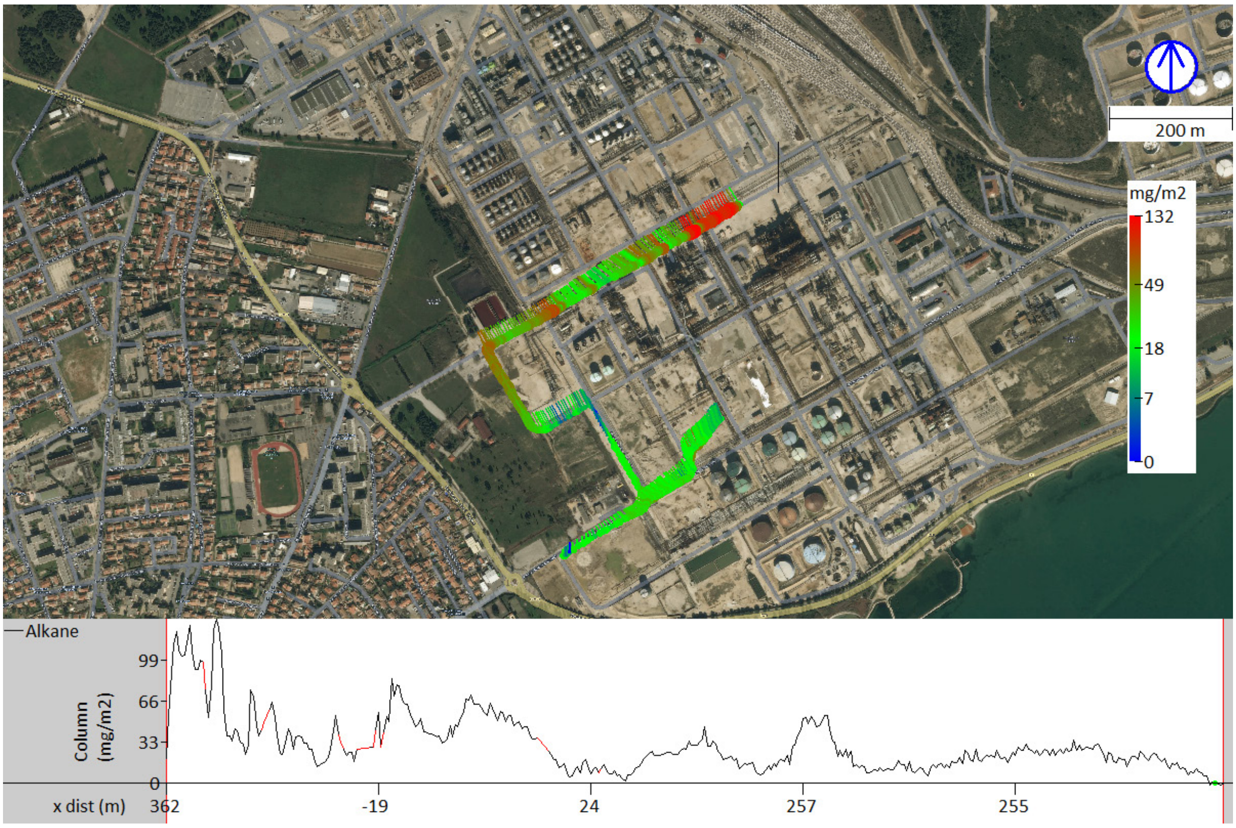

Figure 16. SOF measurement of the northerly background plume during Release 5 on September 26, 10:20. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.6 Controlled release 6

Release number 6 was run on September 26, 12:00-13:30. Release nodes A and C were active, with a total release rate of 9.01 kg/h, where node A released 1.8 kg/h and node C 7.21 kg/h. Winds were south-westerly in the 2-3.5 m/s range. An emission of on average 10.3±4.9 kg/h was measured, based on 10 SOF transects (Table 12). Figure 17 shows a plume transect example during controlled release 6.

Table 12. Summary of SOF measurement results for Controlled Release 6.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160923	115930-130502	10	10.3	4.9	2.1-3.5	204-252
Average			**10.3**	**4.9**		
Median			**9.2**			

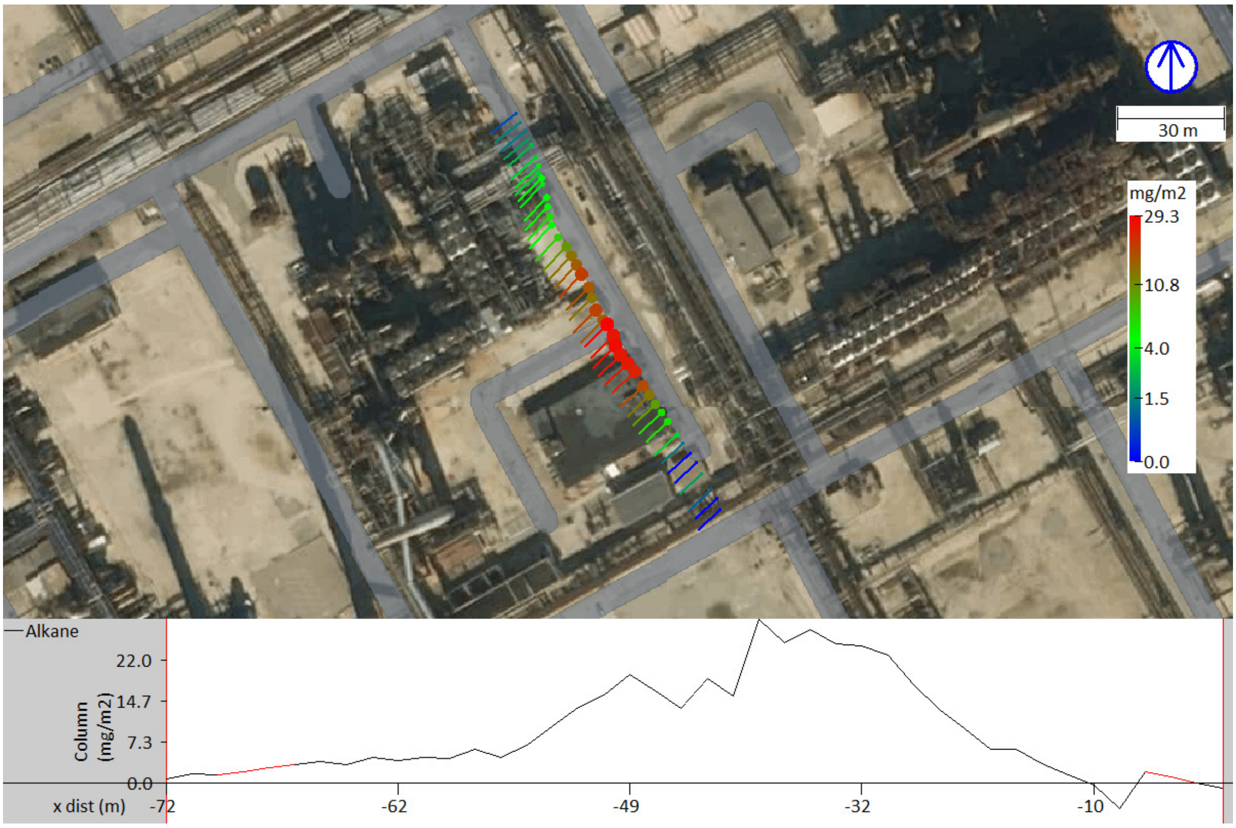

Figure 17. SOF measurement of the emission plume during Release 6 on September 26, 12:15. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.7 Controlled release 7

Release number 7 was run on September 26, 14:30-16:00. Release nodes A, B, C and D were active, with a total release rate of 6.59 kg/h, where each node released 1.65 kg/h. Winds were west-south-westerly in the 3-4 m/s range. An emission of on average 8.6±2.2 kg/h was measured, based on 6 SOF transects (Table 13). Figure 18 shows a plume transect example during controlled release 7. As seen the plume is comparably wide with multiple VOC peaks, reflecting the multi-source node configuration.

Table 13. Summary of SOF measurement results for Controlled Release 7.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160926	145347-155341	6	8.6	2.2	3.3-4.0	214-253
Average			**8.6**	**2.2**		
Median			**8.0**			

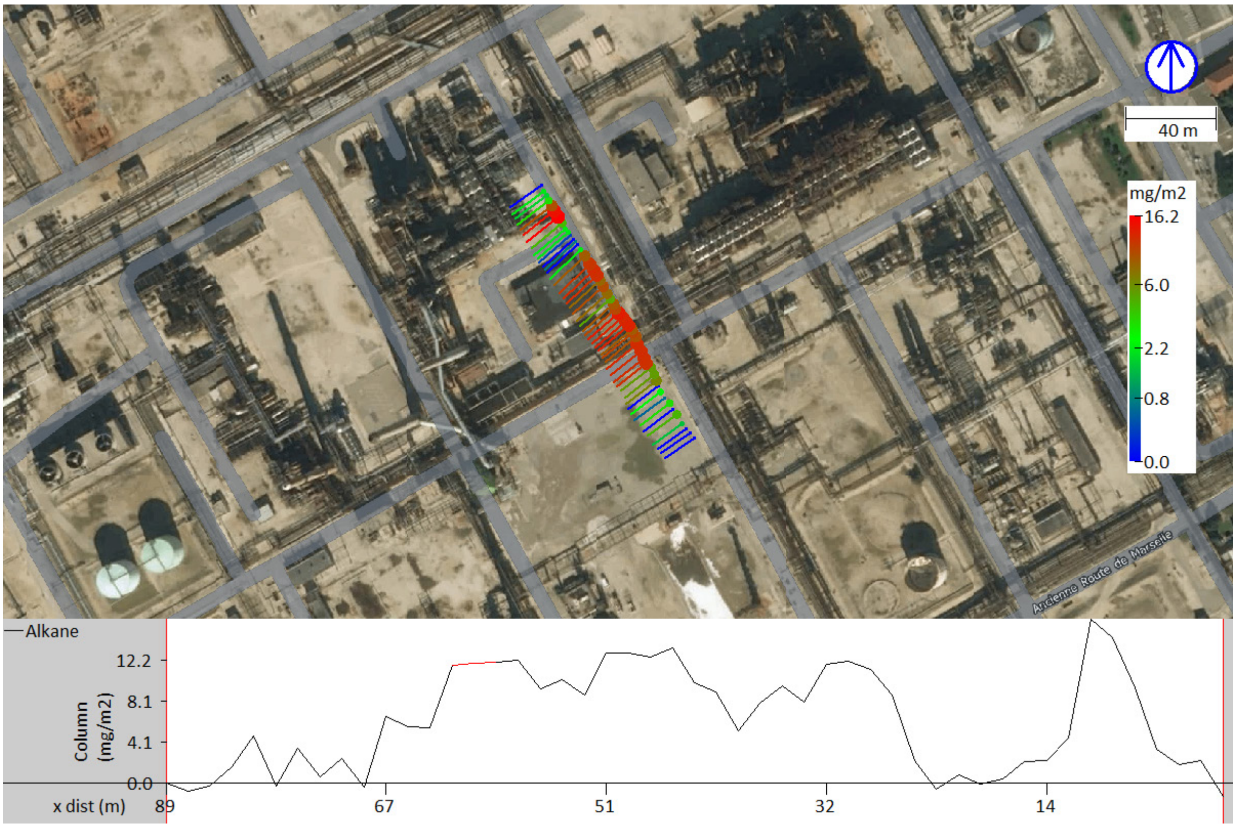

Figure 18. SOF measurement of the emission plume during Release 7 on September 26, 14:54. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.8 Controlled release 8

Release number 8 was run on September 26, 16:05-17:35. Release node C was the only active node, with a total release rate of 8.87 kg/h. Winds were south-westerly in the 3-4 m/s range. About 25 minutes into the experiment the SOF truck got two flat tires (due rusty spikes from the road) and the sampling had to be aborted. Too few transects (<4) were sampled for a valid emission estimate according to protocol.

5.9 Controlled release 9

Release number 9 was run on September 27, 09:35-11:04. Release node E was the only active node, with a total release rate of 11.62 kg/h. Winds were weak north-westerly in the 2-3 m/s range. This experiment suffered from weak winds and strong, variable background plumes from the north, which led to less than four acceptable SOF transects during this configuration, and no acceptable data according to protocol is reported for Release 9. In the first assessment reported, a doublet of the same transect (at 11:00) was included which has now been removed. Figure 19 shows a plume transect of the northerly background plume during controlled release 9. A significant source of cyclohexane blew in from north during this experiment.

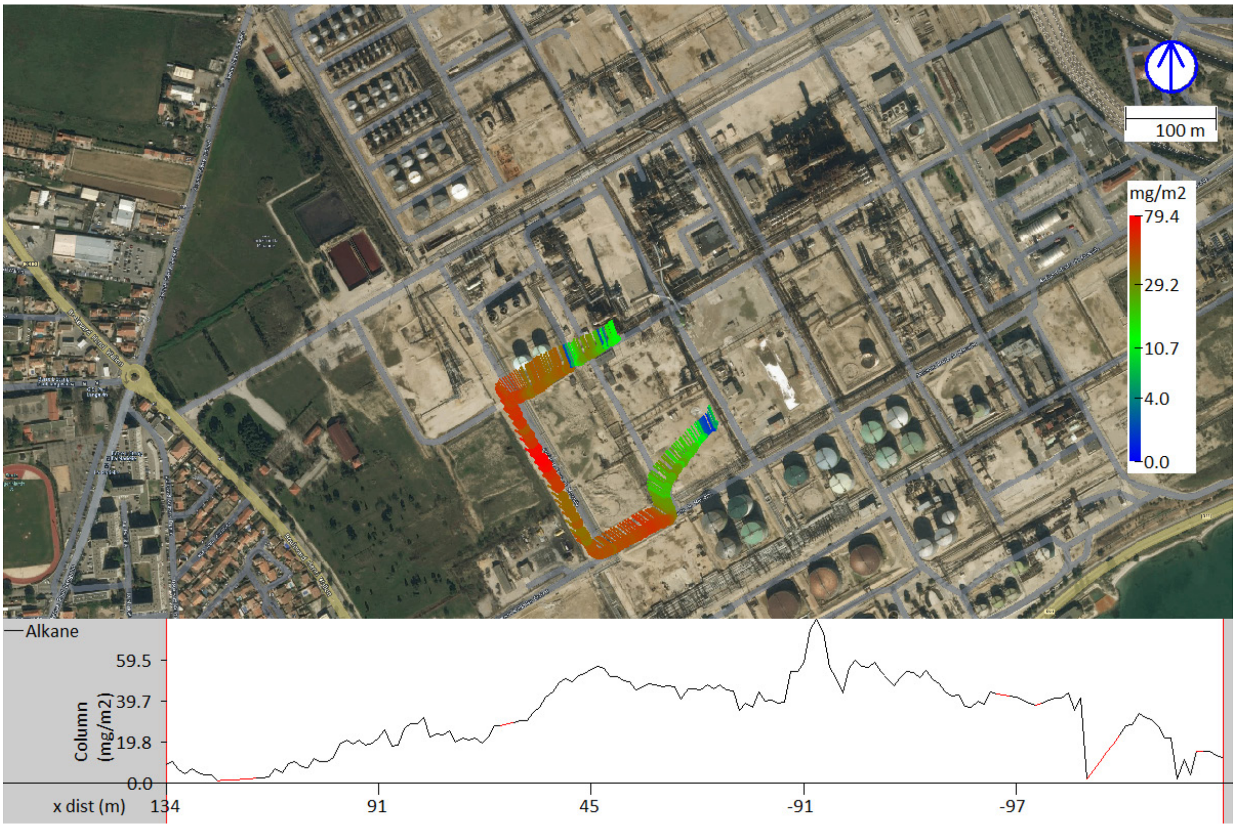

Figure 19. SOF measurement of the strong northerly background plume during Release 9 on September 27, 10:40. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.10 Controlled release 10

Release number 10 was run on September 27, 11:30-13:05. Release nodes A, B, C and D were active, with a total release rate of 18.51 kg/h, where each node released 4.63 kg/h. Winds were weak and variable north-westerly in the 1.5-3 m/s range. This experiment suffered from strong, variable background plumes from the north, which led to less than four acceptable SOF transects during this configuration, and no acceptable data according to protocol is reported for Release 10.

Figure 20 shows a plume transect of the northerly background plume during controlled release 10. The VOC background observed during the Release 10 was in the range 10-160 kg/h, and on average 82±55 kg/h based on 10 SOF transects. A significant source of cyclohexane blew in from north.

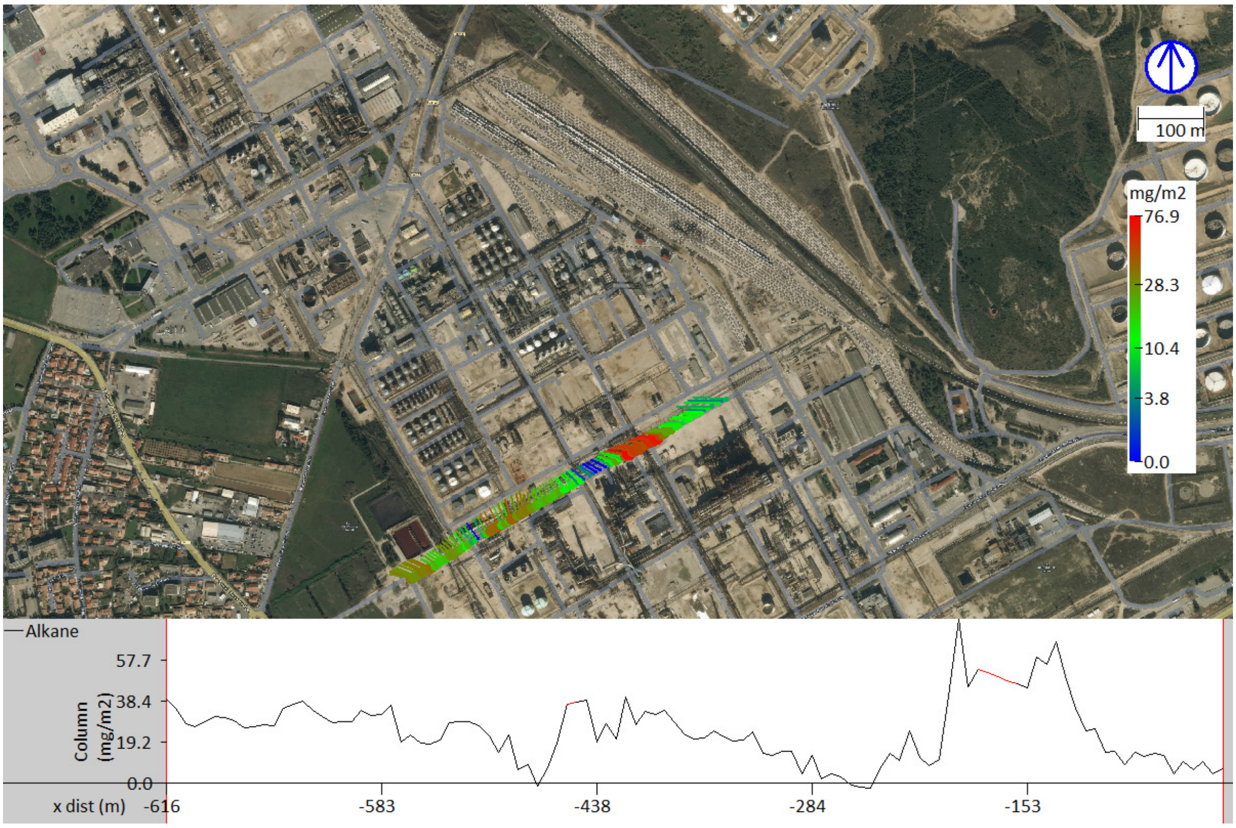

Figure 20. SOF measurement of the strong northerly background plume during Release 10 on September 27, 12:15. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.11 Controlled release 11

Release number 11 was run on September 27, 14:00-15:30. Release nodes A and B were active, with a total release rate of 9.64 kg/h, where node A released 1.93 kg/h and node B 7.71 kg/h. Winds were westerly in the 3-4 m/s range. An emission of on average 10.1±2.9 kg/h was measured, based on 14 SOF transects (Table 14). Figure 21 shows a plume transect example during controlled release 11.

Table 14. Summary of SOF measurement results for Controlled Release 11.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160927	142302-153354	14	10.1	2.9	2.6-4.3	248-287
Average			**10.1**	**2.9**		
Median			**10.2**			

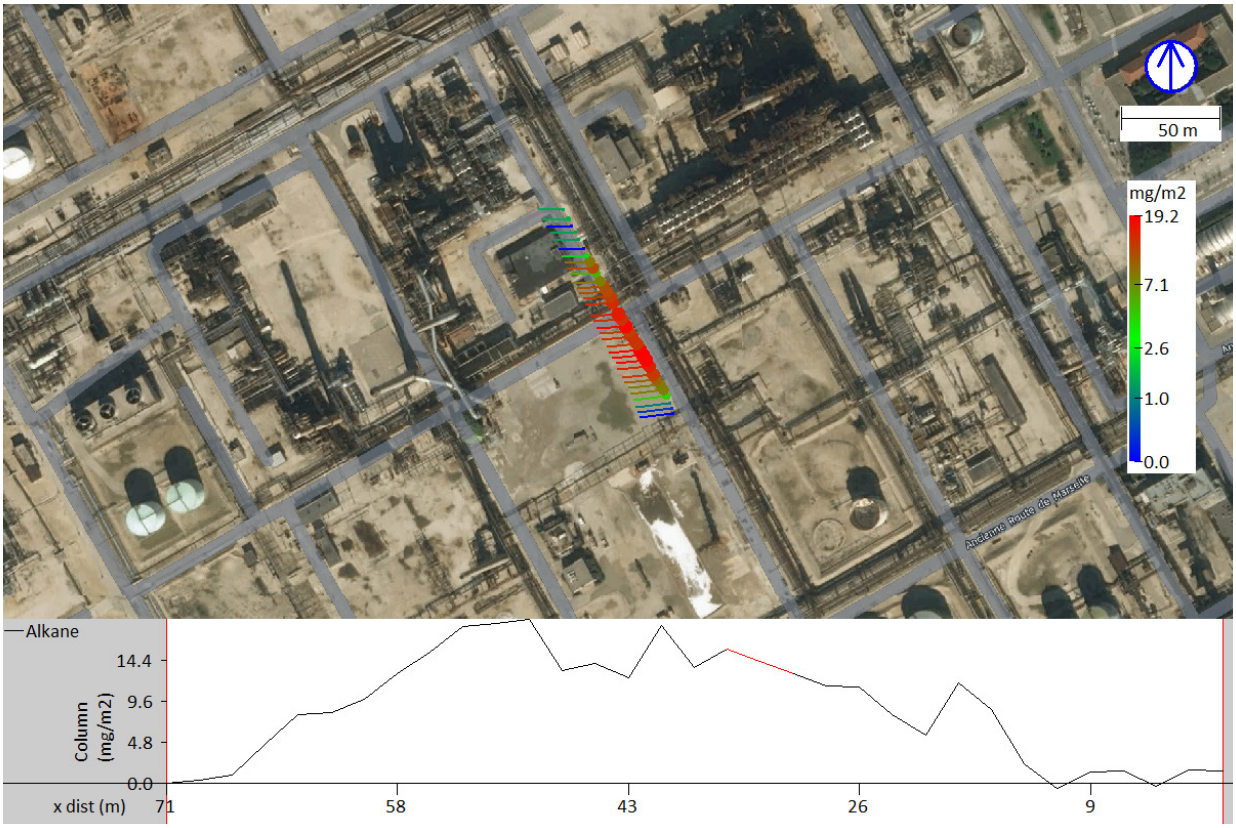

Figure 21. SOF measurement of the emission plume during Release 11 on September 27, 14:48. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.12 Controlled release 12

Release number 12 was run on September 27, 15:55-17:25. Release B were the only node active, with a total release rate of 9.75 kg/h. Winds were westerly in the 3-4 m/s range. An emission of on average 8.3±2.1 kg/h was measured, based on 11 SOF transects (Table 15). Figure 22 shows a plume transect example during controlled release 12.

Table 15. Summary of SOF measurement results for Controlled Release 12.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160927	160104-171658	11	8.3	2.1	2.8-3.8	247-272
Average			**8.3**	**2.1**		
Median			**9.2**			

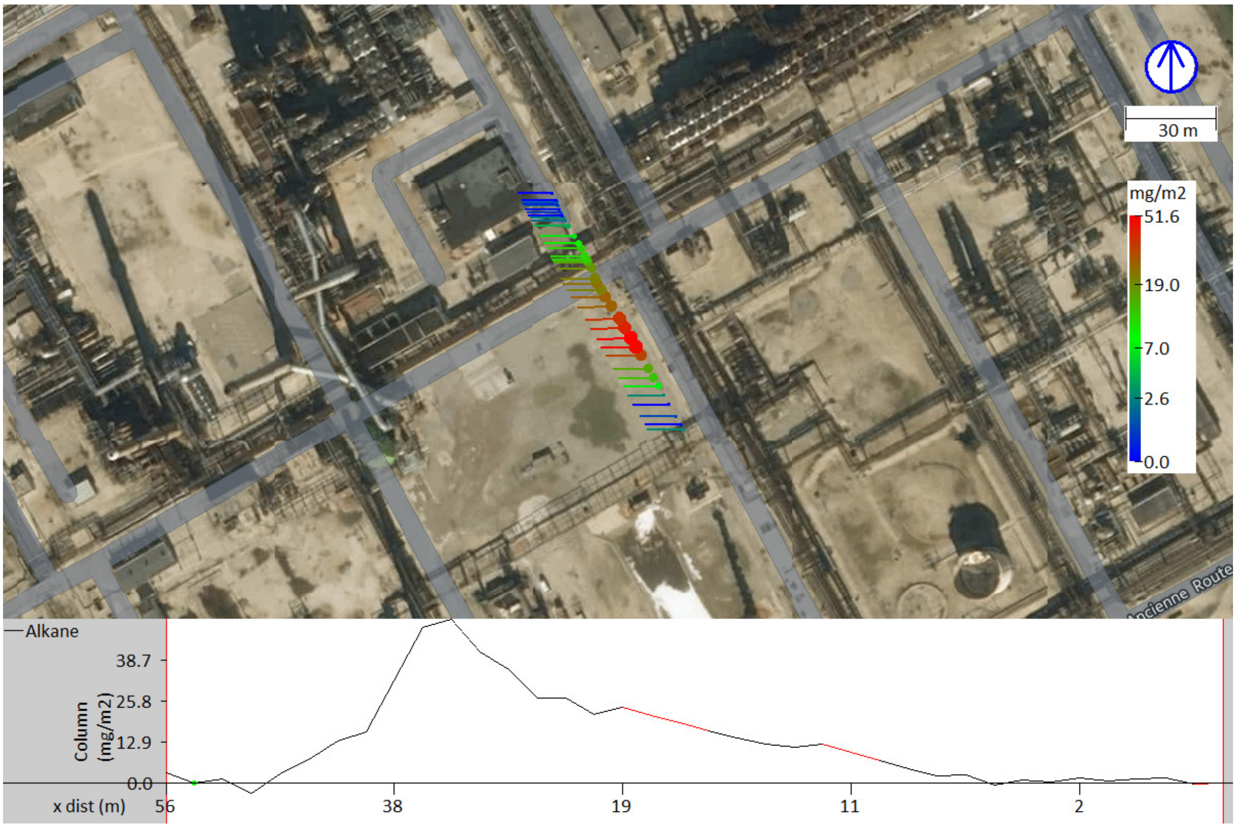

Figure 22. SOF measurement of the emission plume during Release 12 on September 27, 17:15. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.13 Controlled release 13

Release number 13 was run on September 28, 10:07-11:37. Release node E was the only node active, with a total release rate of 14.74 kg/h. Winds were very weak from south to southwest. This experiment suffered from too weak winds (<1.5 m/s) which led no acceptable SOF transects during this configuration, and no valid data according to protocol is reported for Release 13.

5.14 Controlled release 14

Release number 14 was run on September 28, 12:05-13:05. Release node E was the only node active, with a total release rate of 16.61 kg/h. Winds were westerly in the 1.5-3.5 m/s range. An emission of on average 22.7±11.4 kg/h was measured, based on 11 SOF transects (Table 16). Figure 23 shows a plume transect example during controlled release 14. Occasionally when wind turned a bit more north-westerly, stronger upwind plumes were observed during this experiment.

Table 16. Summary of SOF measurement results for Controlled Release 14.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160928	121439-133120	11	22.7	11.4	1.6-3.5	239-284
Average			**22.7**	**11.4**		
Median			**19.1**			

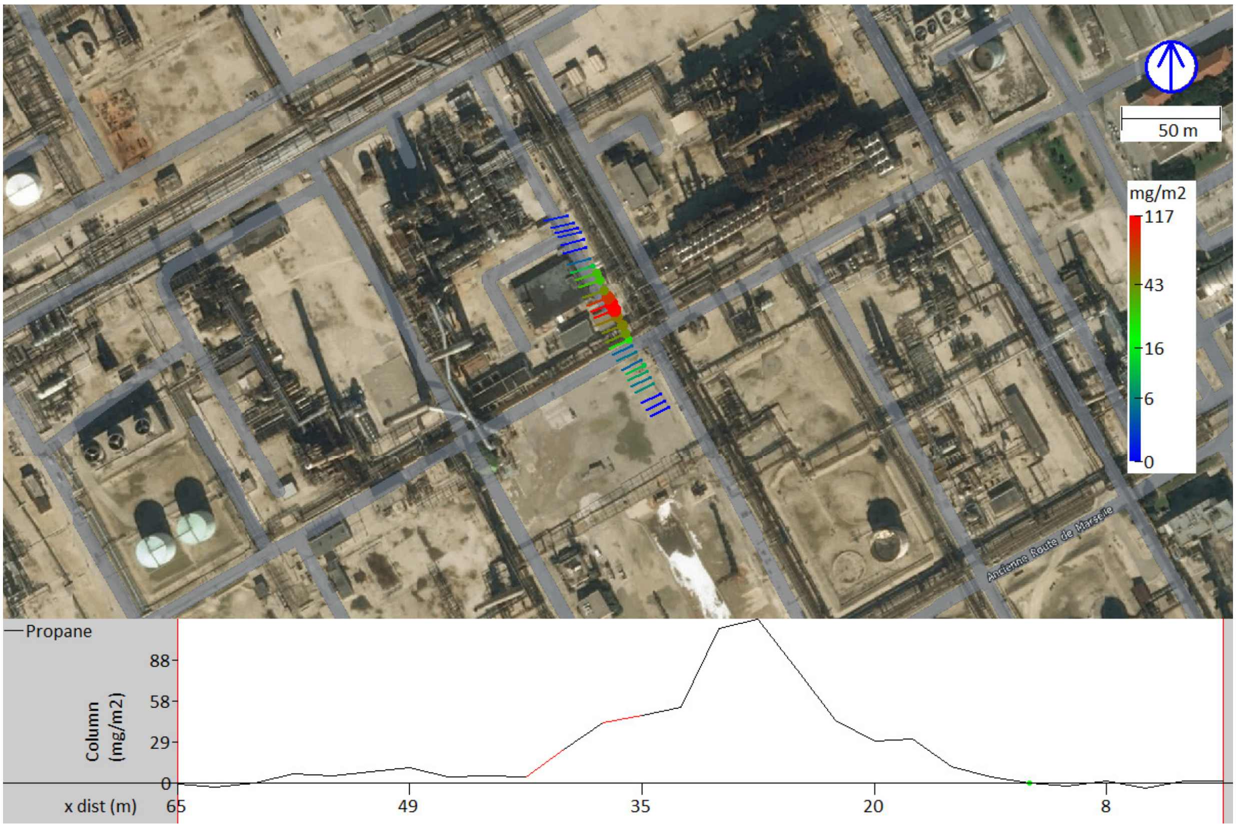

Figure 23. SOF measurement of the emission plume during Release 14 on September 28, 12:55. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

5.15 Controlled release 15

Release number 15 was run on September 28, 14:35-16:00. Release node E was the only node active, with a total release rate of 4.77 kg/h. Winds were westerly in the 2.5-4.5 m/s range. An emission of on average 6.2±2.3 kg/h was measured, based on 13 SOF transects (Table 17). Figure 24 shows a plume transect example during controlled release 15. A strong petroleum/sweet smell and plume was observed in the unit north of the controlled release unit, see Figure 25, sometimes interfering with the controlled release plume on the northern edge. The magnitude of this northern source was 17.5±5.4 kg/h during this experiment, based on 5 SOF transects.

Table 17. Summary of SOF measurement results for Controlled Release 15.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160928	145048-160348	13	6.2	2.3	2.4-4.6	227-268
Average			**6.2**	**2.3**		
Median			**5.8**			

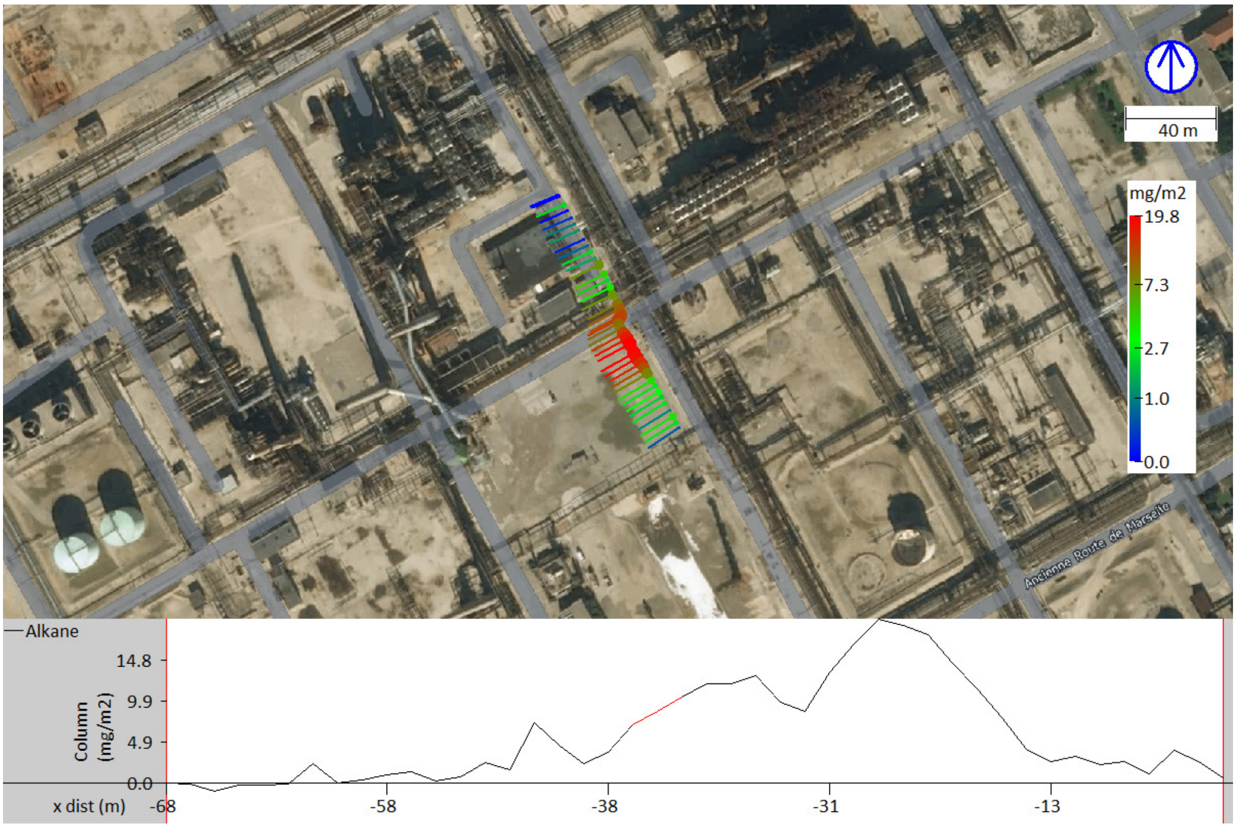

Figure 24. SOF measurement of the emission plume during Release 15 on September 28, 15:00. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

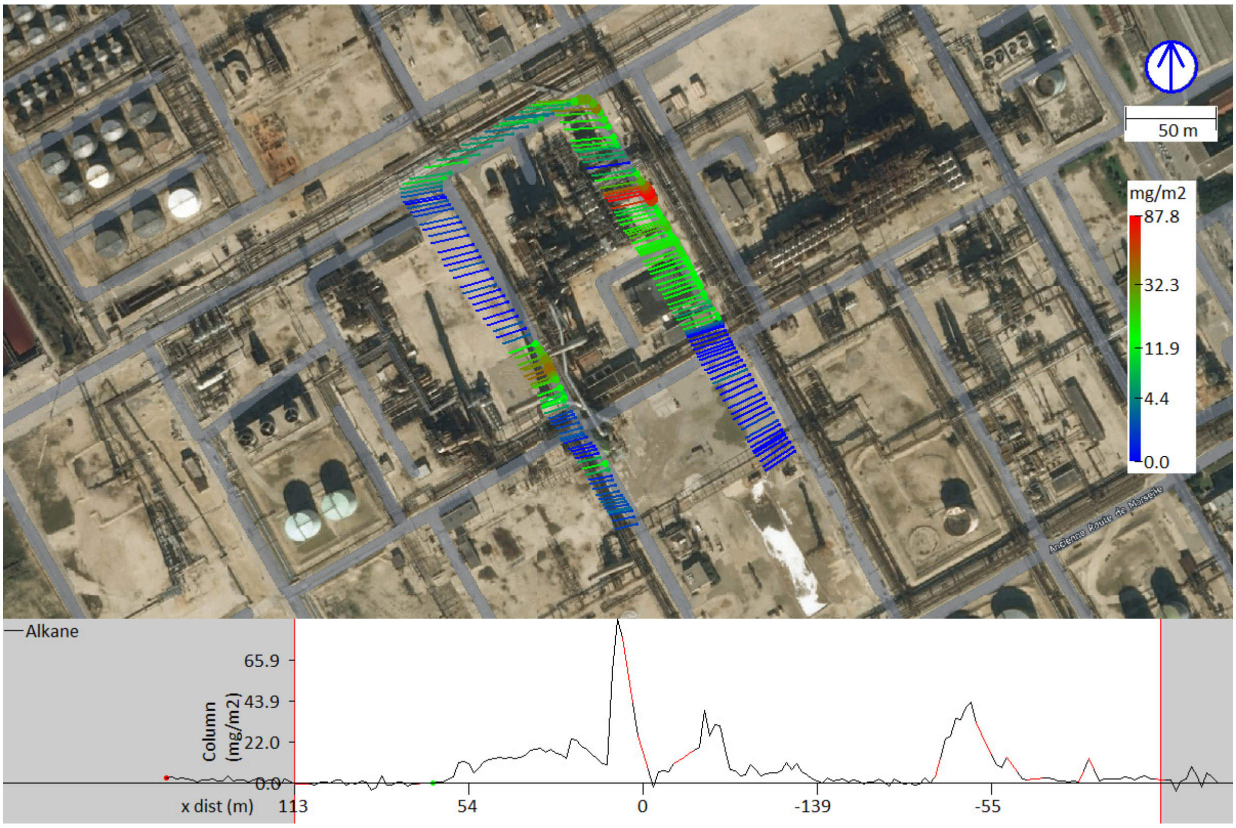

Figure 25. SOF measurement of the emission plume during Release 15 on September 28, 15:15, also showing adjacent source in unit north of the controlled release unit. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m^2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m^2) as a function of the distance travelled through the plume cross section.

5.16 Controlled release 16

Release number 16 was run on September 28, 16:45-17:52. Release node E was the only node active, with a total release rate of 0.78 kg/h. Winds were south-westerly in the 3-5.5 m/s range. This experiment was run late in the day, excluding SOF from the last 30 minutes of the experiment as the sun angle then was below 20 degrees, according to the SOF protocol. This in combination with the more south-westerly wind that merged the controlled release plume with the interfering source discussed for Release 15, limited the number of valid SOF transects. Too few transects (<4) were sampled for a valid emission estimate according to protocol for this release test.

5.17 Controlled release 17

Release number 17 was run on September 29, 10:50-12:15. Release nodes A and D were active, with a total release rate of 9.24 kg/h, where node A contributed with 7.39 kg/h and node D 1.85 kg/h. Winds were weak south-easterly about 1.5-2 m/s. An emission of on average 11.4±5.7 kg/h was measured, based on 11 SOF transects (Table 18). Figure 26 shows a plume transect example during controlled release 17.

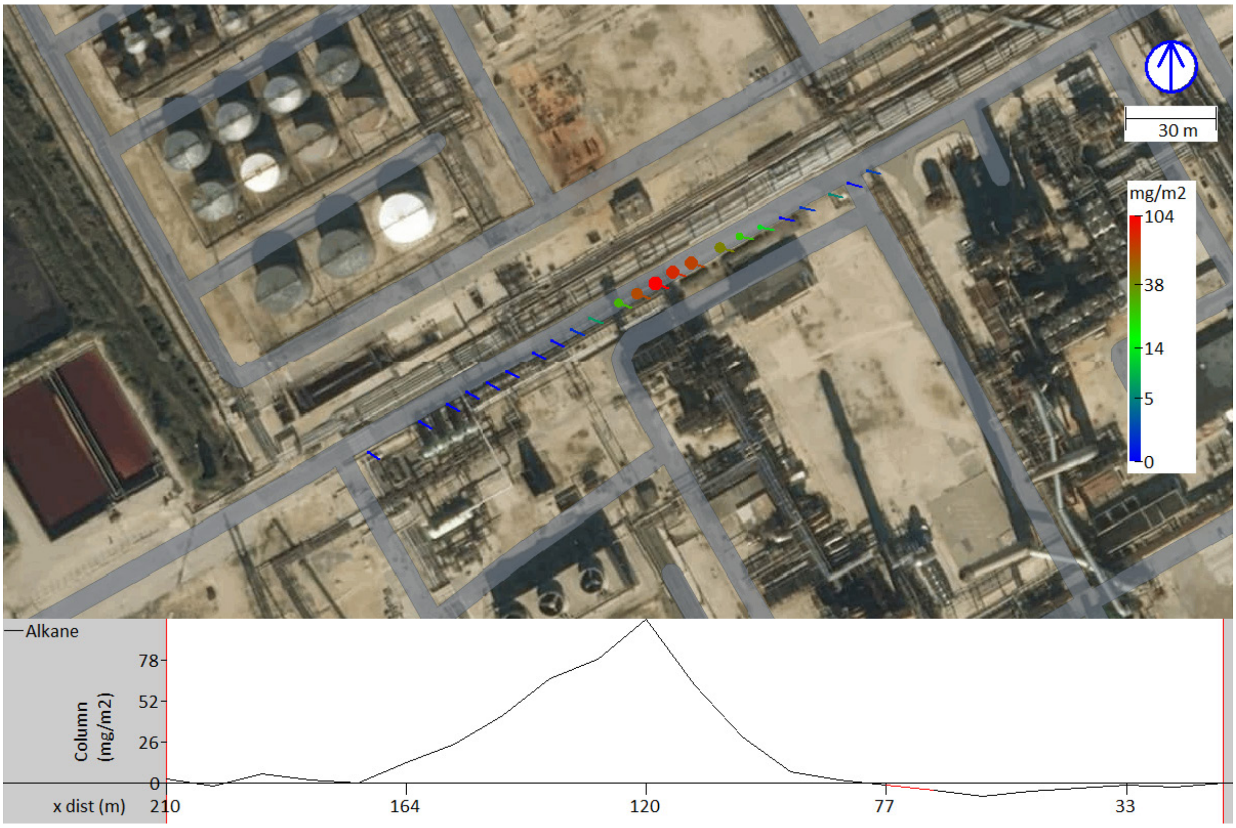

Figure 26. SOF measurement of the emission plume during Release 17 on September 29, 12:12. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

Table 18. Summary of SOF measurement results for Controlled Release 17.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160929	111627-121458	11	11.4	5.7	1.3-1.8	103-209
Average			**11.4**	**5.7**		
Median			**10.1**			

5.18 Controlled release 18

Release number 18 was run on September 29, 12:38-13:52. Release nodes A was the only node active, with a total release rate of 18.86 kg/h. Winds were predominantly south-westerly about 2.5-3.5 m/s. An emission of on average 30.8±9.7 kg/h was measured, based on 16 SOF transects (Table 19). Figure 27 shows a plume transect example during controlled release 18. As seen, the controlled release plume occasionally merged with an interfering plume from the unit northeast of the release unit, increasing uncertainties in the release plume edge allocation and hence in the flux estimate.

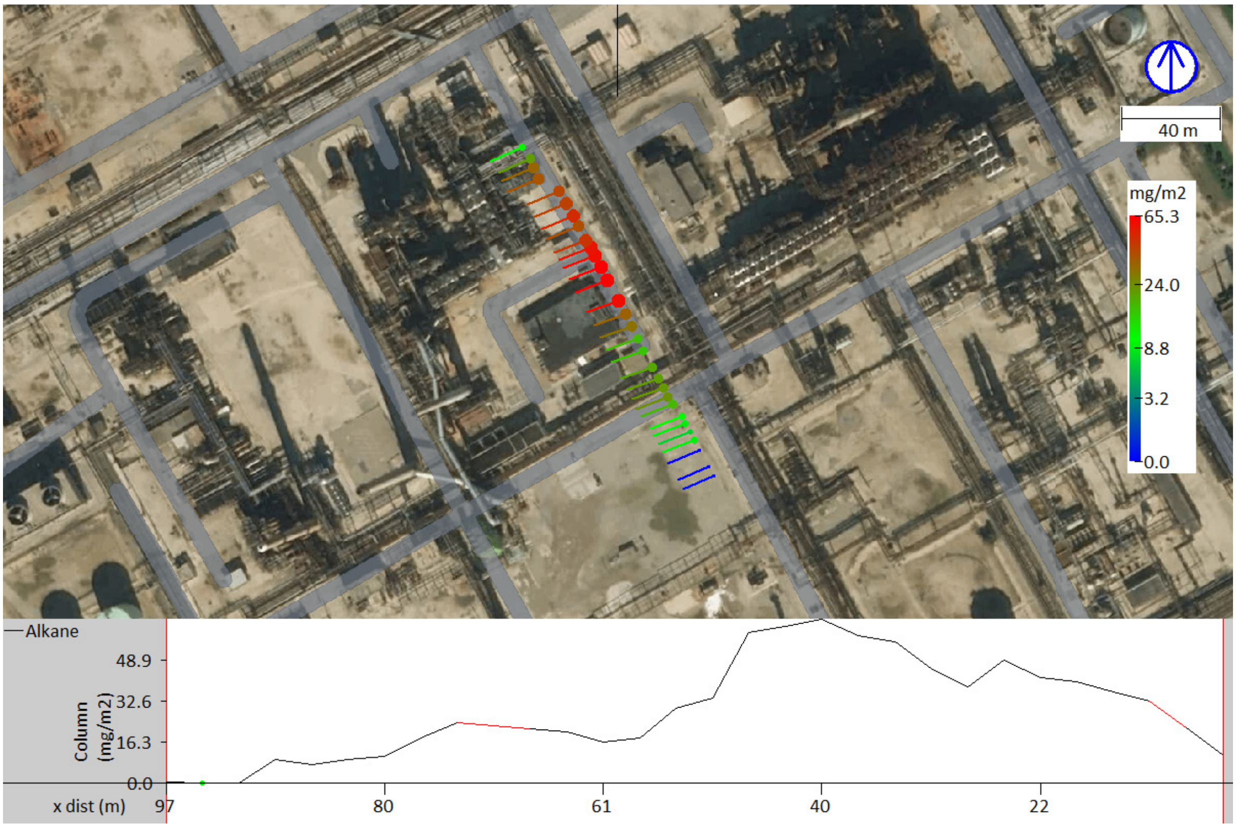

Figure 27. SOF measurement of the emission plume during Release 18 on September 29, 12:58. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

Table 19. Summary of SOF measurement results for Controlled Release 18.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160929	125150-135042	16	30.8	9.7	2.6-3.7	186-248
Average			**30.8**	**9.7**		
Median			**28.8**			

5.19 Controlled release 19

Release number 19 was run on September 29, 14:10-15:10. Release nodes A, B, C and D were active, with a total release rate of 6.59 kg/h and each node released 1.65 kg/h. Winds were predominantly south-westerly about 3-4.5 m/s. An emission of on average 11.3±4.5 kg/h was measured, based on 12 SOF transects (Table 20). Figure 28 shows a plume transect example during controlled release 19. As seen, the controlled release plume occasionally merged with an interfering plume from the unit northeast of the release unit, increasing uncertainties in the release plume edge allocation and hence in the flux estimate. Figure 29 further exemplifies the situation, where the controlled release plume is first measured nearby and then at a more appropriate distance, but where then the plume is merging with the interfering source in the northeast unit.

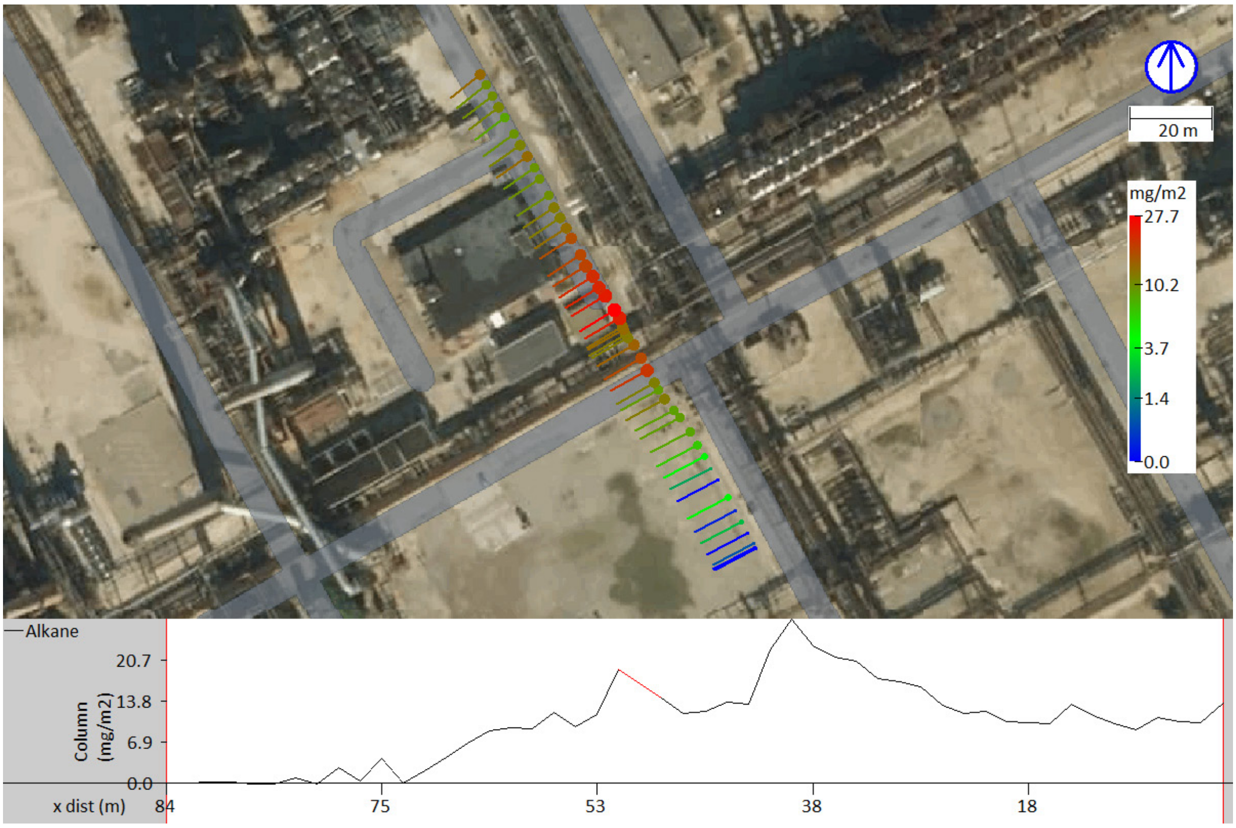

Figure 28. SOF measurement of the emission plume during Release 19 on September 29, 14:31. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

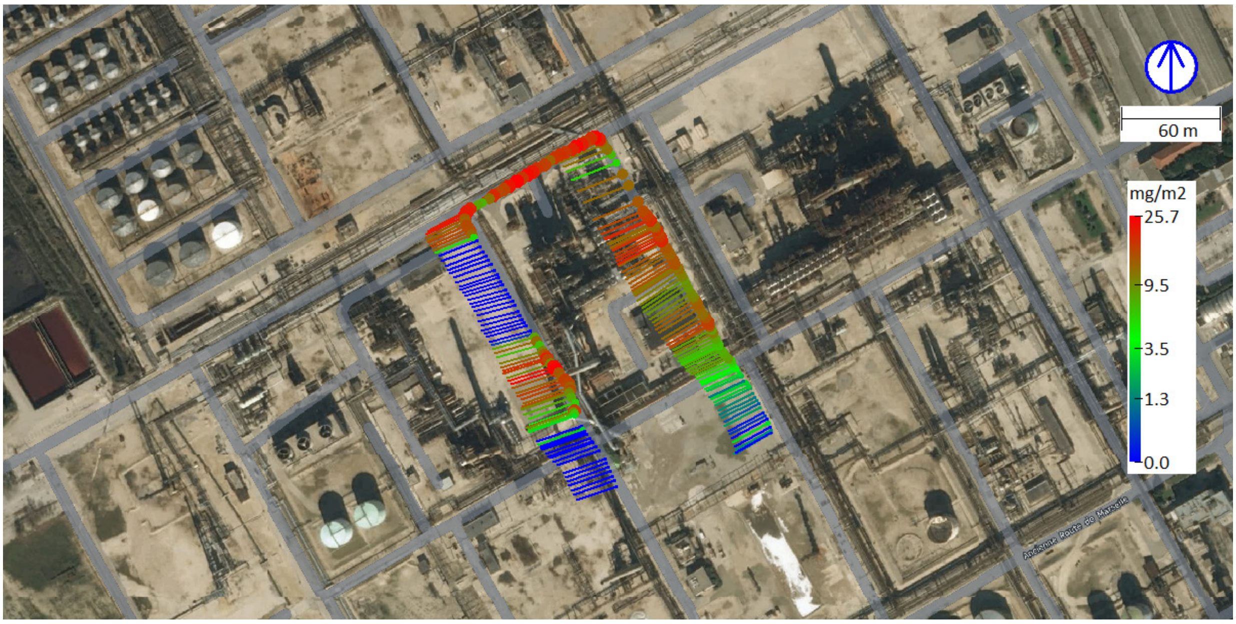

Figure 29. SOF measurement of the emission plume during Release 19 on September 29, 14:40, also showing adjacent source in unit north of the controlled release unit. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m^2. North is upwards, as indicated by the blue arrow.

Table 20. Summary of SOF measurement results for Controlled Release 19.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160929	143135-154704	12	11.3	4.5	2.7-4.6	233-264
Average			**11.3**	**4.5**		
Median			**12.2**			

5.20 Controlled release 20

Release number 20 was run on September 29, 15:30-17:00. Release nodes A, B, C and D were active, with a total release rate of 12.55 kg/h and each node released 3.14 kg/h. Winds were predominantly west-south-westerly about 2.5-3.5 m/s. An emission of on average 13.4±4.0 kg/h was measured, based on 14 SOF transects (Table 21). Figure 30 shows a plume transect example during controlled release 20.

Table 21. Summary of SOF measurement results for Controlled Release 20.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
160929	153807-165608	14	13.4	4.0	2.4-4.0	218-271
Average			**13.4**	**4.0**		
Median			**12.0**			

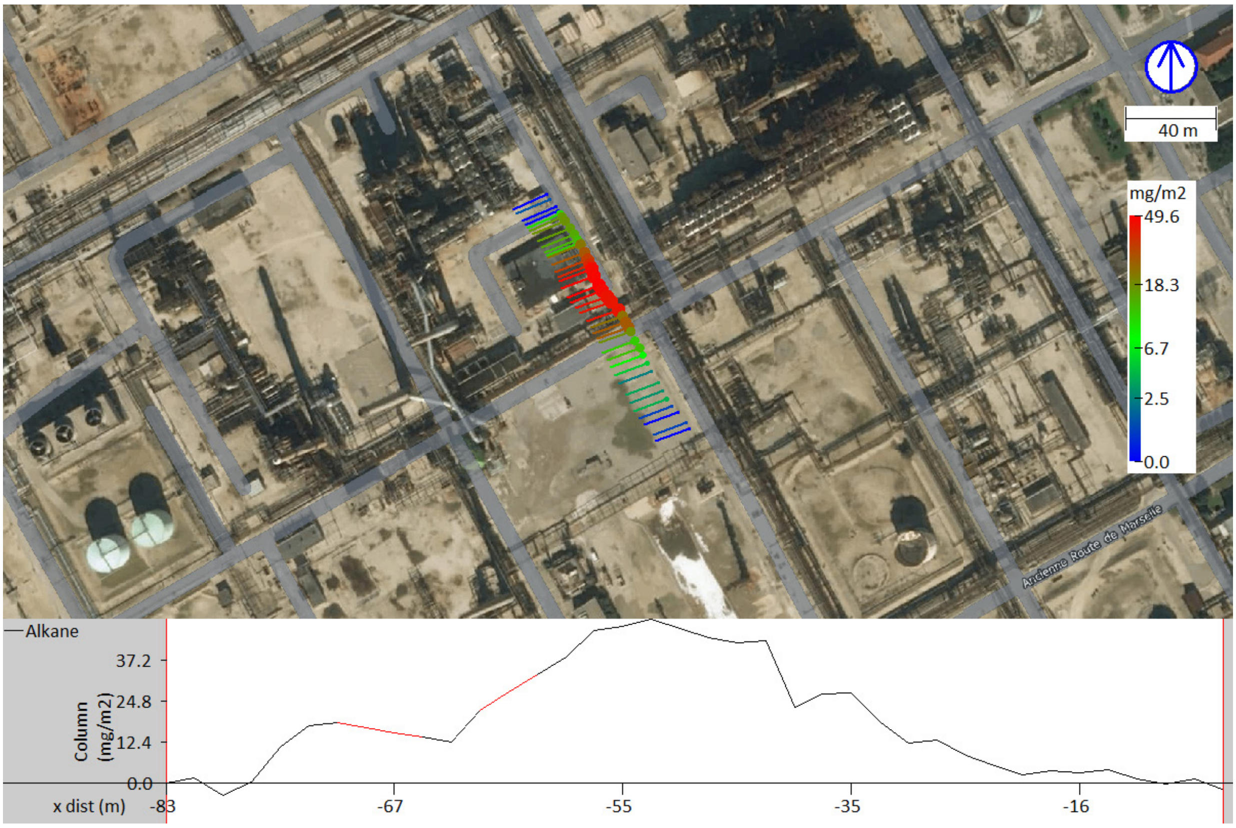

Figure 30. SOF measurement of the emission plume during Release 20 on September 29, 16:25. The sticks on the path plotted on the map points towards the wind at the time of measurement and are color coded to the total concentration column in mg/m2. North is upwards, as indicated by the blue arrow. The lower graph shows the alkane column (mg/m2) as a function of the distance travelled through the plume cross section.

6 Discussion and Conclusion

6.1 Comparison to release rates

Figure 31 shows a linear fit of measured SOF emissions compared to controlled release rates, for the 14 tests valid according to SOF protocol criteria. Overall a positive bias of 1.27 and R^2-value of 0.77 is observed for the fit. Overall the measurements show good response over the covered release rate range of 5-19 kg/h.

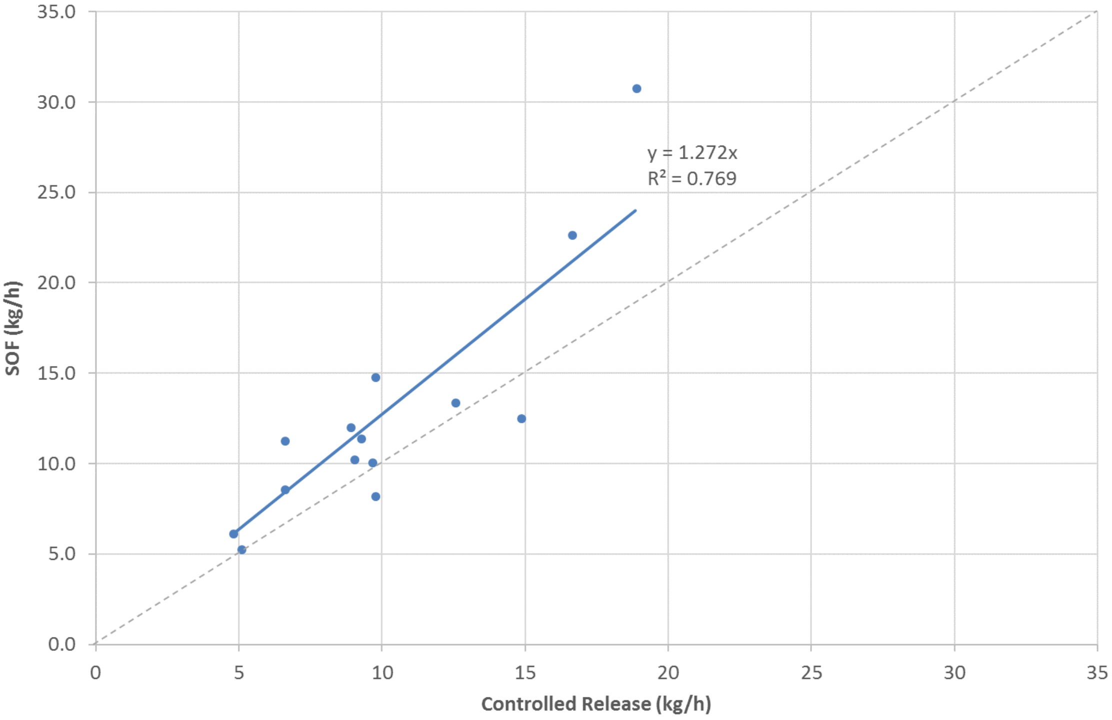

Figure 31. Correlation between measured SOF emission and controlled release rate for the 14 experiments for which the SOF measurements were valid according to the SOF protocol.

Overall the total amount of VOC reported by SOF was within 27% of the total released amount, 178 kg/h versus 142 kg/h, based on the 14 valid tests (Table 6). For individual test configurations, the measured emission rate ranged -15% to +72% compared to the released rate. For the three tests that deviated the most (no. 4, 18 and 19) winds were south-westerly, and in this case the release plume passed a unit in the north eastern part of the measurements area in which a pipeline was being cleaned and this potentially interfered with our measurements. As can be seen in Table 5 the background contribution from C_{6+} alkanes was here 12-16 % but there was also additional alkanes emissions in this source.

For 6 of the 20 release tests, valid SOF criteria were not met either since the wind were too low (<1.5 m/s) or the number of valid SOF plume transects were too few (<4). In the latter case, the reasons limiting the number of useable SOF transects were too low wind speed, too high and variable background plumes or instrument/vehicle issues.

For both the occasions when the reported SOF result underestimated the controlled release (test 2 and 12), source configuration B was run. This node was the only one placed on the upper floor in the process unit, whereas point nodes A, C, D were located on the first floor and the line node E was placed from ground up to second floor. This suggests the plume from node B was dispersed to comparably higher levels above ground, moving at a greater plume speed than emissions from ground level nodes and as compared to the average wind speed (10 m) attributed to the measured SOF mass columns.

Eight of the controlled release tests were run at a rate of about 9.4 kg/h, but with different release node configurations. For six of these, the SOF protocol criteria were met and the repeatability of the SOF result retrieval could be assessed, see Figure 32.

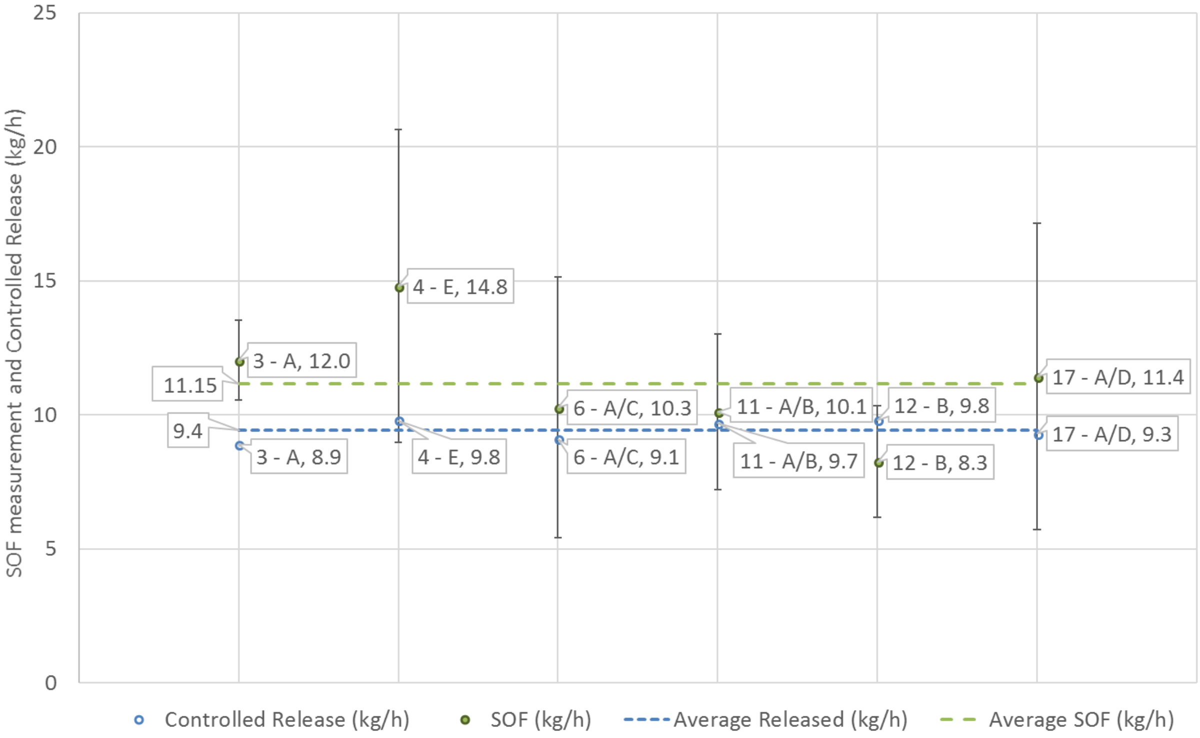

Figure 32. Repeatability of SOF emission estimate for several release node configurations at an average controlled release of 9.38±0.39 kg/h. Six controlled releases were done using different release node configurations denoted A, B, C, D, E attached to the release test number. Vertical bars denote ±1 SD among the SOF transects.

The release rate was on average 9.4±0.4 kg/h for the six tests (test 3, 4, 6, 11, 12 and 17). One or two point nodes (A, B, C, D) at a time, or the linear node (E) alone, were activated during these test configurations and each node was active at least once. On average the measured emission rate was 11.2 kg/h, based om 67 SOF transects, and this is 19% higher than the average release rate, covering effects of release location/distribution as well as inherent measurement variabilities.

6.2 The influence of sampling on the random noise.

The dependence of the random error of the SOF measurements on the number of individual measurements has been studied using the data from the six release tests described above. These measurements were carried out on different days with different metrological conditions and solar height. The variability observed therefore covers most random error sources.

By so called boot-strap methodology, the spread in the obtained average estimate was observed as a function of the number of measurement transects. Repeated sampling of different subset sizes was done based on the 67 SOF transects included in the six release tests with stable emission rate. Each subset of 1-20 measurements was sampled 1 million times, and Figure 33 shows the distribution of the sample mean relative to the total data set mean. When using 4 transects the standard deviation of the random noise is ±20%. From Figure 33 it is evident that the random noise of the measurements gets reduced gradually with the number of samples until it reaches a standard deviation of ± 10 % which is the remaining random noise that can't be accounted for by more samples.

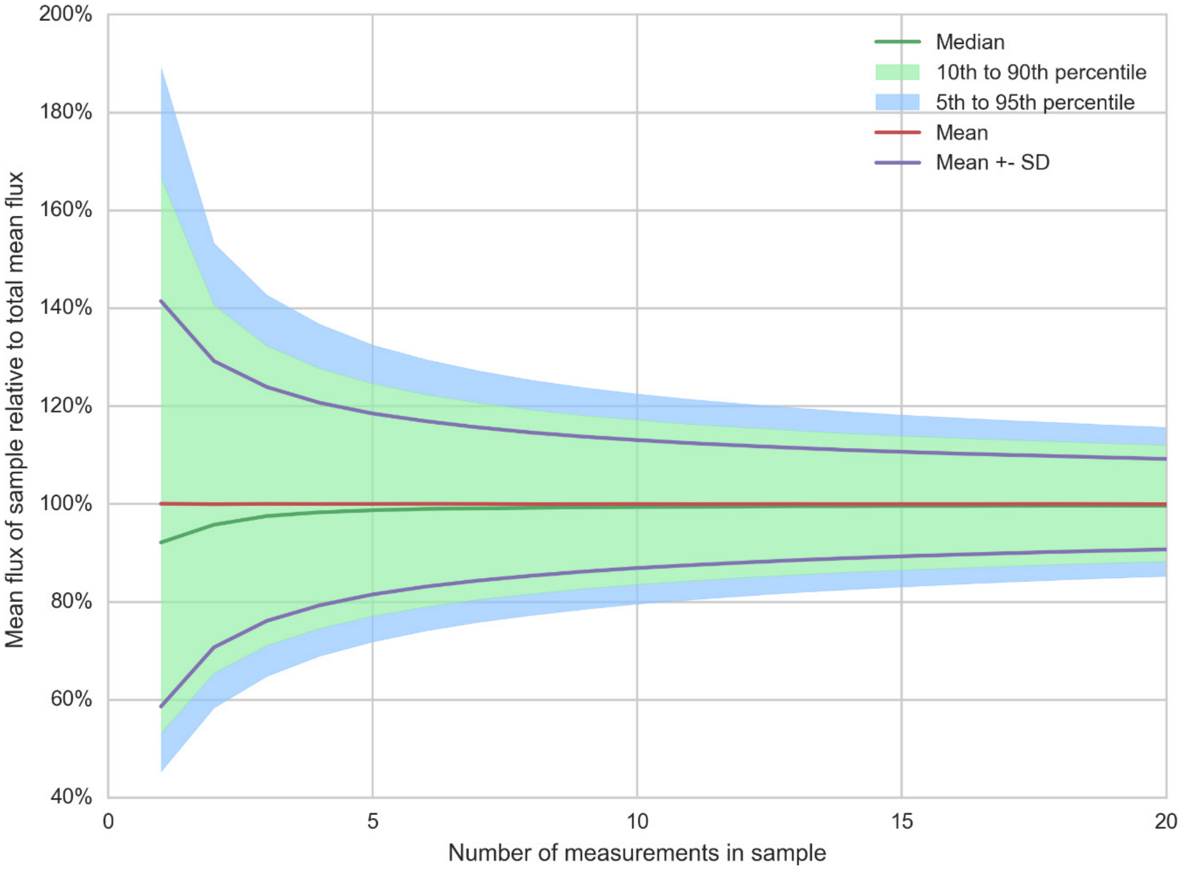

Figure 33. Sensitivity study of number of transects included in the sample. Distribution of the sample mean relative to the total data set mean.

6.3 VOC-composition and retrieval assessment

As specified in Table 5 (section 4), the controlled release gas main constituent was propane (91.2%). Isobutane and n-butane were next in abundance with 3.3 and 2.2 % respectively. In terms of other alkanes i-pentane, n-pentane and ethane were present in the release gas at a content of 0.48%, 0.21% and 0.05%. In other terms, alkanes made up 97.4% of the release gas. The remaining fraction was propene (2.05%), 1-butene (0.25%) and 1,3-butadiene (0.27%).

In order to study the effect of release gas composition on the retrieved amounts by SOF, a spectral analysis including four different compound sets in the SOF evaluation routine was done for a number of plume spectra sampled on different days during the campaign, see Table 22.

A first spectroscopic assessment of the plumes observed at the release site showed presence of cyclohexane and hexane type absorption signatures from heavier hydrocarbons, apart from the evident absorption by propane being the main component released in the experiment itself.

The default method chosen as a basis for the reported emission rate results, included cross sections of propane, hexane and cyclohexane. This spectral evaluation routine was effective in identifying presence of significant background plumes, with a signature of cyclohexane and/or hexane, and thus flag when care had to be taken in assessing the emission plume from the controlled release.

In alternative evaluation method 1 a composite spectrum made up of the constituents and corresponding fractions of the released gas itself was used, fitted as a single VOC cross section to the measured spectra. This reanalysis was done when it was revealed that the released gas was not purely propane, but 91% propane with given impurities as in Table 22.

Alternative evaluation routine 2 was set up with the four most abundant alkane species, in order to compare the VOC retrieval for the default method with this one covering 97.2% of the released VOC mass.

Finally, alternative method 3 was introduced taking method 1 composite mixture combined with hexane and cyclohexane, with the aim of hexane and cyclohexane responding to background sources.

Table 22. Spectrum evaluation methods used in the plume composition sensitivity analysis.

Default method VOC cross sections fitted	**Alternative method 1** Single VOC mixture cross section fitted	**Alternative method 2** VOC cross sections fitted	**Alternative method 3** VOC cross sections fitted
propane	0.05% ethane	propane	Method 1 mixture
hexane	91.17% propane	iso-butane	hexane
cyclohexane	2.05% propene	n-butane	cyclohexane
	3.32% i-butane	iso-pentane	
	2.20% n-butane		
	0.25% 1-butene		
	0.27% 1,3-butadiene		
	0.48% i-pentane		
	0.21% n-pentane		

Figure 34, Figure 35 and Figure 36 show comparisons for plume observation data for the alternative evaluation methods in Table 22 versus the default evaluation method, for measurements on September 22, 28 and 29 respectively.

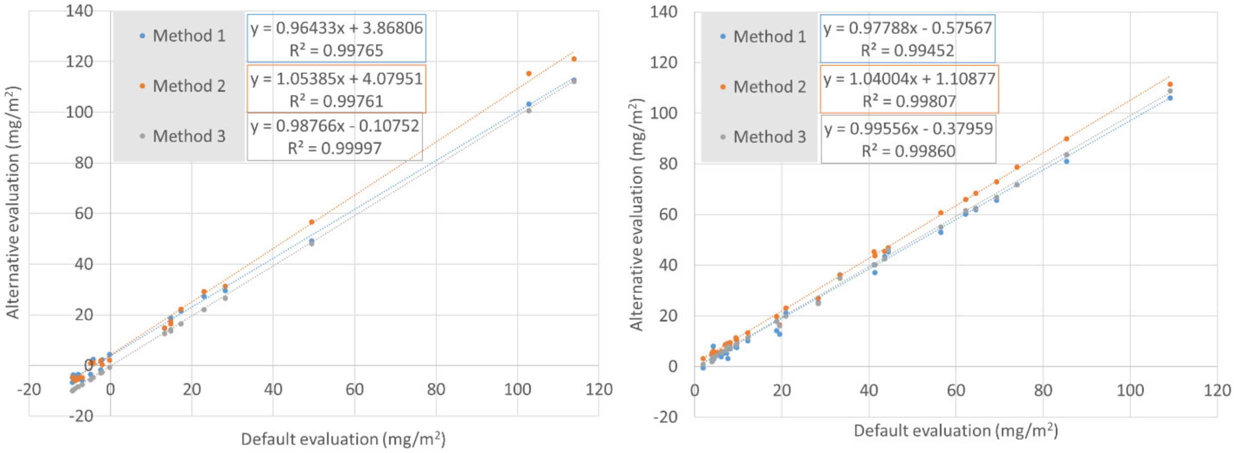

Figure 34. Comparison of three optional SOF VOC-evaluation methods to the default evaluation, for plume observations during September 22, 2016.

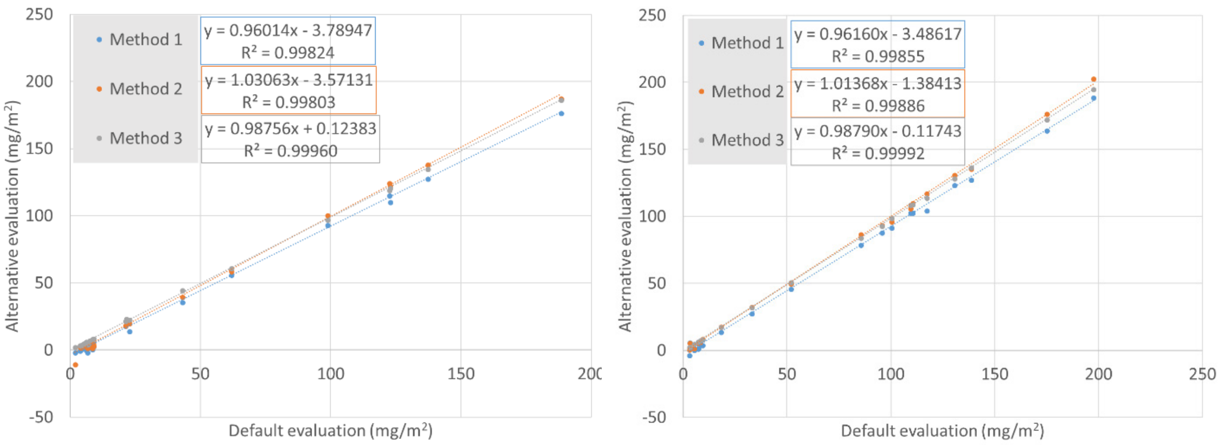

Figure 35. Comparison of three optional SOF VOC-evaluation methods to the default evaluation, for plume observations during September 28, 2016.

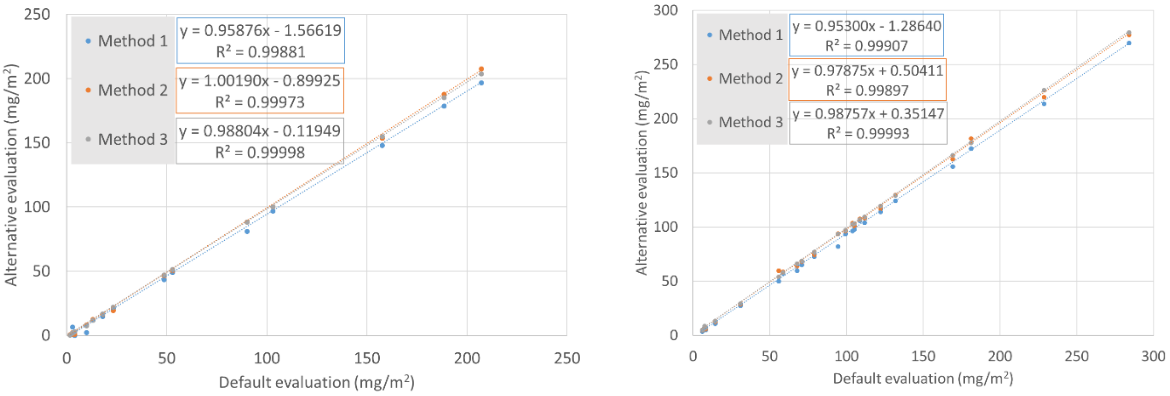

Figure 36. Comparison of three optional SOF VOC-evaluation methods to the default evaluation, for plume observations during September 29, 2016.

When comparing Method 1 against the default method the scale factor varied between 0.953 and 0.978 for the three different dates. Corresponding ranges for method 2 and 3 were 0.978-1.054 and 0.987-0.996 respectively. The larger spread for method 2 can be explained by hexane and cyclohexane not being included in this method, hence having difficulties to fully account for the background sources. Combining the method 1 release gas mixture with hexane and cyclohexane (method 3), improves spread and suggests that the default evaluation method response for the controlled release gas mixture was good. Method 3 was within 1.3% on average compared to the default method. Linearity was close to unity for all method comparisons.

To conclude, the applied default method (of propane, hexane and cyclohexane) retrieved the VOC mass in the release plumes well in comparison to the alternative methods. Observed deviations are within the uncertainty in cross sections. For cases where background plumes (typically cyclohexane and heavier VOCs) blew into the release site and not observed/accounted for, one could expect a positive bias in the reported results (default method).

6.4 Conclusions about uncertainty assessment

As described in section 3 the estimated uncertainty for SOF measurements is in the range 20-35 % with the largest error source corresponding to the assessment of the wind.

When comparing the data against the tracer release data it can be seen that the SOF data on average were within the stated uncertainty range of 20-35% as stated in the SOF measurements protocol but that there were some exceptions with higher deviation possibly caused by problems of reducing the influence of interfering sources and background from the measurements.
In this work we have also been able to show that that the SOF is dependent on the number of transects carried out and that at least for transects should be carried out to reduce the random noise.

Compared to a normal SOF survey, the controlled release experiment was run under more complex and complicating conditions. The duration of every experiment was rather short (1.5 h) compared to normal operation according to the protocol, limiting the number of plume and upwind background transects. In a normal SOF survey measurements are also planned according to conditions, to allow for measurements during different wind directions and optimize the measurements for the site. For the controlled release experiment, measurements were run on a pre-set schedule more or less, irrespective of the conditions being optimal for the site. Consequently, many measurements were done on a tight schedule with limited repetitions. Bumpy, confined roads with shadow patches and disturbed wind fields added uncertainty as well as significant background sources in the area.

7 Acknowledgements

This work was funded by CEN within CEN / TC 264 / WG 38. All partners and external representatives taking part in the project and associated field surveys are greatly acknowledged for their contributions and efforts.

8 Annex A (informative), SOF – description of the method

A.1 Overview

A.1.1 Scope

The Solar Occultation Flux (SOF) method uses solar light to detect gas species that absorb in the infrared (IR), visible and ultraviolet (UV) part of the solar spectrum (Mellqvist, 2009). SOF measurements are carried out using an IR or UV spectrometer that is connected to a solar tracker. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. For the UV channel the measurements are usually carried out by pointing a telescope towards zenith, utilizing the skylight instead of direct solar light. Mass fluxes/emissions are obtained by combining the SOF column measurements with wind measurements. The method is used to quantify and map the location of various gas emission sources over a spatial scale ranging from industrial conglomerates down to sub-areas in individual plants.

A.1.2 Pollutants measured

The SOF method enables simultaneous measurements of a wide range of gas species. Key pollutants that can be measured in the IR spectral region include: alkanes (C_2-C_{10}), alkenes (ethene, propene, 1,3- butadiene), alcohols (methanol, ethanol), alkynes (ethyne), ammonia, carbon-monoxide, formaldehyde, nitrous oxide and hydrogen chloride. Methane and Aromatic VOCs can also be detected but with limited sensitivity due to the high atmospheric background levels in the former case and weak absorption properties and cross interference with CO_2 in the latter case. SO_2, NO_2 and formaldehyde are measured in the UV/visible wavelength region.

The SOF method can be supplemented with concentration measurements of various pollutants (primarily aromatic VOC and methane) in the emission plumes relative to the species quantified directly by SOF (e.g. butane or ethane). In this manner the emissions of various species can be measured indirectly. There are different sensors available for this, including for instance mobile extractive measurements based on infrared (mobile extractive FTIR) and UV/visible absorption (mobile DOAS).

A.1.3 Information provided

A fast solar tracker is combined with an infrared or UV/visible spectrometer and mounted on a mobile platform, such as a van or a boat. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. Measurements are usually carried out by encircling or “boxing” the emission sources while mapping the obtained column data. In this manner the influence of upwind sources can be eliminated.

A.1.4 Scale and limitations

The SOF method is used to map and quantify gas emissions from industrial conglomerates (50 km by 50 km) down to sub-areas in individual plants (20 by 20 m). Flux measurements that are carried out along the fence line of the industries, or further away, have the smallest uncertainties (20-30 %). Measurements close to single storage tanks or other large point sources have larger uncertainties (30-50 %). The SOF measurements require solar light, therefore only daytime measurements can be made. The method has limited sensitivity for methane and aromatic VOCs. However, the emissions of these species can be measured indirectly as described above.

A.2 SOF Measuring principle

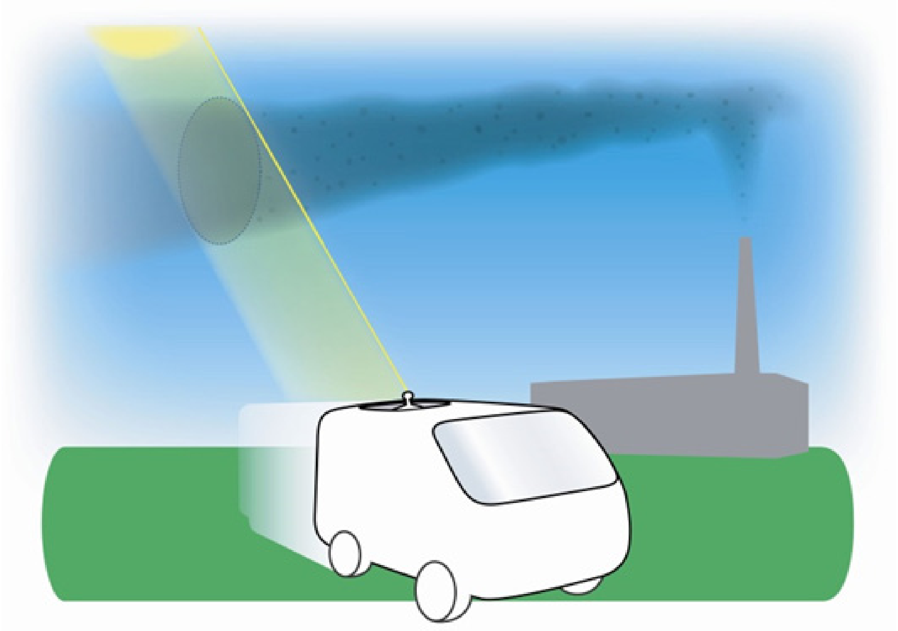

Figure A.1. In the Solar Occultation Flux (SOF) method gases are measured by observing molecular absorption in solar spectra. The instrument is moved across the emission plume using a mobile platform/vehicle. From the integrated molecular mass measured across the plume, the emission flux is obtained by multiplication with the orthogonal wind speed.

Solar occultation flux (SOF) monitors solar radiation in a broad spectral region for the detection and quantification of fugitive and diffuse emissions of the specified VOCs and other species. The SOF technique uses FTIR spectrometry to analyse molecular absorption throughout the atmosphere from a mobile platform. By driving downwind of the emission sources and intersecting the plume with the measurement path, an integrated concentration profile of the emissions is sampled (Figure A.1). The measurements are generally carried out by encircling the emission sources, making it possible to subtract the upwind flux from the downwind flux. The SOF method is used to map and quantify gas emissions from multiple sites down to individual point sources.

A.2.1 Column retrieval

A.2.1.1 Infrared spectral region

The measurements are based on the recording of broadband infrared solar spectra with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of its position. From the solar spectra it is possible to retrieve the path-integrated concentration (column, see Eq. A.1) in the unit mg/m^2 of various species between the sun and the spectrometer. A system consists of a solar tracker, transfer optics and an FTIR spectrometer with a typical spectral resolution of 0.5 cm^{-1} for high-resolved measurements. The spectrometer is equipped with an MCT (mercury cadmium telluride) detector and/or an InSb (indium antimonide) detector. Optical filters are used to reduce the spectral bandwidth in order to reduce stray-light and unwanted wavelengths which improves the signal-to-noise-ratio. The transfer optics is designed to produce an image of the solar disc on the detector plane.

The infrared SOF system is operated in two main spectral regions: i.e. the fingerprint and the CH-stretch region. The fingerprint region corresponds to spectral measurements between 750 to 1000 cm^{-1} at 0.5 cm^{-1} spectral resolution, Figure A.2. Typical measured species here includes alkenes, alkadienes and ammonia. In this spectral region, warm objects radiate (black-body radiation) significantly which creates a thermal background in the absorption spectrum. To correct for this, a thermal background spectrum is recorded at regular intervals by measuring with the solar tracker pointing to the cold sky i.e., away from the sun. The background spectrum is then subtracted from each recorded solar spectrum. In the spectral retrieval, interfering species such as water and CO_2 and others pollutants, are taken into account, depending on the key species.

The CH-stretch mode corresponds to measurements in the infrared region between 2700–3005 cm^{-1}, using the vibrational transition in the carbon and hydrogen (C-H) bond, Figure A.3. In this region most hydrocarbons absorb the infrared light such as alkanes, alcohols, alkenes and aldehydes. For refineries and tank storage, areas the emissions of alkanes are dominant. The absorption features of the different alkanes are similar and interfere with each other, but since the number of absorbing C-H-bonds is directly related to the molecule mass, the total alkane mass can be retrieved despite the interference. In the spectral analysis for refineries, calibration spectra of ethane, propane, n-butane, and n-octane are fitted to the recorded spectra, using a resolution of 2-8 cm^{-1} (Johansson, 2013). Sensitivity studies of the SOF alkane retrieval for refineries shows an uncertainty of around 6 % in the retrieved total VOC mass column (Mellqvist 2009, Johansson 2014) when using this approach. For other industries it is necessary to obtain complementary information about the general VOC composition at the source before choosing the calibration mixture since also aromatic VOCs, alcohols and alkenes have absorption features in the CH-stretch region.

In the spectral retrieval, a reference spectrum is chosen from a section of the measurement transect where it can be assumed that the target gas concentration is near zero and which corresponds to the lowest column value measured, i.e. outside the plume. Instead of calculating the transmittance by dividing all spectra with the reference, which is the common approach in long path FTIR, the logarithm of the reference spectrum is fitted to the measured spectrum together with cross sections of the gas species to be retrieved which are adapted to the instrumental parameters, as shown in equation (Eq. A.1) below, which simply is a rewriting of the Beer Lambert law. This approach makes it possible to account for wavelength shifts in the spectra and also to include several reference spectra in the fit, which results in efficient removal of the influence of the upper atmosphere.

The spectral retrieval is performed by fitting calibration and measured spectra using a nonlinear multivariate fitting routine. One of those schemes, working only for small absorbers is shown below.

$$\ln[I(\nu)] = \sum_j F_j \cdot \ln[I_{o,j}(\nu)] - \sum_i \sigma_i(\nu) \cdot \int conc_i(z) \cdot dz \qquad \text{(Eq. A.1)}$$

Here I(ν) corresponds to the measured light intensity as a function of frequency ν, $I_{0,j}$ corresponds to reference spectra with fitting factors F_j, σ_i corresponds to absorption cross sections for the fitted species and the last part of equation A.1 is the vertically integrated concentration, i.e. column, to be determined.

For the spectral retrieval, high resolution spectra of the key pollutants (VOCs) and interfering species are obtained from databases such as the PNL (Pacific Northwest Laboratory) database (Sharpe 2004). These are degraded to the spectral resolution of the instrument by convolution with the instrument line-shape. The uncertainty in the absorption strength of the calibration spectra is typically around 3 %.

Calibration data from the HITRAN database are used to simulate absorption spectra for atmospheric background species at the actual pressure, temperature and instrumental resolution of the measurements. The same approach is applied for several spectral retrieval codes for high resolution solar spectroscopy (Rinsland 1991; Griffith 1996) and the routine applied here has been tested against the other codes with good results.

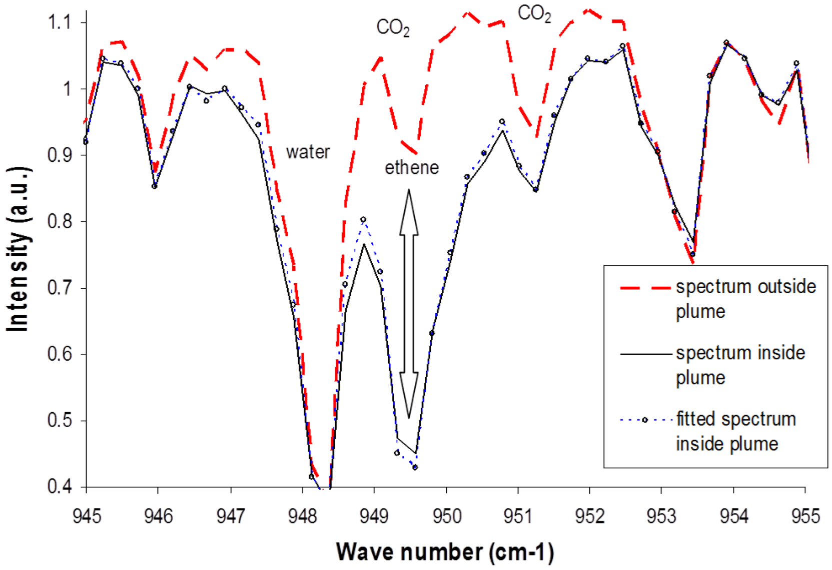

Figure A.2. Solar spectra in the fingerprint region, (left) measured downwind a petrochemical plant. The measured and the fitted mix of calibration spectra are shown (relative to a clean air background reference), obtained using the QESOF spectral retrieval algorithm.

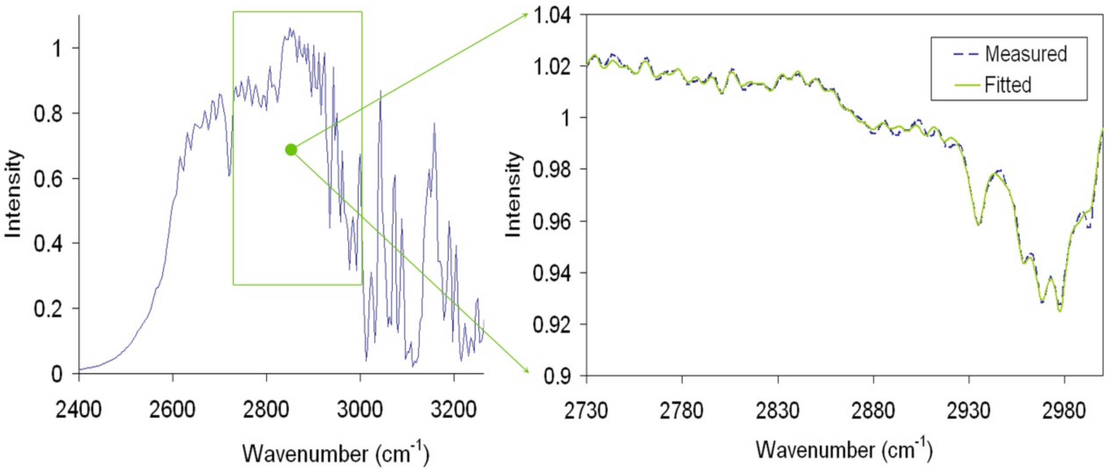

Figure A.3. Solar spectra in the alkane CH-stretch region, (left) measured downwind a refinery. To the right the measured and the fitted mix of calibration spectra are shown (relative to a clean air background reference), obtained using the QESOF spectral retrieval algorithm. Here cross sections of ethane, propane, n-butane, and n-octane have been fitted to the recorded spectra.

A.2.1.2 Ultraviolet and visible spectral region

The SOF measurements in the UV and visible spectral range can be carried out using direct solar light. or scattered zenith sky light to quantify emission fluxes of formaldehyde (HCHO), NO_2 and SO_2., The latter technique is also known as mobile sky-DOAS (Differential Optical Absorption Spectroscopy). The measurements are based on broadband spectroscopy in the wavelength region between 290 and 470 nm using a grating spectrometer connected to a zenith viewing telescope via an optical fibre. The spectral resolution of the spectrometer should be better than 1 nm. Optical filters are used to reduce stray light in order to improve the signal-to-noise of the measurement. There are significant differences in the retrieval method between the UV/visible and the IR spectral region. However, for both wavelength regions, the vertical columns are derived from the spectra and then integrated along the measurement transect and multiplied by the orthogonal wind speed to obtain the flux. The principle of flux measurements using mobile sky-DOAS is the same as for regular SOF, although slant column compensation (as a function of solar elevation) is redundant since the telescope is always pointing toward zenith. The DOAS system also works under cloudy conditions, in contrast to SOF, although higher order scattering within the clouds introduce additional uncertainties especially for patchy clouds.

The spectral retrieval in the UV/visible region corresponds to the DOAS method introduced in the 1970's (Platt 1979) utilizing both artificial light sources and scattered solar light (Heckel 2005; Galle et al., 2002; Johansson 2009; Rivera et al. 2009a, 2009b and 2009c). In the retrieval process, calibration spectra are fitted to the measured spectra. To retrieve SO_2, NO_2 and HCHO in the spectral region 305 to 365 nm, it is necessary to account for absorption features from O_3, O_4 (O_2-O_2 weak complex) and "ring spectra". The latter corresponds to spectral structures from inelastic atmospheric scattering [Fish 1995]. Absorption cross section from published laboratory studies are used in the fitting routines. There are several publicly available software packages that can be used for this analysis, e.g. QDOAS (formerly WINDOAS) [Van Roozendael 2001] from the Belgian Institute for Space Aeronomy (BIRA/IASB) and DOASIS [Kraus 2005] from the University of Heidelberg.

A.2.2 Flux measurement

To obtain the gas emission flux from a source, the measurement vehicle is driven in such way that the analysed solar light cuts through the emission plume, as illustrated in Figure A.1 and Figure A.3. These paths are referred to as SOF measurement transects. The wind speed and direction are also required to calculate the flux and these parameters are usually measured from high masts and towers.

The SOF transects are conducted along roads oriented crosswind and close downwind (0.5–3 km) of the source and give geo-located (lat/long) vertically integrated mass concentrations (vertical mass columns in Si-unit [kg/m^2]) of the target species from the spectral fitting and the optical path geometry The slant angle of the sun is compensated for, by multiplying the concentration with the cosine factor of the solar zenith angle. The gas flux is obtained in two steps; first the vertical columns are integrated along the measurement transect (x1-x2 in the Eq. A.2) which gives the integrated mass of the target species across the plume in Si-unit [kg/m]. Secondly, the true mass flux (Si unit [kg/s]) is given by multiplying this value by the mass weighted average orthogonal wind speed of the plume in Si unit [m/s]. In reality this weighted wind can be obtained if the typical concentration and wind profile versus height is known. Generally, it is approximated as the average wind from ground to the height of the plume see below.

The flux calculation is shown in Eq. A.2. Here, x corresponds to the travel direction, z to the vertical direction, u' to the average wind speed of the transect that is orthogonal to the travel direction (x), u'_{mw} to the mass weighted average wind speed of the plume and H_{mix} to the mixing layer height.

$$flux = \int_{x1}^{x2} \left(\int_{0}^{Hmix} conc(z) \cdot u'(z) \cdot dz \right) dx = u'_{mw} \int_{x1}^{x2} column(x)$$

(Eq. A.2)

$$\text{where } u'_{mw} = \frac{\int^{Hmix} conc(z)u'(z)\cdot dz}{\int_{o}^{Hmix} conc(z)dz} \quad \text{and } column = \int_{0}^{Hmix} conc(z)\cdot dz$$

The wind information is not straightforward to obtain since it is usually complex close to the ground and increases with height. The situation is improved by the fact that SOF measurements always are made in sunny conditions. This is advantageous since it corresponds to unstable meteorological conditions for which vertical wind gradients are smaller due to convection. Over relatively flat terrain w the mean wind varies less than 20 % between 20 and 100 m height as shown by meteorological models and height profile measurements of the wind using balloon soundings (Mellqvist 2010). In addition, for meteorological conditions with considerable convection, the emission plume from an industry mixes rather quickly vertically giving a more or less homogeneous distribution of the pollutant versus height throughout the mixing layer even some kilometres downwind, as shown in airborne studies (Mellqvist 2010). In addition to the atmospheric mixing, the plumes from process industries exhibit an initial lift since they are usually warmer than the surrounding air.

A.2.3 Overall Measurement methodology

The SOF method is used to screen and quantify gas emissions of VOCs (alkanes, alkenes and alcohols) and other species from industrial conglomerates down to sub-areas in individual plants, such as process areas, crude oil storage, product storage tanks, water treatment facilities, flares and loading operations. A typical yearly survey of an industrial facility corresponds to 10 measurement days, preferably spread out over several seasonal periods to better represent mean annual conditions and become less biased by sporadic/intermittent site activities. The annual measurements give a baseline emission for the facility and its sub-areas. Interannual comparisons makes it possible to keep track of the emissions, i.e. to understand whether some parts of the refinery are leaking more relative to last year and whether abatement measures are required. The measurements are also used to evaluate the efficiency of various abatement measures and for tuning flare combustion efficiency. Variations in the daily values can give important information on the emission rates of various site activities. Sporadic emissions are known to contribute significantly to the yearly emissions.

Measurement uncertainty is minimized by conducting measurements outside the fenceline of the refineries, since the wind field is then less disturbed and the plume distribution is more homogenous and extends vertically over a larger height range (typically 100-500 m). Box measurements (where the site is encircled) are necessary to estimate the total facility emissions whenever upwind sources exist. In this manner, upwind emissions are subtracted from the downwind emissions to extract the emissions from the target/encircled facility. Additional on-site measurements are carried out inside the facility using available roads, for estimation of subarea emissions from process areas, product tanks, crude oil tanks, water treatment facility, loading/unloading, flaring and other local sources. The emission values of the sub-areas are usually normalized so that their sum matches the total facility emission value measured at the fence-line. This is need to compensate for the additional uncertainties of near-field measurement (due to a more disturbed wind field) and for different temporal sampling than for the total facility measurements (not done simultaneously and usually fewer measurements).

In order to calculate the flux, the SOF measurements have to be multiplied with the average wind speed of the emission plume as described above. The relevant wind information is usually gathered from several sources: The main wind represents the general non-obscured wind of the plant with a time resolution of 10 minutes (running average). This can be obtained from a 10 m mast positioned in the upwind direction of the plant in a clear and flat area. For special cases of near-field measurements of ground-based sources, such as an open basin of a water treatment area, the ground wind speed downwind the source gives a more representative value for the plume speed. The ground wind speed can be measured using a wind sensor on a 2 m tripod close to the source or with a mobile wind sensor mounted on the measurement vehicle (placed in the front away from the vehicle wind drag and at 2 m altitude).

It is also required to obtain information of the typical wind profile. This can be obtained by real-time measurements using a wind Doppler LIDAR, wind radar or SODAR or frequent radio sondes (wind balloons) combined with ground measurements or by extrapolating an appropriate (logarithmic) wind profile from multiple wind sensors on a high taller mast (at least 20 m). A common approach is to use scaling factors applied to the continuous 10 m wind mast data based on empirical relationships between mast wind and the vertical profiles.

To estimate the average wind speed of the plume, information about the plume height is also needed. Usually an assumption of the general plume height dispersion is made, based on previous airborne studies (Mellqvist 2010) assuming that the plume mixes with at vertical speed of 0.5 m/s. E.g. if the measurements are carried out 200 s downwind the source (corresponding to a distance of 1000 m at a wind speed of 5 m/s), the plume is assumed to be homogenously mixed in height over the first 100 m. The appropriate wind information to use in the flux calculation is then the average from the ground to 100 m. An estimate of the plume height can also be obtained by combining SOF measurements with parallel ground concentration measurements using a mobile extractive FTIR system (Mellqvist 2016, Mellqvist 2017, Galle 2001). In this case, the average ratio between column measurements of alkanes [mg/m^2] and the concentration measurements [mg/m^3] yields the average plume height [m], assuming a well-mixed plume (Mellqvist 2016, Mellqvist 2017).

Wind speed and direction vary constantly over a range of time scales. This may cause horizontal shifts (meandering) in the position of the emission plume in the measurement plane. Hence it is important to apply a statistical approach to the SOF-technique where an increasing number of measurement transects improves the estimate of the actual emission. Therefore, only statistical measures (i.e. average or median) are given in the data reports while single/individual transects are considered too uncertain and generally excluded. In Figure A.5, individual measurement transects obtained from the fence-line of a Swedish refinery are shown as histograms (binned into different emission intervals). Measurements of a constant source would produce a normal distribution while a skewed shape and/or long tails are due to intermittent emissions due to upsets or sporadic activities such as tank cleaning etc. The refinery corresponding to the data in Figure A.5. has been measured 12 times since 1989 (DIAL four times and SOF nine times) and with exception for the first occasion the average emission has varied within 30 %.

The SOF measurements can be combined with extractive FTIR (Galle 2001) and UV measurement of VOCs (Mellqvist 2016, Mellqvist 2017), to calculate inferred fluxes of other species such as aromatic VOCs and methane by measuring the mass ratio of a specific specie against alkanes and multiplying this ratio with measured alkane flux. The ratio of the column and the concentration measurements also provides an estimate of the average plume height for well mixed plumes as mentioned above.

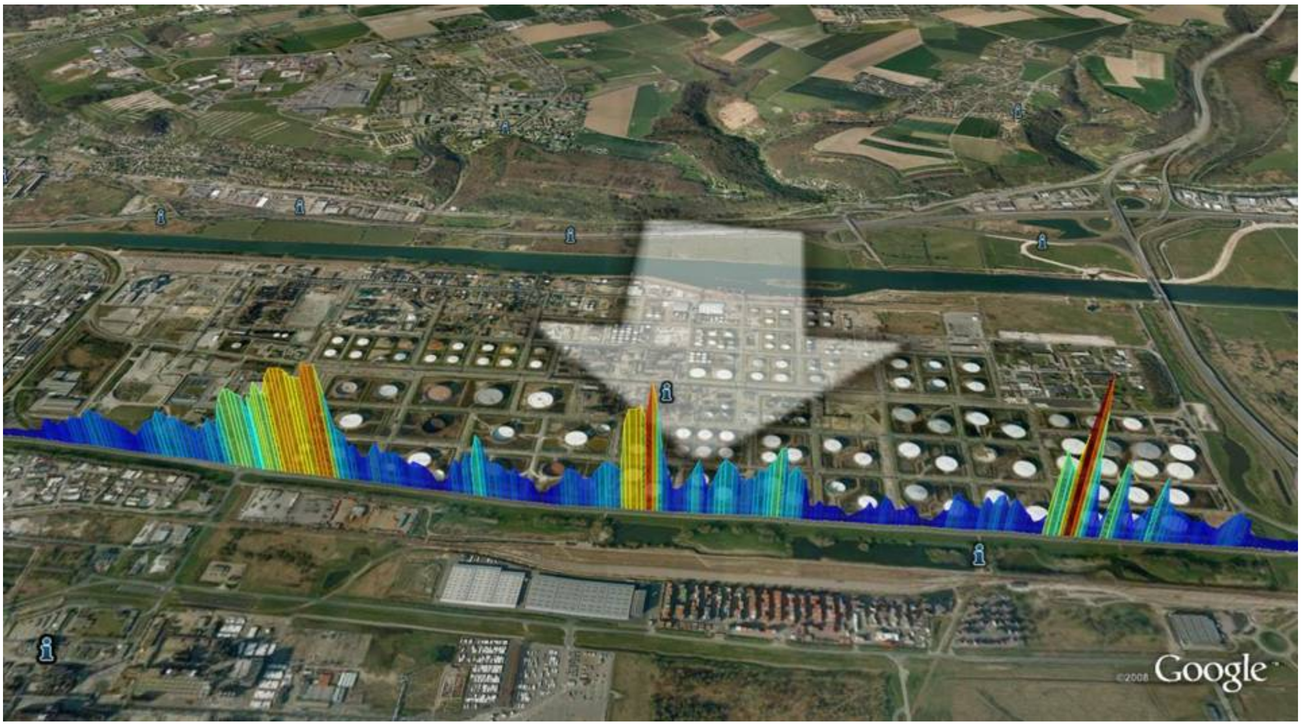

Figure A.4. A SOF transect downwind a refinery. The staples and colours show the vertical mass columns of butane, as retrieved from molecular absorption in the solar spectra. The average wind direction during the transect is indicated by the white arrow. The mass flux is obtained by multiplying the integrated mass columns with the orthogonal wind speed.

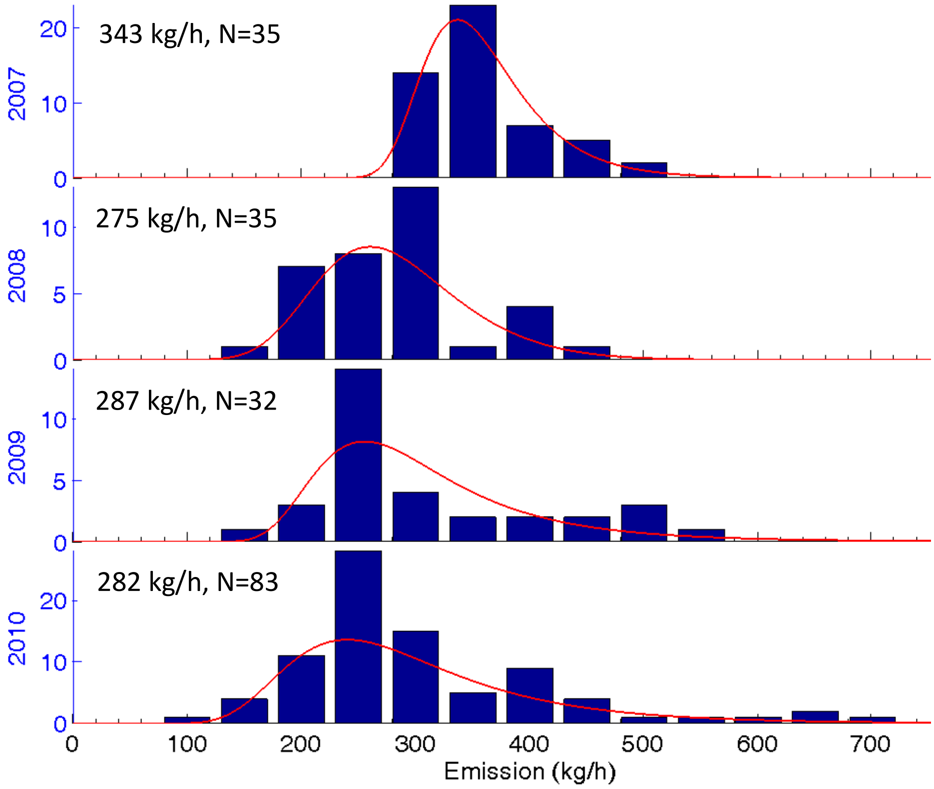

Figure A.5. A Histograms of individual SOF transects of alkanes (mass flux [kg/h]) from a Swedish refinery over four years. The red curve is an empirical probability distribution fitted to the data. The emissions data in the graph corresponds to the median values.

A.2.4 Advantages and constrains

The SOF method provides real time information about the location and magnitude of the emissions. Under favourable meteorological conditions, the technique can cover a large facility, such as a refinery, in a single day, providing information about the location of the largest emissions sources with a 50x50 m spatial precision.

The SOF technique is constrained by meteorological conditions. The measurements can only be carried out under sunny conditions (or also a homogenous cloud cover for SkyDOAS) and are restricted to accessible roads and therefore only certain wind directions may work. Measurements are less certain at low (and very high wind speeds and at low solar angles. With low and variable winds it is difficult to determine and separate the sources and both wind speed and direction are relatively more uncertain. At high wind speeds, the gas concentration is diluted and this may lead to underestimation of the emission if the concentration drops below the detection limit. Also, the wind shear (the gradient of the vertical wind profile) increases at high wind velocities which increases the potential uncertainties of near-field measurements and the estimation of the plume height. The restriction to daytime measurements may lead to biased annual emissions. According to a recent study based on the conventional AP-42 model (US-EPA 2013) developed by the US EPA, the effect of daytime and summer season sampling bias due to diurnal and annual temperature variations gives a 30-40 % maximum overestimation in the emissions for an external floating roof tank, compared to the annual average (Johansson 2014). As only a portion of the total emissions are affected (only tank emissions), the daytime bias for the whole facility will be less, and generally much less. Subsequent implementation of emission control devices (such as inter breathing tanks) also tend to minimize emissions from temperature variations.

Another limitation of the SOF method is lack of vertical resolution which means that the plume height cannot be determined directly from the measurement. Parallel concentration measurements can remedy this as mentioned above. Still, the uncertainty of the plume height leads to an uncertainty in the plume wind speed and subsequently the emission flux.

A.2.5 Validation and comparisons

The performance of the SOF method has been tested in side-by-side comparisons to other methods and in controlled gas release experiments. The results are given in Table A. 1. and Figure A. 6.

In one experiment, tracer gas (SF_6) was released from a 17 m high mast on a wide parking lot. The emission rate was then quantified by SOF measurements 50–100 m downwind the source, yielding a 10 % accuracy for these measurements when averaging 5–10 transects (Kihlman 2005b). More difficult measurement geometries have also been tested by conducting tracer gas releases of SF_6 from the top of crude oil tanks. For instance, in an experiment at Nynas refinery in Sweden, tracer gas was released from a crude oil tank. In this case, near-field measurements in a disturbed wind field at a downwind distance of about 5 tank heights, the overestimation was 30 %, applying wind data from a 20 m mast (Kihlman 2005a; Samuelsson 2005b). A similar experiment was carried out by releasing SF_6 in the process area of a petrochemical plant, using 5 different release points. The SF_6 release was measured 300 m downwind using SOF with meteorological data from a nearby mast. The SOF data were 15% higher than the actual released data, i.e. 2.18±0.3 kg/h compared to 1.89 kg/h.

Several controlled source release experiment have been carried out with external referees. This includes a blind exercise with the French institute INERIS as reviewer. Controlled releases of the

source gas ammonia were here carried out from a single point in a farmland measurement in France with measurements 50-150 m downwind.
In spring of 2015, a blind exercise with an external reviewer from city of Longview was carried out in Mont Belvieu, Texas (USA). Controlled source releases of ethylene were carried out from a 10 m tower in a parking lot. SOF-measurements were made 50-75 m downwind.

In the fall of 2015, a blind exercise was carried out with an external reviewer from the SCAQMD (South Coast Air Quality Management District, California, USA) at the parking lot of the Anaheim football stadium. Controlled releases of propane were here carried out from a single point at 5-10 m altitude and SOF measurements were performed 50-100 m downwind. As part of this study, comparative measurements between the SOF and DIAL technique were also carried out.

In 2016 a blind exercise was carried out at an abandoned French refinery with an external reviewer (French standardisation institute INERIS), as part of European standardisation CEN TC264 WG 38 validation. Controlled source releases of propane were carried out from 4 nodes inside a process unit with dimension 50m×25m×25m. Measurements were carried out at 50-300 m distance from the source, on roads inside the process unit.

The SOF method has also been compared to other methods. In an experiment at the Nynas refinery, a fan was mounted outside the ventilation pipe, blowing out a controlled VOC flow from the tank. The pipe flow was measured using a so called pitot pipe and the concentration was analysed by a FID (Flame ionization detector) which made it possible to calculate the VOC emission rate. In parallel, SOF measurements were carried out at a distance corresponding to a few tank heights. Similar measurements from a joint ventilation pipe from several bitumen cisterns were also carried out (Samuelsson 2005b). The SOF method was used in parallel to airborne measurements of ethene fluxes from a petrochemical industrial area in Mont Belvieu, TX (De Gouw 2009).

The Mobile sky DOAS (UV SOF) has been validated by Rivera et al. (2009c) who performed SO_2 measurements on a power plant in Spain.

Furthermore, the SOF method has been validated as part of the CEN standardisation, by controlled source releases in an decommissioned refinery, see separate report on this.

Table A. 1. Validation experiments and instrument comparisons for the SOF technique.

Experiment	**Comment**	**SOF [kg/h]**	**Reference [kg/h]**	**Diff**
Controlled source releases of **sulphur hexafluoride** from a mast at a parking	SOF measurements on a parking lot 100 m away from a tracer release point in a 17 m mast. Tracer release rate from weighing. (Fransson, 2002)	2.2	1.97	10 %
Controlled source releases of **sulphur hexafluoride** from the top of crude oil tank	SOF measurements 3 tank heights away (Samuelsson, 2005)	13 +5.4	9.5	36%

Controlled source releases of **sulphur hexafluoride** from multiple position in a Petrochemical plant	Blind experiment together with the company Borealis. SOF measurements 500 m away (Unpublished)	2.18±0.3	1.89	15%
Controlled source releases of **ammonia** from a single point in farmland	Blind exercise together with the French institute INERIS (Unpublished). Releases of the tracer ammonia were carried out from a single point in a farmland	0.4	0.3	44%
		0.41	0.5	-15%
		0.43	0.6	-31%
		0.83	1.0	-19%
		1.27	1.1	14%
Controlled source release of **ethylene** from a 10 m tower in a parking lot	Blind experiment together with city of Longview and TCEQ (Yarwood 2015)	2.1	1.85	14%
		3.6	3.99	-10%
		3.3	6	-45%
		11	10.85	1.40%
Controlled source release of **propane** from a single point	Blind exercise at Anaheim football stadium as part of a SCAQMD study. Releases of propane from a single point at 5-10 m height without downwind obstacles. Measurements were carried out 50-100 m downwind. (Mellqvist 2017)	0.6	1.6	-63%
		2	4.6	-57%
		4.4	9.3	-53%
		6.6	13.9	-53%
		11.7	18	-35%
		14.7	23.9	-38%
		15.2	25.4	-40%
Controlled **VOC** emission from bitumen pipe	Blind exercise together with the company ÅF-IPK. SOF measurements downwind bitumen tank park (Samuelsson 2005). Blind comparison with different instrument operators and external reviewers.	7	7.1	+1%
Controlled **VOC** emission from crude tank.	Blind exercise together with the company ÅF-IPK. Heated tank with single vent. A fan was mounted and then the flow and concentration were measured in the vent using FID and a pitot tube. SOF measurements 3 tank heights away. (Samuelsson, 2005). Blind comparison with different instrument operators and external reviewers.	9	12	-26%

Comparative measurements of **ethylene** from a petrochemical conglomerate in Mont Belvieu, E Texas.	SOF measurements 3 km downwind compared to airborne measurement from a WP 3 Orion aircraft by NOAA. (Mellqvist, JGR 2009; De Gouw, 2009).	390	480	-20%
Comparative measurement of **alkanes** from tanks	SOF against DIAL in real measurement on several tanks. Externally reviewed by SCAQMD. Blind comparison with different instrument operators and external reviewers. (Mellqvist 2017)	9.4 21.7 103.5 348	13.7 46 122.9 289	-31% -53% -16% 20%

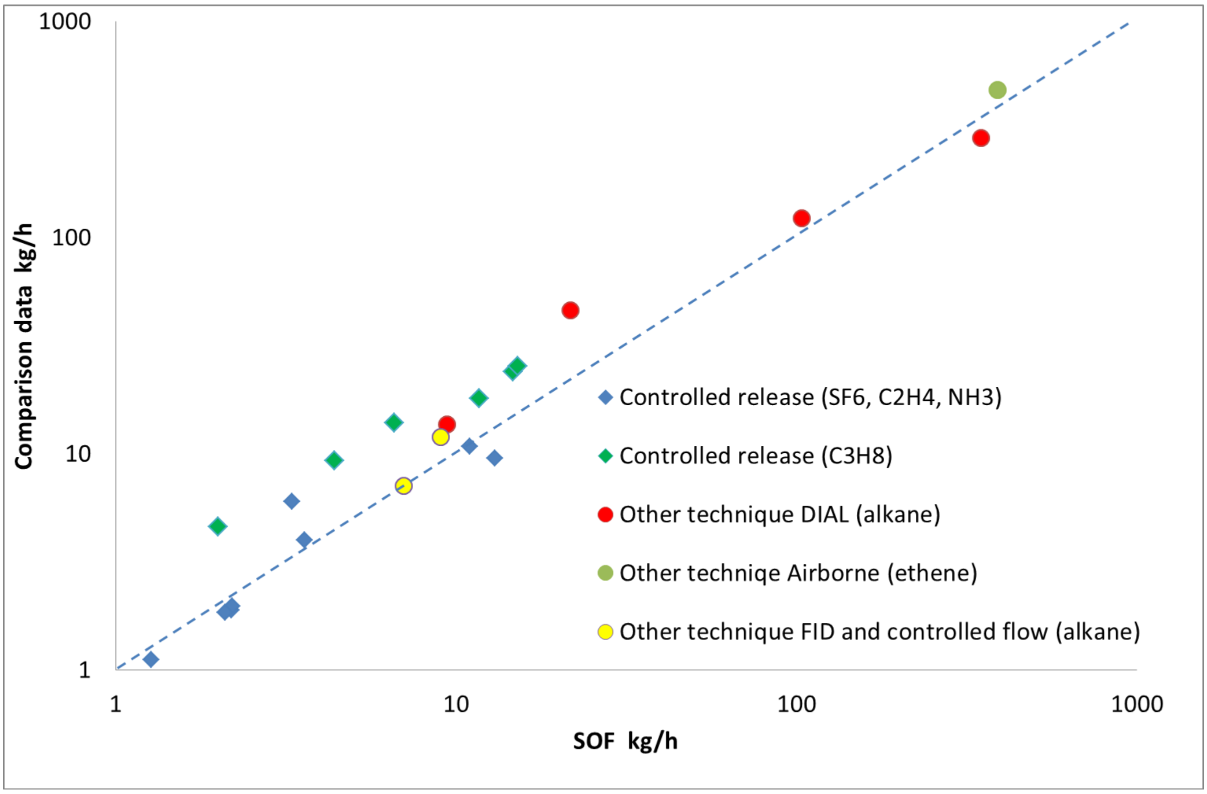

Figure A. 6. Summary of nine SOF validation experiments, based on controlled gas releases from a mast or comparative measurements of real fugitive emission sources.

A.3 Technical performance / Performance requirements

A.3.1 Performance characteristics

A summary of the performance capabilities of a typical SOF system under normal conditions are given in Table A. 2. The values provided are based on the actual levels of performance of existing SOF systems, determined from the typical absolute precision for column measurements in earlier studies when driving 40 km/h downwind of industries in Houston. The numbers in Table A. 2 are applicable given that there is enough solar radiation (relatively clear conditions and the solar elevation is more than 20^o. The performance will improve for small sources and slower measurement speed. For the species measured in the UV region, the numbers are based on measuring zenith scattered light in clear sky conditions. The column accuracy is the combined effect of instrument and retrieval stability on the total columns for a plume transect in real conditions.

The flux is determined by multiplying the column across the gas plume with the orthogonal wind speed as described in A.2.2. The main uncertainty of the flux measurements of diffuse emission sources comes from the uncertainty in the wind field in relation to the emission plume. For elevated point sources (stack) emissions, applicable to measurements of SO_2 and NO_2, this uncertainty is considerably lower. Table A. **3** shows the estimated uncertainty for flux measurements in various field conditions when measuring alkane emission from refineries and petrochemical industries. This estimate is obtained as the root-sum-square of various error sources estimated from a one-month campaign in Texas (Mellqvist et al., 2010), but the numbers are representative for other campaigns as well.

The infrared cross sections for alkane have an uncertainty of 3–3.5 % (Sharpe et al., 2004) and retrieval errors of 10 % have been estimated for the different species. This is the combined effect of instrument and retrieval stability on the total columns for a plume transect. For the alkane retrieval this also includes a 6 % mass retrieval uncertainty due to limited specificity. All these uncertainty sources have been combined by root-sum-square to a composite flux measurement uncertainty range for each species and study. The maximum and minimum for each range was calculated using the maximum and minimum uncertainties of both wind speed and wind direction. In most cases, the composite uncertainty is approximately 20-35 %.

The typical precision and accuracy of the complementary measurements which are used to derive the flux rates is shown in Table A. 4.

Table A. 2. Capability of a typical SOF column measurement based on direct solar measurements in the IR region and zenith scattered light in the UV.

Parameter	Precision (1σ)	Accuracy
Alkanes (C_2-C_8) (IR)	3 mg/m^2	10%
Ethene (IR)	1 mg/m^2	10%
Propene (IR)	2 mg/m^2	10%
NH_3	0.5 mg/m^2	10%
SF_6	0.2 mg/m^2	10%
SO_2 (UV)	1 mg/m^2	10%
NO_2 (UV)	1 mg/m^2	10%
HCHO (UV)	0.2 mg/m^2	10%

(1) Precision in ppb, assuming 50 m path length and C_4 mixture.

Table A. 3. Typical uncertainty estimation of alkane flux measurements for diffuse emission sources (the variability of the sources not taken into account).

	Wind Speed a)	**Wind direct** b)	**Spectroscopy (cross sections)** c)	**Retrieval error** d)	**Composite flux measurement uncertainty** e)
Alkanes	15–30 %	5–10 %	3.5 %	10 %	20–35 %

f) Comparing mast wind averages with the 0–500 m GPS sonde averages, the max data spreads 16–30 % (1σ, 30 %).

g) The 1σ deviation among the wind data compared to the 0–500 m sonde is 18º. For a plume transect orthogonal to the wind direction, which is always the aim, this would give a 6 % error. For a measurement in 75º angle the error is 9 %.

h) Includes systematic and random errors in the cross section database.

i) The combined effects of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect and error of the SOF alkane mass retrieval. Estimated for SOF.

j) The composite square root sum of squares uncertainty.

Table A. 4. Requirements of complementary measurement devices to the SOF method.

Parameter	**Precision/Detection Limit (1σ)**	**Accuracy**
Air temperature	n/a	±1 degrees C
Atmospheric Pressure	0.01 mb	±2 mb
Relative Humidity	n/a	±4 % RH
Wind direction	1 degree	±1 degrees
Wind speed	0.5 m/s	±0.5 m/s for winds 0-5 m/s ±1 m/s for winds 5-40 m/s

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Annex B
(normative)

SOF – Performance requirements and QA/QC

B.1 Performance requirements

For practical applications in order to be able to monitor gas emissions from an industrial scale site, the SOF (both IR and UV) system shall be:

- firmly mounted on a mobile platform that enables direct infrared solar measurements for IR-SOF, direct UV solar measurements or zenith sky measurements for UV-SOF.
- equipped with a global positioning system with at least 1 s temporal sampling time.
- able to perform high temporal sampling (< 5 s) and vibrational noise levels below the specified criteria while moving up to 70 km/h.
- capable of showing real time column data and platform position on a map.
- used together with continuous wind measurements (unobstructed wind at 10 m) and frequent vertical profiling of the wind.

For practical applications in order to be able to monitor general VOC emissions (alkanes, alcohol, alkenes) and other species (e.g. NH3), from an industrial scale site, the SOF system shall be:

- equipped with a fast infrared spectrometer (typically FTIR) with spectral resolution of 1 cm^{-1} or better covering the spectral region 800 cm^{-1} to 3100 cm^{-1} (3.2-12.5 µm).
- equipped with fast response solar tracker with a precision of 1 mrad while moving.

For practical applications in order to be able to monitor SO_2, NO_2 and HCHO emissions from an industrial scale site, the system shall be:

- equipped with a fast UV/visible spectrometer with a spectral resolution of 1 nm or better covering the spectral region 305 to 365 nm.
- equipped with an optical fibre and a zenith viewing telescope.

B.2 Application of the method

B.2.1 Measurements planning

It is critical to thoroughly plan the survey before carrying out the measurements. This includes the following:

- Campaign logistics: this includes site pre-visit meeting (if required) or checklists for ensuring the site are aware of the logistics of the measurements. A SOF methodology description may be provided if required. Also make sure that the site is operating normally during the time of the measurements. Periods of major plant revisions should be avoided. Ask staff for a detailed site map/overview. Site orientation: Identifying site areas and measurement roads considering different wind directions and solar paths (to predict where shadows exists during the course of the day). Ask site staff about how to get access to roads in any ATEX-areas. Extract, based on this information, ideal wind conditions for measurements of the site and areas.

- Identification of likely emission sources: this requires information from the site, usually including site plans and existing emissions information. Potential background sources off-site should also be considered.

- Potential interfering species: for complex sites this may require process information or preliminary air-sample analysis taken as part of the campaign measurements.

- Meteorology assessment: get information on typical wind directions and solar conditions and other relevant meteorological data. Try to access data from any nearby meteorological stations.

B.2.2 Selection of gas species to be measured

Selection of optical channels for SOF:

- Obtain information about the typical gas-mixture in the emissions and handled products of the site de Make complementary composition measurements, such as canister analysis or high-resolution MeFTIR, if needed.

- Decide on the time sharing between the different optical channels (alkanes, alkenes or other species).

B.2.3 Measurement strategy

Identify an optimal meteorological mast location, preferably a clear and flat area on the upwind side of the facility. If site topography is complex and different wind directions are anticipated, deploy a second and possibly third meteorological station to ascertain that the unobscured wind is always available. The unobscured (main) wind should be measured at 10 m altitude. Optionally deploy or use an available on-site mast with a height of +30 m to get above tank height. Combine with wind profiler or frequent balloon wind soundings.

Figure out ideal SOF measurement transects for each site area based on the weather forecast for the actual measurements period. Use the following daily strategy:

a) Communicate each day to the site the possible SOF locations facilitating the work permit.

b) Quickly react if the actual wind direction during the day deviates from the forecast.

For a given wind direction, the area to measure should be chosen such as:

a) The area under investigation is clear from strong upwind/background sources. Avoid areas with high inflows or where the background cannot be estimated.

b) When measuring at close distance from the emission source, i.e. close to low level sources, such as water treatment ponds and sewers, a ground level wind sensor should be deployed close to the SOF measurement transect.

B.2.4 Set-up and initial tasks

General:

☐ Site specific requirements such as safety inspection and introduction course.
☐ Agree on the procedure for changing SOF location with site operators and prepare any special permits to drive in ATEX areas (with a safety guard).
☐ Assure safe operation of the SOF vehicle.

Vehicle:

☐ Check SOF vehicle status according to safety and performance.
☐ Check that warning lights and signage are mounted and operational.
☐ For measurements inside industrial areas the equipment should be equipped with a single safety switch by which all instruments can be turned off, in case of emergency.
☐ Make sure that car battery pack is fully charged.
☐ Make sure any loose items are stowed away securely.

Instruments:

☐ Turn on instruments and make sure that detectors are properly cooled.
☐ Optimize signals by optical alignment.
☐ Clean mirrors and optics if necessary
☐ Make a rotational alignment test and determine the resulting column. Tolerance: ±2 mg/m^2 in any direction while standing still.
☐ Check spectral resolution and intensity response. Check that the width of narrowest absorption lines in the measured solar spectra are within the set spectral resolution. Tolerance within 20%.
☐ For the UV/visible spectrometer run a daily line shape test to calibrate the wavelength and to convert the absorption cross sections to the appropriate special resolution.
☐ Check the time synchronization of all instruments and computers against GPS-time, tolerance 1s.

GPS:

☐ Check that the GPS data are available and correct.

Wind:

☐ Set-up the meteorological sensors at the agreed locations and check the functionality.
☐ Align sensor correctly (toward magnetic north) using a compass. Tolerance: ±5^{o}.
☐ Erect the wind mast vertically and secure it firmly
☐ Check that wind information is available and reasonable.
☐ Check the time difference of logger and computer. Tolerance 1 s.

B.2.5 Measurements

Before starting the measurements, ensure:

☐ Staff is signed in on site (if required).

☐ If necessary, apply for a work permit.

☐ Ensure that staff is familiar with local safety protocols.

☐ Logging of the meteorological data is started.

☐ Determine the measurement plan/strategy for the day.

Measurement procedure:

☐ During the measurements check that the retrieved columns change less than 5 mg/m^2 when turning in different directions. If the changes are larger a recalibration of the rotational alignment should be done or a note to account for this in the uncertainty evaluation during post analysis. Note that this effect usually depends on the solar angle and the offset is usually worse for low solar angles.

☐ For each source multiple measurement transects per day are required with accepted quality. The solar angle above horizon should be sufficiently high and the average wind during the transects within the required wind speed.

☐ For each area source, the inflow from the background should be determined. This should be done by measuring in a “box” around the source area for at least half of the measurements. In a dense industrial area it is necessary to make box measurements while for more isolated sources the background levels can also be determined from the baseline of the downwind SOF measurements, if upwind roads are not available. Extra care should be taken if there is large source upwind the area source. Such sources can meander in and out of the area source relatively quickly and this effect is more pronounced the bigger source and the further away it is located. If such a source is identified it is important to localize and quantify it, in order to be able to discard its effect in later measurements.

☐ The measurements should be done at highest driving speed possible, taking into account speed limits and the noise of the retrieved columns, in order to “freeze” horizontal movement of the plume during the scan. Higher speed causes vibrational noise, depending on the quality of the road, and it also increases the influence of shadows. For instance, one should adapt the speed to minimize the effect from periodically occurring shadows, such as light posts.

☐ Avoid measurement situations when the observed sun cuts through the emission plume from the upwind side, and when it goes below high emitting objects, such as flares. This is usually a problem when measuring too close to high structures or process area with plume lift, in combination with low solar angles.

☐ Keep track of wind directions and measured columns/concentrations so that the entire plume from a facility is captured.

☐ Always try to start new measurements outside the plume. Although this can be fixed in the post analysis, it significantly improves the real time interpretation and analysis.

☐ When measuring in the alkene channel around 10 µm, one should measure dark spectra that will be subtracted from all other spectra. Such measurements, carried out by pointing the solar tracker away from the sun toward typical sky, should be carried out frequently, at least every hour, with the same settings as the solar measurements.

☐ Take notes and photos on interesting findings and events.

☐ If unexpected measurement results are obtained, such as high emissions or higher than previously experienced, try to check in real time whether these could be explained by for instance intermittent emissions due to for instance maintenance activity such as tank cleaning operation or ship or truck loading. If feasible, take contact with the industrial site and discuss whether the emissions can be explained by some known activity.

☐ Check the wind meter on a regular basis to make sure that it is operational.

☐ Check the GPS sensor on a regular basis to make sure that it is operational.

At the end of the measurement day ensure that:

☐ All SOF data are saved and backed up.

☐ All met data are downloaded, saved and backed up.

☐ Demount the wind mast if it is not in a secure location

☐ Update survey documents. If feasible discuss measurements results with the industrial site and collect complementary data such as tank height level, flaring activity, etc.

☐ Turn off instruments.

☐ Charge measurement vehicle, and data logger batteries.

☐ Make sure that instruments are well protected inside the vehicle from rain/moisture.

B.3 Quality control

B.3.1 General

Quality checks and quality assurance and measures are performed at several levels. In general, most checks are done prior to measurement, including powering up the equipment, checking operating parameters, and test the instruments. The purpose is to run operational checks to catch problems prior to field deployment and repair all malfunctioning equipment.

B.3.2 Spectroscopic calibration procedures

B.3.2.1 General

The SOF instrument does not need calibration prior to the measurements and instead one relies on published line parameters or absorption cross sections from the literature available in data bases. This is appropriate as long as the instrument is well aligned and its spectral response is well characterized. It should have the same response in all pointing directions relative to the sun.

B.3.2.2 Calibration

Published line parameters, for instance from the HITRAN database (Rothman 2003) should be used to simulate absorption spectra for atmospheric background species (H_2O, HDO, CO_2, CH_4) at the actual pressure, temperature and instrumental resolution of the measurements. For the retrievals of the VOC species, high resolution calibration spectra can be obtained from data bases, such as the PNL (Pacific Northwest Laboratory) database (Sharpe, 2004). The uncertainty in the absorption strength of the calibration spectra is here about 4 %. To use these cross sections they have to be degraded to the spectral resolution of the instrument by convolution with the instrument line-shape. The advantage with this approach is the traceability since it does not require calibration. However, the actual line shape of the instrument is not measured and instead one relies on the accuracy of the theoretical line shape in the retrieval. An optional way to obtain calibration spectra of VOCs is to measure absorbance spectra directly by using a calibration cell containing calibration mixtures of VOCs in the solar beam.

B.3.3 Meteorological sensors calibration

The meteorological sensor should be calibrated once a year by the manufacturer or by a reference wind meter. The calibration certificates may provide a calibration factor for the wind speed and wind direction readings. If data loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.

In addition, the different sensors should be compared side-by-side in the field to provide a further check on their correct function. For instance, if mechanical anemometers are being used the bearings can be worn causing lower apparent wind speeds which is difficult to identify afterwards. This must therefore be checked by relatively short-term comparisons in the field or lab to a reference anemometer once per year.

B.3.4 Required QC checks in the field

For the SOF instrument several QC procedures should be carried out prior to conducting the spectral measurements on each day. This includes checking that the instruments work in general and that the spectral response is appropriate and independent on the positioning of the instrument, relative to the sun.

This should be done by measuring solar spectra at the highest resolution and investigate the maximum intensity and width and line position of narrow absorption lines which have an apparent linewidth which is similar to the spectral resolution of the instruments. There are many such narrow lines. For instance, the solar absorption line at around 2158 cm^{-1} at high solar angles is suitable for this purpose, corresponding to the atmospheric absorption of CO. Note that the width of the atmospheric lines is usually dependent on the solar angle. In the QC procedure it should be checked that the width of the measured narrow absorption lines is not more than 20 % wider than the nominal theoretical width of the instrument and that the line position is not shifted more than 0.2 cm^{-1} towards lower wavenumbers. If this is not the case, a realignment of the SOF instrument is required. If the linewidth and line position is acceptable, the next step is to make sure that the same line shape is achieved when the SOF system is directed in four 90^o directions relative to the sun. If the linewidth is within 5 % and the position is not shifted more than 0.2 cm^{-1} and intensity is within 10 % for all four directions then the quality is acceptable. If not, the instruments should be rotationally aligned. The above-mentioned procedure should be performed on each measurement day.

The next step in the QC procedure is to run the instrument with the actual resolution used for measuring the VOCs, typically 8 cm^{-1}. Measurements are again carried out with the instrument positioned in four 90^o directions relative to the sun and then the columns (path integrated concentration) of VOCs should be retrieved. These should change less than 2 mg/m^2 in the different directions. The same test should be carried out several times every measurement day to be used for the error estimation in the reporting.
During the measurements it should be checked in the real time data that the precision of the instruments is normal, and whether upwind emission sources or other short-term activities influence the measurements.

Prior to each SOF transect it should be checked that the spectra have an intensity which is less than 25 % from saturation. If one uses an FTIR, saturation effects can also be seen as baseline effects in dark spectral regions.

For the UV/visible spectrometer run a daily lineshape test by holding a low-pressure mercury lamp in front of the zenith viewing telescope. The emission lines should be used for wavelength calibration and to convert the cross section to the appropriate special resolution of the instrument.

B.4 Data analysis

B.4.1 General

General data analysis is based on the following:

- Retrieve the path average concentration (column) of VOCs from the solar spectra
- Retrieve gas fluxes
- Identify source emission areas and make statistics over their emissions over multiple days for the different source areas

B.4.2 Calculation of path-integrated concentration

The retrieval of the path integrated concentration (column) from the infrared spectra should be performed by spectral fitting of calibration spectra to the measured SOF spectra. In addition to the fitting of VOC spectra, one should also fit background species such as H_2O CO_2 and CH_4.

In the spectral retrieval a reference spectrum should be chosen from a region of the measurement transect where it can be assumed that the target gas concentration is near zero and which corresponds to the lowest column value measured, i.e. typically and upwind spectrum.

The spectral retrieval shall be based on the Beer-Lambert law, which states that the logarithm of the intensity ratio for the light which is absorbed by the gas is proportional to the path averaged concentration. The retrieval algorithm can be implemented in different ways, but usually some kind of nonlinear fitting scheme is required. One solution is to work directly in the logarithmic space. Here the logarithm of the reference spectrum is fitted to the measured spectrum together with absorption cross sections of the gas species to be retrieved. This approach makes it possible to account for wavelength shifts in the spectra and also to include several reference spectra in the fit, which results in efficient removal of the influence of the upper atmosphere. However, such a scheme is suitable only for small absorbers.

For measurements of alkenes, alkadienes and ammonia the spectral region between 750cm^{-1} and 1000 cm^{-1} should be used with a spectral resolution corresponding to 1 cm^{-1} or better, for sufficient specificity. In the spectral evaluation routine it is required that background species, such as H_2O and CO_2, are fitted with good precision together with the main absorbing VOC species in the spectral region, e.g. ethene, propene, 1-butene, 1,3-butadiene and ammonia. A thermal background spectrum should be recorded at regular intervals by measuring with the solar tracker pointed to the cold sky. The background thermal spectrum should be subtracted from each recorded solar spectrum.

For measurements of alkanes, the spectral region between 2700 cm^{-1} and 3005 cm^{-1} (CH- stretch region) should be used with a resolution of 4 cm^{-1} to 8 cm^{-1}, for improved signal to noise. The absorption features of the different alkanes are similar and interfere with each other and specificity is therefore poor. However, since the number of absorbing C-H-bonds is directly related to the molecular mass, the total alkane mass can be retrieved with good accuracy despite the interference. In addition, since the absorption structures of the different alkane species change systematically with the number of carbon atoms, it is possible in the spectral retrieval to evaluate also the average carbon number in the measured VOC plume. The VOC's that are emitted from a typical refinery correspond mostly to light alkanes (90%). The composition of the alkanes is however usually complex and it may consist of many tenths of species. Even so, to obtain the total alkane mass and average number, it is in the spectral retrieval sufficient to fit only a few VOC calibration spectra (ethane, propane, n-butane, and n-octane) together with the atmospheric background species of CO_2, HDO, H_2O and CH_4. For other industries it is necessary to obtain complementary information about the general VOC composition at the source before choosing the calibration mixture to use in the spectral evaluation since also aromatic VOCs, alcohols and alkenes have absorption features in the CH-stretch region.

For measurements of SO_2, NO_2 and HCHO in the UV/visible the spectral region between 305 and 365 nm should be used with a resolution better than 1 nm. In the retrieval it is also necessary to take into account absorption features of O_3, O_4 (O_2-O_2 weak complex) and "ring spectra", the latter corresponding to spectral structures coming from inelastic atmospheric scattering [Fish 1995]. In the data retrieval it is preferable to use published cross sections.

B.4.3 Calculation of gas fluxes

The flux should be obtained as the product of the SOF column measurements integrated across the plume and the average wind speed for the VOC plume.

For inside refinery measurements the wind used should be obtained from the non-obscured 10-minute average wind at the plant. For special cases the ground wind speed downwind the source should instead be used, i.e. from the water treatment area.

For measurement beyond the fence-line of the site or on-site measurements covering a larger area such as tank farm, the plume wind speed should be obtained as the average wind speed from the ground to the upper mixing height of the plume. The upper mixing height is obtained as the product of the assumed vertical mixing speed (0.5 m/s) and the time it takes for an air parcel to travel between the main source and measurement position. The latter is obtained as the ratio between distance to source and the wind speed. For a tank area the position of the source is assumed to be in the middle of the tank farm. The mixing height can optionally be measured indirectly, by making use of complementary alkane concentration measurements on the ground. From the ratio between the measured column by SOF and the measured ground concentration, an estimate of the upper mixing height of the plume is obtained, assuming a well-mixed plume from ground and upward.

The wind height profile is needed to calculate the average wind speed from ground to upper mixing height. The profile should either be obtained directly from (a) a wind profiler running continuously, (b) a combination of the 10 m measurement wind from a mast and statistical scaling factors obtained from wind balloon soundings or wind profiler measurements, (c) mast measurements at different heights and logarithmic extrapolation or d) equivalent methods. If variant b is chosen the balloon sounding should be taken over several full measurements days, with 3-6 soundings per day. The days should be chosen so that they cover the different wind conditions occurring during the SOF measurements.

B.4.4 Estimation and localization of emission sources

From spatial mapping of the flux measurements together with wind measurements, the source areas causing the measured gas fluxes can be interpreted. It is important to measure over several days and ideally in different wind directions to be able to pinpoint the sources.

The SOF measurements has the smallest uncertainty when carrying out measurements outside the fenceline of the refinery, since the wind field is then less disturbed and most of the emissions plume has had time to distribute itself over several hundred meters in height. For the subarea measurements performed close to the source inside the refinery, the wind field is more complex and using an unobscured 10 m wind risks overestimating the emissions. . The emission values obtained by SOF inside the refinery should therefore be rescaled to the appropriate plume speed, so that their sum matches the emission value measured at the fenceline. In this manner the uncertainty of the wind field close to tanks etc. is minimized.

The SOF measurements are influenced by turbulence in the wind field, causing apparent horizontal shifts in the position of the plume in the measurement plane. One shall therefore average over at least 4 measurements during the same day to mitigate this effect.

Industrial sites, such as refineries are complex and include both continuous emissions from tanks and process areas as well as intermittent ones from various activities such as cleaning and repair, ship and truck loading and flaring. To get an understanding of the emissions at a site one should measure over 5-10 days, depending on the size of the site, for varying wind directions. The obtained data from various areas should be analysed in a statistical manner. The wind turbulence normally causes an emission curve that follows a normal distribution while a skew shape of these curves is due to intermittent emissions due to tank cleaning etc. The best estimate of the continuous emissions is the median value, given that intermittent emissions only have occurred infrequently during the measurement study, while the average emissions is the best estimate for the total emissions during the period. However, since intermittent emissions can be very high, it is important to understand the origin of these before including them in any emission assessment. Once the source of the intermittent emission is understood one should assess, if possible together with the industrial site, how frequent such emissions occur during the year.

Indirect flux measurements of aromatics, methane and other gases not measured solely by SOF are also possible. By combining SOF measurements with complementary concentration measurement techniques based on optical (infrared and ultraviolet) absorption in multi-reflection cells in the same measurement vehicle fluxes of the gases are obtained. The measured ratio of the gas (aromatic species, methane, etc.) concentration to total alkane concentration is multiplied with the measured alkane flux to indirectly measure the gas emissions. The ratio of the column and the concentration measurements also provides an estimate of the average plume height for well mixed plumes as mentioned above.

If the total emission values obtained at the fence line of the industry differs to the total estimated emissions in the refinery of sub areas and tanks, the inside measurements should be rescaled to match the outside. The rational for this is that the fenceline measurements are considered more accurate since the wind field is then less disturbed compared to on-site measurements, caused primarily by the fact that the plume has had time to rise to higher altitudes where the wind field is more stable.

B.4.5 Data validation procedures

One shall maintain records that include sufficient information to reconstruct measurement from the variables originally gathered in the measurement process. This includes, but is not limited to, information (raw data, electronic files, and/or hard copy printouts) related to sampler calibration, sample collection, measurement instrument calibration, quality control checks of sampling or measurement equipment, "as collected" or “raw” measurement values, an audit trail for any modifications made to the "as collected" or “raw” measurement values, and traceability documentation for reference standards. Difficulties encountered during sampling or analysis, such as interference between adjacent plumes, large upwind fluxes or highly variable wind fields should be documented.

To ensure high quality data an internal audit procedure of the data shall be carried out. In this procedure, the completed SOF measurements shall be reviewed by an experienced SOF-operator that has not been involved in the actual data evaluation. At least one of the persons involved in the data processing must have been present while the actual measurements were made.

The final emission data should be presented as daily means and standard deviations for each measured source. Histograms, showing all individual measurements of a source, may also be presented to analyse the emission distributions.

Extreme outliers should generally not be excluded, unless non-typical conditions/operations at the facility are reported. In this case, the outliers should be reported separately so that these conditions/operations can be followed up. However, since the median is used as the best estimate of the continuous emissions, the outliers will generally not include this value.

The criteria below shall be used to flag uncertain SOF measurement data and these data should either be discarded, tagged with higher uncertainty, as requiring complementary information or new spectroscopic retrieval:

1. For each reported source emission, at least 4 measurement transects are required per day.
2. Noise levels above the detection limits, tolerance less than 3×detection limit
3. Significant baseline variations, tolerance <10 mg/m^2.
4. Significant data gaps in the plume, tolerance < 20 % of the spatial extent of emission plume
5. Extended vehicle stops, tolerance < 20% of the of the time extent of emission plume measurement
6. Nearby upwind plumes are of significant magnitude, tolerance < 50% of downwind emissions
7. Average wind speed during the transects included in the average emission value, tolerance 1.5 m/s to 12 m/s
8. Highly varying wind directions, tolerance < 30^o in standard deviation of 10 min wind direction
9. Low solar angle, tolerance > 20^o above horizon
10. Upwind measurements close to high structures, or process area, for which the solar beam cuts through the gas plume from the upwind side or goes below the emission plume, such as a flare.
11. Data corresponding to significant systematic residual in the spectral fitting, tolerance 2× typical spectral residual noise.

B.5 Reporting

The report should include the following:

- Overview and description of measurement method.
- Description of emission quantification procedure.
- Measurements objectives.
- Factors influencing detection limit and accuracy.
- Emission for each area measured.
- Meteorological and other data collected pertaining to the SOF measurement:
    - date, time and duration of measurement
    - wind velocity and direction
    - geographic location (GPS coordinates)
    - description of areas observed
- Two-dimensional column data for the measurements
- Display of the data overlaid on a site plan (2D plot) to aid visualization of the plume and to identify emission sources.
- Conclusion: which areas were measured and total emission rate. Emission rates should be presented as statistical data (daily means, standard deviations, median).

TOTAL
COMMITTED TO BETTER ENERGY

MEMO

Raffinage-Chimie
Direction R&D
Laboratoire Qualité de l’Air

Destinataire : CEN WG38 group *To* :		Expéditeur : Olivier DUCLAUX.... *From* Jonathan LEMUS.... Pierre MANGEON... ....
Copie : Equipe LQA .... *Copy* Sylvie SUTTER................		Date : 12/05/2018 ....
Object : *Subject*	**RESULTATS RDM in CEN campaign #1 : blind test with emission controlled**	

Reference CEDRE : HSE -2018- ENV –024

Sommaire

1. Contexte

In the framework of CEN WG38, an emission quantification campaign with controlled emissions has been carried out in south of France in a mothballed refinery.
The emission quantification was conducted using several technics, including macroscale optical tools (Lidar from NPL, SOF from Fluxsense), mobile FTIR using tracer operated by Fluxsense and Reverse Dispersion Modeling operated by TOTAL LQA.
The study was conducted on TOTAL funding for a participation in the first two weeks of testing (# test 1 to 4 and # test 6 to 14).

All the emission estimates were sent to INERIS before knowing the true emissions, with a presentation of the results in Powerpoint format.

This report summarizes the emission estimates originally submitted, modifications related to protocol adaptation, and actual emissions provided thereafter.

The report is divided into three parts:

- Preparatory work and measurement campaign
- RDM methodology : Direct Modeling and Reverse dispersion estimation
- Comparisons with real emissions, definition of validity criteria

2. Preparatory work and measurement campaign

- The preparatory work was done in August – September 2016 :
  - Meetings and prior visits of the unit with photography.
  - Safety training.
  - Retrieval of geometry information (Map of the installations, pictures, height measurements with laser …)

- During the measurement campaign, emission estimations involved:
  - Staff :
    - 2 persons from TOTAL for Met Mast installation
    - Measurements (#test 1 to 4) : 3 persons (2 for RDM and one for FLIR IR camera (not necessary for RDM))
    - Measurements (test#6 to 14) : 2 person for RDM and IR camera
  - On-site materials
    - Weather station METEK USA-1 - 3 D with turbulence measurement, installed on a10 meters mast (carbon) (see picture).
    - Portable Foxboro Analyzer (FID / PID) (see picture).
    - Infrared camera (FLIR) for VOC detection and pictures
    - 1 vehicle for transportation (a car)
    - Gas for calibration (Propane + Air zero)
    - Computer
    - Personal protective equipment

  - Off-site materials:
    - Hydrogen bottle for FID refueling.

Protocol:

- Before measurements, a calibration of the FID detector was performed with propane standard.
- The emission tests lasted 1h30, and safety conditions had to be met in order to move in the unit (use of ladders, all parts of the unit were not accessible due to the decrepitude…), so the number of measurement points was variable for each test. The location of measurement point chosen were:
    - first, a up wind measurement is done for background before the authorization to go in the unit
    - in or downwind of the unit to be in the plume of each source for quantification
    - not to close for safety reasons (max concentration accepted 1000 ppm)
    - not to close for representativeness of dispersion model reasons (minimum 2 meters)
    - Following the path, the strategy is to obtain a transversal section of each plume (with the objective to have 7 significative points in each plume)

Figure 1 : views of FID Measurements

Figure 2 : METEK Meteo Station and location of met stations (the METEK is close to the Station North)

Exact measurement locations and timing were recorded.

The minimum measurement duration at a point was 30 seconds for FID measurements. According to the wind variability, the duration could reach several minutes in the same point. All measurement locations are reported in each test annexe.
An example of a measurement pathway (measurement points in red) in the modelled structure is reported in next Figure.

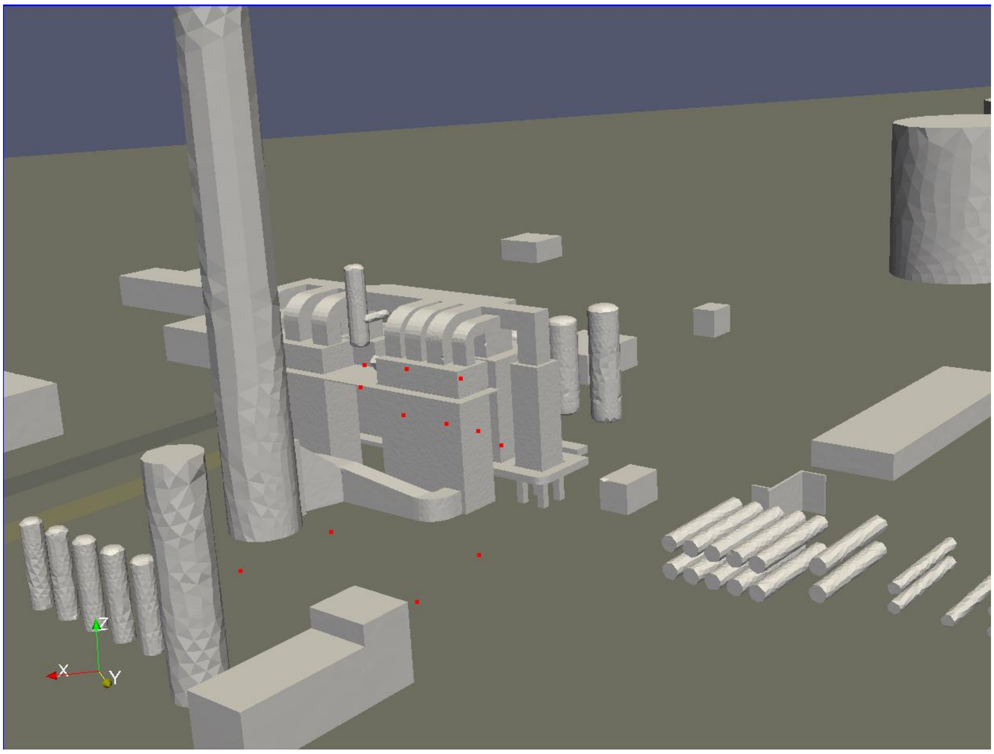


Figure 3 : Measurement points (red dots) during a path

From the 22/06/2016 to the 28/09/2016 14 :00, the TOTAL team participated in 13 Tests. For all the tests in which TOTAL RDM participated, an RDM estimation was performed and sent to INERIS.

	Date	Start time (local)	End time (local)	TOTAL Measurements	TOTAL RDM estimations	Sources
Test 1	22/09/2016	13:18:00	14:48:00	yes	yes	Lvl1M
Test 2	22/09/2016	15:10:00	16:46:00	yes	yes	Lvl2
Test 3	23/09/2016	11:27:00	12:57:00	yes	yes	Lvl1N
Test 4	23/09/2016	14:00:00	15:30:00	yes	yes	Tube
Test 5	26/09/2016	09:41:00	11:11:00	no	no	
Test 6	26/09/2016	12:00:00	13:30:00	yes	yes	Lvl1N + Lvl1S
Test 7	26/09/2016	14:30:00	16:00:00	yes	yes	4 sources
Test 8	26/09/2016	16:05:00	17:35:00	yes	yes	Lvl1S
Test 9	27/09/2016	09:35:00	11:04:00	yes	yes	Tube
Test 10	27/09/2016	11:30:00	13:05:00	yes	yes	4 sources
Test 11	27/09/2016	14:00:00	15:30:00	yes	yes	Lvl1N + Lvl2
Test 12	27/09/2016	15:55:00	17:25:00	yes	yes	Lvl2
Test 13	28/09/2016	10:07:00	11:37:00	yes	yes	Tube
Test 14	28/09/2016	12:05:00	13:35:00	yes	yes	Tube
Test 15	28/09/2016	14:35:00	16:00:00	no	no	
Test 16	28/09/2016	16:45:00	17:52:00	no	no	
Test 17	29/09/2016	10:50:00	12:15:00	no	no	
Test 18	29/09/2016	12:38:00	13:52:00	no	no	
Test 19	29/09/2016	14:10:00	15:10:00	no	no	
Test 20	29/09/2016	15:30:00	17:00:00	no	no	

Tableau 1 : list of tests with participation of TOTAL team, and sources

3. RDM methodology : Direct Modeling and Reverse dispersion estimations

The RDM methodology was applied after the measurement campaign. To reproduce dispersion conditions specific of the measurement period, direct dispersion calculation was performed with unitary emission.

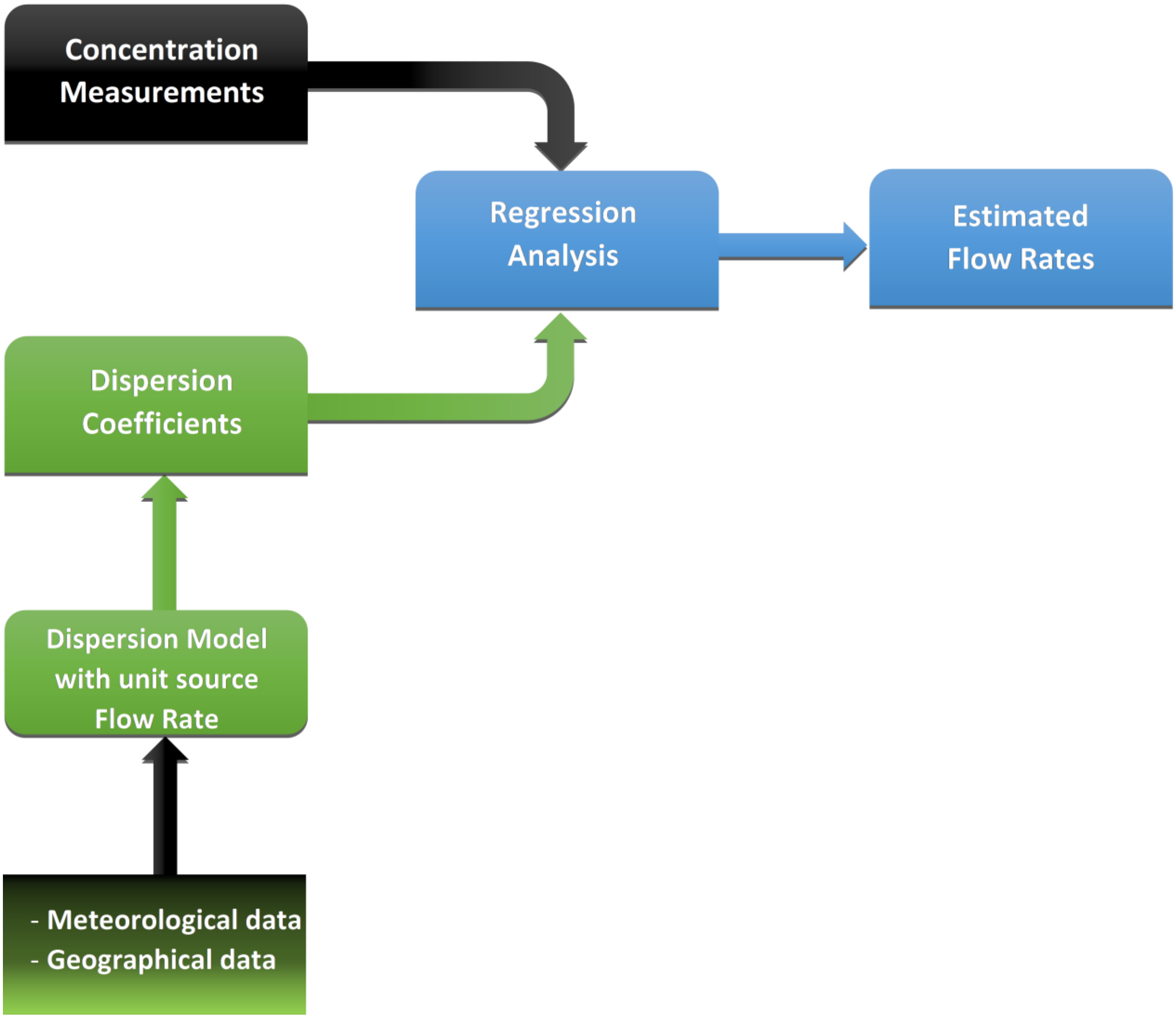


Figure 4 : Reverse Dispersion Methodology

Direct model description :

Following RDM standard, the model must be adapted to the situation. In presence of obstacles (building, tanks, industrial units …), the selected model must be able to reproduce effects of obstacles in the wind field.

The model selected for the CEN campaign is a combination of a CFD model and a Lagrangian dispersion model.

CFD calculation :

In complex area, CFD model is a solution to reproduce wind fields and turbulence variability. The model requires parameterizations adaptated to studied atmospheric turbulences, and uses the meteorological parameters (wind direction, speed and turbulence) to construct a 3D wind field data base. This database is used for dispersion calculation to obtain unstationnary evolution of meteorological conditions.

A specific domain was defined to represent the unit where the controlled emissions are located and the main obstacles around, which could influence the local wind field. The domain is represented in the next pictures, as as the satellite view, modeled structure and meshing (all domain and a zoom on the unit). An example of CFD model results for 2 meters above ground wind is also reported.

Figure 5 : View of the real site

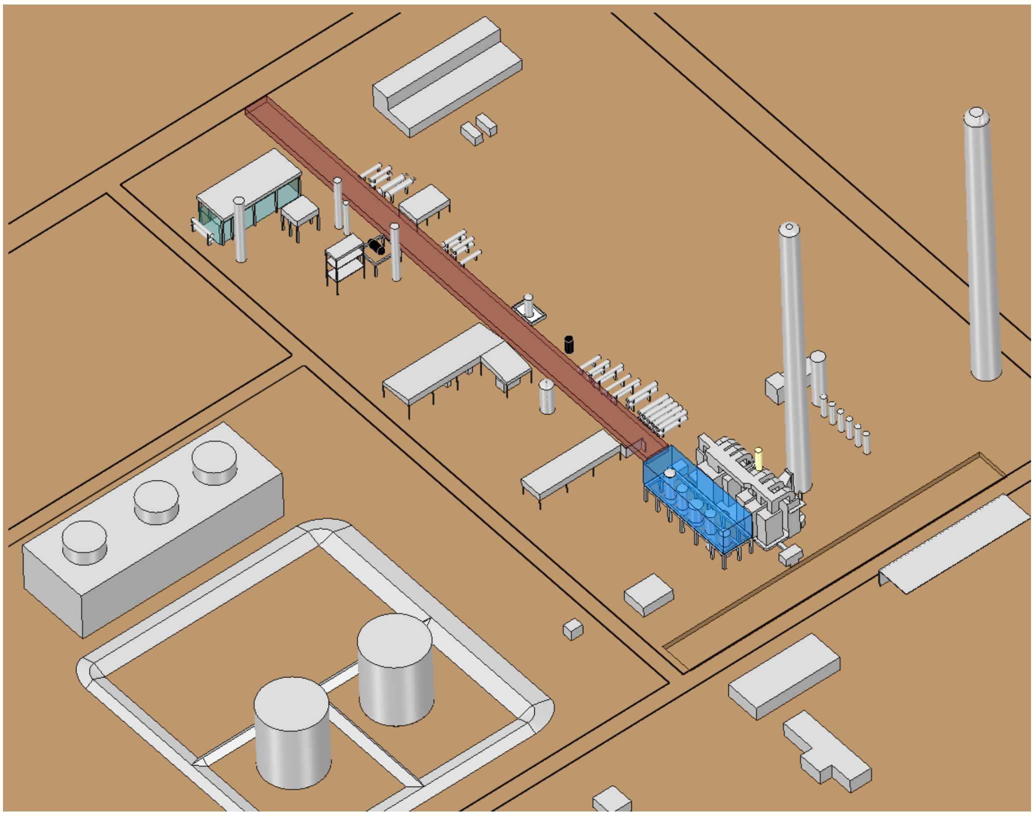


Figure 6 : View of the modeled site

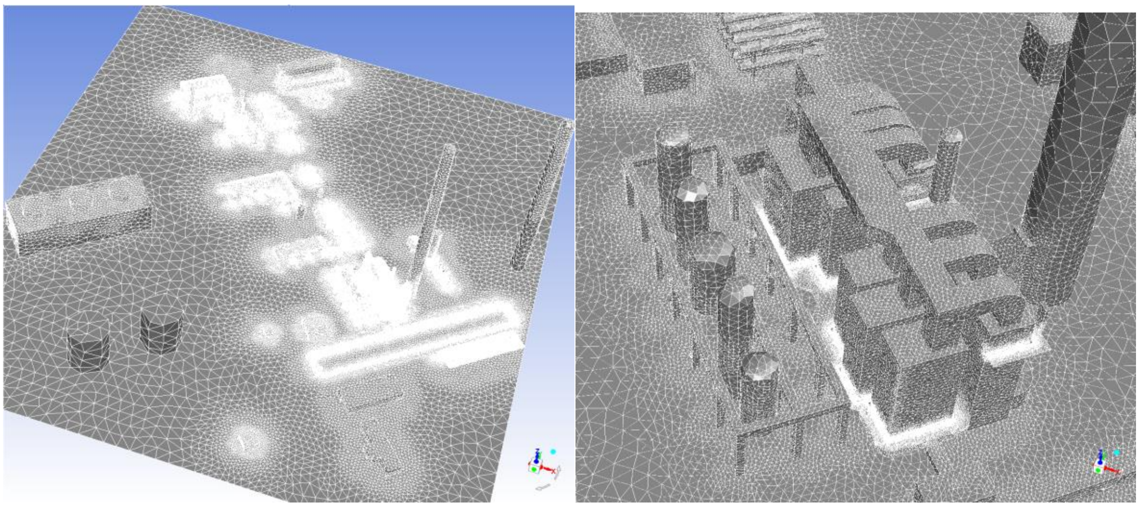


Figure 7 : View of the real site

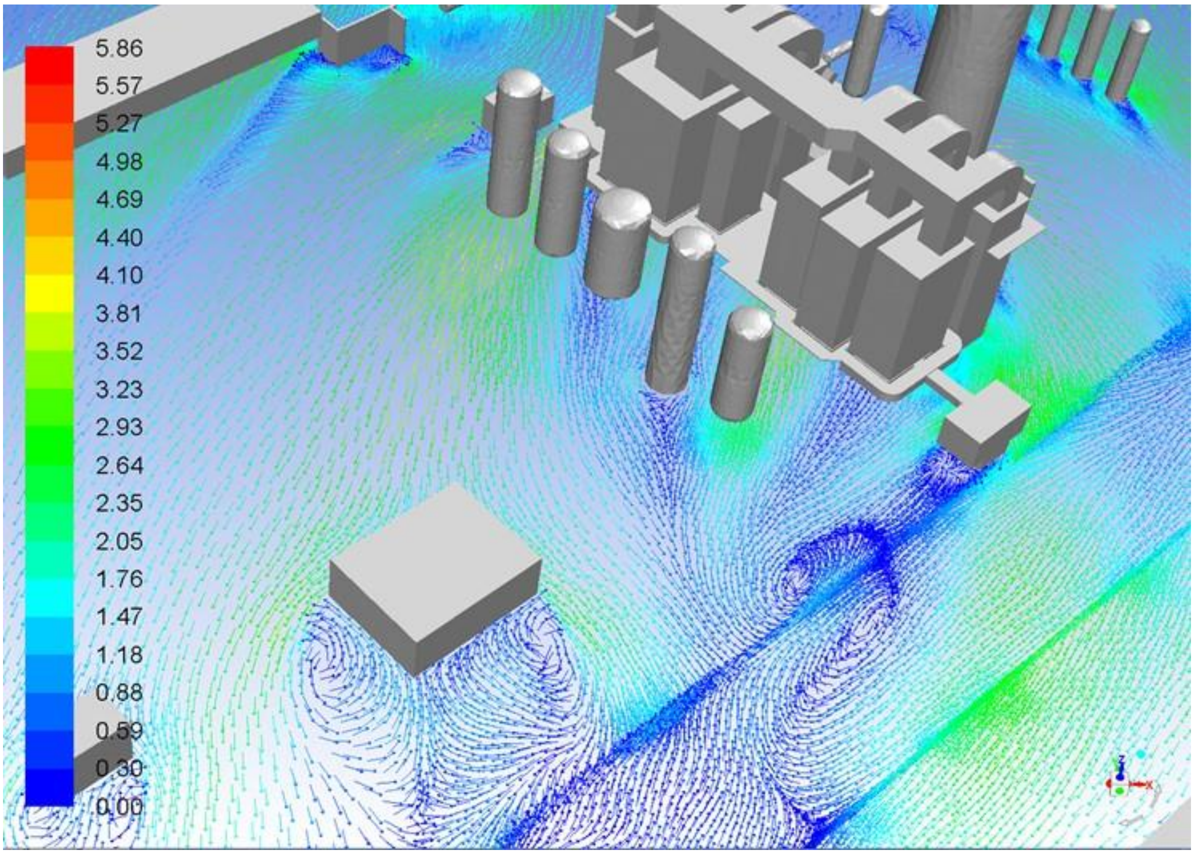


Figure 8 : View of wind field calculate by CFD model (Fluent)

- The combination of the data base with measured real meteorological conditions allows to construct a variable wind field.

- The next work is the dispersion. The dispersion is based on the recombined 3d wind field and the use of a lagrangian model (SLAM). The emission sources are represented by volume or area sources. Classical direct dispersion is performed with a theoretical emission flux set at 1 g/s for each source, in order to obtain the dispersion factor matrix at each monitoring point.

Dispersion :

- The emission sources are used in the dispersion model (SLAM) with the combination of CFD wind and turbulence fields corresponding to a specific meteorological condition (station measurement).

- **Representation of emission sources :**

  - The parameters of the 5 emission sources are described in Table 1 according to their position in the modeling domain and their geometry. The discs are represented by a circle with a radius of 0.4 m. The tube is modeled as a cylinder. The positions are defined as the center of each source.
  - An example of instantaneous dispersion with the tube is reported.

Source name	X	Y	Z	R	H
source_disk_Level1 - Mid	-148.62701	2275.6492	5.6	0.4	0
source_disk_Level1_Nord	-158.0824	2277.4313	3.5	0.4	0
source_disk_Level1_Sud	-139.25529	2258.8154	3.5	0.4	0
source_disk_Level2	-143.94633	2274.8085	10.6	0.4	0
source_tube	-144.8	2273.3	7.5	0.1	5

Table 1 : characteristics of emission sources

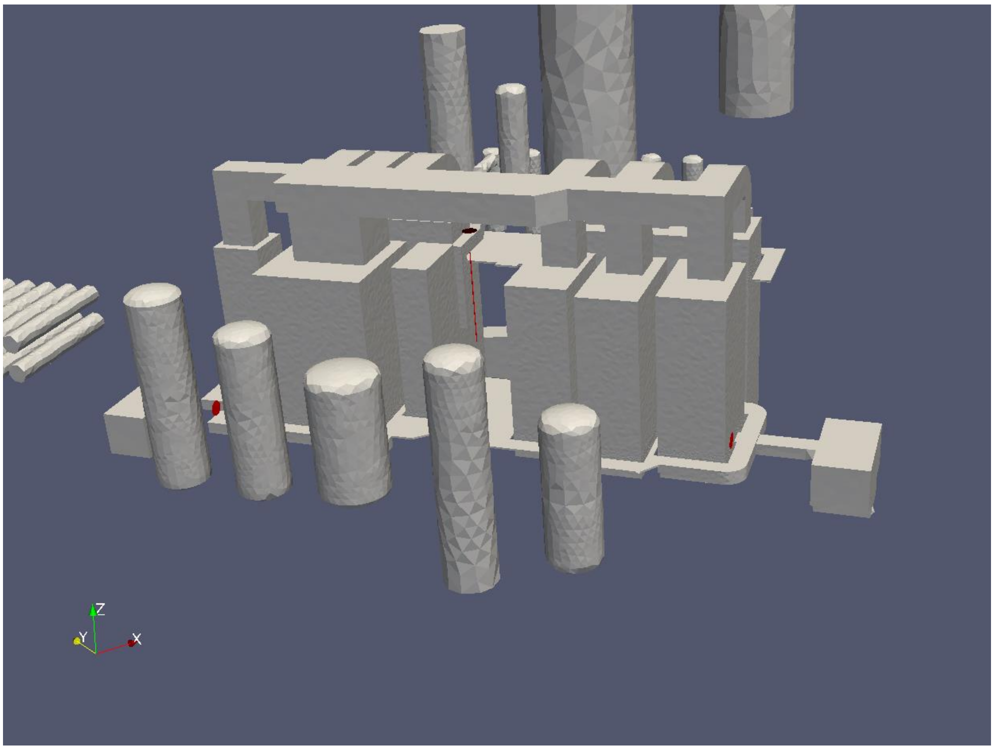


Figure 9 : Emissions sources

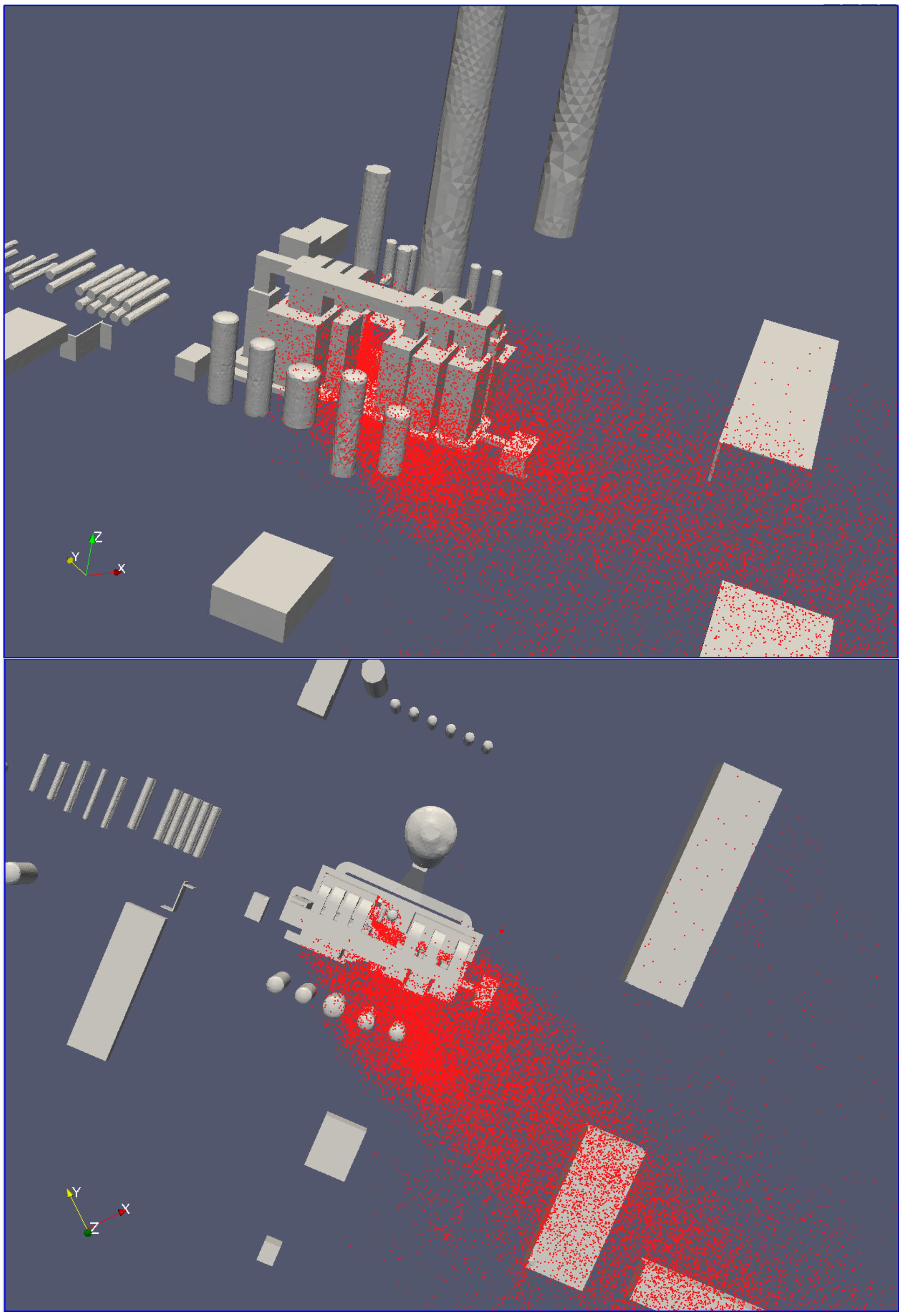


Figure 10 : View of Lagrangian dispersion of the tube emission

RDM :

The dispersion coefficients (defined as the concentrations simulated with an unitary emission per source, ex : 1 g/s or 1k/h), are specific at each time and measurement location point.

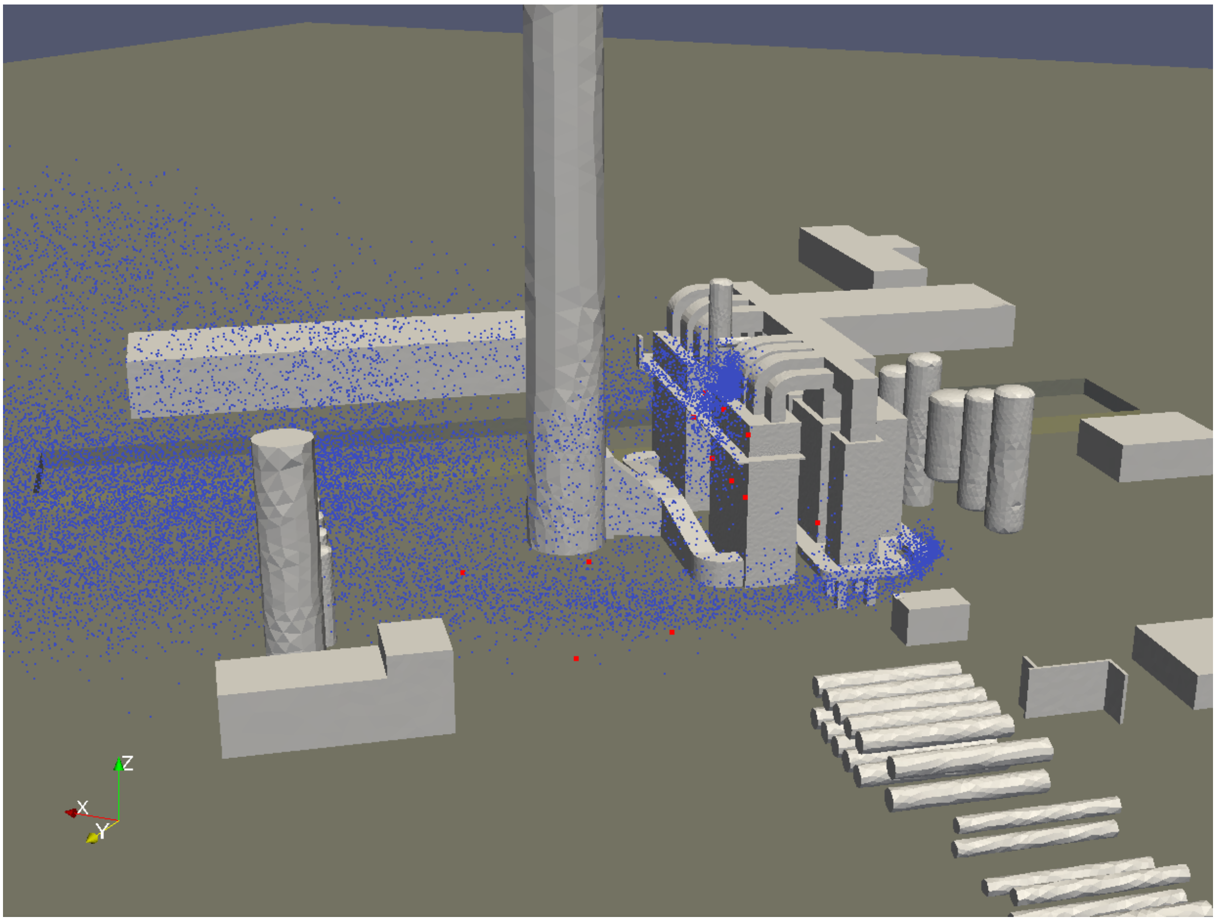


Figure 11 : View of Lagrangian dispersion with two sources (red dot are measurement points but at different times)

Multilinear regression is applied to the dataset (Measured concentrations = function of simulated concentrations). Result of RDM is reported according to different meteorological station information and measurement integration times (30 seconds and 2 minutes). For size reasons, only 2 minutes averaged measurements are reported in annex.

Validation of RDM is describe by comparison against validation criteria (see next part).

4. . Results for each test

For each test, main data are in annex describe test by test.
The results obtain with RDM sended to INERIS (blind test) are summarized in the table and figures below. Two different RDM tests were done :

- one using the METEK meteo station (for wind direction and speed, and turbulence as Lmo)
- one using the INERIS South Est Station for wind (direction and speed) and turbulence from METEK.

The preferred MET station for each test is reported in Table 2 chosen based on the wind direction, and data consistency (best fit between measurement and model before knowledge of the real emission).

In comparison with the real emissions, we can highlight three different test typologies:

- tests with same RDM estimations than the two met stations and realistic emission estimations (test #1,2,9,10,11)
- tests with significant differences with the two met stations and realistic estimation of emissions (test #6)
- tests with unrealistic emission estimations with the two stations (test#3, 4,7,8,12,13,14)

test number	METEK	INERIS	Main Wind direction	Vent moyen METEK	Chosen station	real emission
Test1	**7**	7	224	2,2	METEK	5,07
Test2	**17,1**	17,6	203	2,8	METEK	14,85
Test3	2,2	**3,1**	243	1,4	INERIS SE	8,87
Test4	**1,5**	3	251	2,4	METEK	9,75
Test6	12,5	**5,6**	234	1,7	INERIS SE	9,01
Test7	16,4	**26,8**	233	1,9	INERIS SE	6,59
Test8	45	**23,7**	230	1,9	INERIS SE	8,87
Test9	**9,7**	9,7	332	2,4	METEK	11,62
Test10	**14,1**	14,1	300	2	METEK	18,51
Test11	**8,5**	9,2	267	2,6	METEK	9,64
Test12	**4**	6,5	254	2	METEK	9,75
Test13	**3,2**	1,6	223	0,9	METEK	14,74
Test14	**2,8**	1,7	243	1,5	METEK	16,61

Table 2 : Emission estimation by RDM

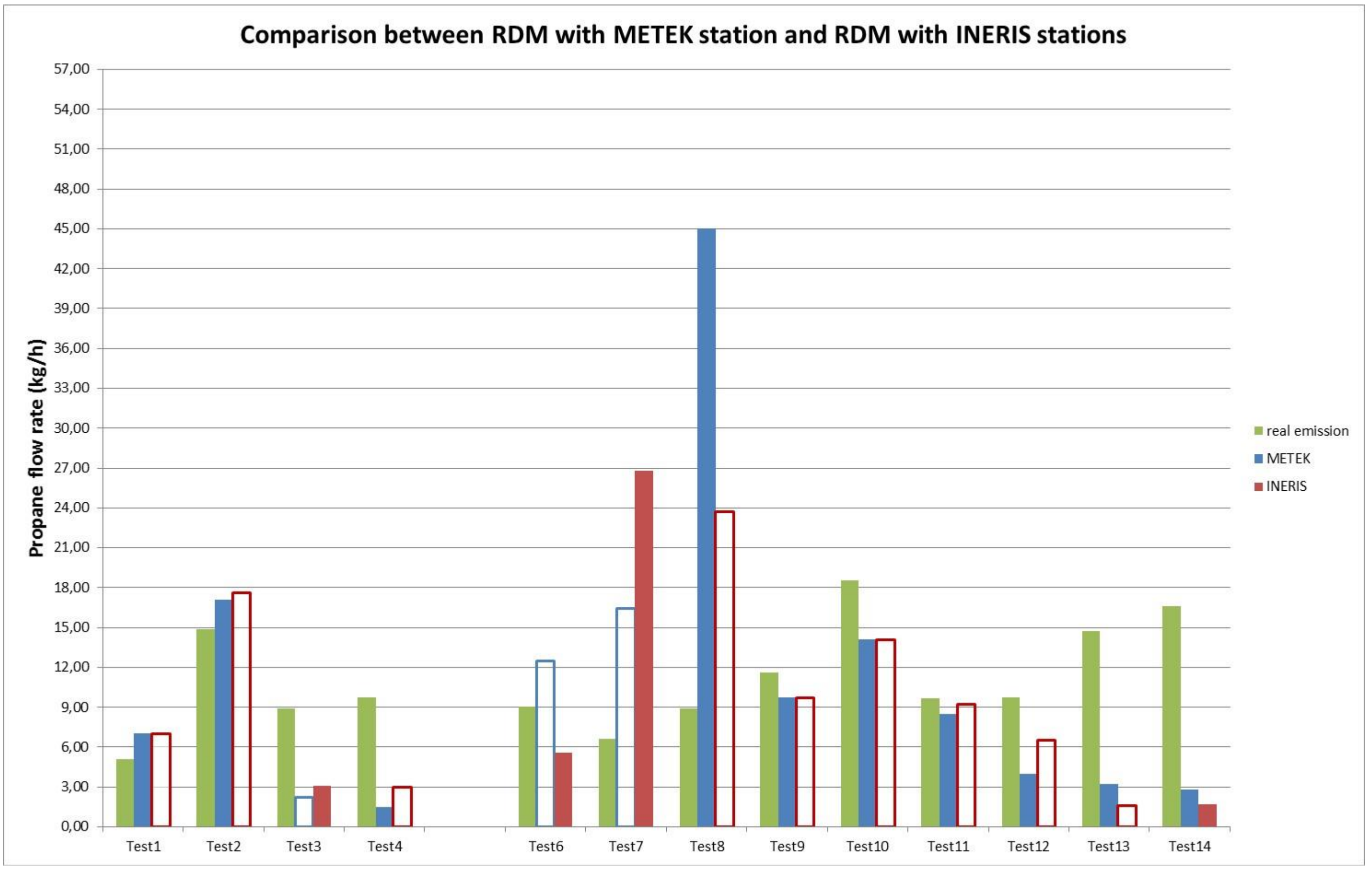


Figure 12 : for each test, real emission (green), first RDM estimation with METEK met station (blue) or INERIS SE met station (red). A full plot indicate the RDM estimation retained for blind test.

To define the criteria of RDM application, an analysis of results was done according to meteorological condition

The first clear criteria is related to the wind speed. As dispersion model have a limit in low wind conditions, all RMD estimations in wind speed conditions below 2 meter / second must be treated with care (see next Figure for a comparison of normalize emissions in function of wind speed) .
Wind speed was above 2 meters / seconds during all the test of the first typology (# test 1,2,9,10,11,).

Only tests 4 & 12 are not correct despite a wind speed above 2 meters / second. Further investigations were carried out for these tests :

- Test#4 : there was a problem with the ejection velocity from the tube in the first dispersion calculation (emission tube too close to the structure). After bug correction, the new RDM calculation leads to an estimation of around 8 kg/h, but without a good correlation criteria.
- Test#12 : an elimination of points measured below 2 meters / second leads to a RDM estimation of around 9,85 (real emissions 9,75).

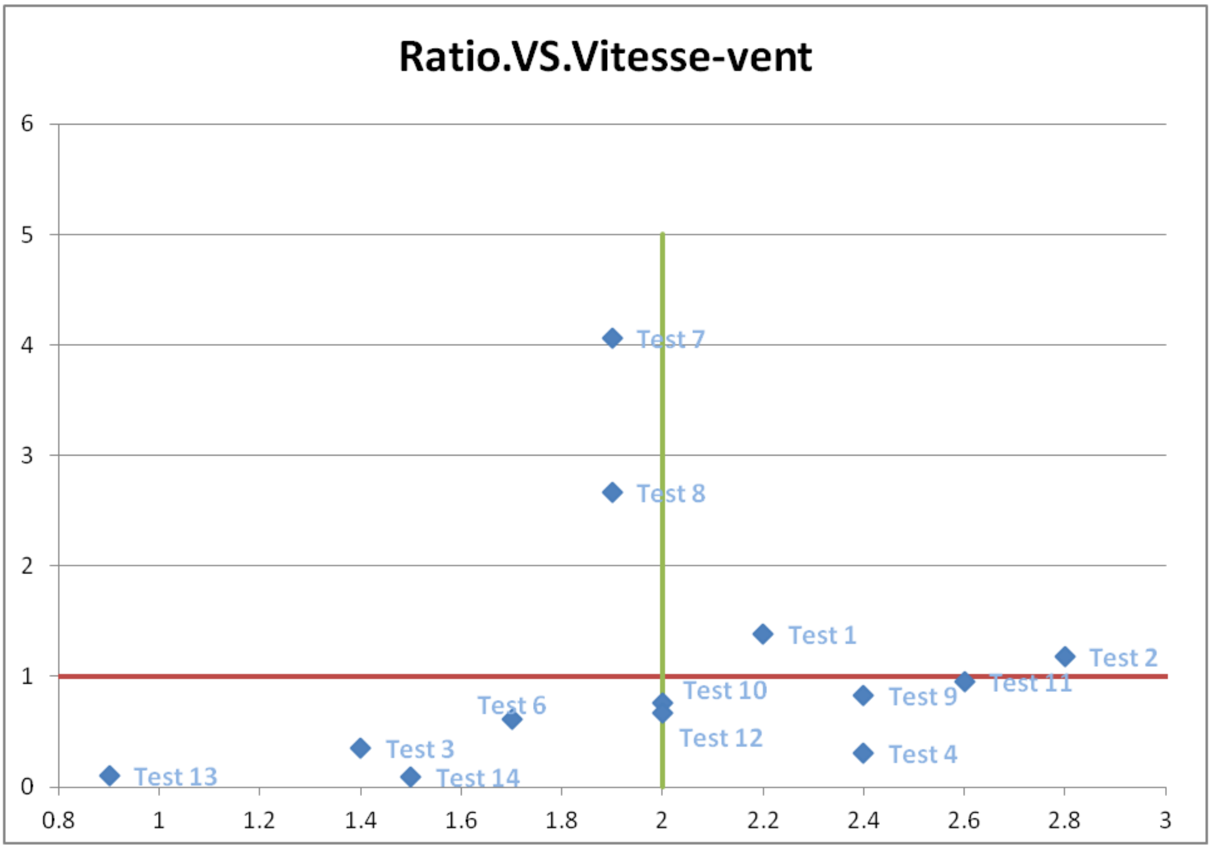


Figure 13 : for each test, normalized emissions (RDM estimations / real emissions) in function of wind speed (METEK station).

To have a full view of the results, several XY plot were done :

- The first estimations send with all results (13 tests) lead to an averaged overestimation of 0,76 and a negative regression coefficient (-0,3).

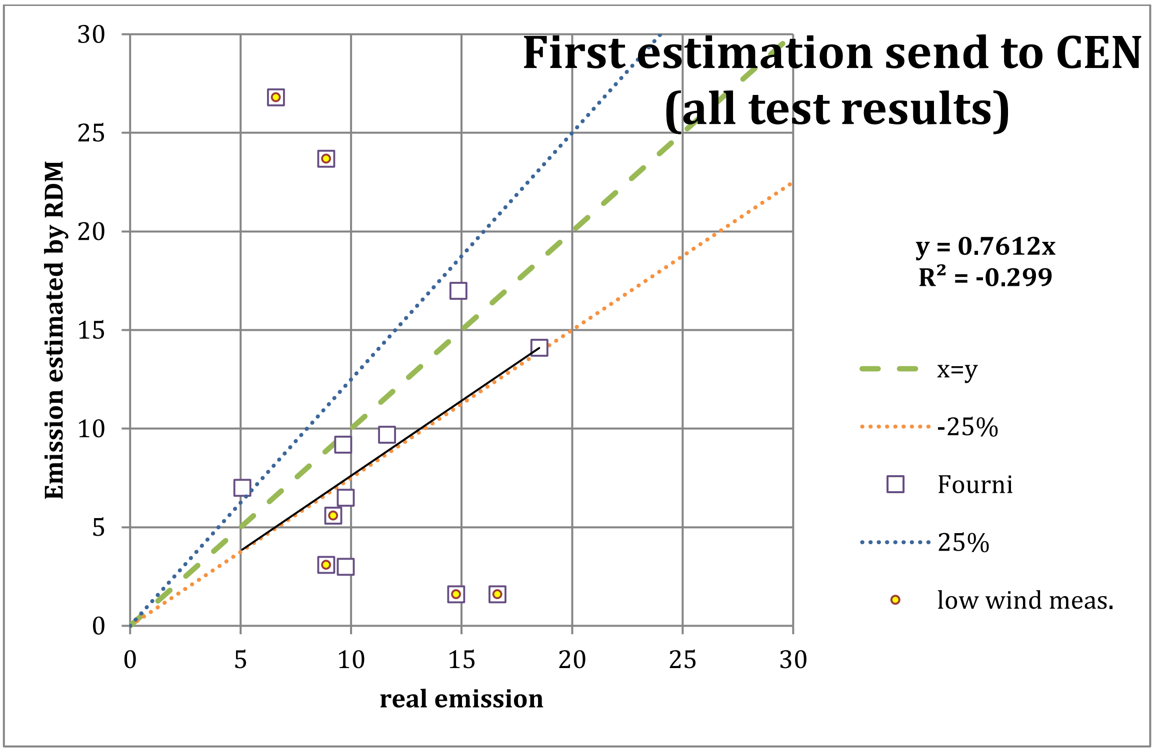


Figure 14 : RDM estimations in comparison of real emissions (all test)

- If we only take in account test with average wind speed above 2 meter / second, the second RDM estimation is more realistic with an overestimation of 0,84 and a regression coefficient of 0.68.

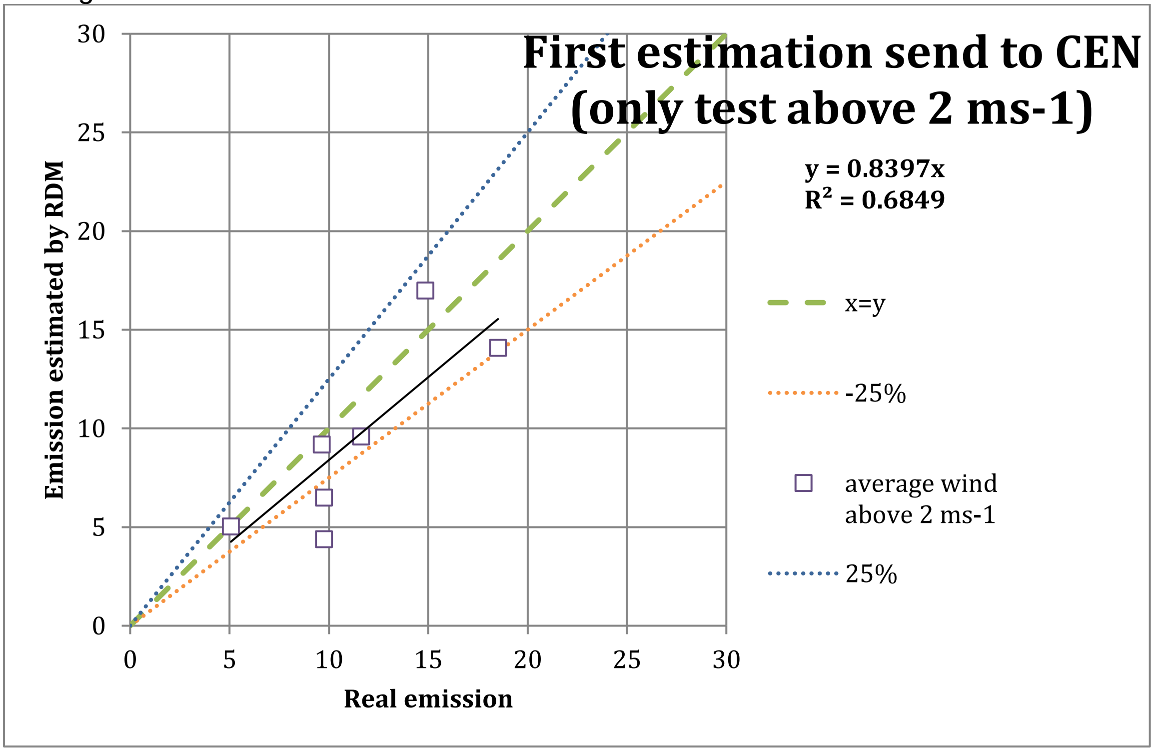


Figure 15 : RDM estimations in comparison of real emissions (only test above 2 ms-1)

- Elimination of test#4 (data not consistent) and calculations limited to test with wind speed conditions above 2 ms-1 lead to better estimations. The overestimation is only 0,92 with a regression coefficient of 0,72.With respect to these two criteria (data consistency and no measurement below 2 meter/second), all the estimations are within +/- 25 % of the real emissions.

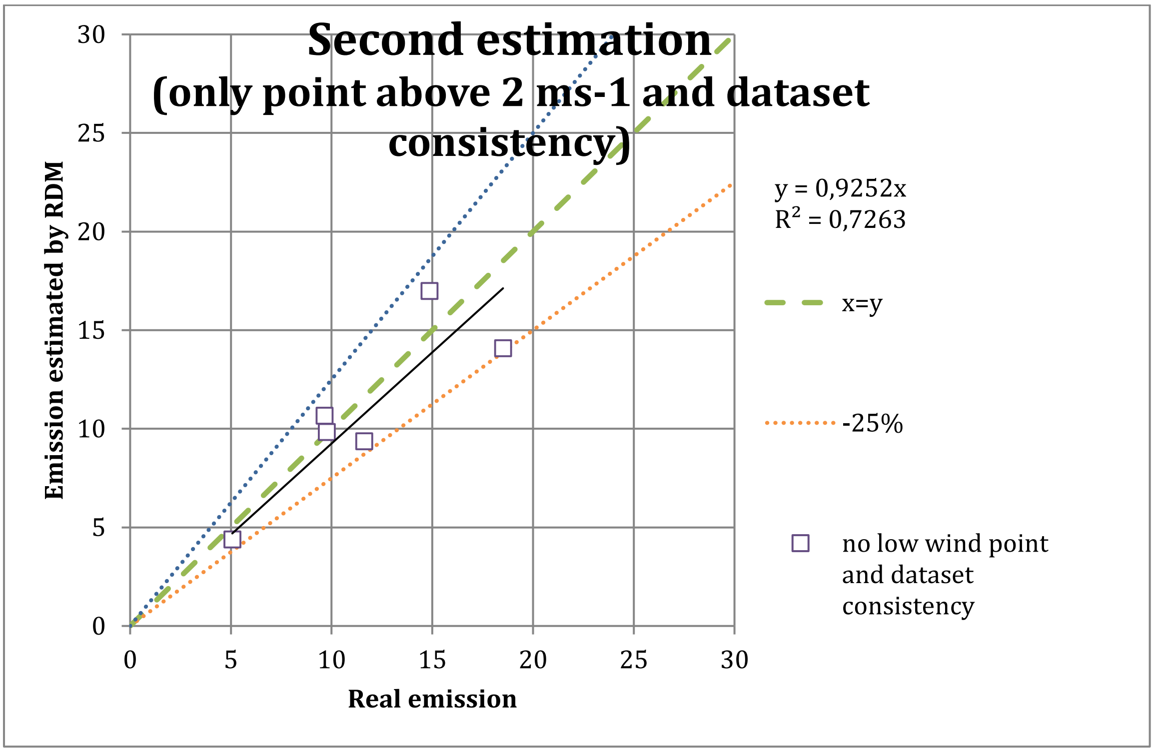


Figure 16 : RDM estimations in comparison to real emissions (only test above 2 ms-1 and data consistency)

- A final correction of the FID response according to real gas compositions (not only propane) leads to an emission increase of +2.5 %, and the overestimation is only 0.948, with a regression coefficient of 0.72.

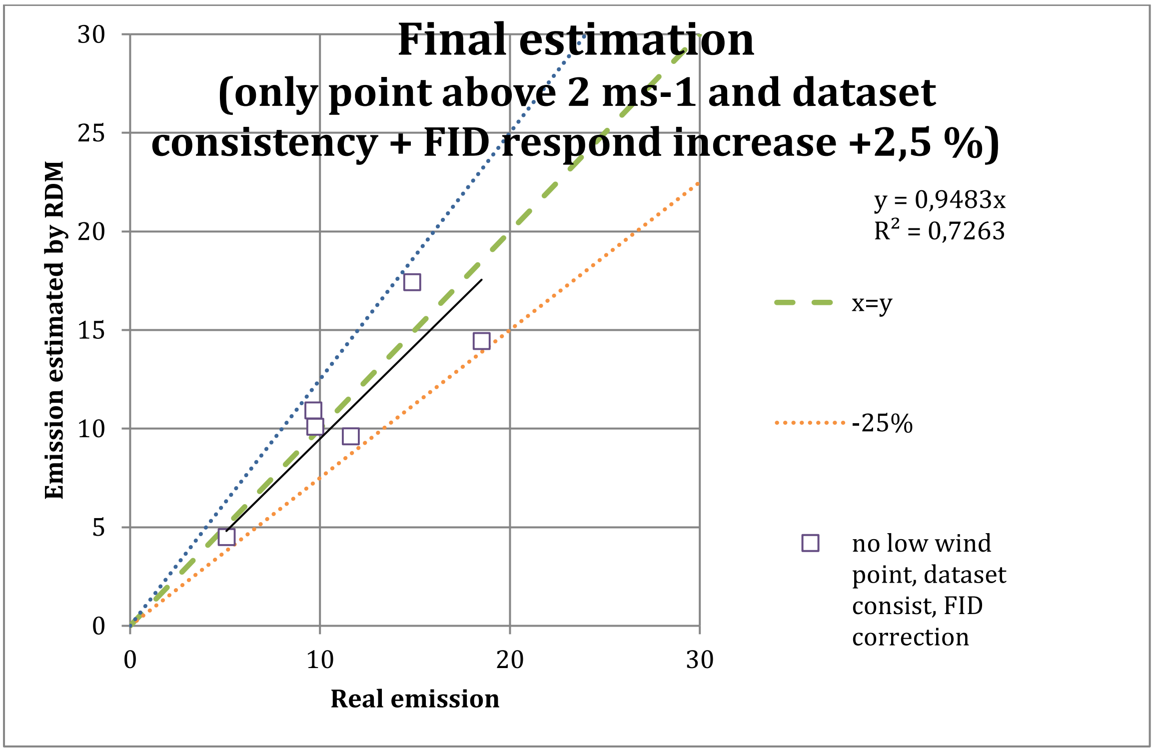


Figure 17 : RDM estimations in comparison to real emissions (only test above 2 ms-1 and data consistency) with correction of FID factor (+2.5 %)

5. Assessment of the method protocol :

Despite the complexity of the meteorological conditions (low wind and high atmospheric instability), the RDM methodology was able to quantify the emissions with an uncertainty of +/- 25 %. The main validity criteria added to the initial protocol are :

- In the previous protocol, measured concentrations bellow 0.5mg/m3 above the background were filtered in the raw data, in order to limit near background measurement error. This conducted to an overestimation of estimated emissions. It is now better to use all measurement data, corrected with the background.
- The best estimation is obtained with the highest frequency measurement data (30 seconds for FID, 30 seconds for wind met data). In the past a smoothing for 2 minutes was used, but it was not benefiting.
- Selection of measurements with wind above 2 meters / second at 10 meters, with a station close to the measurements area.

- Taking into account the ejection speed if measurements are close to the sources (less than 3 meters) or high ejection speed are identified (like some stack emission)

- For modeled concentrations, the averaged concentrations were calculated in the volume of a 2 meters radius sphere at each point, centered on the point coordinate. This volume must be lower (Radius : 0.5 meters) near the sources (less than 4 meters), and 1 meter radius between 4 to 10 meters from the sources. After 10 meters, a 2 meter radius can be used.
- A global evaluation of the quality of the RDM is obtained by comparing a linear regression between measured and simulated concentrations :
    - The slope of the linear regression directly gives the emission for mono source test.

    - For multi sources test, the slope represent the emissions if each source has the same emissions. Only RDM program can give the emissions

- The emission (or equivalent emission in multi sources case) is obtained with the coefficient of the slope, with the regression is forced to pass by zero. The quality of the estimation is obtained with the coefficient of the slope without the zero forcing. A negative slope is a bad estimation, and estimation must be treated with care.

With respect to these criteria, the RDM was able to quantify 6 Tests.

6. ANNEXES

Annexe : CFD description

Description of modeling choices retained for the specific campaign:

The CFD calculations are done with the ANSYS FLUENT code, using preprocessor Space Claim for meshing.

MESHING :

For the present case, we retains the strategy to obtain a good meshing quality:
- Layout of the unit with as much precision as possible
- Management of fine detail levels (like pipes) via porous volumes

- Size function: Proximity and curvature
- Size imposed on the faces of ovens and platforms (20cm)
- Size imposed at the interstices (4cm)
- Directed design at ground level (2m)
- Result: ~ 7 million meshes with precise refinement in the complex areas of the unit,

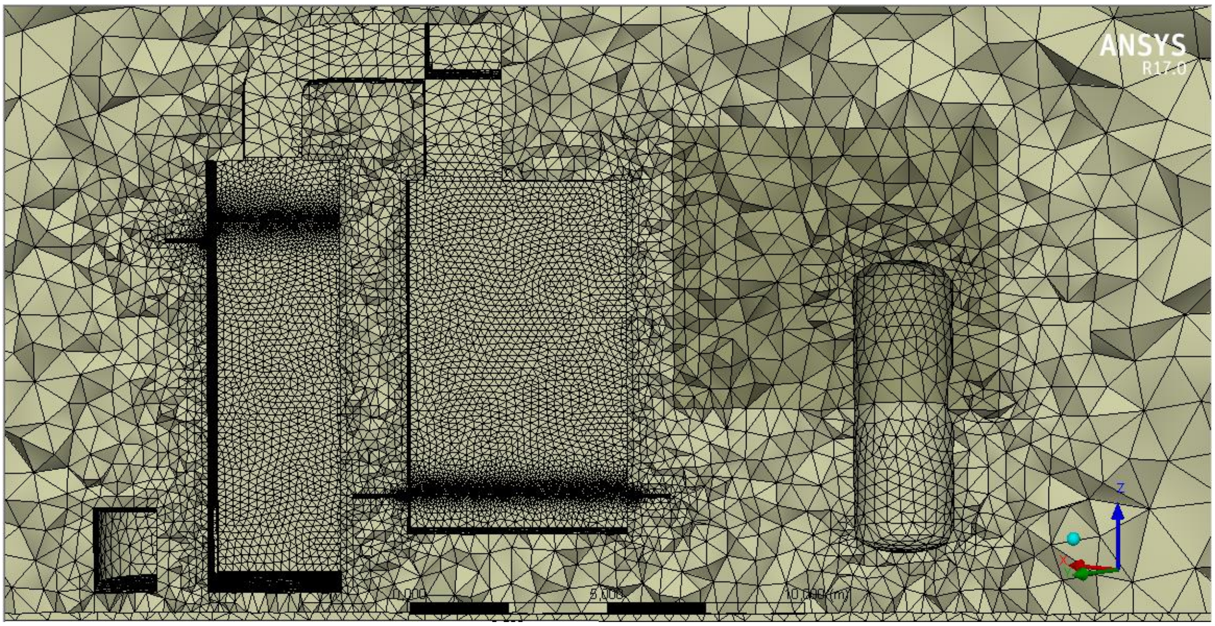


Figure 18 : view of meshing variability

CFD calculation

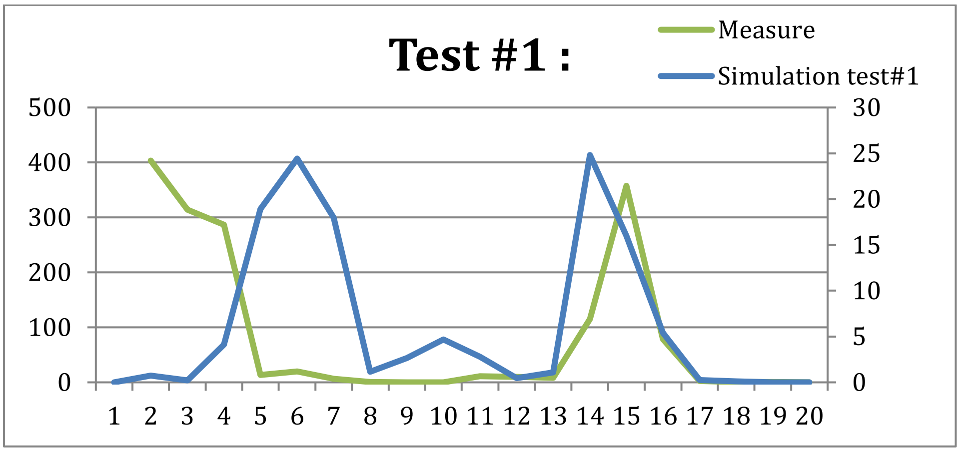
- Establishment of profiles based on observed weather data
- Launch of test calculations and validation of the vertical wind profiles at the end of the domain (South) in comparison with the profiles measured by LiDAR wind (see INERIS)
- Bibliography carried out to evaluate the coefficients of resistance law in the Gryning model. (see French GT3D “good practice guide”)
- Retention: Vachat model (gives formulation according to k, u *, f and LMO.
- One pair (A, B) per stability class

ANNEXE : TEST #1

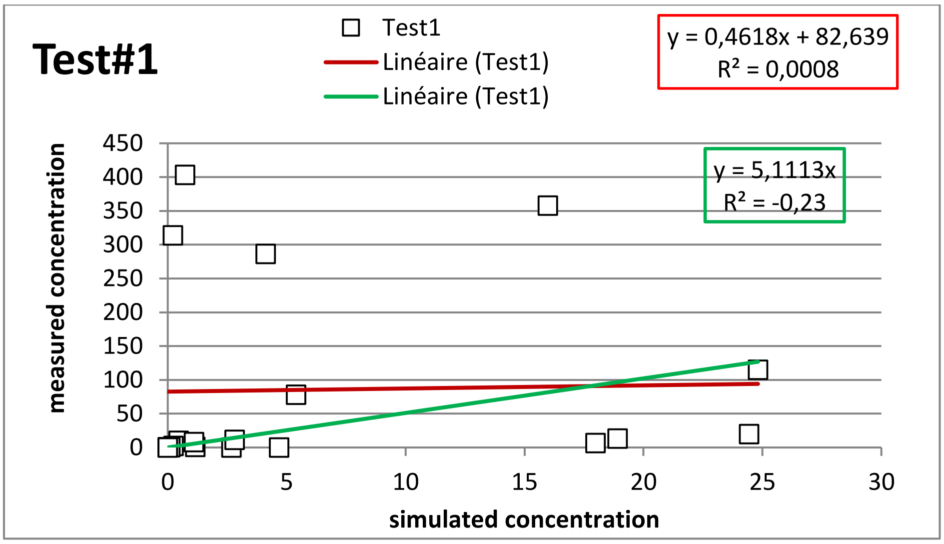
Measurements point test#1 :

Id	X	Y	Z	R
1	-144.9029	2272.0782	4.75	1.0
2	-151.5139	2280.0879	4.75	1.0
3	-153.4930	2282.5331	4.75	1.0
4	-147.9822	2276.1272	4	1.0
5	-144.9659	2279.9073	10.5	1.0
6	-147.0505	2274.9030	4.5	1.0
7	-137.4871	2284.7848	1.5	1.0
8	-150.9637	2284.3157	1.5	1.0

Time serie of measurement and simulation with dispersion factor for test#1



XY plot and slope calculation for the validity criteria : : OK valid

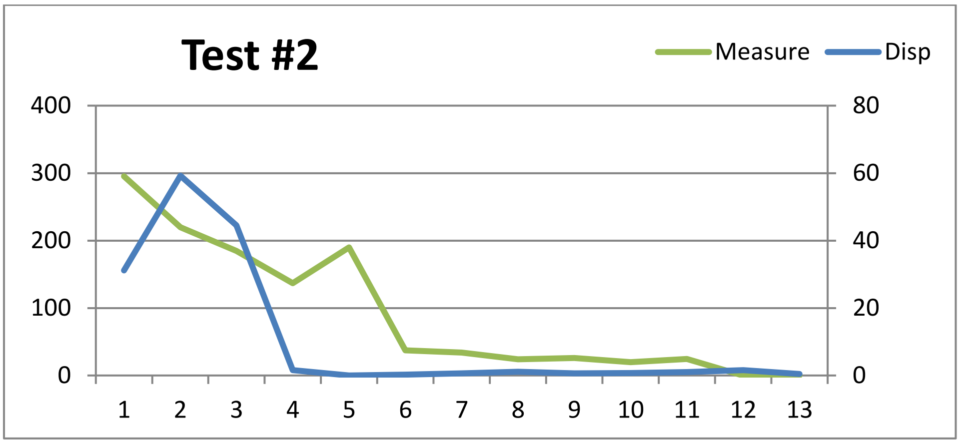


ANNEXE : TEST #2

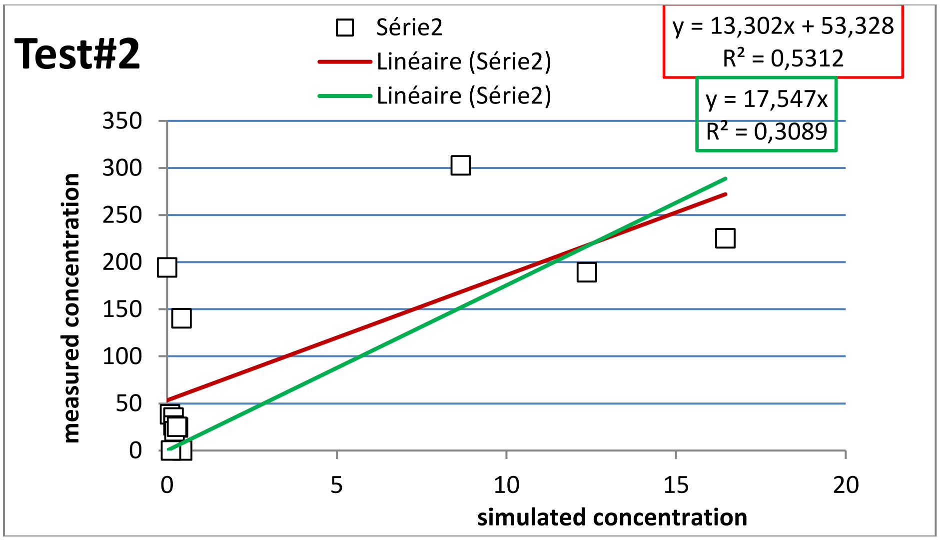
Measurements point test#2 :

Id	X	Y	Z	R
1	-142.1312	2276.5437	11	1.0
2	-142.7951	2277.2698	11.25	1.0
3	-144.8476	2279.7577	11.25	1.0
4	-147.5483	2282.9337	11.25	1.0
5	-148.1286	2283.8040	11.25	1.0
6	-149.7470	2282.0818	11.25	1.0
7	-128.8961	2286.8918	1.75	2.0

Time serie of measurement and simulation with dispersion factor for test#2



XY plot and slope calculation for the validity criteria : Test#2OK valid



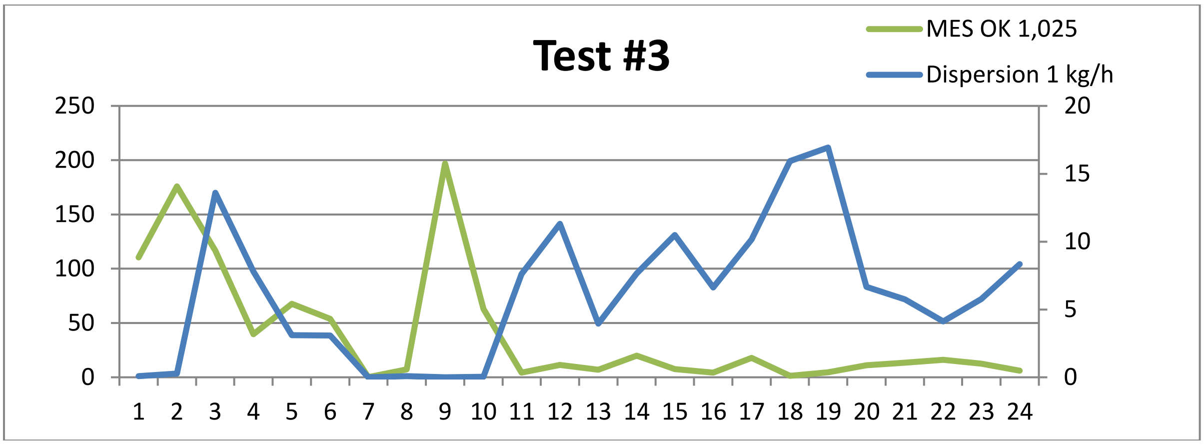
ANNEXE : TEST #3

Measurements point test#3 :

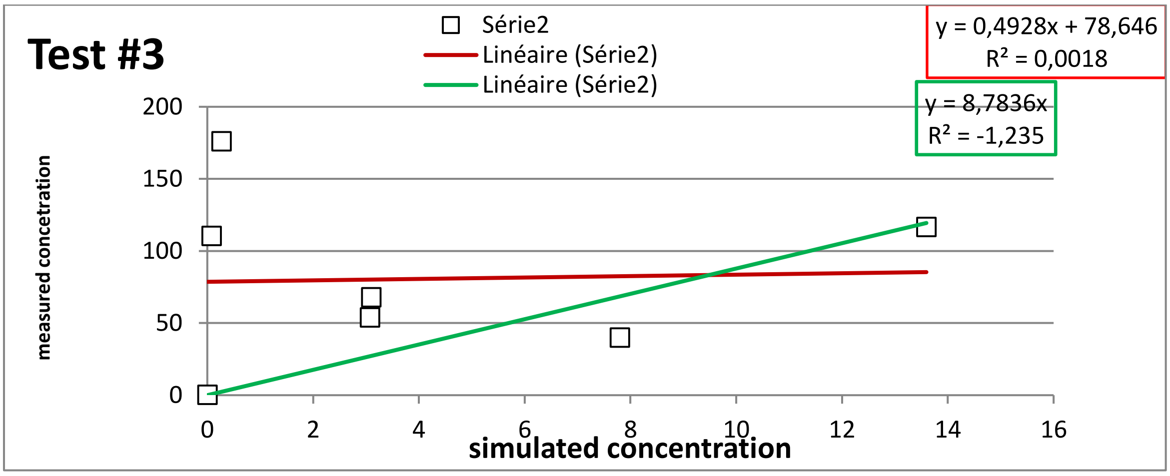
Id	X	Y	Z	R
1	-154.1290	2277.6722	4.75	1.0
2	-156.4770	2280.7558	4.75	1.0
3	-153.7544	2282.6691	4.75	1.0
4	-150.6962	2281.7167	11	1.0
5	-144.8172	2279.79515	11	1.0
6	-156.6255	2275.5922	4.5	1.0
7	-142.2168	2294.1038	1.75	2.0
8	-139.3088	2289.3358	1.75	2.0

9	-135.8702	2291.6227	1.75	2.0
10	-131.5539	2296.7782	1.75	2.0

Time serie of measurement and simulation with dispersion factor for test#3



XY plot and slope calculation for the validity criteria : OK valid



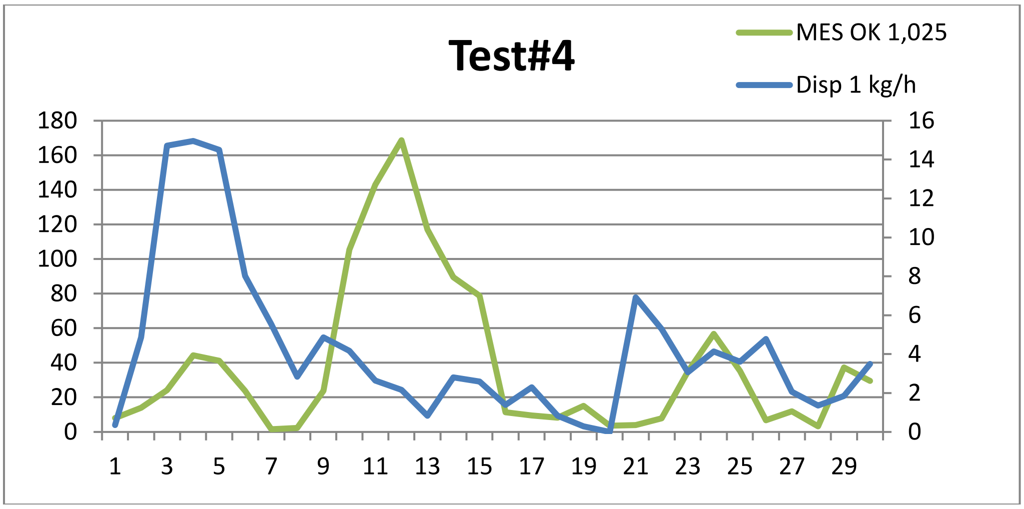
ANNEXE : TEST #4

Measurements point test#4 :

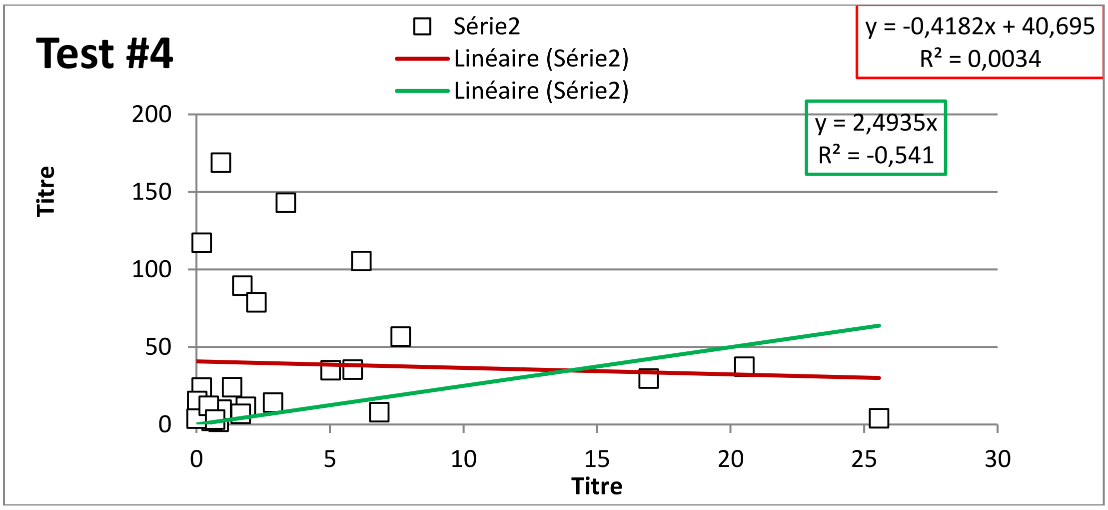
Id	X	Y	Z	R
1	-140.3874	2274.3116	11.25	1.0
2	-141.7294	2276.4409	8.5	1.0
3	-139.8602	2274.4026	8.5	1.0
4	-143.2222	2278.5342	8.5	1.0
5	-144.7939	2280.1733	8.5	1.0
6	-147.3544	2283.0783	8.5	1.0
7	-140.3874	2274.3116	11.25	1.0
8	-140.6847	2277.2656	6.5	1.0

9	-141.0332	2277.6140	6.5	1.0
10	-139.2263	2275.3425	6.5	1.0
11	-141.9309	2278.6880	6.5	1.0
12	-136.2593	2287.0243	1.75	2.0

Time serie of measurement and simulation with dispersion factor for test#4



XY plot and slope calculation for the validity criteria : invalid



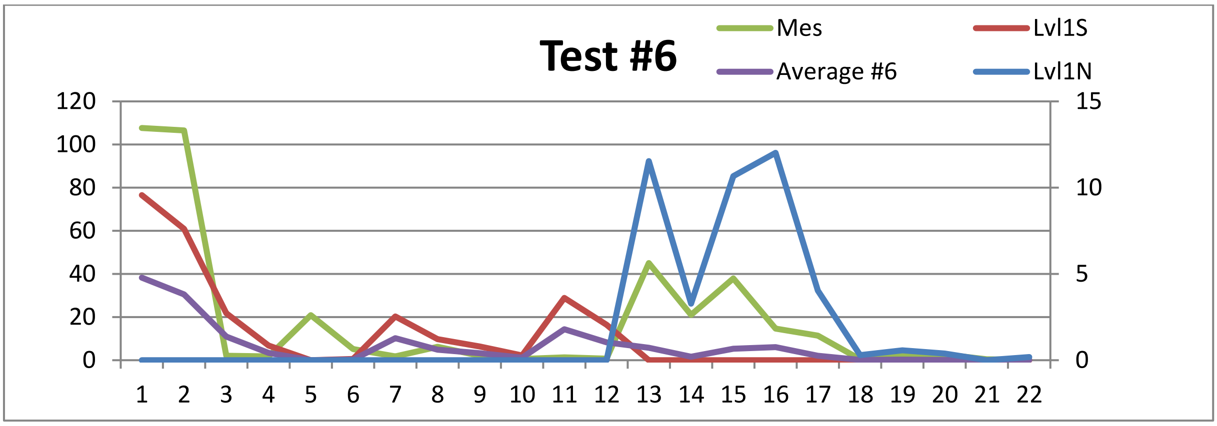
ANNEXE : TEST #6

Measurements point test#6 :

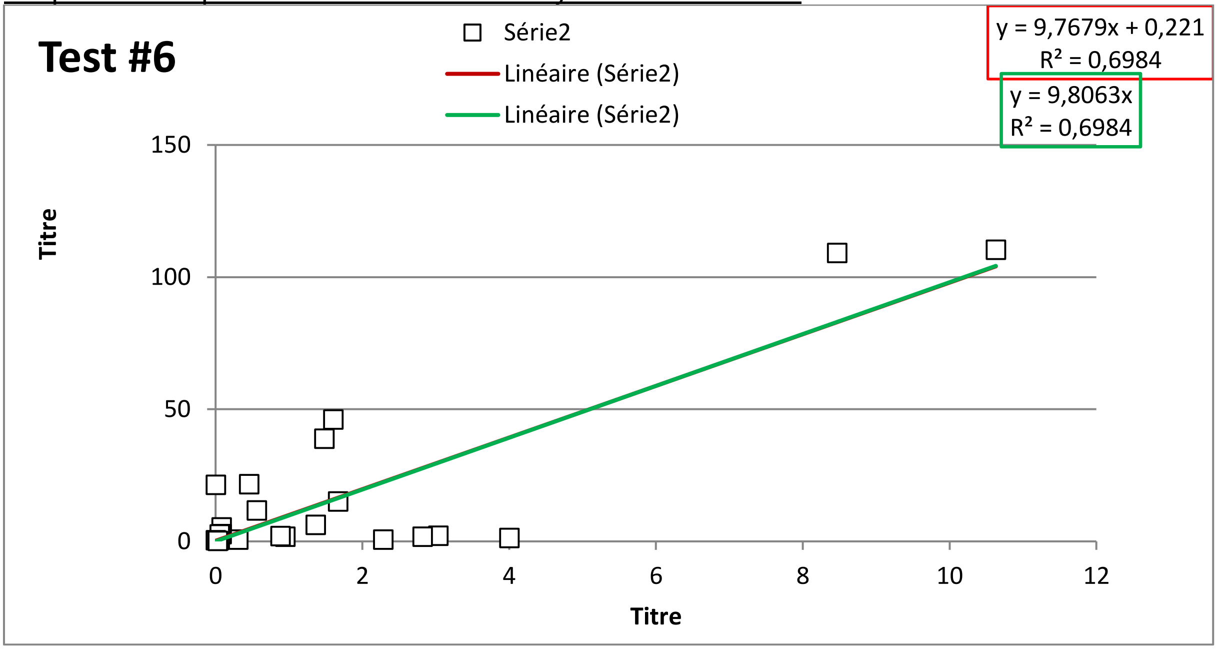
Id	X	Y	Z	R
1	-136.1083	2261.6261	4.75	1.0
2	-135.0169	2262.0468	11	1.0

3	-135.7988	2268.8132	11	1.0
4	-132.0014	2264.4580	1.75	1.0
5	-128.0198	2266.7634	1.75	2.0
6	-153.5743	2282.6161	4.5	1.0
7	-156.8387	2282.3916	5	1.0
8	-148.8593	2285.7141	8	1.0
9	-148.1119	2283.8649	10.5	1.0

Time serie of measurement and simulation with dispersion factor for test#6



XY plot and slope calculation for the validity criteria : OK valid



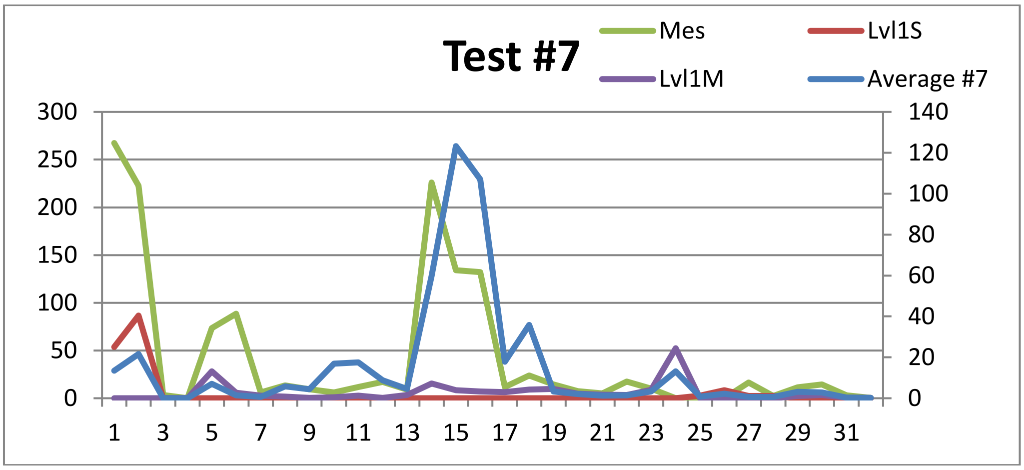
ANNEXE : TEST #7

Measurements point test#7 :

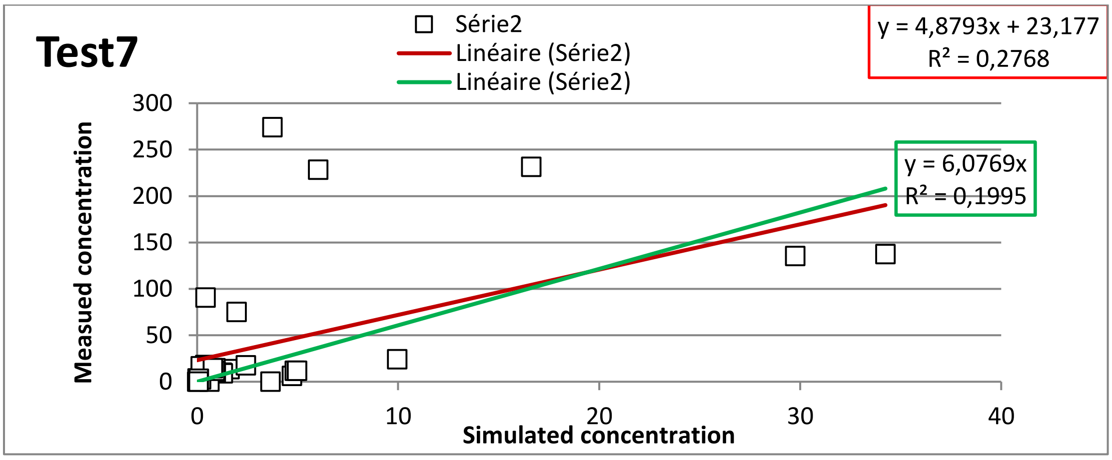
Id	X	Y	Z	R
1	-135.9628	2261.8097	4.5	1.0
2	-146.0877	2273.8244	4.75	1.0

3	-150.8739	2279.5725	4.75	1.0
4	-153.5853	2282.6773	4.75	1.0
5	-156.4624	2280.7809	4.5	1.0
6	-156.4673	2282.5739	5	1.0
7	-142.2691	2276.7727	11.25	0.5
8	-144.9672	2279.9051	11.25	1.0
9	-150.5443	2287.2906	8	1.0
10	-149.3447	2285.4833	8	1.0
11	-140.7298	2275.6764	8	1.0
12	-130.7675	2264.0131	8	1.0
13	-131.5598	2265.6112	6	1.0
14	-148.3256	2285.6174	6	1.0
15	-148.9687	2286.3582	1.75	1.0

Time serie of measurement and simulation with dispersion factor for test#7



XY plot and slope calculation for the validity criteria : Test # 7 OK valid

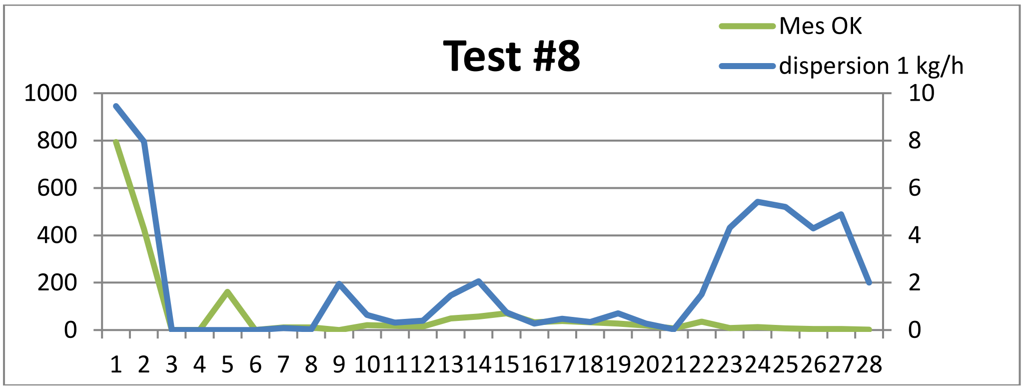


ANNEXE : TEST #8

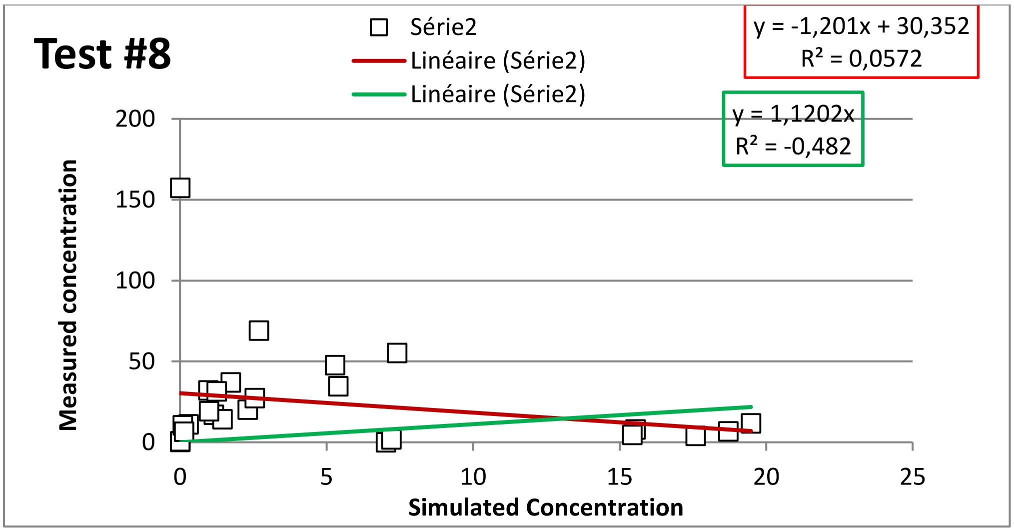
Measurements point test#8 :

Id	X	Y	Z	R
2	-136.0032	2261.7034	4.75	1.0
3	-156.3477	2278.2465	4	1.0
4	-142.0746	2276.4312	11	1.0
5	-138.6880	2272.4738	11	1.0
6	-135.3280	2268.5912	11	1.0
7	-130.8489	2264.2297	8	1.0
8	-134.9182	2269.0305	8	1.0
9	-131.1092	2264.8418	6	1.0
10	-134.7715	2269.7543	6	1.0
11	-127.2707	2275.9363	1.75	2.0
12	-127.4495	2266.0713	1.75	2.0
13	-120.4472	2271.0853	1.75	2.0

Time serie of measurement and simulation with dispersion factor for test#8



XY plot and slope calculation for the validity criteria : Test#8 Invalid

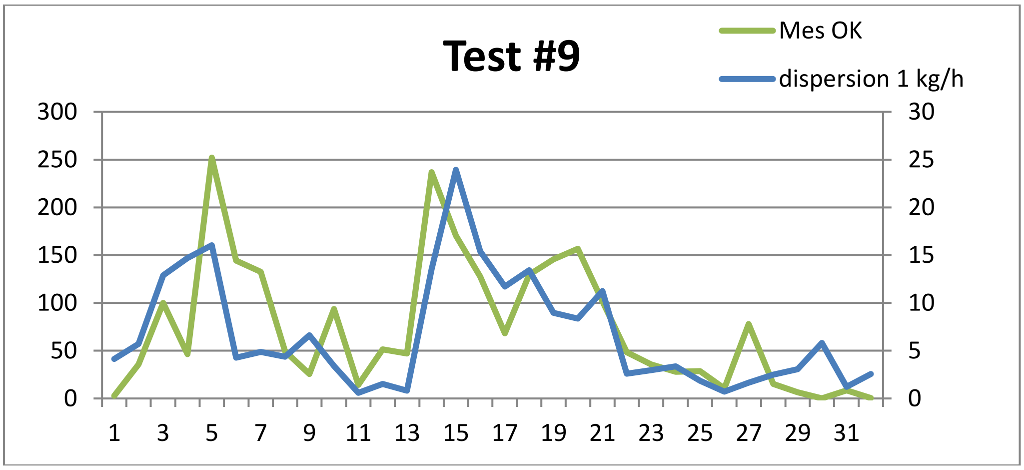


ANNEXE : TEST #9

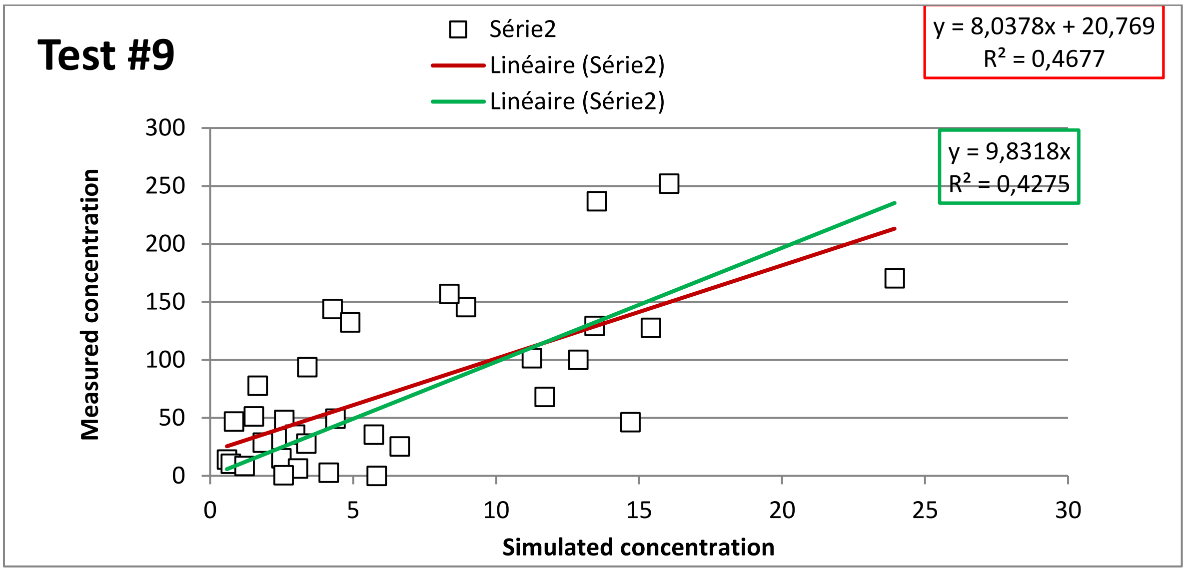
Measurements point test#9 :

Id	X	Y	Z	R
1	-147.7297	2267.2145	4.75	1.0
2	-142.8628	2269.8835	4.75	1.0
3	-138.3462	2264.4249	4.75	1.0
4	-135.7376	2261.3816	4.75	1.0
5	-140.3207	2257.5099	4.75	1.0
6	-143.7666	2270.3906	6.75	1.0
7	-143.1142	2271.7485	11.25	1.0
8	-141.8422	2272.5407	11	1.0
9	-134.9672	2262.0615	11	1.0
10	-139.3782	2266.7784	12	1.0
11	-145.9644	2263.4591	4.75	1.0
12	-131.0311	2256.6136	1.75	1.0
13	-128.4632	2263.3644	1.75	1.0

Time serie of measurement and simulation with dispersion factor for test#9



XY plot and slope calculation for the validity criteria : test#9 OK valid

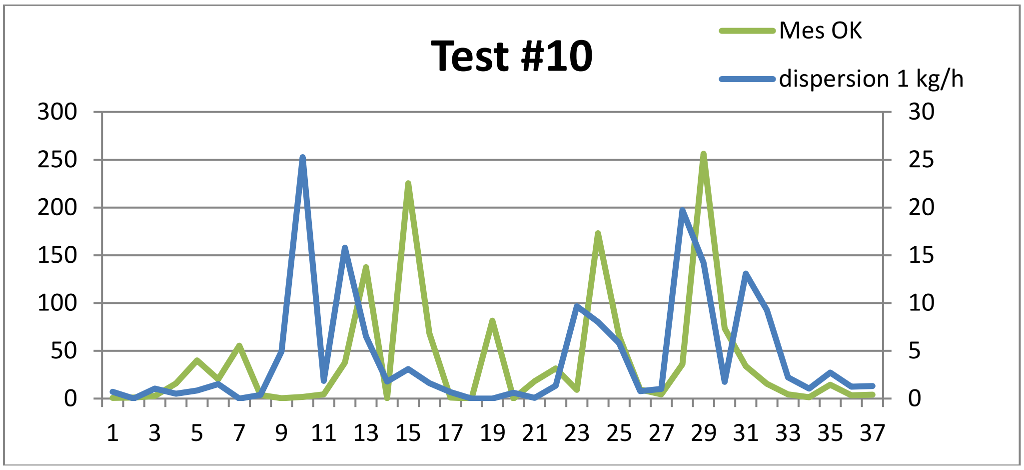


ANNEXE : TEST #10

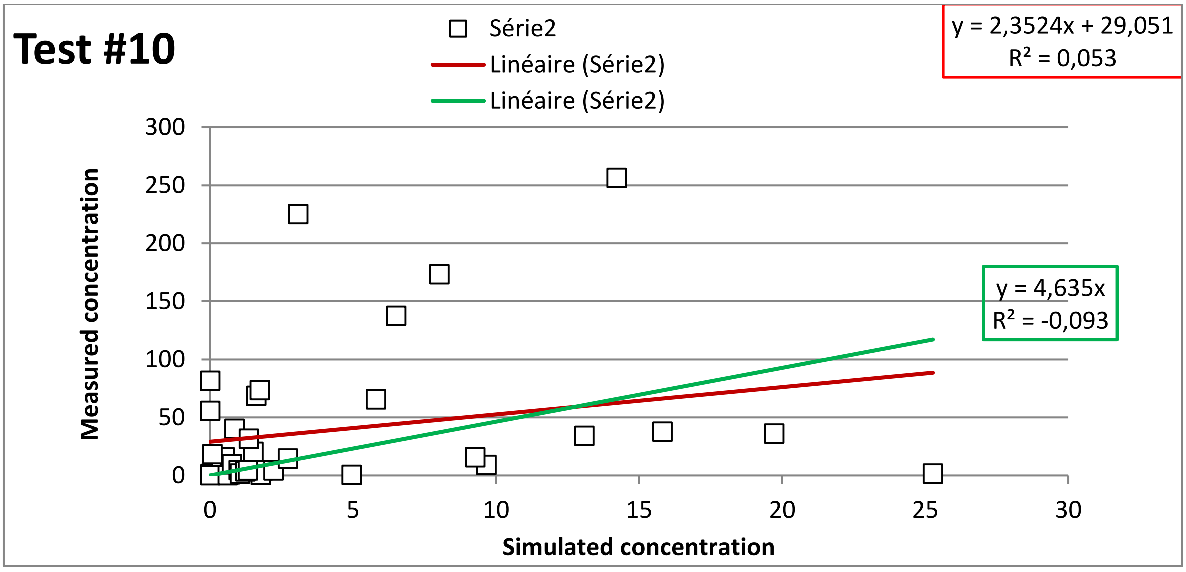
Measurements point test#10 :

Id	X	Y	Z	R
1	-124.9073	2247.4279	1.75	2.0
2	-130.1994	2260.9533	1.75	1.0
3	-140.0509	2252.5232	1.75	1.0
4	-150.6176	2265.6708	1.5	1.0
5	-147.5623	2265.8122	4.75	1.0
6	-152.1790	2270.0455	4.75	1.0
7	-156.4033	2274.9781	4.75	1.0
8	-156.8452	2280.4316	4.75	1.0
9	-151.7269	2280.4944	4.75	1.0
10	-142.6925	2269.6250	4.75	1.0
11	-145.3455	2272.4642	4.75	1.0
12	-151.7269	2280.4944	4.75	1.0
13	-140.9225	2273.9896	11.25	1.0
14	-135.6419	2268.8292	11.25	1.0
15	-134.9948	2262.0408	11	1.0
16	-134.1998	2287.4068	1.75	2.0

Time serie of measurement and simulation with dispersion factor for test#10



XY plot and slope calculation for the validity criteria test#10 : OK valid



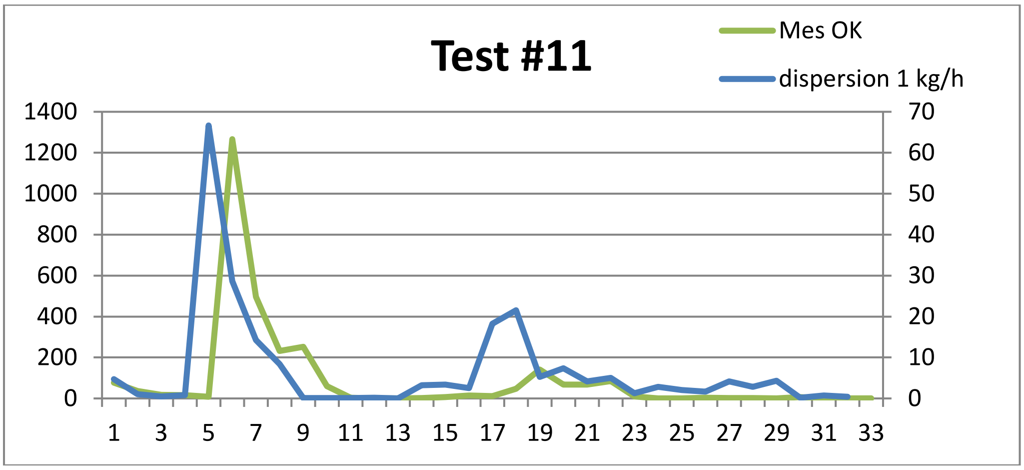
ANNEXE : TEST #11

Measurements point test#11 :

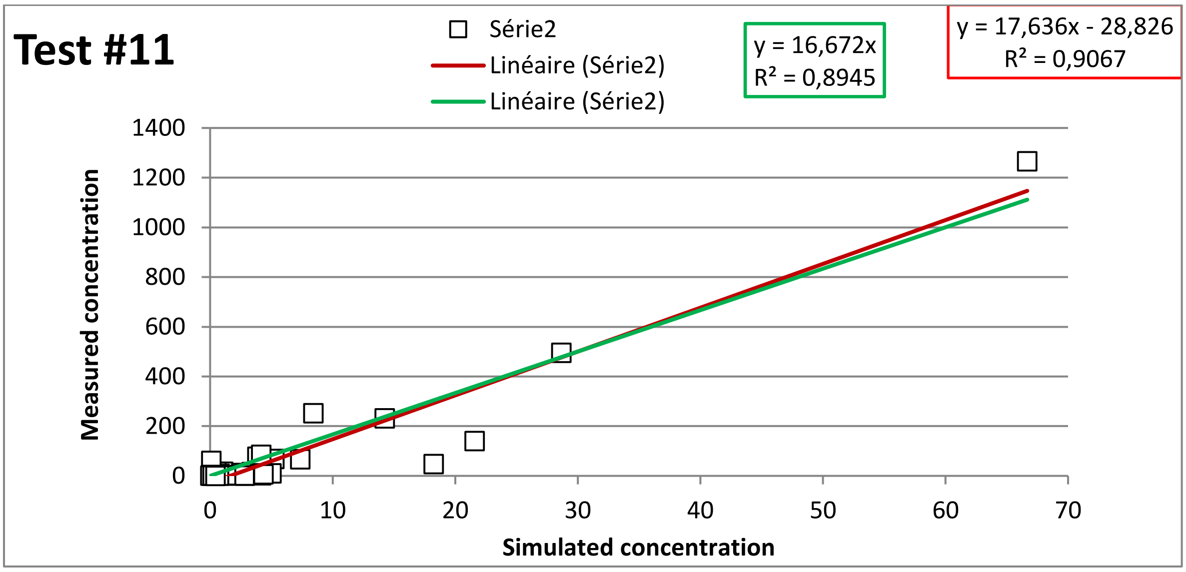
Id	X	Y	Z	R
1	-154.4149	2277.4205	4.5	1.0
2	-151.4009	2279.8255	4.75	1.0
3	-142.0937	2276.4869	11	0.5
4	-144.8699	2279.8382	11.25	1.0
5	-148.1614	2283.8646	11.25	1.0
6	-148.8792	2285.9341	8	1.0
7	-146.9980	2283.4792	8	1.0
8	-144.3154	2280.2692	8	1.0
9	-141.6095	2277.1707	9.5	1.0

10	-147.4131	2292.9231	1.75	2.0
11	-138.2455	2285.6336	1.75	2.0
12	-132.0208	2290.7767	1.75	2.0
13	-142.8459	2296.2318	0.5	2.0

Time serie of measurement and simulation with dispersion factor for test#11



XY plot and slope calculation for the validity criteria : test#11 OK valid

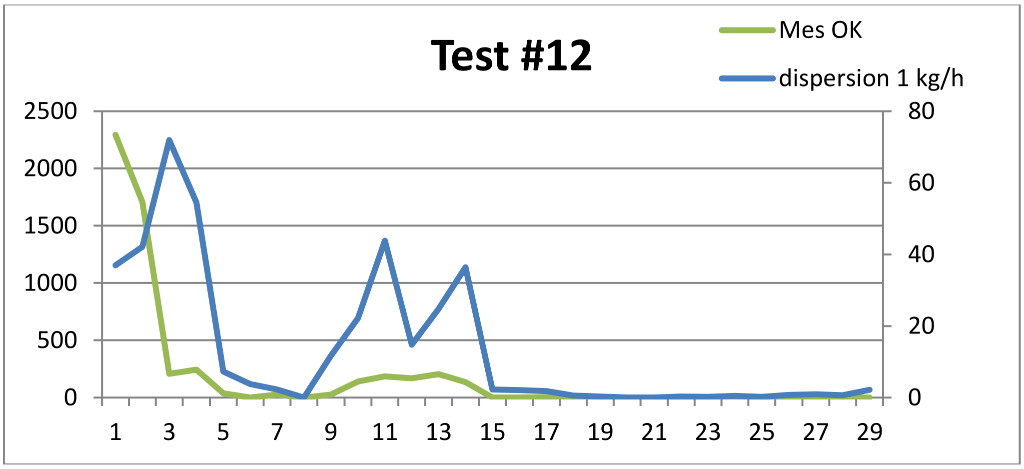


ANNEXE : TEST #12

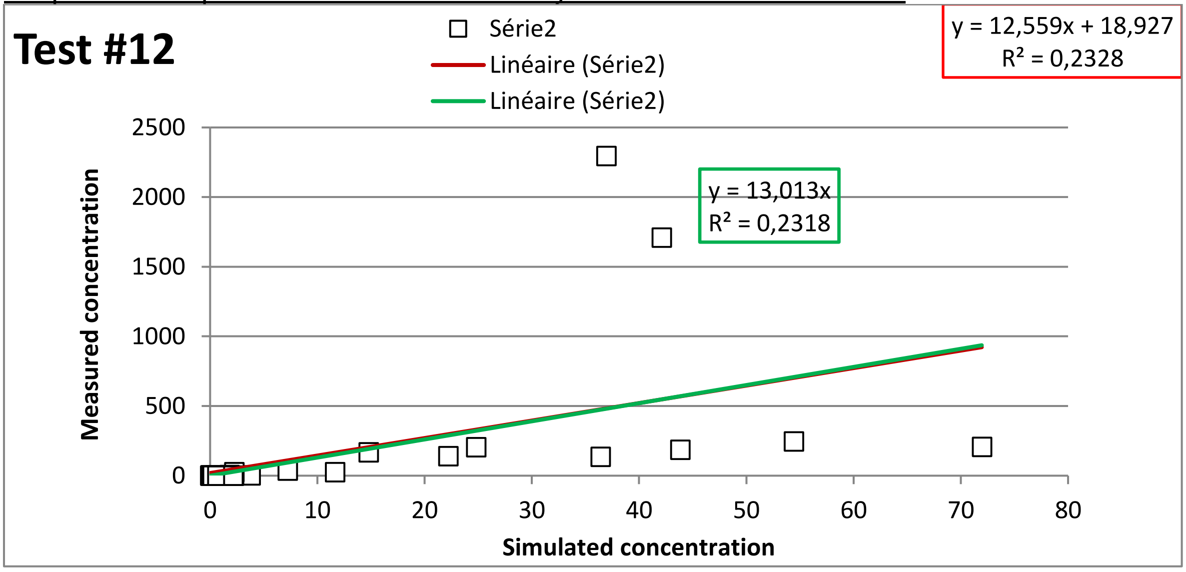
Measurements point test#12 :

Id	X	Y	Z	R
1	-141.9954	2276.4487	11	0.5
2	-144.7332	2279.8172	11.25	1.0
3	-148.0926	2283.8951	11.25	1.0
4	-149.3419	2286.6944	8	1.0
5	-143.9515	2279.7343	8	1.0
6	-141.5259	2276.7245	9.5	1.0
7	-137.3091	2285.2979	1.75	1.0
8	-128.0117	2287.1397	1.75	1.0
9	-112.1672	2293.8920	1.75	2.0
10	-101.8108	2302.6083	1.75	2.0
11	-89.2125	2292.3081	1.9	2.0
12	-108.3992	2282.7562	1.75	2.0

Time serie of measurement and simulation with dispersion factor for test#2



XY plot and slope calculation for the validity criteria : test#12 OK valid

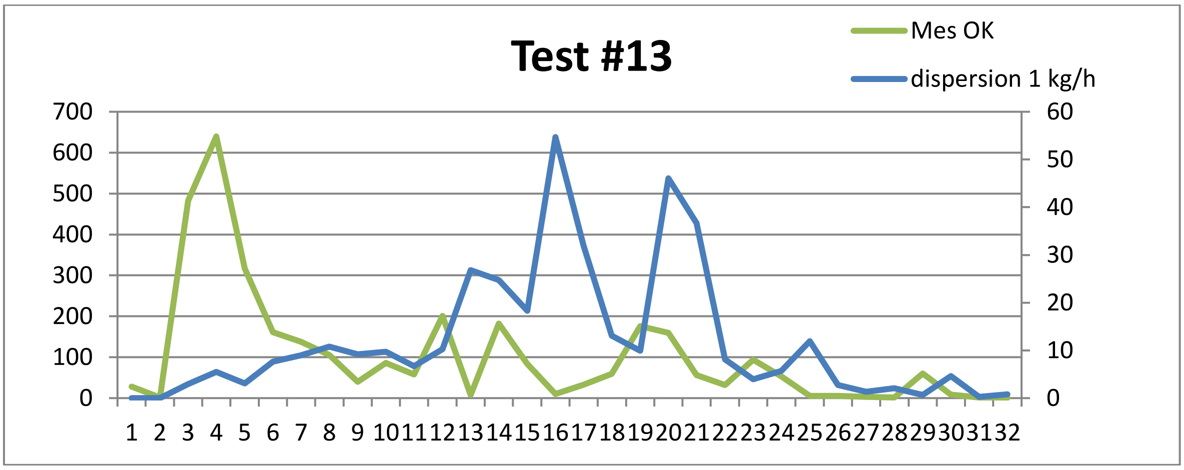


ANNEXE : TEST #13

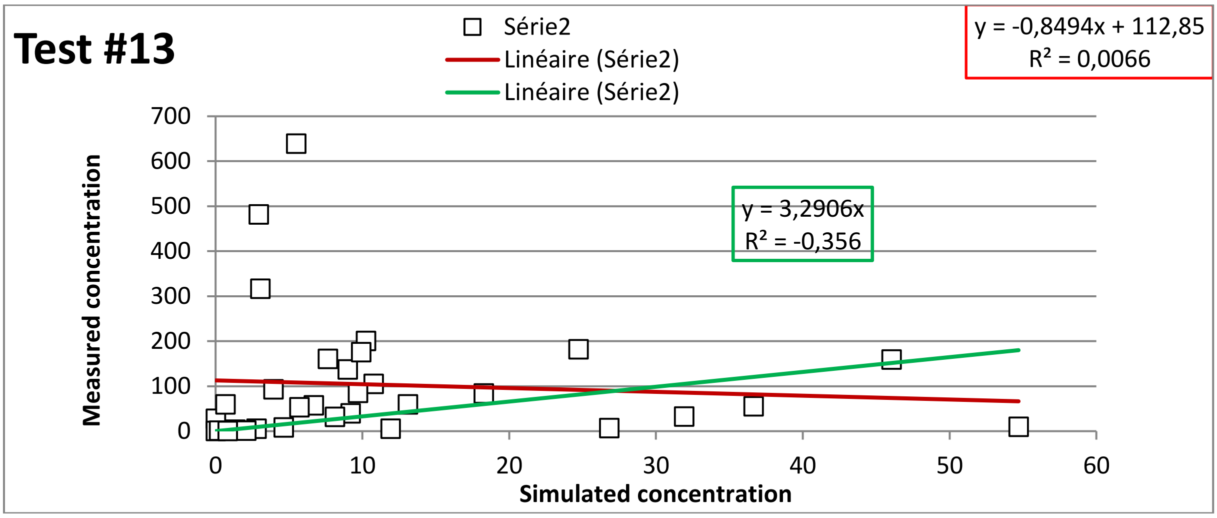
Measurements point test#13 :

Id	X	Y	Z	R
1	-141.4766	2274.5791	11.25	1.0
2	-141.8867	2276.2692	11.25	1.0
3	-144.9029	2279.9490	11.25	1.0
4	-148.0329	2283.9030	11.25	1.0
5	-141.2704	2276.4724	8	1.0
6	-144.2969	2280.1638	8	1.0
7	-141.2392	2277.5883	6	1.0
8	-143.6629	2280.4996	6	1.0
9	-140.6873	2276.9219	6	1.0
10	-133.2084	2289.8498	1.75	2.0
11	-129.1996	2292.3681	1.75	2.0
12	-119.2222	2301.3208	1.75	2.0
13	-117.2060	2278.1945	1.75	2.0
14	-142.2406	2296.8899	0.5	2.0

Time serie of measurement and simulation with dispersion factor for test#13



XY plot and slope calculation for the validity criteria : Test#13 Invalid

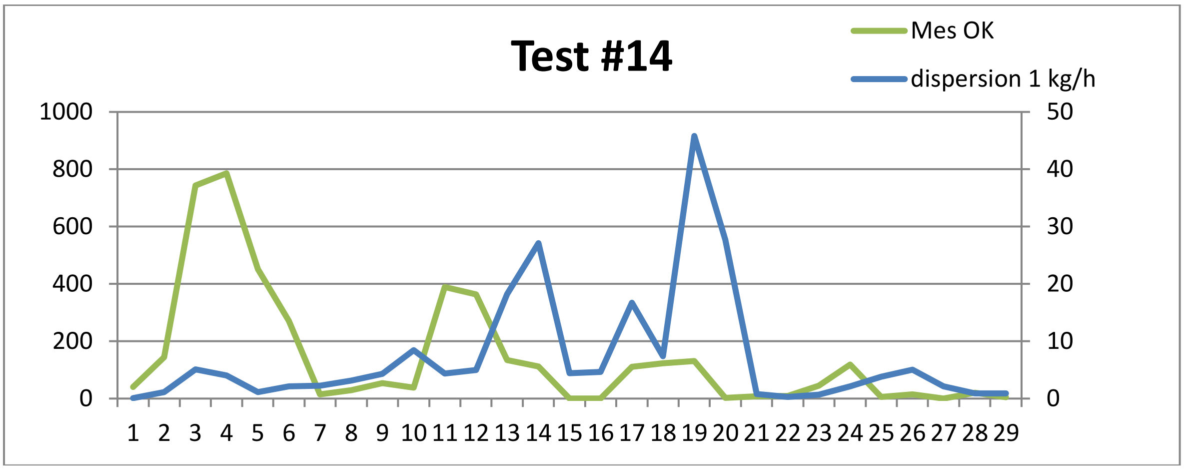


ANNEXE : TEST #14

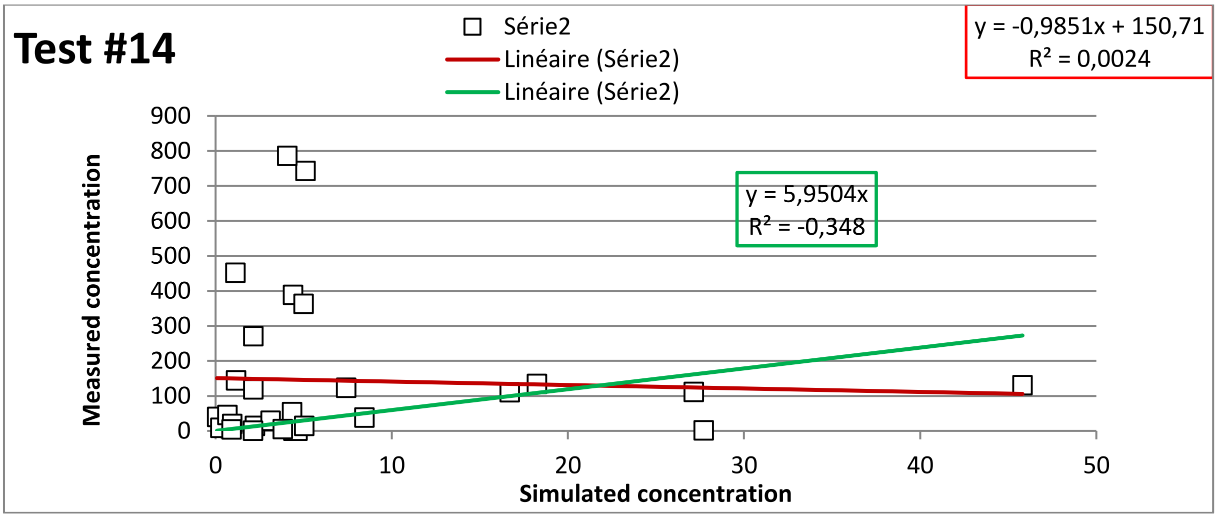
Measurements point test#14 :

Id	X	Y	Z	R
1	-141.1985	2274.7572	11	1.0
2	-141.8883	2276.3049	11.25	1.0
3	-144.8833	2279.9561	11.25	1.0
4	-148.1170	2283.9461	11.25	1.0
5	-138.4492	2272.2987	11.25	1.0
6	-147.0911	2283.4299	8	1.0
7	-144.4276	2280.3893	8	1.0
8	-141.1672	2276.5414	8	1.0
9	-146.8628	2284.6534	6	1.0
10	-144.0739	2281.1920	6	1.0
11	-140.7410	2277.0938	6	1.0
12	-139.6374	2291.1155	1.75	2.0
13	-136.3933	2287.0737	1.75	2.0
14	-129.8132	2292.5226	1.75	2.0
15	-111.7738	2293.7824	1.75	2.0

Time serie of measurement and simulation with dispersion factor for test#14



XY plot and slope calculation for the validity criteria : Test#14 Invalid



NPL REPORT CMES (RES) 024

DIFFERENTIAL ABSORPTION LIDAR (DIAL) RESULTS FOR THE SECOND WG38 FIELD VALIDATION STUDY IN THE NETHERLANDS, JUNE 2017

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NPLML - COMMERCIAL

JUNE 2018

Differential Absorption Lidar (DIAL) Results for the Second WG38 Field Validation Study in the Netherlands, June 2017

F Innocenti, R A Robinson, A Finlayson and N Howes
Chemical, Medical & Environmental Science Division

ABSTRACT

This report presents the results of VOC emission measurements from a refinery site in the Netherlands, carried out using the NPL Differential Absorption Lidar (DIAL). This study was the second WG38 validation test aimed at the development and validation of standardized test methods for the elaboration of a European Standard, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere”. The measurements were conducted from the 8th to the 22nd June 2017.

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Approved on behalf of NPL by
Alan Brewin, Director, Operations Division.

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EXECUTIVE SUMMARY

Background

The European Commission's standardisation mandate M/514 under the Directive 2010/75/EU on industrial emissions, was accepted by CEN/BT, and a decision has been taken to establish this standardisation work within CEN/TC264/WG38.

The control of the emissions of Volatile Organic Compounds (VOCs) to atmosphere due to their losses during storage or transport is covered by both EU legislation and international protocols. The legislation on industrial emissions (Directive 2010/75/EU) is supported by the Best Available Techniques Reference documents (BREFs), which set out at an EU level the best available techniques for defined industrial activities and/or across these activities. Several BREFs also cover the prevention and control of fugitive and diffuse emissions of VOCs from industrial storage and transfer activities, in particular the BREFs concerned with mineral oil and gas refineries, large volume organic chemicals, and the "horizontal" BREF on the emissions from storage. The mandate for this work requests the European standardisation organisations to develop a European Standard that can be used in the determination of VOC emissions to be regulated within permits that are issued according to the Directive.

Total VOC emissions are also regulated at the EU and Member States levels under the National Emission Ceilings Directive (2001/81/EC) which sets total emission ceilings for such emissions at specific levels to be met from 2010 onwards.

VOCs are emitted by a wide range of sources including transport and industrial processes, as well as biogenic and other natural sources, and also by associated storage and handling activities, and the industrial and domestic use of VOC containing products.

VOCs are emitted to a significant extent by fugitive and diffuse sources (including non-point sources), although this is difficult to quantify accurately. This requirement for more accurate determination of these important VOC emissions creates a challenge because of their area emissions, and they require specific measurement and estimation methods that are currently not standardised. However, improving the accuracy of determining these VOC emissions should enable an improved assessment of these losses, and may provide an incentive to reduce such losses, as well as the benefits to their effects on the environment and human health. This should also contribute to the more uniform application of EU regulations and EU guidance documents.

Objectives

Mandate M/514 requires CEN to prepare and validate a standard for the determination of diffuse and fugitive emissions from oil and gas facilities. It should be complementary to the existing standard for the determination of leaks from piping and equipment EN 15446:2008.

This European Standard specifies the framework for determining emissions to the atmosphere of VOCs. It defines a system of methods to detect and/or identify and/or quantify diffuse/fugitive emissions from industrial sources. These methods include Optical Gas Imaging (OGI), Differential Absorption Lidar (DIAL), Solar Occultation Flux (SOF), tracer correlation, flux chamber measurement techniques, calculation and estimation methods.

Two validation studies have been undertaken. The first used a controlled release, able to replicate typical industrial emission levels, at an industrial location to challenge the remote sensing techniques with a known release of VOC under typical industrial conditions. A second validation study deployed the suite of techniques at an industrial facility to validate the combined framework of techniques defined in the standard and demonstrate their operation at a typical site.

An operational refinery in the Netherlands was selected as the location for the second validation study, taking place from 8th to 22nd June 2017. Four measurement providers participated in the tests, running a total of five methods, covering five of the proposed techniques. The results obtained with the DIAL method are described in this report.

Method

DIAL is a well-established and proven optical remote sensing technique that has been used by NPL in numerous emission surveys around the globe. The DIAL method allows to make spatially resolved concentration measurements of a target gas along the path of an eye-safe laser beam transmitted into the atmosphere. During the measurement, the laser is operated alternately at two adjacent carefully chosen wavelengths. One, called the ‘on- wavelength’, is a wavelength which is strongly absorbed by the target species. The other, the ‘off-wavelength’, is a wavelength which is not absorbed significantly by the target species. The difference in the absorption of the two wavelengths is related to the concentration of the gas. Spatial resolution is obtained by pulsing the laser beam. Emissions rates are determined by scanning the laser beam through the atmosphere to build up a concentration map, and combining this with measurements of the wind speed and direction.

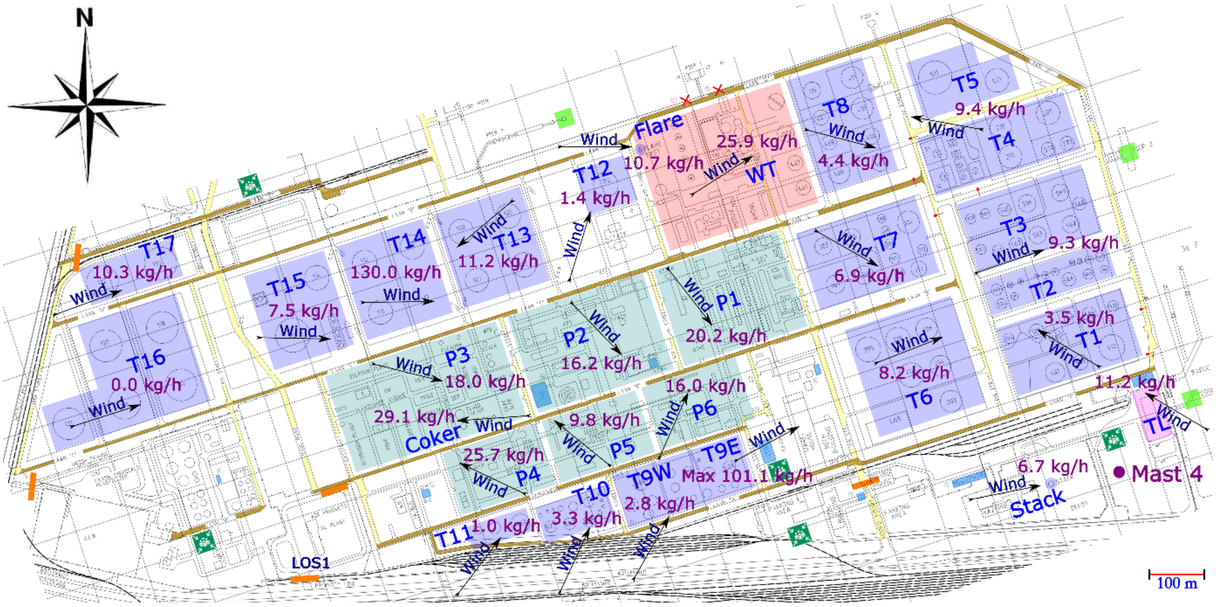
Results and Discussion

The field validation programme was aimed to independently assess each technique protocol. The remote sensing techniques objective was to measure the whole site VOCs emissions as well as the emissions from targeted smaller areas.

DIAL measurements were made by determining the concentration of VOC in vertical measurement planes downwind of the area being measured, and combining these concentrations with wind measurements to determine the emission rate. A total of 154 vertical DIAL scans were made with only three scans not used because of unfavourable wind direction.

Ambient air samples were taken to provide an indication of the VOC speciation around the site and to calculate the scaling factor to go from the standard DIAL VOC emission rate to the actual C2+ emission rate. The measured site-averaged mixture scaling factor was 1.04 ± 0.06 while the specific waste water treatment area scaling factor was 1.68 ± 0.11.

The DIAL was able to measure all the site C2+ emissions divided in several areas as shown in the figure below and summarised in the table below. Some areas had other site areas as upwind sources and the values reported in the table are after the subtraction of the background contribution. In these cases, the reported standard deviation (stdev) is the sum in quadrature of two sets of measurements. For this reason, these reported standard deviations are relatively high, particularly when the emission rates are low.



After the measurement campaign ended we were informed by the site's operator that the content of two tanks (T603 and T614) in the east part of area T9 was cyclohexane. The DIAL VOC measurement is not particularly sensitive to cyclohexene, therefore the correction factor from VOC to C2+ is relatively high. If the composition of these two tanks was known in advance as specified in the protocol, the measurements would have been carried out in a different way: either the DIAL wavelength would have been tuned to cyclohexane to measure it directly (like it is usually performed with methane and ethane), or the generic VOC measurement would have made minimising any other upwind source by cutting through the two tanks to isolate their emission form the other nearby tanks or by doing the measurement with different wind direction, specifically from south. For this validation campaign, the latter approach would have been used since the aim was to measure generic VOC that there would have not been time to switch to any other measurement species. Unfortunately, without the pre-knowledge of the tanks composition, the measurements of this area were carried out with westerly wind so that upwind VOC sources contributions from T10, T11 and the tanks in the west area of T9 needed to be subtracted to estimate the emission from east area of T9. This estimated VOC emission was 3.2 kg/h and, by applying the cyclohexane correction factor, the C2+ (cyclohexane) emission rate was 101.1 ± 79.7 kg/h for a 95% level of confidence. This is a very uncertain measurement and even only 0.5 kg/h of VOC contribution from tanks nearby would make a significant difference. Therefore, this value can only be a maximum emission rate if all the VOC assigned to this area was from the two cyclohexane tanks.

Emission Area	**Emission Rate**	**Standard Uncertainty**	**95% Level of Confidence**
	kg/h	**kg/h**	**kg/h**
T1	3.5	0.3	0.8
T2 & T3	9.3	0.8	1.9
T4 & T5	9.4	1.2	3.3
T6	8.2	0.9	2.3
T7	6.9	0.7	1.6
T8	4.4	1.2	3.1
T9 West	2.8	0.3	0.8
T10	3.3	0.5	1.6
T11	1.0	0.2	0.6
T12	1.4	0.2	0.4
T13	11.2	0.8	1.6
T14 - Temp Source	130.0	21.3	59.9
T15	7.5	0.9	2.5
T16	0.0	0.6	1.8
T17	10.3	0.9	2.0
P1	20.2	3.5	9.8
P2	16.2	1.9	4.8
P3	18.0	1.1	2.2
P4	25.7	3.0	7.7
P5	9.8	3.0	7.1
P6	16.0	2.4	5.7
WT	25.9	2.7	5.9
Flare - Temp Source	10.7	0.7	1.4
Stack SE Site Area - Temp Source	6.7	0.8	1.9
Truck Loading - Temp Source	11.2	1.1	2.4
Coker - Temp Source	29.1	3.0	7.3
T9 Est - T603 & T614 Cyclohexane *	101.1	31.4	79.7
Total - No Temp Sources	**211.6**	**7.1**	**14.4**
Total - Including Temp Sources	**399.4**	**22.7**	**64.4**
Total - Including Cycloexane Estimate*	**500.5**	**38.8**	**88.4**

* This estimate should be treated as maximum value if all the VOC assigned to this area was from the two cyclohexane tanks.

The highest single emission source was a tank in area T14 with a known issue that the site operator was addressing, therefore this source should be considered as a temporary source. The emissions measured from the flare, the stack on the SE site area, the truck loading area and the Coker can also be considered as temporary sources since the emission rate can vary significantly during the day while the DIAL measurements cover approximately one-hour period. The total site emission measured during the three weeks campaign was 211.6 ± 14.4 kg/h excluding the temporary sources and 399.4 ± 64.4 kg/h with the inclusion of the temporary sources. By adding the estimated maximum emission rate from the two cyclohexane tanks T603 and T614 the total emission rate was 500.5 ± 88.4 kg/h.

Overall the protocol was successfully followed and a significant amount of DIAL and wind data was recorded and analysed. These data confirmed the validity of several of the DIAL protocol strategies and technique assumptions as discussed in Section 7.

1 INTRODUCTION

This report presents the results carried out using the National Physical Laboratory's (NPL) differential absorption lidar (DIAL) system (shown in Figure 1.1) to measure emission rates of VOC gas from a refinery site in the Netherlands from the 8th to the 22nd June 2017. This was part of the second validation study to prepare and validate a standard for the determination of diffuse and fugitive emissions from oil and gas facilities within CEN/TC264/WG38, "Stationary source emissions - Standard method to determine fugitive and diffuse emissions of volatile organic compounds into the atmosphere" for which NPL was selected to conduct validation and intercomparison work using the DIAL method. The objective was to obtain critically important quality assurance information on measurement protocols for all participating optical remote sensing methods.

Figure 1.1 NPL DIAL facility.

In the following Section 2 a description of the site is provided. An overview of the DIAL technique is given in Section 3. A brief overview of the measurement approach and the DIAL measurement locations used during the campaign is given in Section 4. Section 5 presents the summary tables and figures for each day of measurement and Section 6 presents a discussion of the results of the VOC emission rate measurements. Section 7 presents an assessment of the DIAL protocol and strategy. The conclusions are presented in Section 8. Technical details for the DIAL technique are presented in Appendix 1, including a discussion of the calibration and validation procedures. Annex 2 presents a series of wind roses to provide a summary of the wind conditions present during the campaign. Annex 3 presents the results of speciation measurements of air samples using pumped absorption tubes.

2 SITE DESCRIPTION

A pre-test visit to the refinery in the Netherlands has been carried out by all the participants in March 2017 to perform the pre-campaign activities identified in the protocol such as health and safety, campaign logistic and identification of suitable measurement locations.

2.1 OVERVIEW

The locations where all the participant's meteorological stations would be deployed were identified during the pre-test visit with the DIAL fixed meteorological mast located in the southeast corner of the site as shown in Figure 2.1.

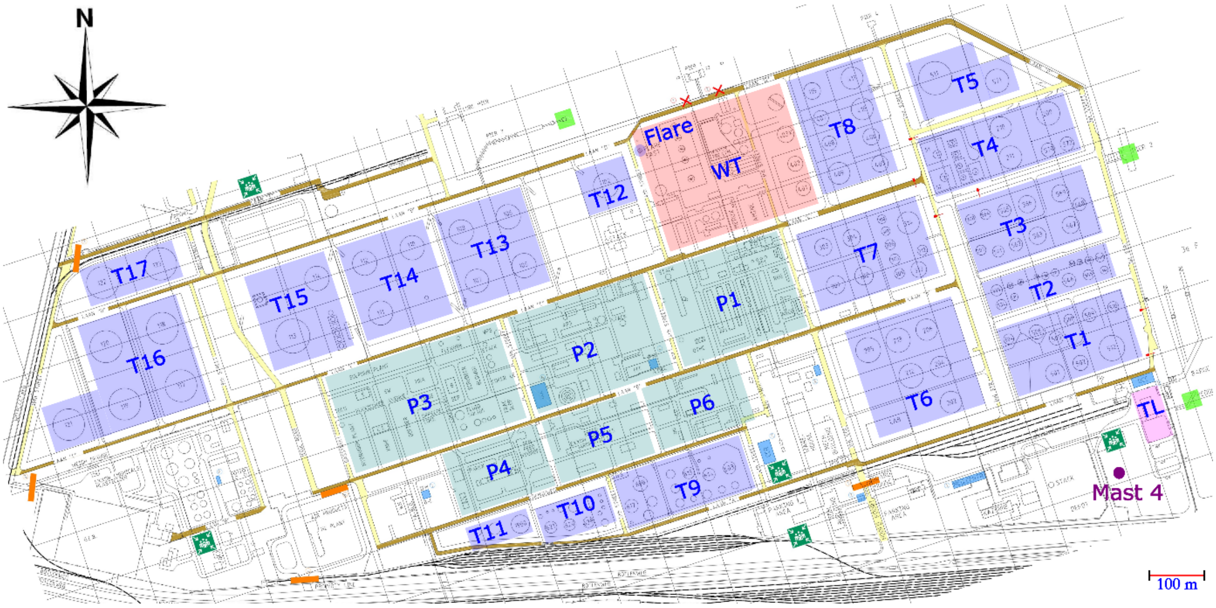


Figure 2.1 Locations of the fixed meteorological station

As part of the protocol the customer should list and identify all the areas to be measured but in this validation project it was agreed by all partners to measure the whole site emission. Each technique would then carry out the measurements following its own protocol and, in the DIAL case, the site was divided in 26 areas shown in Figure 2.1, 17 tank areas, 6 process areas, water treatment, flare and truck loading. The dimensions of these areas were chosen to be representative of typical DIAL measurements that have been carried out in last few decades by NPL at several refineries for different customers.

During the measurement campaign, the selection of the area(s) to be measured depends on several factors driven by wind conditions, available parking locations and line-of-sights (LOS). To assist the implementation of the protocol measurement strategy, following the site visit, the checklist of the areas to be measured was created as shown in Table 2.1. In this table is noted:

- if the DIAL could be parked around the four corners of the area to be measured and be able to scans along all 8 LOS - two from each corner;
- if the measurement of the area of interest could be performed with any wind direction i.e. identify areas that can only be measured with a specific wind direction;
- ideal wind direction/s to measure each area considering available DIAL parking locations and potential upwind sources that should be minimised when possible.

Table 2.1 Checklist table showing all the areas to be measured and the ideal wind condition to carry out the measurements.

Nr.	Plant	Locations /LOS	Wind Directions	Ideal WD
1	Tanks T1	4/8	Any	1)SSE 2)ENE
2	Tanks T2	4/8	Any	1)SSE 2)ENE
3	Tanks T3	4/8	Any	1)SSE 2)ENE
4	Tanks T4	4/8	Any	1)SSE 2)ENE
5	Tanks T5	4/8	Any	1)SSE 2)ENE
6	Tanks T6	4/8	Any	1)SSE 2)ENE
7	Tanks T7	4/8	Any	1)SSE 2)ENE
8	Tanks T8	4/8	Any	1)SSE 2)ENE
9	Tanks T9	4/4	SSE/NNW	SSE
10	Tanks T10	4/4	SSE/NNW	SSE
11	Tanks T11	4/4	SSE/NNW	SSE
12	Tanks T12	4/8	Any	1)WSW 2)SSE
13	Tanks T13	4/6or8?	Any	1)WSW 2)SSE
14	Tanks T14	4/6or8?	Any	1)WSW 2)SSE
15	Tanks T15	4/7or8?	Any	1)WSW 2)SSE
16	Tanks T16	4/8	Any	1)WSW 2)SSE
17	Tanks T17	4/8	Any	1)WSW 2)SSE
17	Water Treatment	4/6or8?	Any	1)WSW 2)SSE
18	Flare	2/4	Any	Any
19	Process Area P1	4/8	Any	1)SSE 2)WSW
21	Process Area P2	4/7or8?	Any	1)SSE 2)WSW
22	Process Area P3	4/7or8?	Any	1)SSE 2)WSW
23	Process Area P4	4/6	N/S/W	SSE
24	Process Area P5	4/6	N/S/E	SSE
25	Process Area P6	4/8	Any	SSE
26	Truck Loading	3/4?	Any?	SSE to WSW

3 DIAL MEASUREMENT TECHNIQUE

This section describes the principles for applying the DIAL technique, a more detailed description of the DIAL methodology can be found in Appendix 1.

3.1 THE DIAL TECHNIQUE

The DIAL technique is a remote sensing method capable of making spatially resolved measurements of concentrations of a target gas (in this case VOC) along the path of an eye-safe laser beam transmitted into the atmosphere.

In the DIAL technique, the laser is operated alternately at two adjacent wavelengths (in the 3.3 µm region for VOC). One of these, the ‘on-wavelength’, is chosen to be at a wavelength which is absorbed by the target species. The other, the ‘off-wavelength’, is chosen to be a wavelength which is not absorbed significantly by the target species. The difference in the absorption of the two wavelengths allows the concentration of the gas to be calculated. Spatial resolution is obtained by pulsing the laser beam. DIAL VOC measurement is targeted on C2+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. A scaling factor to go from the standard DIAL VOC mass to the measured C2+ VOC mass is then applied.

Emissions rates are determined by scanning the laser beam through the atmosphere to build up a concentration map, and combining this with measurements of the wind speed and direction as shown in Figure 3.1. Range-resolved remote DIAL measurements enable total site emissions and area-specific emissions to be measured, with no disruption to normal operational activities. The DIAL data quantify emission rates in kg/hr and provide 2D/3D mapping of emission concentrations in ppm.

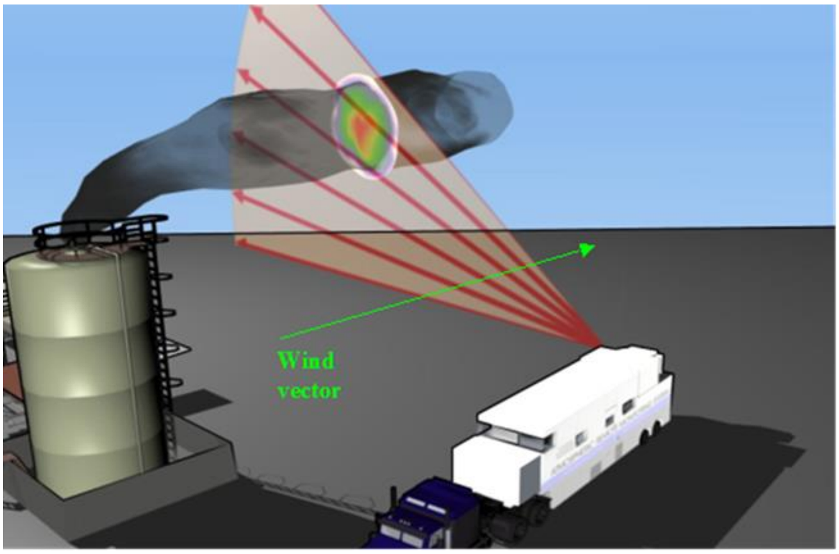


Figure 3.1 DIAL Measurement Configuration

3.2 DIAL TRAILER LOCATION

To measure the emission rate from identified target source, the DIAL is first placed so that a series of downwind scans can be obtained, and then, if possible, DIAL is moved to another position to monitor the upwind emission rate (Figure 3.2a). In some cases, upwind and downwind emission rates can be obtained from a single location (Figure 3.2b). In order to perform measurements, the DIAL has to ‘stand-off’ by a minimum measurement distance of 50 m (measurements cannot be undertaken in the first 50 m from the trailer) so the DIAL does not have to be located in the emission plume.

For each source, the DIAL placement location is chosen by taking into consideration the availability of unobstructed view of the different areas of the site and the current wind direction. The DIAL can be moved during the day if the wind direction changes and if different areas of the site can be measured from other locations.

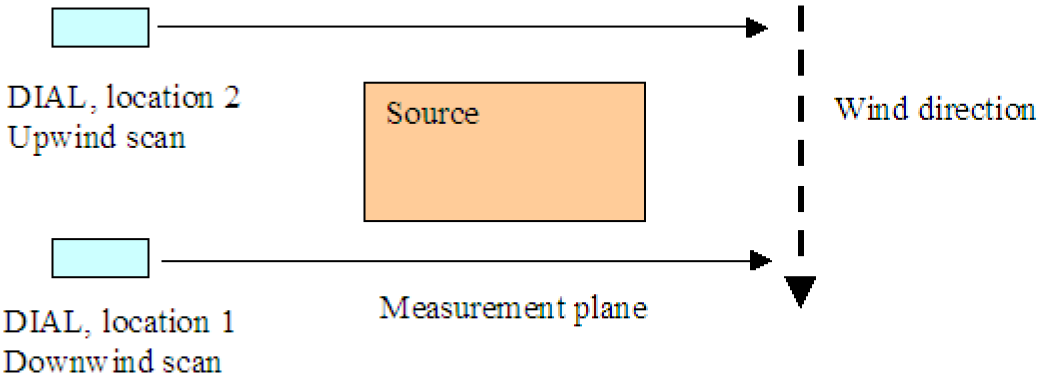


Figure 3.2a Measurement of emissions from two DIAL locations

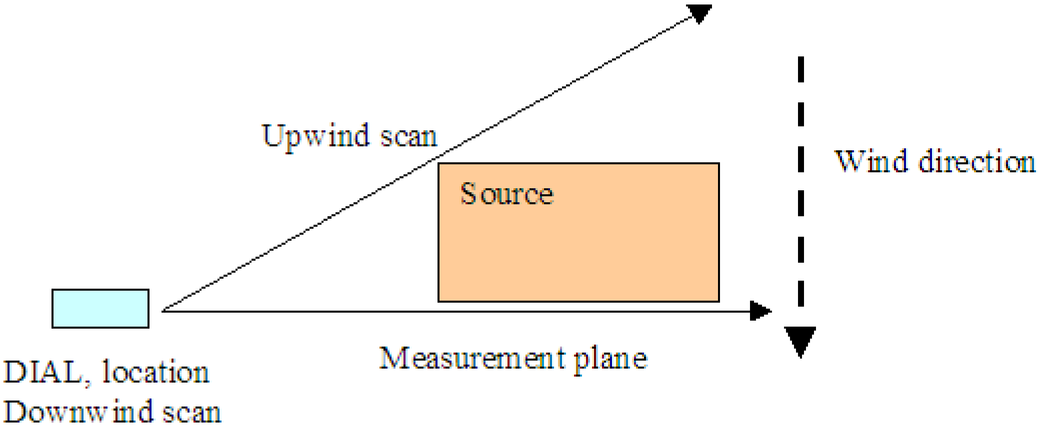


Figure 3.2b Measurement of emissions from one DIAL locations

The strength of the returning DIAL radiation depends on atmospheric conditions as the transmitted infrared radiation is returned by scattering from aerosol/dust particles in the atmosphere. Therefore, the maximum scan range of the DIAL system depends on the atmospheric conditions, and varies from day to day and can also change throughout the day. For VOC the range is typically between 300 m and 600 m. During the three weeks study the weather was variable, wet at the beginning of the campaign and dry with long spells of sunshine and clear view at the end of the campaign. In the latter case not many aerosol/dust particles were present in the atmosphere resulting in a lower strength DIAL return signal.

As the suitability of a measurement location is dependent on wind direction, the choice of measurement locations was made daily following the protocol measurement strategy and the checklist in Table 2.1.

3.3 LINES-OF-SIGHT AND NUMBER OF SCANS

From each location, DIAL scans can be carried out using different LOS to perform downwind and upwind measurements when necessary and to have different cuts through the area of interest. In general, approximately four scans (individual emission measurements) are made along each LOS. The majority of the scans recorded during a DIAL campaign are downwind of different areas of the site. The rest of the scans are upwind or background measurements. For this study only 3 of the 154 recorded scans were not used because of unfavourable wind direction.

3.4 EMISSIONS FROM DIFFERENT AREAS OF THE SITE

Emissions from other areas of the site or other upwind sources may have been upwind of the measured sources and therefore contributing to the measured emission rates. However, generally upwind sources can be excluded in three ways:

1) If the upwind sources to be excluded were close to the measured sources and produced localised plumes, these were discriminated spatially from the measured rates by selecting the regions of the scanned region to integrate, in order to calculate the emission rate only from the area of interest.
2) Conversely, if the upwind sources could not be spatially discriminated and the emissions from them have been measured separately in upwind scans then these values were subtracted from the downwind emission rate.
3) If the upwind sources were further away (typically more than ~300m - 500 m) and relatively low, they normally would be diffuse and below the measurement noise or detection limit or subtracted as a fixed background slope.

This study all the three techniques were used during the data analysis. When the second technique is used the reported stdev is the sum in quadrature of at least two sets of measurements. Consequently, these reported standard deviations are relatively high, particularly when the emission rates are low.

3.5 METEOROLOGICAL MEASUREMENT

The location of meteorological monitoring stations is usually determined in advance of arriving at the site by examining the local historical meteorology data. For this campaign, the fixed meteorological mast, located in the southeast corner of the site, supported four wind sensor packages at 11.9 m, 9.0 m, 6.2 m and 3.4 m elevation from the ground. A 2.3 m high portable mast was also deployed near the DIAL truck or along the measurement LOS. The DIAL truck was equipped with an integral 10.5 m high meteorological mast. The fixed mast’s wind sensors were calibrated Vector Instrument wind vanes and cup anemometers. These instruments were also checked prior to deployment. Wind data were recorded using battery powered loggers, with two second sampling rate. The meteorological data were then processed to provide vector averaged wind data for the periods of each DIAL scan. The wind speed data is used to construct a logarithmic vertical wind profile as described in Appendix 1 (Section 3).

3.6 CALIBRATION PROCEDURE

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. The gas cells were filled with known concentrations of the target species, from NPL standard gas mixtures, which are directly traceable to national standards. A fraction of the transmitted beam was split off and half was directed straight to a detector, the other half was directed through the gas cell and then onto a detector. This provided a direct measurement of the differential absorption at the operating wavelengths. The ratio between the energy on each detector was continuously monitored during the operation of the system to detect any possible drift in the laser wavelengths. Additionally, once a day the wavelength was scanned through the absorption peak of methane and then tuned to appropriate wavelengths for DIAL measurements. The calibration cells were also periodically placed in the output beam to check that the concentration response of the whole system was as expected.

3.7 MEASUREMENT UNCERTAINTY

In previous NPL validation studies, DIAL measurements of total emission rate have shown agreement with known emission sources of between 5% and 20% as described in Appendix 1 (Section 7). The uncertainty of the measurements in this study was estimated based on the stdev of the individual emission rate measurements from which each mean emission rate value has been determined. The 95% t-based confidence interval for the mean is also reported.

The DIAL estimated uncertainty for a single measurement is about 30% - 40%, and some of this uncertainty will be included in the reported stdev. A set of measurements is usually made which reduces the uncertainty typically below 30%; during the first validation study carried out using controlled releases the DIAL uncertainty for a set of four scans was demonstrated to be less than 10%. The reported uncertainty is the variability of the measured results. As such it encapsulates variability occurring during the measurements which will include the measurement itself (random DIAL measurement uncertainty), variability in the source emissions, and variability in the wind direction and speed used since for each scan a different wind profile is calculated from the wind mast data.

When the reported average emission rate for an area is obtained after the subtraction of the upwind contributions the stdev is the sum in quadrature of at least two sets of measurements. These standard deviations can be relatively high, particularly when the resulting emission rates are low.

4 OVERVIEW OF MEASUREMENT APPROACH

The NPL DIAL measurements were conducted from a series of locations around the site in order to determine VOC emission rates from all the identified areas. These locations and the locations of the fixed meteorological station (indicated by ‘Mast 4’) are shown in Figure 4.1.

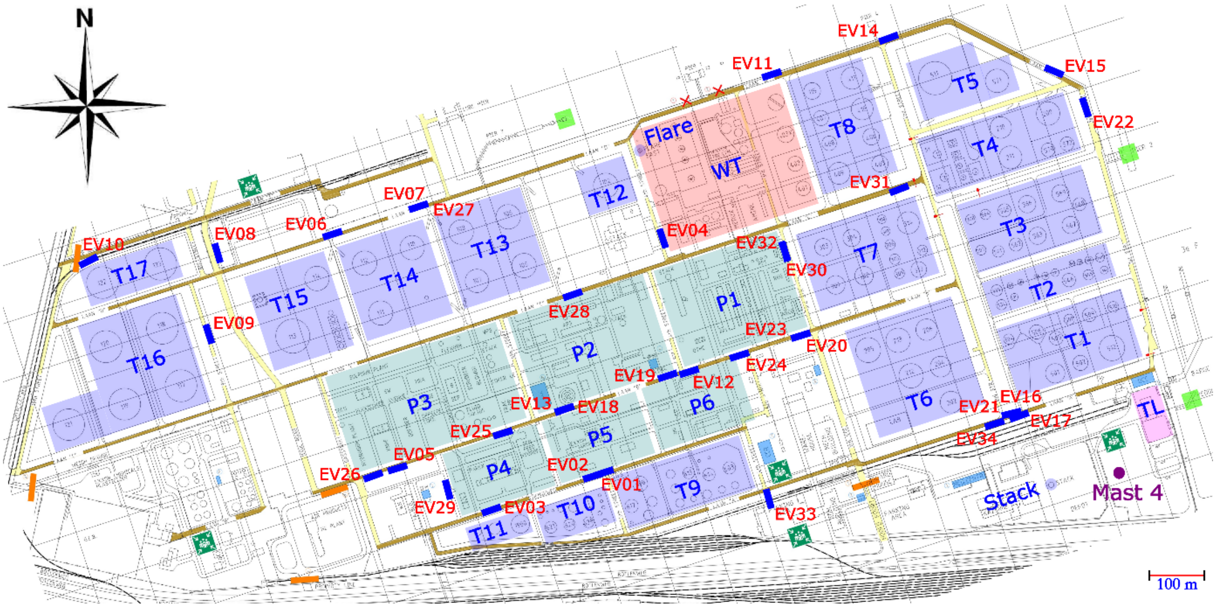


Figure 4.1 DIAL measurement locations and location of fixed meteorological mast

Emission rates were determined using the procedure described in Sections 3.2 - 3.3 and Appendix 1, by scanning the DIAL measurement beam in a vertical plane downwind of the target areas, and measuring the total VOC concentration in that plane.

The logarithmic wind field profile used for the emission rate calculations (see Appendix 1) was determined either from the speeds on the fixed mast sensors located at the southeast corner of the site or from the speeds of the portable and fixed mast sensors or from the speeds of the portable and DIAL sensors. The wind sensor used to define the wind direction for the emission rate calculation was dependant on location, typically the top Mast 4 or the DIAL sensors were used.

During the three weeks study the wind direction was variable and it covered most of the directions although a westerly component was predominant during the campaign. The wind directions over the period of each measurement location are summarized in Annex 2. The wind roses reported in Annex 2 for each location are from the wind sensor used to define the wind direction for the emission rate calculations.

5 SUMMARY TABLES AND FIGURES

5.1 EMISSION RATE RESULTS

The LOS used at each measurement location are shown in Figures 5.1 through 5.32. The figures also show the average wind direction measured over the full-time frame during which the measurements from a given location took place.

Figures designated a1 and a2 are exemplar contour plots and visualizations of the emissions observed in the downwind DIAL measurements. The contour plots (a1 figures) are scaled to the maximum concentration value in each plot while all the 3D visualizations (a2 figures) use a common colour scale (shown below the first scan result) which was 1.0 ppm. Therefore, the colour scale of the contour plot is different with respect to the colour scale of the 3D visualization. In some cases this difference in scaling leads to a slight difference in apparent plume shapes between a contour plot and the 3D visualization.

Tables 5.1 to 5.32 report the emission rates determined for each scan made during the measurement campaign. The scan numbers are not necessarily sequential because they exclude scans recorded for data quality checks and scans aborted by the operator. No valid scan has been eliminated from the report. The tables also list the locations and the LOS used for each measurement. The wind directions reported in the tables are from the sensor used for the emission rate calculations. The wind speeds reported in the tables are from the higher of the sensors used to determine the wind profile. The notes in each table are only indicative of the area measured in a specific LOS to aid the reader in visualising the general location from where the emissions are coming. Reference should be made to the results discussion (Section 6) for more detailed explanations.

Table 5.1 VOC emission rates determined from EV01 on 8th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
1	EV01/LOS1	09:19	09:30	3.0	213.1	0.96	Downwind T11
2	EV01/LOS1	09:30	09:42	3.2	217.3	0.85	Downwind T11
3	EV01/LOS1	09:42	09:53	3.2	219.3	0.47	Downwind T11
4	EV01/LOS1	10:17	10:29	2.4	213.3	1.44	Downwind T11

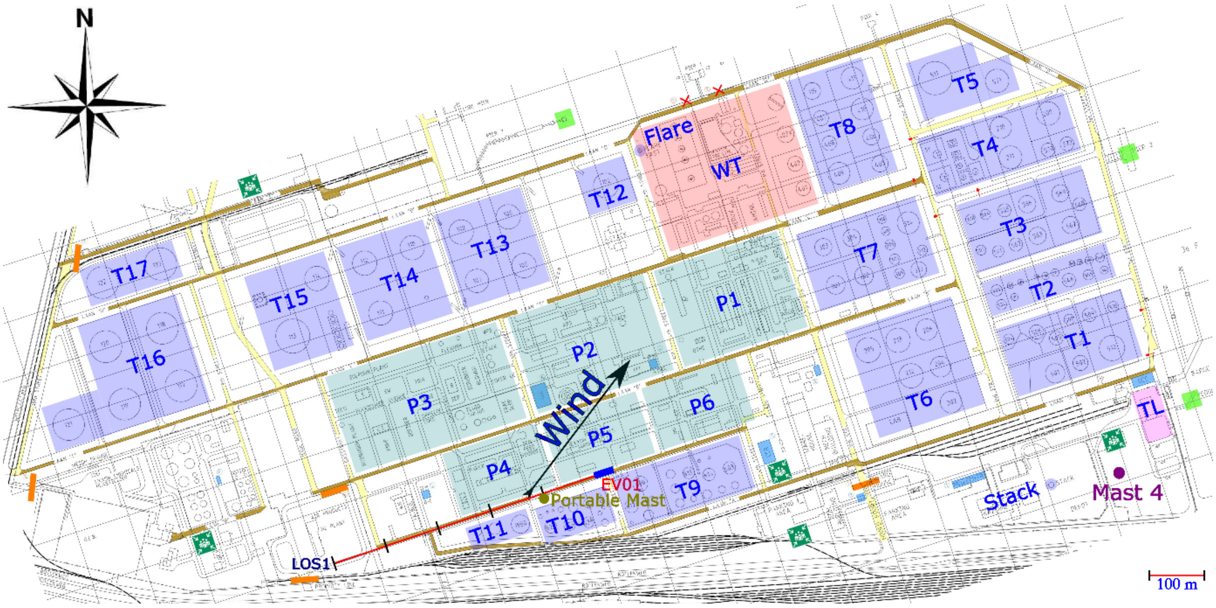


Figure 5.5.1 Measurement configuration for location EV01 on 8th June.

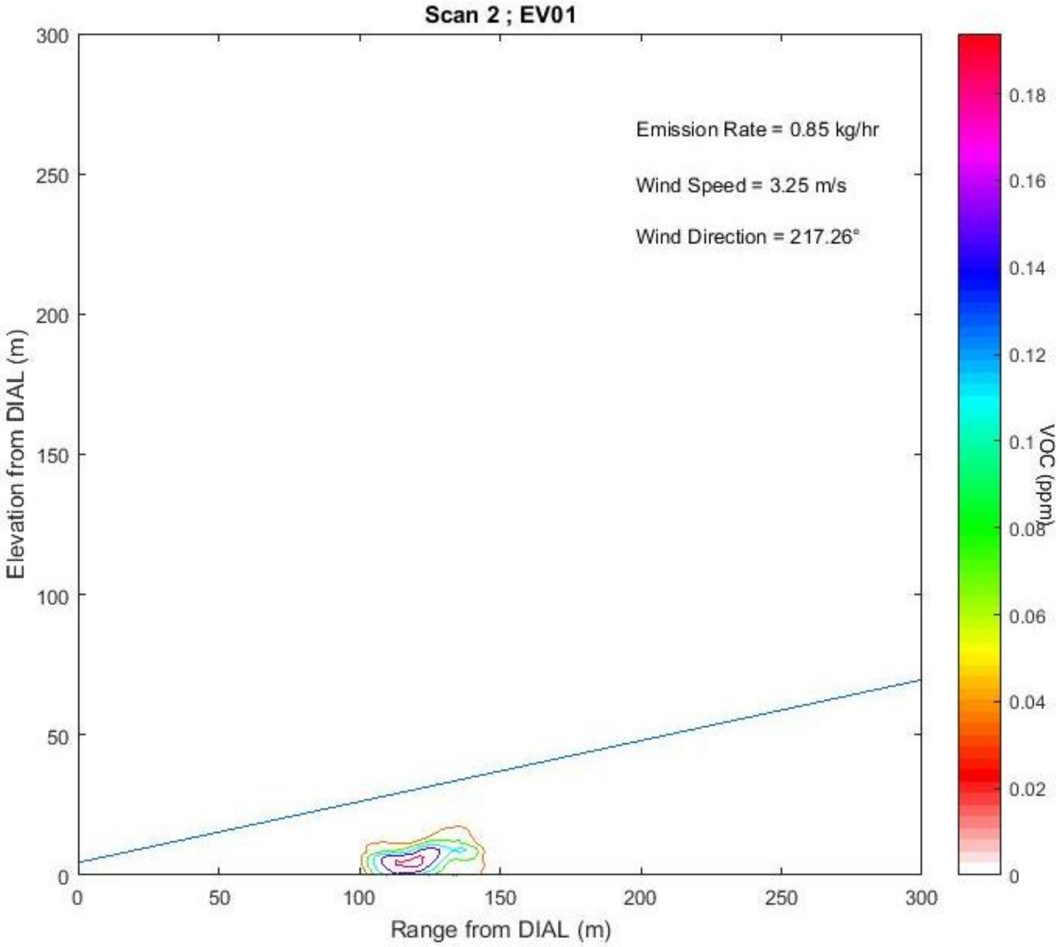


Figure 5.1a1 Observed VOC concentration for Scan 2 representing EV01/LOS1.

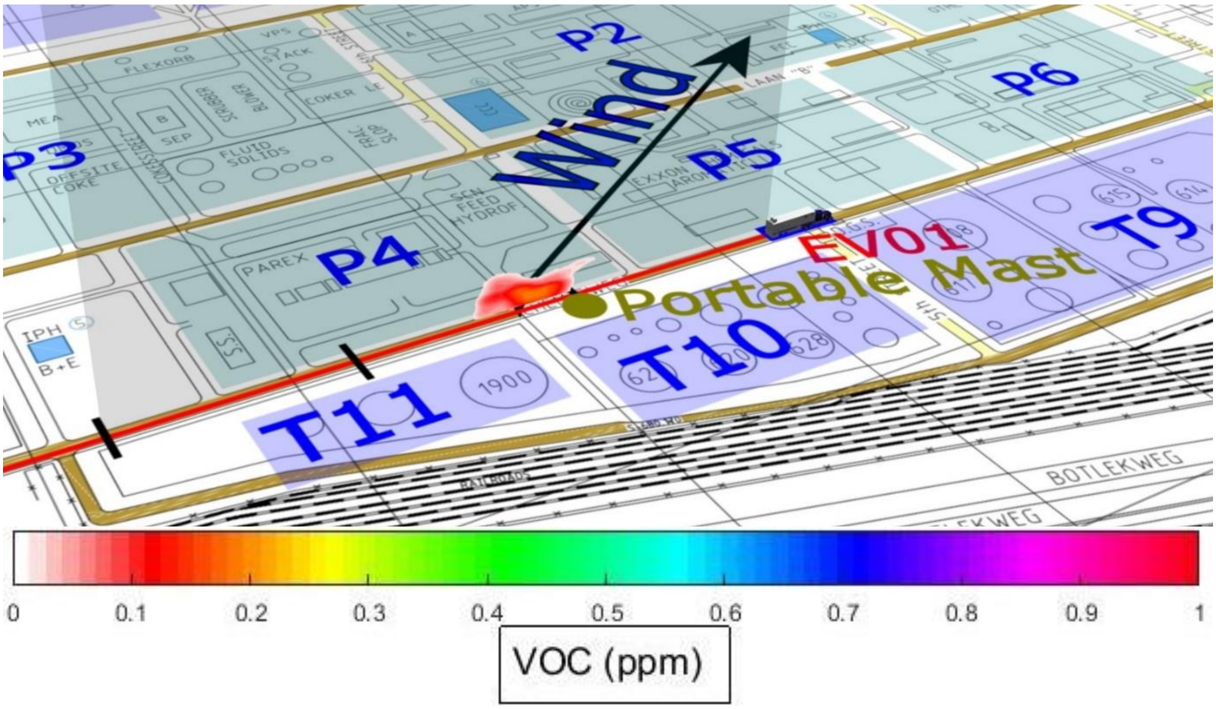


Figure 5.1a2 Visualisation of emission rate for Scan 2 representing EV01/LOS1.

Table 5.2 VOC emission rates determined from EV02 on 8th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
6	EV02/LOS1	11:08	11:21	3.1	210.5	1.95	Downwind West Area T9
7	EV02/LOS1	11:26	11:39	3.8	222.0	3.10	Downwind West Area T9
8	EV02/LOS1	11:40	11:53	4.1	213.7	2.81	Downwind West Area T9
9	EV02/LOS1	11:53	12:07	3.6	210.5	2.90	Downwind West Area T9

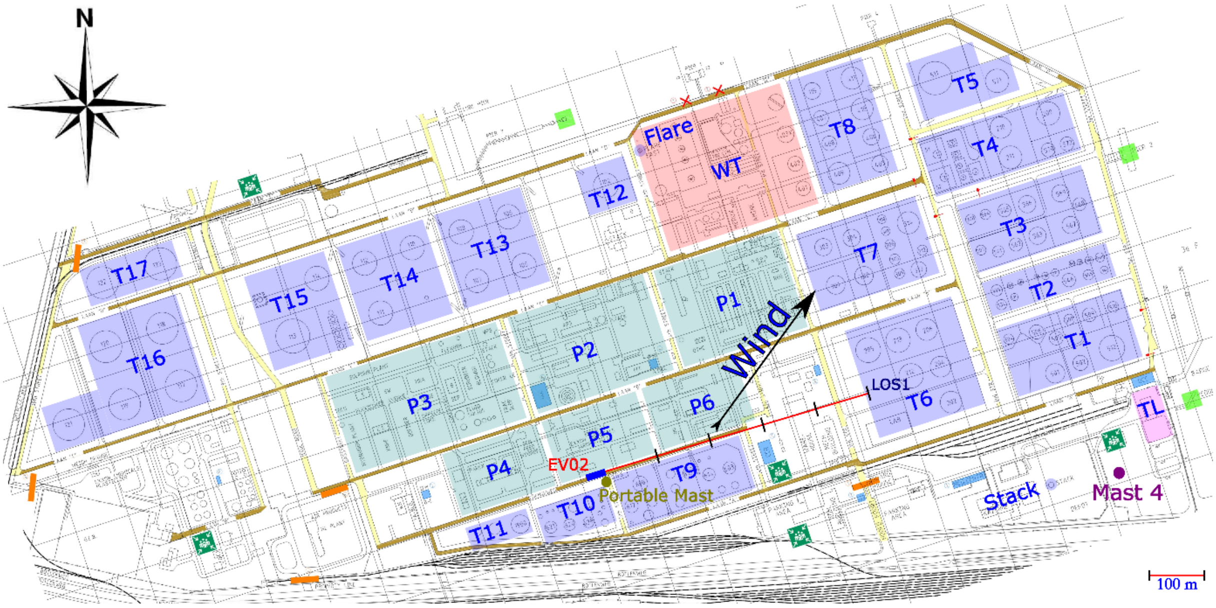


Figure 5.2 Measurement configuration for location EV02 on 8th June.

Table 5.3 VOC emission rates determined from EV03 on 8th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
10	EV03/LOS1	12:36	12:48	5.3	202.7	3.42	Downwind T10
11	EV03/LOS1	12:48	13:01	4.1	210.1	2.35	Downwind T10
12	EV03/LOS1	13:01	13:13	5.0	213.1	3.71	Downwind T10
13	EV03/LOS1	13:14	13:26	5.2	194.1	9.08	Downwind T10 - Intermittent Source?

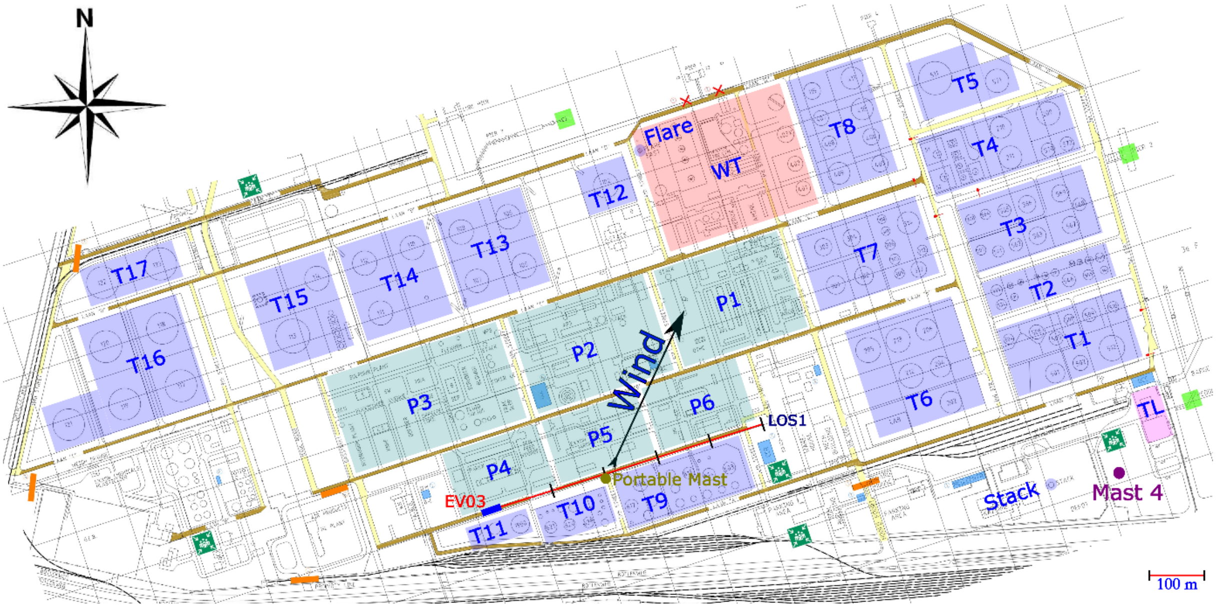


Figure 5.3 Measurement configuration for location EV03 on 8th June.

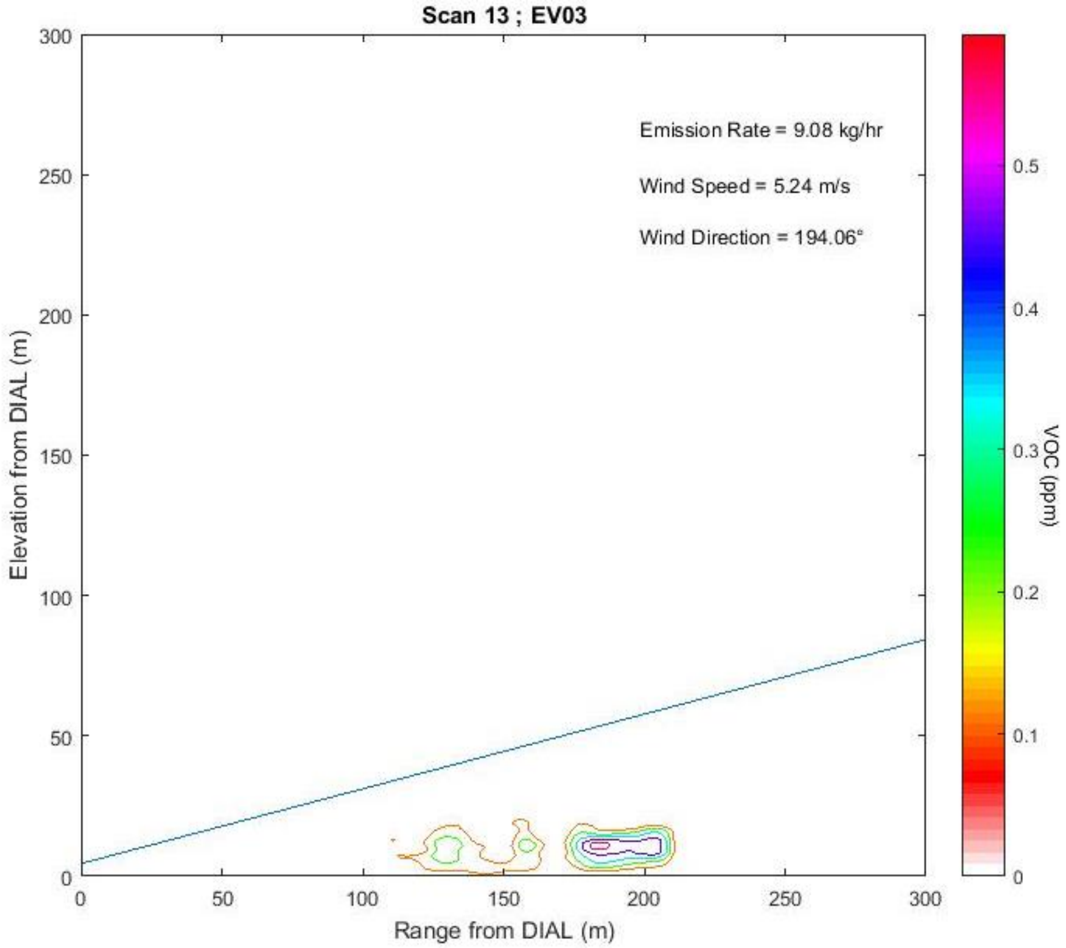


Figure 5.3a1 Observed VOC concentration for Scan 13 representing EV03/LOS1.

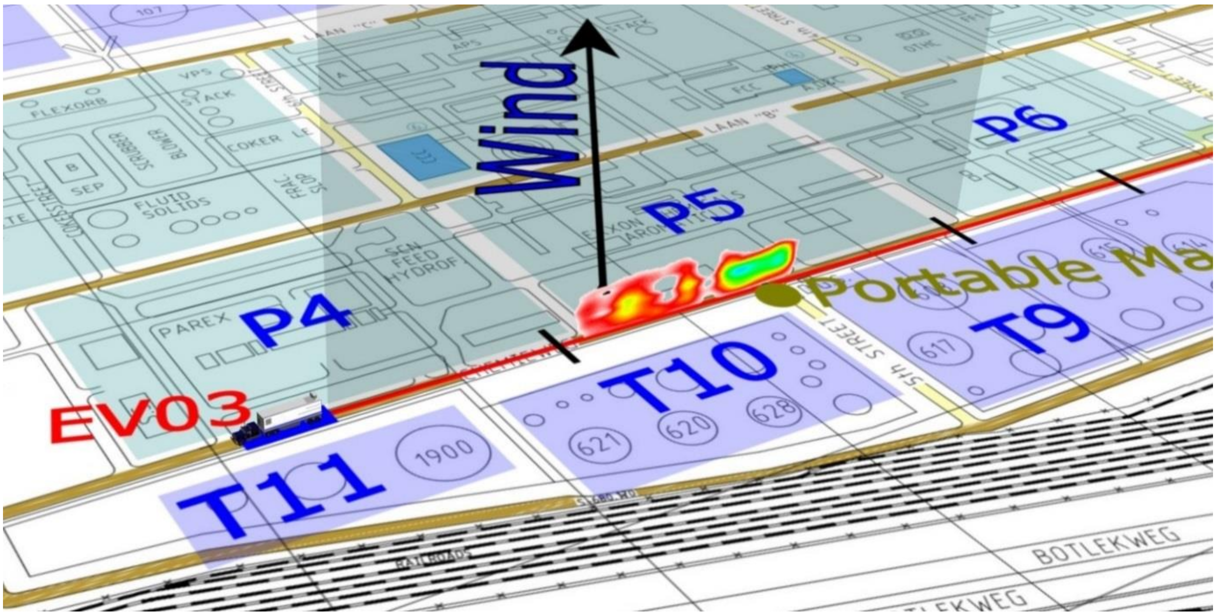


Figure 5.3a2 Visualisation of emission rate for Scan 13 representing EV03/LOS1.

Table 5.4 VOC emission rates determined from EV04 on 8th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
14	EV04/LOS1	14:48	14:56	5.3	196.5	1.32	Downwind T12
15	EV04/LOS1	14:56	15:04	5.9	189.9	1.14	Downwind T12
16	EV04/LOS1	15:04	15:13	6.0	197.1	1.76	Downwind T12
17	EV04/LOS1	15:13	15:21	4.8	206.4	1.16	Downwind T12

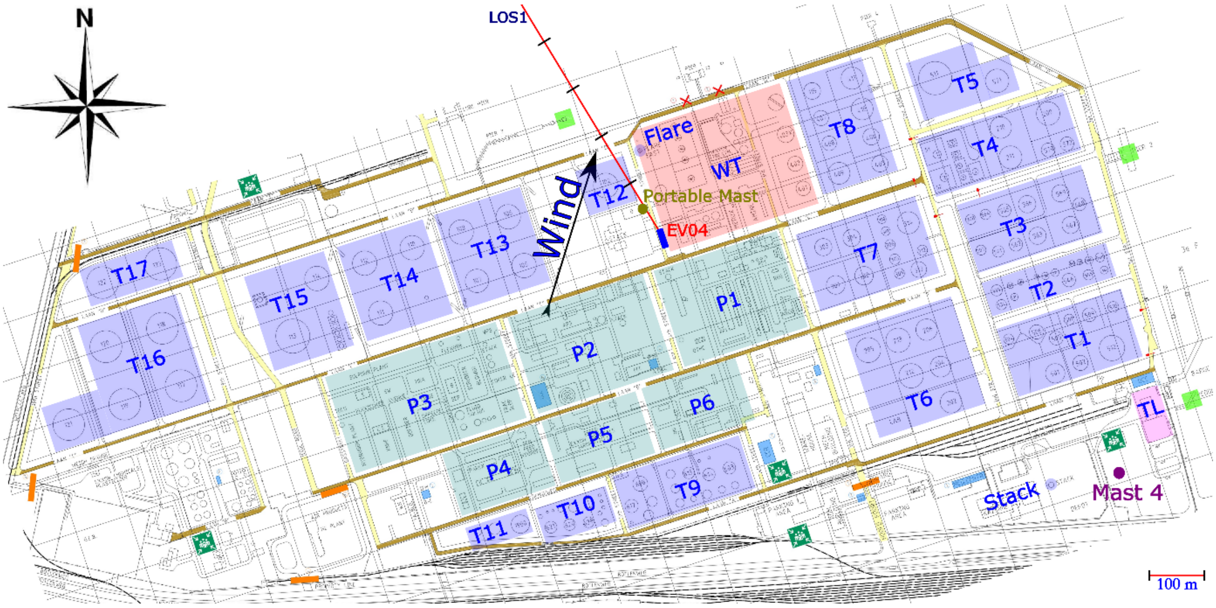


Figure 5.4 Measurement configuration for location EV04 on 8th June.

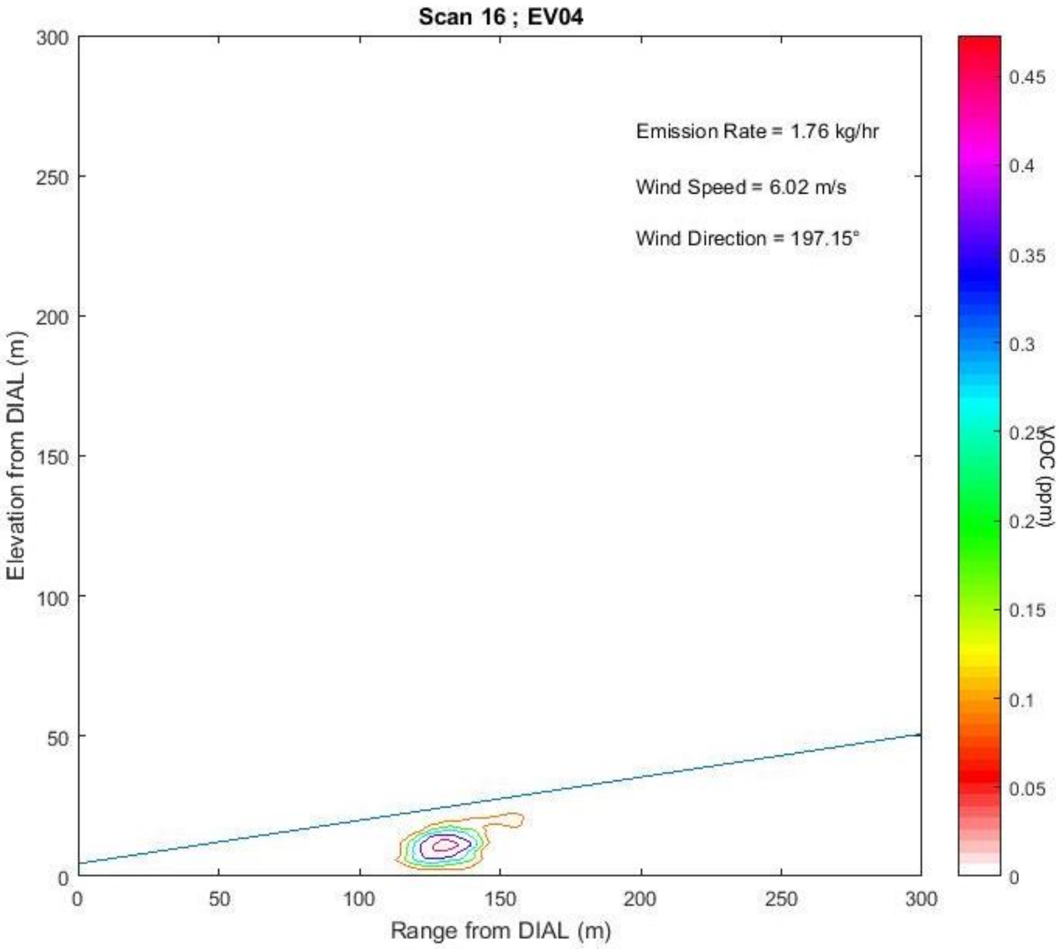


Figure 5.4a1 Observed VOC concentration for Scan 16 representing EV04/LOS1.

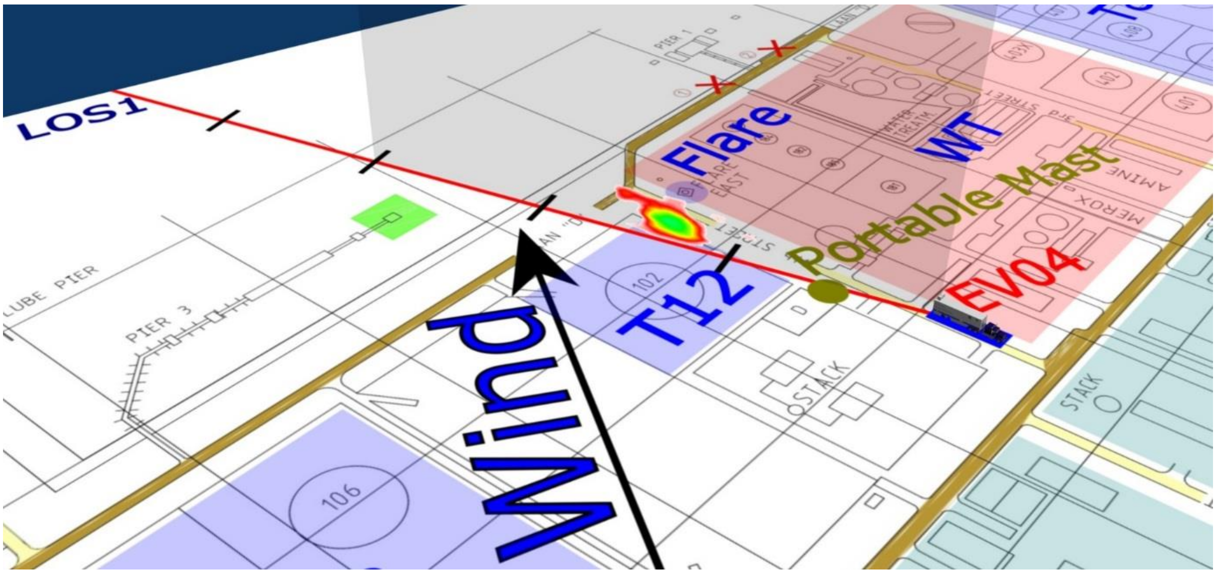


Figure 5.4a2 Visualisation of emission rate for Scan 16 representing EV04/LOS1.

Table 5.5 VOC emission rates determined from EV06 on 9th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
20	EV06/LOS1	10:32	10:45	6.0	276.7	8.33	Downwind T15
21	EV06/LOS1	10:46	10:59	5.2	268.3	4.83	Downwind T15
22	EV06/LOS1	10:59	11:11	6.9	270.6	8.04	Downwind T15
23	EV06/LOS1	11:12	11:24	6.4	267.4	7.55	Downwind T15

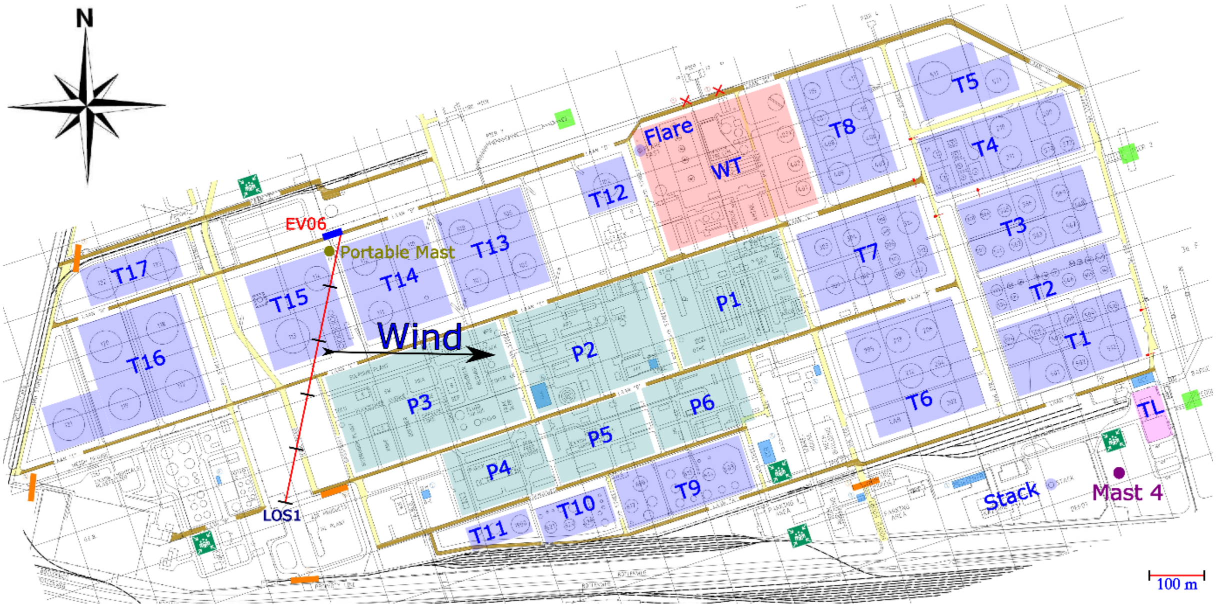


Figure 5.5 Measurement configuration for location EV06 on 9th June.

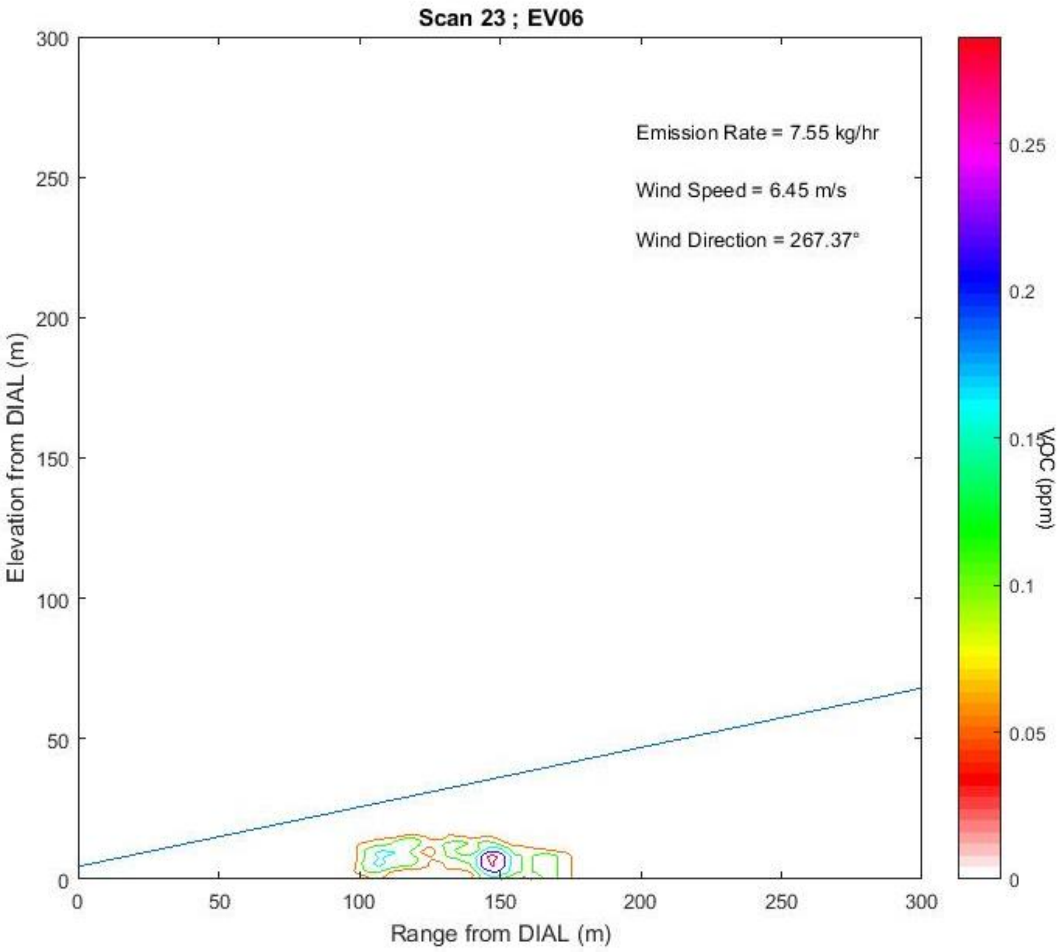


Figure 5.5a1 Observed VOC concentration for Scan 23 representing EV06/LOS1.

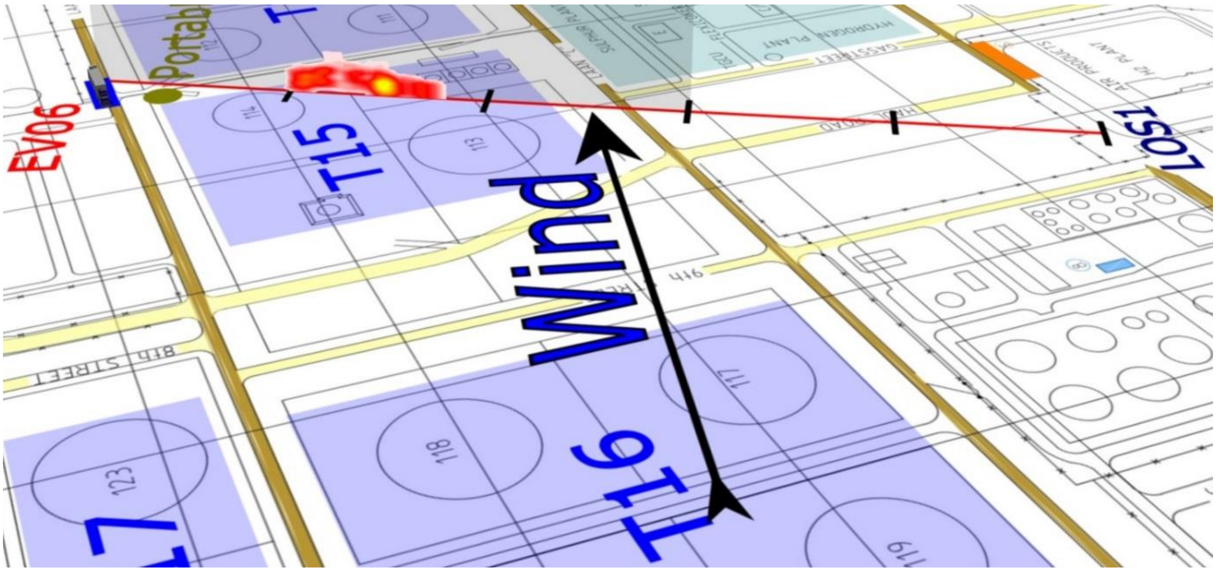


Figure 5.5a2 Visualisation of emission rate for Scan 23 representing EV06/LOS1.

Table 5.6 VOC emission rates determined from EV07 on 9th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
26	EV07/LOS1	12:03	12:17	7.0	276.1	128.51	Downwind T14 - Temp Source
27	EV07/LOS1	12:17	12:32	7.2	267.7	83.67	Downwind T14 - Temp Source
28	EV07/LOS1	12:33	12:48	7.6	269.3	174.99	Downwind T14 - Temp Source
29	EV07/LOS1	12:49	13:05	6.6	263.8	111.88	Downwind T14 - Temp Source

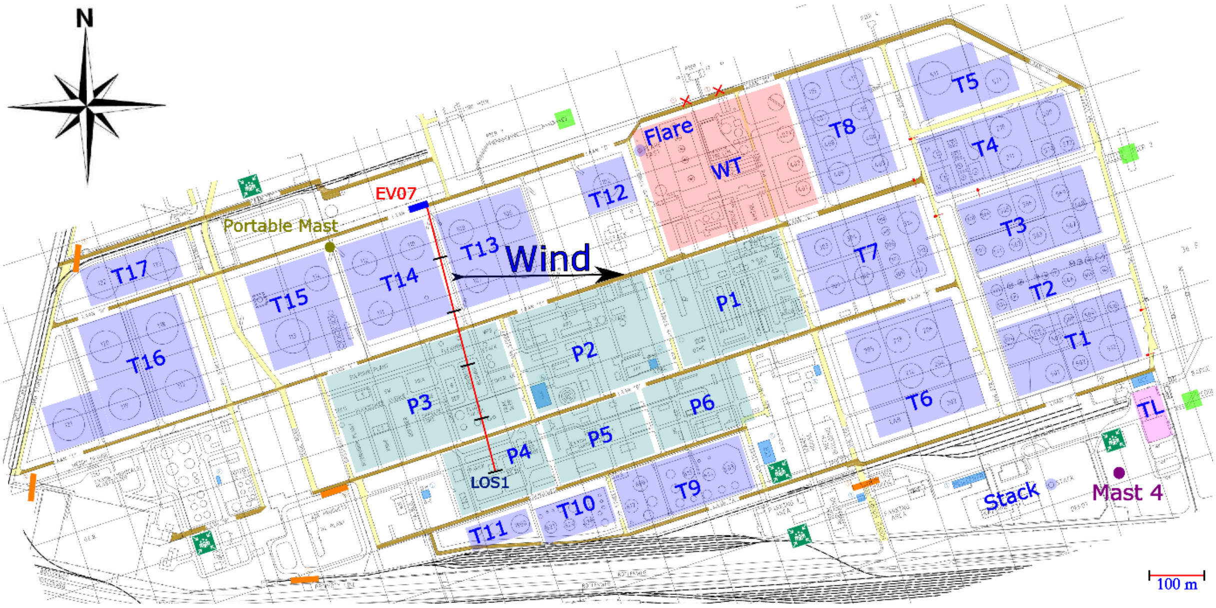


Figure 5.6 Measurement configuration for location EV07 on 9th June.

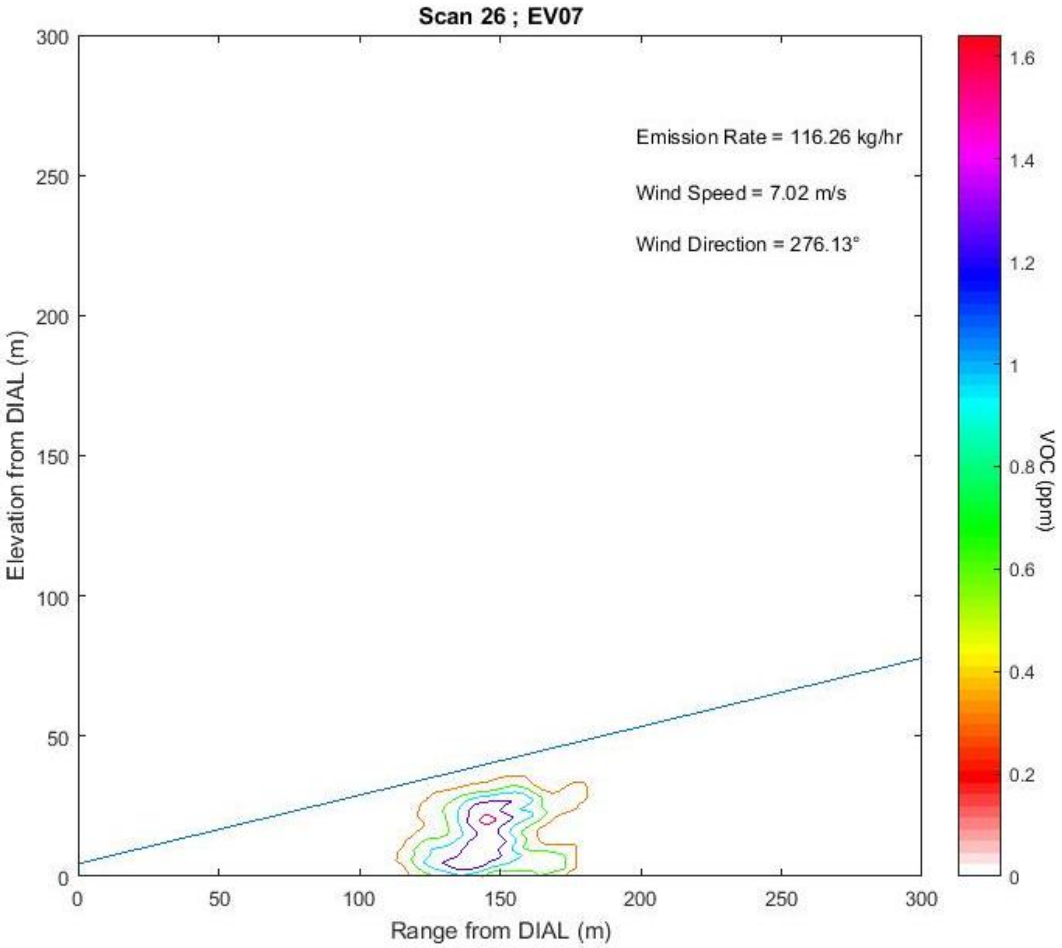


Figure 5.6a1 Observed VOC concentration for Scan 26 representing EV07/LOS1.

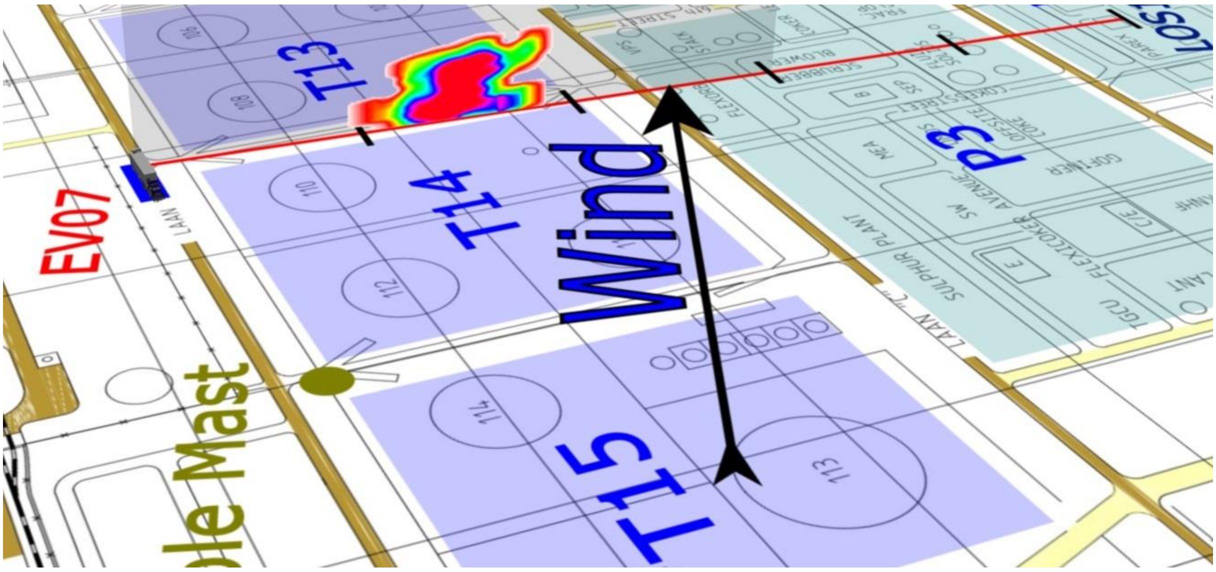


Figure 5.6a2 Visualisation of emission rate for Scan 26 representing EV07/LOS1.

Table 5.7 VOC emission rates determined from EV08 on 9th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
31	EV08/LOS1	13:43	13:54	6.7	243.8	0.70	Downwind T16
32	EV08/LOS1	13:54	14:06	6.1	246.6	-0.43	Downwind T16
33	EV08/LOS1	14:06	14:17	6.7	249.4	1.04	Downwind T16
34	EV08/LOS1	14:18	14:29	7.5	264.0	-1.37	Downwind T16

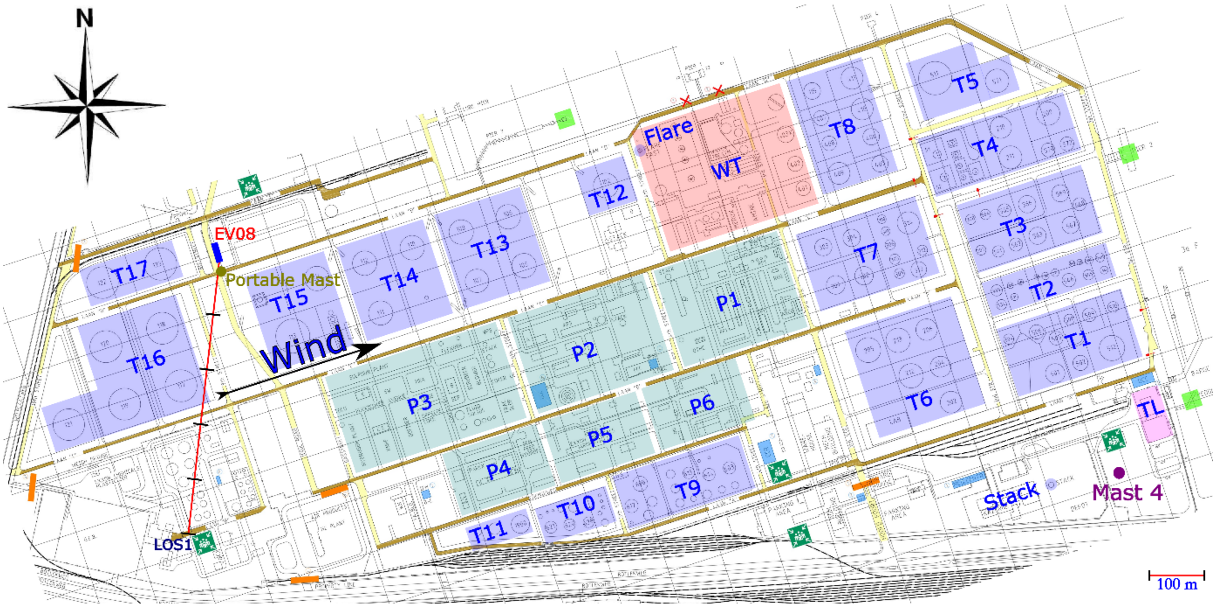


Figure 5.7 Measurement configuration for location EV08 on 9th June.

Table 5.8 VOC emission rates determined from EV09 on 12th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
35	EV09/LOS1	09:41	09:54	8.2	255.6	11.52	Downwind T17
36	EV09/LOS1	09:54	10:07	8.7	250.6	9.44	Downwind T17
37	EV09/LOS1	10:07	10:19	7.3	245.6	9.86	Downwind T17
38	EV09/LOS1	10:19	10:32	7.3	248.5	8.57	Downwind T17

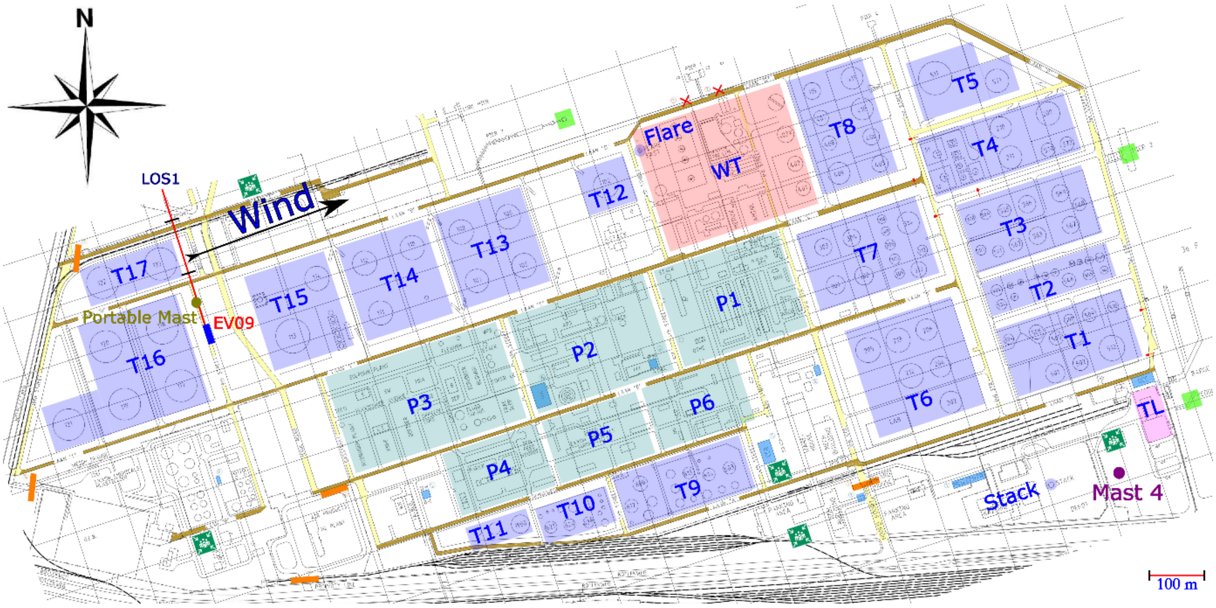


Figure 5.8 Measurement configuration for location EV09 on 12th June.

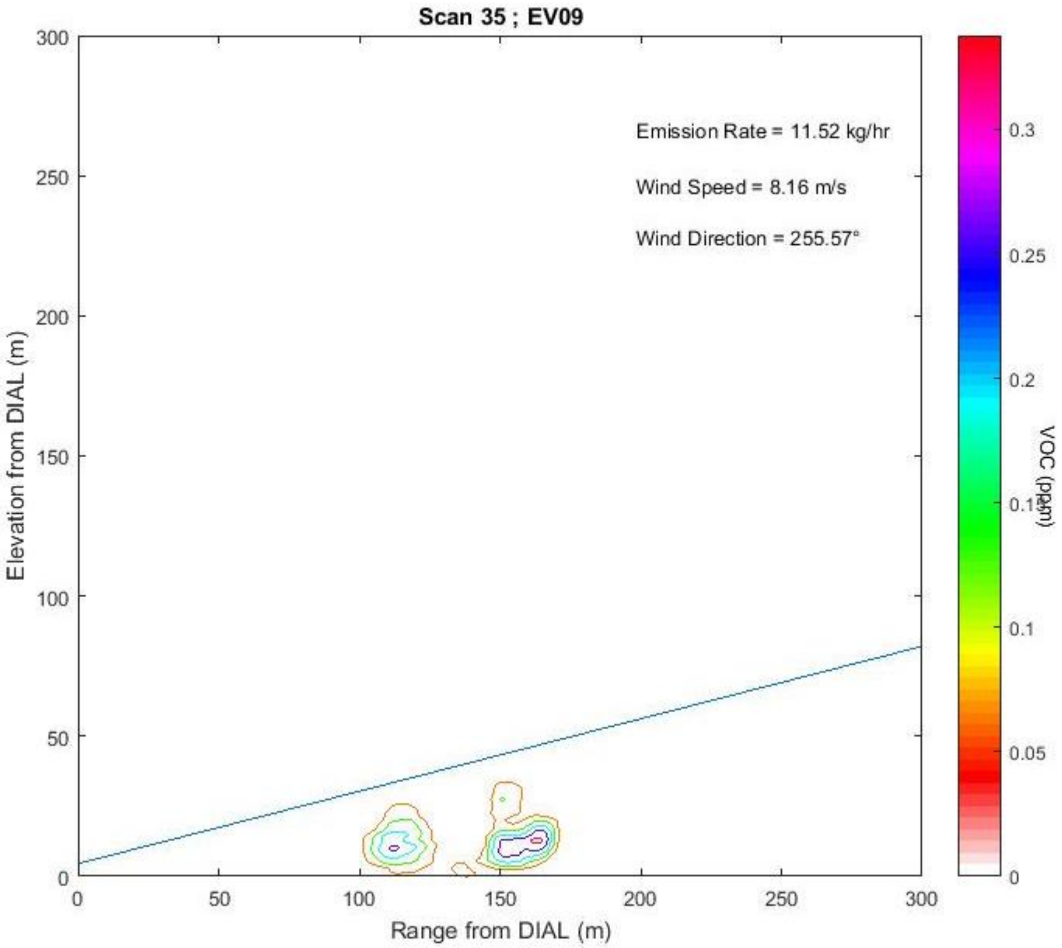


Figure 5.8a1 Observed VOC concentration for Scan 35 representing EV09/LOS1.

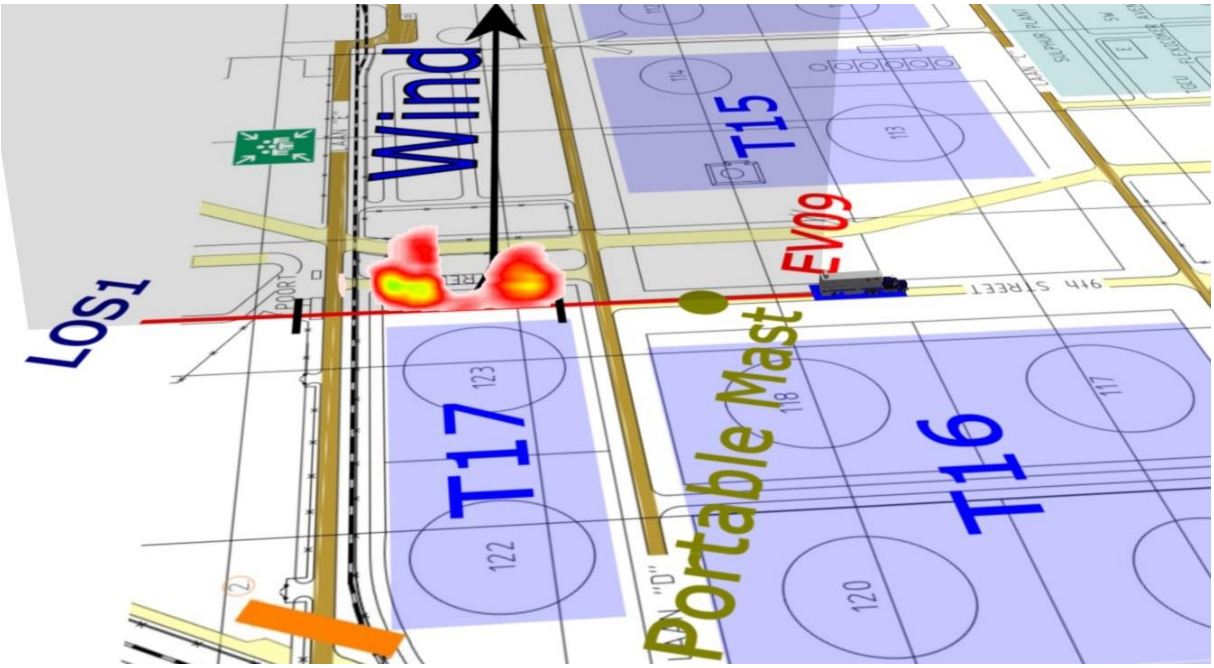


Figure 5.8a2 Visualisation of emission rate for 35 representing EV09/LOS1.

Table 5.9 VOC emission rates determined from EV10 on 12th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
41	EV10/LOS1	11:40	11:51	7.0	262.5	0.02	Upwind
42	EV10/LOS1	11:58	12:09	7.6	263.8	-0.47	Upwind
43	EV10/LOS1	12:14	12:26	8.1	267.1	-0.52	Upwind
44	EV10/LOS1	12:30	12:42	7.3	251.8	0.82	Upwind

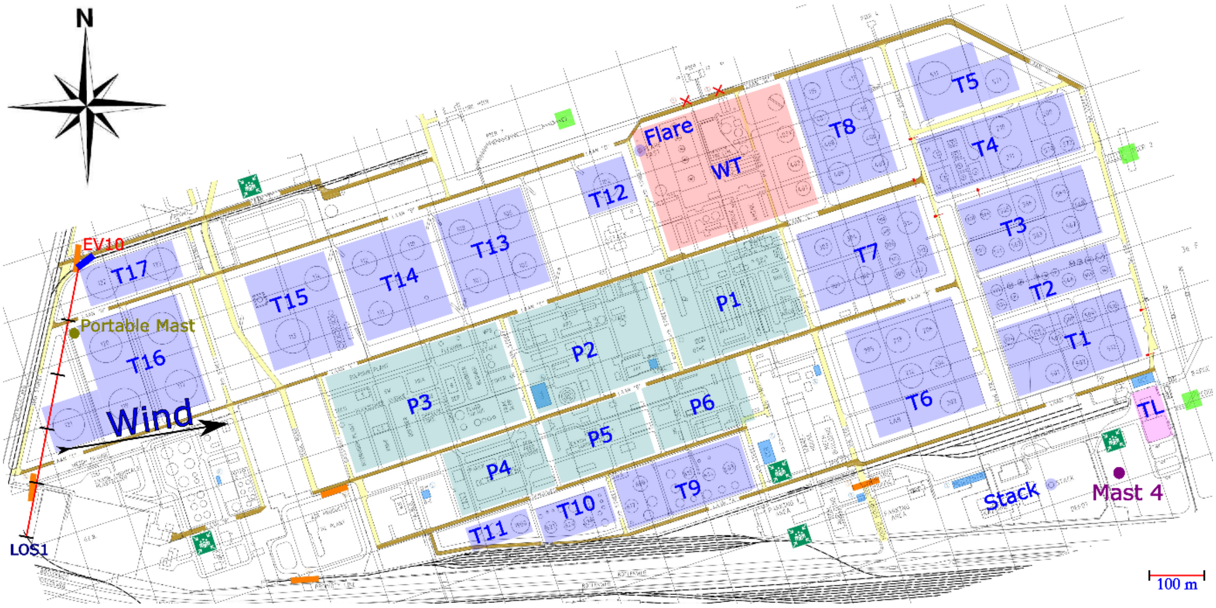


Figure 5.9 Measurement configuration for location EV10 on 12th June.

Table 5.10 VOC emission rates determined from EV11 on 12th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
45	EV11/LOS1	13:59	14:12	7.9	262.9	13.89	Downwind WT
46	EV11/LOS1	14:13	14:26	8.8	267.8	14.93	Downwind WT
47	EV11/LOS1	14:27	14:40	7.6	274.2	16.76	Downwind WT
48	EV11/LOS1	14:40	14:54	8.5	269.8	14.24	Downwind WT
49	EV11/LOS2	15:03	15:08	8.7	277.9	10.82	Downwind Flare
50	EV11/LOS2	15:09	15:16	7.6	269.8	10.01	Downwind Flare
51	EV11/LOS2	15:16	15:24	8.8	267.0	9.91	Downwind Flare
52	EV11/LOS2	15:24	15:31	6.9	277.1	10.29	Downwind Flare

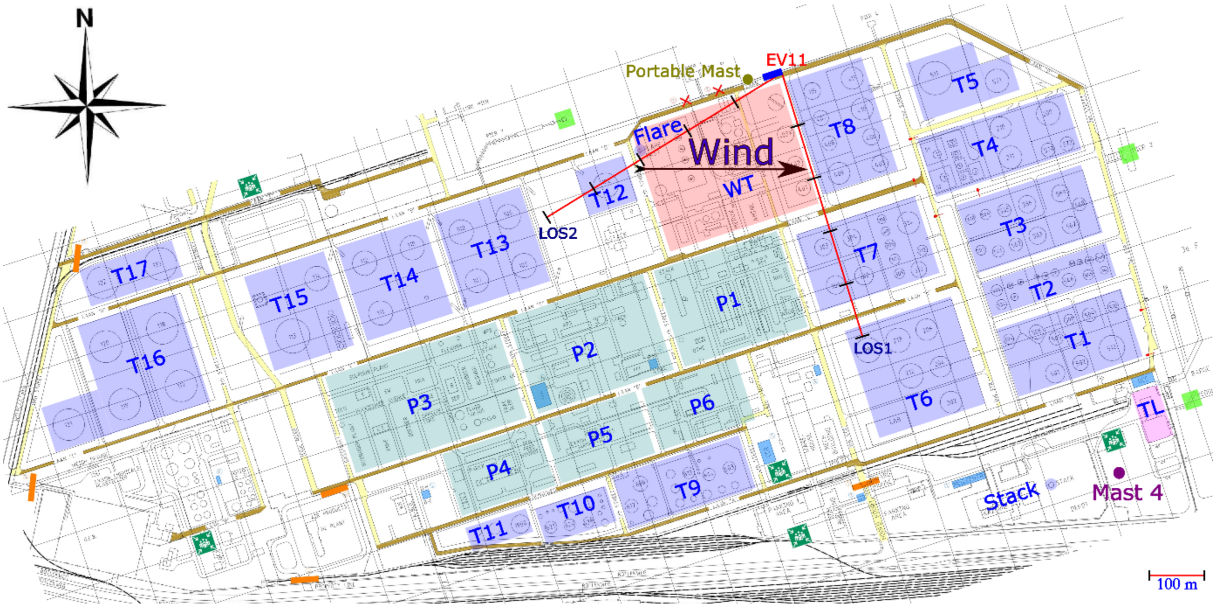


Figure 5.10 Measurement configuration for location EV11 on 12th June.

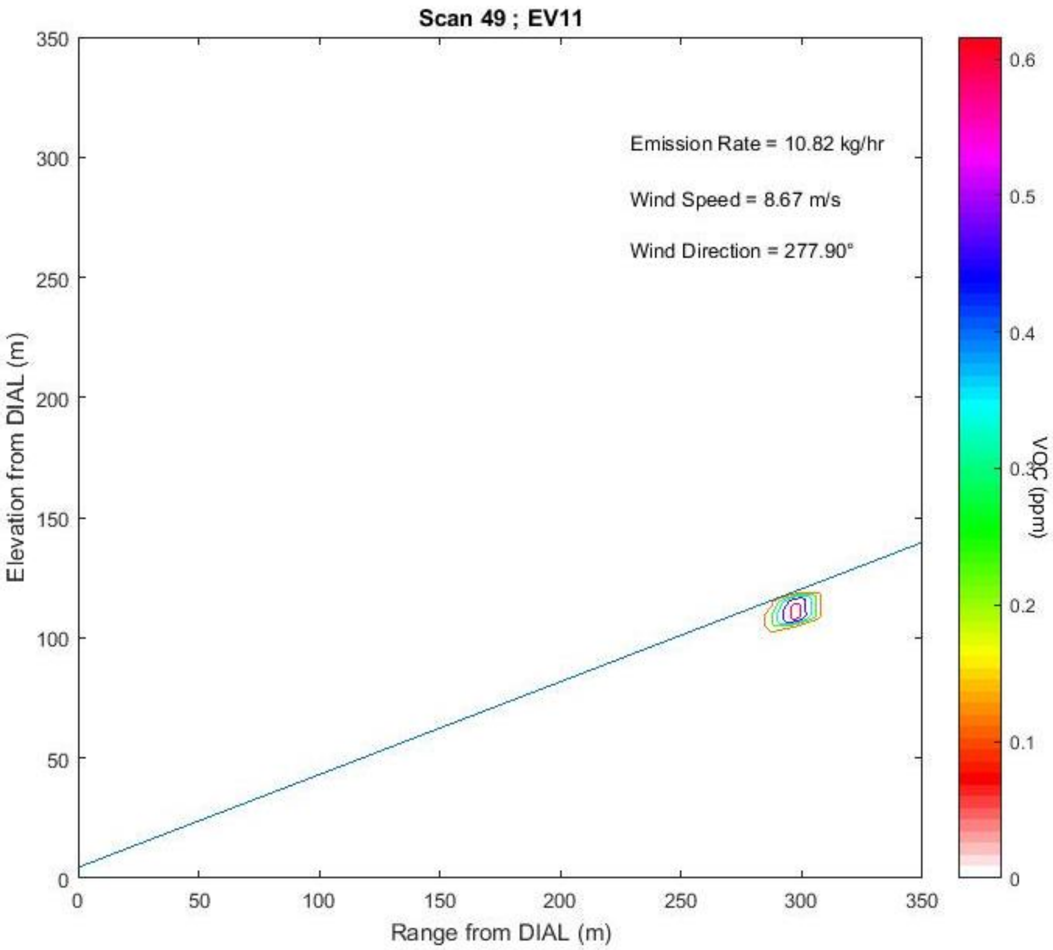


Figure 5.10a1 Observed VOC concentration for Scan 49 representing EV11/LOS2.

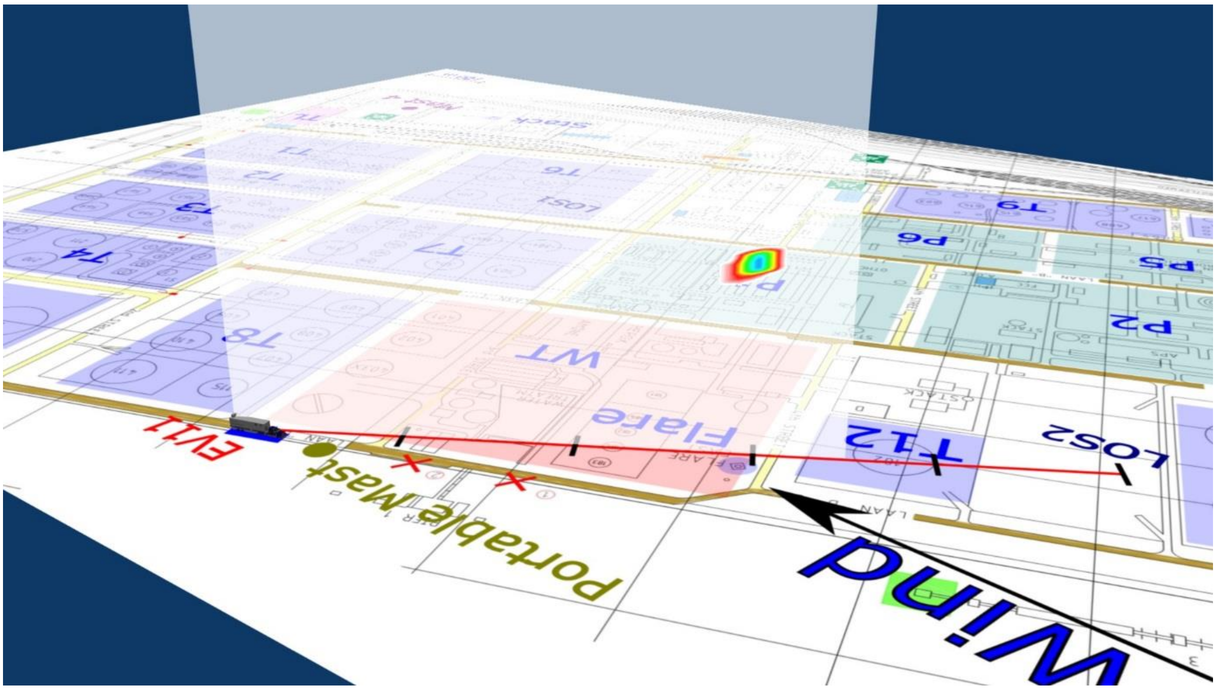


Figure 5.10a2 Visualisation of emission rate for Scan 49 representing EV11/LOS2.

Table 5.11 VOC emission rates determined from EV12 on 13th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
54	EV12/LOS1	09:06	09:23	2.6	323.1	13.84	Downwind P1
55	EV12/LOS1	09:24	09:41	2.6	314.1	14.15	Downwind P1
56	EV12/LOS1	09:41	09:59	2.8	324.7	25.48	Downwind P1
57	EV12/LOS1	09:59	10:17	2.7	331.0	23.97	Downwind P1

Figure 5.11 Measurement configuration for location EV12 on 13th June.

Table 5.12 VOC emission rates determined from EV14 on 13th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
60	EV14/LOS1	12:37	12:51	3.5	264.0	18.58	Downwind T8 + WT
61	EV14/LOS1	12:52	13:06	4.2	292.5	21.68	Downwind T8 + WT
62	EV14/LOS1	13:07	13:21	4.9	292.6	19.54	Downwind T8 + WT
63	EV14/LOS1	13:22	13:36	4.1	291.4	17.10	Downwind T8 + WT

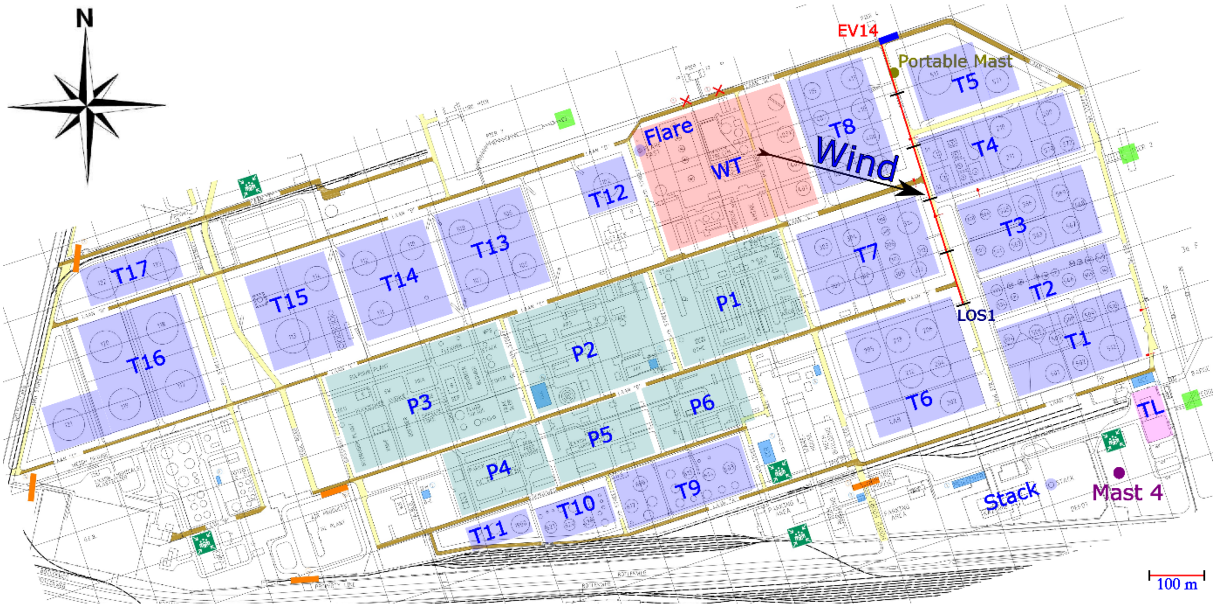


Figure 5.12 Measurement configuration for location EV14 on 13th June.

Table 5.13 VOC emission rates determined from EV15 on 13th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
64	EV15/LOS1	14:13	14:29	4.0	277.8	32.17	Downwind Most T4 + Upwind
65	EV15/LOS1	14:29	14:46	3.4	290.0	17.95	Downwind East Area T4 + Upwind
66	EV15/LOS1	14:46	15:03	3.2	303.1	6.93	Downwind East Area T4
67	EV15/LOS1	15:03	15:20	3.0	320.9	0.90	Wind // LOS

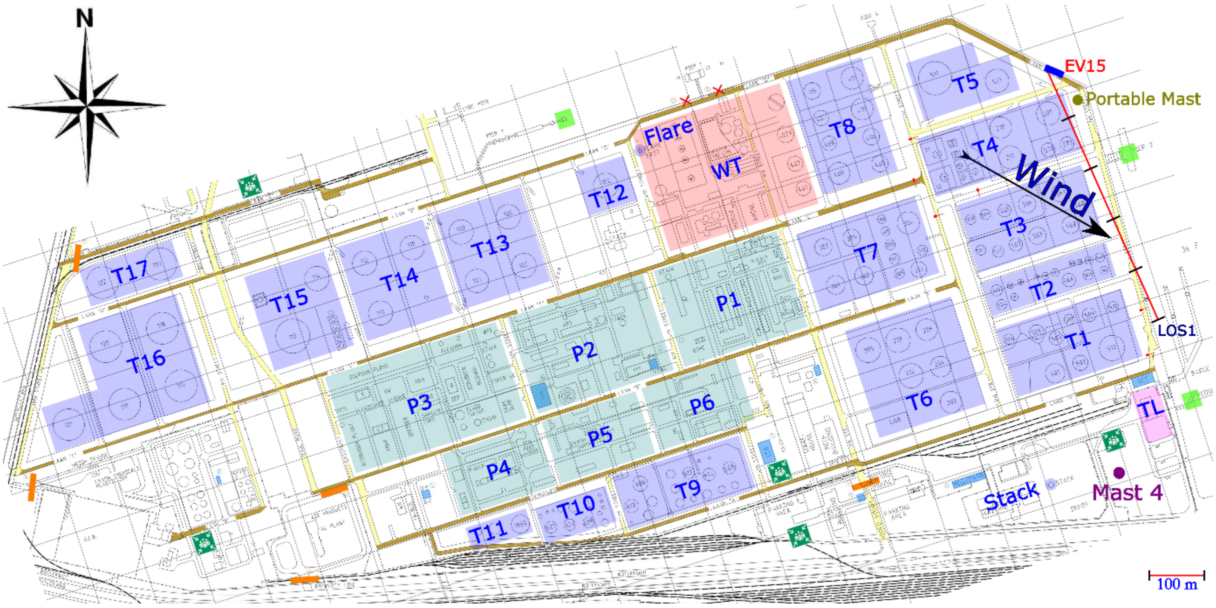


Figure 5.13 Measurement configuration for location EV15 on 13th June.

Table 5.14 VOC emission rates determined from EV16 on 14th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
69	EV16/LOS1	08:54	09:06	3.4	118.1	3.71	Downwind West Area T1
70	EV16/LOS1	09:07	09:19	3.2	118.2	3.72	Downwind West Area T1
71	EV16/LOS1	09:20	09:32	3.4	127.6	3.48	Downwind West Area T1
72	EV16/LOS1	09:32	09:45	2.7	117.4	2.67	Downwind West Area T1

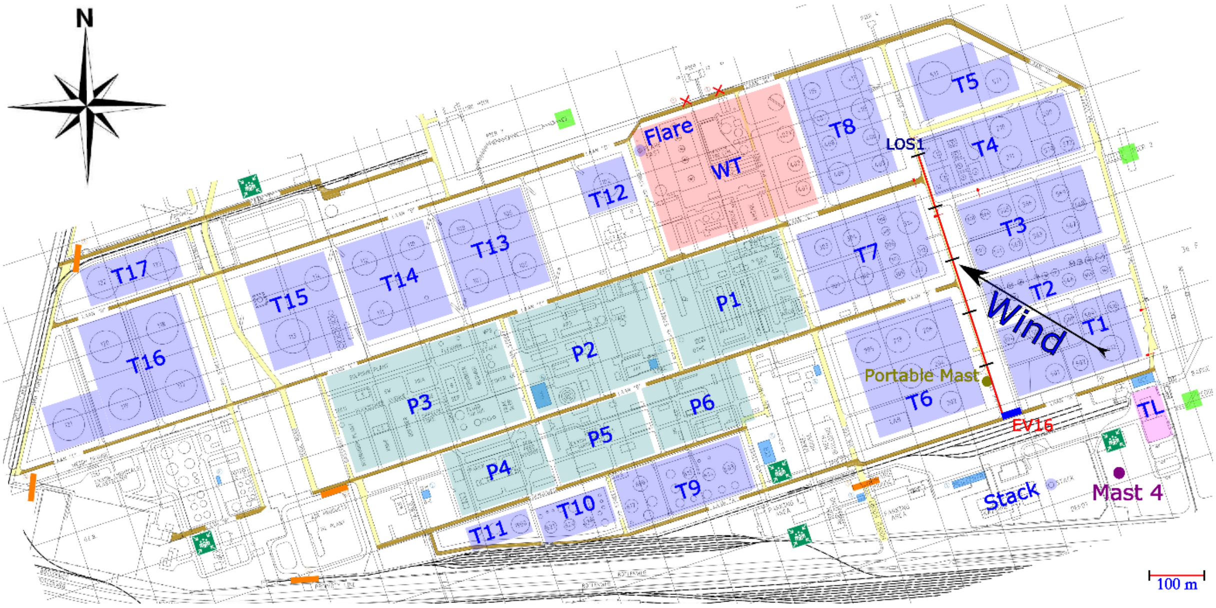


Figure 5.14 Measurement configuration for location EV16 on 14th June.

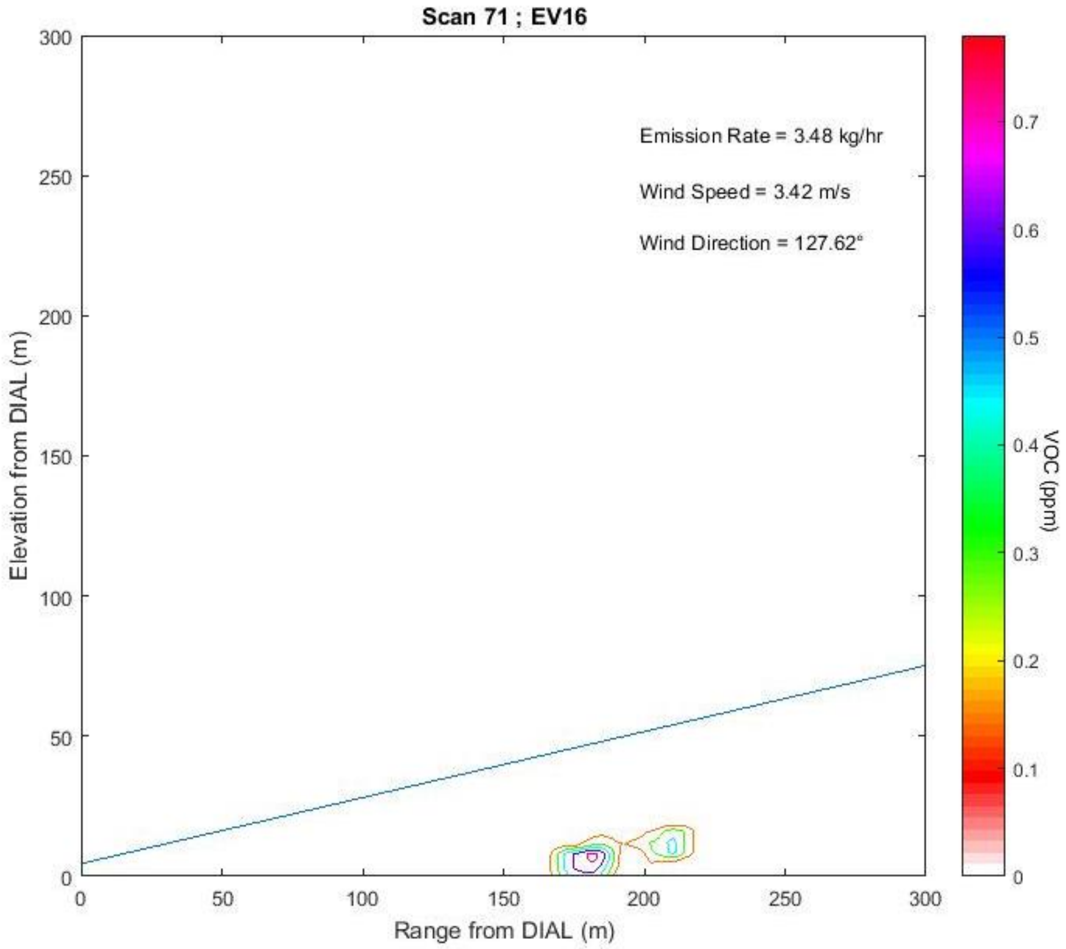


Figure 5.14a1 Observed VOC concentration for Scan 71 representing EV16/LOS1.

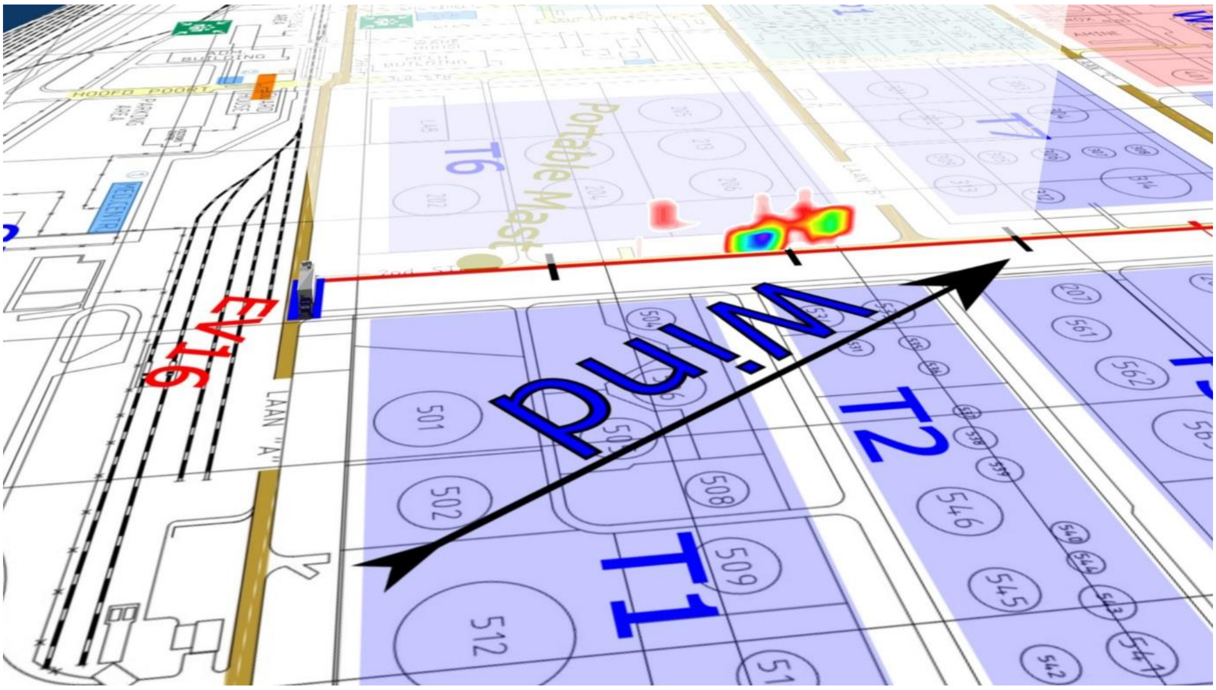


Figure 5.14a2 Visualisation of emission rate for Scan 71 representing EV16/LOS1.

Table 5.15 VOC emission rates determined from EV17 on 14th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
74	EV17/LOS1	10:35	10:47	3.2	127.0	8.32	Downwind Truck Loading Area
75	EV17/LOS1	10:47	11:01	3.6	117.3	12.18	Downwind Truck Loading Area
76	EV17/LOS1	11:01	11:13	3.6	113.4	9.46	Downwind Truck Loading Area
77	EV17/LOS1	11:14	11:27	3.5	117.7	11.75	Downwind Truck Loading Area
78	EV17/LOS1	11:28	11:41	3.5	123.4	12.18	Downwind Truck Loading Area

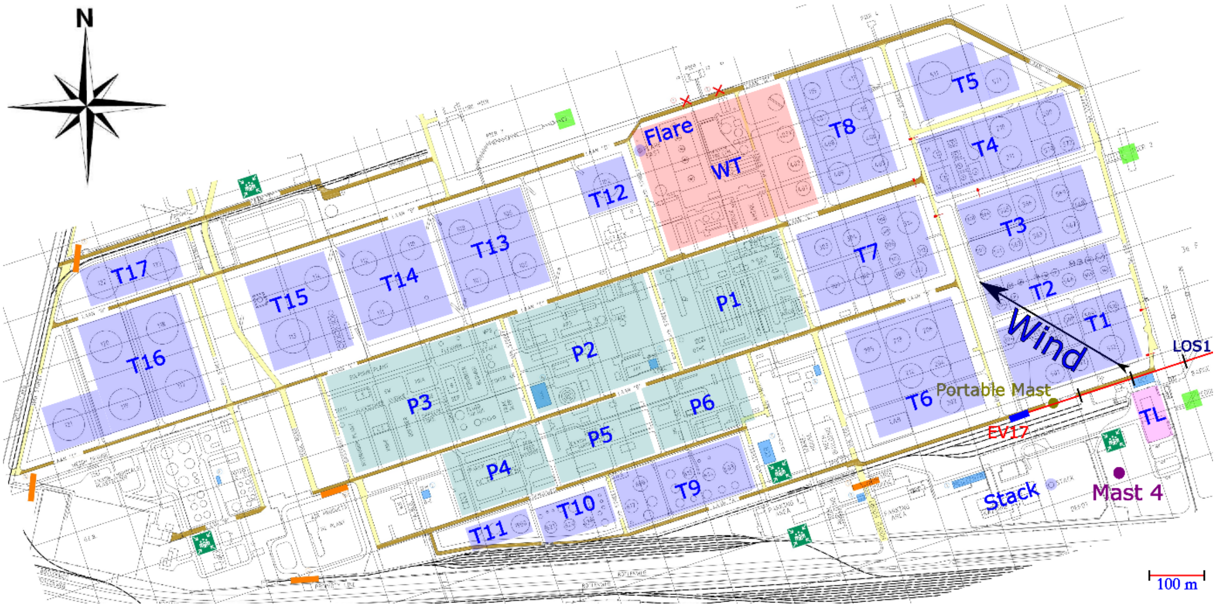


Figure 5.15 Measurement configuration for location EV17 on 14th June.

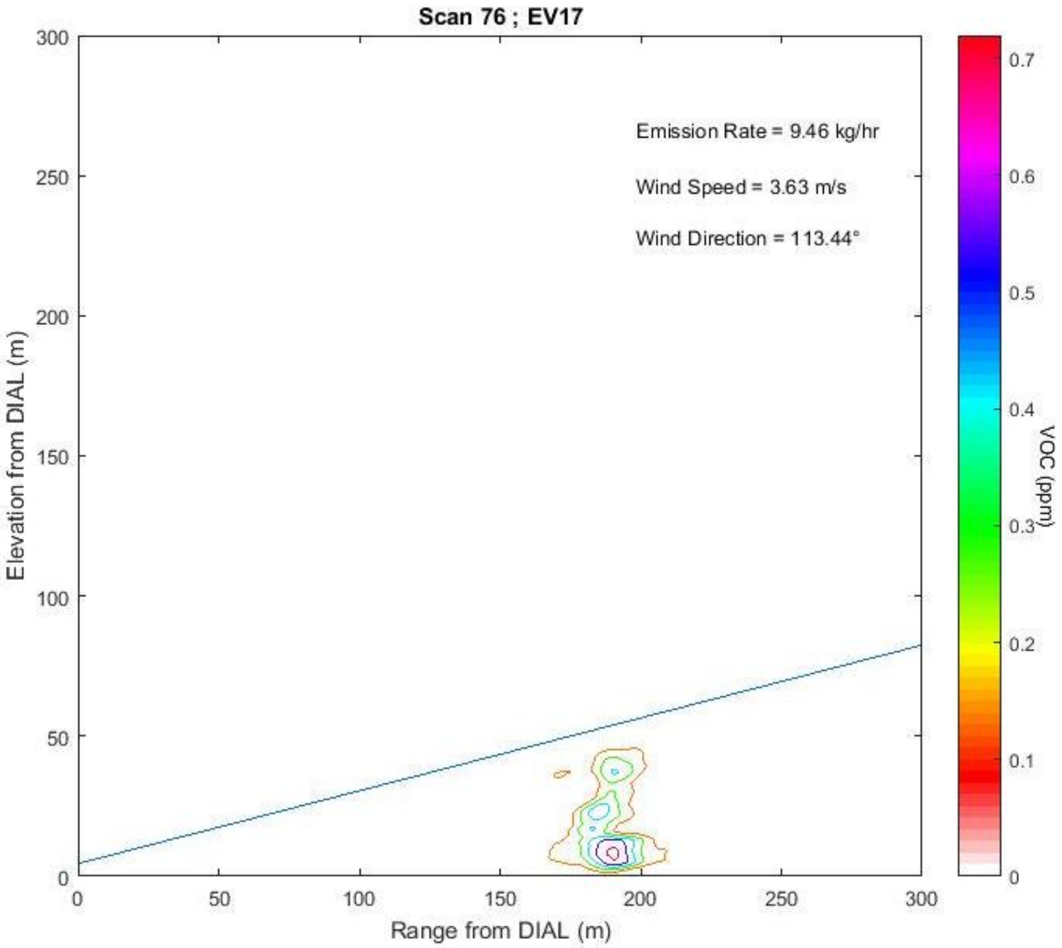


Figure 5.15a1 Observed VOC concentration for Scan 76 representing EV17/LOS1.

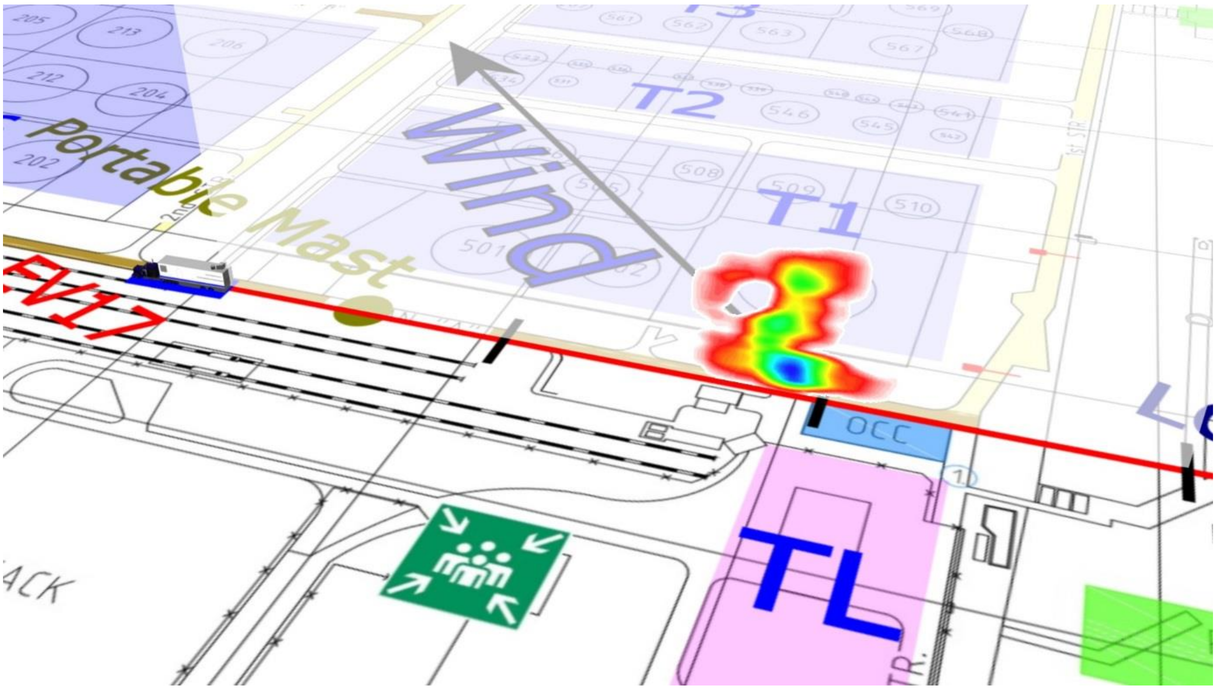


Figure 5.15a2 Visualisation of emission rate for Scan 76 representing EV17/LOS1.

Table 5.16 VOC emission rates determined from EV18 on 14th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
80	EV18/LOS1	12:28	12:45	3.4	111.5	23.49	Downwind P4 & T10 & T11
81	EV18/LOS1	12:45	13:01	4.0	105.9	35.01	Downwind P4 & T10 & T11
82	EV18/LOS1	13:02	13:18	3.2	114.5	26.47	Downwind P4 & T10 & T11
83	EV18/LOS1	13:22	13:38	3.4	134.6	29.94	Downwind P4 & T10 & T11

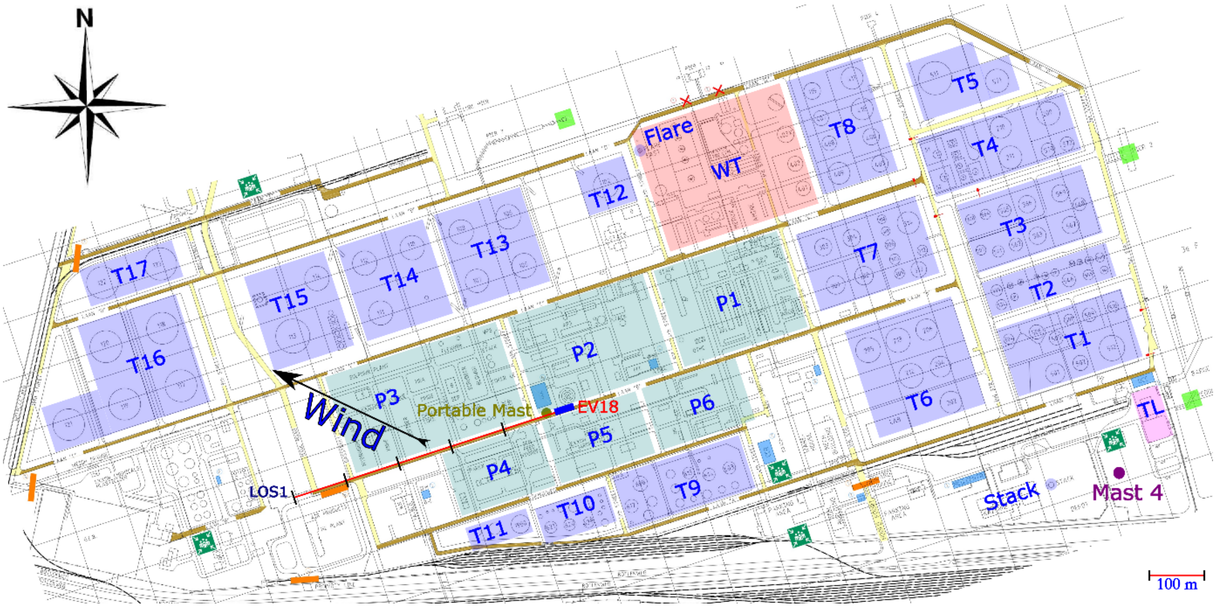


Figure 5.16 Measurement configuration for location EV18 on 14th June.

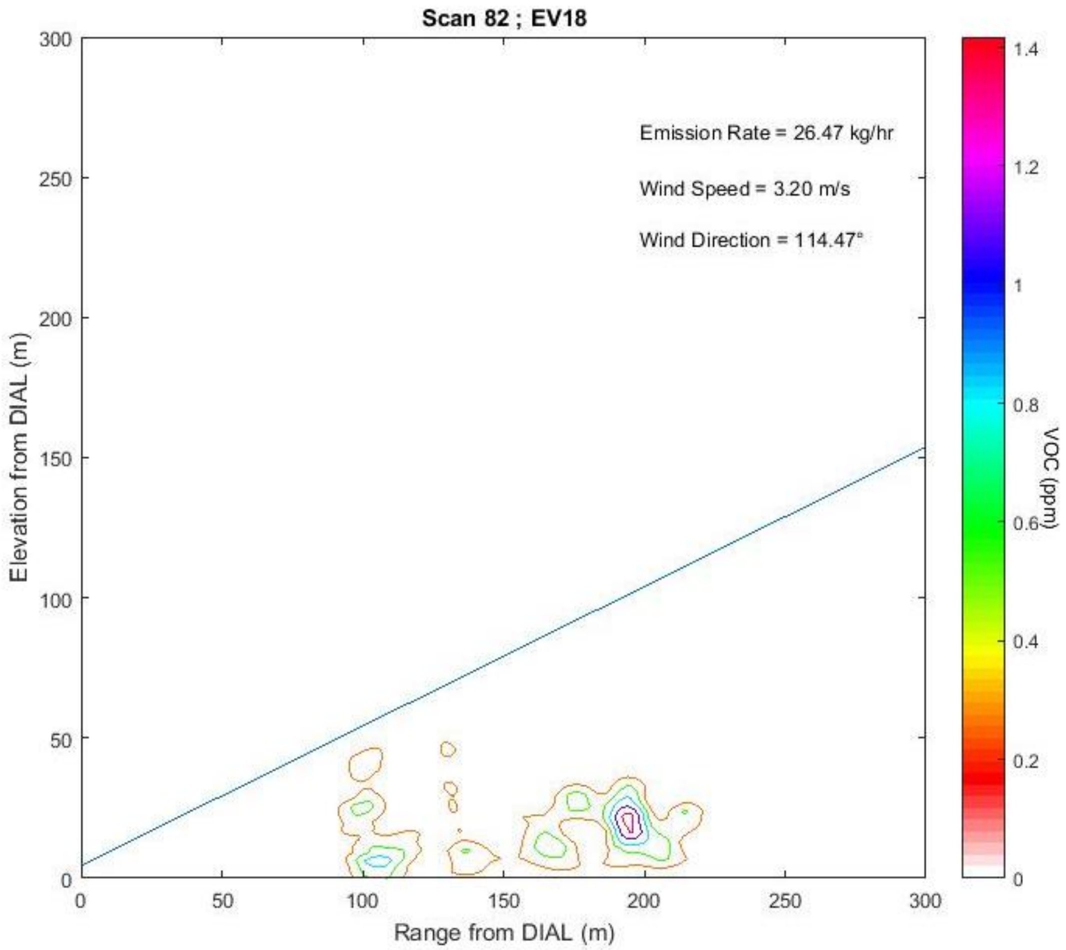


Figure 5.16a1 Observed VOC concentration for Scan 82 representing EV18/LOS1.

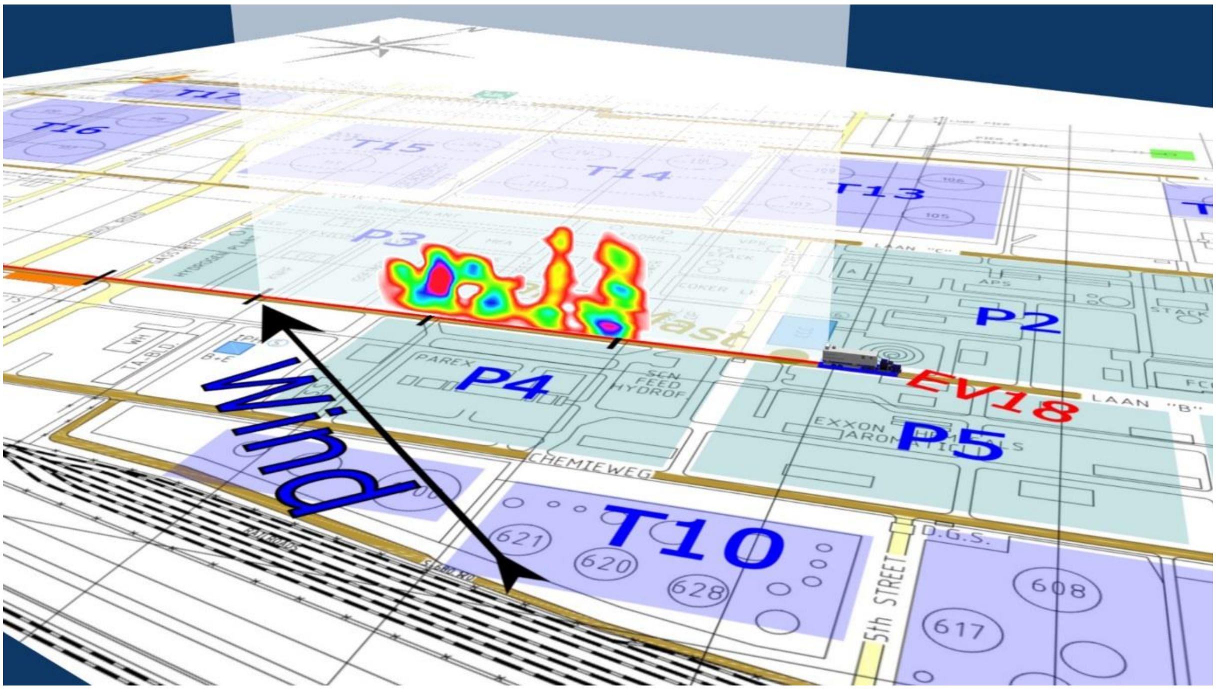


Figure 5.16a2 Visualisation of emission rate for Scan 82 representing EV18/LOS1.

Table 5.17 VOC emission rates determined from EV19 on 14th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
84	EV19/LOS1	14:19	14:32	3.1	128.5	13.85	Downwind P5 & T9
85	EV19/LOS1	14:34	14:47	2.9	135.6	18.16	Downwind P5 & T9
86	EV19/LOS1	14:47	15:01	2.3	130.6	15.29	Downwind P5 & T9
87	EV19/LOS1	15:01	15:14	3.2	127.8	14.14	Downwind P5 & T9

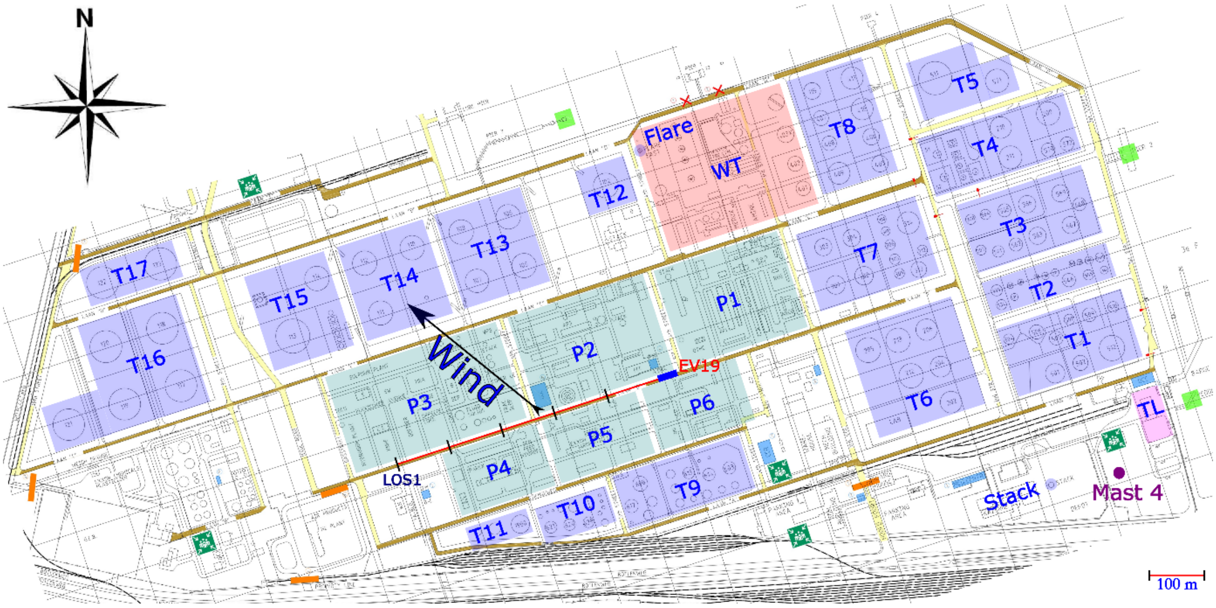


Figure 5.17 Measurement configuration for location EV19 on 14th June.

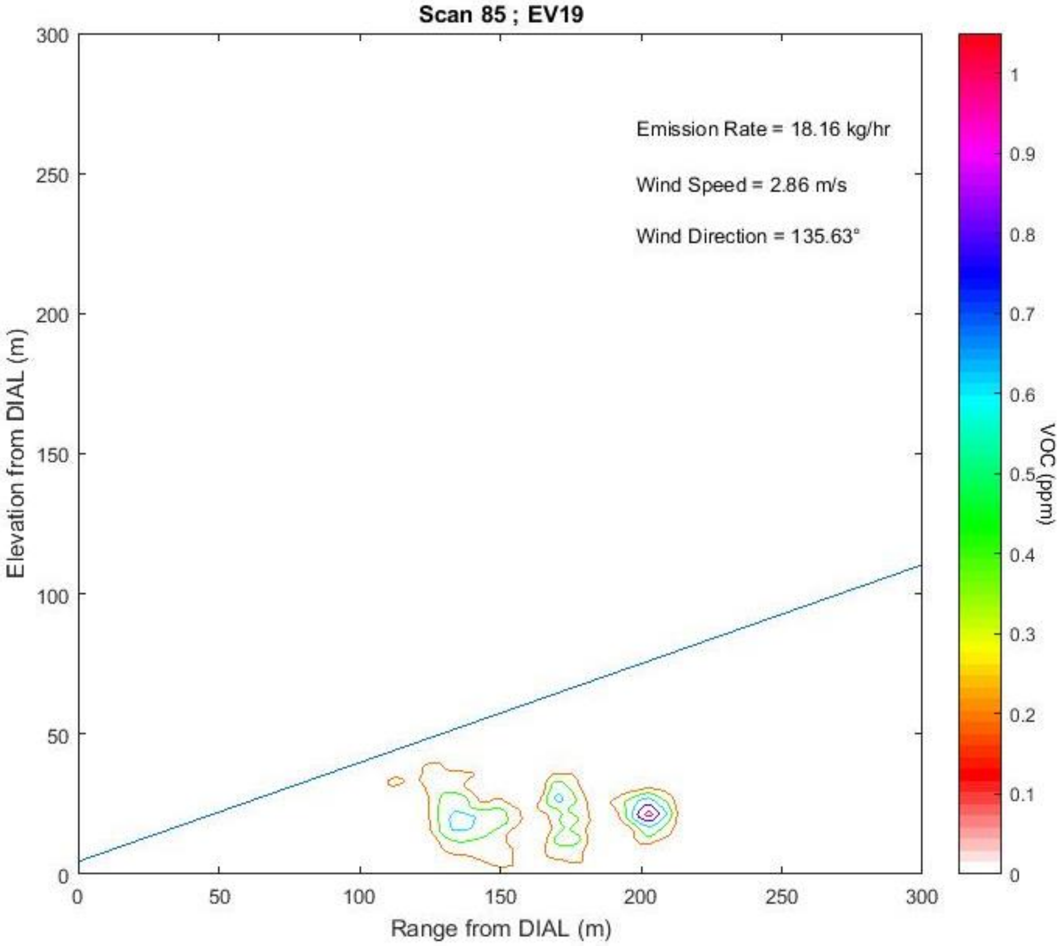


Figure 5.17a1 Observed VOC concentration for Scan 85 representing EV19/LOS1.

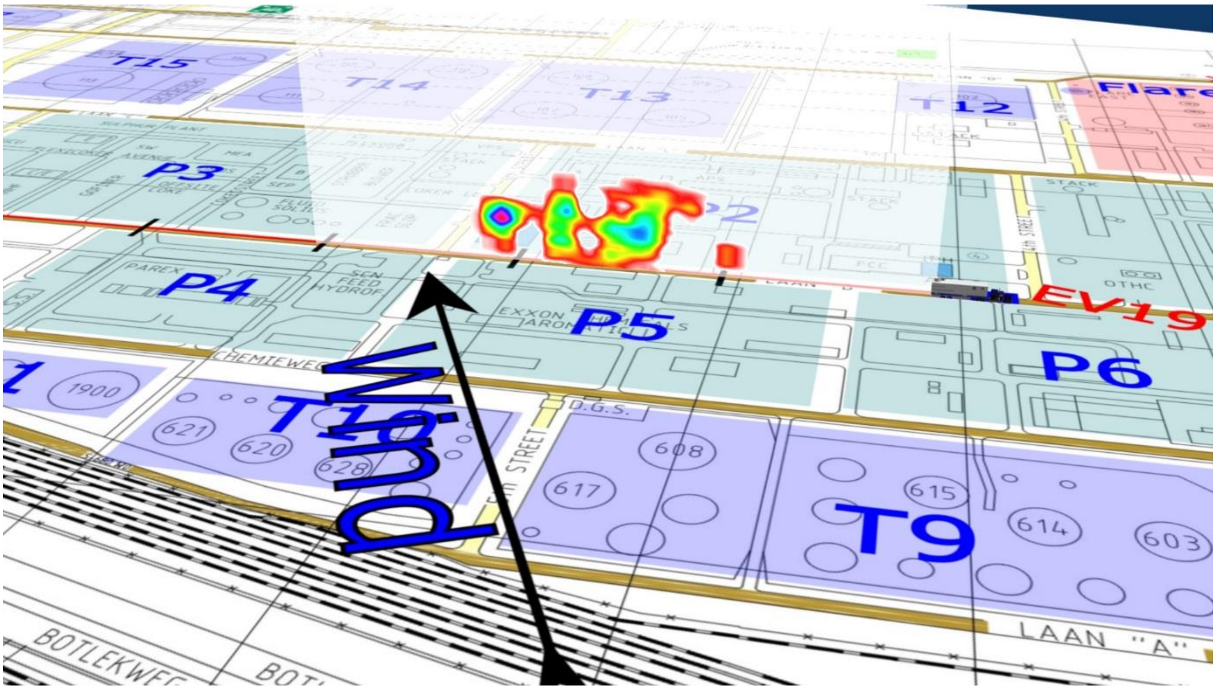


Figure 5.17a2 Visualisation of emission rate for Scan 85 representing EV19/LOS1.

Table 5.18 VOC emission rates determined from EV20 on 15th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
90	EV20/LOS1	11:22	11:36	4.8	202.4	27.47	Downwind P6 & T9
91	EV20/LOS1	11:37	11:51	6.0	201.0	19.64	Downwind P6 & T9
92	EV20/LOS1	11:52	12:06	4.6	199.2	20.95	Downwind P6 & T9
93	EV20/LOS1	12:07	12:21	4.9	215.1	19.68	Downwind P6 & T9

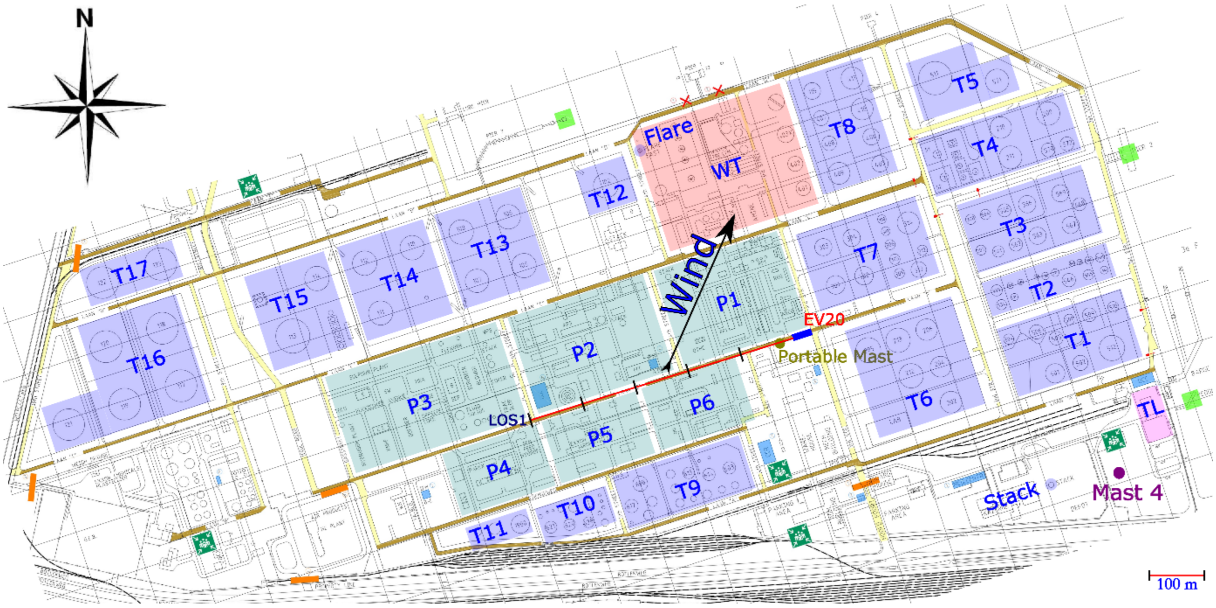


Figure 5.18 Measurement configuration for location EV20 on 15th June.

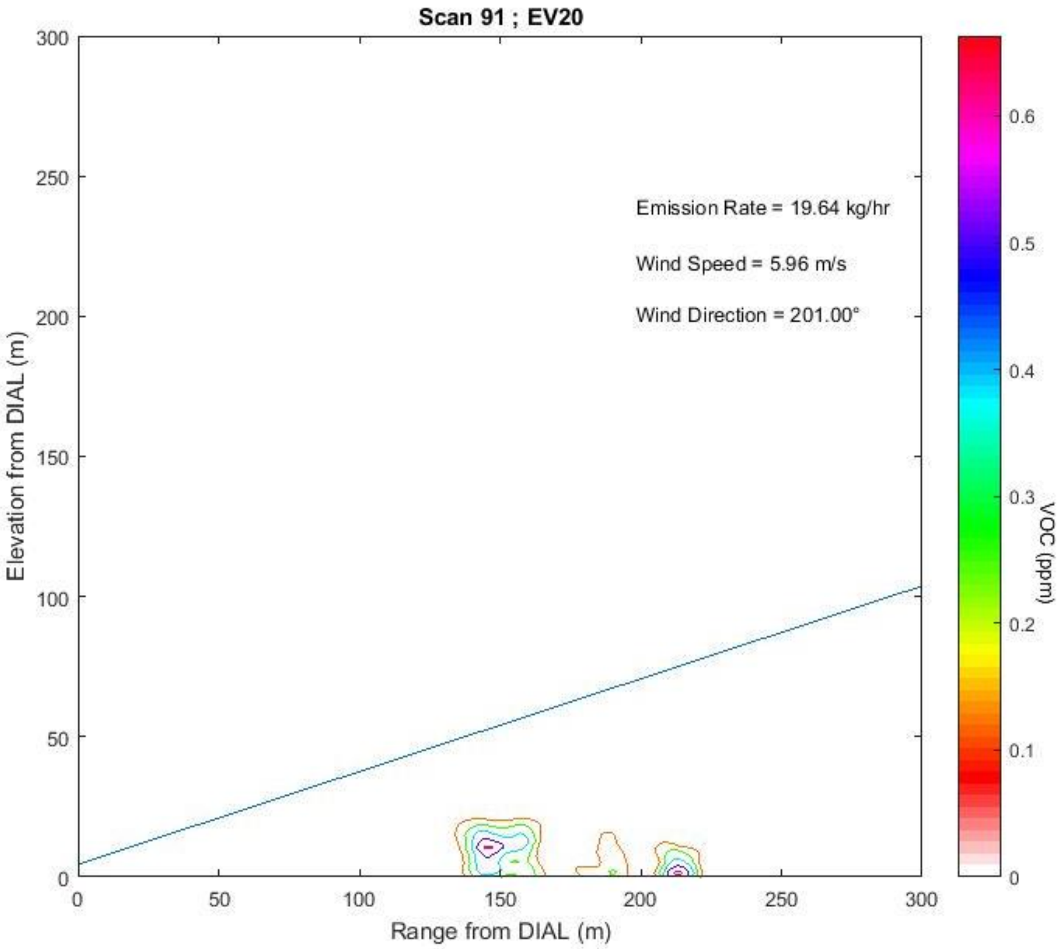


Figure 5.18a1 Observed VOC concentration for Scan 91 representing EV20/LOS1.

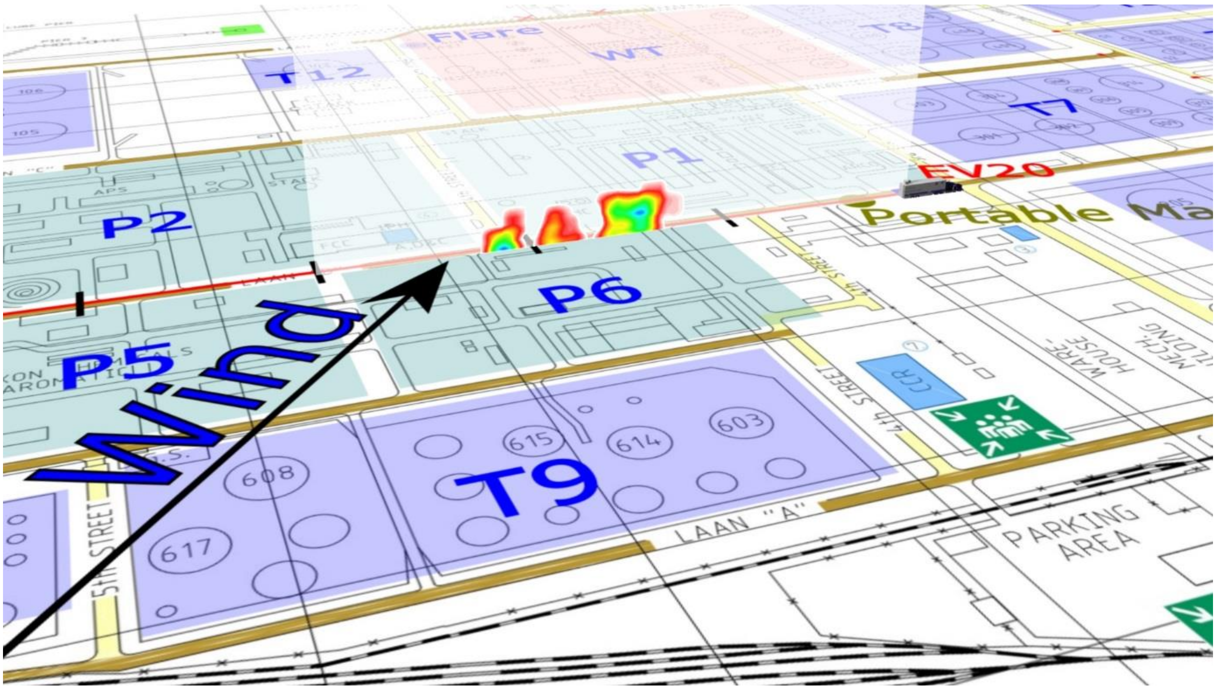


Figure 5.18a2 Visualisation of emission rate for Scan 91 representing EV20/LOS1.

Table 5.19 VOC emission rates determined from EV21 on 15th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
95	EV21/LOS1	13:33	13:45	6.5	249.0	7.56	Downwind T6
96	EV21/LOS1	13:46	13:58	7.0	253.8	9.93	Downwind T6
97	EV21/LOS1	13:58	14:11	6.4	248.8	7.60	Downwind T6
98	EV21/LOS1	14:11	14:23	7.0	242.8	6.24	Downwind T6

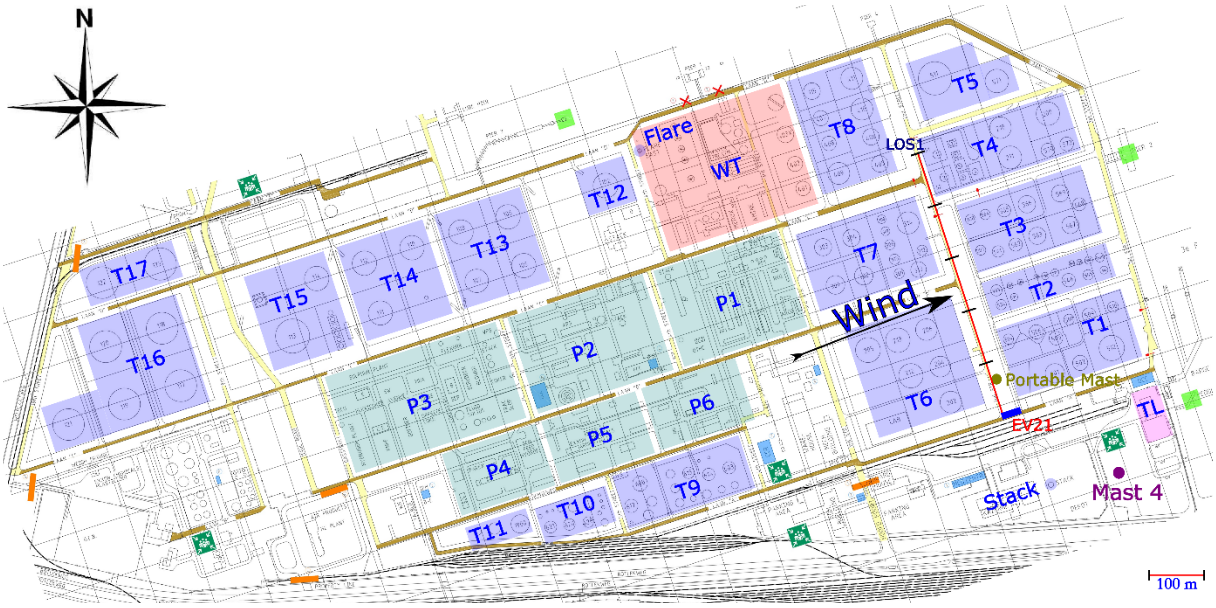


Figure 5.19 Measurement configuration for location EV21 on 15th June.

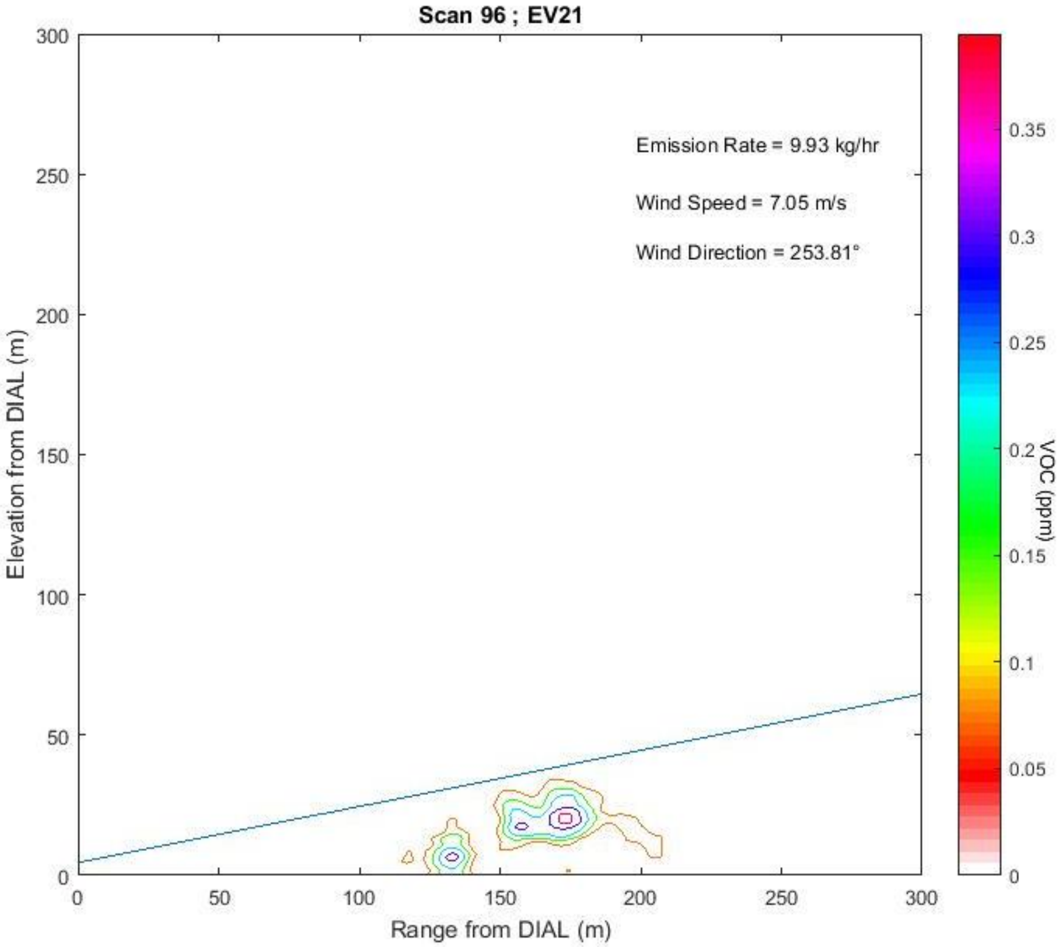


Figure 5.19a1 Observed VOC concentration for Scan 96 representing EV21/LOS1.

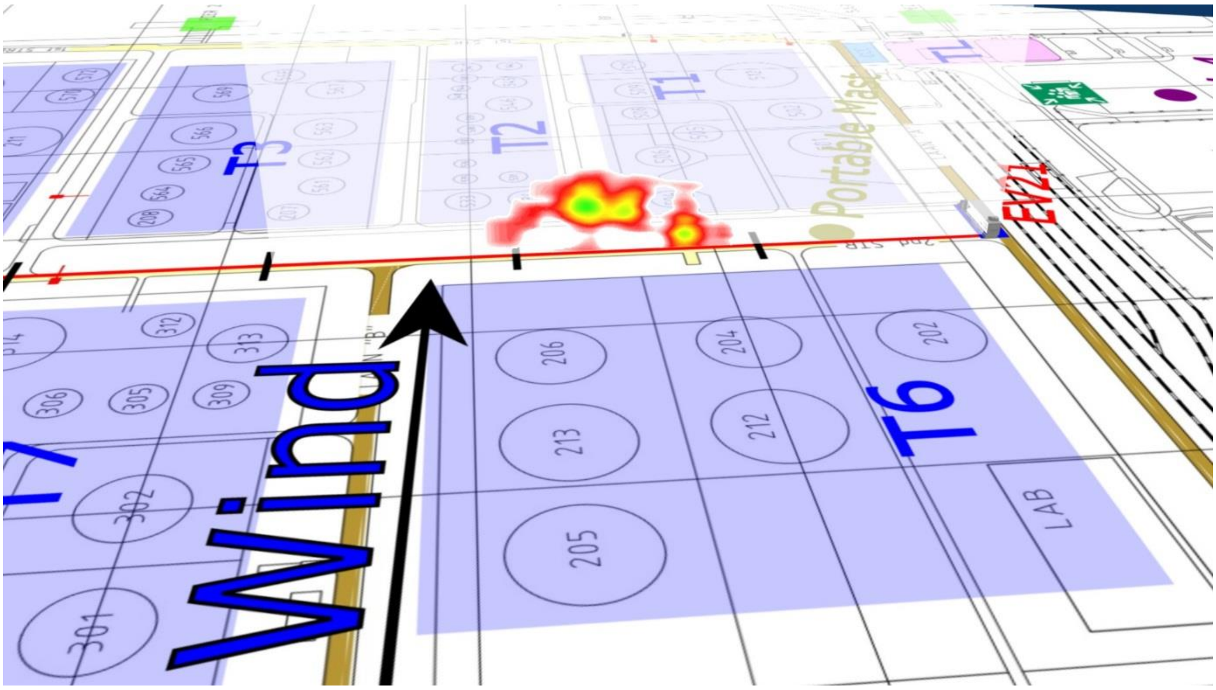


Figure 5.19a2 Visualisation of emission rate for Scan 96 representing EV21/LOS1.

Table 5.20 VOC emission rates determined from EV22 on 15th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
99	EV22/LOS1	14:54	15:04	5.8	236.3	10.49	Downwind T2 & T3
100	EV22/LOS1	15:04	15:13	6.3	258.2	9.16	Downwind T2 & T3
101	EV22/LOS1	15:13	15:22	5.7	248.2	7.97	Downwind T2 & T3
102	EV22/LOS1	15:23	15:32	7.5	259.5	8.05	Downwind T2 & T3

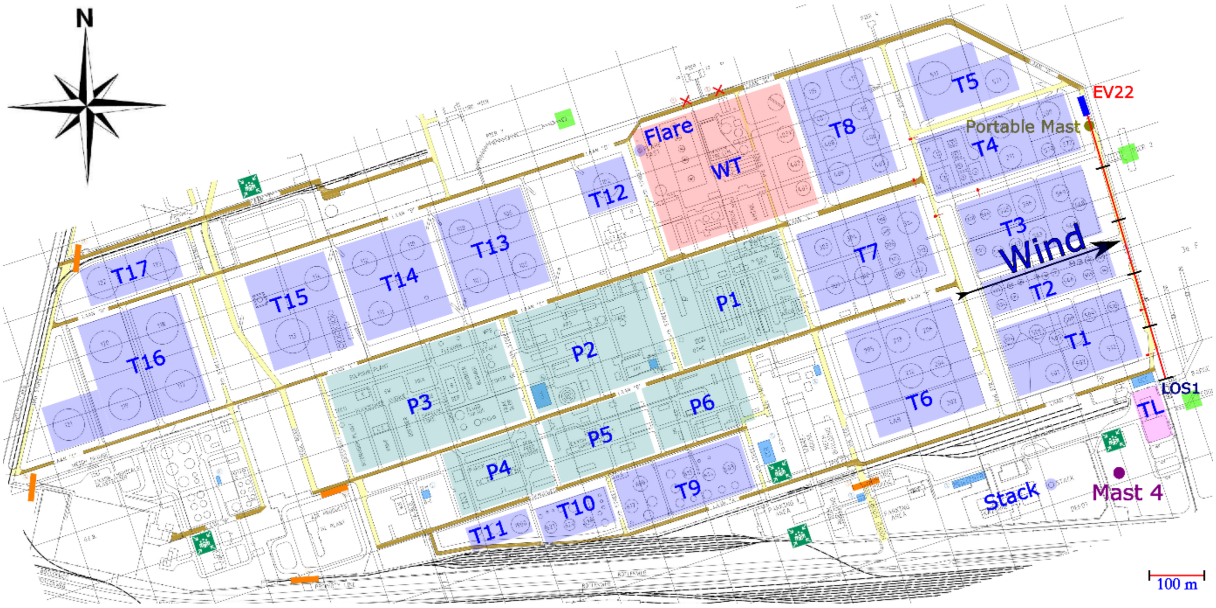


Figure 5.20 Measurement configuration for location EV22 on 15th June.

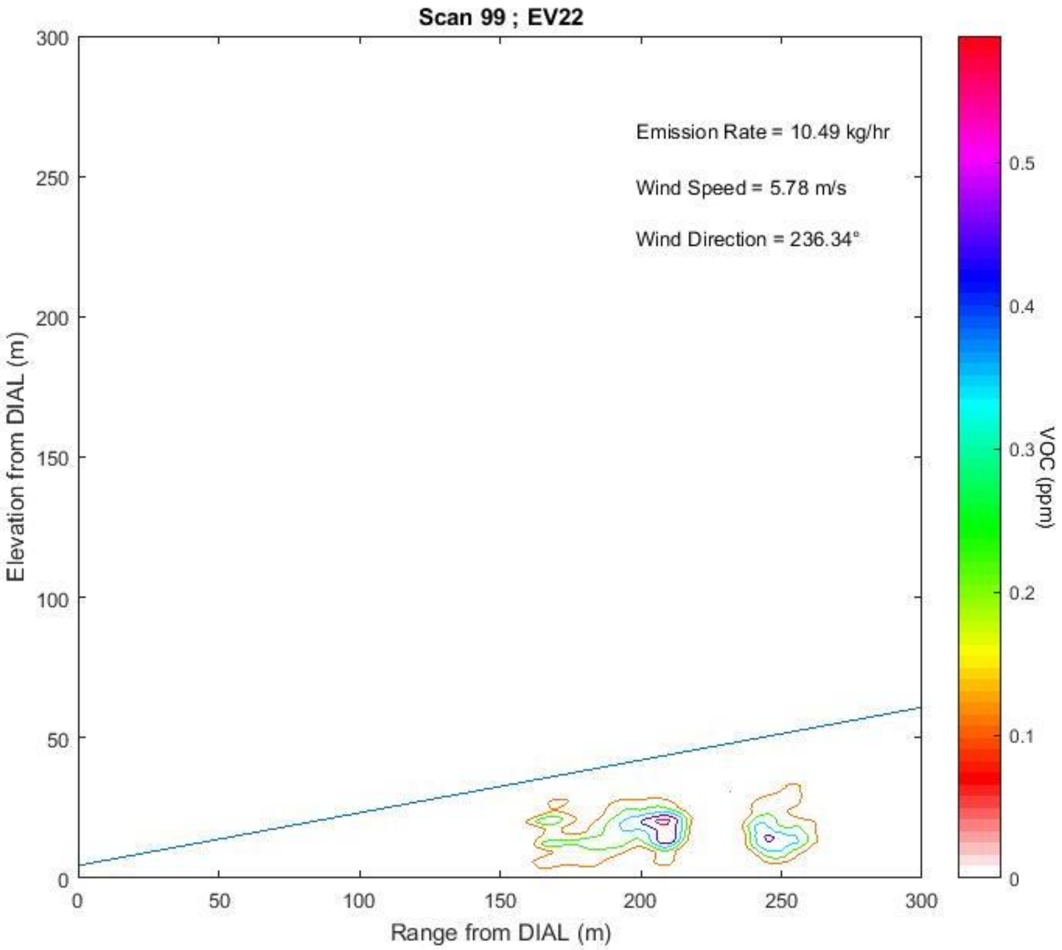


Figure 5.20a1 Observed VOC concentration for Scan 99 representing EV22/LOS1.

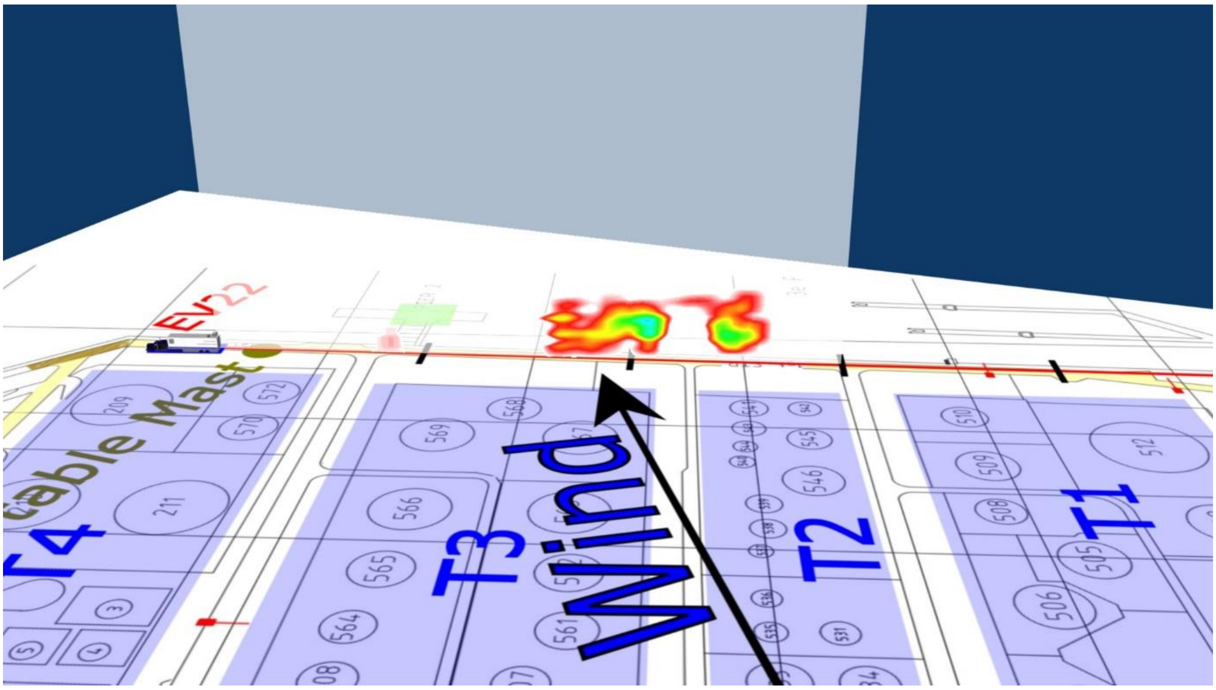


Figure 5.20a2 Visualisation of emission rate for Scan 99 representing EV22/LOS1.

Table 5.21 VOC emission rates determined from EV23 on 16th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
105	EV23/LOS1	09:02	09:14	5.4	316.7	7.21	Downwind T7
106	EV23/LOS1	09:20	09:33	4.5	315.0	5.85	Downwind T7

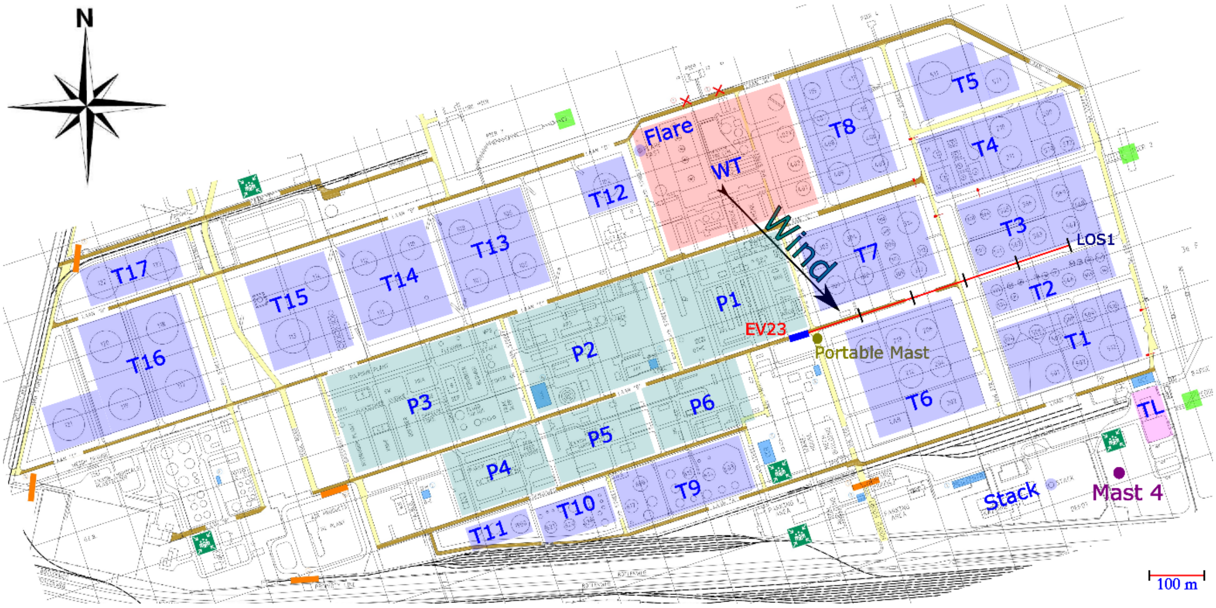


Figure 5.21 Measurement configuration for location EV23 on 16th June.

Table 5.22 VOC emission rates determined from EV24 on 16th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
107	EV24/LOS1	09:56	10:06	4.0	303.6	6.83	Downwind T7
108	EV24/LOS1	10:06	10:17	4.8	301.3	5.06	Downwind T7
109	EV24/LOS1	10:17	10:27	5.9	302.8	9.61	Downwind T7
110	EV24/LOS1	10:27	10:37	5.4	289.9	5.29	Downwind T7
111	EV24/LOS1	10:38	10:48	5.1	302.6	6.46	Downwind T7

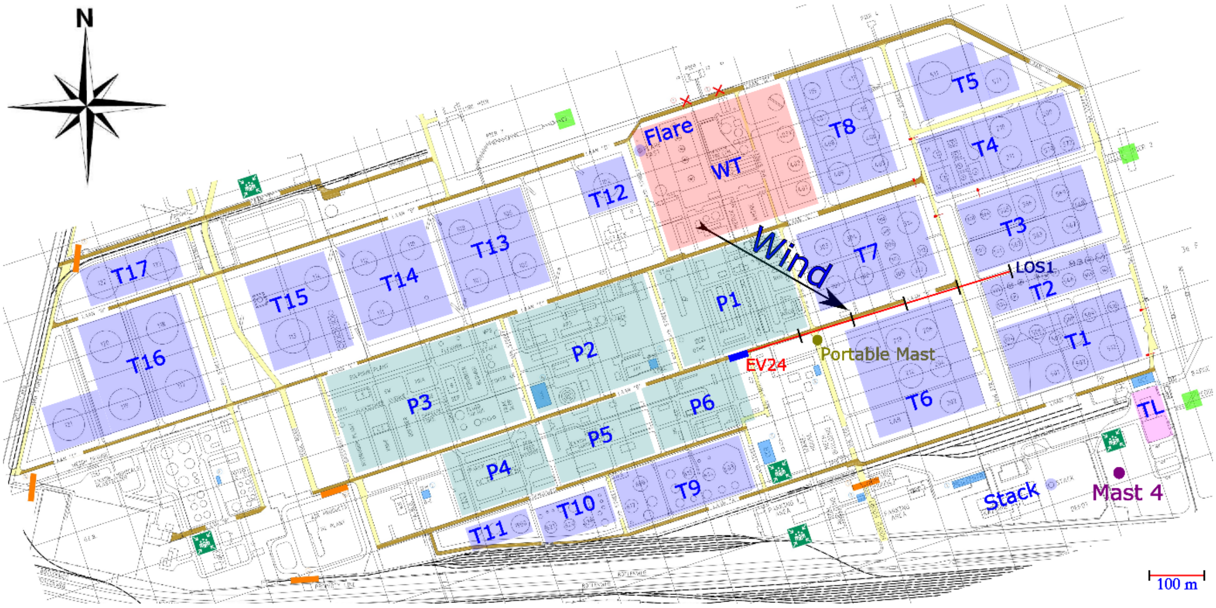


Figure 5.22 Measurement configuration for location EV24 on 16th June.

Table 5.23 VOC emission rates determined from EV25 on 16th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
115	EV25/LOS1	11:33	11:47	5.6	316.7	26.70	Downwind P2 & T13
116	EV25/LOS1	11:47	12:01	5.5	308.4	27.53	Downwind P2 & T13
117	EV25/LOS1	12:01	12:14	5.9	320.2	29.05	Downwind P2 & T13
118	EV25/LOS1	12:14	12:28	5.6	318.9	21.96	Downwind P2 & T13

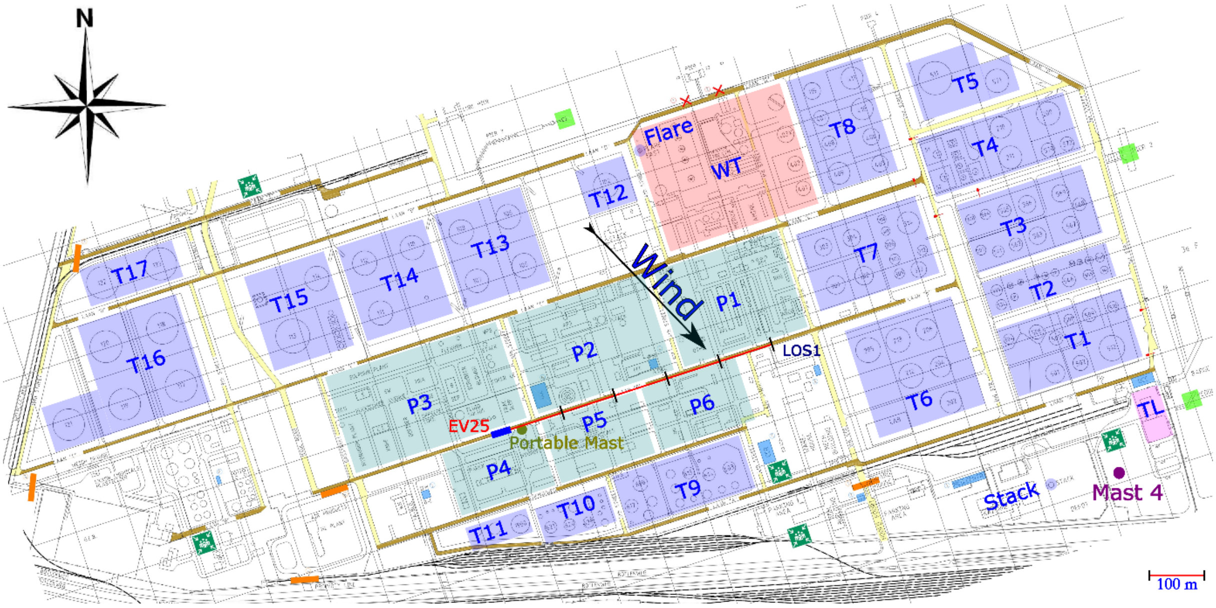


Figure 5.23 Measurement configuration for location EV25 on 16th June.

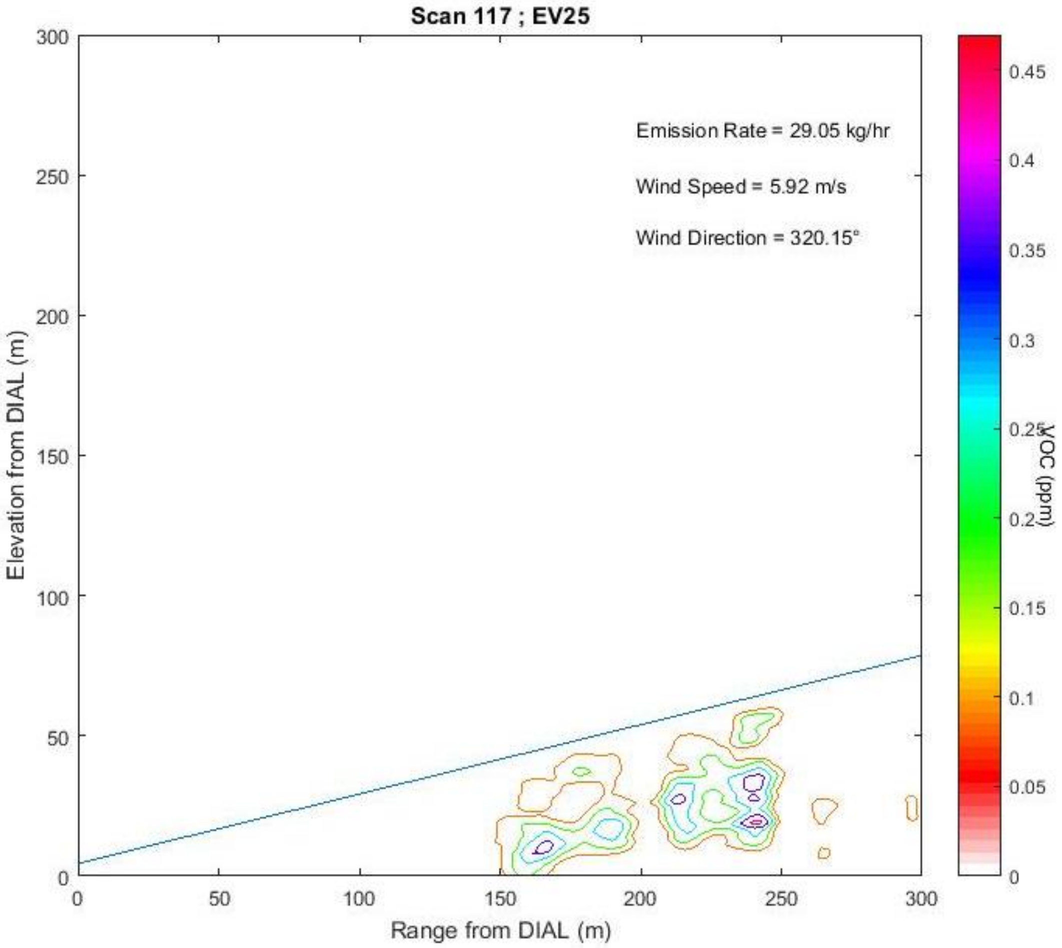


Figure 5.23a1 Observed VOC concentration for Scan 117 representing EV25/LOS1.

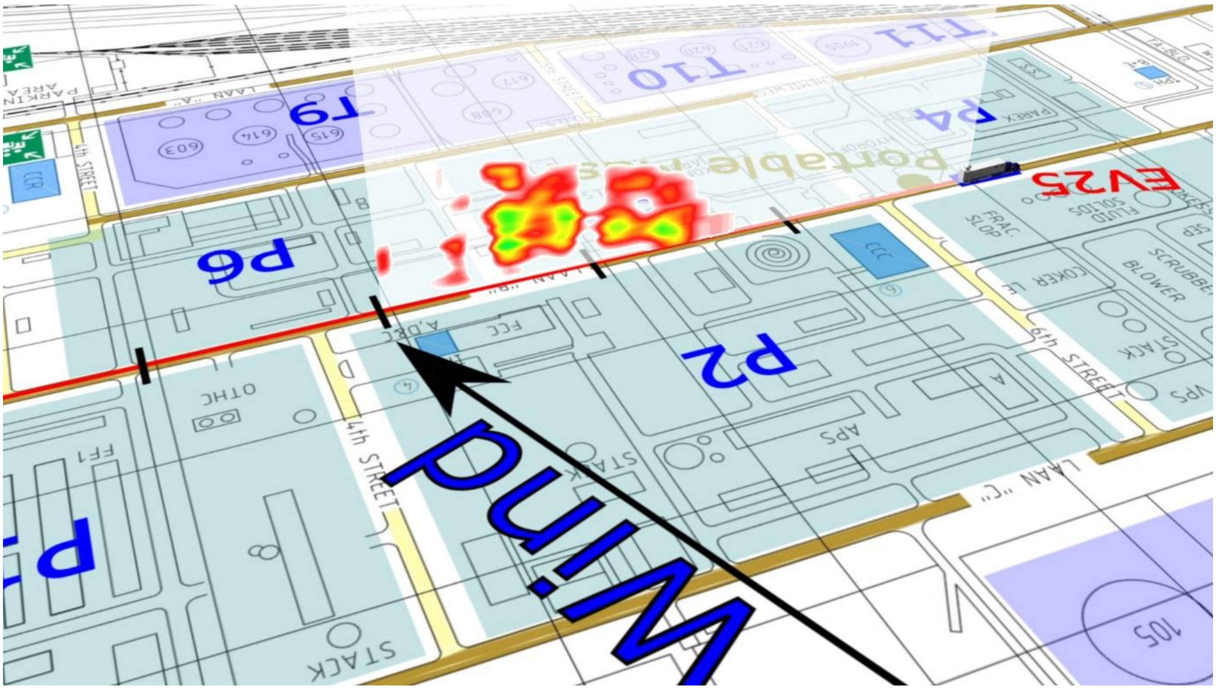


Figure 5.23a2 Visualisation of emission rate for Scan 117 representing EV25/LOS1.

Table 5.24 VOC emission rates determined from EV26 on 16th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
120	EV26/LOS1	12:51	13:11	6.3	323.7	83.19	Downwind P3 + Upwind
121	EV26/LOS1	13:12	13:33	6.2	319.3	103.44	Downwind P3 + Upwind
122	EV26/LOS1	13:37	13:57	6.2	321.9	45.25	Coker Plume - Possibly No Upwind
123	EV26/LOS1	13:58	14:18	5.9	318.5	52.33	Coker Plume - Possibly No Upwind
124	EV26/LOS1	14:29	14:41	5.5	284.0	17.31	P3 - Wind Changed & No Coker Plume

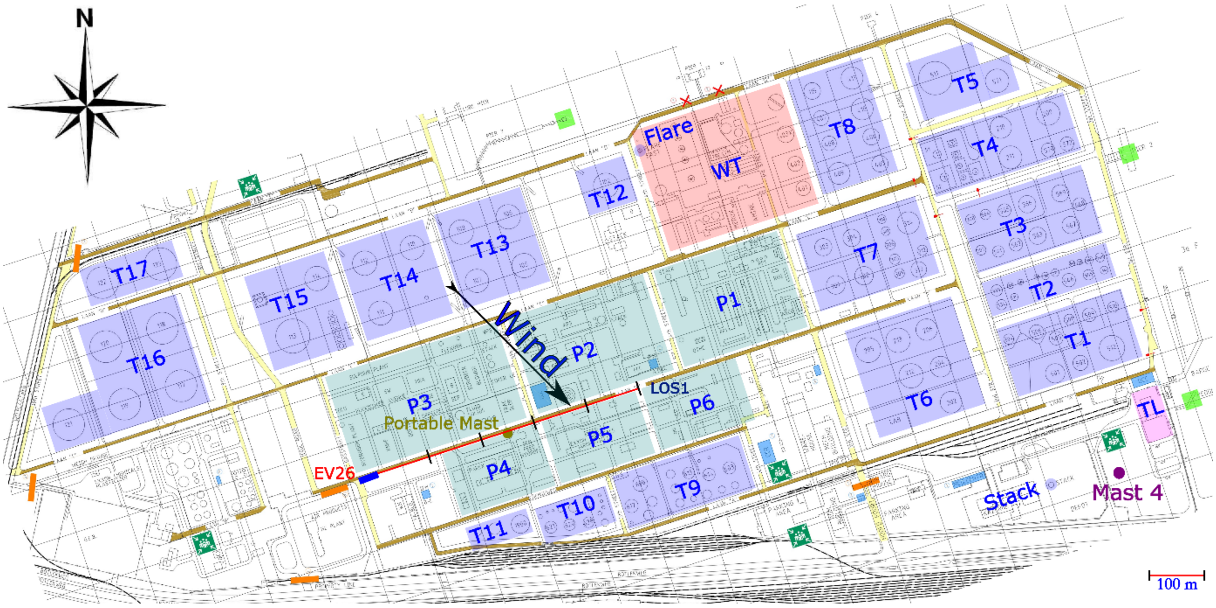


Figure 5.24 Measurement configuration for location EV26 on 16th June.

Table 5.25 VOC emission rates determined from EV27 on 20th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
127	EV27/LOS1	10:40	10:54	3.8	47.5	11.04	Downwind T13
128	EV27/LOS1	10:57	11:12	3.7	50.9	10.60	Downwind T13
129	EV27/LOS1	11:12	11:27	3.8	54.9	9.38	Downwind T13
130	EV27/LOS1	11:27	11:42	3.4	58.9	11.21	Downwind T13
131	EV27/LOS2	11:50	12:02	2.9	48.2	-0.64	Downwind Tank 106
132	EV27/LOS2	12:03	12:15	3.7	45.0	0.49	Downwind Tank 106
133	EV27/LOS2	12:15	12:28	3.5	53.4	-0.03	Downwind Tank 106
134	EV27/LOS2	12:28	12:40	3.3	51.1	0.22	Downwind Tank 106
135	EV27/LOS1	12:44	12:58	3.8	37.3	12.01	Downwind T13
136	EV27/LOS1	12:59	13:13	3.9	51.1	10.09	Downwind T13

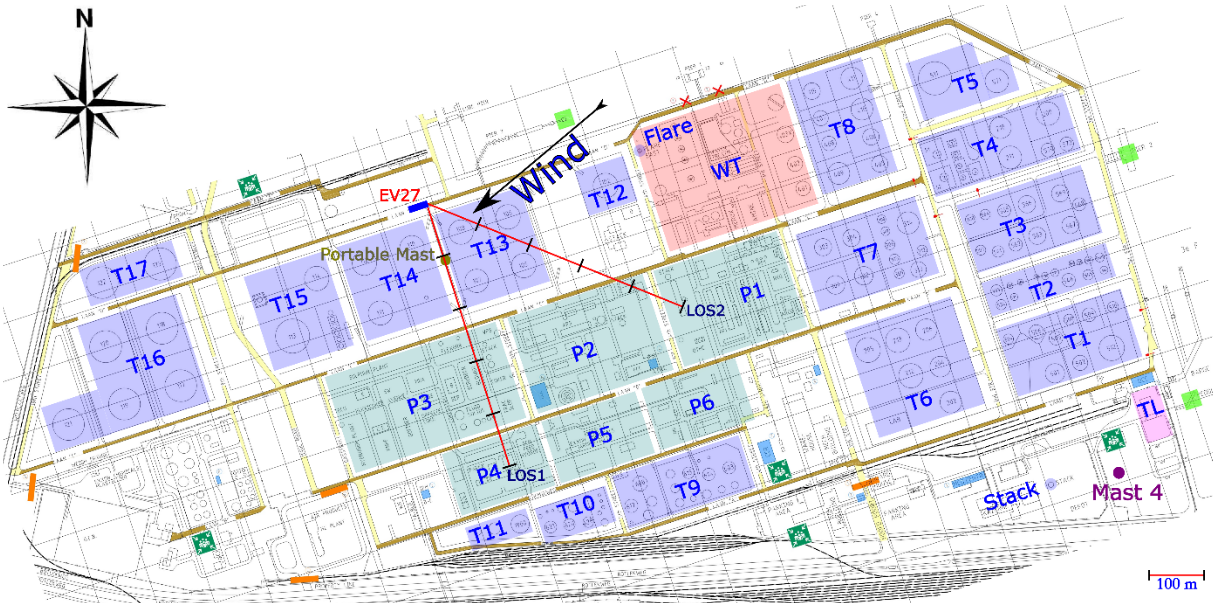


Figure 5.25 Measurement configuration for location EV27 on 20th June.

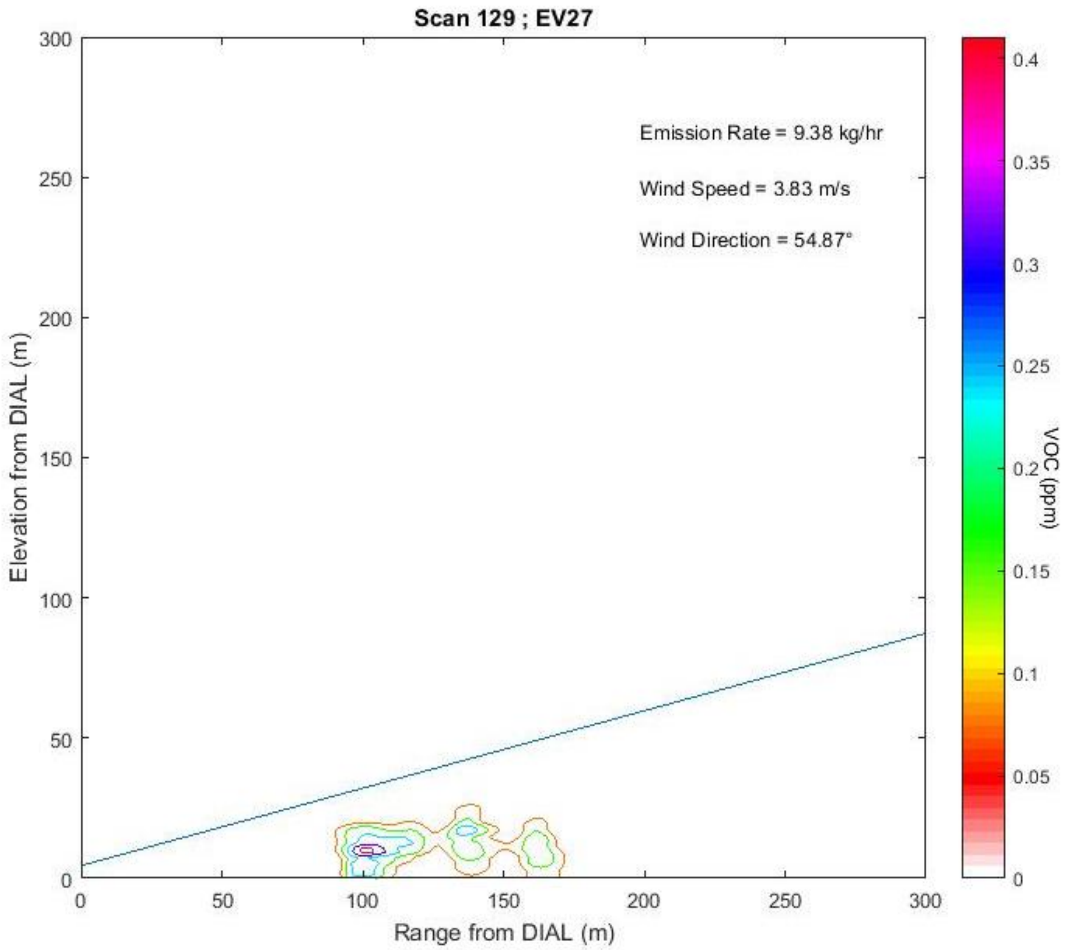


Figure 5.25a1 Observed VOC concentration for Scan 129 representing EV27/LOS1.

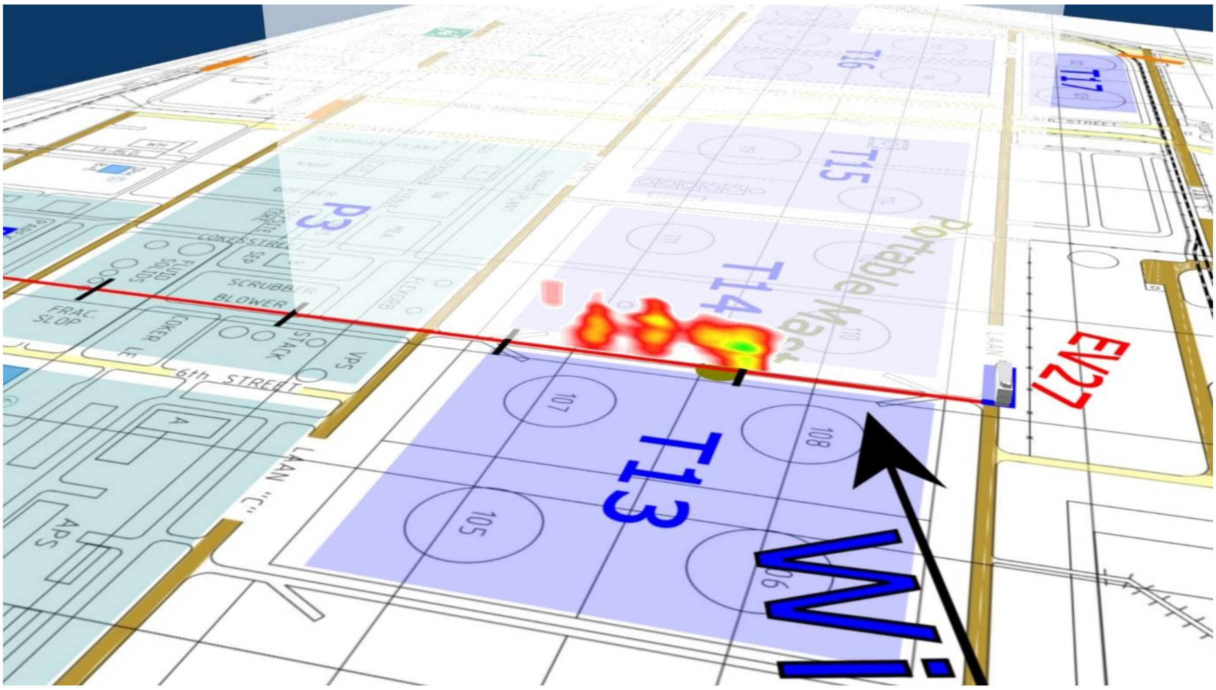


Figure 5.25a2 Visualisation of emission rate for Scan 129 representing EV27/LOS1.

Table 5.26 VOC emission rates determined from EV28 on 20th June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
138	EV28/LOS1	14:12	14:21	3.5	37.7	0.93	Upwind T13
139	EV28/LOS1	14:23	14:32	4.3	32.2	-0.76	Upwind T13
140	EV28/LOS1	14:35	14:45	3.6	25.5	-0.15	Upwind T13
141	EV28/LOS1	14:45	14:54	3.8	31.3	0.02	Upwind T13

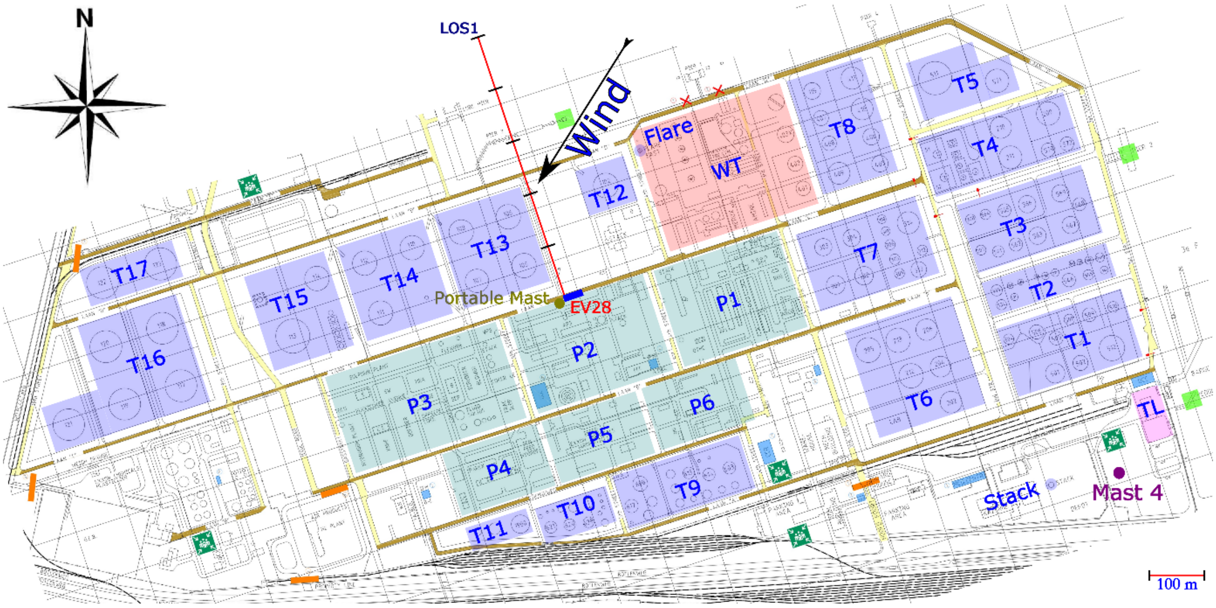


Figure 5.26 Measurement configuration for location EV28 on 20th June.

Table 5.27 VOC emission rates determined from EV29 on 21st June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
143	EV29/LOS1	09:21	09:43	5.0	80.8	25.03	Downwind Coker
144	EV29/LOS1	09:43	10:05	4.5	88.1	34.21	Downwind Coker
145	EV29/LOS1	10:05	10:27	4.1	89.8	28.89	Downwind Coker
146	EV29/LOS1	10:28	10:50	4.5	86.3	23.63	Downwind Coker

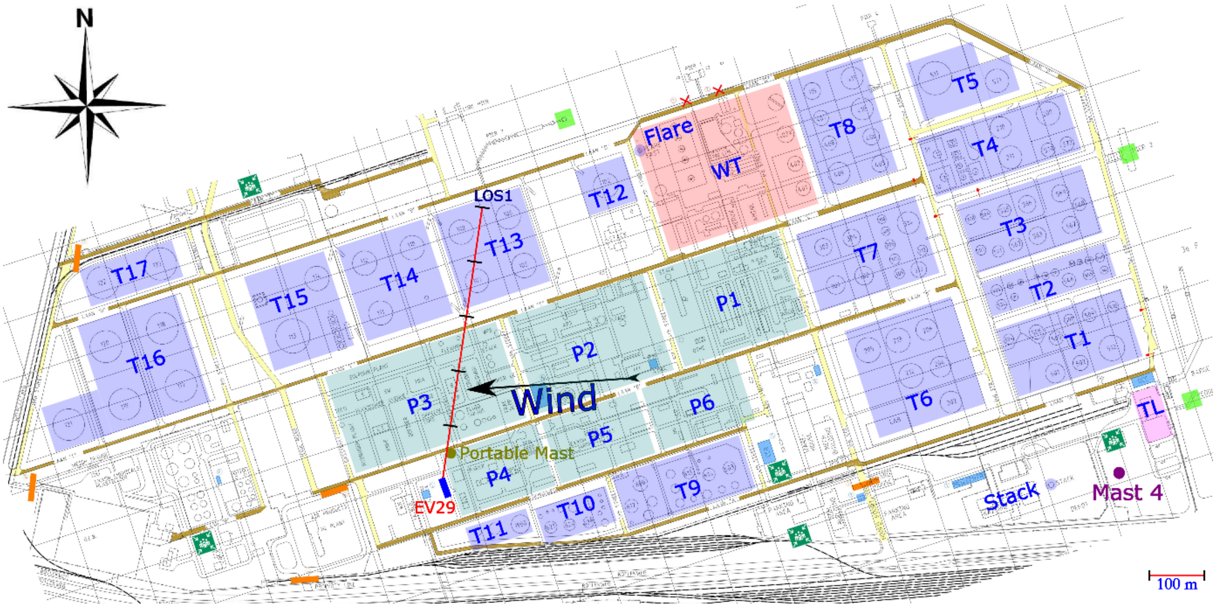


Figure 5.27 Measurement configuration for location EV29 on 21st June.

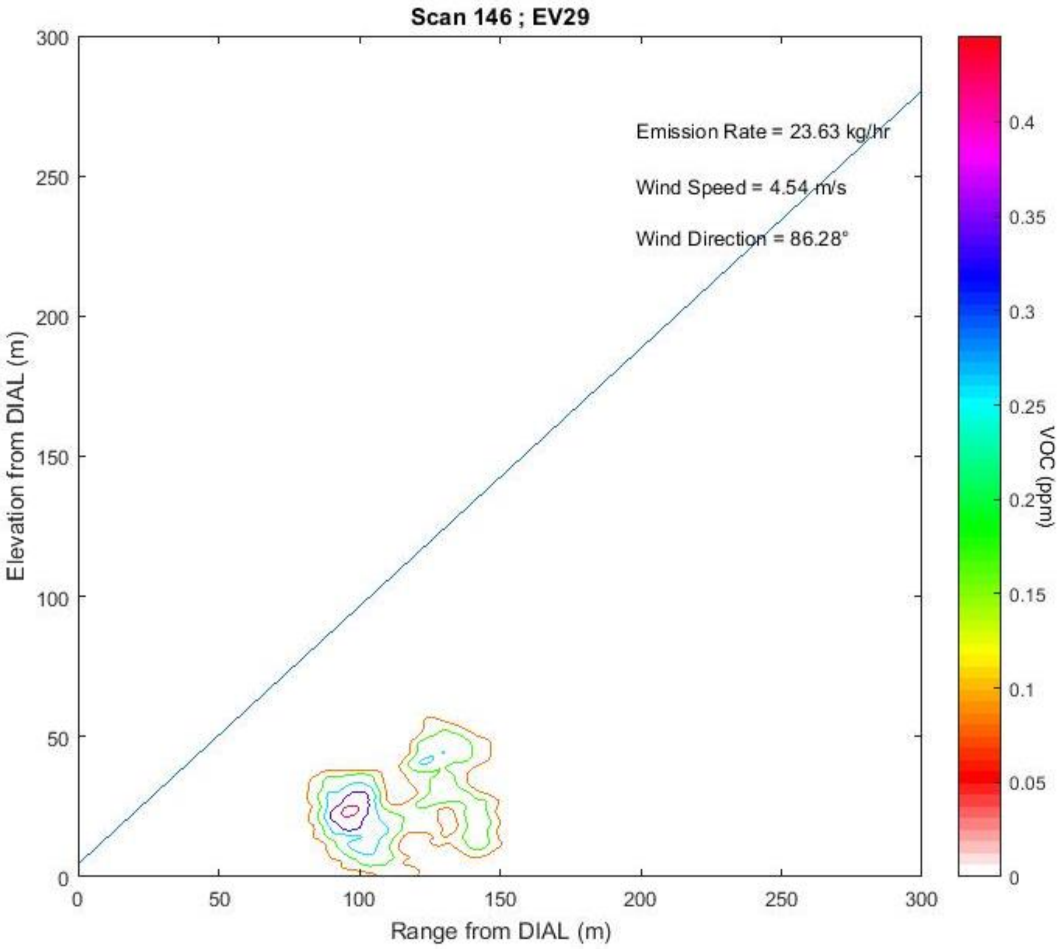


Figure 5.27a1 Observed VOC concentration for Scan 146 representing EV29/LOS1.

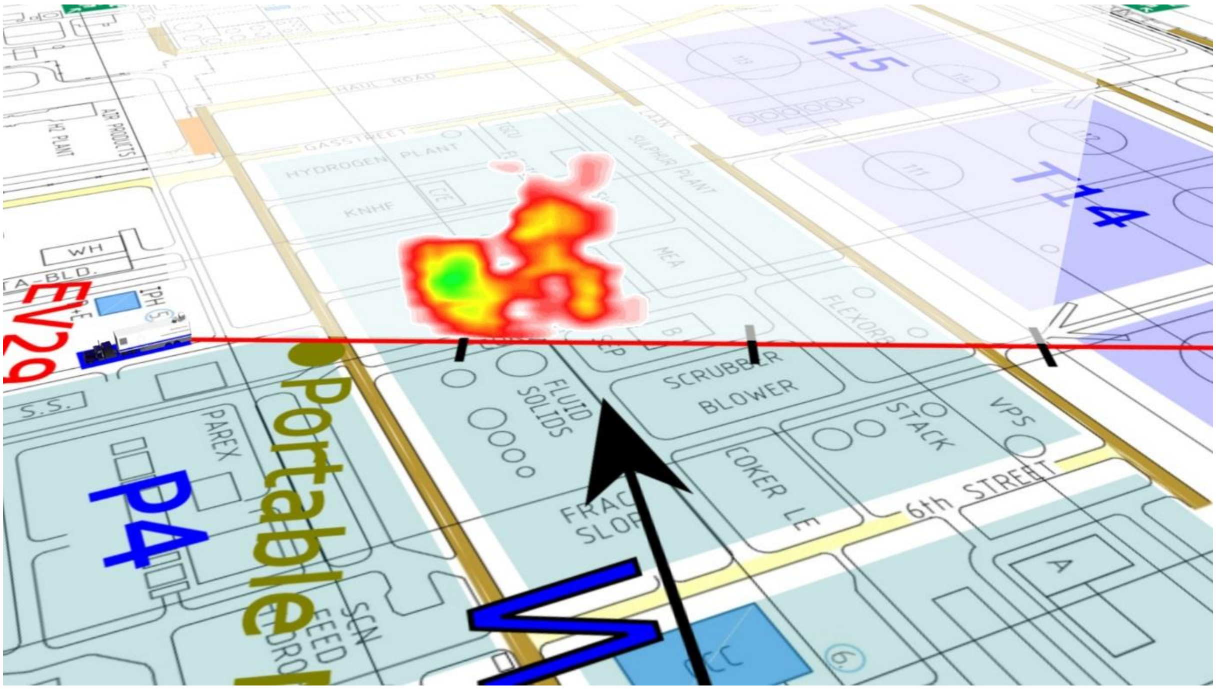


Figure 5.27a2 Visualisation of emission rate for Scan 146 representing EV29/LOS1.

Table 5.28 VOC emission rates determined from EV30 on 21st June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
149	EV30/LOS1	11:43	11:54	4.2	78.5	8.87	Downwind WT Tanks & T8
150	EV30/LOS1	11:55	12:07	4.2	82.9	8.95	Downwind WT Tanks & T8
151	EV30/LOS1	12:08	12:20	3.8	78.0	10.33	Downwind WT Tanks & T8
152	EV30/LOS1	12:21	12:33	4.3	86.3	8.09	Downwind WT Tanks & T8

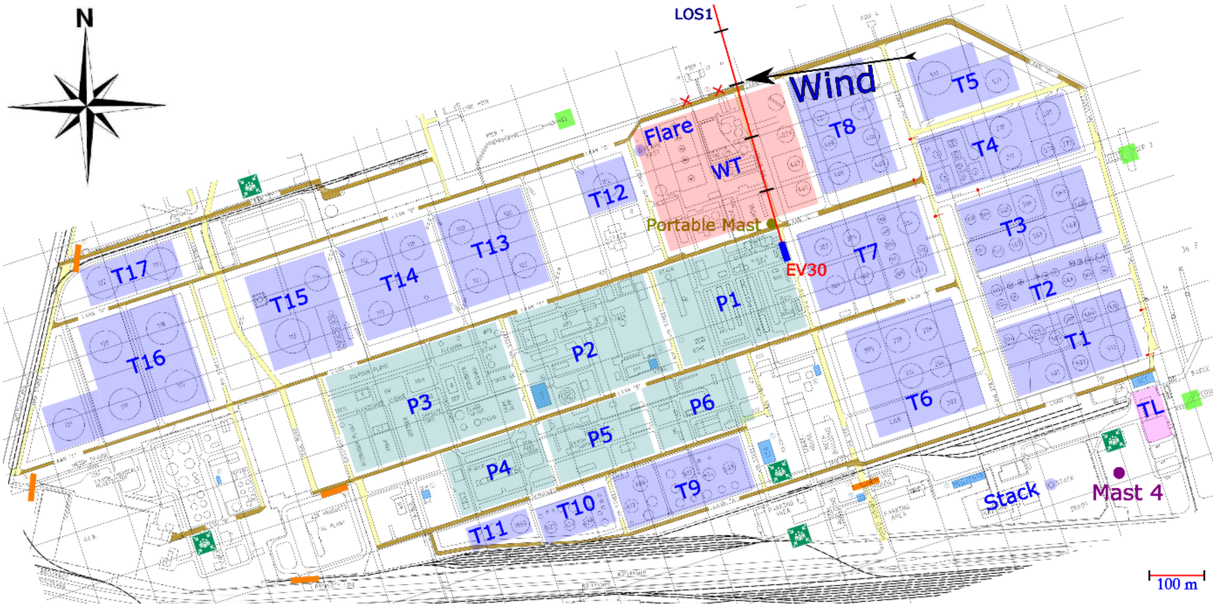


Figure 5.28 Measurement configuration for location EV30 on 21st June.

Table 5.29 VOC emission rates determined from EV31 on 21st June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
153	EV31/LOS1	13:12	13:23	4.1	87.9	10.08	Downwind T5 & Most of T4
154	EV31/LOS1	13:25	13:38	4.2	91.2	11.48	Downwind T5 & Most of T4
155	EV31/LOS1	13:39	13:53	4.4	110.7	7.24	Downwind T5 & Most of T4
156	EV31/LOS1	13:59	14:13	4.2	103.1	7.11	Downwind T5 & Most of T4
157	EV31/LOS2	14:22	14:31	4.1	102.3	3.86	Downwind T2 & SW Corner T3
158	EV31/LOS2	14:31	14:40	4.0	96.6	3.16	Downwind T2 & SW Corner T3
159	EV31/LOS2	14:41	14:50	4.1	112.9	4.77	Downwind T2 & SW Corner T3
160	EV31/LOS2	14:50	14:59	4.3	111.5	4.37	Downwind T2 & SW Corner T3

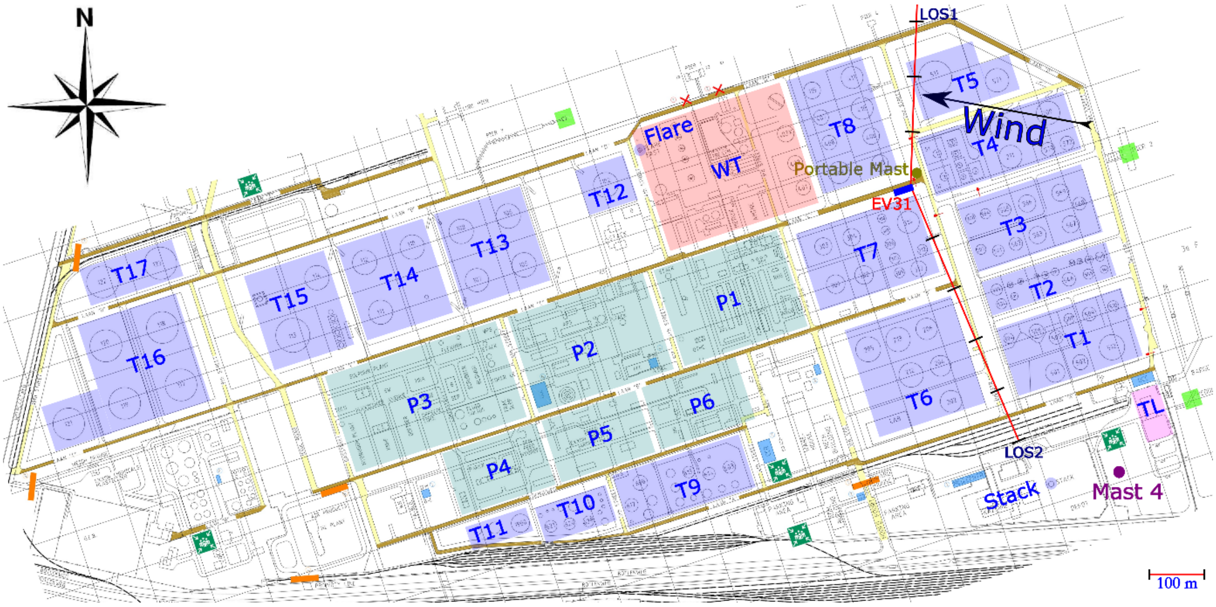


Figure 5.29 Measurement configuration for location EV31 on 21st June.

Table 5.30 VOC emission rates determined from EV32 on 22nd June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
162	EV32/LOS1	08:52	09:06	5.3	239.8	17.54	Downwind WT
165	EV32/LOS1	09:30	09:39	4.4	231.8	12.44	Downwind WT
166	EV32/LOS1	09:42	09:50	3.3	231.2	11.45	Downwind WT
167	EV32/LOS1	09:50	09:58	3.9	237.9	14.84	Downwind WT
168	EV32/LOS1	09:59	10:07	5.0	242.8	18.03	Downwind WT
169	EV32/LOS1	10:08	10:16	5.5	237.7	15.99	Downwind WT
170	EV32/LOS1	10:17	10:25	5.3	244.3	16.22	Downwind WT
171	EV32/LOS1	10:25	10:33	5.2	243.9	16.51	Downwind WT
172	EV32/LOS1	10:34	10:42	5.4	240.4	12.14	Downwind WT
173	EV32/LOS1	10:43	10:51	6.2	241.8	14.72	Downwind WT
174	EV32/LOS1	10:51	10:59	5.5	231.1	12.50	Downwind WT
175	EV32/LOS1	11:00	11:08	5.5	235.0	13.00	Downwind WT
176	EV32/LOS1	11:24	11:32	6.7	239.1	13.70	Downwind WT
177	EV32/LOS1	11:33	11:42	6.9	246.7	20.42	Downwind WT
178	EV32/LOS1	11:42	11:52	6.9	238.1	23.44	Downwind WT

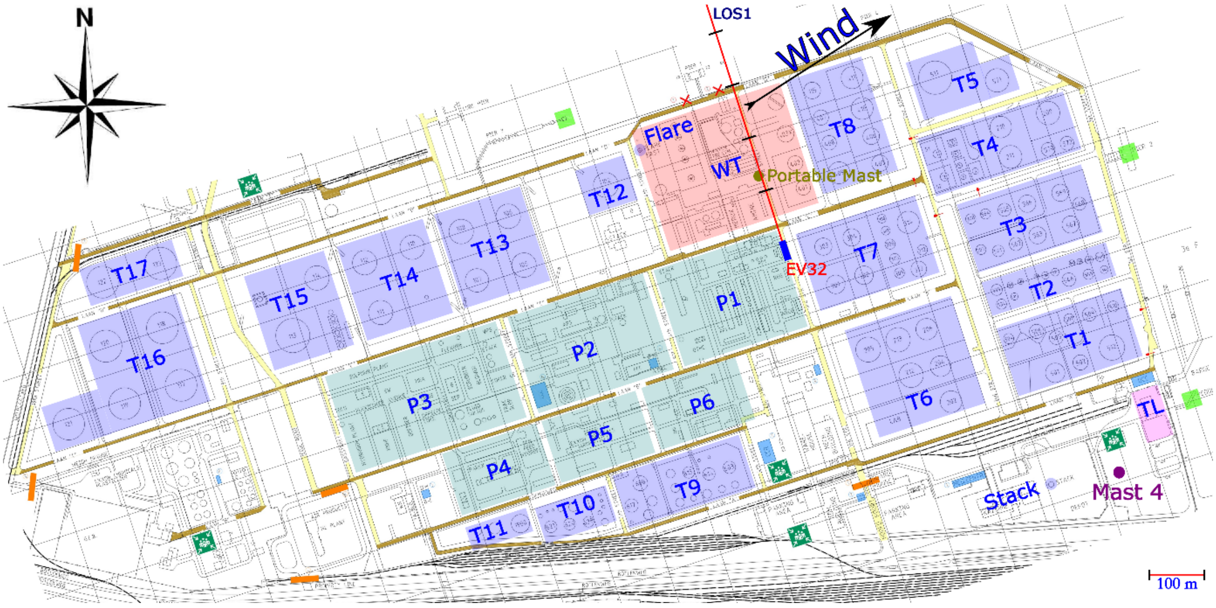


Figure 5.30 Measurement configuration for location EV32 on 22nd June.

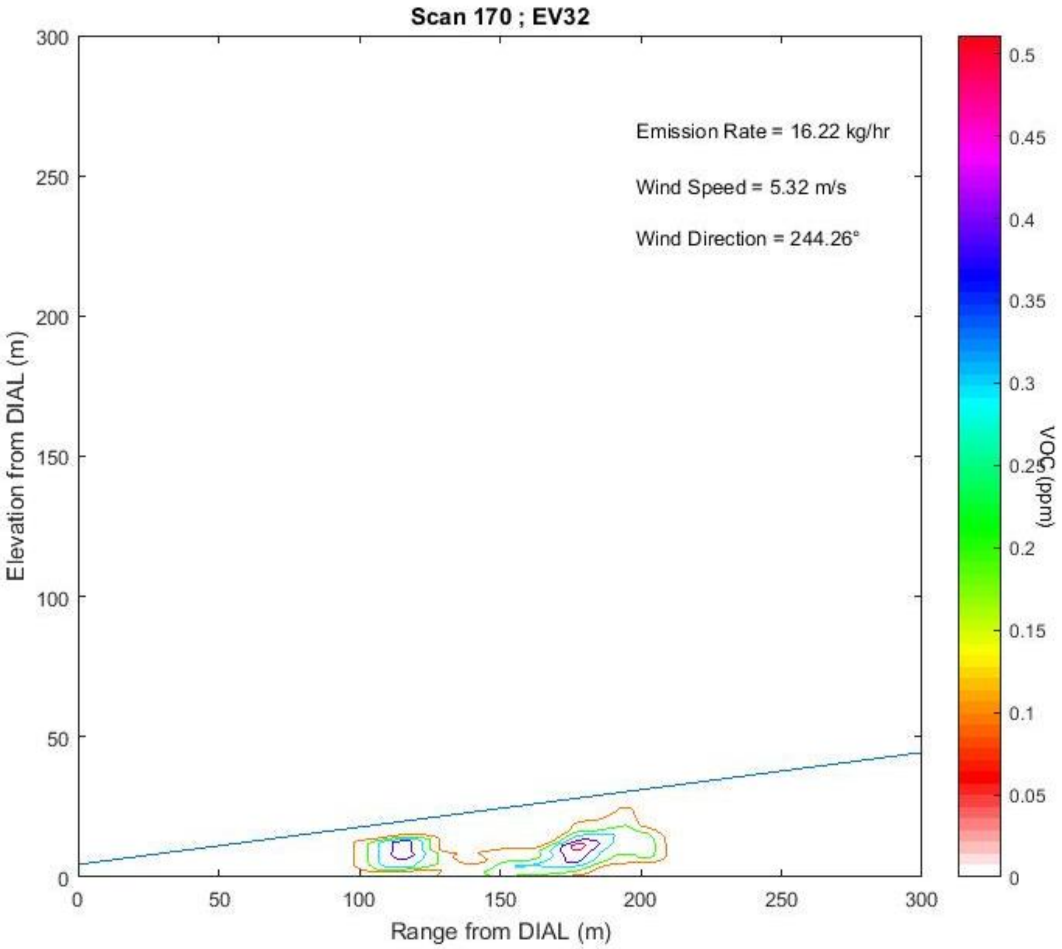


Figure 5.30a1 Observed VOC concentration for Scan 170 representing EV32/LOS1.

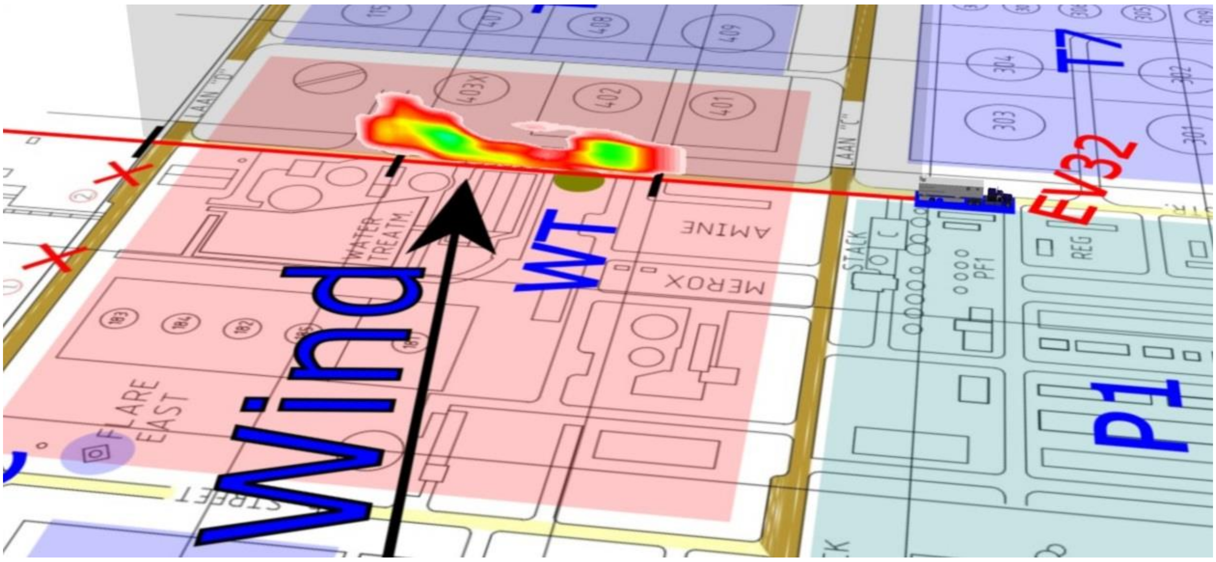


Figure 5.30a2 Visualisation of emission rate for Scan 170 representing EV32/LOS1.

Table 5.31 VOC emission rates determined from EV33 on 22nd June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
180	EV33/LOS1	12:32	12:45	7.4	245.6	10.20	Downwind T9
181	EV33/LOS1	12:45	12:59	6.7	244.9	11.54	Downwind T9
182	EV33/LOS1	12:59	13:12	5.8	238.3	10.96	Downwind T9
183	EV33/LOS1	13:13	13:27	6.1	236.5	7.29	Downwind T9

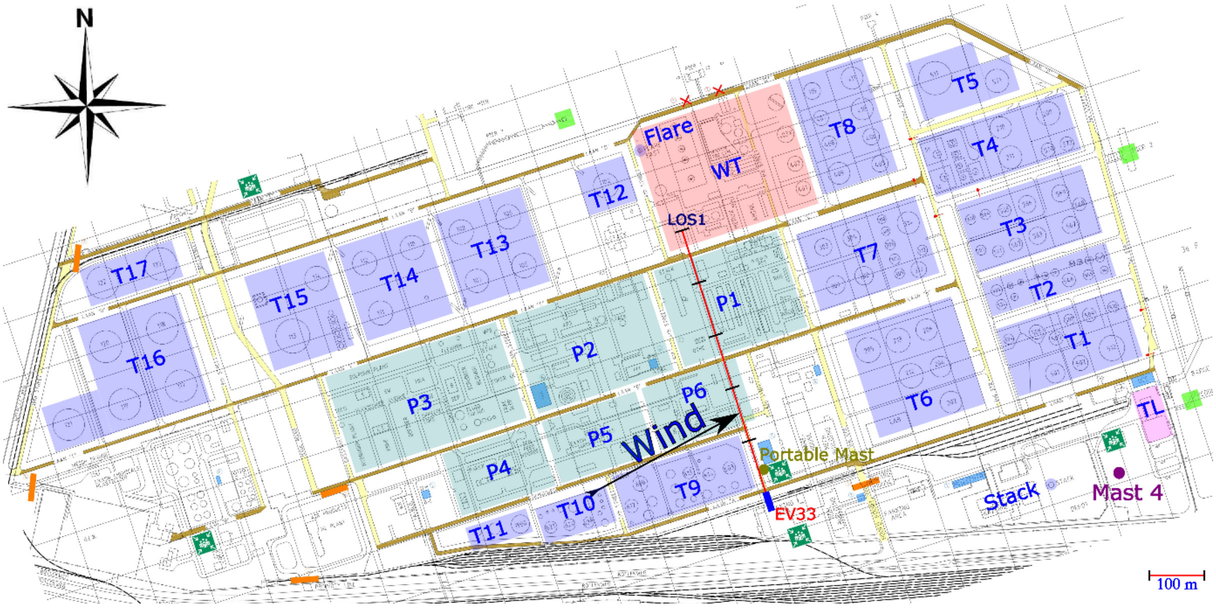


Figure 5.31 Measurement configuration for location EV33 on 22nd June.

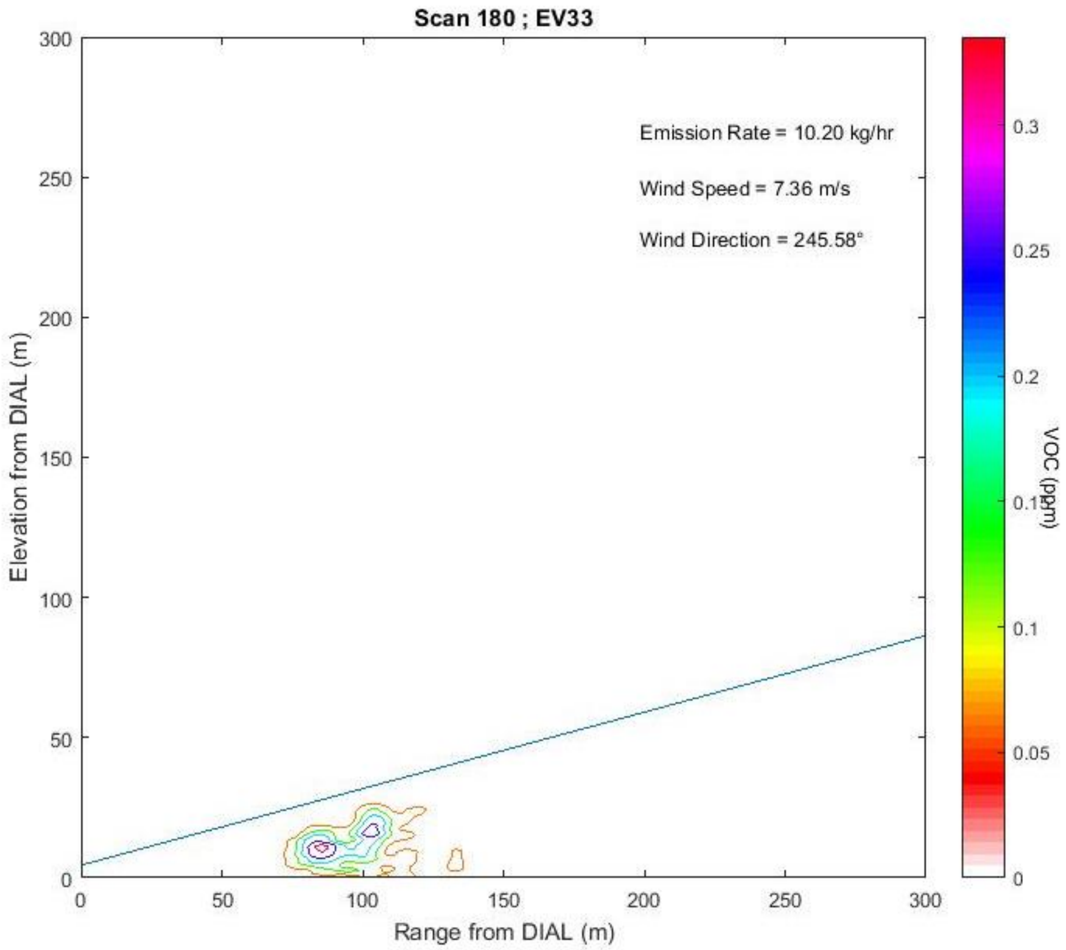


Figure 5.31a1 Observed VOC concentration for Scan 180 representing EV33/LOS1.

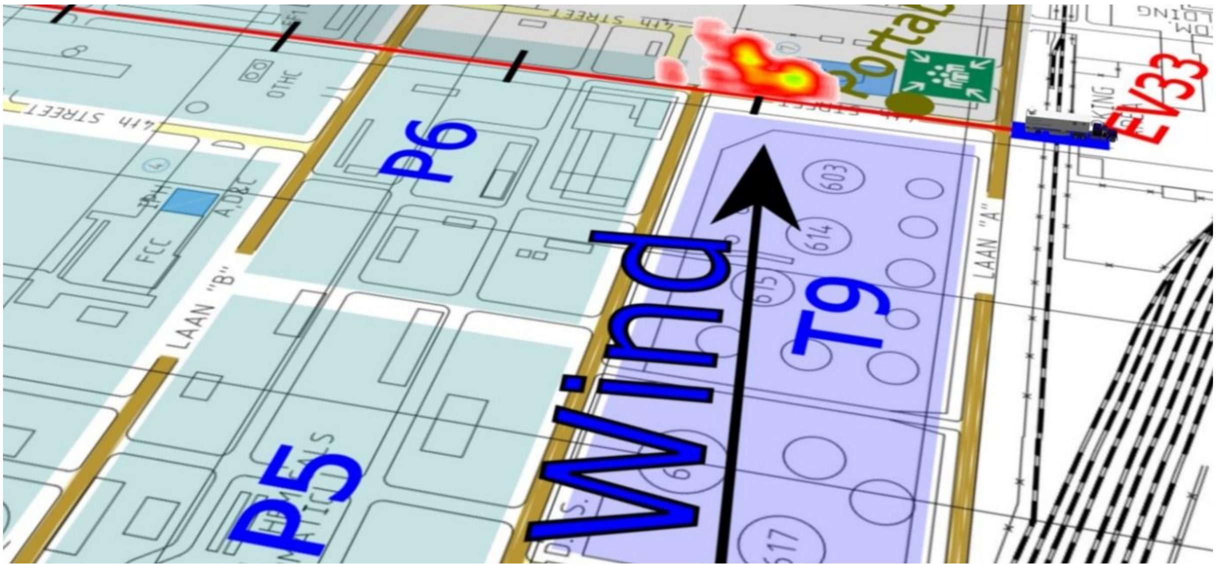


Figure 5.31a2 Visualisation of emission rate for Scan 180 representing EV33/LOS1.

Table 5.32 VOC emission rates determined from EV34 on 22nd June.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
184	EV34/LOS1	14:25	14:30	6.3	248.1	6.94	Downwind Stack SE Site Area
185	EV34/LOS1	14:32	14:38	8.7	260.0	5.59	Downwind Stack SE Site Area
186	EV34/LOS1	14:39	14:45	9.5	257.0	4.76	Downwind Stack SE Site Area
187	EV34/LOS1	14:45	14:51	8.1	254.1	7.18	Downwind Stack SE Site Area
188	EV34/LOS1	14:51	14:57	8.5	267.8	9.30	Downwind Stack SE Site Area
189	EV34/LOS1	14:57	15:04	9.3	262.4	4.98	Downwind Stack SE Site Area

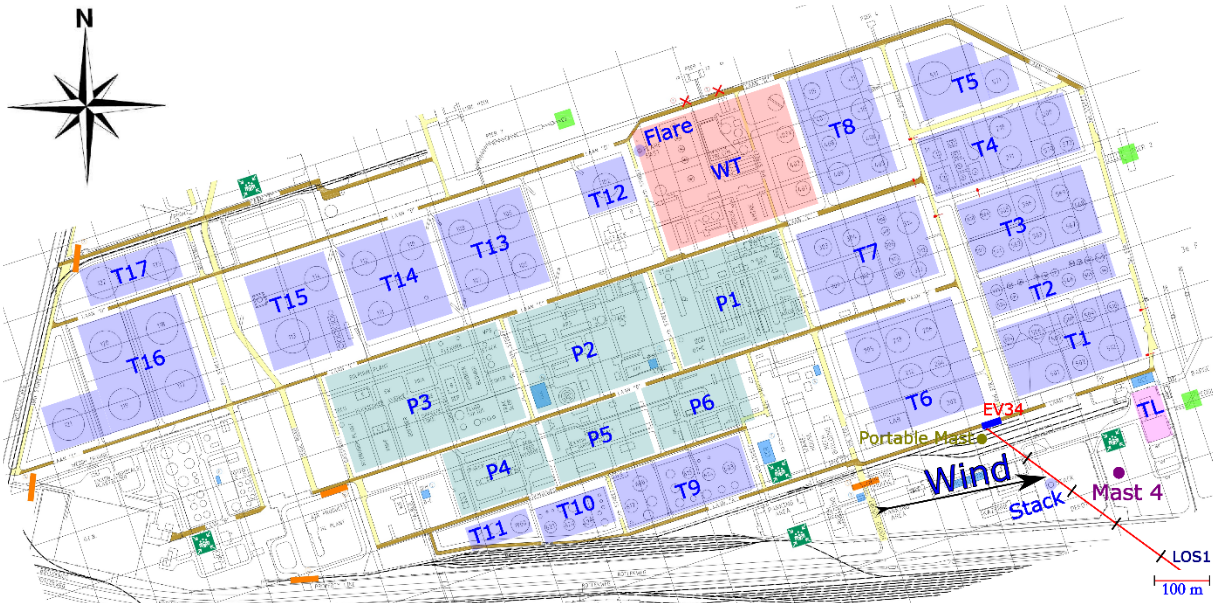


Figure 5.32 Measurement configuration for location EV34 on 22nd June.

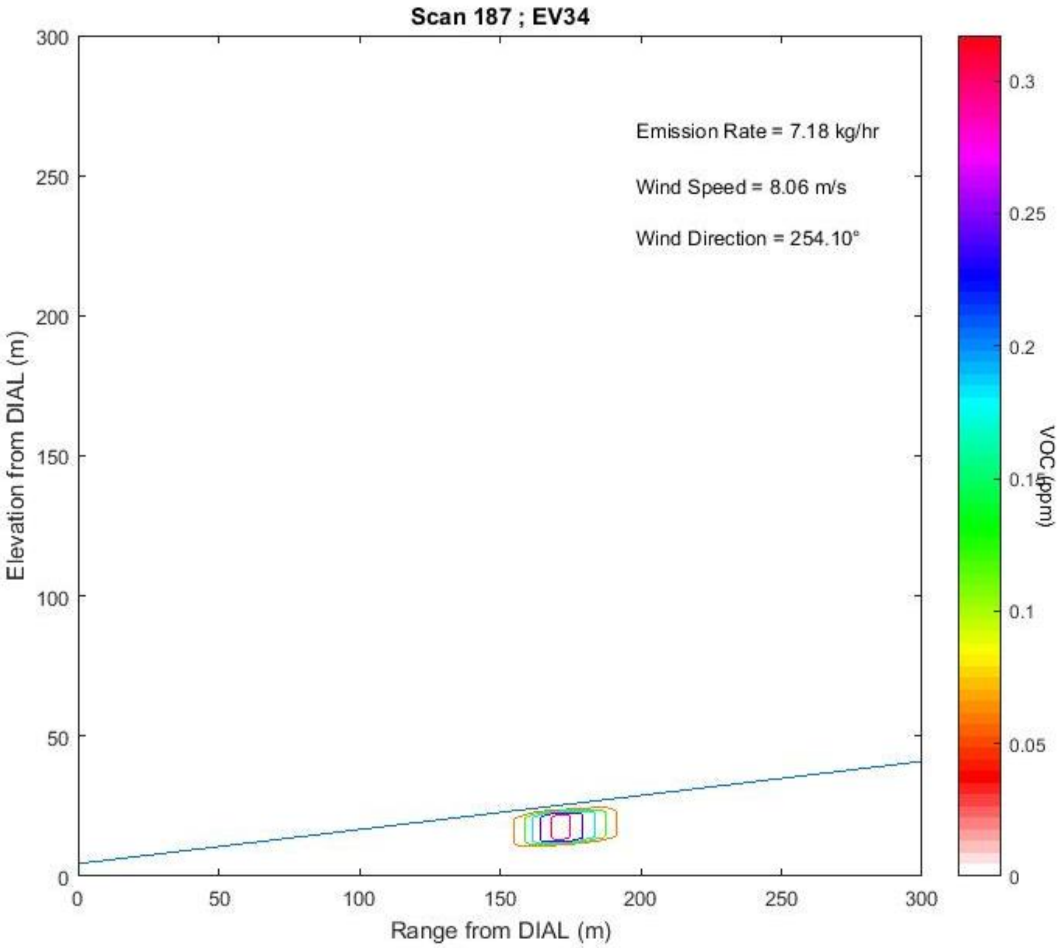


Figure 5.32a1 Observed VOC concentration for Scan 187 representing EV34/LOS1.

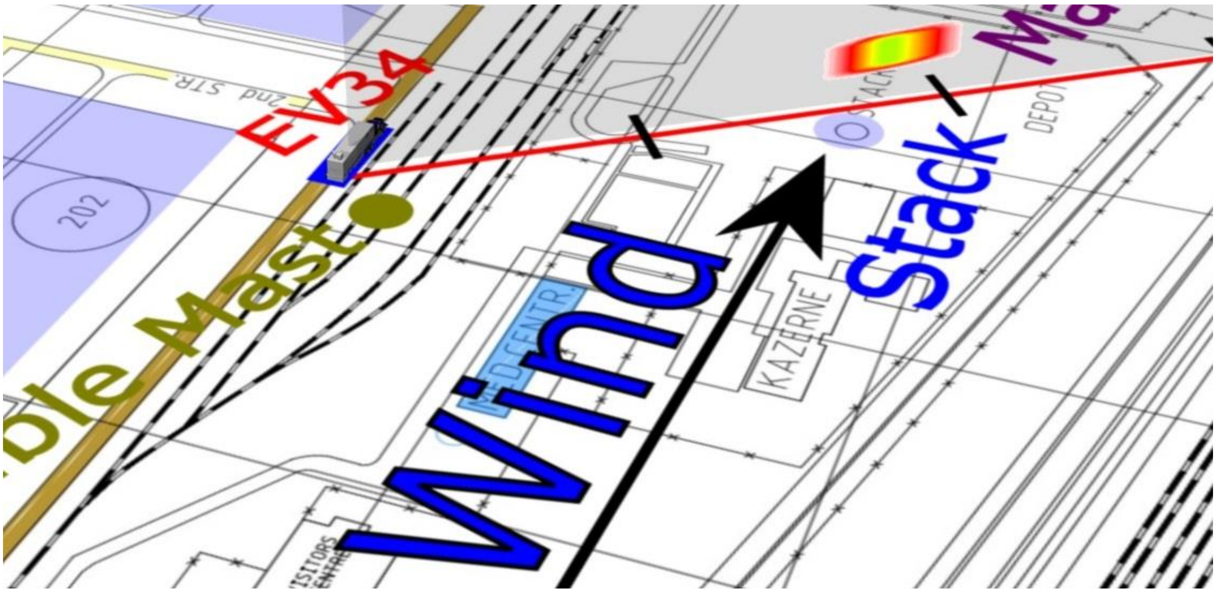


Figure 5.32a2 Visualisation of emission rate for Scan 187 representing EV34/LOS1.

6 RESULTS DISCUSSION

The calculations of the VOC emission rates from the different locations from the 8th to 22nd June are described in the following sections. Table 6.1 presents the mean and stdev of the measured VOC emission rates determined from each location for each LOS. The stdev values include the effects of the source variability, DIAL measurement uncertainty and the influence of other factors such as the wind speed and direction variability during the course of individual measurements.

Table 6.1 Summary of determined VOC emission rates. For each location and LOS the average flux and stdev (when more than one scan is available) are reported.

Date	Location / LOS	Notes	Emission Rate	Standard Deviation	95% Level of Confidence	Scans	Wind Direction Sensor	Wind Speed Sensors
			kg/h	kg/h	kg/h	#		
8-Jun	EV01/LOS1	Downwind T11	0.9	0.4	0.6	4	DIAL	Port-DIAL
8-Jun	EV02/LOS1	Downwind West Area T9	2.7	0.5	0.8	4	DIAL	Port-DIAL
8-Jun	EV03/LOS1	Downwind T10	3.2	0.7	1.8	3	Mast	Port-Mast
8-Jun	EV03/LOS1	Downwind T10 - Intermittent Source	9.1	-	-	1	Mast	Port-Mast
8-Jun	EV04/LOS1	Downwind T12	1.3	0.3	0.5	4	Mast	Port-Mast
9-Jun	EV06/LOS1	Downwind T15	7.2	1.6	2.6	4	DIAL	Mast
9-Jun	EV07/LOS1	Downwind T14 - Temp Source	124.8	38.3	60.9	4	DIAL	Mast
9-Jun	EV08/LOS1	Downwind T16	0.0	1.1	1.8	4	DIAL	Mast
12-Jun	EV09/LOS1	Downwind T17	9.8	1.2	2.0	4	DIAL	Port-Mast
12-Jun	EV10/LOS1	Upwind	0.0	0.6	1.0	4	DIAL	Mast
12-Jun	EV11/LOS1	Downwind WT	15.0	1.3	2.0	4	DIAL	Mast
12-Jun	EV11/LOS2	Downwind Flare	10.3	0.4	0.6	4	DIAL	Mast
13-Jun	EV12/LOS1	Downwind P1	19.4	6.2	9.9	4	DIAL	Port-Mast
13-Jun	EV14/LOS1	Downwind T8 + WT	19.2	1.9	3.1	4	DIAL	Port-Mast
14-Jun	EV16/LOS1	Downwind West Area T1	3.4	0.5	0.8	4	Mast	Port-Mast
14-Jun	EV17/LOS1	Truck Loading - Temp Source	10.8	1.8	2.2	5	Mast	Mast
14-Jun	EV18/LOS1	Downwind P4 & T10 & T11	28.7	4.9	7.9	4	Mast	Port-Mast
14-Jun	EV19/LOS1	Downwind P5 & T9	15.4	2.0	3.1	4	Mast	Port-Mast
15-Jun	EV20/LOS1	Downwind P6 & T9	21.9	3.7	6.0	4	Port	Mast
15-Jun	EV21/LOS1	Downwind T6	7.8	1.5	2.4	4	Mast	Port-Mast
15-Jun	EV22/LOS1	Downwind T2 & T3	8.9	1.2	1.9	4	Mast	Mast
16-Jun	EV23/LOS1	Downwind T7	6.5	1.0	8.6	2	Mast	Port-Mast
16-Jun	EV24/LOS1	Downwind T7	6.7	1.8	2.3	5	Mast	Port-Mast
16-Jun	EV25/LOS1	Downwind P2 & T13	26.3	3.1	4.9	4	Mast	Port-Mast
16-Jun	EV26/LOS1	Downwind P3	17.3	-	-	1	Mast	Port-Mast
20-Jun	EV27/LOS1	Downwind T13	10.7	0.9	1.0	6	DIAL	Mast
20-Jun	EV27/LOS2	Downwind Tank 106	0.0	0.5	0.8	4	DIAL	Mast
20-Jun	EV28/LOS1	Upwind T13	0.0	0.7	1.1	4	Mast	Mast
21-Jun	EV29/LOS1	Downwind Coker - Temp Source	27.9	4.7	7.5	4	Mast	Mast
21-Jun	EV30/LOS1	Downwind WT Tanks & T8	9.1	0.9	1.5	4	Mast	Mast
21-Jun	EV31/LOS1	Downwind T5 & Most of T4	9.0	2.2	3.4	4	Mast	Port-Mast
21-Jun	EV31/LOS2	T2 & SW Corner T3	4.0	0.7	1.1	4	Mast	Port-Mast
22-Jun	EV32/LOS1	Downwind WT	15.5	3.3	1.8	15	Mast	Port-Mast
22-Jun	EV33/LOS1	Downwind T9 & T10 & T11	10.0	1.9	3.0	4	Mast	Port-Mast
22-Jun	EV34/LOS1	Downwind Stack SE Site Area	6.5	1.7	1.8	6	Mast	Mast

Because the DIAL emission rate measurement depends on several different experimental conditions, the detection limit can be experimentally estimated when the measured stdev is similar to the measured value. The stdev therefore defines the detection limit for a given set of measurements.

Ambient air samples were taken to provide an indication of the VOC speciation around the site and to calculate the scaling factor to go from the standard DIAL VOC emission rate to the actual C2+ VOC emission rate. The measured site-averaged mixture scaling factor was 1.04 ± 0.06 while the specific waste water treatment area scaling factor was 1.68 ± 0.11.

Table 6.2 Summary of determined C2+ emission rates. For each location and LOS the average flux and standard uncertainty are reported.

Date	Location / LOS	Notes	Emission Rate	Standard Uncertainty	95% Level of Confidence
			kg/h	kg/h	kg/h
8-Jun	EV01/LOS1	Downwind T11	1.0	0.2	0.6
8-Jun	EV02/LOS1	Downwind West Area T9	2.8	0.3	0.8
8-Jun	EV03/LOS1	Downwind T10	3.3	0.5	1.6
8-Jun	EV03/LOS1	Downwind T10 - Intermittent Source	9.5	0.6	1.2
8-Jun	EV04/LOS1	Downwind T12	1.4	0.2	0.4
9-Jun	EV06/LOS1	Downwind T15	7.5	0.9	2.5
9-Jun	EV07/LOS1	Downwind T14 - Temp Source	130.0	21.3	59.9
9-Jun	EV08/LOS1	Downwind T16	0.0	0.6	1.8
12-Jun	EV09/LOS1	Downwind T17	10.3	0.9	2.0
12-Jun	EV10/LOS1	Upwind	0.0	0.3	1.0
12-Jun	EV11/LOS1	Downwind WT	25.1	2.6	5.7
12-Jun	EV11/LOS2	Downwind Flare	10.7	0.7	1.4
13-Jun	EV12/LOS1	Downwind P1	20.2	3.5	9.8
13-Jun	EV14/LOS1	Downwind T8 + WT	29.6	2.8	6.1
14-Jun	EV16/LOS1	Downwind West Area T1	3.5	0.3	0.8
14-Jun	EV17/LOS1	Truck Loading - Temp Source	11.2	1.1	2.4
14-Jun	EV18/LOS1	Downwind P4 & T10 & T11	29.9	3.1	7.6
14-Jun	EV19/LOS1	Downwind P5 & T9	16.0	1.4	3.1
15-Jun	EV20/LOS1	Downwind P6 & T9	22.9	1.7	4.0
15-Jun	EV21/LOS1	Downwind T6	8.2	0.9	2.3
15-Jun	EV22/LOS1	Downwind T2 & T3	9.3	0.8	1.9
16-Jun	EV23/LOS1	Downwind T7	6.8	0.8	5.3
16-Jun	EV24/LOS1	Downwind T7	6.9	0.9	2.3
16-Jun	EV25/LOS1	Downwind P2 & T13	27.4	2.3	5.0
16-Jun	EV26/LOS1	Downwind P3	18.0	1.1	2.2
20-Jun	EV27/LOS1	Downwind T13	11.2	0.8	1.6
20-Jun	EV27/LOS2	Downwind Tank 106	0.0	0.2	0.5
20-Jun	EV28/LOS1	Upwind T13	0.0	0.3	0.7
21-Jun	EV29/LOS1	Downwind Coker - Temp Source	29.1	3.0	7.3
21-Jun	EV30/LOS1	Downwind WT Tanks & T8	9.4	0.7	1.6
21-Jun	EV31/LOS1	Downwind T5 & Most of T4	9.4	1.2	3.3
21-Jun	EV31/LOS2	T2 & SW Corner T3	4.2	0.4	1.1
22-Jun	EV32/LOS1	Downwind WT	26.1	2.8	6.1
22-Jun	EV33/LOS1	Downwind T9 & T10 & T11	10.4	1.2	2.9
22-Jun	EV34/LOS1	Downwind Stack SE Site Area	6.7	0.8	1.9

In the following sections of this report the average C2+ emission rate and standard uncertainty will be quoted unless otherwise specified.

6.1 TANK AREA T1

The C2+ emissions from T1 were measured from location EV16 on the 14th of June. During this measurement the wind speed was approximately 3.5 m/s, coming from a south-easterly direction, as shown in Figure 5.14. The average C2+ emission rate measured of the 4 scans taken was 3.5 ± 0.3 kg/h as reported in Table 6.2. Figures 5.14a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 71; from these plots it is seen that the highest plume concentration is between 175-200 m relative to the DIAL with the source located in SW corner of T1.

6.2 TANK AREAS T2 & T3

On the 15th of June C2+ emissions from T2 and T3 were measured from location EV22. During this measurement the wind speed was approximately 5.5 m/s, coming from a W/SW direction, as shown in Figure 5.20. The average C2+ emission rate measured of the 4 scans taken was 9.3 ± 0.8 kg/h as reported in Table 6.2. Figures 5.20a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 99, these plots suggest the majority of the emissions come from the SE area of T2 area and the very south side of T3.

6.3 TANK AREAS T4 & T5

The C2+ emissions from T4 and T5 were measured from location EV31, LOS1 on the 21st of June. During this measurement the wind speed was approximately 4 m/s, coming from E/SE direction, as shown in Figure 5.29. The average C2+ emission rate measured of the 4 scans taken was 9.4 ± 1.2 kg/h and as reported in Table 6.2. From the position of the plume relative to the DIAL, it was thought that the emission sources were most likely located in the east-side of T4, this was later confirmed by OGI camera investigation carried out by Bureau Veritas.

6.4 TANK AREA T6

On the 15th of June C2+ emissions from T6 were measured from location EV21. During this measurement the wind speed was approximately 7.5 m/s, coming from a W/SW direction, as shown in Figure 5.19. The average C2+ emission rate measured of the 4 scans taken was 8.2 ± 0.8 kg/h as reported in Table 6.2. Figures 5.19a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 96. These plots suggest the largest emission sources are from the north tanks in area T6.

6.5 TANK AREA T7

On the 16th of June two different measurements of the T7 area were carried out from locations EV23 and EV24. During both sets of measurements the wind speed was approximately 5 m/s, coming from a north-westerly direction, as shown in Figures 5.21 and 5.22. The average C2+ emission rates measured from locations EV23 and EV24 were 6.8 ± 0.8 kg/h and 6.9 ± 0.9 kg/h respectively, as reported in Table 6.2. Both measurements were very consistent with each other and the overall average emission rate was 6.9 ± 0.7 kg/h as reported in the summary Table 6.3.

6.6 TANK AREA T8

The C2+ emissions from the T8 were measured from location EV14, LOS1 on the 13th of June. During this measurement the wind speed was approximately 4 m/s, coming from a W/NW direction, as shown in Figure 5.12. Notably, the emissions from the water treatment area were also upwind during these measurements. To determine the emissions contribution from area T8 the water treatment VOC emission measured from location EV11 was subtracted from the emissions calculated from location EV14. The conversion factor from VOC to C2+ was then applied and the resulting average C2+ emission rate measured for area T8 was 4.4 ± 1.2 kg/h as reported in the summary Table 6.3.

6.7 TANK AREA T9

Initial measurements of the west side of the T9 area were made on the 8th of June from location EV02. For these measurements the wind was S/SW with a speed of approximately 3.5 m/s as shown in

Figure 5.2. The average C2+ emission rate measured of the 4 scans taken at EV02 was 2.8 ± 0.3 kg/h as reported in Table 6.2.

On the 22nd of June C2+ emissions for the whole T9 area was measured from location EV33. During this measurement the wind speed was approximately 6.5 m/s, coming from a W/SW direction, as shown in Figure 5.31. After the measurement campaign ended we were informed by the site's operator that the content of two tanks (T603 and T614) in the east part of area T9 was cyclohexane. The DIAL laser wavelength used for VOC measurement is not very sensitive towards cyclohexane C-H vibrations, therefore the correction factor from VOC to C2+ (cyclohexane) is relatively high. If the composition of these two tanks was known in advance as specified in the protocol, the generic VOC measurement would have made minimising any other upwind source by cutting through the two tanks to isolate their emission form the other nearby tanks or by carrying out the measurement with different wind direction, specifically from south. Without the prior knowledge of the composition of these tanks, the measurements of this area were carried out with westerly wind, so that upwind VOC emission contributions from T10, T11 and the west side of T9 needed to be subtracted to estimate the emission from east area of T9 increasing the measurement uncertainty. The average VOC emission rate measured of the 4 scans taken at EV02 was 10.0 ± 1.9 kg/h as reported in Table 6.2. This led to an estimated VOC emission rate of 3.2 kg/h for the east side of T9. By then applying the cyclohexane correction factor the C2+ (cyclohexane) emission rate was 101.1 ± 79.7 kg/h for a 95% level of confidence. This measurement has a large associated uncertainty and even a small change of about 0.5 kg/h in the VOC contribution from the upwind tanks would make a significant difference to the estimated cyclohexane emission rate. Therefore, this value is thought to be the maximum possible emission rate for this area, as all the VOC measured was assumed to originate from the two cyclohexane tanks.

6.8 TANK AREA T10

On the 8th of June C2+ emissions from T10 were measured from location EV03. During this measurement the wind speed was approximately 4.5 m/s, coming from a S/SW direction, as shown in Figure 5.3. An intermittent source was observed during the last scan (Scan 13) of this measurement set. Figures 5.3a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 13 where the intermittent source was identified in the 180 m - 200 m range from the DIAL, originated from the tanks in the east area of T10. The average C2+ emission rate measured from the other 3 scans, excluding Scan 13, was 3.3 ± 0.5 kg/h as reported in Table 6.2.

6.9 TANK AREA T11

The C2+ emissions from area T11 were measured from location EV01, LOS1 on the 8th of June. During this measurement the wind speed was approximately 3 m/s, coming from a S/SW direction, as shown in Figure 5.1. The average C2+ emission rate measured of the 4 scans taken was 1.0 ± 0.2 kg/h as reported in Table 6.2. Figures 5.1a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 2, these plots suggest the emission was coming from the SE tank 1900.

6.10 TANK AREA T12

On the 8th of June C2+ emissions from T12 were measured from location EV04. During this measurement the wind speed was approximately 5.5 m/s, coming from a S/SW direction, as shown in Figure 5.4. The average C2+ emission rate measured of the 4 scans taken was 1.4 ± 0.2 kg/h as reported in Table 6.2. Figures 5.4a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 16, these plots clearly suggest the emission was coming from tank 102.

6.11 TANK AREA T13

The C2+ emissions from the T13 area were measured from location EV27/LOS1 on the 20th of June. During this measurement the wind speed was approximately 3.5 m/s, coming from a north-easterly direction, as shown in Figure 5.25. The average C2+ emission rate measured of the 6 scans taken was 11.2 ± 0.8 kg/h as reported in Table 6.2. Figures 5.25a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 129, in these plots several plumes are observed in the 100 m - 200 m region from the DIAL. This suggests all the tanks but tank 105 (SE corner) are potential emission sources. Additional scans were performed along LOS2 to separately measure the emission from tank 106, the average C2+ emission rate measured of the 4 scans taken was 0.0 ± 0.2 kg/h as reported in Table 6.2. This indicates that the emission sources from area T13 were tanks 107 and 108.

6.12 TANK AREA T14

On the 9th of June C2+ emissions from T14 were measured from location EV07. During this measurement the wind speed was approximately 7 m/s, coming from a westerly direction, as shown in Figure 5.6. The average C2+ emission rate measured of the 4 scans taken was 130 ± 21.3 kg/h as reported in Table 6.2. Figures 5.6a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 26. From these plots a large plume is observed between 125-175 m from the DIAL, directly downwind of tank 112. Notably, this was a known issue that site operators were addressing, hence this source has been included as temporary in the summation of the total site emissions, see Section 6.24.

6.13 TANK AREA T15

Emissions from the T15 area were measured from location EV06 on the 9th of June. During this measurement the wind speed was approximately 6 m/s, coming from a westerly direction, as shown in Figure 5.5. The average C2+ emission rate measured of the 4 scans taken was 7.5 ± 0.9 kg/h as reported in Table 6.2. Figures 5.5a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 23 showing the main emission source was tank 113 and the area between tanks 113 and 114.

6.14 TANK AREA T16

On the 9th of June C2+ emissions from T16 were measured from location EV08. During this measurement the wind speed was approximately 6.5 m/s, coming from a W/SW direction, as shown in Figure 5.7. No significative C2+ emission was measured from the 4 scans taken, 0.0 ± 0.6 kg/h as reported in Table 6.2.

6.15 TANK AREA T17

The C2+ emissions from the T17 area were measured from location EV09 on the 12th of June. During this measurement the wind speed was approximately 8 m/s, coming from a W/SW direction, as shown in Figure 5.8. The average C2+ emission rate measured of the 4 scans taken was 10.3 ± 0.9 kg/h as reported in Table 6.2. Figures 5.8a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 35. From these plots, plumes are seen either side of Tank 123. This suggests the emission sources were from Tank 122 and/or the west side of Tank 123.

6.16 PROCESS AREA P1

On the 13th of June C2+ emissions from the main process area P1 were measured from location EV12. During this measurement the wind speed was approximately 2.5 m/s, coming from a north-westerly direction, as shown in Figure 5.11. The average C2+ emission rate measured of the 4 scans taken was 20.2 ± 3.5 kg/h as reported in Table 6.2. Multiple emission sources can be expected from this area since several plumes were observed in the 100 m - 250 m range from the DIAL.

6.17 PROCESS AREA P2

The C2+ emissions from the main process area P2 were measured from location EV25 on the 16th of June. During this measurement the wind speed was approximately 5.5 m/s, coming from a north-westerly direction, as shown in Figure 5.23. The measurement plane LOS1 was also downwind of area T13. Therefore, to determine the emissions from P2 the contribution from T13, measured from location EV27, was subtracted from the total emissions measured from location EV25, 27.4 ± 2.3 kg/h as reported in Table 6.2. The average C2+ emission rate for P2 measured from the 4 scans taken was 16.2 ± 1.9 kg/h as reported in the summary Table 6.3. Figures 5.23a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 117. Similar to area P1, multiple emission sources can be expected from area P2 since several plumes were observed in the 150 m - 250 m range from the DIAL.

6.18 PROCESS AREA P3

On the 16th of June C2+ emissions from the main process area P3 were measured from location EV26. Throughout this measurement the wind speed was approximately 6 m/s, varying between north-westerly and westerly directions, as shown in Figure 5.24. Notably, during most of this measurement significant emissions were measured from the Coker and the upwind source area T14. From the position of the plume relative to the DIAL, it was thought that the Coker was a significative emission source, in particular for Scans 122 and 123. Area T14 was not an upwind source during the last Scan 124 measured with more westerly wind direction and the C2+ emission rate measured from area P3 was 18.0 ± 1.1 kg/h as reported in Table 6.2. No specific plume from the Coker area was observed during this scan. It should be noted that this single measurement does not meet the requirement for a valid measurement of a set of four scans as stated in the DIAL protocol.

6.19 PROCESS AREA P4

The C2+ emissions from the petrochemical area P4 were measured from location EV18 on the 14th of June. During this measurement the wind speed was approximately 3.5 m/s, coming from a E/SE direction, as shown in Figure 5.16. The measurement plane LOS1 was not only downwind of P4, but also of areas T10 and T11. Therefore, to determine the emission from P4 the contributions from T10 and T11, measured from locations EV03 and EV01 respectively, was subtracted from the total emissions measured from location EV18, 29.9 ± 3.1 kg/h as reported in Table 6.2. The average C2+ emission rate calculated for P4 was 25.7 ± 3.0 kg/h as reported in the summary Table 6.3. Figures 5.16a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 82. Multiple emission sources can be expected from this area since several plumes were observed in the 100 m - 200 m range from the DIAL.

6.20 PROCESS AREA P5

On the 14th of June C2+ emissions from the petrochemical area P5 were measured from location EV19. During this measurement the wind speed was approximately 2.5 m/s, coming from a south-easterly direction, as shown in Figure 5.17. The measurement plane LOS1 was not only downwind of P5, but also of area T9. Therefore, to determine the emission from P5, the contribution from area T9 needs to be subtracted from the total emissions measured from location EV19, 16.0 ± 1.4 kg/h as reported in Table 6.2. Area T9 VOC emission contribution can be calculated by subtracting from the VOC measured from EV33 (downwind of T9, T19 and T11) the contributions from T10 and T11, measured from locations EV03 and EV01 respectively. The VOC emission from P5 can then be calculated by subtracting T9 VOC contribution from the VOC emission measured from location EV19. The conversion factor from VOC to C2+ can then be applied to calculate the average C2+ emission rate from P5, 9.8 ± 1.6 kg/h as reported in the summary Table 6.3. Figures 5.17a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 85. Multiple emission sources can be expected from this area since several plumes were observed in the 130 m - 220 m range from the DIAL.

6.21 PROCESS AREA P6

The C2+ emissions from the petrochemical area P6 were measured from location EV20 on the 15th of June. During this measurement the wind speed was approximately 5 m/s, coming from a S/SW direction, as shown in Figure 5.18. The measurement plane LOS1 was not only downwind of P5, but also of area T9 as in the case of the measurements of area P5. Therefore, to determine the emission from P6, the contribution from area T9 needs to be subtracted from the total emissions measured from location EV20, 22.9 ± 1.7 kg/h as reported in Table 6.2. The contribution from T9 was calculated as described in Section 6.20 and the calculate average C2+ emission rate from P6 was 16.0 ± 2.4 kg/h as reported in the summary Table 6.3. Figures 5.18a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 91. Two main emission sources were observed at about 150 m and 220 m from the DIAL

6.22 WATER TREATMENT (WT) AREA

The C2+ emissions were measured for the water treatment area on two separate occasions. The first set of measurement was made on the 12th of June from location EV11/LOS1, during this measurement period a westerly wind of approximately 8 m/s was observed, as shown in Figure 5.10. The second set of measurement were carried out on the 22nd of June from location EV32, for these measurements the wind was from W/SW, as shown in Figure 5.30. From this location 15 scans were recorded and over this period the wind varied between approximately 4 m/s and 7 m/s. Both sets of measurements were consistent with each other and the average C2+ emission rate over all 19 scans recorded from locations EV11 and EV32 was 25.9 ± 2.7 kg/h as reported in the summary Table 6.3. Figures 5.30a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 170. Multiple emission sources can be expected from this area since several plumes were observed in the 100 m - 200 m range from the DIAL.

6.23 TEMPORARY SOURCES

All of the emissions from the following locations are assumed to be temporary sources, dependent upon site activity and operations.

6.23.1 Flare

On the 12th of June C2+ emissions from the flare were measured from location EV11/LOS2. Throughout this measurement period the wind speed varied was approximately 8 m/s, coming from a westerly direction, as shown in Figure 5.10. The average C2+ emission rate measured of the 4 scans taken was 10.7 ± 0.7 kg/h as reported in Table 6.2. Figures 5.10a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 49.

6.23.2 Stack to South-East of Site

The C2+ emissions from a stack to the south-east of the site were measured from location EV34 on the 22nd of June. During this measurement period the wind speed varied between approximately 6.5 m/s and 9.5 m/s, coming from a W/SW direction as shown in Figure 5.32. The average C2+ emission rate measured of the 6 scans taken was 6.7 ± 0.8 kg/h as reported in Table 6.2. Figures 5.32a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 187.

6.23.3 Truck Loading

On the 14th of June C2+ emissions from the flare were measured from location EV17. Throughout this measurement the wind speed was approximately 3.5 m/s, coming from a south-easterly direction, as shown in Figure 5.15. The average C2+ emission rate measured of the 5 scans taken was 11.2 ± 1.1 kg/h as reported in Table 6.2. Figures 5.15a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 76.

6.23.4 Coker

The C2+ emissions from the Coker were measured from location EV29 on the 21st of June. During this measurement the wind speed was approximately 4.5 m/s, coming from an easterly direction, as shown in Figure 5.27. The average C2+ emission rate measured of the 4 scans taken was 6.7 ± 0.8 kg/h as reported in Table 6.2. Figures 5.27a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 146. The plume extends to roughly 40 m in elevation along the whole Coker area.

6.24 SUMMARY OF THE RESULTS

The DIAL successfully measured the site C2+ emissions from several areas as shown in the Figure 6.1 and the average emission rates from each of these areas are summarised in Table 6.3. Some areas had other site areas as upwind sources and the values reported in the table are after the subtraction of the background contribution. In these cases, the reported stdev is the sum in quadrature of two sets of measurements. For this reason, these reported standard deviations are relatively high, particularly when the emission rates are low.

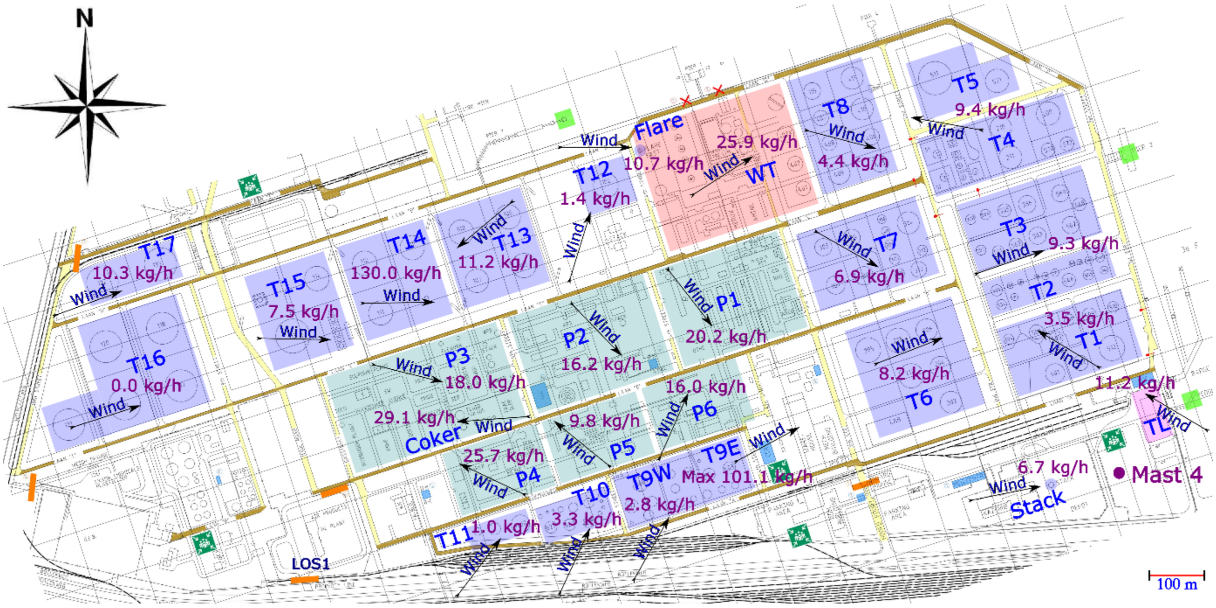


Figure 6.1 Summary of the C2+ emissions expected from the different areas of the site.

The highest single emission source was tank 112 in area T14 with a known issue that the site operator was addressing, therefore this source should be considered as a temporary source. The emissions measured from the flare, the stack on the SE site area, the truck loading area and the Coker can also be considered as temporary sources since the emission rate can vary significantly during the day while the

DIAL measurements cover approximately one-hour period. After the measurement campaign ended we were informed by the site's operator that the content of two tanks (T603 and T614) in the east part of area T9 was 100% cyclohexane. The DIAL laser wavelength used for VOC measurement is not very sensitive to cyclohexane and therefore the correction factor from VOC to C2+ (cyclohexane) is relatively high. Consequently, this is a very uncertain measurement and the average C2+ (cyclohexane) emission rate was 101.1 ± 79.7 kg/h for a 95% level of confidence. Even a small VOC contribution of 0.5 kg/h from tanks nearby would make a significant difference. Therefore, this reported emission rate should only be considered as the maximum possible emission rate for this area, as all the VOC measured is assumed to originate from the two cyclohexane tanks.

The total site emission measured during the three weeks campaign was 211.6 ± 14.4 kg/h excluding the temporary sources and cyclohexane tanks. With the inclusion of the temporary sources (but not the cyclohexane tanks) a total site emission of 399.4 ± 64.4 kg/h was calculated. By adding the estimated maximum emission rate from the two cyclohexane tanks T603 and T614 the total emission rate was 500.5 ± 88.4 kg/h.

Table 6.3 Summary of C2+ emission rate measurements from all the measured areas.

Emission Area	Emission Rate	Standard Uncertainty	95% Level of Confidence
	kg/h	kg/h	kg/h
T1	3.5	0.3	0.8
T2 & T3	9.3	0.8	1.9
T4 & T5	9.4	1.2	3.3
T6	8.2	0.9	2.3
T7	6.9	0.7	1.6
T8	4.4	1.2	3.1
T9 West	2.8	0.3	0.8
T10	3.3	0.5	1.6
T11	1.0	0.2	0.6
T12	1.4	0.2	0.4
T13	11.2	0.8	1.6
T14 - Temp Source	130.0	21.3	59.9
T15	7.5	0.9	2.5
T16	0.0	0.6	1.8
T17	10.3	0.9	2.0
P1	20.2	3.5	9.8
P2	16.2	1.9	4.8
P3	18.0	1.1	2.2
P4	25.7	3.0	7.7
P5	9.8	3.0	7.1
P6	16.0	2.4	5.7
WT	25.9	2.7	5.9
Flare - Temp Source	10.7	0.7	1.4
Stack SE Site Area - Temp Source	6.7	0.8	1.9
Truck Loading - Temp Source	11.2	1.1	2.4
Coker - Temp Source	29.1	3.0	7.3
T9 Est - T603 & T614 Cyclohexane *	101.1	31.4	79.7
Total - No Temp Sources	**211.6**	**7.1**	**14.4**
Total - Including Temp Sources	**399.4**	**22.7**	**64.4**
Total - Including Cycloexane Estimate*	**500.5**	**38.8**	**88.4**

* This estimate should be treated as maximum value if all the VOC assigned to this area was from the two cyclohexane tanks.

7 PROTOCOL ASSESSMENT AND LESSONS LEARNED

7.1 DIAL PROTOCOL

To assist the implementation of the protocol measurement strategy the initial checklist shown in Table 2.1 was continuously updated in the field marking which areas were measured, if the potential upwind sources were measured and further notes such as the wind direction during the measurement periods. The final version of this table at the end of the measurement campaign is shown in Table 7.1.

Table 7.1 Checklist tables showing all the areas to be measured and the ideal wind condition to carry out the measurements.

Nr.	Plant	Locations /LOS	Wind Directions	Ideal WD	VOC Measured?	Upwind Measured?	Notes/Wind
1	Tanks T1	4/8	Any	1)SSE 2)ENE	Y	TL	SE wind shifted more southerly
2	Tanks T2	4/8	Any	1)SSE 2)ENE	Y	T6	Measured with W/SW wind; T2/T3 together
3	Tanks T3	4/8	Any	1)SSE 2)ENE	Y	T7	Measured with W/SW wind; T2/T3 together
4	Tanks T4	4/8	Any	1)SSE 2)ENE	Y	No Need	Measured with E/SE wind; T4/T5 together
5	Tanks T5	4/8	Any	1)SSE 2)ENE	Y	No Need	Measured with E/SE wind; T4/T5 together
6	Tanks T6	4/8	Any	1)SSE 2)ENE	Y	T9/P6 (far)	Measured with W/SW wind
7	Tanks T7	4/8	Any	1)SSE 2)ENE	Y	WT	Measured with NW wind
8	Tanks T8	4/8	Any	1)SSE 2)ENE	Y	WT	Measured with W/NW wind
9	Tanks T9	4/4	SSE/NNW	SSE	Y	T10 & T11	Measured with S/SW wind & W/SW wind
10	Tanks T10	4/4	SSE/NNW	SSE	Y	No Need	Measured with S/SW wind
11	Tanks T11	4/4	SSE/NNW	SSE	Y	No Need	Measured with S/SW wind
12	Tanks T12	4/8	Any	1)WSW 2)SSE	Y	P2	Measured with S/SW wind
13	Tanks T13	4/6or8?	Any	1)WSW 2)SSE	Y	T12	Measured with NE wind
14	Tanks T14	4/6or8?	Any	1)WSW 2)SSE	Y	T15	Measured with W wind
15	Tanks T15	4/7or8?	Any	1)WSW 2)SSE	Y	T16	Measured with W wind
16	Tanks T16	4/8	Any	1)WSW 2)SSE	Y	Offsite	Measured with W/SW wind
17	Tanks T17	4/8	Any	1)WSW 2)SSE	Y	Offsite	Measured with W/SW wind
17	Water Treatment	4/6or8?	Any	1)WSW 2)SSE	Y	T12	Measured with W wind & W/SW
18	Flare	2/4	Any	Any	Y	No Need	Measured with W wind
19	Process Area P1	4/8	Any	1)SSE 2)WSW	Y	T12	Measured with NW wind
21	Process Area P2	4/7or8?	Any	1)SSE 2)WSW	Y	T13	Measured with NW wind
22	Process Area P3	4/7or8?	Any	1)SSE 2)WSW	Y	T14/T15	NW wind shifted more westerly
23	Process Area P4	4/6	N/S/W	SSE	Y	T10/T11	Measured with E/SE wind
24	Process Area P5	4/6	N/S/E	SSE	Y	T9	Measured with SE wind
25	Process Area P6	4/8	Any	SSE	Y	T9	Measured with S/SW wind
26	Truck Loading	3/4?	Any?	SSE to WSW	Y	No need	Measured with SE wind

The DIAL successfully quantified the emission rates from all the 26 planned target areas (green boxes in Table 7.1) from 34 different locations carrying out at least a set of four scans for each measurement. The only exception was area P3 since the wind was variable during the measurement period and with a strong upwind source. Nonetheless, the main source from this area, the Coker was correctly measured on a different day with a set of four scans.

Several areas were measured with a wind direction similar to the expected ideal wind direction, therefore minimising the impact of any potential upwind source. For some areas such as T4, T5, T10, T11, Truck Loading and Flare there was no need to carry out upwind measurements since the wind direction was such that no potential upwind sources were present. T16 and T17 were also measured with an ideal wind direction so that potential upwind sources were from offsite and upwind scans were carried out showing no VOC emissions. For all the other measured areas other plant areas were potential upwind sources that were noted in the checklist table that was also updated once these areas were measured. During the analysis stage it was then decided how to exclude these upwind sources following one or more of the three ways described in Section 3.4:

1) Upwind sources produce localised plumes that are spatially discriminated and are not analysed. This has been applied for example for area T1 where the TL emission was upwind of it but it was not analysed by stopping the analysis range up to about 200 m from the DIAL, see Figure 5.14.
2) Upwind sources are separately measured and subtracted from the area under investigation. This was the case for areas T8, T9, P2, P4, P5 and P6 with the emission rates calculated by subtracting the contribution from the upwind areas reported in Table 7.1.
3) Upwind sources are more than ~300 m away from the measuring plane and it is reasonable to assume the emission are diffuse such that the concentration is lower than the detection limit/noise or constant in the analysis range and therefore subtracted as a fixed background slope. This was the case, for example, for area T6 measurements with the potential upwind sources P6 and T9 being more than 500 m away from the measuring plane, see Figure 5.19. The measured plumes, see Figures 5.19a and 5.19b, were also localised and small enough to be unlikely associated to sources more than 500 m away from the measuring plane. The emission rate from these localised plumes from T6 was also lower than the potential upwind sources emission rates. Another example is area T7 with a small localised plume with an average emission rate much lower than the emission rate expected from WT upwind contribution that was take into account with the background slope subtraction. Other areas where this approach has been used were: T2, T3, T12, T13, T15, WT and P1.

For area T13 the third method was used and it is worth noting that in this case a second measurement along LOS2 was made to separate emissions from the tanks in area T13, see Figure 5.25. No emission was measured along LOS2 confirming the assumption that the upwind source T12 was correctly excluded from the measurement along LOS1, which is further downwind with respect to LOS2. Area T14 was the highest emission source on site and when it was measured T15 was potentially an upwind source. In this case it is possible that the third method would apply but it is difficult to assess if it would be more accurate to subtract T15 upwind contribution according to method 2. It was chosen to report T14 emission rate without subtracting T15 emission rate mainly because this was very low, 7.5 kg/h, particularly when compared with T14 stdev of 38.3 kg/h.

The repetition of extra sets of measurements of the same area from different location or on a different day was not required by the operator for this field campaign. Nonetheless some areas such as WT and T9 were repeated as part of the objective to carry out measurements at the same time as other measurement techniques involved in this field validation campaign.

All the data quality assurance and quality checks described in the protocol and briefly summarised in Section 3.6 were successfully carried out on a daily basis over the duration of the campaign.

Air samples were collected at different locations providing an indication of the actual speciation of the emission sources sampled by the DIAL.

7.2 DIAL METEROLOGICAL DATA AND COMPARISON TO WIND LIDAR

A logarithmic wind profile is typically used to describe the vertical distribution of the wind by using at least two wind speed sensors at different heights preferably located in an unperturbed area. During this field validation campaign four sensors were used, mounted on a 12 m fixed meteorological mast (Mast 4) located at the southeast corner of the site as reported in Section 4. A wind Lidar sensor was deployed at the same location by the Institut national de l'environnement industriel et des risques (Ineris) and the wind Lidar data from 40 m to 200 m were made available to all the participants. These data were recorded with a minute interval from late 13th June to the 21st June. Table 7.2 shows the average wind Lidar speeds at 40 m, 70 m, 90 m and 120 m measured over several scan periods at six different DIAL locations. For the same scan periods the wind speed at 40 m, 70 m, 90 m and 120 m can be calculated using the logarithmic profile obtained by fitting the wind speeds measured by Mast 4 at elevations of 3.4 m, 6.2 m, 9.0 m and 11.9 m. The differences between the Lidar data and Mast 4 logarithmic fitted profiles are very small, up to a maximum of about 10% for locations EV18 and EV24 as can be seen in Table 7.2. The average difference over the 27 scans between the Lidar and Mast 4 wind speeds at 120 m was only 2.2% which is remarkably small considering the top sensor on Mast 4 was at an elevation of 11.9 m. Moreover, wind Lidar data also has associated uncertainties in the reported elevations, wind speeds and directions that should be taken into consideration when comparing the two datasets.

Table 7.2 Wind Lidar data compared with Mast 4 logarithmic fitted wind profiles over several scan periods at six different DIAL locations for wind speeds at elevations of 40 m, 70 m, 90 m and 120 m.

Day	Location	Start Time	End Time	Lidar Wind Speed (m/s)				Mast 4 Wind Speed (m/s)				Lidar-Mast 4 Wind Speed Difference (%)			
				120 m	90 m	70 m	40 m	120 m	90 m	70 m	40 m	120 m	90 m	70 m	40 m
14	EV16	08:54	09:45	3.83	3.84	3.84	3.71	3.87	3.78	3.71	3.54	**-1.0**	**1.4**	**3.5**	**4.9**
14	EV18	12:28	13:38	4.68	4.59	4.53	4.41	4.26	4.17	4.08	3.89	**9.8**	**10.1**	**11.0**	**13.2**
15	EV21	13:33	14:23	9.65	9.48	9.33	8.77	9.73	9.36	9.04	8.33	**-0.8**	**1.2**	**3.2**	**5.3**
16	EV24	09:56	10:48	7.25	7.01	6.91	6.39	6.59	6.39	6.22	5.83	**10.0**	**9.6**	**11.2**	**9.7**
20	EV27	10:40	13:13	4.97	4.86	4.79	4.51	5.00	4.84	4.70	4.40	**-0.5**	**0.4**	**1.9**	**2.5**
21	EV30	11:43	12:33	5.05	4.96	4.96	4.88	5.30	5.15	5.02	4.74	**-4.6**	**-3.8**	**-1.3**	**2.9**
Average All Scans (27)				5.89	5.76	5.70	5.41	5.76	5.59	5.43	5.09	**2.2**	**3.2**	**4.9**	**6.2**

The overall averages over the 27 scan periods are also reported in this table.

Table 7.3 shows the ratio between the average Lidar and Mast 4 wind data at 40 m and 120 m over the same scan periods at six different DIAL locations. For each location the stdev is also reported which represents the variability of Lidar/Mast 4 wind speed ratio over the four to six scans carried out at each location. The overall averages and standard deviations over the 27 scan periods are also reported. The observed variability at each location can be up to about 10%, this is approximatively the expected contribution of the wind speed to the average emission rate variability, i.e. the emission rate stdev measured at each location. As mentioned in the previous paragraph, wind Lidar data also has associated uncertainties and their contribution is included in the stdev reported in Table 7.3.

Table 7.3 Average ratio and stdev between the Lidar and Mast 4 extrapolated wind data at 40 m and 120 m over same scan periods at six different DIAL locations.

Day	Location	Start Time	End Time	Lidar 40m/Mast 4 40m		Lidar 120m/Mast 4 120m	
				Average	St Dev (%)	Average	St Dev (%)
14	EV16	08:54	09:45	1.05	6.9%	1.00	9.5%
14	EV18	12:28	13:38	1.13	0.8%	1.10	5.1%
15	EV21	13:33	14:23	1.05	7.2%	0.99	10.4%
16	EV24	09:56	10:48	1.11	12.1%	1.11	11.3%
20	EV27	10:40	13:13	1.03	5.6%	1.00	8.1%
21	EV30	11:43	12:33	1.03	2.2%	0.96	6.3%
Average All Scans (27)				**1.07**	**7.6%**	**1.03**	**9.9%**

The overall averages over the 27 scan periods are also reported in this table.

The DIAL average emission rate is obtained multiplying all points within the measured gas concentration profile by the fitted logarithmic wind speed profile. Each elevation point has an associated uncertainty due to the wind speed as reported in Table 7.2 that could have different values and signs at different elevations and therefore the overall wind profile uncertainty can be expected to be lower than the uncertainty reported for a single point in Table 7.2. If this is the case, it is also likely that the random variabilities reported in Table 7.3 have components that are uncorrelated at different elevations. Therefore, the overall fitted logarithmic wind speed profile variability contribution to the average emission rate variability can be expected to be lower than the variability reported for single points in Table 7.3.

These results show that the uncertainty and variability due to fitted logarithmic wind speed profile, potentially one of the main sources of uncertainty of a DIAL measurement, can be relatively low for a set of four DIAL scans. Each DIAL scan consists of a concentration plane that is measured over the whole scan period of about 10 minutes, therefore the wind speed uncertainties and variabilities reported in Tables 7.2 and 7.3 over a set of at least four scans for each location are continuously sampled by DIAL concentration measurements. This would have not been the case if the DIAL measurement was a snapshot, i.e. a few seconds concentration measurement every several minutes. This would mean that only several seconds of the wind speed uncertainty and variability reported in Tables 7.2 and 7.3 would have been sampled with only four scans. In this case the number of scans should be higher in order to have a statistical significant sample of the wind speed uncertainty and variability reported in Tables 7.2 and 7.3.

The continuous measurement of the emission concentration over the period the wind is averaged to calculate the mass emission rate. This is the main reason the DIAL method is typically less affected by meteorological conditions when compared to other methods that use wind measurements for the calculation of mass emission rates. This has been shown during the first CEN validation study using controlled releases but also during other intercomparison and validation studies reported in Section A.6. All these results confirm that the DIAL provides measurements of mass emission rates which are linear with release rate, fall within the stated variability for the measurements, and most critically, that the systematic biases in the DIAL measured emission estimates are very low, typically less than 4%. Each of the controlled release studies showed that the dominant DIAL uncertainties sources had a random behaviour since the sum of all the controlled release emission rates was always very close to the sum of all the reported DIAL emission rates. This also simulates DIAL measurements of different areas on a site that are then summed together to obtain an estimate of the total emission rate. Therefore, since typically the dominant DIAL uncertainties sources have a random behaviour the reported total emission rate as a sum of several sets of at least four DIAL scans can be expected to have significantly lower associated uncertainty in comparison to each independent set of measurement. This is consistent with the 95% level of confidence reported in Table 6.3 for each set of measurement and for the total site emission. For the total site emission (without temporary emission sources) this is only about 7% of the reported value while no single site area measured by the DIAL has such a low 95% level of confidence.

At a close range from the emission source the wind field could potentially have a complex behaviour due to the presence of buildings increasing the uncertainty in the determination of the emission rate. This can be reduced by deploying a portable wind sensor along the DIAL measuring LOS to either use this wind speed for the wind profile determination or to modify the wind profile derived from the unperturbed fixed mast sensors to match the portable wind speed at the portable elevation. This can be achieved by extrapolating unperturbed wind speeds at a few elevations using the Mast 4 fitted logarithmic profile and then calculating a new fitted logarithmic wind profile using the extrapolated points and the portable wind sensor. This method was applied several times during this campaign, see Table 6.1, when the local portable wind speed was significatively different from the Mast 4 unperturbed wind speed at the same elevation. The extrapolated elevations used here were 30 m, 60 m and 90 m for measurements downwind of tank areas and 40 m, 80 m and 120 m for measurements downwind of process areas. The new logarithmic wind speed profile calculated using the wind speeds at these elevations and the portable wind speed at 2.3 m has the following characteristics:

- At 2.3 m the wind speed matches the speed measured by the portable sensor.
- As the elevation increases the effect of the local wind speed measured by the portable sensor on the wind speed profile decreases when compared to the Mast 4 unperturbed wind speed profile.
- At the first extrapolated elevation used (30 m or 40 m at this site) the wind speed is very close to the unperturbed wind speed measured by Mast 4. This elevation is therefore chosen to be representative of the obstacle elevation, for example 30 m for tanks, where it is reasonable to expect the wind speed being close to the unperturbed wind speed measured by Mast 4.

- At the second extrapolated elevation used (60 m or 80 m at this site) the wind speed matches the unperturbed wind speed measured by Mast 4.
- As the elevation increases from the second extrapolated elevation to the third extrapolated elevation (90 m or 120 m at this site) the wind speed overestimation of the unperturbed wind speed measured by Mast 4 gradually increases. It is therefore important to assess that no significative gas concentrations are measured by the DIAL at elevations higher than the second extrapolated elevation.

Table 7.4 shows the average VOC emission rates and standard deviations reported at six different DIAL locations for which the wind Lidar data has been analysed (these are the same values as reported in Table 6.1). The sensors used for the wind profile calculations are also reported together with extrapolated elevations used from the unperturbed Mast 4 fitted logarithmic profile. The average emission rates and standard deviations were then recalculated using logarithmic wind profiles obtained by fitting the portable wind sensor speed and the wind Lidar speed measured at 40 m and 70 m. These values can be directly compared with the emission rates and standard deviations recalculated using logarithmic wind profiles obtained by fitting the portable wind sensor speed and the unperturbed Mast 4 wind speed projected at 40 m and 70 m. Notably, the difference in emission rate between these two sets of data is smaller than the standard deviations of the measurements. This difference is usually very small in absolute terms (less than 1 kg/h) apart from location EV18 with a difference of 3.5 kg/h.

Location EV18 was also the only location where there was a difference, albeit small (~1.5 kg/h), between the emission rate calculated using the portable wind speed and extrapolated unperturbed Mast 4 wind speed at 40 m, 80 m and 120 m and the emission rate calculated using the portable wind speed and extrapolated unperturbed Mast 4 wind speed at 40 m and 70 m. This is because in the latter case the effect of the portable sensor on the wind speed profile at 40 m is smaller when compared to former case. These measurements were downwind of the process area P4 which has tall buildings and emission measured up to about 50 m. It is therefore plausible that the wind profile that is affected most up to 40 m by the portable sensor wind speed is more representative of the real wind speed. The mass emission rate obtained using the unperturbed Mast 4 fitted logarithmic profile was 35.0 kg/h, therefore the actual emission rate measured downwind area P4 buildings is expected to be lower than this value. Nonetheless, the differences in emission rates calculated using these different wind profiles are all smaller than the measured stdev. This, as mentioned before, encapsulates all the sources of variability occurring during the measurements including the variability in the wind speed used since for each scan a different wind profile is calculated.

Table 7.4 Average VOC emission rates and standard deviations calculated using different wind profiles at six different DIAL locations for which the wind Lidar data has been analysed.

Day	Location	Sensors Used P = Portable M = Mast 4	Emission Rate (kg/h)		P-Lidar @ 40m & 70m Emission Rate (kg/h)		P-Mast @ 40m & 70m Emission Rate (kg/h)		P-Mast P-Lidar Diff (kg/h)
			Average	St Dev	Average	St Dev	Average	St Dev	
14	EV16	P-M @ 30m, 60m ,90m	3.40	0.50	3.32	0.76	3.39	0.49	0.1
14	EV18	P-M @ 40m, 80m ,120m	28.73	4.95	33.71	5.58	30.24	5.34	-3.5
15	EV21	P-M @ 30m, 60m ,90m	7.83	1.53	8.03	1.11	7.83	1.54	-0.2
16	EV24	P-M @ 30m, 60m ,90m	6.65	1.82	7.35	1.95	6.66	1.82	-0.7
20	EV27	M	10.72	0.92	10.90	1.01	10.71	0.80	-0.2
21	EV30	P-M @ 30m, 60m ,90m	9.06	0.93	9.13	1.15	9.05	0.94	-0.1

The sensors used for the wind profile calculations are reported together with extrapolated elevations used from the unperturbed Mast 4 fitted logarithmic profile. The average emission rates and standard deviations are recalculated using two different wind profiles. The first profile is calculated using the portable wind sensor speed and the wind Lidar speed measured at 40 m and 70 m, the second one using the portable wind sensor speed and the unperturbed Mast 4 wind speed projected to 40 m and 70 m.

The emission rate reported for the measurements at location EV27 were calculated using the unperturbed wind speed profile from Mast 4. The main reason for using only Mast 4 wind data was that the local portable wind speed was not significatively different from the Mast 4 unperturbed wind speed at the same elevation. This is confirmed by the fact that when the average emission rate is recalculated using the wind speed profile obtained by fitting the portable wind sensor speed and the unperturbed Mast 4 wind speed at 40 m and 70 m, this is 10.71 kg/h and almost identical to the reported average emission rate of 10.72 kg/h.

The discussion of the results presented in Table 7.4 indicates that for most DIAL measurements the use of different wind profiles is more a refinement than a necessity. As described before, the uncertainty and variability due to fitted logarithmic wind speed profiles can be relatively low for a set of four DIAL scans since the gas concentration is continuously measured over the period the wind is measured and averaged to calculate the mass emission rate. This variability is then encapsulated in the reported mass emission measurement stdev which is typically higher than the mass emission rates differences observed using different wind profiles.

The first CEN validation study using controlled releases, and also other intercomparison and validation studies reported in Section A.6, showed that the dominant DIAL uncertainties sources had a random behaviour, not only the wind speed profiles as demonstrated above. The most important factor that allows a set of four DIAL scans to be a statistically significative sample minimising the measurement uncertainty is, apart from the continuous concentration sampling over the period the wind is measured and averaged, the DIAL's specific knowledge of the plume location in space. Table 7.5 shows the average VOC emission rate and stdev reported at seven different DIAL locations (these are the same values as reported in Table 6.1). From the plots presented in Section 5 of the plumes observed at these locations it can be inferred that centre of mass of these plumes were approximatively between 10 m and 15 m. The average emission rates and standard deviations were then recalculated using the fixed wind speed measured by the top sensor of Mast 4 at 11.9 m. Notably, the difference in emission rate between these two sets of data is smaller than the measurements standard deviations confirming that the use of logarithmic wind speed profiles is mostly a measurement refinement if the plume location is known.

Table 7.5 Average VOC emission rates and standard deviations calculated using the fitted logarithmic wind profile and the fixed wind speed measured by the top sensor of Mast 4 at 11.9 m.

Day	Location	Reported Emission Rate (kg/h)		Mast 4 12m Speed Emission Rate (kg/h)		DIAL-12m Speed Diff (kg/h)
		Average	St Dev	Average	St Dev	
9	EV07	124.76	38.26	119.82	32.76	4.95
14	EV18	28.73	4.95	32.75	5.46	-4.02
15	EV21	7.83	1.53	7.16	0.75	0.67
16	EV24	6.65	1.82	6.54	1.93	0.11
20	EV27	10.72	0.92	10.36	0.83	0.37
21	EV30	9.06	0.93	9.56	0.64	-0.50
22	EV33	10.00	1.89	11.80	2.34	-1.80

Without the knowledge of the plume location a set of several scans could have a significative bias if the incorrect plume elevation was inferred, for example 50 m in the case of the measurements reported in Table 7.5. Then in order to attempt to minimise this bias uncertainty several more scans would be necessary over several different days and meteorological conditions if the plume elevation varies during these different sets of measurements in such a way to randomise the uncertainty from the lack of knowledge of the plume location. In this case when different emission rates are measured on different days and meteorological conditions it would be difficult to assess if it was because the uncertainty bias due to the lack of knowledge of the plume location was different or because the source emission rate varied. On the other hand, the DIAL method, as a consequence of the knowledge of the source location, is well suited to assess temporally varying sources. This has demonstrated several times in past for example measuring ship loading emissions and batch processes such as delayed Cokers.

7.3 WIND DIRECTION

The sensor selected for the wind direction was:

- A local wind sensor (DIAL or portable) when it better represented the local wind direction, particularly when the main emission plume is at low elevation, affected by the local terrain and buildings.
- The top sensor from Mast 4 when the plumes were elevated and in an area where there was not much local building obstruction or when it was not observed any significant wind direction difference between the wind sensors deployed.

The assumptions made in the DIAL protocol when selecting the wind sensor to be used for the wind direction measurement were demonstrated during the first CEN validation study using controlled releases. It was also demonstrated that when two sets of wind directions from different sensors are used to calculate the average emission rate, the set of data with significantly lower stdev should be preferably used.

Table 7.6 shows the average VOC emission rate and stdev reported for the main site source T14 measured from location EV07 using the wind direction from the local DIAL sensor (these are the same values as reported in Table 6.1). The average emission rate and stdev were recalculated using two different wind directions: from the local portable sensor and from Mast 4 top sensor. The difference in emission rate between these three sets of data are negligible, particularly when compared to the measurements' standard deviations. The standard deviations are also comparable confirming that, in this case, there was no significant difference between the choice of a local sensor or Mast 4 sensor located approximatively 1.3 km away from the measured area.

Table 7.6 Average VOC emission rates and standard deviations calculated using wind direction measured from different sensors for area T14 measured from location EV07.

Day	Location	Measured Area	DIAL Wind Dir Emission Rate (kg/h)		Portal Wind Dir Emission Rate (kg/h)		Mast 4 Wind Dir Emission Rate (kg/h)	
			Average	St Dev	Average	St Dev	Average	St Dev
9	EV07	T14 - Main Source	124.8	38.3	123.3	37.2	128.8	40.1

Table 7.7 shows the average VOC emission rate and stdev reported for the water treatment area measured from location EV32 using the wind direction from Mast 4 top sensor (these are the same values as reported in Table 6.1). The average emission rate and stdev were recalculated using the wind directions from the local portable sensor. In this case the Mast 4 top sensor was chosen since the average wind direction during the measurement period didn't show any significant difference when compared to the wind direction measure by the portable sensor. The results in Table 7.7 confirm this choice was correct since the difference in emission rate and stdev between these two sets of data are negligible.

Table 7.7 Average VOC emission rates and standard deviations calculated using wind direction measured from different sensors for the water treatment area measured from location EV32.

Day	Location	Measured Area	Mast 4 Wind Dir Emission Rate (kg/h)		Portal Wind Dir Emission Rate (kg/h)	
			Average	St Dev	Average	St Dev
22	EV32	WT	15.5	3.3	15.7	3.3

The averages reported in Table 7.7 are from emission rates measured over 15 scans. For the individual scans the variability between the emission rates calculated using Mast 4 top sensor and portable sensor was up to a maximum of about 10% while the average emission rate difference was only about 1% as reported in Table 7.7. This confirms the random behaviour of the uncertainties associated with wind direction measurements. The variability in the wind direction measurements, like in the case of wind speed, is propagated to the emission rate measurements since it is continuously sampled by the DIAL concentration measurements over the period the wind is measured and averaged to calculate the mass emission rate.

7.4 LESSONS LEARNED

Overall the protocol was successfully followed and a significant amount of DIAL and wind data was recorded and analysed. This confirmed the validity of several of the DIAL protocol strategies and technique assumptions as discussed in previous Sections.

It is part of the DIAL protocol to discuss with site operators the type of emission sources and interfering species before the campaign and on a daily basis since this would allow to optimise the measurement approach and strategy. In this case unfortunately it didn’t happen mainly because the measurement campaign was organised on behalf of all participants by Bureau Veritas. While this was very useful and successfully facilitated the execution of the measurements, it also meant that NPL personnel had no daily communication with the main site contact and site operators. This overall was not an issue apart from the measurement of the east part of T9 where the composition of two tanks was later found to be 100% cyclohexane. Because the DIAL generic VOC measurement is not particularly sensitive to cyclohexene this lead to a very uncertain measurement of this area as described in Section 6.7. With pre-knowledge of these tanks composition, the measurements of this area would have been carried out with a different optimised strategy and the typical DIAL accuracy levels could have been achieved. This reinforces the importance of emission composition knowledge when measuring with DIAL in order to optimise the measurement strategy and to obtain mass emission rates that are as accurate as possible. It also reinforces the need of communication with site operators to obtain precise information on a daily basis regarding the possible emission composition in the areas to be measured.

8 CONCLUSIONS

This field validation programme was aimed to independently assess each technique protocol. DIAL measurements were made by determining the concentration of VOC in vertical measurement planes downwind of the area being measured, and combining these concentrations with wind measurements to determine the emission rate. A total of 154 vertical DIAL scans were made with only three scans not used because of unfavourable wind direction.

Ambient air samples were taken to provide an indication of the VOC speciation around the site and to calculate the scaling factor to go from the standard DIAL VOC emission rate to the actual C2+ emission rate. The measured site-averaged mixture scaling factor was 1.04 ± 0.06 while the specific waste water treatment area scaling factor was 1.68 ± 0.11.

The DIAL was able to measure all the site C2+ emissions divided in several areas. The highest single emission source was a tank in area T14 with a known issue that the site operator was addressing, therefore this source should be considered as a temporary source. The emissions measured from the flare, the stack on the SE site area, the truck loading area and the Coker can also be considered as temporary sources since the emission rate can vary significantly during the day while the DIAL measurements cover approximately one-hour period. The total site emission measured during the three weeks campaign was 211.6 ± 14.4 kg/h excluding the temporary sources and 399.4 ± 64.4 kg/h with the inclusion of the temporary sources. By adding the estimated maximum emission rate from the two cyclohexane tanks T603 and T614 the total emission rate was 500.5 ± 88.4 kg/h.

Overall the protocol was successfully followed and a significant amount of DIAL and wind data was recorded and analysed. These data confirmed the validity of several of the DIAL protocol strategies and technique assumptions as discussed in Section 7.

ANNEX A: DESCRIPTION OF THE DIAL TECHNIQUE

A.1 OVERVIEW OF THE DIAL TECHNIQUE

The Differential Absorption Lidar (DIAL) technique is a laser-based remote monitoring technique which enables range-resolved concentration measurements to be made of a wide range of atmospheric species. This section explains the theory of the DIAL technique and describes the NPL system in detail.

A.2 DESCRIPTION OF THE THEORY OF DIAL MEASUREMENTS

The atmospheric return signal, P, measured by a DIAL system from range r and at wavelength x is given by the Light Detection and Ranging (Lidar) equation, a simplified form of which is given in Equation 1.

$$P_x(r) = E_x \frac{D_x}{r^2} B_x(r) \exp\{-2\int_0^r [\,A_x(r') + \alpha_x C(r')]dr'\,\} \qquad \textbf{(1)}$$

where D_x is a range independent constant, C(r) is the concentration of an absorber with absorption coefficient α_x and $A_x(r)$ is the absorption coefficient due to all other atmospheric absorption, E_x is the transmitted energy and B_x is the backscatter coefficient for the atmosphere.

The equation has three basic components:

- a backscatter term based on the strength of the signal scattering medium
- parameters associated with the DIAL system
- a term which is a measure of the amount of absorption of the signal which has occurred due to the presence of the target species.

In the DIAL technique, the laser is operated alternately at two adjacent wavelengths. One of these, the "on-resonant wavelength", is chosen to be at a wavelength which is absorbed by the target species. The other, the "off-resonant wavelength", is chosen to be at a wavelength which is not absorbed significantly by the target species, and is not interfered with by other atmospheric constituents.

Pairs of on- and off-resonant signals are then acquired and averaged separately until the required signal to noise ratio is achieved.

The two wavelengths used are close together, hence the atmospheric terms $A_x(r)$ and $B_x(r)$ in the lidar equation can be assumed to be the same for both wavelengths. These terms are then cancelled by taking the ratio of the two returned signals.

The path-integrated concentration (CL) may be derived (Equation 2) by multiplying the logarithm of the ratio of the signals by the ratio of the absorption of the two wavelengths by the target species.

$$CL(r) = \frac{1}{2\Delta\alpha} \frac{1}{N} \sum_{i=1}^{N} \log \frac{S_{ON,i}(r)}{S_{OFF,i}(r)} \qquad \textbf{(2)}$$

where N is the number of pulse pairs averaged, $\Delta\alpha = \alpha_{OFF}-\alpha_{ON}$ is the differential absorption coefficient and S represents the received power after energy normalisation of the on- and off-resonant signals respectively.

This path-integrated concentration represents the total concentration of the target species in the atmosphere along the measured line-of-sight out to the range r.

The range-resolved concentration can then be derived by differentiating the path-integrated concentration (Equation 3).

$$C(r) = \frac{dCL(r)}{dr} \tag{3}$$

where C(r) is the concentration at range r along the line-of-sight averaged over the spatial resolution of the DIAL along its line-of-sight (typically 3.75 m).

A.3 DESCRIPTION OF FACILITY OPERATED BY NPL

The DIAL system operated by NPL is housed in a mobile laboratory. It can operate in the infrared and ultraviolet spectral regions allowing coverage of a large number of atmospheric species. A scanner system directs the output beam and detection optics, giving almost full coverage in both the horizontal and vertical planes.

The system also contains ancillary equipment for meteorological measurements, including an integral 10 m meteorological mast with wind speed, direction, temperature and humidity measurements.

The system is fully self-contained, with power provided by an on board generator, and has full air conditioning to allow operation in a range of ambient conditions.

The following sections describe the DIAL system in more detail.

Source
The source employs a combination of Nd-YAG and dye lasers together with various non-linear optical stages to generate the tuneable infrared and ultraviolet wavelengths. The source has a pulse repletion rate of 10 Hz and an output laser pulse duration of ~10 ns. A small fraction of the output beam in each channel is split off by a beam splitter and measured by a pyroelectric detector (PED) to provide a value for the transmitted energy with which to normalise the measured backscatter return.

Detection
The returned atmospheric backscatter signal is collected by the scanning telescope. This directs the collected light into separate paths for the infrared and ultraviolet channels. The returned light passes through band pass filters relevant to each detection channel and is then focused onto the detection elements. Solid-state cryogenically-cooled detectors are used in the infrared channel and low-noise photomultipliers in the ultraviolet.

After amplification the signals from these detectors are digitised using a high speed digitiser. The digitiser is clocked using a clock generator triggered by the same trigger used to fire the lasers. This ensures the range gating is correctly synchronised to the laser pulse transmission. The signals from the PED monitoring the transmitted energy are also digitised and stored.

Data Analysis
The data acquired are analysed, using the DIAL techniques described below, to give the range-resolved concentration along each line-of-sight.

The data analysis process consists of the following steps:
i) Background subtraction
Any DC background value is subtracted from the signals. This measured background takes account of any DC signal offset which may be present due to electronic offsets and from incident background radiation. The background level is derived from the average value of the far field of the returned lidar signal where no significant levels of backscattered light is present.

ii) Normalisation for variation in transmitted energy
The two signal returns are normalised using the monitored values of the transmitted energy for the on and off resonant wavelength pulses. The mean transmitted energy is used to normalise the averaged return signal. For this application, this has been shown to be equivalent to normalising individual shots against transmitted energy and then averaging the normalised values.

iii) Calculation of path-integrated concentration
The path-integrated concentration of the target species, out to the range r, is calculated using equation 2.

The absorption coefficients used in this calculation are derived from high-resolution spectroscopy carried out using reference gas mixtures at NPL.

iv) Derivation of range-resolved concentrations.
The integrated concentration profiles are piecewise differentiated with a selectable range resolution, to give the range-resolved concentration along the line-of-sight, as in equation 3.

v) Calculation of emission rates
Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile. This is carried out using algorithms developed at NPL which reduce artefacts due to the difference in data density at different ranges, due to the polar scanning format of the data. The emission rate is then determined using the concentration profile together with meteorological data.

The emitted rate is calculated using the following mathematical steps:
(a) The product is formed of the gas concentration measured with the DIAL technique at a given point in space, and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.
(b) This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.
(c) This array of results is then integrated over the complete concentration profile to produce a value for the total emitted rate.

Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large spatial variations since, for example, errors in the wind speed in regions where large concentrations are present will significantly affect the accuracy of the results. A logarithmic wind profile is used to describe the vertical distribution of the wind. At least two wind speeds at different heights, usually from sensors on a fixed meteorological mast, are used to calculate the wind profile. The calculated wind field is then combined with the measured gas concentration profile using the procedure described above.

A summary of the ultraviolet and infrared performance capabilities of the NPL DIAL facility are given in Tables A.1 and A.2. The values given in these tables are based on the actual levels of performance of the system obtained during field measurements, rather than calculations based on theoretical noise performances. For simplicity the numbers are presented as a single concentration sensitivity and maximum range values. However, the detailed performance behaviour of a DIAL system is much more complex and there are a number of key points that should be noted:

- The DIAL measurement is of concentration per unit length rather than just concentration. So the sensitivity applies for a specified pathlength – 50 metres in this case. Measurements over a shorter path would have a lower sensitivity, and would be more sensitive over a longer path length.
- Since the backscattered lidar signal varies with range, generally following a $(\text{range})^{-2}$ function, the sensitivity is also a function of range. The sensitivity values given in the tables apply at a range of 200 metres, and these will get poorer at longer ranges.

- The maximum range of the system is generally determined by the energy of the emitted pulse and the sensitivity of the detection system, except in the case of nitric oxide where range is limited by oxygen absorption at the short ultraviolet wavelengths required for this species.
- In all cases the performance parameters are based on those obtained under typical meteorological conditions. For the ultraviolet measurements the meteorological conditions do not have a great effect on the measurements as the backscattered signal level is predominantly determined by molecular (Rayleigh) scattering, and this does not vary greatly. However, in the infrared the dominant scattering mechanism is from particulates (Mie scattering). So the signal level, and therefore the sensitivity, is dependent on the particular loading of the atmosphere, and this can vary dramatically over relatively short timescales.
- The optical configuration of the DIAL system means there is a minimum range between 40-100 m before measurements can be made.

The NPL DIAL has a theoretical range resolution of 3.75 metres along the measurement beam, and a vertical and horizontal scan resolution which can be less than 1 metre at 100 metres. However, the actual range resolution determined by the signal averaging used, will depend on atmospheric conditions and the concentration of the measured pollutant, and may be of the order of 20-30 m.

Table A.1 Ultraviolet capability of NPL DIAL Facility

Species	**Concentration sensitivity (ppb km) (1)**	**Max Range (m) (2)**
NO	1	500
N_2O	10	500
SO_2	3	1000
O_3	1.5	1000
Xylene	1	500
Toluene	0.5	600
Benzene	0.5	600

Table A.2 Infrared capability of NPL DIAL Facility

Species	**Concentration Sensitivity (ppb km) (1)**	**Max Range (m) (2)**
CH_4	20	600
VOCs	3	600
C_2H_6	3	600
C_2H_4	15	600
C_2H_2	3	600
HCl	2	800
N_2O	25	600
CH_3OH	45	500

(1) The concentration sensitivities apply for measurements of a 50 metre wide plume at a range of 100m to 200m from the DIAL, under typical meteorological conditions.

(2) The range value represents the typical working maximum range for the NPL DIAL system.

A.4 GENERAL HYDROCARBON SCALING FACTOR

The DIAL is able to make measurements of a wide range of compounds, including benzene and other aromatics, individual VOCs and total VOCs, see Tables A.1 and A.2. The methodology for obtaining measurements of the total VOC content from C3 to C15 is provided below. It consists of the combination of DIAL measurements with air sampling and GC analysis. The system is able to monitor individual aromatic compounds and VOC species, which have absorption features in the IR and UV spectral regions covered by the DIAL system. NPL has the spectral expertise, access to spectral libraries and an in-house spectroscopic capability to assess the DIAL sensitivity for additional individual species.

The general hydrocarbon measurement listed in Table A1.2 uses an infrared absorption that is similar for all hydrocarbons with three or more carbon atoms, linked to the stretch frequency of the carbon-hydrogen bond. The line strengths for these species are proportional to the number of carbon-hydrogen bonds present and this enables a total mass emission to be determined. As such it provides a measure of the mixture of volatile organic compounds (VOCs) that are present at an oil or petrochemical site. The pair of infrared wavelengths used for this DIAL measurement are selected so that the absorption per unit mass is relatively invariant with respect to the mix of different hydrocarbons that are present. However, the sensitivity of this measurement in terms of ppb of hydrocarbon depends on the mixture of species present, and the value given in the table reflects the typical mix of hydrocarbons found at oil refineries.

Although the general hydrocarbon measurement provides a good estimate of the overall amount of hydrocarbons present, the accuracy of this measurement can be improved, and the total VOC concentration calculated, by combining the DIAL measurements with the results of gas chromatography (GC) analysis of the emitted gases. The standard procedure for this involves taking whole air samples around the site in locations where the DIAL measurements show the emitted plumes are present. The VOCs present in these samples are identified and quantified by GC analysis. The results provide the relative levels of all the VOCs present with a concentration of 0.1 ppb or higher. The results of this analysis are combined with NPL's unique spectral library of quantified infrared absorptions of an extensive set of VOCs to calculate the combined absorption coefficient for the actual VOC mixture present at the site. Appling this absorption coefficient to the DIAL results enables the total VOC emission rates to be calculated.

A.5 RELATIONSHIP BETWEEN EMISSION RATE AND CONCENTRATIONS

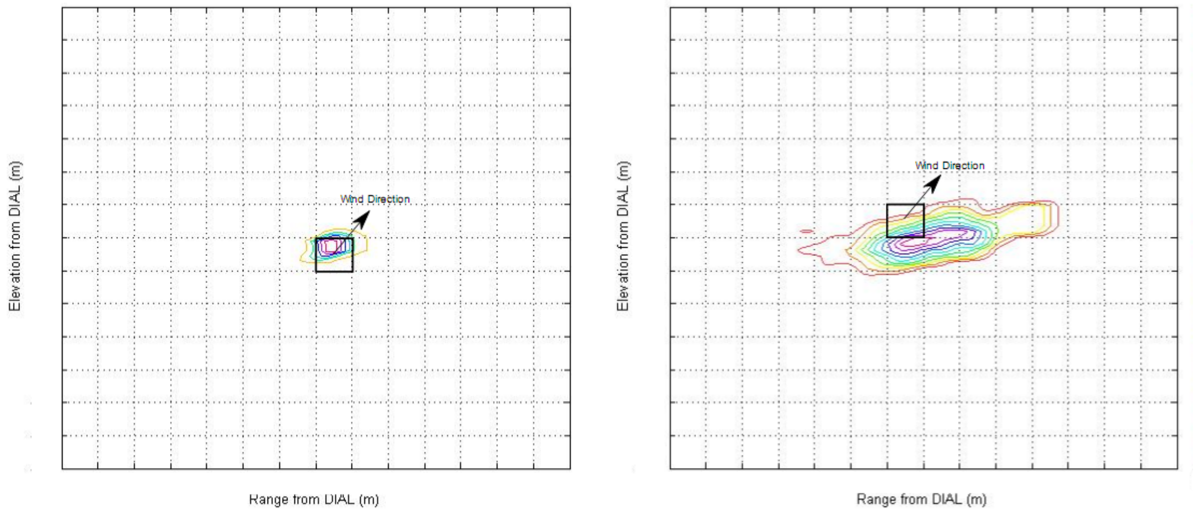


Figure A.1 Illustration of the emission rate calculation approach

Where concentrations are provided as an indication of the levels observed in a measurement scan, the reported concentration in the measurement plane is the maximum concentration seen in a cell in the measurement plane. The resolution of the planes used is equal to the DIAL system resolution and is 3.75 m, so each cell is 3.75 m square. Figure A.1 shows how plume size affects the emission rate that is calculated. The concentration assigned to each cell is multiplied by the perpendicular wind field determined for that cell, and then the individual cell emission rates are summed to give the total emission rate through the plane. This figure shows two example plumes (the cell grids are for indication and are not to scale), one which has a small plume, and therefore a small integrated emission rate, and the other which has a larger plume, and therefore represents a larger emissions rate, although the peak concentration in both is similar, and indeed may even be higher in the small plume than the large plume.

Figure A.2 shows a schematic representation of two measurement plane configurations observing the same plume. One has a nearly perpendicular orientation to the plume, and the wind direction is therefore also perpendicular to the measurement plane. The other is at an angle through the plume, and therefore the wind is not perpendicular to the plane of the measurements. If only the concentration profile were observed the right hand measurement configuration would show a larger plume (as it cuts obliquely through the plume). However, when the wind direction is taken into account, the normal component of the wind vector is used, and this therefore reduces the emission rate determined from this scan, resulting in the same emission rate being determined for both measurement orientations.

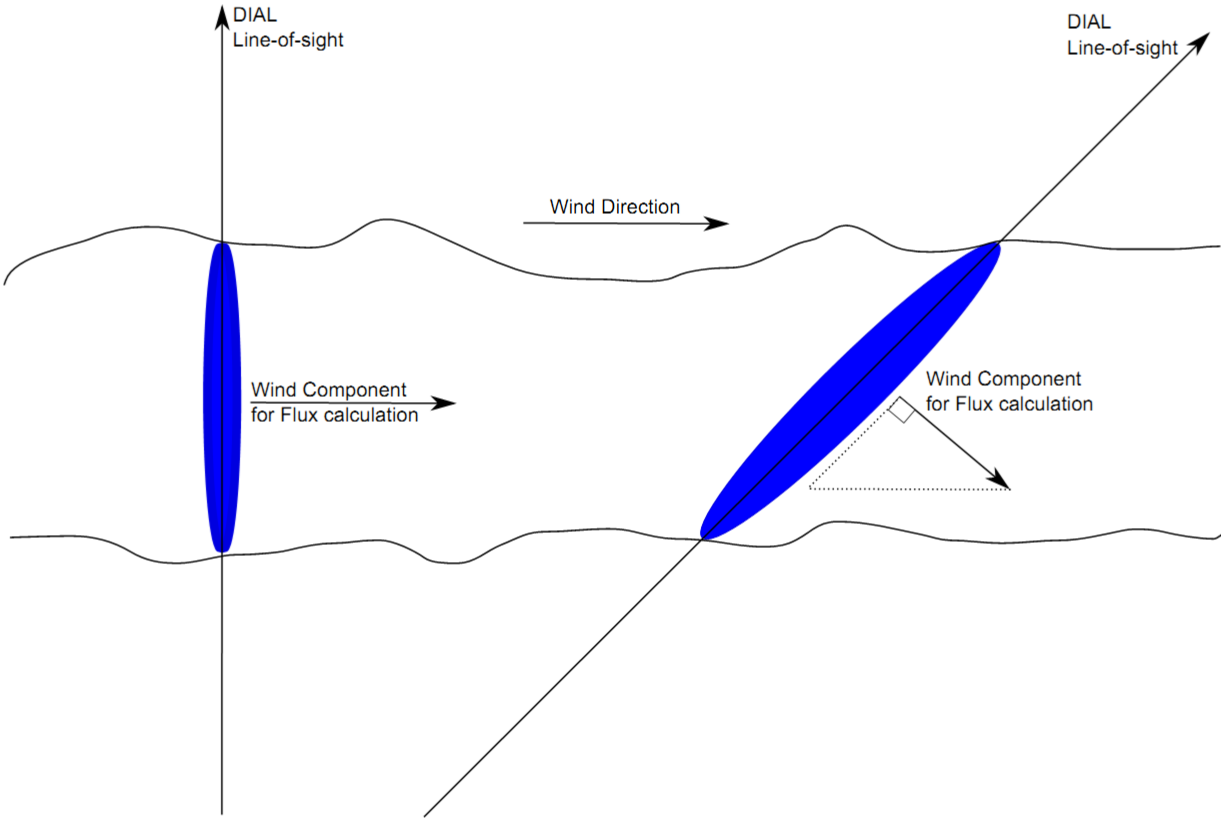


Figure A.2 Schematic showing relationship between emission rate and wind direction

A.6 CALIBRATION AND VALIDATION

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. The gas cells are filled with known concentrations of the target species, obtained from NPL standard gas mixtures, which are directly traceable to national standards. A fraction of the transmitted beam is split off and directed through a gas cell to a PED, in the same way as with the beam for the transmitted energy monitors. This provides a direct measurement of the differential absorption at the operating wavelengths by the target gas. The transmission through the gas cells is continuously monitored during the operation of the system to detect any possible drift in the laser wavelengths. The calibration cells are also periodically placed in the output beam to show the concentration response of the whole system is as expected.

A number of field comparisons have been undertaken to demonstrate the accuracy of the measurements obtained with DIAL. Examples of these carried out by NPL are summarized below:

i) Intercomparisons have been carried out on chemical and petrochemical plants where a large number of different volatile organic species are present. In these intercomparisons, the DIAL beam was directed along the same line-of-sight as a line of point samplers. The point samplers were operated either by drawing air into internally-passivated, evacuated gas cylinders or by pumping air at a known rate, for a specified time, through a series of absorption tubes which efficiently absorb all hydrocarbon species in the range C_2 - C_8. The results obtained for the total concentrations of VOCs measured by the point samplers and those measured by the infrared DIAL technique agreed within ± 15%. The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within ± 20%.

ii) The ultraviolet DIAL system was used to monitor the emission rates and concentrations of sulphur dioxide produced from combustion and emitted by industrial stacks. These stacks were instrumented with calibrated in-stack sampling instruments. The results of the two sets of measurements agreed to within ± 12%.

iii) DIAL Measurements of controlled releases of methane from a stack agreed with the known emission rates to within ± 15%.

iv) The California Air Quality Regulator (SCAQMD) commissioned in 2015 a series of field tests at refineries and small retail petrol stations as part of a larger research programme. The NPL area source facility was used to separately validate several standard methods to determine fugitive and diffuse emissions at these sites. The following techniques were validated NPL IR DIAL, Open-Path FTIR (OP-FTIR) Spectroscopy, Tunable Diode Laser Absorption (TDL) Spectroscopy, and Solar Occultation Flux (SOF). During the SCAQMD blind controlled release study the DIAL demonstrated to be very accurate. The DIAL method was not affected by meteorological conditions and it was able to report emissions from all the test releases. For each release the difference between the released and DIAL rates was less than the stdev of the DIAL measurements, see Table A.3. This includes Release 7 that was quite low and close to the DIAL detection limit that during this experiment can be estimated to be between 0.5 kg/hr and 1 kg/hr. The emission rates measured by the DIAL were also linear as shown in Figure A.3 with an excellent R^2 value of 0.99.

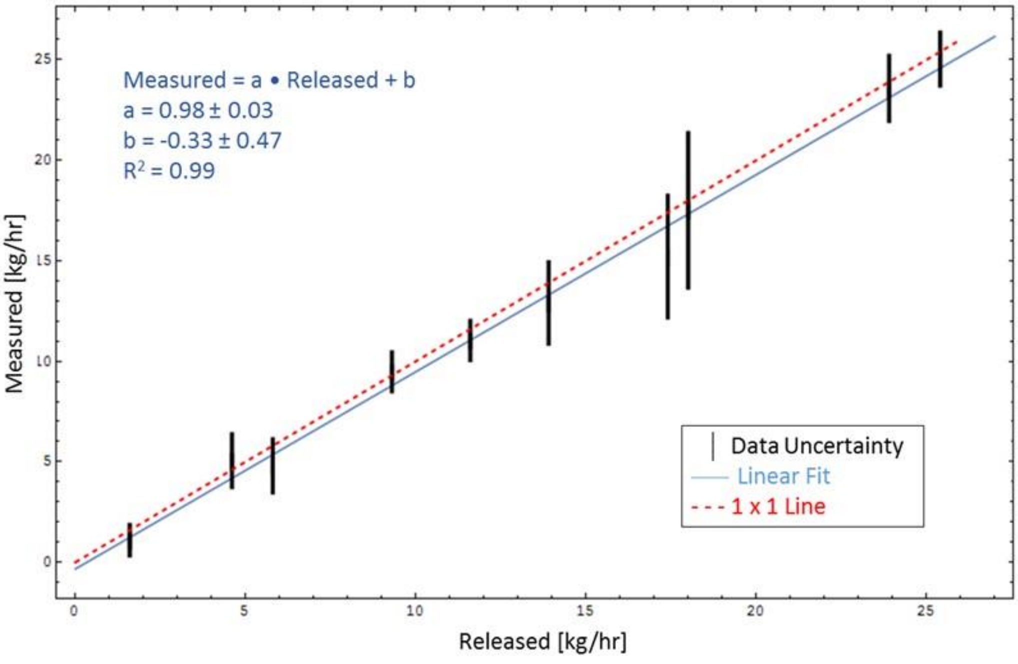


Figure A.3 Comparison of actual propane release rates with DIAL measurements

Table A.3 Summary of determined propane emission rates, for each controlled release the average emission and stdev are reported. Positive and negative % difference between measured and released rates corresponds to overestimation and underestimation of emissions respectively

Notes	Average Flux	Standard Deviation	Scans	Controlled Release	Difference DIAL-Release	
	kg/hr	kg/hr	#	kg/hr	Kg/hr	%
Release 1 13:02-13:56 - 3m	4.8	1.3	6	5.8	-1.0	-17.3
Release 2 14:00-14:55 - 3m	11.0	1.0	4	11.6	-0.6	-4.8
Release 3 15:00-15:58 - 3m	15.2	3.0	3	17.4	-2.2	-12.6
Release 5 10:44-11:43 - 3m	12.9	2.0	4	13.9	-1.0	-7.2
Release 6 11:47-12:40 - 6.4m	5.1	1.3	4	4.6	0.5	10.0
Release 7 12:48-13:41 - 7.9m	17.5	3.9	4	18.0	-0.5	-2.8
Release 8 13:43-14:38 - 7.9m	1.1	0.8	3	1.6	-0.5	-31.1
Release 9 14:44-15:39 - 7.9m	9.5	1.0	3	9.3	0.2	1.9
Release 10 15:44-16:29 - 7.9m	25.0	1.3	3	25.4	-0.4	-1.5
Release 11 16:34-17:16 - 3m	23.6	1.6	3	23.9	-0.3	-1.4

The sum of all the DIAL emission rates and the release rates are 125.7 kg/hr and 131.5 kg/hr respectively, with a difference of only -4.4%. This is equivalent to an approximately ten hour long controlled release experiment but also it simulates DIAL measurements of different areas on a site that are then summed together to obtain an estimate of the total emission rate. This also shows that the dominant DIAL uncertainties sources during this field validation campaign had a random behaviour and therefore by increasing the number of DIAL scans the uncertainty can be expected to decrease accordingly.

v) Validation of the DIAL against controlled releases at NPL. As a part of research and development programmes NPL have a continuous development programme for the DIAL technology and have conducted a number of validation studies using the NPL controlled release facility (CRF). The results of a series of these have been assessed and published in the peer review literature. These results confirm that the DIAL provides measurements of mass emission rates which are linear with release rate, fall within the stated variability for the measurements, and most critically, that the systematic biases in the DIAL measured emission estimates are less than 4% as illustrated in Figure A.4.

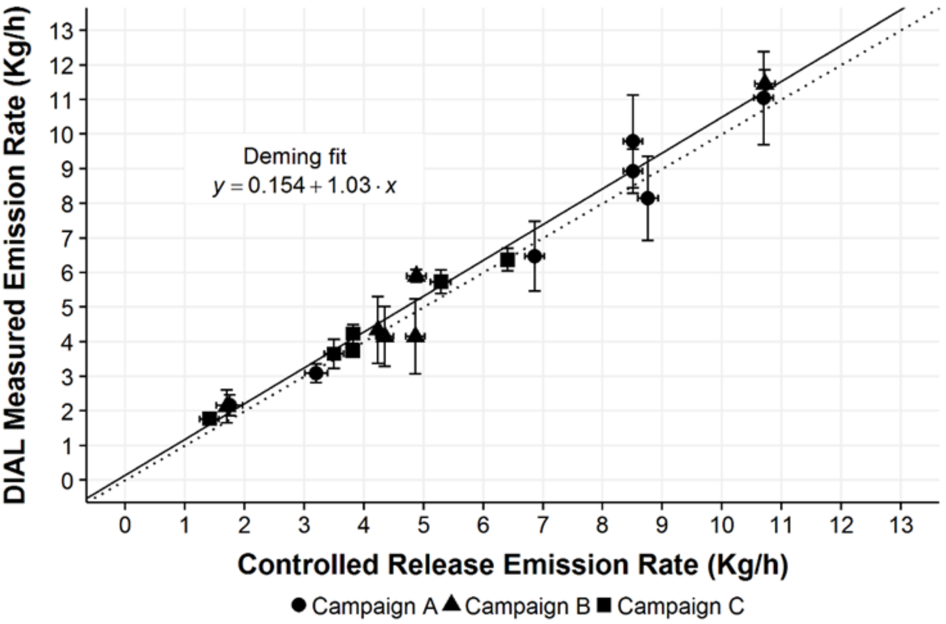


Figure A.4 Results of three validation campaigns comparing the NPL DIAL emission rate measurements to 20 CRF release rates (solid line: Deming regression fit; dotted line: 1:1 fit)

ANNEX B: METEOROLOGICAL MEASUREMENTS

Wind data were collected from a 4-channel fixed mast (located in the southeast corner of the site at the position ‘Mast 4’ identified in Figure 2.1) that supported four wind sensor packages, at 11.9 m, 9.0 m, 6.2 m and 3.4 m local elevation. Figure A2.1 shows an example of the meteorological mast. The DIAL (10.5 m), meteorological station (3 m) and portable (2.3 m) wind sensors were also deployed.

Figure B.1 Example NPL meteorological mast.

The following figures present the average wind roses for the measurement periods on each location from the 21st to the 29th of September.

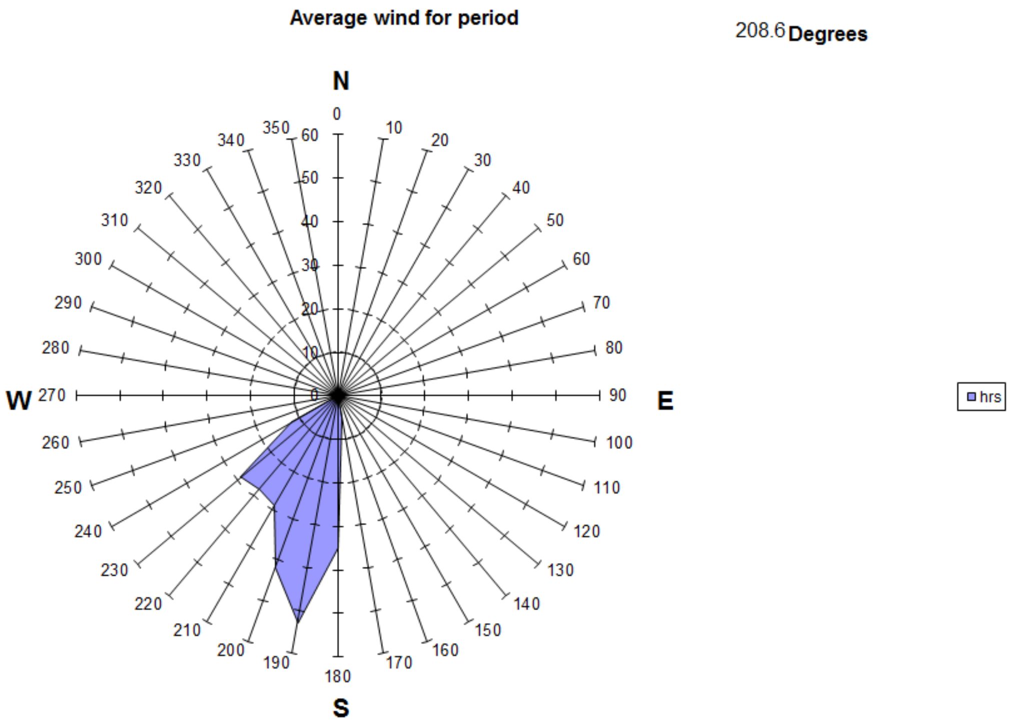


Figure B.2 Wind rose for 22nd September during measurements from BV02, 13:17 - 17:22

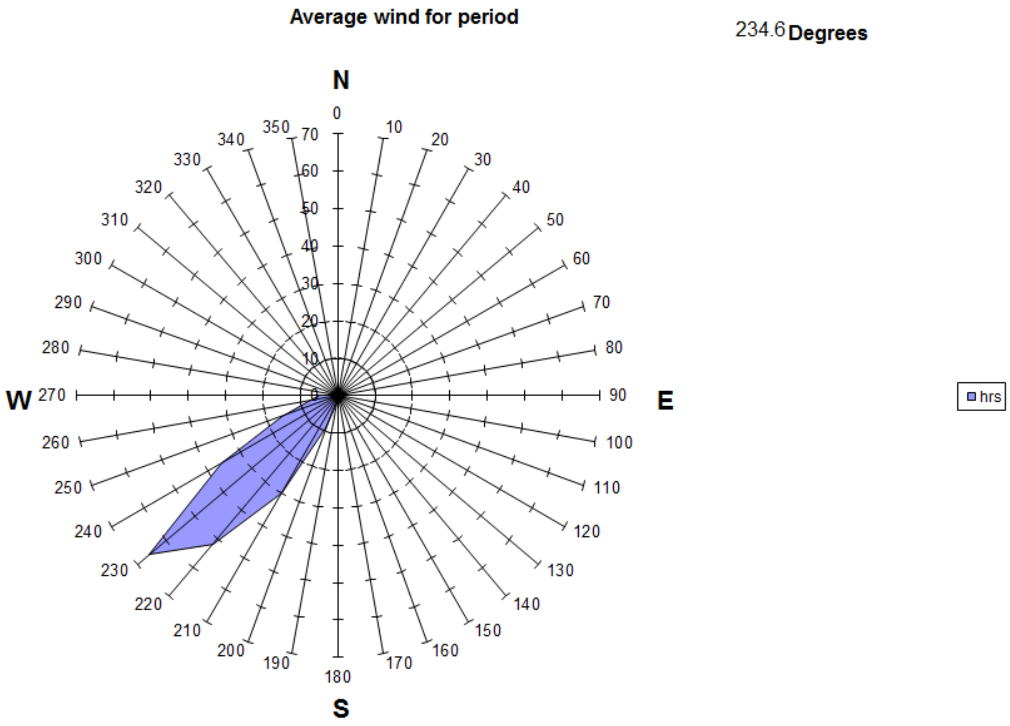


Figure B.3 Wind rose for 23rd September during measurements from BV03, 11:29 - 15:40

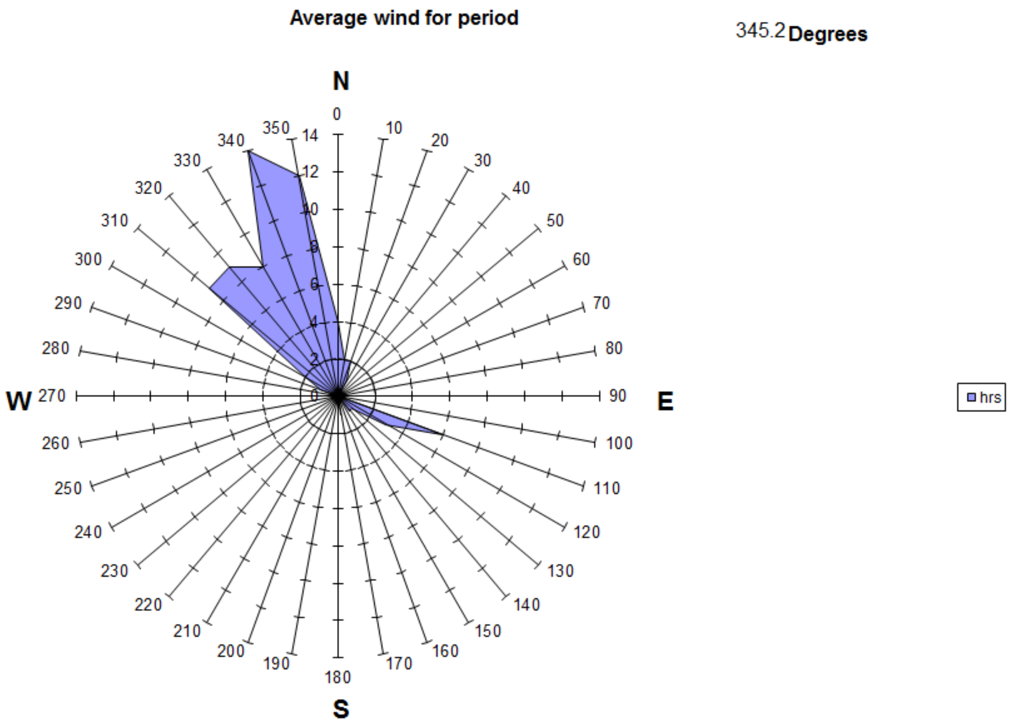


Figure B.4 Wind rose for 26th September during measurements from BV04, 9:41 - 11:06

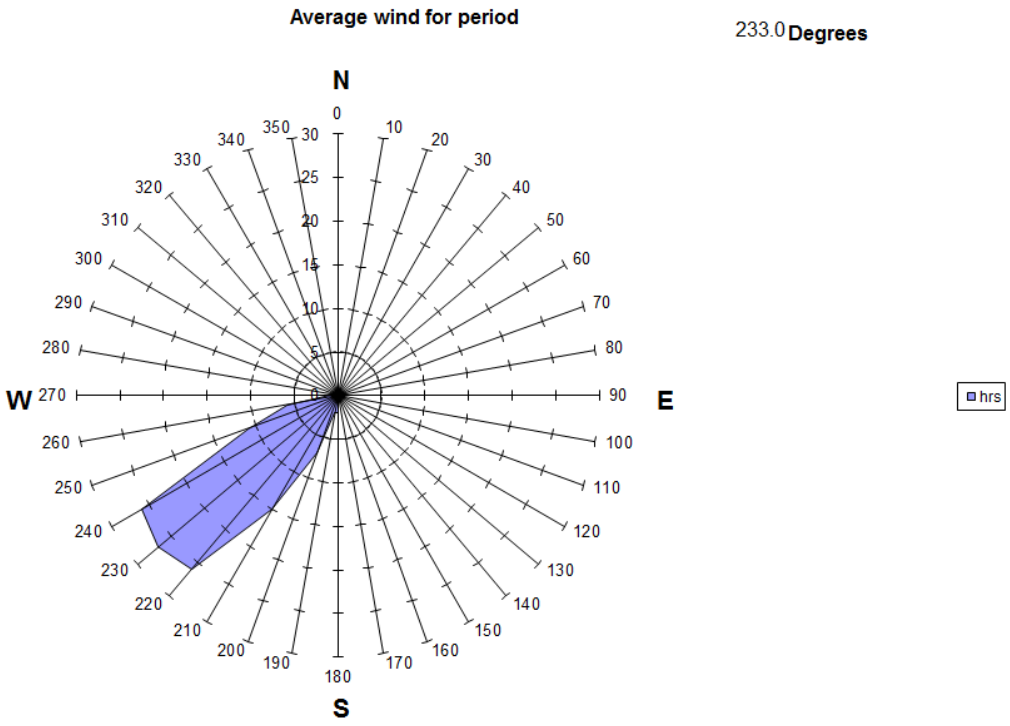


Figure B.5 Wind rose for 26th September during measurements from BV06, 12:22 - 14:35

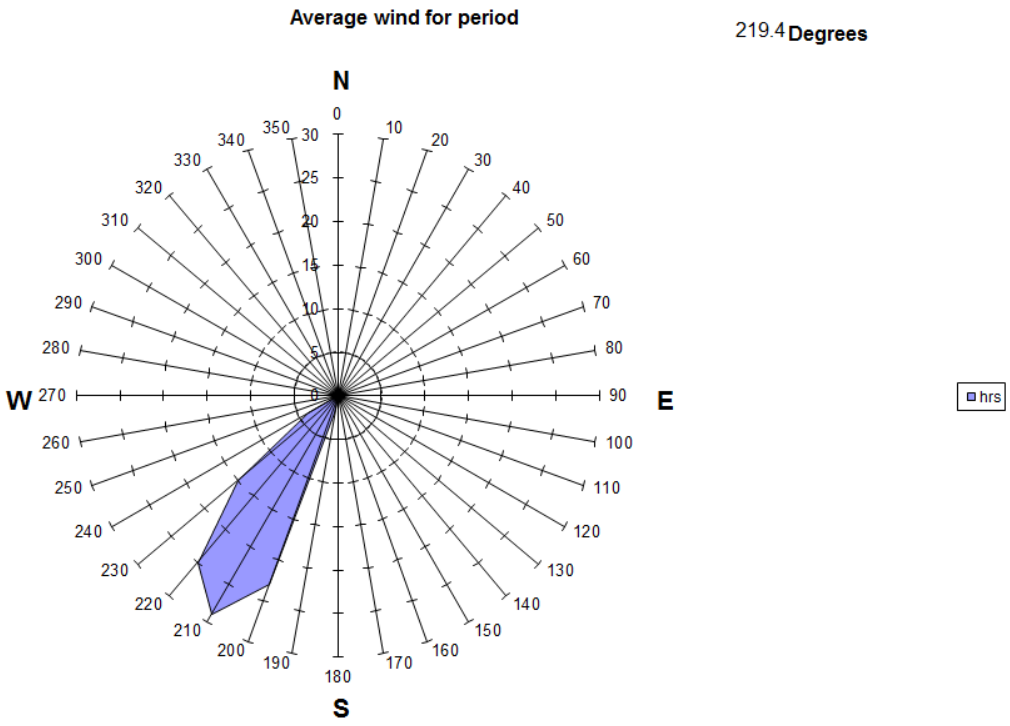


Figure B.6 Wind rose for 26th September during measurements from BV09, 16:05 - 17:50

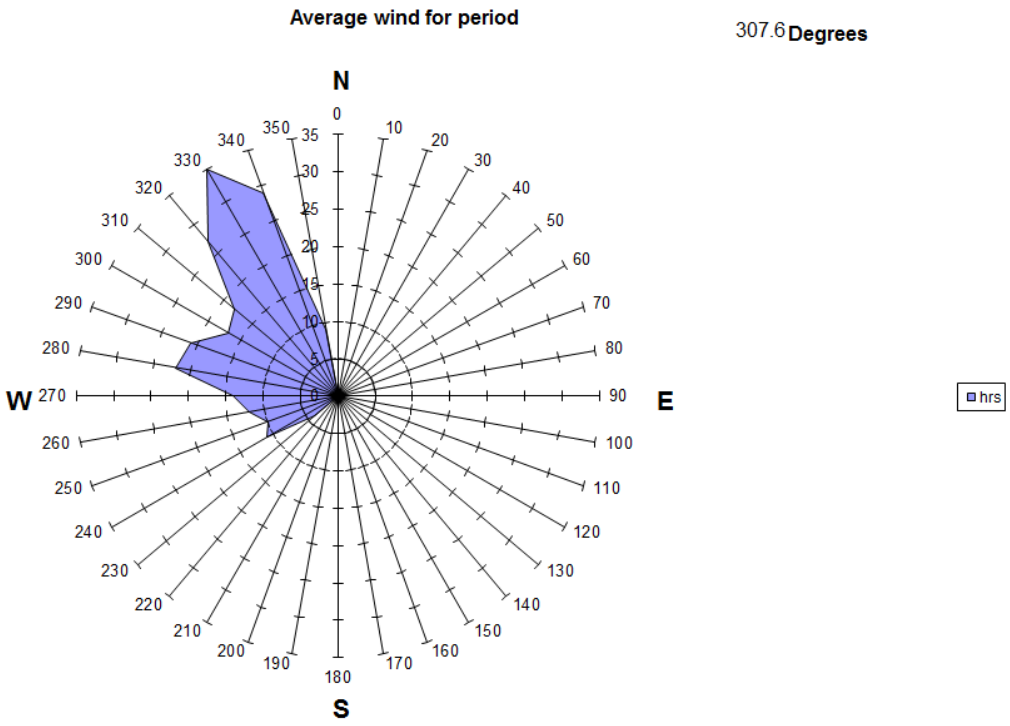


Figure B.7 Wind rose for 27th September during measurements from BV10, 9:14 - 13:26

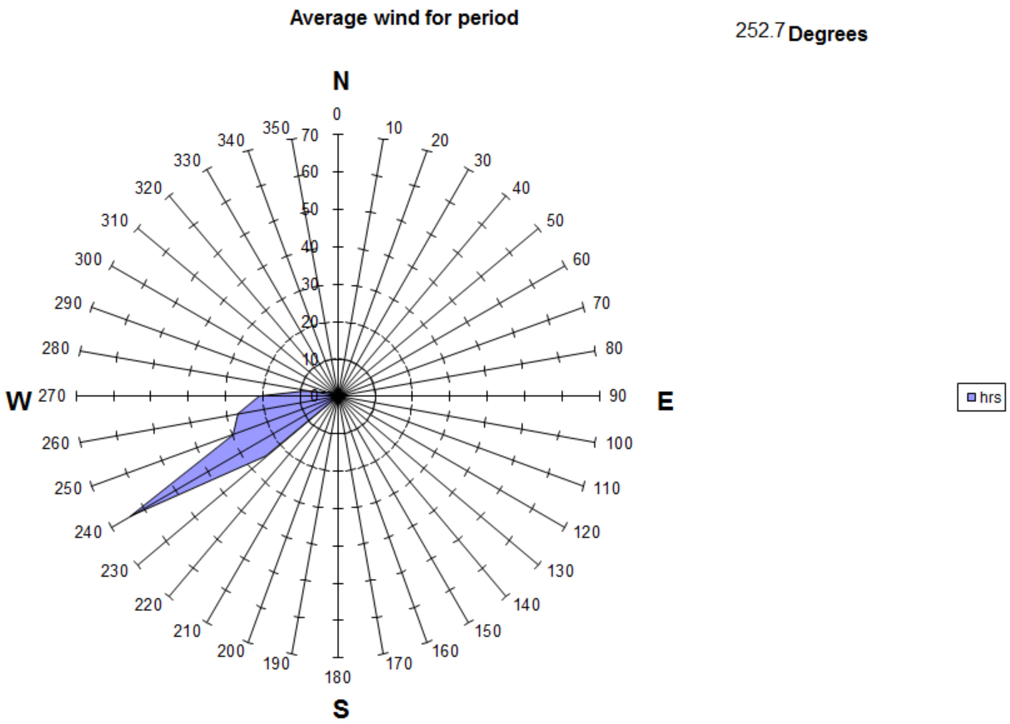


Figure B.8 Wind rose for 27th September during measurements from BV11, 14:20 - 17:44

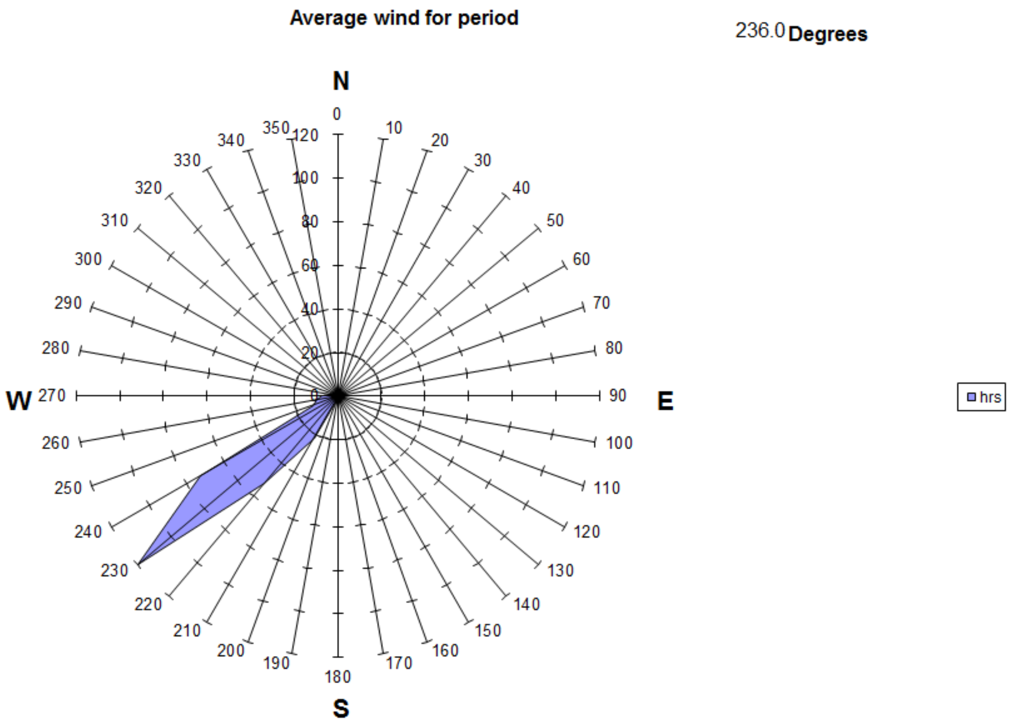


Figure B.9 Wind rose for 28th September during measurements from BV13, 12:05 - 17:48

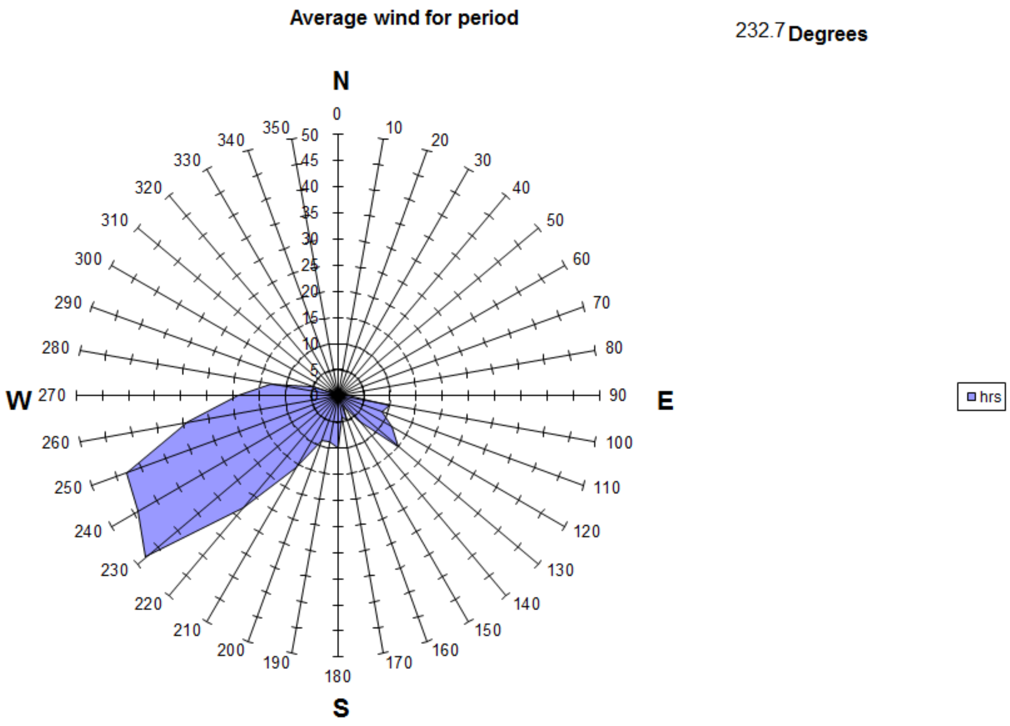


Figure B.10 Wind rose for 27th September during measurements from BV14, 10:51 - 17:21

ANNEX C: VOC SPECIATION USING PUMPED SORPTION TUBES

The DIAL measures C2+ VOCs by measuring the differential absorption of two wavelengths of light. The wavelengths used, at around 3000 cm^{-1}, are chosen to measure, in effect, the C-H stretch in the hydrocarbons for C2 and above. The sensitivity of the DIAL is slightly different for different hydrocarbons, and for example an oxygenated hydrocarbon will give a different absorption per mass than a straight chain alkane. The differential absorption strength used in the DIAL VOC measurements was calibrated to give a mass emission rate for gasoline vapour. A different 'cocktail' of hydrocarbons could give a slightly different response per unit mass. Air samples were taken at locations which would provide an indication of the actual speciation of the emission fluxes sampled by the DIAL. If the actual (relative) composition is known from the air sample analyses, then it is possible to check that the absorption coefficients used are appropriate for the actual hydrocarbon mixture present, and adjust the coefficients if necessary.

Air samples were taken at a total of 8 locations around the site over the course of the measurement campaigns. Figure C.1 shows the locations of each numbered sample taken during the campaign, ET1 to ET8. The figure also indicates the wind direction that was present during each sample. The air samples were taken using pumped Perkin Elmer Automatic Thermal Desorption (ATD).

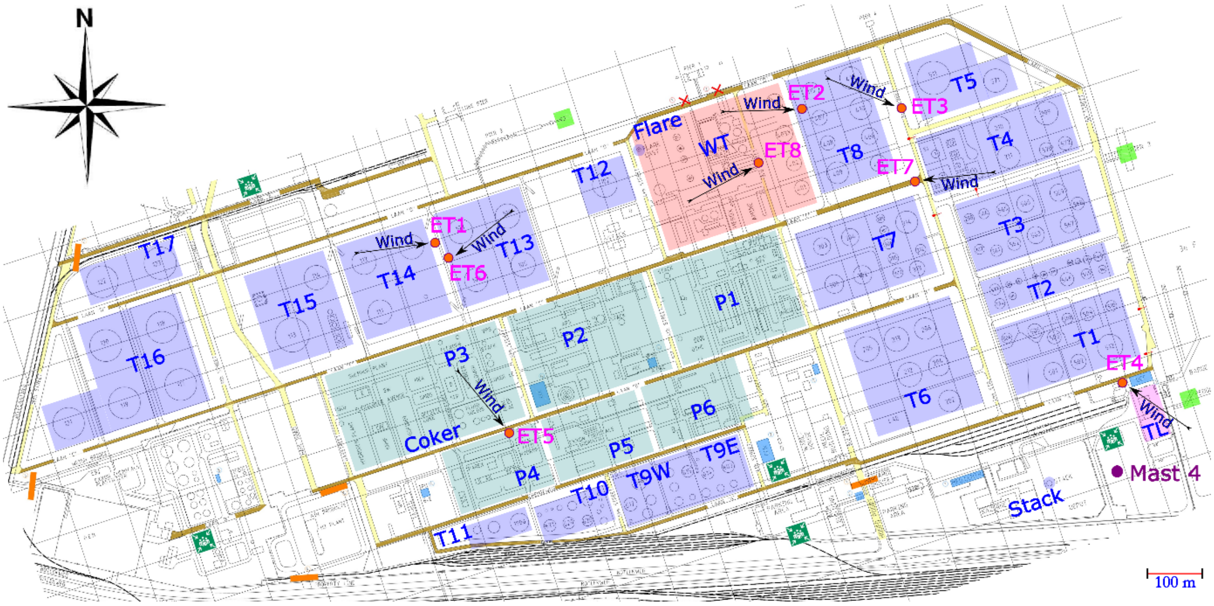


Figure C.1 Pumped sample tube locations and wind directions during campaign.

The ATD tubes were sampled at a flow rate of 40ml/min to enable a reasonable duration of sample to be taken - typically 30 to 40 minutes. The samples were taken at a height of approximately 2 m by mounting the sampling array on a tripod.

The sampler tubes were approximately 6 mm in diameter and 90 mm long. The sampler tubes contained approximately 200 milligrams to 300 milligrams of sorbent. Three sorbent tubes were used: a carbon molecular sieve (CarboSieve S3) to measure the lightest species and two in series containing different sorbent materials, a porous polymer (Tenax TA) and a carbon black (Carbopack X). Different sorbents are needed to cover the diverse boiling point ranges and chemical functional groups of VOCs, and this combination gives a maximum Carbon number range of C_2-C_{22}.

8.1 SPECIATION RESULTS FROM THE ATD TUBE SAMPLES

The tube analyses were carried out by NPL's in house accredited analysis laboratory. Different methods of analysis were used for the CarboSieve S3 and Carbopack X (light hydrocarbons) tubes and the Tenax (heavy hydrocarbons) tubes.

The CarbonSieve S3 and Carbopack X method of analysis was based on EN ISO 16017-2 and was carried out using UKAS (United Kingdom Accreditation Service) accredited method QPDQM/B/526. This method combines Automatic Thermal Desorption with Gas Chromatography (GC), with a Flame Ionisation Detector (FID).

The analysis instrument used is an Automated Thermal Desorber autosampler coupled to a Gas Chromatograph usually with a flame ionisation detector. The VOCs are released from the sampler tube using a heated oven in an inert gas stream of helium. The VOCs are refocused onto a small cold trap prior to transfer onto the gas chromatography column. Generally a coated fused silica gas chromatography column of diameter 320 micrometers and length 60 meters is used to separate the individual VOCs collected. Using VOC standard materials, the identification of the individual VOC components is compared to the column elution time (retention time) of the standard VOC materials. The mass of VOCs collected is quantified using the flame ionisation detector. A series of calibrations standards are used to calibrate the flame ionisation detector response. The concentration of the VOC in ambient air is then calculated using from the mass collected and the volume of air sampled.

A similar procedure was used for the Tenax analyses, but in this case mass spectrometric (MS) detection was used after the GC separation instead of a FID. MS detection provides additional information on the mass of ionized fragments from the different species while retaining the elution separation of the gases, which assists in the species identification within the potentially complex mixture of heavy organic components.

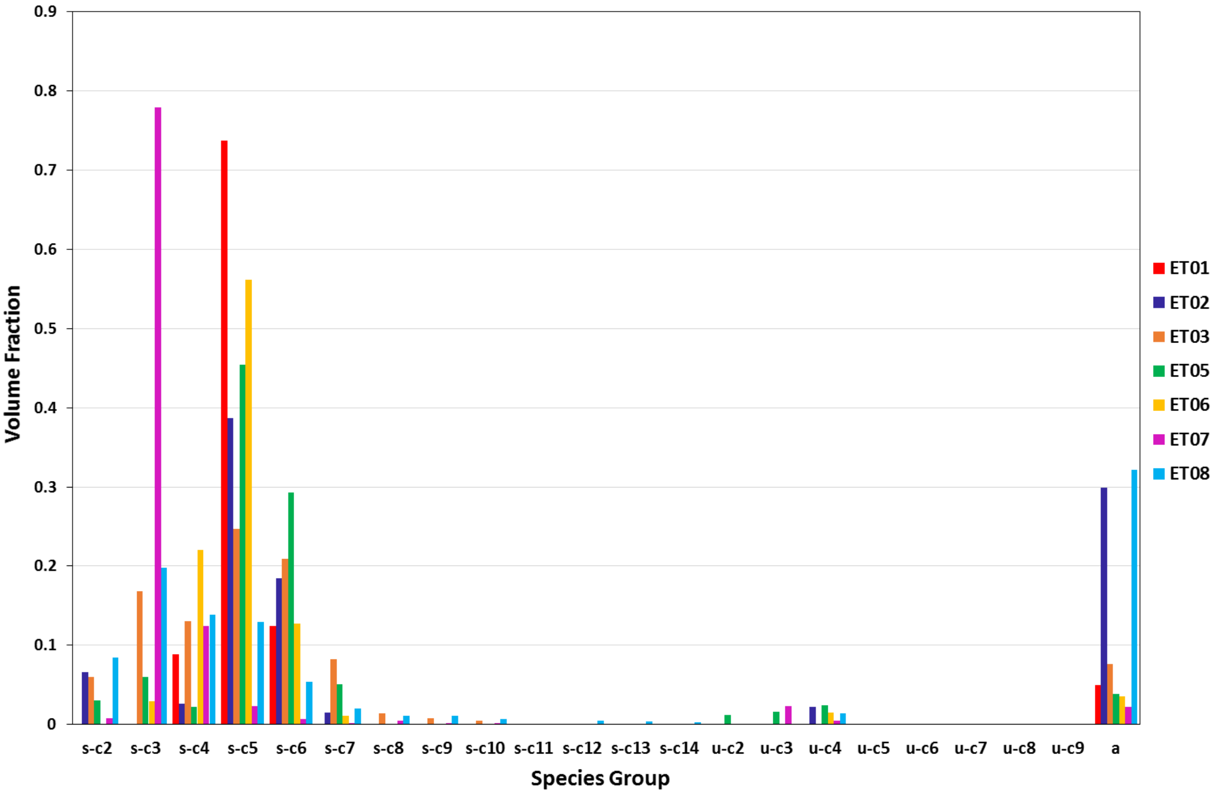


Figure C.2 Volume fraction of VOCs in selected samples

Upon return to NPL it was observed that the tubes used for sample ET04 were slightly damaged, this sample was therefore omitted from the tube analysis. The remaining seven samples were selected for further analysis and to check the DIAL C2+ VOC absorption coefficient. Forty different VOCs were identified in these samples and to simplify the presentation of the data the aliphatic species have been separated into saturated and unsaturated compounds and then grouped by carbon number (from C2 to C10), and the aromatic species have also been grouped together. The summarised results for the selected samples are given in Figure C.2.

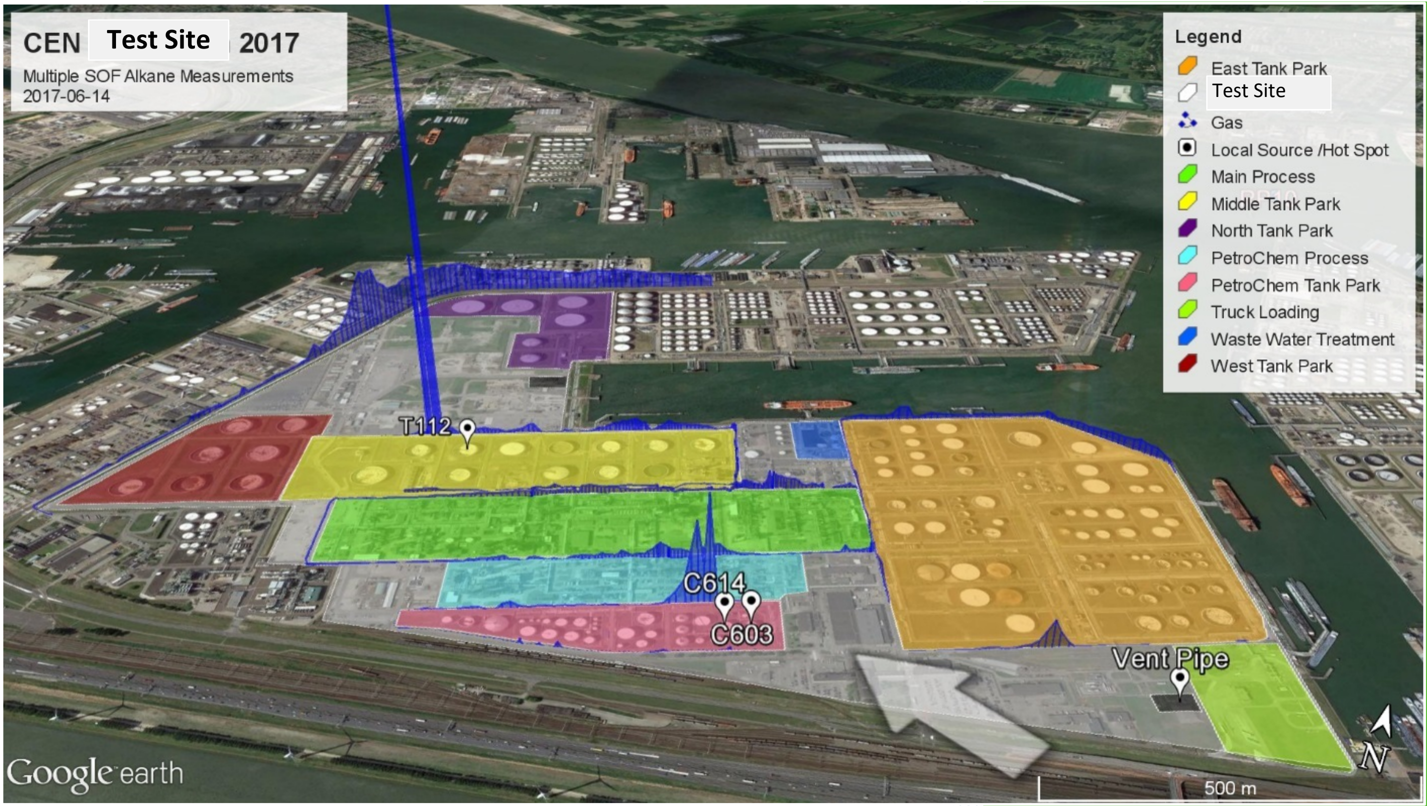
Samples ET02 and ET08 have comparatively higher fractions of aromatic compounds (a). Notably, both these sample were located downwind of the waste water treatment area. The other tube samples were all dominated by C3 to C6 saturated hydrocarbons. Due to the different speciation observed, two different scaling factors from standard VOC to C2+ were calculated; one for measurements of the waste water treatment and the other for measurements of the rest of the site.

As highlighted above, the standard DIAL VOC measurement is targeted on C2+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. For the tube measurements ET02 and ET08, the scaling factor to go from the standard DIAL VOC measurements to C2+ is 1.68 ± 0.11. This scaling factor was applied to the reported DIAL VOC measurements of the water treatment area. For the other tube measurements, the scaling factor to go from the standard DIAL VOC measurements to the measured site-averaged C2+ mixture is 1.04 ± 0.06. Even though this scaling factor is not significantly different from one, it was still applied to all the reported DIAL VOC measurements apart from the water treatment area and the cyclohexane tanks in area T9.

CEN 2017

FluxSense Report

Demonstration of the Solar Occultation Flux measurements at a refinery in the Netherlands as part of CEN validation, CEN WG 38 TC 264



FINAL REPORT

FluxSense AB

5 October 2019

Date: 5 October 2019

Title: Demonstration of the Solar Occultation Flux measurements at a refinery in the Netherlands as part of CEN validation

Authors: Johan Mellqvist[1,2], Samuel Brohede[1,] John Johansson[1], Jerker Samuelsson[1] and Eva Emanuelsson[1]

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This work is carried out as part of CEN WG 38 TC 264.

[Cover: Multiple SOF measurements at a refinery site in port of The Netherlands conducted 14 June 2017. The height of the blue curve is proportional to the atmospheric alkanes gas column (1 m is equivalent to 1 mg/m^2). The wind direction is indicated by the white arrows. Map from GoogleEarth™ 2017.]

Summary

This report describes a validation experiment in the Netherlands 2017 as part of standardizing methods to measure fugitive VOC emissions. The work has been carried out as part of CEN WG 38 TC 264. The campaign was carried out from June 5 to June 22, at a refinery in The Netherlands. The main objective was to demonstrate different methods in a real facility and compare these if possible. The methods should follow their measurements protocol, as derived within the CEN project. This report describes measurements with the Solar Occultation Flux method which was carried out during 8 days. This mobile remote sensing method requires sunny conditions and the possibility of moving around the industrial site, inside and outside the site.

The campaign highlighted the advantages of the SOF technique. During a few days with favorable conditions, i.e. mostly clear sky and distinct wind (in the 1.5-12 m/s range), the emissions from the entire facility and all sub-areas/sources were quantified and hotspots quickly detected due to the mapping ability. SOF measurements were conducted both on site and along the fence-line and spanned a wide range of spatial scales, from small point sources to large multi-site regions.

The sum of the alkane emissions from the 11 identified sources/subareas within the Test Site was 630 kg/h when using median values. An alternative (top-down) approach, where the majority of the total facility emissions was measured along the fence-line, gave very consistent results (666 kg/h). The emissions were dominated by the Middle Tank Park with half of the total emissions. This tank park was, in turn, dominated by a single tank.

In addition to the diffuse area emissions several distinct sources, “hotspots”, were identified within the first three measurement days and compared to independent gas imaging measurements with good agreement. These includes a major leaking tank, two tanks in the petrochemical area, a vent pipe connected to the truck loading an oil pit and the eastern flare (intermittent source).

Table of Contents

1 Introduction

This report describes a validation experiment as part of standardizing methods to measure fugitive VOC emissions. This work is carried out as part of CEN WG 38 TC 264. The campaign was carried out from June 5 to June 22 2017 at a refinery in The Netherlands. The main objective was to demonstrate different methods in a real facility and compare these if possible. The methods should follow their measurements protocol, as derived within the CEN project. This report describes measurements with the Solar Occultation Flux method (Figure 1 and Figure 2) which was carried out during 8 days. This mobile remote sensing method requires sunny conditions and the possibility of moving around the industrial site, inside and outside the site.

The measurements were obstructed by the fact that there was heavy construction work going on at the site during the campaign which restricted the movement of the SOF vehicle and the possibility to obtain backgrounds. In addition, there was a major source at the site corresponding to a faulty tank that caused rather high background values. Despite these circumstances, we believe we have understood the major sources at the facility and that we have reasonable understanding of the total VOC emissions from the whole site

2 SOF method

The Solar Occultation Flux (SOF) method uses solar light to detect gas species that absorb in the infrared (IR), visible and ultraviolet (UV) part of the solar spectrum (Mellqvist, 2009). SOF measurements are carried out using an IR or UV spectrometer that is connected to a solar tracker. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. For the UV channel the measurements can instead be carried out by pointing a telescope towards zenith, utilizing the skylight instead of direct solar light. Mass fluxes/emissions are obtained by combining the SOF column measurements with wind measurements. The method is used to quantify and map the location of various gas emission sources over a spatial scale ranging from industrial conglomerates down to sub-areas in individual plants. The technique is described in detail on the informative annex of the protocol (see Appendix B: SOF Protocol v 2.0).

Figure 1. The SOF van used for the measurements.

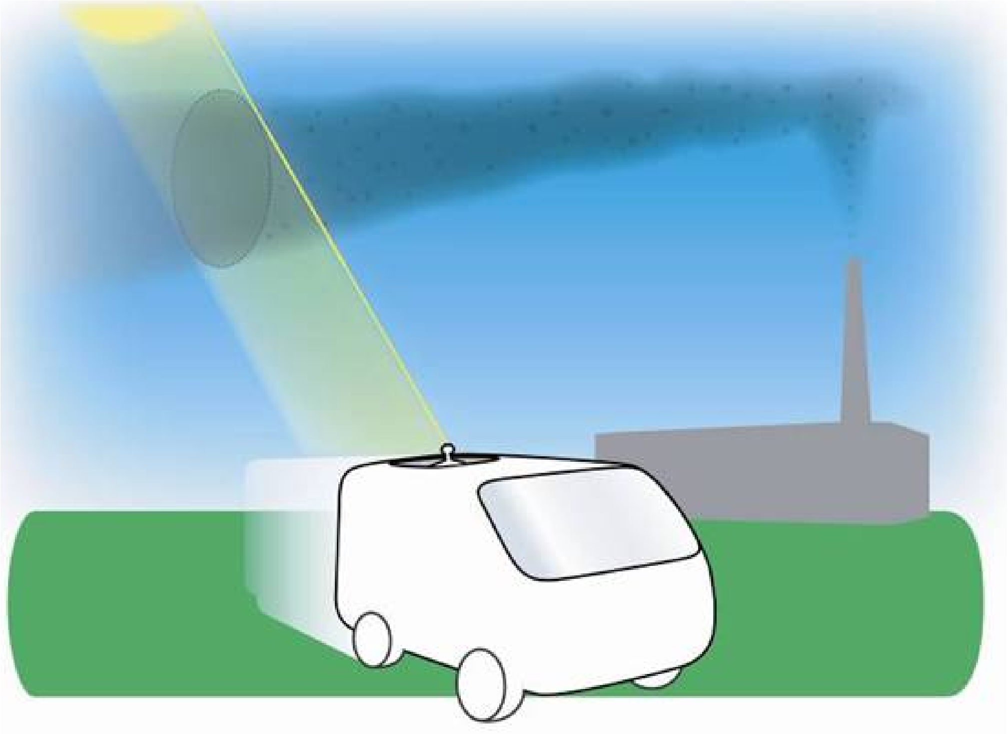


Figure 2. Illustration of the SOF method. The vehicle is driven across the prevailing wind so that the solar beam cuts through the emission plume while the sun is locked into the FTIR spectrometer by the solar tracking device on the roof. The VOC mass (or other compound of interest) is integrated through the plume cross section. See Appendix A for complete equations.

2.1 Performance Characteristics

A summary of the performance capabilities of a typical SOF system under normal conditions are given in Table 1. The values provided are based on the actual levels of performance of existing SOF systems, determined from the typical absolute precision for column measurements in earlier studies when driving 40 km/h downwind of industries in Houston. The numbers in Table 1 are applicable given that there is enough solar radiation (relatively clear conditions and at least an hour away from sunset or sunrise). The performance will improve for small sources and slower measurement speed. For the species measured in the UV region, the numbers are based on measuring zenith scattered light in clear sky conditions. The column accuracy is the combined effect of instrument and retrieval stability on the total columns for a plume transect in real conditions. The flux is determined by multiplying the column across the gas plume with the orthogonal wind speed. The main uncertainty of the flux measurements of diffuse emission sources comes from the uncertainty in the wind field in relation to the emission plume. For elevated point sources (stack) emissions, applicable to measurements of SO_2 and NO_2, this uncertainty is considerably lower.

Table 2 shows the estimated uncertainty for flux measurements in various field conditions when measuring alkane emission from refineries and petrochemical industries. This estimate is obtained as the root-sum-square of various error sources estimated from a one month campaign in Texas (Mellqvist et al., 2010), but the numbers are representative for other campaigns as well

The infrared cross sections for alkane have an uncertainty of 3–3.5 % (Sharpe et al., 2004) and retrieval errors of 10 % have been estimated for the different species. This is the combined effect of instrument and retrieval stability on the total columns for a plume transect. For the alkane retrieval this also includes a 6 % mass retrieval uncertainty due to limited specificity. All these uncertainty sources have been combined by root-sum-square to a composite flux measurement uncertainty range for each species and study. The maximum and minimum for each range was calculated using the maximum and minimum uncertainties of both wind speed and wind direction. In most cases, the composite uncertainty is approximately 20-35 %.

Table 1— Capability of a typical SOF column measurement based on direct solar measurements in the IR region and zenith scattered light in the UV

Parameter	**Precision/Detection (1σ)**	**Accuracy**
Alkanes (C2-C8) (IR)	3 mg/m^2	10%
Ethene (IR)	1 mg/m^2	10%
Propene (IR)	2 mg/m^2	10%
NH_3	0.5 mg/m^2	10%
SF_6	0.2 mg/m^2	10%
SO_2 (UV)	1 mg/m^2	10%
NO_2 (UV)	1 mg/m^2	10%
HCHO (UV)	0.2 mg/m^2	10%

(1) Precision in ppb, assuming 50 m path length and C4 mixture.

Table 2. Typical uncertainty estimation of alkane flux measurements for diffuse emission sources (the variability of the sources not taken into account).

	Wind Speed [a)]	**Wind direct** [b)]	**Spectroscopy (cross sections)** [c)]	**Retrieval error** [d)]	**Composite flux measurement uncertainty** [e)]
Alkanes	15–30 %	5–10 %	3.5 %	10 %	20–35 %

a) Comparing mast wind averages with the 0–500 m GPS sonde averages, the max data spreads 16–30 % (1σ, 30 %)

b) The 1σ deviation among the wind data compared to the 0–500 m sonde is 18º. For a plume transect orthogonal to the wind direction, which is always the aim, this would give a 6 % error. For a measurement in 75º angle the error is 9 %.

c) Includes systematic and random errors in the cross section database.

d) The combined effects of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect and error of the SOF alkane mass retrieval. Estimated for SOF.

e) The composite square root sum of squares uncertainty

3 Survey Setup and Implementation

The main objective of this study was to demonstrate the SOF technique for measurements of fugitive VOC emissions in a real measurement situation. The measurements were based on a measurements protocol developed as part of the CEN WG 38 TC 264 work.

The main activities performed during the 8 days were the following:

1. Measurements at the fence-line of facility, or further away, to estimate the total VOC emissions from the full site. As discussed in the previous section this was sometimes difficult to carry out due to few sunny days and the on-going construction work which limited our capability to measure on the fence-line of the plant. It was therefore only possible to measure the total emissions from western part of the facility and then add the contribution from the eastern park, obtained from independent measurements. It was also possible to measure in a bigger circle around the facility but then also two neighboring sites denoted, N1 and N2 contributed to the emissions.

2. Overview measurement to map inside the facility to find potential VOC leaks and hot spots. When hotspots were found another group taken part in the campaign, Bureau Veritas, was notified and they thereafter performed leak search inside the given unit with optical gas imaging to find the actual leak. However, since it was a “blind” campaign these results were not communicated to us.

3. Comparative measurements between SOF and DIAL (operated by NPL) at 3 emission sources.

The general methodology followed, as given in the SOF CEN-protocol, is:

- Carry out the SOF measurements in a box around the area investigated, subtracting the measured VOC inflow from the outflow. Both inside and outside of the plant.
- The wind is obtained from an upwind mast of approximately 10 m, corresponding to a relatively undisturbed flow at 10 m.
- The wind LIDAR is used to calculate the systematic difference between mast and higher heights. This is used to post-correct data or in the uncertainty estimate.
- The alkane composition for the background sources and source was evaluated by comparing to propane, butane, and octane with exception for the petrochemical site where we also added cyclohexane to the spectroscopic retrieval. The cyclo-hexane could be identified from the measured spectra.

Following the SOF protocol, a data screening was done in the post analysis, requiring a solar angle above 20^o, average wind speed above 1.5 m/s and below 12 m/s and at least 4 transects passed a given source per day. Additional criteria are found in Appendix B: SOF Protocol v 2.0.

3.1 Emission Quantification

The sources below were quantified according to the objectives of the survey. The number of successful measurements vary significantly depending on road accessibility, wind directions, background plumes and priority. See locations in Figure 3.

Sources quantified with SOF:

- Area1: East Tank Park
- Area 2: West Tank Park
- Area 3: Middle Tank Park
- Area 4: North Tank Park
- Area 5: Petro-Chemical Tank Park
- Area 6: Main Process
- Area 7: Petro-Chemical Process
- Area 8: Waste Water Treatment (WWT)
- Area 9: Oil Pit
- Area 10: Vent Pipe
- Area 11: Truck Loading Area
- Tank 112 (in Area 3)
- Flare East
- External Facility: E1
- External Facility: E2 (
- West Part (Area: 2-9 and External Facilities: E1+E2)
- Test Site + N1 Site+ N2 Site (All three sites and E1 +E2!)

Measurements were conducted along the periphery of the sources and box-measurements were performed (when possible) to account for background emissions. The measurement objects were selected based on the current wind direction and interfering background plumes.

Altogether, measurements were carried out during 9 days, however the number of successful and quality assured measurements varied substantially from day to day and from source to facility depending on weather conditions, local measurement conditions (e.g. road accessibility), priority and time sharing between different sources.

Figure 3. Map showing the measured sources of the Test Site areas during the CEN THE NETHERLANDS 2017 survey. Local sources are denoted as white pins and area sources as shaded regions. Map from Google Earth © 2017.

Figure 4. Map showing the West Part area of the Test Site during the CEN THE NETHERLANDS 2017 survey. Map from Google Earth © 2017.

Figure 5. Map showing the Test Site + N1 Site + N2 Site area during the CEN THE NETHERLANDS 2017 survey. Map from Google Earth © 2017.

Wind measurements were carried out by INERIS with three portable 10m wind masts a wind-Cube LIDAR located according to Figure 6. Most of the wind data used was taken from the truck loading area.

The wind LIDAR was set to give data in an altitude span from 40 to 200 m and was used to scale wind mast data to represent different altitudes. Note that LIDAR data have not been used directly in the flux calculations. See section 4 for wind statistics and plots.

Wind velocities were generally steady during the survey and some typical wind directions were represented. The wind direction was, however, never optimal for total facility measurements of the Test Site with SOF without site access to the adjacent sites N1 or N2.

4 Wind Statistics and Analysis

Wind measurements were carried out by INERIS with three portable 10 m wind masts and a wind-Cube LIDAR located according to Figure 6. Most of the wind data used was taken from the truck loading area in the SE, since the wind generally was unobscured here.

The wind LIDAR was set to give data in an altitude span from 40 to 200 m and was used to scale wind mast data to represent different altitudes. Wind speed data below 40 meter (where no LIDAR data exists) are linearly interpolated using a combination of LIDAR and the Truck Loading 10 m wind. This gives scaling factors that represents the average wind speed from 10 m and upwards see Table 3. Wind information below 10 m are not used for calculating scaling factors. Note that LIDAR data have not been used directly in the flux calculations in this survey.

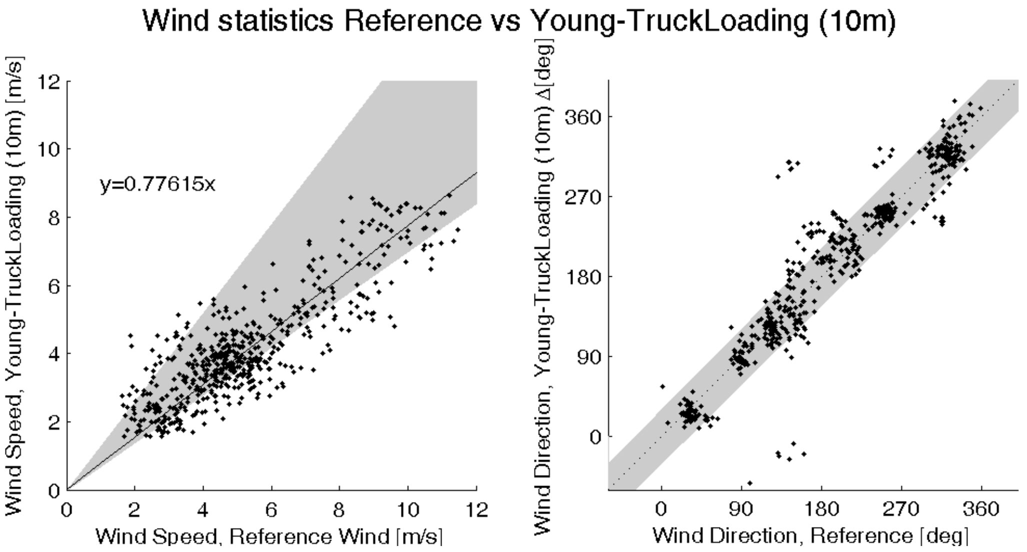
Wind velocities were generally steady during the survey and some typical wind directions were represented. The wind direction was, however, never optimal for total facility measurements of the Test Site with SOF without site access to the adjacent sites N1 or N2

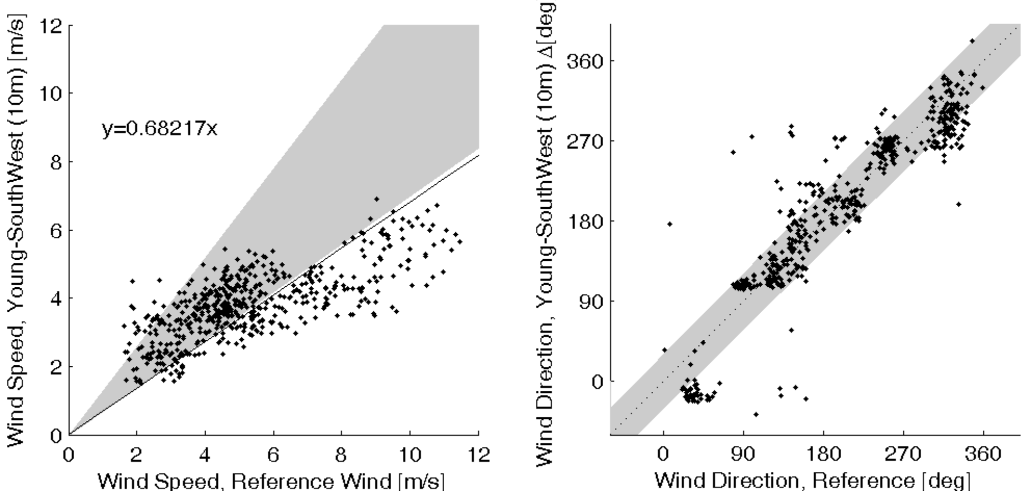
The obtained scaling factors between the different wind mast and various levels of the wind LIDAR are shown in Table 3. In this project we generally used data from the 10 m wind mast at the truck loading scaled to the 10-40 m LIDAR wind for all inside area measurements, with the exception for strong point sources for which the 10 m wind was directly used. For the large-scale measurements at the fence-line, we used the wind data from the 10 m mast at the truck loading scaled up with the 10-200 m wind LIDAR factor. Average LIDAR wind profile and variability for the survey is found in Figure 9. Daily wind LIDAR profile plots are found in Appendix A: LIDAR Profile Plots.

Figure 6. Map showing the extent of the Test Site in the CEN THE NETHERLANDS 2017 survey. Also noted are local meteorological stations (white dart boards). Map from Google Earth © 2017.

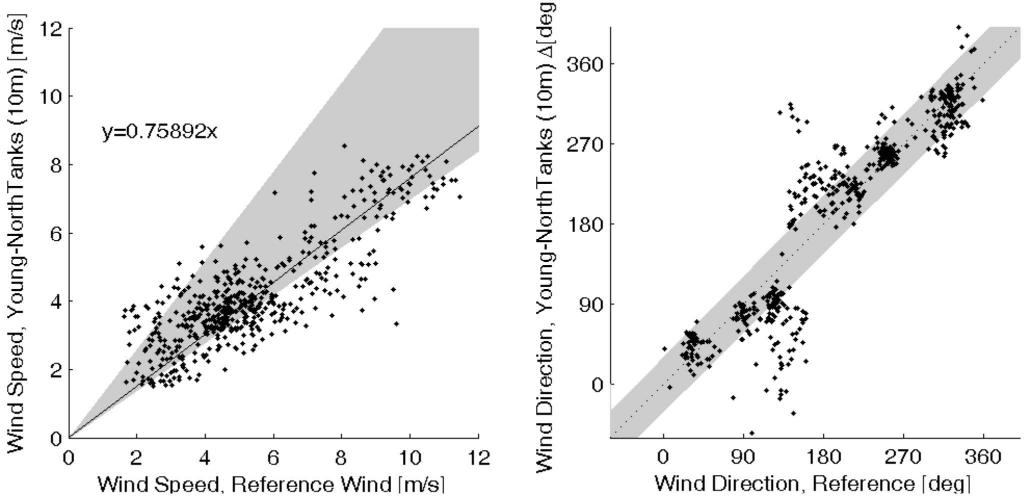
Table 3. Wind speed scaling factors for the CEN campaign (10-21 June 2017). Total least squares fitting slope (forced through zero) of wind mast versus LIDAR references. Only daytime data (09:00-17:00) and wind speeds between 1.5 and 12 m/s included in the fit.

Wind Sensor Name	**Sensor Type**	**Sensor Altitude**	**LIDAR 40m Ref.**	**LIDAR 10-40m Ref.**	**LIDAR 40-100m Ref.**	**LIDAR 10-100m Ref.**	**LIDAR 40-200m Ref.**	**LIDAR 10-200m Ref.**
Wind Mast – Truck Loading	Sonic	10 m	1.205	1.102	1.288	1.240	1.343	1.316
Wind Mast – South West	Sonic	10 m	1.369	1.253	1.466	1.411	1.529	1.498
Wind Mast – North Tanks	Sonic	10 m	1.232	1.127	1.318	1.269	1.373	1.346
DCMR Geulhaven	?	?	0.917	0.839	0.983	0.946	1.025	1.005
DCMR Rozenburg	?	?	0.937	0.857	1.006	0.968	1.047	1.026

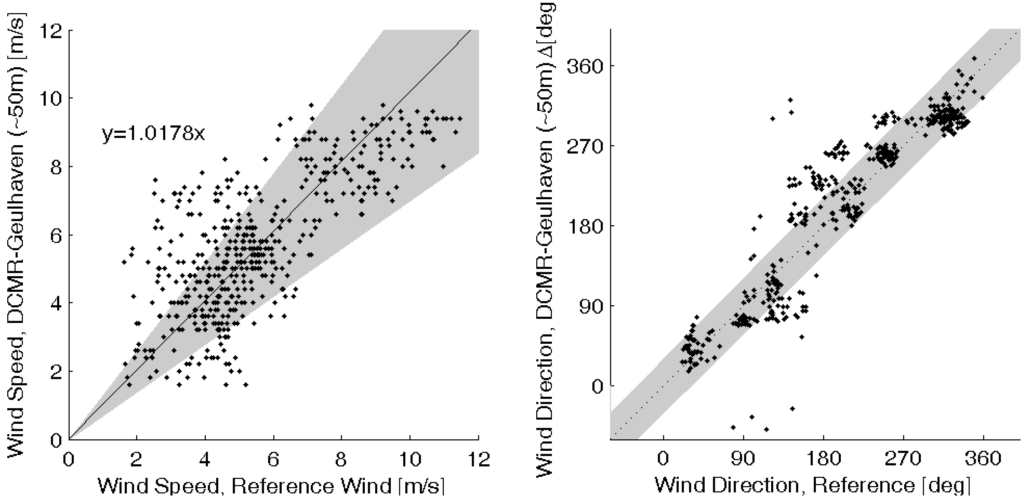




Wind statistics Reference vs Young-SouthWest (10m)



Wind statistics Reference vs Young-NorthTanks (10m)



Wind statistics Reference vs DCMR-Geulhaven (~50m)

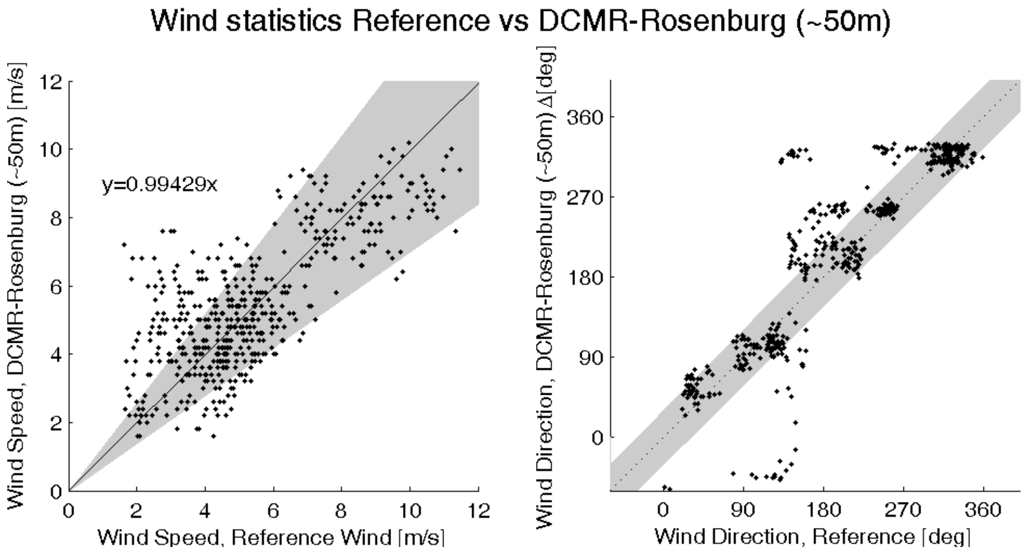
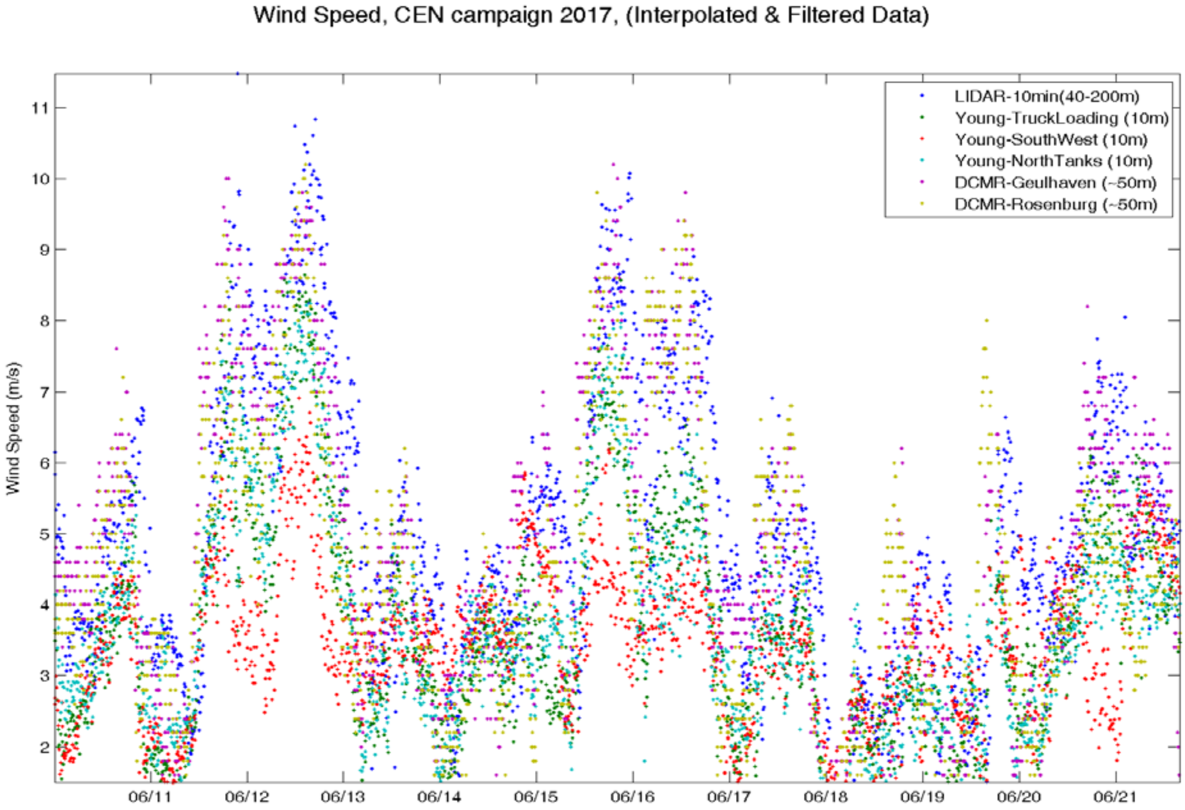


Figure 7 XY-plots of wind sensors versus LIDAR Reference (40-100m) for the CEN The Netherlands campaign 10-21 June 2017. Total least squares fitting slope (forced through zero) of wind mast versus LIDAR references. Only daytime data (09:00-17:00) and wind speeds between 1.5 and 12 m/s included in the fit. Grey shaded areas correspond to a 30% difference from the 1-1-line (left) and ±30 degrees (right).



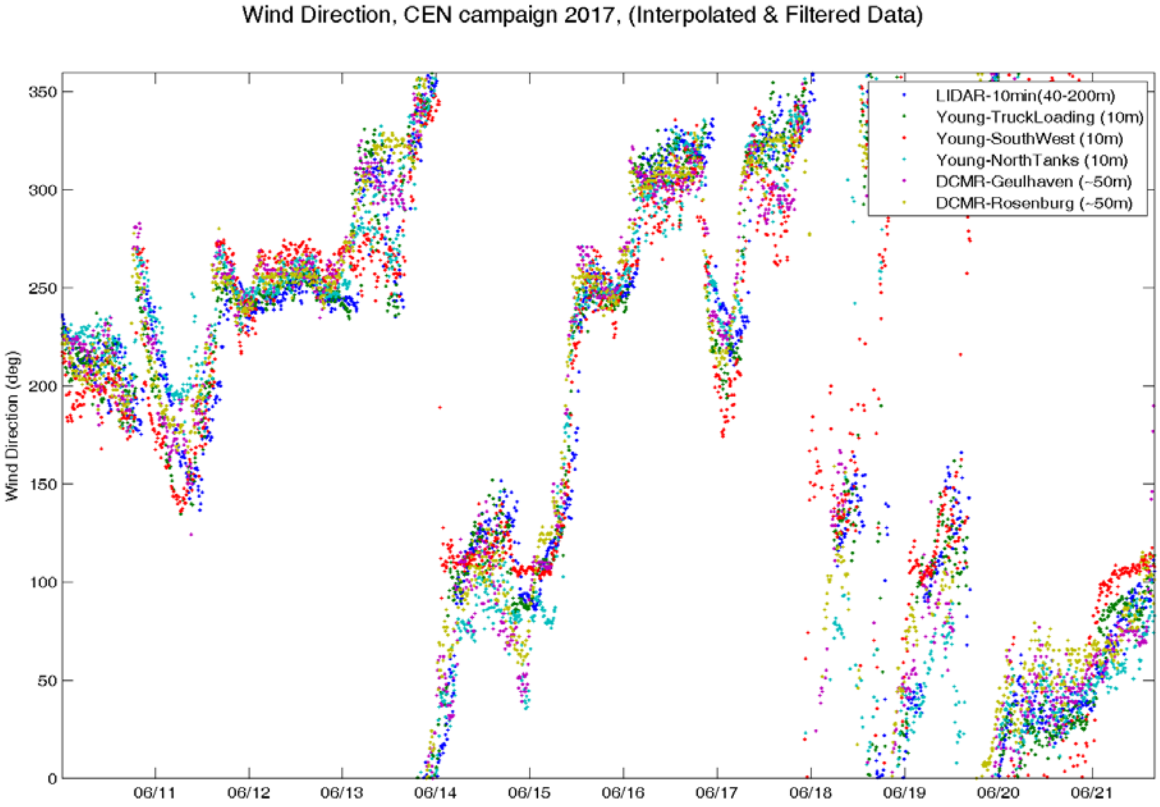


Figure 8 Wind data from various wind stations during the CEN The Netherlands campaign 10-21 June 2017 sampled on the LIDAR 10 min time grid.

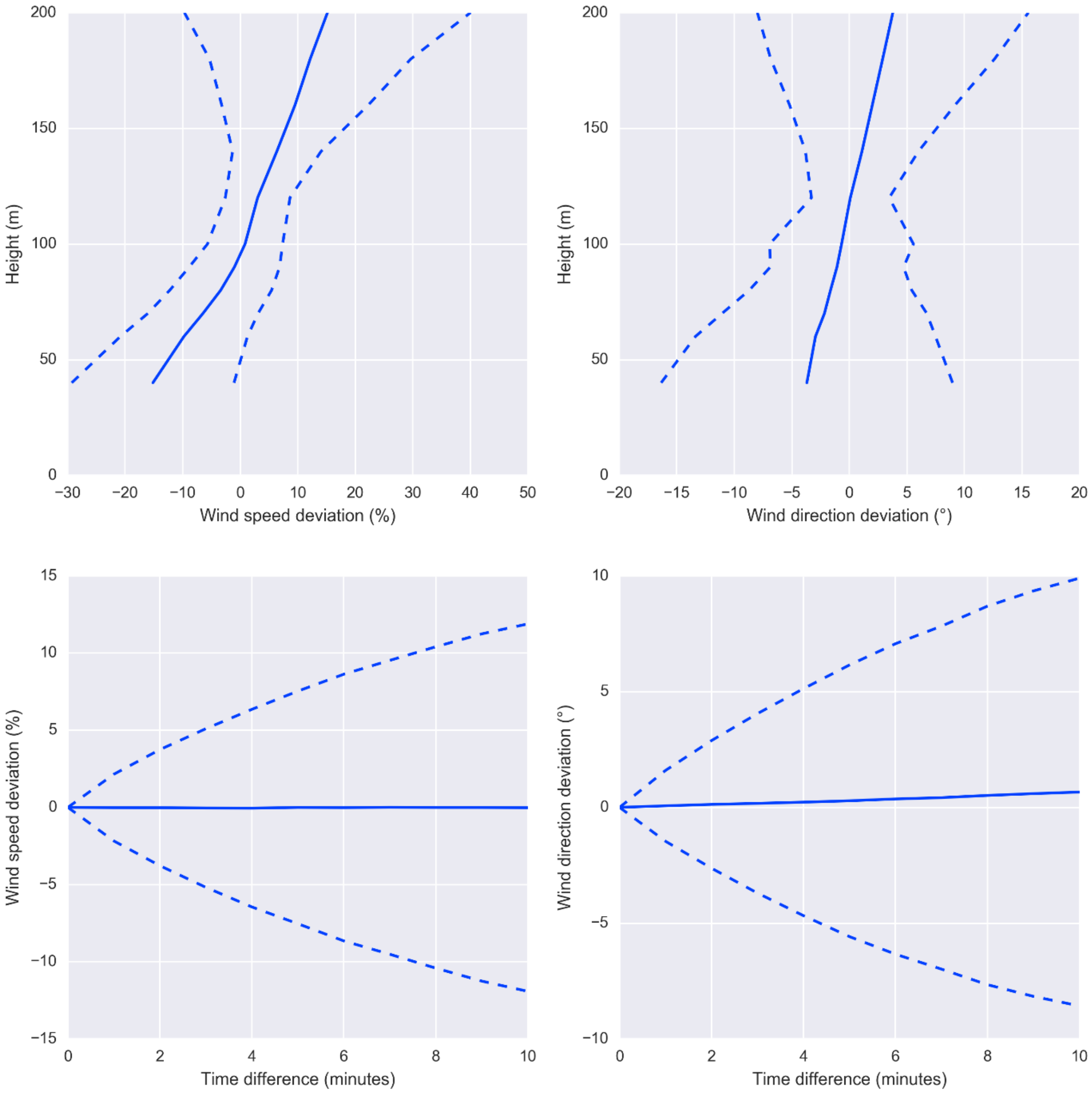


Figure 9 Wind LIDAR data for the CEN The Netherlands 2017 survey. Average (solid lines) and ± one standard deviation (dashed lines) of 10-min data. The top panels show altitude information of relative wind speed (left) and wind direction (right) deviations over the 40-200 m range. The bottom panels show time dependence in the wind speed (left) and wind direction (right).

5 Results – SOF Emission Quantification and Leak Search

All together 243 quality assured SOF transects were carried out during 9 different days. Emission fluxes were quantified from 16 different sources with SOF during the CEN THE NETHERLANDS 2017 campaign as summarized in Table 4 and Figure 10. Daily values and typical plume distributions are fund in the subsections below.

Results are presented as different statistical measures such as averages, standard deviations and medians. Both daily and total survey values are given for each site. The median survey values should primarily be used since it is less sensitive to outliers from intermittent emissions and thus a more conservative measure of the typical emissions. The daily average value is, however, considered the best estimate of the actual emissions during the time of the measurements.

For some sources, not all quality criteria in the SOF protocol could be fulfilled (see all criteria in Appendix B: SOF Protocol v 2.0). One reason was limited daily statistics with less than 4 measurements per day per source. For other sources, the background emission (upwind flux) were higher than the emissions from the source itself (downwind flux) which introduced uncertainties beyond the given limits for SOF. These measurements are presented in gray in the tables and should be considered as indicative only.

The emission from the whole facility can be derived in two ways; from a top down or a bottom up approach. Either the measurements from the west part of the facility are used together with additional sources in the east, with upwind sources subtracted (top down), corresponding to an overall emission of 666 kg/h, see Table 4. Or instead the individual areas and sources are summed up (bottom up), corresponding to an aggregate emission of 630 kg/h.

The distribution of the survey median emissions from different sources within the Test Site is found in Figure 11. Emissions were dominated by the Middle Tank Park with 51% of the total, followed by the East Tank Park (12%), the Petro-Chemical Tank Park (10%), the Petro-Chemical and the Main Process (6% each), the West Tank Park (5%) and the Vent Pipe (3%). Other sources contributed insignificantly (less than 2%).

Besides the source quantification, SOF can also be used to map the emission and identify leaks or hotspots. Figure 12 and Figure 13 are good examples what information can be obtained from SOF column transects during different wind directions. Significant peaks are found downwind of Tank 211, Tank C603 & C613 of the Petro-Chemical Tank Park and the Vent-Pipe for both wind directions (south-easterly on June 14 and westerly on June 15 and 22).

Table 4. Summary of SOF emission flux measurements during the CEN The Netherlands 2017 survey. Results are reported here as total survey statistics in the form of median, mean, 1-σ standard deviation (SD) and 95% Confidence Interval for the mean (Mean +/- 95% CI). Days with less than 4 measurements are excluded in the statistical analysis. Results in gray do not fulfill all quality criteria in the CEN-protocol (for the reason stated in the comments column) and should be treated as indicative measurements only. See Appendix B: SOF Protocol v 2.0 for a complete list of quality criteria. N/A= not applicable. *T=Truck Loading Wind Station, N= North Tanks Wind Station

CEN The Netherlands 2017 Measured Sources with SOF	**Counts**		**SOF Survey Results**				**Wind**	**Comments**
	Days	**No**	**Median** Flux [kg/h]	**Mean** Flux [kg/h]	**SD** Flux [kg/h]	**95% CI** Flux [kg/h]	**Station Info*** [m]	SOF Protocol deviations etc
Test Site Semi-Total								See Figure 4
West Part	3	15	580	610	221	122	T10-40	
Estimated Test Site Total *(West Part+1+10+11-E1-E2)*			***666***	***716***	**N/A**		various	
Test Site Sources								See Figure 3
1. East Tank Park	3	15	76	91	46	28	T10-40	
2. West Tank Park	1	4	27	27	10	16	T10-40	
3. Middle Tank Park	5	17	334	400	283	171	T10-40	
Tank 112	*4*	*24*	*248*	*272*	*200*	3.1	*T10*	
4. North Tank Park	2	11	12	13	4.0	8.1	T10	No boxes but clear bkg
5. Petro-Chemical Tank Park	6	50	58	60	27	26	T10-40	Eval. with cyclo-hexane
6. Main Process	2	5	35	38	16	33	T10-40	
7. Petro-Chemical Process	3	7	34	42	27	3.4	T10-40	Eval. with cyclo-hexane
8. WWT	2	6	14	12	3.2	15	T10	No upwind meas.
9. Oil Pit	3	6	12	13	4.0	2.1	N10	Limited daily statistics
10. Vent Pipe	4	55	21	22	7.7	6.9	T10	
11. Truck Loading Area	3	13	5.2	9.8	12	28	T10	
Sum Sources (1 to 11)		**189**	**630**	**730**	**N/A**		various	
External Sources								
E1 External Facility 1	4	6	9.4	8.8	4.9	5.1	T10	Limited daily statistics
E2 External Facility 2	2	2	6.5	6.5	0.8	6.9	T10	Limited daily statistics
Intermittent Sources								
Flare East	1	4	125	115	48	76	T10-40	Flare Event?
Large Scale Measurements								See Figure 5
Test Site + N1 Site + N2 Site	2	9	1025	1087	338	354	T10-	

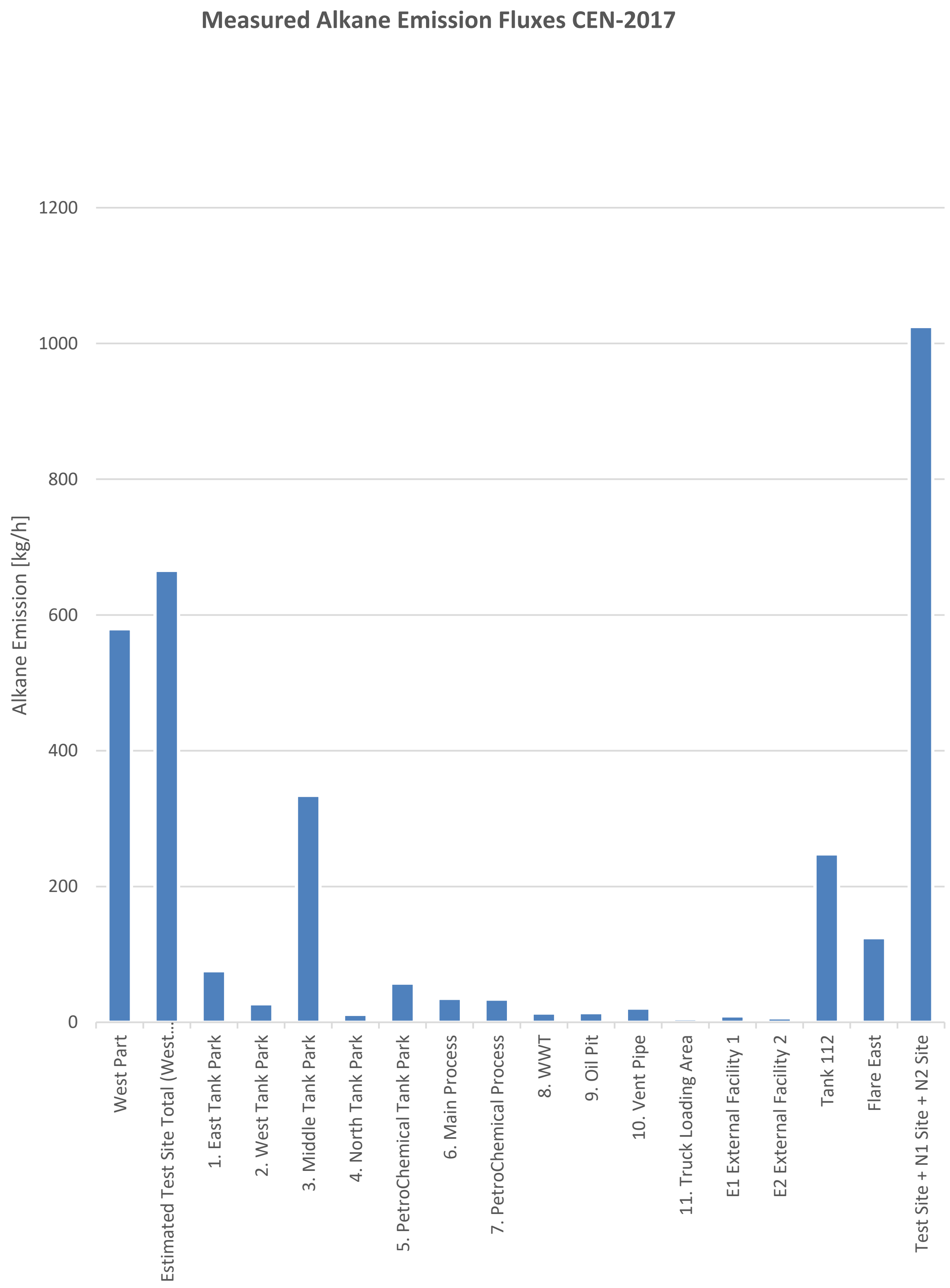


Figure 10 Histogram of measured survey median values of alkane mass emission fluxes as measured by SOF during the CEN The Netherlands 2017 survey.

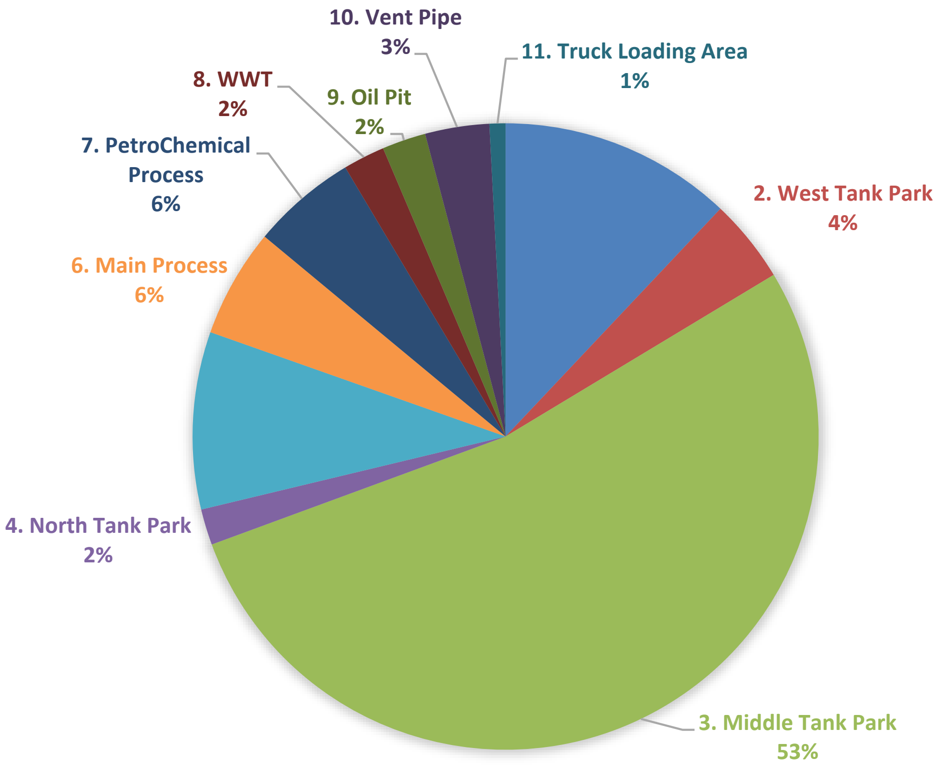


Figure 11 Pie chart of measured (median values) alkane emission fluxes from Test Site sources during the CEN 2017 survey in The Netherlands as measured by the FluxSense SOF instruments.

Figure 12 Multiple SOF measurements at the Test Site conducted on 14 June 2017. The height of the blue curve is proportional to the atmospheric alkanes gas column (1 m is equivalent to 1 mg/m^2). The wind direction is indicated by the white arrows. Map from GoogleEarth™ 2017.

Figure 13 Multiple SOF measurements at the Test Site conducted 15 and 22 June 2017. The height of the blue curve is proportional to the atmospheric alkanes gas column (1 m is equivalent to 1 mg/m^2). The wind direction is indicated by the white arrows. Map from GoogleEarth™ 2017.

5.1 Result Tables and Examples per Source

Daily averages and standard deviations (SD) for all quality assured SOF data are presented per site in the sub-sections/tables below together with figures of typical transects. Calculated survey average and median are also found in the last row of each table. Days with less than 4 measurements do not fulfil the SOF protocol criterium and are excluded in the calculations of these values but are presented as indicative values. Histogram plots of individual transects are presented for sources with a sufficient number of measurements. The histograms give an idea of the statistical distribution of the measured emissions.

5.1.1 West Part of the Test Site

The West Part of the Test Site cover the entire Test Site excluding the East Tank Park, Truck Loading and the Vent Pipe but including the External Facilities E1 and E2, see Figure 4. According to the results of SOF measurements, emissions from this area correspond to around 90 percent of the Test Site emissions.

Alkane emissions from this area were measured with 15 quality assured SOF transects during 3 days as presented in Table 5. The survey median was 580 kg/h with a daily average variation from 509 kg/h (10 June) to 738 kg/h (13 June).

The transects showed a typical column peak directly downwind of Tank 112 in the Middle Tank Park, see example in Figure 14.

Table 5. SOF alkane measurements of **West Part of the Test Site** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 4 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170610	153621-173923	5	508.9	135.9	4.5-5.3	175-181
170613	172823-183542	4	738.4	319.2	3.0-3.9	324-350
170614	165146-180534	6	607.9	193.7	2.4-3.7	106-160
Average		15	609.7	221.1		
Median		**15**	**579.7**			

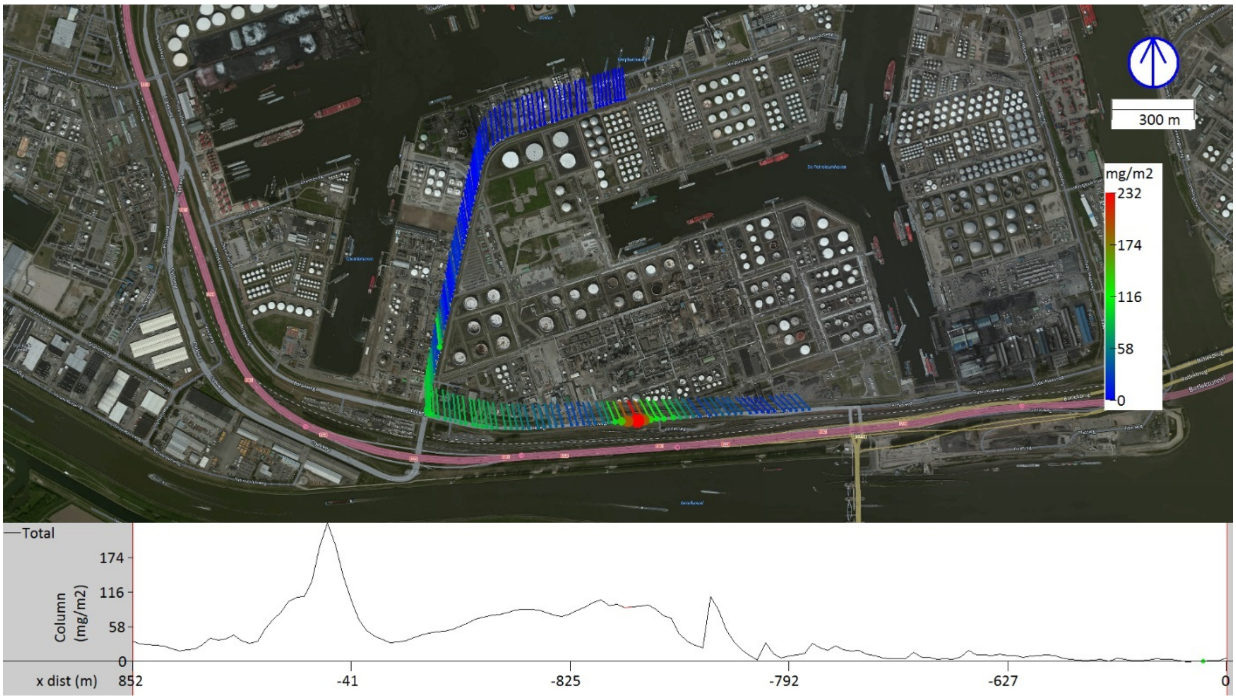


Figure 14 Example of SOF alkane transect from the West Part, 2017-06-13 at 18:22. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.2 East Tank Park

The East Tank Park is located in the east of the Test Site and contains storage tanks with various products, see Figure 4.

Alkane emissions from this area were measured with 15 quality assured SOF transects during 3 days as presented in Table 6. The survey median (based on 13 measurements from 14 and 19 June) was 76 kg/h with a daily average variation from 70 kg/h (14 June) to 116 kg/h (19 June). Results from 15 June are based on limited daily statistics and are indicative only.

The transects showed peaks downwind various tanks with different daily patterns, see example from 14 June in Figure 15.

Table 6 SOF alkane measurements of **East Tank Park** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. See Figure 3 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170614	090239-155820	7	69.7	42.2	2.8-4.2	113-126
170615	*091836-093724*	*2*	*49.0*	2.9	*3.3-3.7*	*151-154*
170619	114109-131743	6	115.5	41.0	1.8-3.2	88-155
Average		13	90.8	46.4		
Median		**13**	**75.9**			

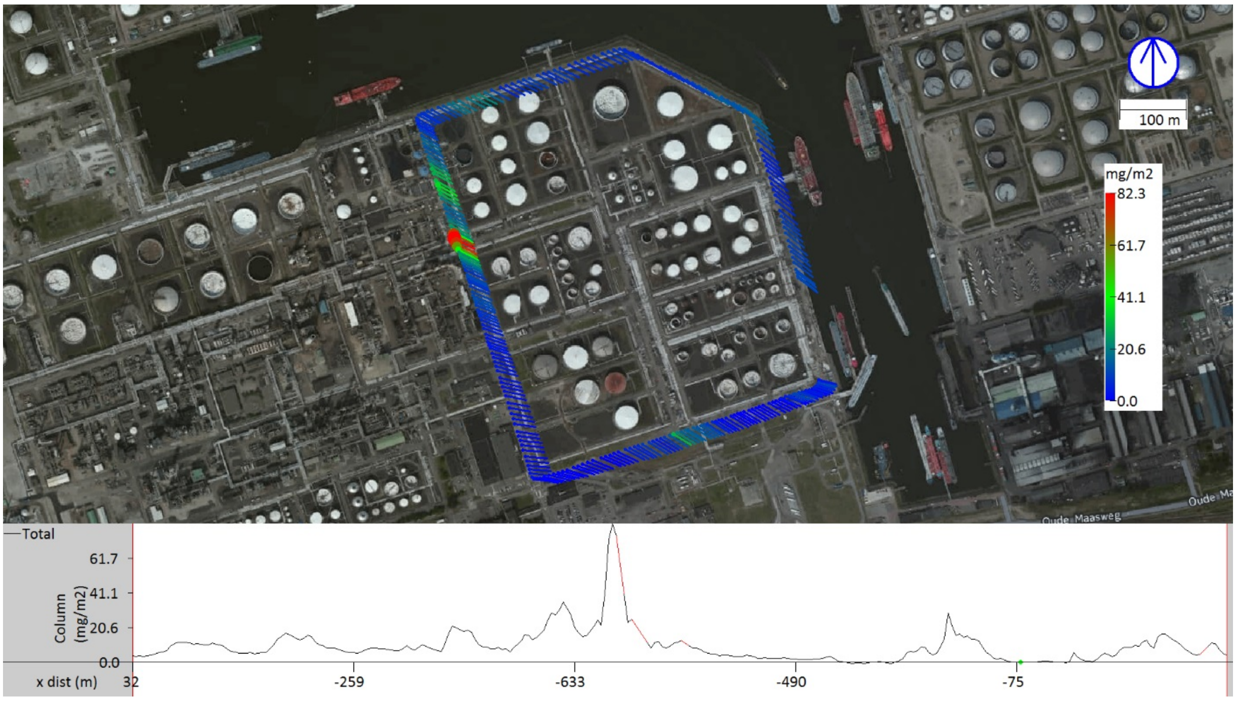


Figure 15 Example of SOF alkane transect from the East Tank Park, 2017-06-14 at 15:41. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.3 West Tank Park

The West Tank Park is located in the west part of the Test Site and contains seven large storage tanks with floating roof, see Figure 4.

Alkane emissions from this area were measured with 4 quality assured SOF transects 15 June as presented in Table 7. The daily/survey median was 27 kg/h and the standard deviation 10 kg/h.

The transects showed a broad peak downwind the area no clear signature from individual tanks, see example in Figure 16.

Table 7 SOF alkane measurements of **West Tank Park** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 3 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170615	131058-141055	4	27.3	9.8	6.9-8.2	238-247
Average		4	27.3	9.8		
Median		**4**	**27.3**			

Figure 16 Example of SOF alkane transect from the West Tank Park, 2017-06-15 at 13:10. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind.

5.1.4 Middle Tank Park

The Middle Tank Park is located north of the Main Process and east of the West Tank Park and west of the Waste Water Treatment area. It contains various large and medium size storage tanks, see Figure 4.

Alkane emissions from this area were measured with 17 quality assured SOF transects during 5 days as presented in Table 8. The survey median (based on 13 measurements from 13-15 June) was 334 kg/h with a daily average variation from 222 kg/h (14 June) to 643 kg/h (13 June). Results from 9 and 22 June are based on limited daily statistics and are indicative only. The high daily value for 13 June was significantly influenced by a single outlier of >1000 kg/h.

The transects showed a large peak downwind Tank 112 and multiple additional smaller peaks from other tanks with different daily patterns, see example from 14 June in Figure 17. The outlier on 13 June showed the largest peak NOT downwind 112. See section 5.1.15 for specific measurements on 112.

Table 8 SOF alkane measurements of **Middle Tank Park** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only, See Figure 3 for area localizations.

Day [yymmdd]	**Time span [hhmmss-hhmmss]**	**Num Meas**	**Emission avg [kg/h]**	**Emission SD [kg/h]**	**Wind Speed Min-Max [m/s]**	**Wind Dir Span [deg]**
170609	*131222-134444*	*2*	*265.3*	11.4	*7.0-7.3*	*237-243*
170613	114757-155907	4	643.2	373.0	2.9-5.1	239-324
170614	134100-150609	5	222.4	138.3	2.2-3.4	118-143
170615	130348-155818	4	378.7	150.8	6.2-9.1	236-261
170622	*114637-123059*	*2*	*182.5*	2.9	*6.1-8.0*	*232-243*
Average		13	400.0	282.6		
Median		**13**	**334.3**			

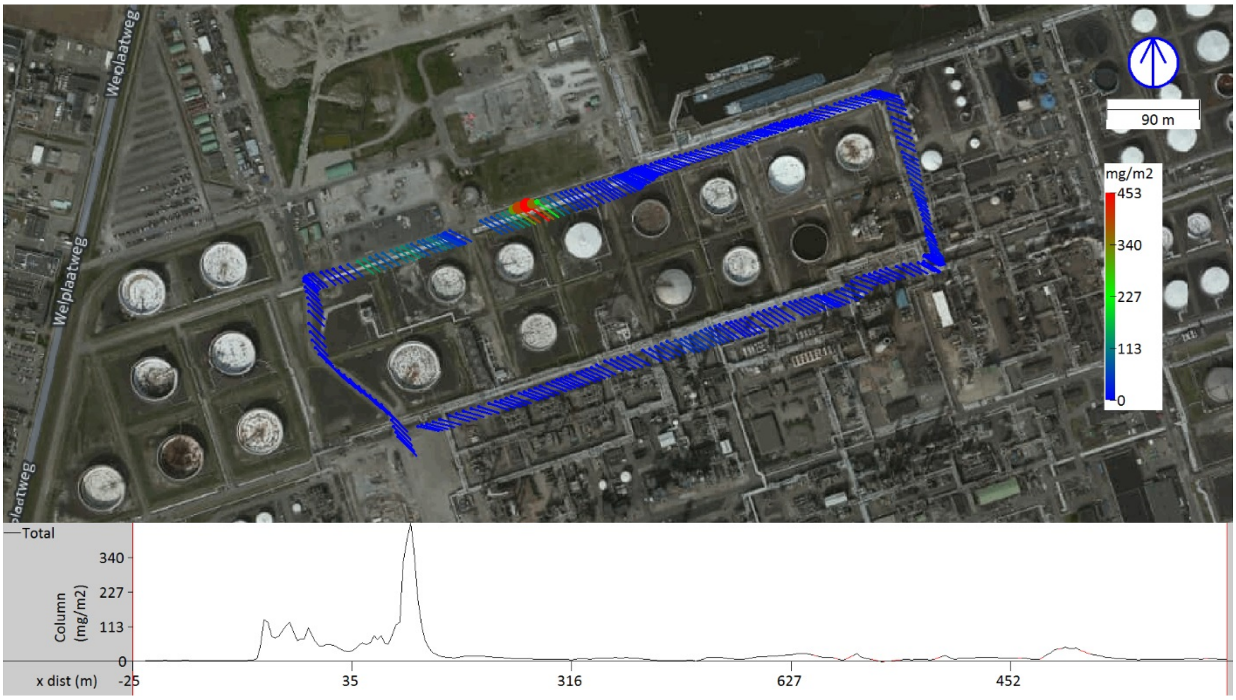


Figure 17 Example of SOF alkane transect from the Middle Tank Park, 2017-06-14 starting at 13:41. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.5 North Tank Park

The North Tank Park is located in the north of the Test Site and contains four large and two small storage tanks with domes, see Figure 4. Complete encircling (boxing) of the area was not possible due to limited road access, but no significant background sources existed during the time of the measurements. This was assured by making separate upwind measurement in connection to the downwind measurements

Alkane emissions from this area were measured with 11 quality assured SOF transects during 2 days as presented in Table 9. The survey median (based on 9 measurements from 10 June) was 12 kg/h. Results from 10 June are based on limited daily statistics and are indicative only, but shows a similar average value.

The transects showed one large peak downwind the area but pointing toward different tanks on the two days (probably the tank that was active at the moment), see example from 15 June in Figure 18.

Table 9. SOF alkane measurements of **North Tank Park** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only See Figure 3 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170610	154945-175328	9	12.5	4.0	3.4-4.7	174-207
170615	*143516-143739*	*2*	*11.4*	0.1	*5.7-5.7*	*247-248*
Average		9	12.5	4.0		
Median		**9**	**11.7**			

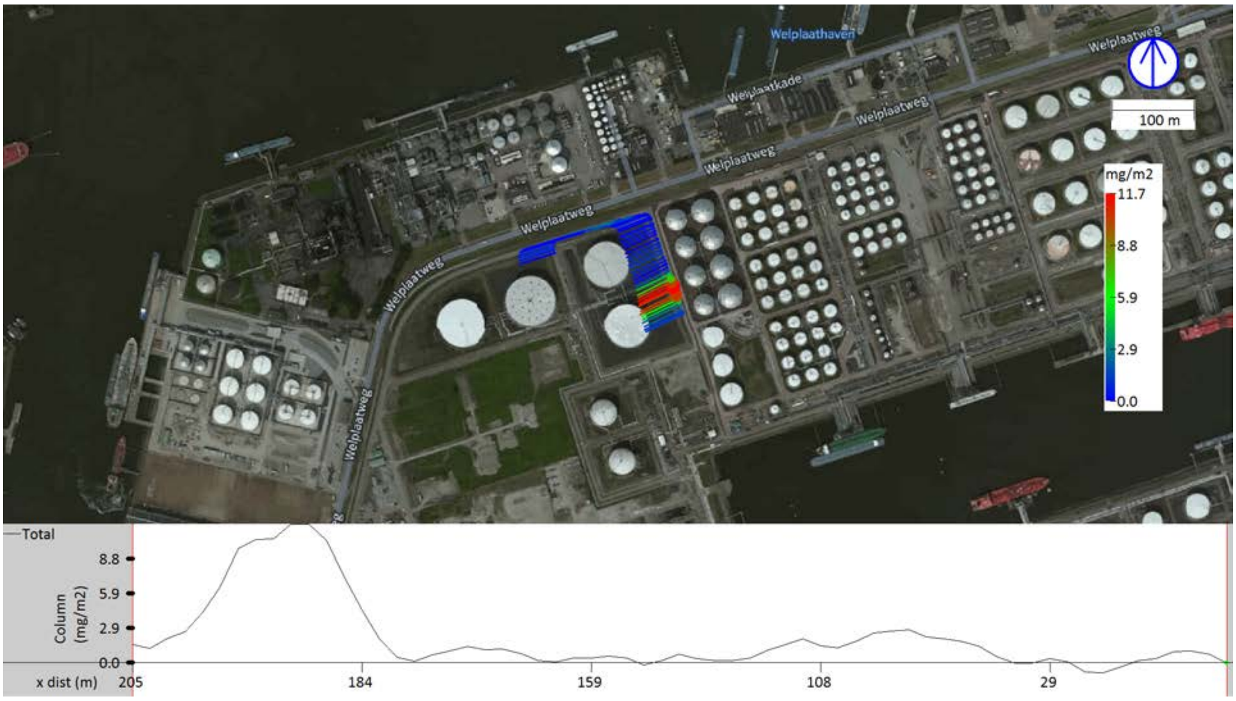


Figure 18 Example of SOF alkane transect from the North Tank Park, 2017-06-15 at 14:35. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The

lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.6 Petro-Chemical Tank Park

The Petro-Chemical Tank Park is located in the south of the Test Site and contains storage tanks with petrochemical products, mainly CyHex, see Figure 4. Cross section of cyclo-hexane was added to the spectral evaluation of measurements from this area since this gas was expected to represent a significant part of the emissions. The spectral fits indicate that the emissions were almost purely in the form of cyclo-hexane.

Alkane emissions from this area were measured with 50 quality assured SOF transects during 6 days as presented in Table 6. The survey median (based on 46 measurements from 9, 13, 14 and 22 June) was 58 kg/h with a daily average variation from 47 kg/h (9 June) to 66 kg/h (14 June). Results from 8 and 12 June are based on limited daily statistics and are indicative only. Histograms of individual transects show a distribution around 60 kg/h and a few outlier above 120 kg/h, see Figure 20.

The transects showed that the emissions were totally dominated by the east part (mainly tank C603 and C614), see example from 14 June in Figure 19.

Table 10. SOF alkane measurements of **Petrochemical Tank Park** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. See Figure 3 for area localizations.

Day [yymmdd]	**Time span [hhmmss-hhmmss]**	**Num Meas**	**Emission avg [kg/h]**	**Emission SD [kg/h]**	**Wind Speed Min-Max [m/s]**	**Wind Dir Span [deg]**
170608	*132334-150815*	*3*	*69.2*	30.1	*4.9-5.9*	*196-210*
170609	130137-155221	4	46.7	13.7	5.4-7.4	245-257
170612	*150821-150929*	*1*	*143.5*	0.0	*8.6-8.6*	*256-256*
170613	112655-160503	14	53.3	29.8	3.4-5.7	234-290
170614	111420-123951	12	66.3	29.3	3.4-4.3	95-140
170622	100759-134856	16	63.8	26.1	5.1-7.8	228-249
Average		46	59.8	27.4		
Median		**46**	**57.7**			

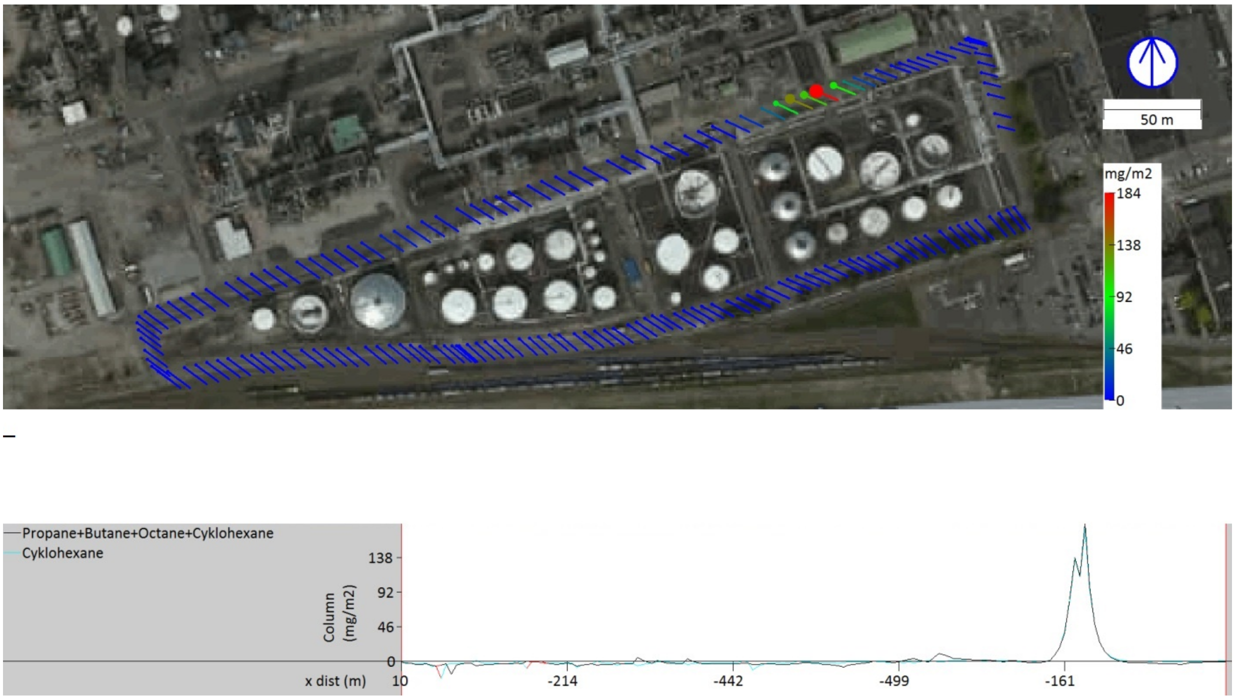


Figure 19 Example of SOF alkane transect from the Petro-Chemical Tank Park, 2017-06-14 at 11:42. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

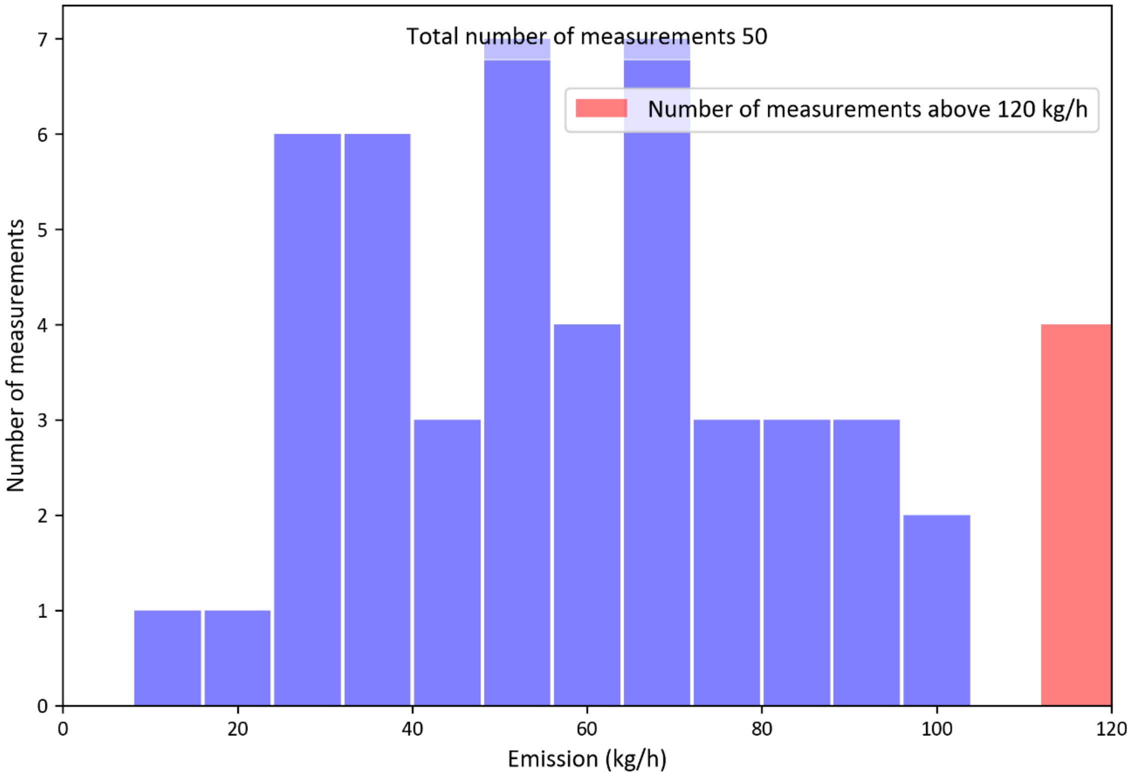


Figure 20 Histograms of SOF individual alkane measurements at the Petro-Chemical Tank Park during the CEN 2017 survey in The Netherlands.

5.1.7 Main Process

The Main Process is located in the center of the Test Site, totally surrounded by other areas/sources, see Figure 4. This implies complete encircling (boxing) of the area every time. Construction work at the site made boxing impossible or extremely difficult during large parts of the campaign which limits the statistics of this area.

Alkane emissions from this area were measured with 5 quality assured SOF transects during 2 days as presented in Table 11. The daily/survey median from 14 June was 38 kg/h with a daily standard deviation of 16 kg/h. Results from 8 June is based on a single transect and are indicative only.

The transects showed that the emissions were dominated by the east part, see example from 14 June in Figure 21.

Table 11. SOF alkane measurements of **Main Process** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. See Figure 3 for area localizations.

Day [yymmdd]	**Time span [hhmmss-hhmmss]**	**Num Meas**	**Emission avg [kg/h]**	**Emission SD [kg/h]**	**Wind Speed Min-Max [m/s]**	**Wind Dir Span [deg]**
170608	*143848-144826*	*1*	*49.4*	*N.A.*	*6.1-6.1*	*199-199*
170614	124321-133855	4	37.7	16.2	3.8-4.6	123-138
Average		4	37.7	16.2		
Median		**4**	**35.4**			

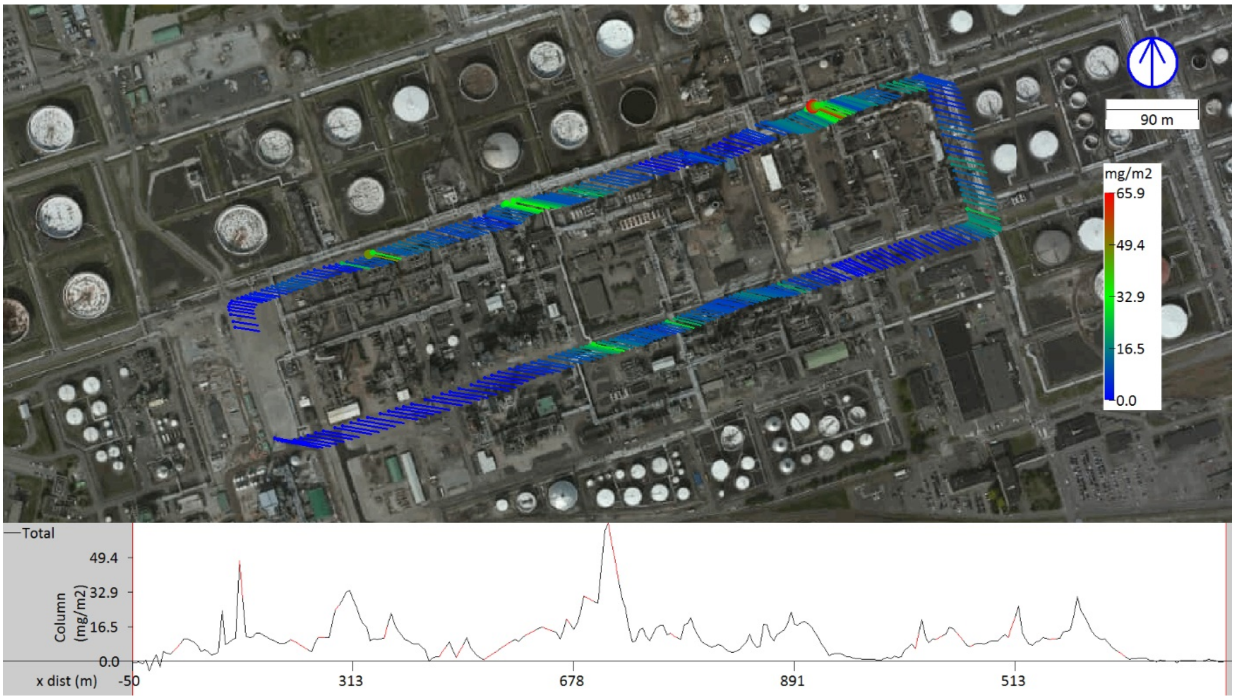


Figure 21 Example of SOF alkane transect from the Main Process, 2017-06-14 at 12:43. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.8 Petro-Chemical Process

The Petro-Chemical Tank Park is located south Main Process and North of the Petro-Chemical Tank Park (see Figure 4). Complete encircling (boxing) of the area was necessary due to significant background plumes. Construction work at the site made this difficult during large parts of the campaign which limits the statistics of this area. The area contains process facilities related to the petrochemical products, mainly CyHex. Cross section of cyclo-hexane was therefore added to the spectral evaluation of measurements from this. The spectral fits indicate that the emissions contained high fractions of cyclo-hexane.

Alkane emissions from this area were measured with 7 quality assured SOF transects during 3 days as presented in Table 12. The daily/survey median based on 5 measurements from 14 June was 34 kg/h. Results from 8 and 9 June are based on single transects and highly uncertain. As explained above, a small emission plume had to be detected overlaid on a large and variable background plume. This introduces large uncertainties that cannot be compensated for by box-measurements. Hence, these measurements did not follow the SOF standard protocol and should be treated as indicative only.

The transects showed sharp incoming emissions plumes from the Petro-Chemical Tank Park (east part) on the upwind side and somewhat larger and wider plumes on the downwind side, see example from 14 June in Figure 22.

Table 12. SOF alkane measurements of **Petro-Chemical Process** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. See Figure 3 for area localizations.

Day [yymmdd]	**Time span [hhmmss-hhmmss]**	**Num Meas**	**Emission avg [kg/h]**	**Emission SD [kg/h]**	**Wind Speed Min-Max [m/s]**	**Wind Dir Span [deg]**
170608	*144415-145229*	*1*	*34.1*	*N.A.*	*5.8-5.8*	*194-194*
170609	*131043-131125*	*1*	*18.4*	*N.A.*	*6.9-6.9*	*257-257*
170614	115052-125438	5	41.7	26.6	4.0-4.5	104-136
Average		5	41.7	26.6		
Median		**5**	**34.2**			

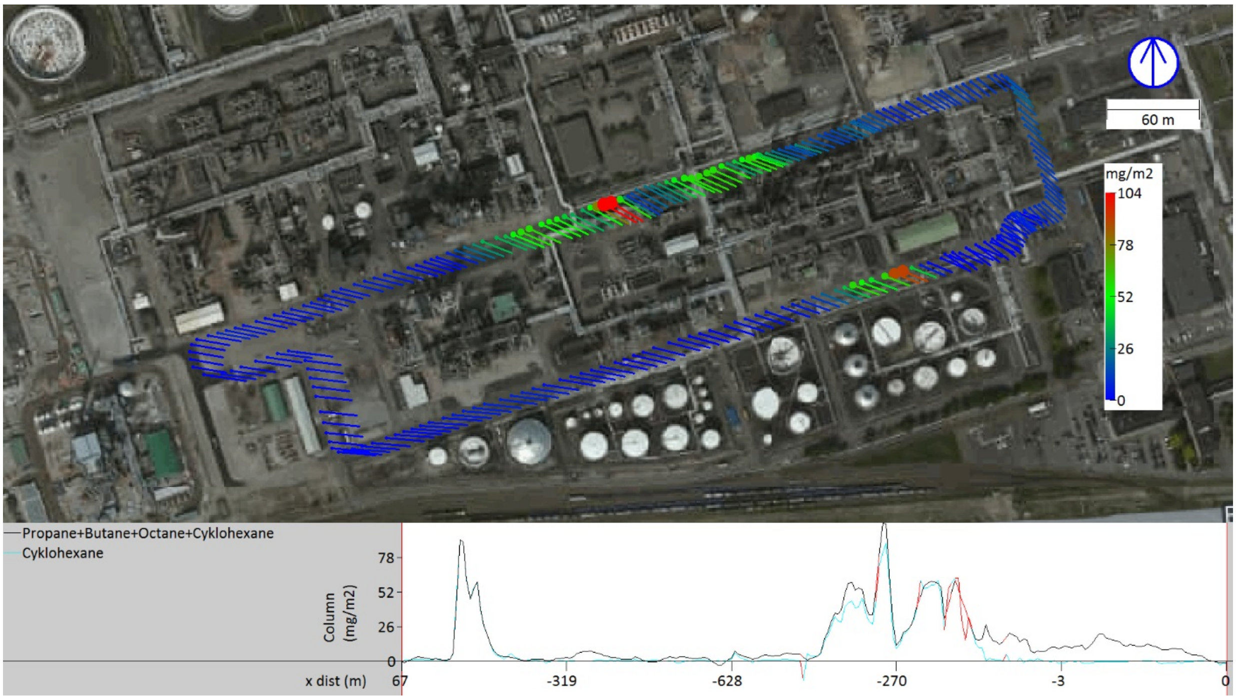


Figure 22 Example of SOF alkane transect from the Petro-Chemical Process, 2017-06-14 at 12:28. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.9 Waste Water Treatment

The Waste Water Treatment is positioned northeast of the Main Process and east of the Middle Tank Park. Complete encircling (boxing) of the area was necessary due to significant background plumes at the current wind directions. However construction work at the site made this largely impossible during the campaign. In addition, all measurements were carried out with strong background emissions from the Middle Tank Park (see 5.1.4) and none of the measurements therefore fulfilled the requirements of a stable background.

The transects showed typically one small emission plume from the Waste Water Treatment against the background, see example in Figure 23, but there are possibly also other small sources within the area. The plume distributions in the SOF data do, however, clearly show that no major sources exist in this area.

Table 13. SOF alkane measurements of **Waste Water Treatment (**See Figure 3 for area localizations) during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic do not fulfill quality criteria and are indicative only. † All measurements were made against high background emissions and do not fulfill the "relatively clear background"-criteria of the SOF standard CEN protocol.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170615	124030-155522	5	11.8	3.2	5.3-7.1	226-255
170622	*113801-113834*	*1*	*8.1*	*N.A.*	*8.0-8.0*	*237-237*
Average†		5	11.8	3.2		
Median†		**5**	**13.6**			

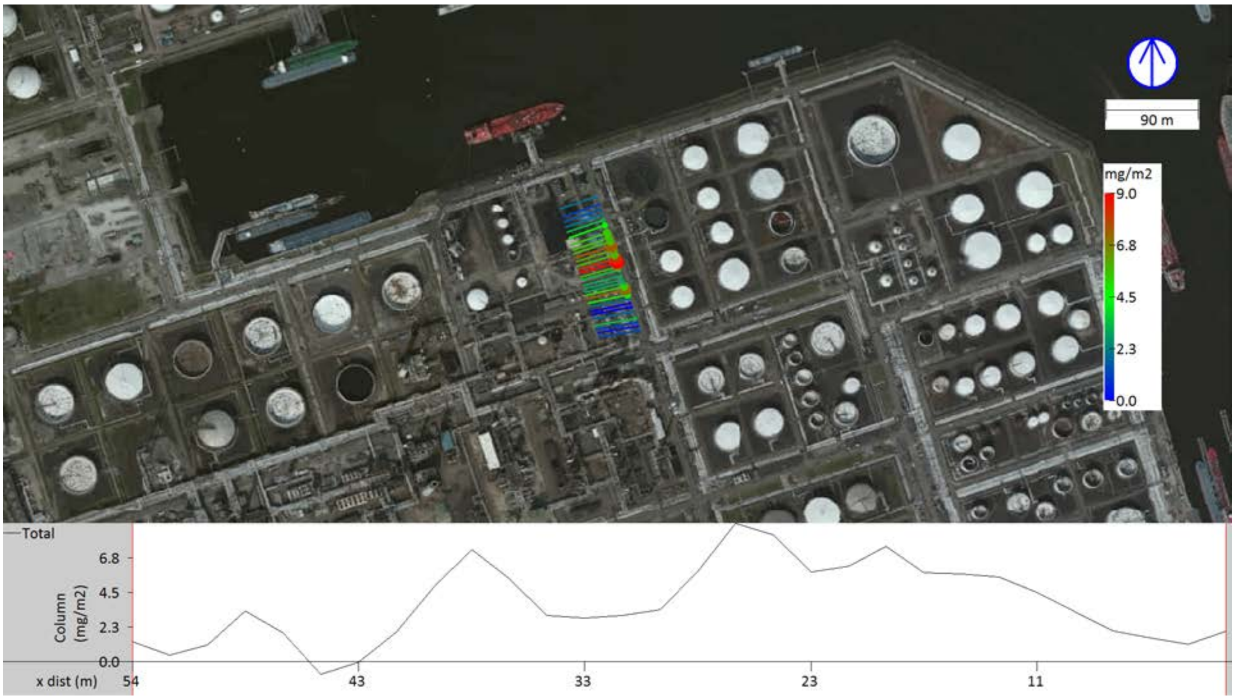


Figure 23 Example of SOF alkane transect from the North Tank Park, 2017-06-15 at 12:47. The dots show the trace of the vehicle and the colors indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.10 Oil Pit

The Oil Pit was an intermittent point source located in between the Middle Tank Park and the North Tank Park, see Figure 4.

Alkane emissions from this area were measured with 6 quality assured SOF transects during 3 days as presented in Table 14. All days have, limited statistics and should be considered indicative only. Hence, the survey median (based on all 6 measurements) should also be considered indicative (outside the SOF standard protocol for quantification).

The transects showed an isolated but variable peak downwind the pit, see example from 13 June in Figure 24.

Table 14. SOF alkane measurements of **Oil Pit** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. *Survey Average and Medians are calculated using data with limited daily statistics and do not fulfill the SOF standard CEN protocol. See Figure 3 for area localizations.

Day [yymmdd]	**Time span [hhmmss-hhmmss]**	**Num Meas**	**Emission avg [kg/h]**	**Emission SD [kg/h]**	**Wind Speed Min-Max [m/s]**	**Wind Dir Span [deg]**
170612	*154835-155029*	*2*	*3.2*	0.1	*8.5-8.6*	*254-258*
170613	*140059-140547*	*3*	*29.0*	8.6	*3.8-4.3*	*241-279*
170615	*144112-144223*	*1*	*9.4*	N.A.	*6.9-6.9*	*239-239*
*Average**		*6*	*17.1*	*14.3*		
Median*		***6***	***14.2***			

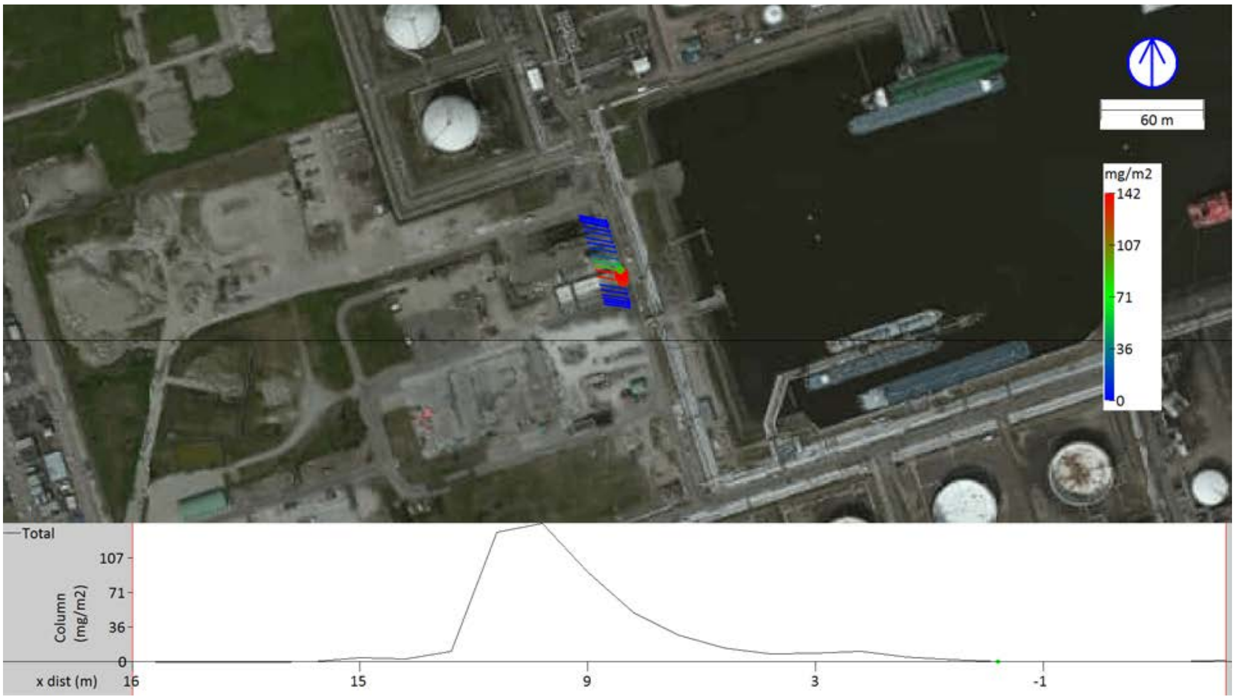


Figure 24 Example of SOF alkane transect from the Oil Pit, 2017-06-13 at 14:00. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.11 Vent Pipe

The Vent Pipe was a continuous and significant point source located south of the East Tank Park, see Figure 4. The source was selected for a side-by-side comparison between the different measurement techniques (22 June) because it is isolated and easily accessible.

Alkane emissions from this source were measured with 55 quality assured SOF transects during 4 days as presented in Table 15. The survey median was 21 kg/h with a small daily average variation from 17 kg/h (15 June) to 26 kg/h (14 June). Histograms of individual transects show a narrow distribution peaking at 20 kg/h with a small tail toward higher values, see Figure 26.

The transects showed a typical isolated sharp peak downwind the source, see example in Figure 25.

Table 15. SOF alkane measurements of **Vent Pipe** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 3 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170614	085528-155326	12	21.5	8.2	2.2-4.5	112-125
170615	090331-095154	6	17.4	4.7	2.5-3.4	149-173
170619	115908-131529	4	25.6	10.1	1.8-2.7	111-154
170622	123733-145324	33	21.7	7.7	5.7-11.1	239-264
Average		55	21.5	7.7		
Median		**55**	**20.9**			

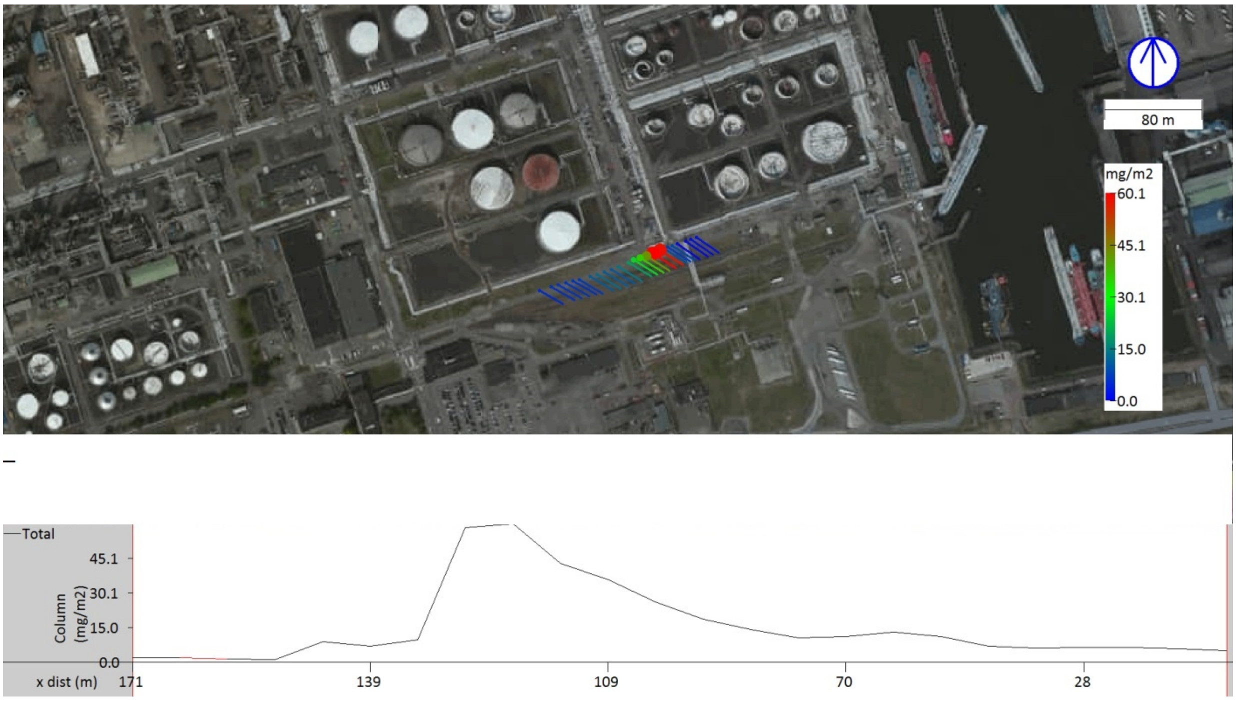


Figure 25 Example of SOF alkane transect from the Vent Pipe, 2017-06-14 at 10:49. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

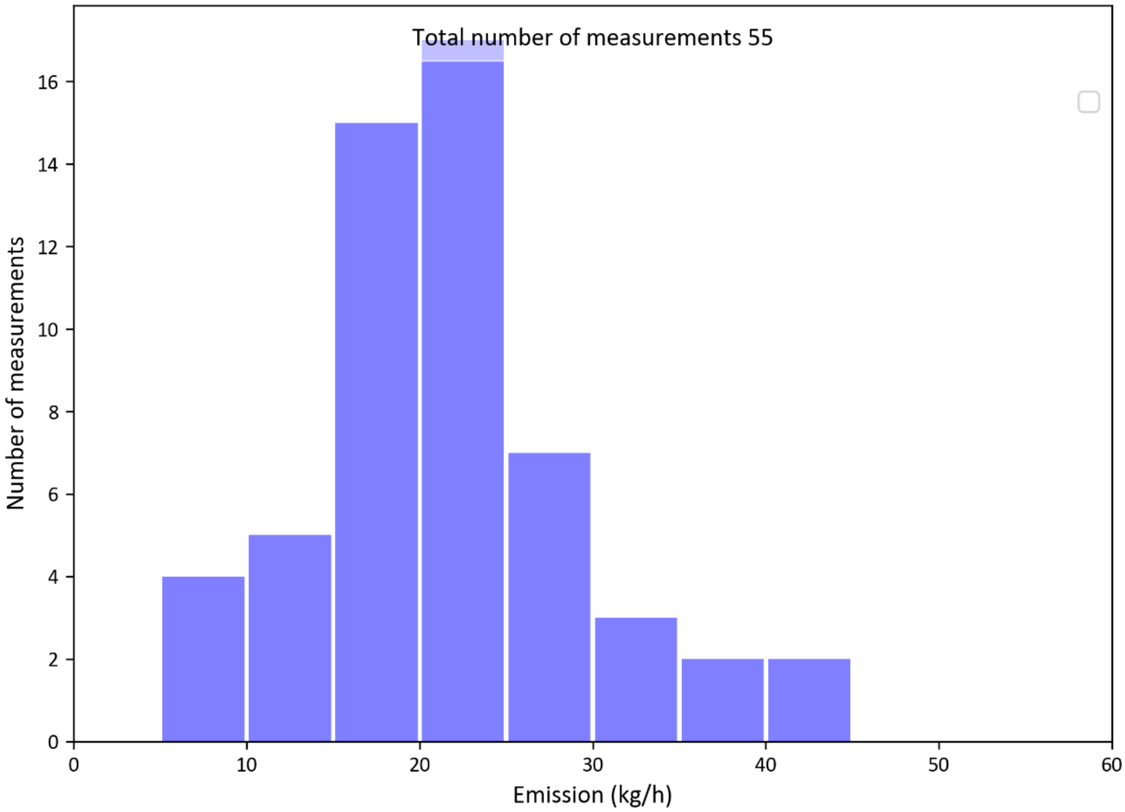


Figure 26 Histograms of SOF individual alkane measurements of the Vent Pipe during the CEN 2017 survey in The Netherlands.

5.1.12 Truck Loading

The Truck Loading is located south of the East Tank Park (see Figure 4) and is a variable source depending on the truck loading activity.

Alkane emissions from this source were measured with 13 quality assured SOF transects during 4 days as presented in Table 16. The survey median was 5.2 kg/h with a daily average variation from 4 kg/h (14 June) to 21 kg/h (19 June).

The transects showed a typical peak downwind the source but variable in magnitude, see example in Figure 27.

Table 16. SOF alkane measurements of **Truck Loading Truck Loading** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 3 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170614	090226-155229	5	4.0	2.9	2.7-4.1	106-128
170615	090534-095051	4	6.2	3.5	2.5-3.5	160-172
170619	120018-131747	4	20.7	16.6	2.2-3.0	98-134
Average		13	9.8	11.5		
Median		**13**	**5.2**			

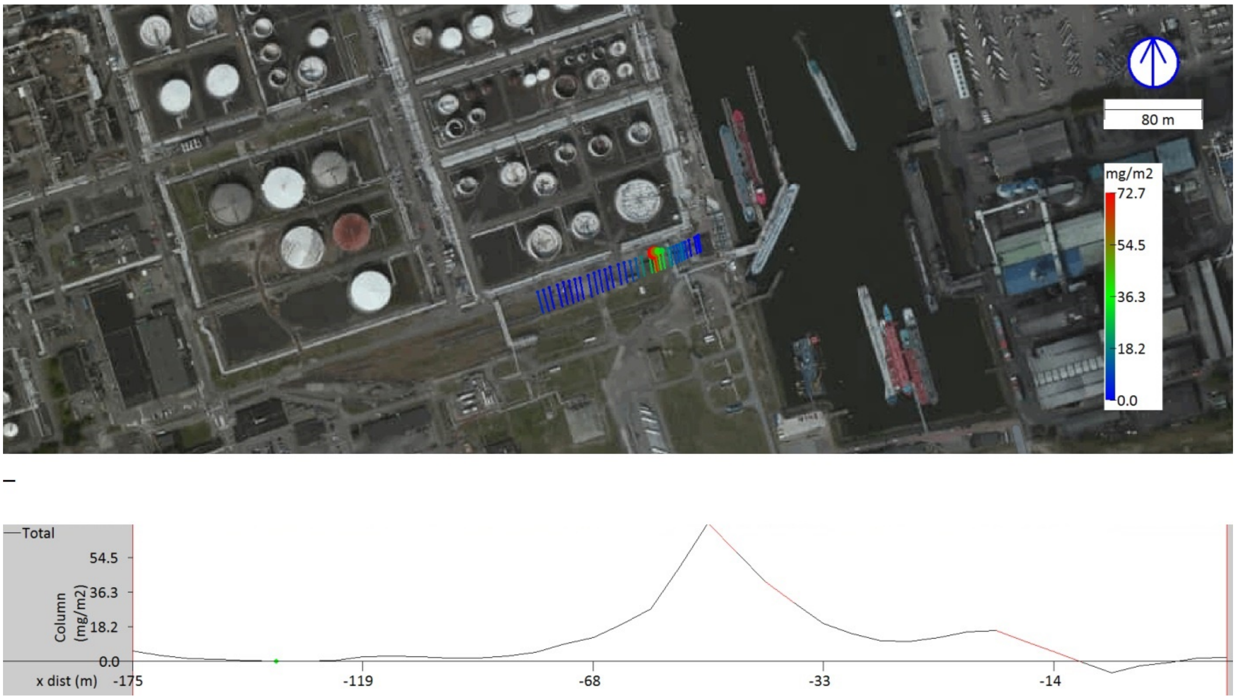


Figure 27 Example of SOF alkane transect from the Truck Loading, 2017-06-15 at 09:45. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.13 External Facility-1

The External Facility-1 is located south-west of the Main Process area, see Figure 4. This source does not belong to the Test Site and was not a scope of the campaign. However, it contributed theoretically to the measured total emissions.

Alkane emissions from this area were measured with 2 quality assured SOF transects during 2 days as presented in Table 17. Both days contain only single transects and the results should be considered indicative only since they are too few to fulfil the requirements in the SOF standard protocol. However, the measurements of 7 and 6 kg/h indicate that the magnitude of this source is insignificant in comparison to the emissions from the Test Site. Measured columns were close to the detection limit are not shown in the report.

Table 17. SOF alkane measurements of **External Facility-1** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. *Survey Average and Medians are calculated using data with limited daily statistics and do not fulfill the SOF standard CEN protocol. See Figure 3 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170613	*141849-142039*	*1*	*7.0*	*N.A.*	*3.6-3.6*	*234-234*
170622	*120114-120249*	*1*	*6.0*	*N.A.*	*5.1-5.1*	*230-230*
*Average**		*2*	*6.5*	*0.5*		
Median*		***2***	***6.5***			

5.1.14 External Facility-2

The External Facility-2 is located west of the Petro-Chemical Process, see Figure 4. This source does not belong to the Test Site and was not a scope of the campaign. However, it contributed theoretically to the measured total emissions.

Alkane emissions from this area were measured with 6 quality assured SOF transects during 4 days as presented in Table 18. All days have, limited statistics and should be considered indicative only since they are too few to fulfil the requirements in the SOF standard protocol. However, the measurements of around 9.4 kg/h (based on all 6 measurements) indicate that the magnitude of this source is insignificant in comparison to the emissions from the Test Site. Measured columns were small and are not shown in the report.

Table 18. SOF alkane measurements of **External Facility-2** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. *Survey Average and Medians are calculated using data with limited daily statistics and do not fulfill the SOF standard CEN protocol. See Figure 3 for area localizations.

Day [yymmdd]	**Time span [hhmmss-hhmmss]**	**Num Meas**	**Emission avg [kg/h]**	**Emission SD [kg/h]**	**Wind Speed Min-Max [m/s]**	**Wind Dir Span [deg]**
170609	*135730-135833*	*1*	*3.5*	*N.A.*	*5.8-5.8*	*253-253*
170612	*153047-153146*	*1*	*11.3*	*N.A.*	*6.8-6.8*	*249-249*
170613	*115417-142127*	*3*	*9.2*	*6.4*	*2.5-4.9*	*222-252*
170622	*120030-120110*	*1*	*10.6*	*N.A.*	*5.9-5.9*	*226-226*
*Average**		*6*	*8.8*	*4.5*		
Median*		***6***	***9.4***			

5.1.15 Tank 112

Tank 112 in the Middle Tank Park (see Figure 4) was a strong but variable local source during the campaign. In fact, this single tank contributed to almost 40% of the Test Site's total emissions (see Table 4). The tank had a mechanical failure and maintenance was ongoing during the campaign which explains the high (non-typical) emission rates.

Alkane emissions from this source were measured with 26 quality assured SOF transects during 4 days as presented in Table 19. The survey median was 248 kg/h with a daily average variation from 482 kg/h (8 June) to 196 kg/h (14 June). A possible downward trend in the daily means is possible, especially if considering the mean value for 22 June, 70 kg/h. This value is, however, based on limited daily statistics and is indicative only (outside the SOF standard protocol for quantification).

A histogram of the individual transects shows signs of a bi-modal distribution, one peaking slightly below 100 kg/h and the other above 200 kg/h, see Figure 29.

The transects showed typically a huge peak downwind the source, see example in Figure 25, which was also clearly visible in the fence-line measurements (see Figure 14).

Table 19. SOF alkane measurements of **Tank 112 (Middle Tank Park)** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. See Figure 3 for area localizations.

Day [yymmdd]	**Time span [hhmmss-hhmmss]**	**Num Meas**	**Emission avg [kg/h]**	**Emission SD [kg/h]**	**Wind Speed Min-Max [m/s]**	**Wind Dir Span [deg]**
170608	134352-143602	5	481.8	326.9	5.1-6.9	188-218
170613	115018-155823	5	261.8	43.2	2.7-5.1	210-279
170614	134331-153051	13	196.0	110.1	2.2-4.2	94-157
170622	*095526-122048*	*3*	*69.4*	37.4	*3.3-7.1*	*231-241*
Average		23	272.4	199.6		
Median		**23**	**248.1**			

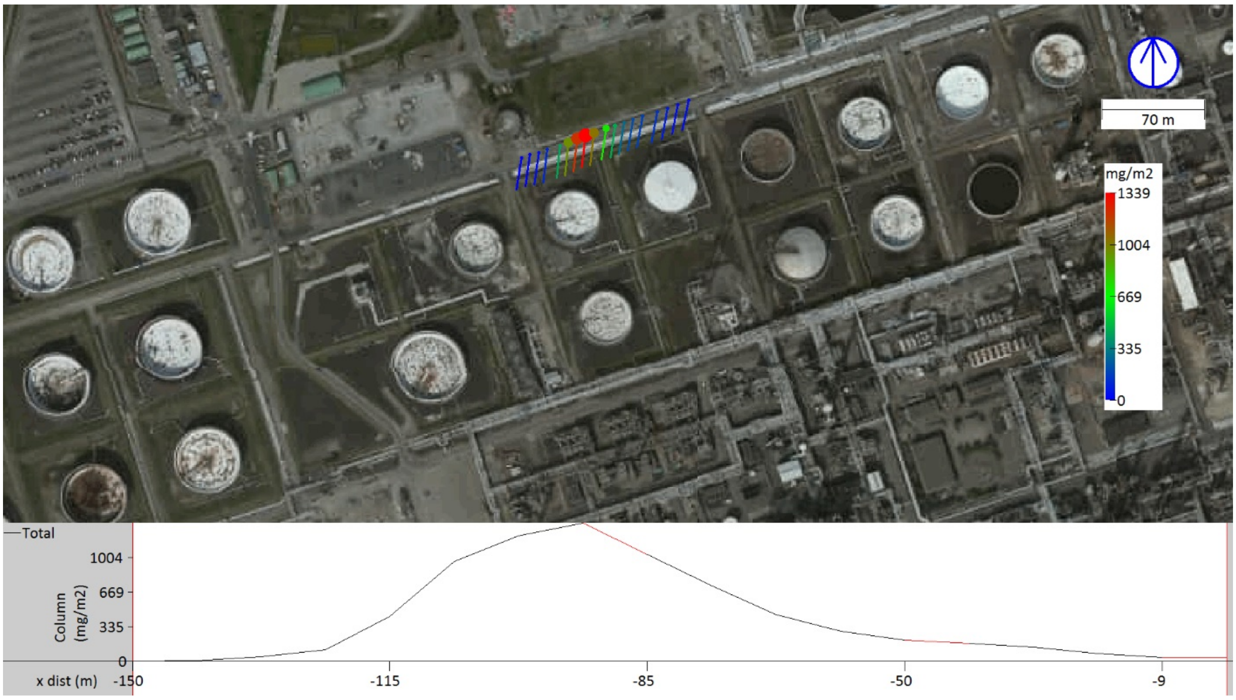


Figure 28 Example of SOF alkane transect from the Tank 112, 2017-06-08 at 13:38. The dots show the trace of the vehicle and the color indicates the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

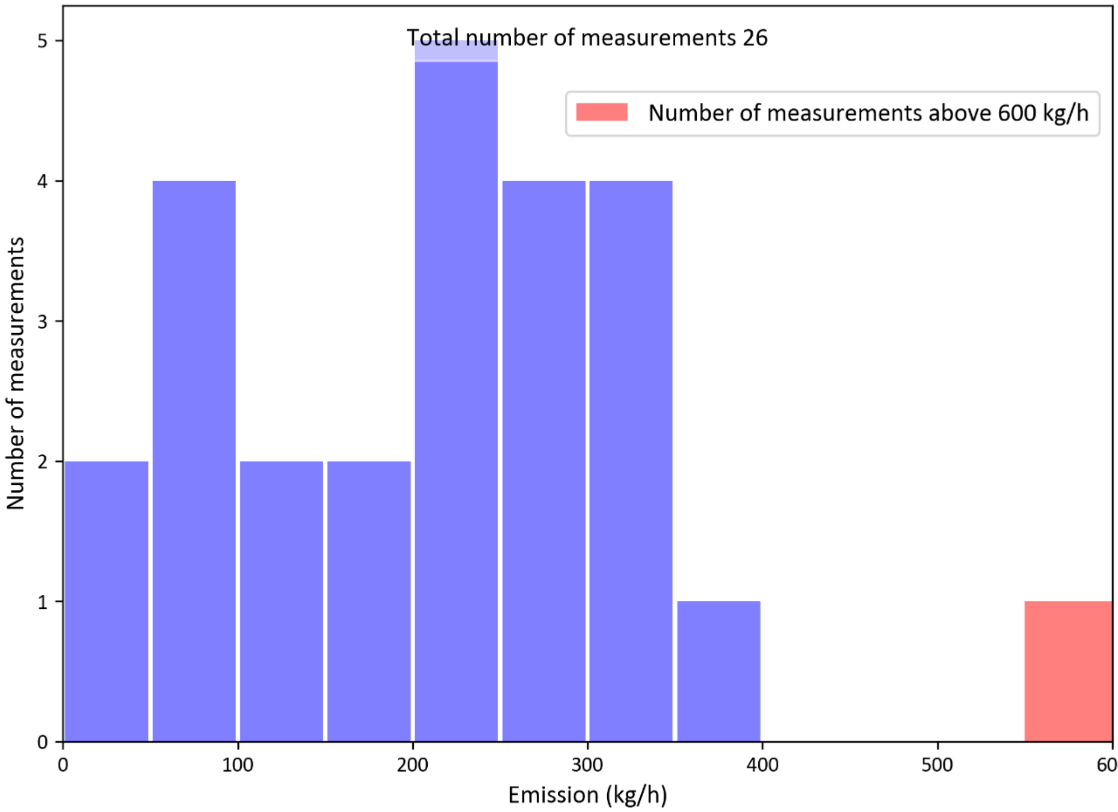


Figure 29. A histogram of SOF individual alkane measurements of Tank 112 during the CEN 2017 survey in The Netherlands.

5.1.16 Flare East

The Flare East is located between the Waste Water Treatment Area and the Middle Tank Park, see Figure 4.

Alkane emissions from this source were measured with 4 quality assured SOF transects 15 June as presented in Table 20. The median value of 125 kg/h is quite significant compared to other sources of the Test Site, but is relevant only for a short period of time, probably related to a flaring event. Intermittent sources, such as flares, are difficult to assess statistically due to observational bias (only detectable when in operation), especially in this environment with large background sources in all directions. Periods of no emissions (i.e. no flaring) are simply not represented. Hence, emission from the Flare East is not included in the total estimate but reported separately (see Table 4).

The transects 15 June showed a sharp peak downwind the flare, see example in Figure 30.

Table 20. SOF alkane measurements of **Flare East** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 3 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170615	145552-160332	4	115.1	47.8	5.4-8.8	233-247
Average		4	115.1	47.8		
Median		**4**	**124.7**			

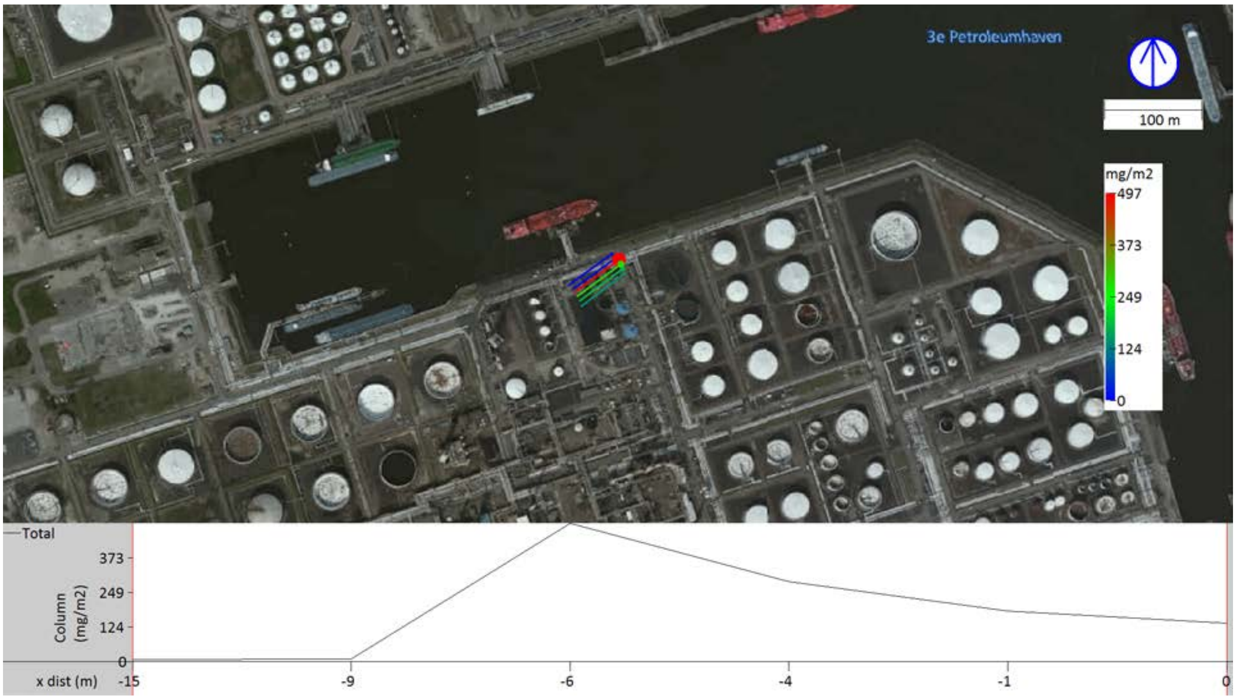


Figure 30 Example of SOF alkane transect from the East Flare, 2017-06-15 at 14:43. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

5.1.17 Test Site + N1 Site + N2 Site

This multi-site area contains the entire Test Site and two adjacent sites, N1 to the north and N2 to the east, see Figure 5.

Alkane emissions from this area were measured with 9 quality assured SOF transects during 2 days as presented in Table 21. The survey median (based on 6 measurements from 15 June) was 1025 kg/h. Results from 13 June are based on limited daily statistics and are indicative only (outside the SOF standard protocol for quantification) but show a very similar value.

The transects, especially in northerly wind showed a broad peak directly downwind the Middle tank Park of the Test Site which indicates that this is a significant source even in comparison to other sites, see example in Figure 31.

Table 21. SOF alkane measurements of **Test Site + N2 + N1** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. Results in italic are based on limited daily statistics and are indicative only. See Figure 5 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170613	*181723-185421*	*3*	*1186.6*	382.4	*3.7-4.3*	*335-352*
170615	164800-183017	6	1087.4	337.7	8.3-9.3	241-255
Average		6	1087.4	337.7		
Median		**6**	**1024.9**			

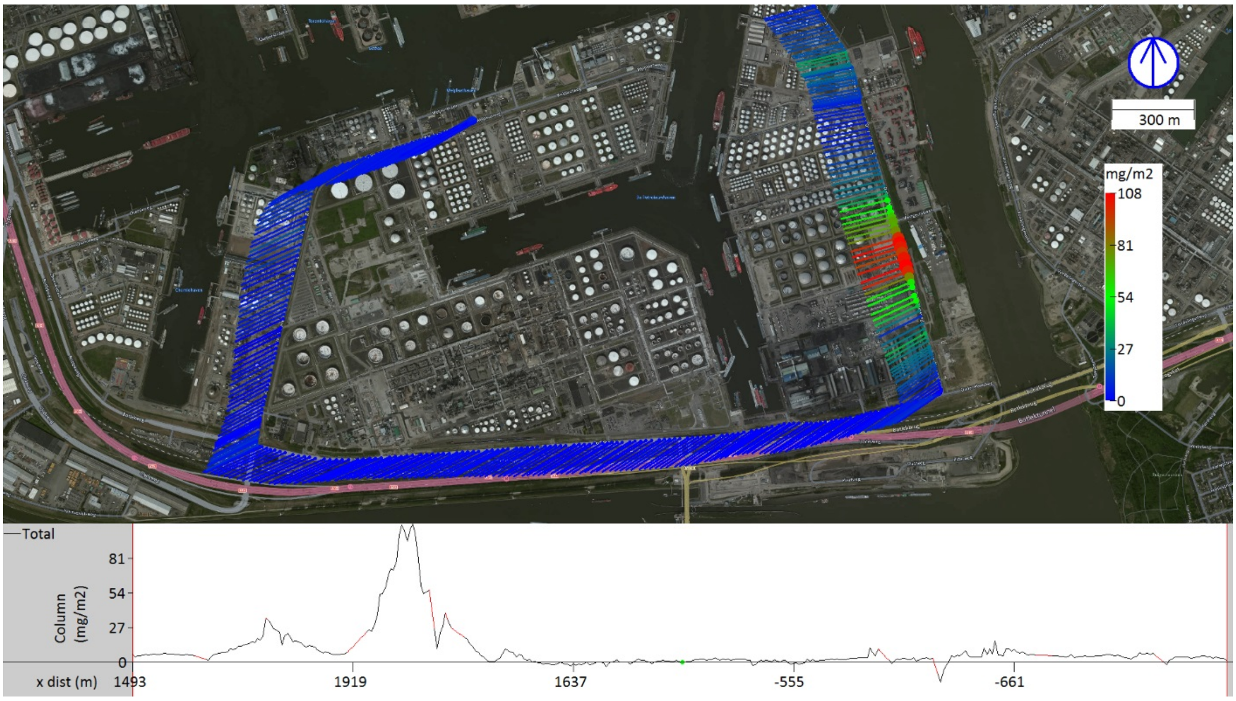


Figure 31 Example of SOF alkane transect from the Test Site + N2 + N1 area, 2017-06-15 at 18:15. The dots show the trace of the vehicle and the color indicate the local alkane column (mg/m^2) according to the color bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the alkane columns as a function of distance from the start.

6 Discussion and Conclusion

The CEN measurement campaign in The Netherlands 2017 highlighted the advantages of the SOF technique. During a few days with favorable conditions, i.e. mostly clear sky and distinct wind (in the 1.5-12 m/s range, the emissions from the entire facility and all sub-areas/sources were quantified and hotspots quickly detected due to the mapping ability. Large-scale measurements of the Test Site and surrounding facilities were also performed during the campaign which put the emissions in a broader context. The SOF measurements spanned a wide range of spatial scales, from small point sources to large multi-site regions.

The number of measurements per source varies significantly, from a single measurement to more than 50. The final data are presented as daily means with standard deviations for each source and as total survey medians. The reported values are representative of the time period of the observations and the uncertainty will also depend on the number of samples. Daily values based on less than 4 transects are not according to protocol and should be considered indicative only. The standard deviation of the source emission is a combination of measurement uncertainties (mainly from wind uncertainties) and actual variability in the emissions.

The standard SOF procedure is a top-down approach where total emissions from an entire site are quantified and the measured emissions from subareas and internal sources normalized to match this. The reason for this is that near-field measurements from subareas have higher uncertainty. Isolated measurements of the entire site were, however, not possible during the campaign due to limited road access (for the current wind directions). Measurements at the West Part (see 5.1.1) containing around 90% of the total emissions were, on the other hand, possible. Comparing the total emissions based on West Part measurements (~top-down approach) with the sum of emissions from all subareas and sources (bottom-up approach) gave very consistent numbers for this campaign, 666 kg/h vs 630 kg/h. This shows that both approaches are feasible and can be applied for SOF measurements.

This survey clearly points out the importance of assessing the relevant gas species in the SOF spectral evaluation. The SOF protocol (Annex B.2.2) states that information about the typical gas-mixture in the emissions must be obtained or complementary measurements made. Since SOF measures broadband infrared spectra, significant absorption by an atypical plume composition of species not included in the standard spectral fit can be detected in the residual of the fit. In such a case, the species included in the evaluation routine are updated to match the observed absorption signal. Plumes from the Petro-chemical areas of the Test Site contained large fractions of cyclo-hexane which is not included in the standard SOF alkane evaluation. A sensitivity study showed that the standard evaluation would give a median flux from the Petro-chemical Tank Park of less than half (44%) of the actual value when cyclohexane was included in the spectral fitting routine. For the large-scale measurements, in which cyclo-hexane is a minor (insignificant) constituent, the effect was only 1%. Hence, the addition of cycle-hexane in the spectral fit were only applied for the Petro-Chemical areas.

A careful selection of the wind information for different areas/sources need to be done to avoid biases in the flux calculations. In this campaign, the unobscured 10 m wind at the truck-loading area has been used, scaled to match LIDAR-profiles for various altitude ranges using least-squares linear fits (See section 4). Wind directions from this mast were generally matching the expected plume position from the hotspots during the campaign which indicate the validity of the mast position and sensor altitude. For ground-based sources, such as the Waste Water Treatment, the unscaled 10 m wind has been used while the scaled 10-40 m wind were used for elevated (tanks, process, flares, e t c) sources. The 10-200m scaled wind was used for large-scale measurements. A sensitivity study for fence-line measurements of the West Part reveals that the flux decreases with 10% if using the 10 m wind instead of the 10-40 m wind and increases with around 20%. if using the 10-200 m wind. Both these values are within the given wind uncertainty of 30% for SOF flux measurements.

Emissions from the Test Site were dominated by the Middle Tank Park (with around half of the total emissions) in which one single source (Tank 112) stood out. Even for measurements at fence-line distance showed a clear signature plume peak downwind Tank 112. Emissions from this single source were so strong that measurements of sources/areas further downwind were sometimes impossible. Emissions from the sources simply drowned in the background plumes from Tank 112. This was particularly the case for the Waste Water Treatment area where a small emission plume had to be detected overlaid on a large and variable background plume. This introduces large uncertainties that cannot be compensated for by encircling the area (box-measurements). Hence, measurements of the Waste Water Area did not follow the SOF standard protocol and should be treated as indicative only, relying on the fact that the plumes were very narrow and repeatedly were present at the same position. The plume distributions in the SOF data do however also clearly show that no major sources exist in this area. Quantification of the area are preferably done when emissions from the Middle Tank Park are more modest or during northerly winds since no strong upwind sources exist in this direction.

Intermittent (highly variable) sources need additional consideration and statistical sampling as compared to more stable/continuous sources. Area sources generally belong to the latter category since they contain multiple sources. The Middle Tank Park of the Test Site (during the time of the measurement) was, however, an exception since it was dominated by a single and variable source (Tank 112). The histogram of all individual measurement transects (Figure 29) for Tank 112 indicates two different emission states or at least not a typical normal distribution. The SOF protocol states at least 4 acceptable transects per source and day to account for variable sources. This is a conservative measure which also reduces the statistical basis for the survey medians of areas with low variability such as the North Tank Park. Extreme intermittent sources (binary sources) are even more difficult to assess statistically due to observational bias (only detectable during operations), especially with large background sources in all directions which was the case for the Flare East source in this campaign. Periods of no or insignificant emissions (i.e. no flaring) are simply not represented. Hence, emission from this intermittent source are not included in the total estimate but reported separately (see Table 4). Emissions from flares can, as measured here, be significant and experience from other studies show that flaring efficiency can vary substantially between sites. A special flare study, with additional measurements, is needed to gain relevant knowledge on how to optimize the operation to minimize the VOC emissions.

The measurement statistics were compromised for some areas/sources due to limited road access from construction- and revision work at the Test Site. This was particularly a problem for the Waste Water Area, the Middle Tank Park, the Main Process and the Petro-chemical Process. Due to background plumes, these areas need to be completely encircled which was impossible at many occasions. Also the fact that the work permit expired at 16:00, loosing several hours of possible SOF measurements per day, limited the measurement statistics in this campaign compared to a standard SOF survey.

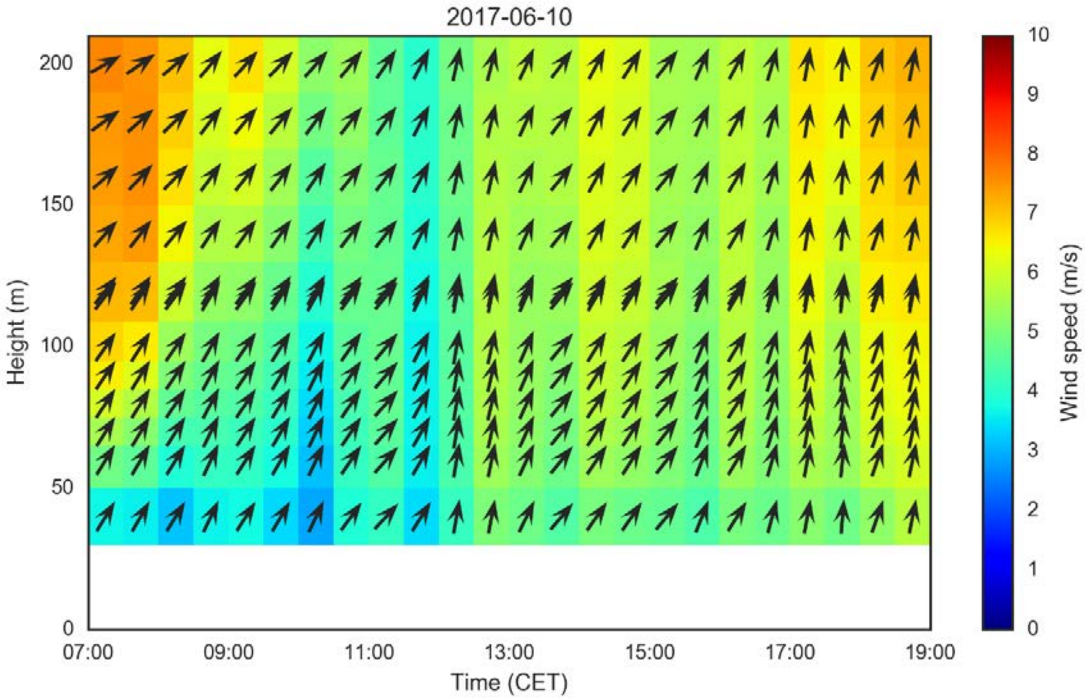
The campaign was successful, with measurements for all sources of the Test Site and quantitative emission values (within the quality criteria) for almost all the sources, although the measurement planning and set-up was not optimal for SOF. A standard SOF survey would, for example, be planned based on the weather forecast so that measurements were done during optimal wind directions. Also, the road access and work permits would have been set up to assure complete box-measurements of all areas and thus avoiding periods of major construction work. Finally, periods with non-typical operations, such as the maintenance of Tank112 (which gave extreme emissions), would have been avoided, unless these emissions were of particular interest.

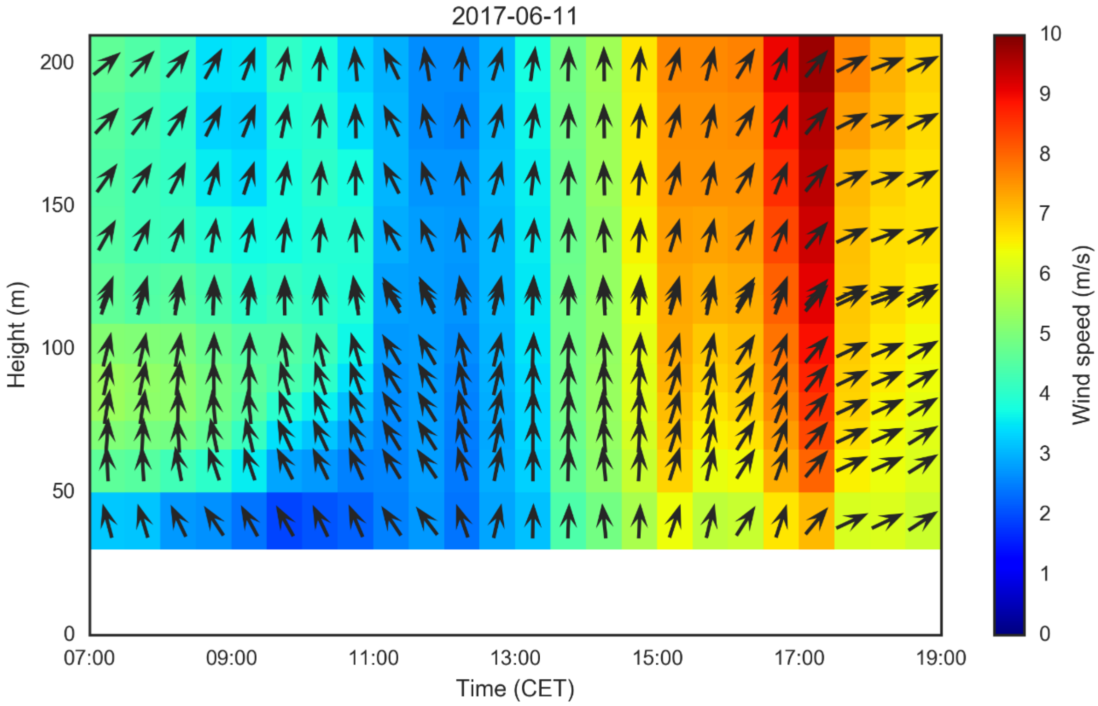
7 Acknowledgement

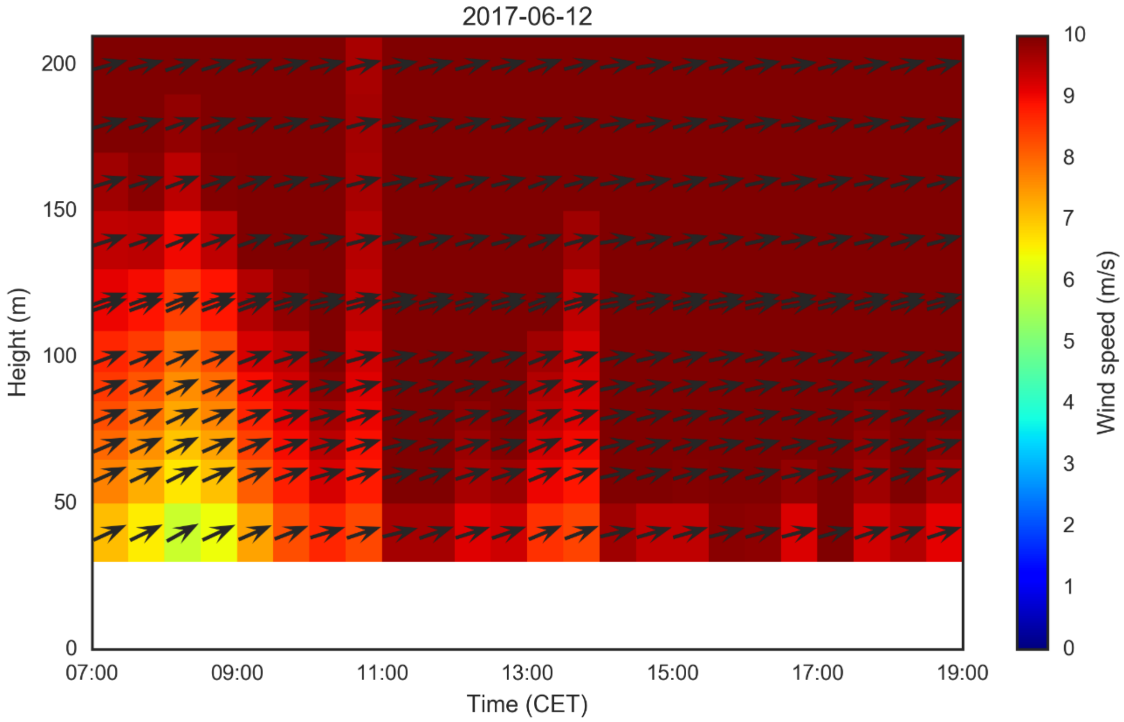
This work is a part (WP6) of the CEN WG 38 TC 264 standardization project, funded by the European Commission/EFTA. The measurement campaign was administrated by INERIS. Special thanks to the staff of the Test Site in The Netherlands for cooperation and to the other measurement teams for fruitful collaboration.

8 Appendix A: LIDAR Profile Plots.

Daily wind profiles from the WindCube LIDAR at the Test Site during the CEN The Netherlands campaign 10-21 June 2017 are found in the panels below. Wind speed for altitudes between 40 and 200 m are plotted as colored squares and the corresponding wind directions as black arrows.






2017-06-12
Height (m)
200
150
100
50
0
07:00
09:00
11:00
13:00
15:00
17:00
19:00
Time (CET)
Wind speed (m/s)
10
9
8
7
6
5
4
3
2
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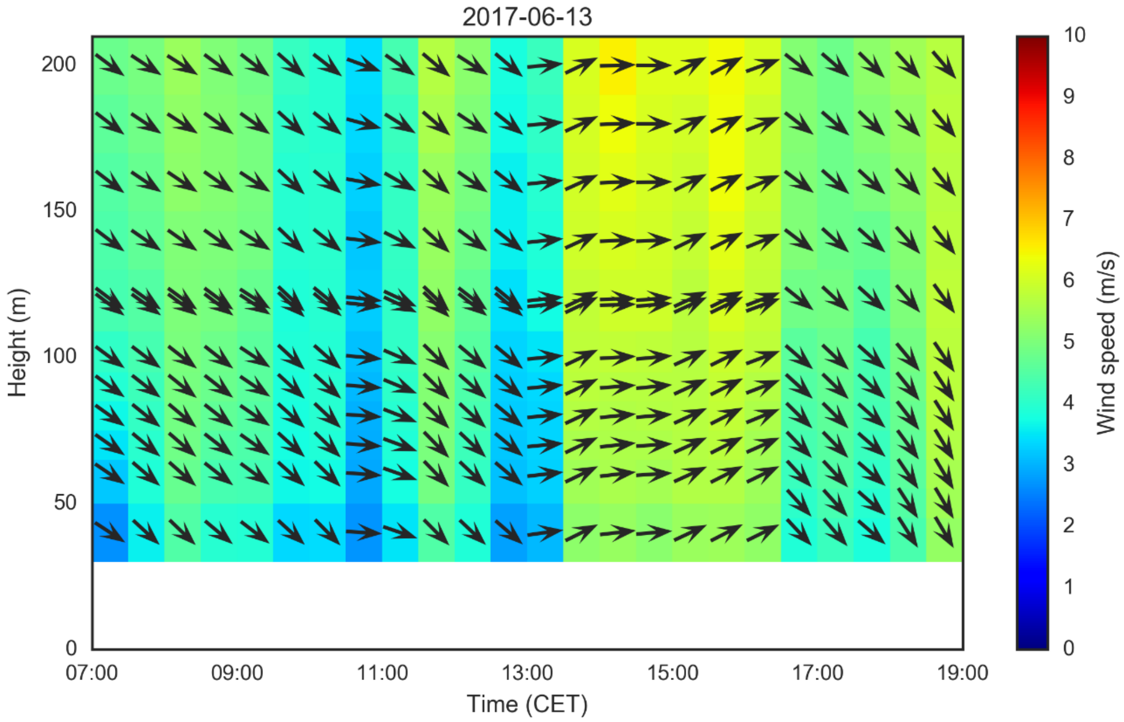
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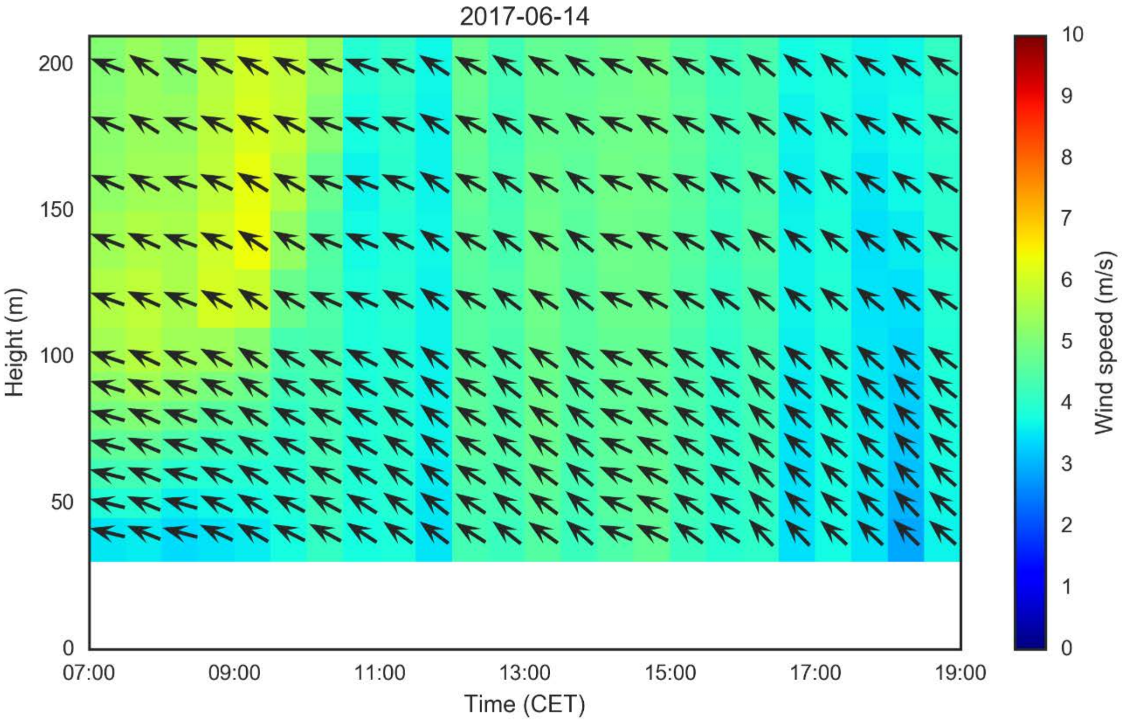
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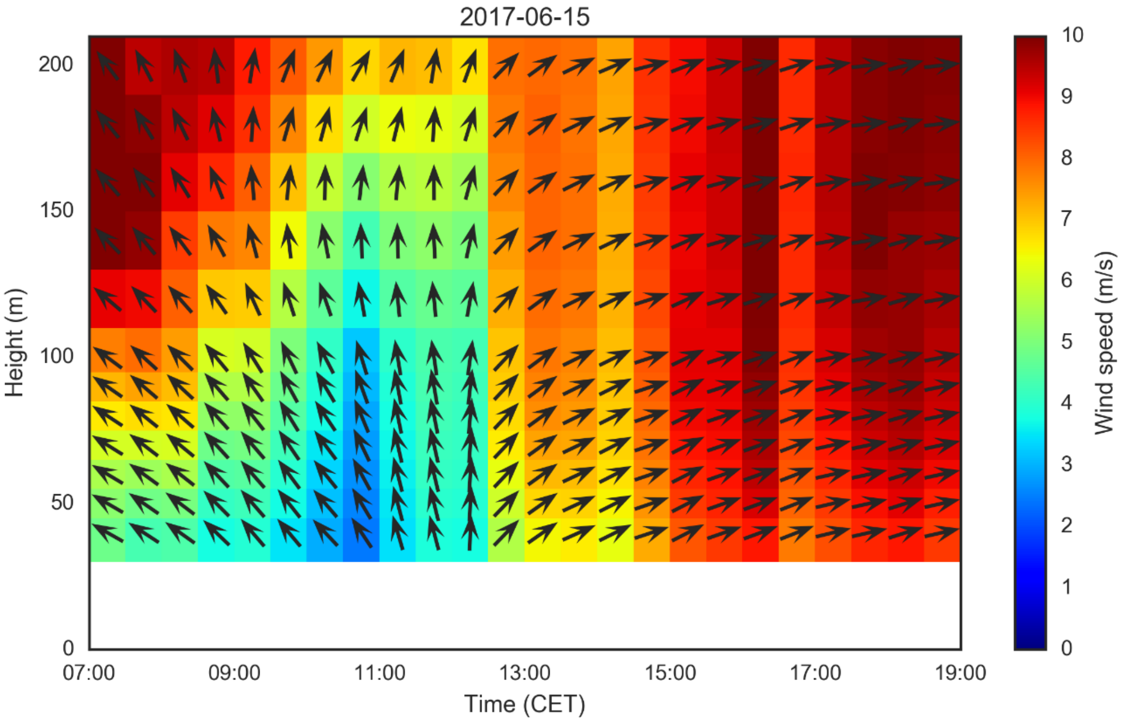
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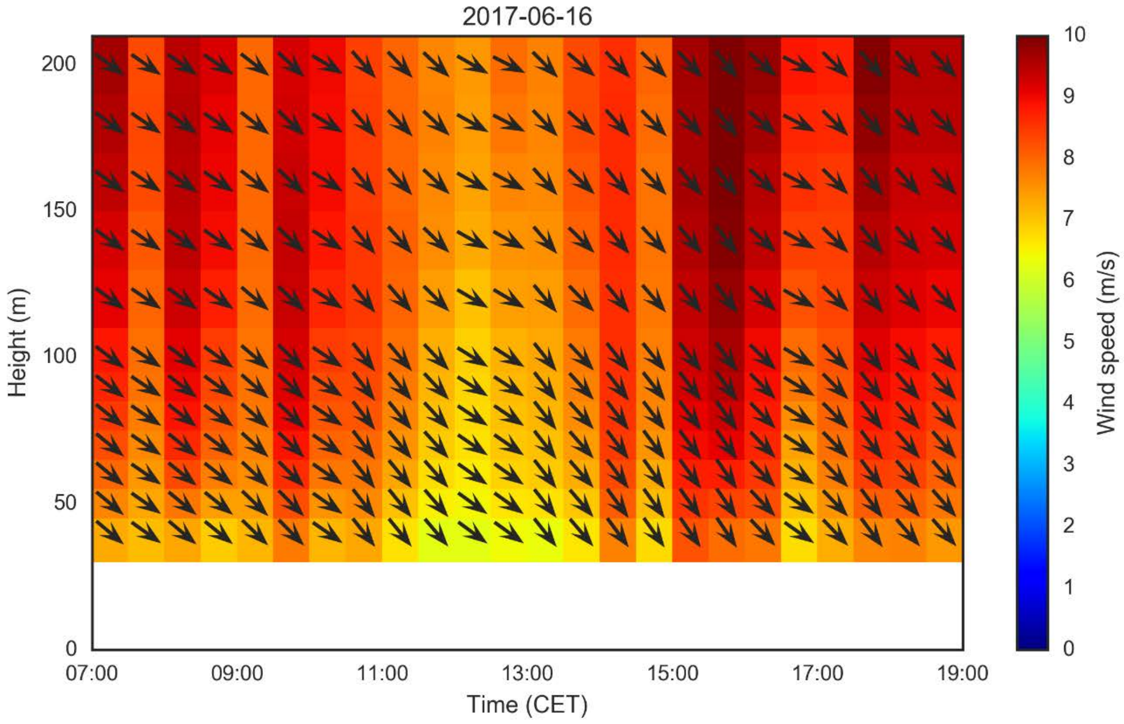
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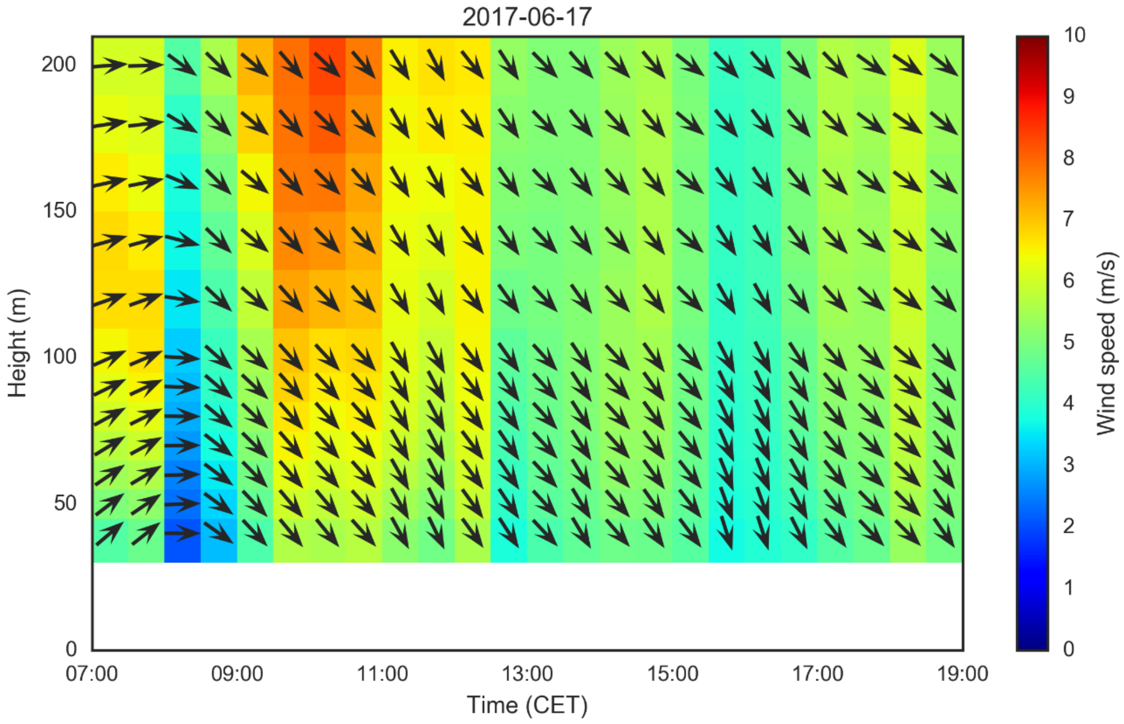
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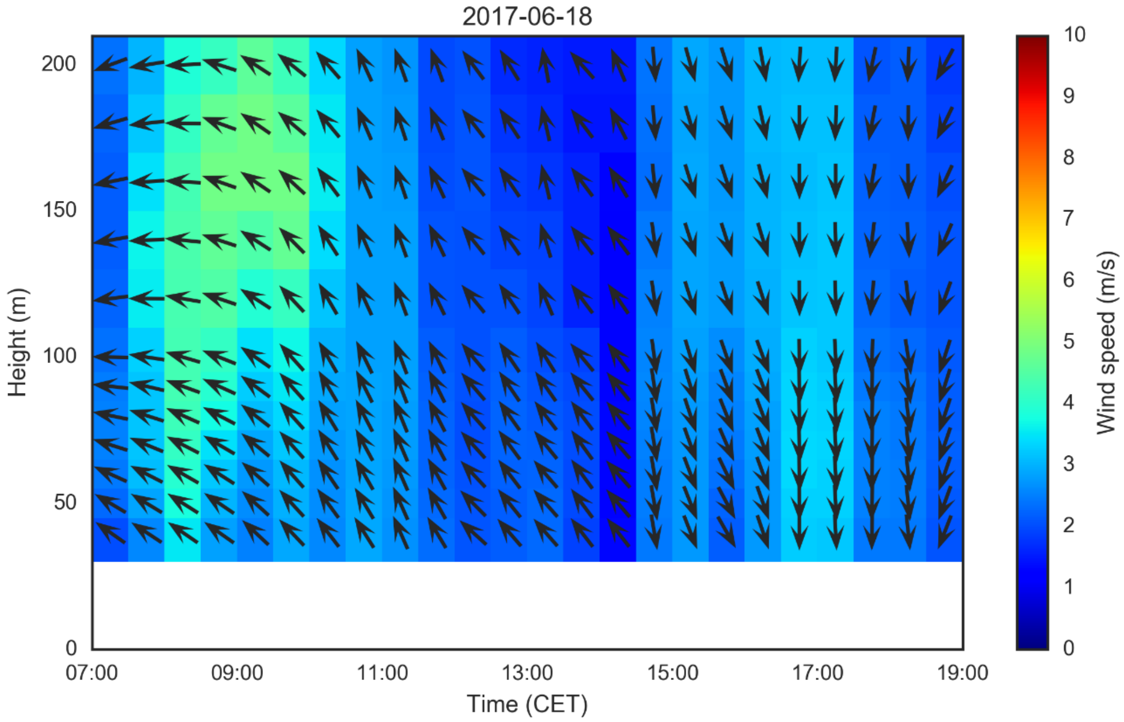
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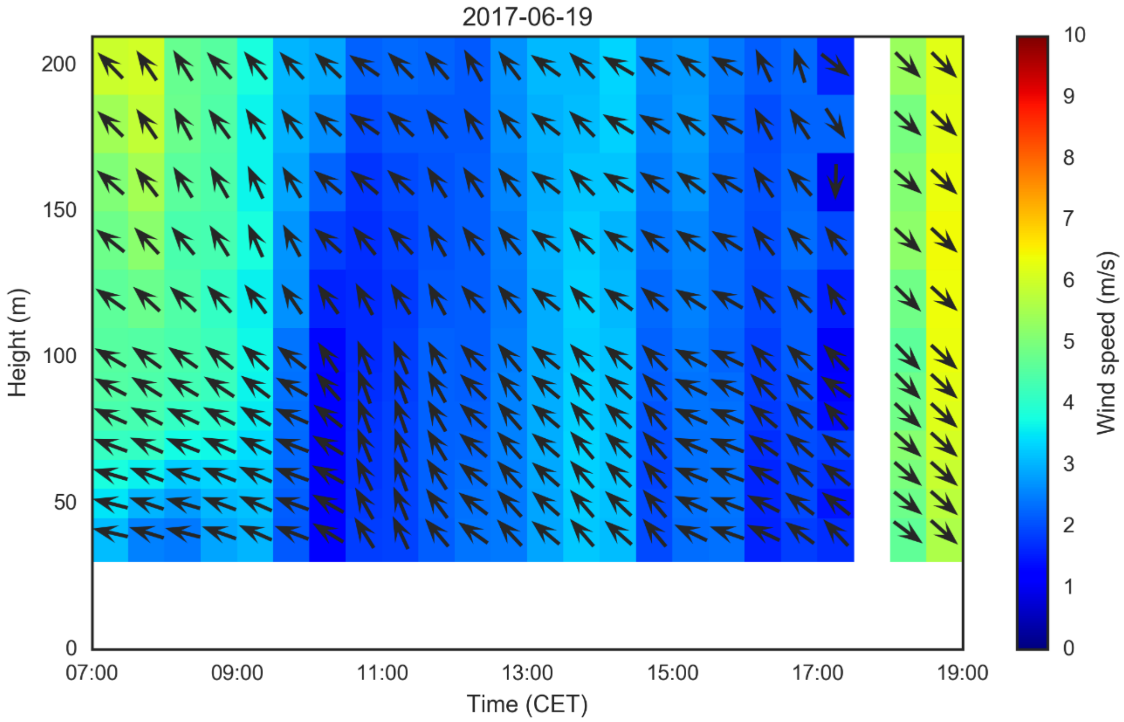
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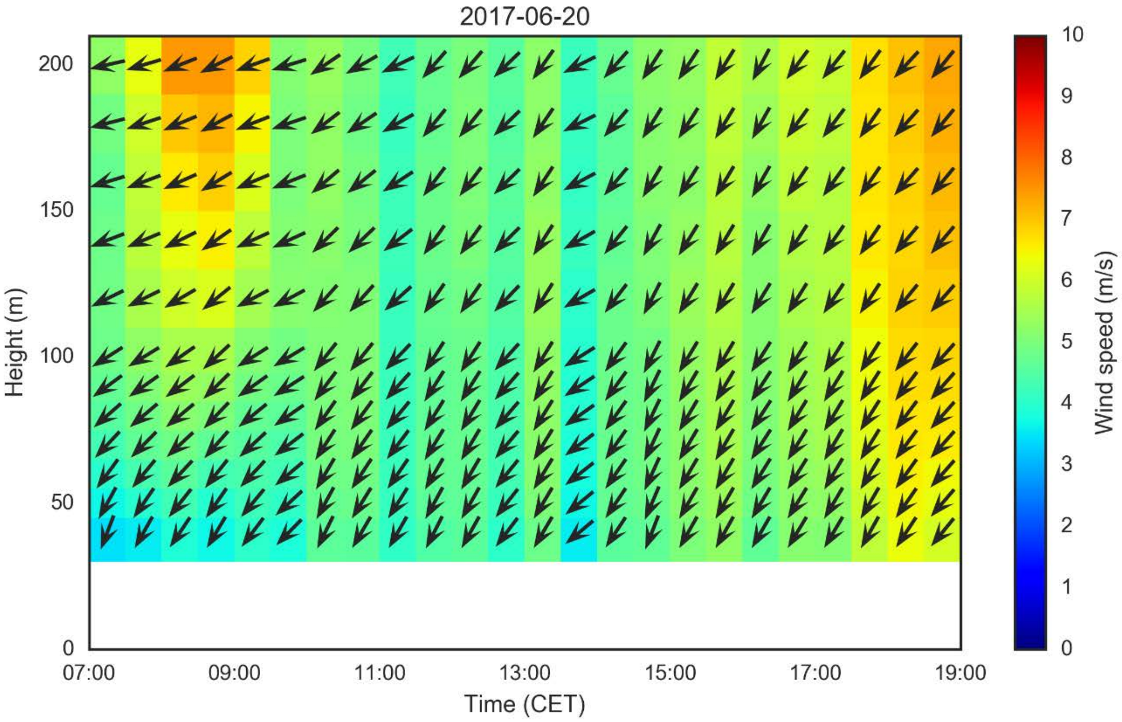
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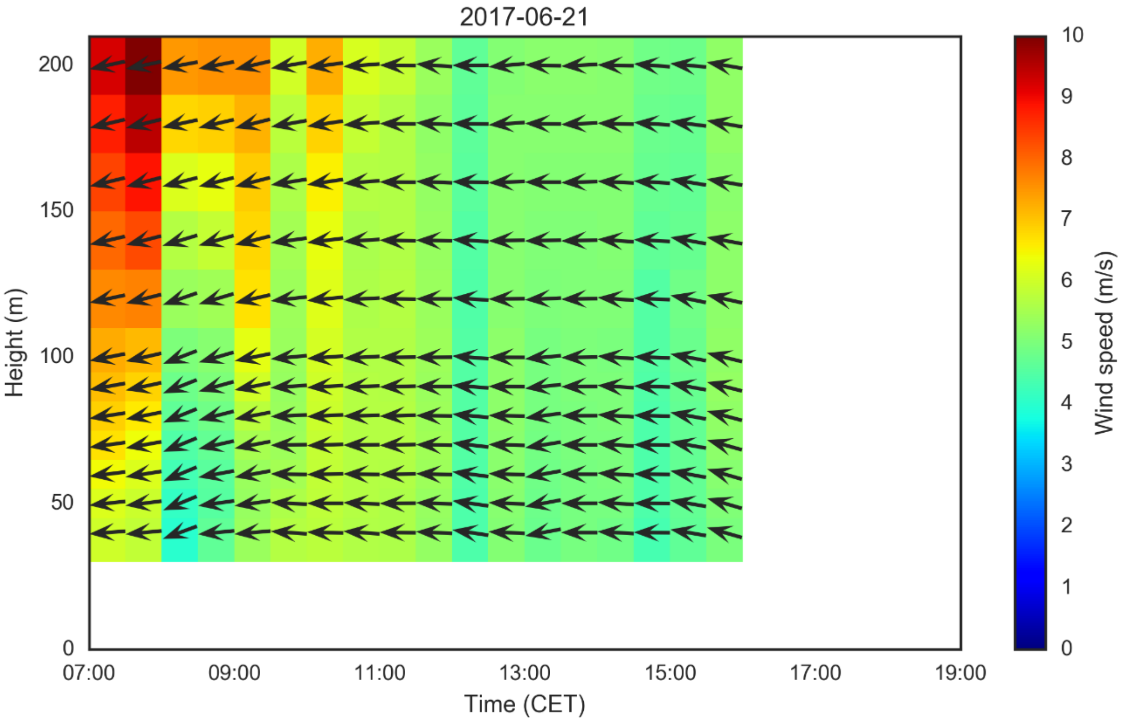
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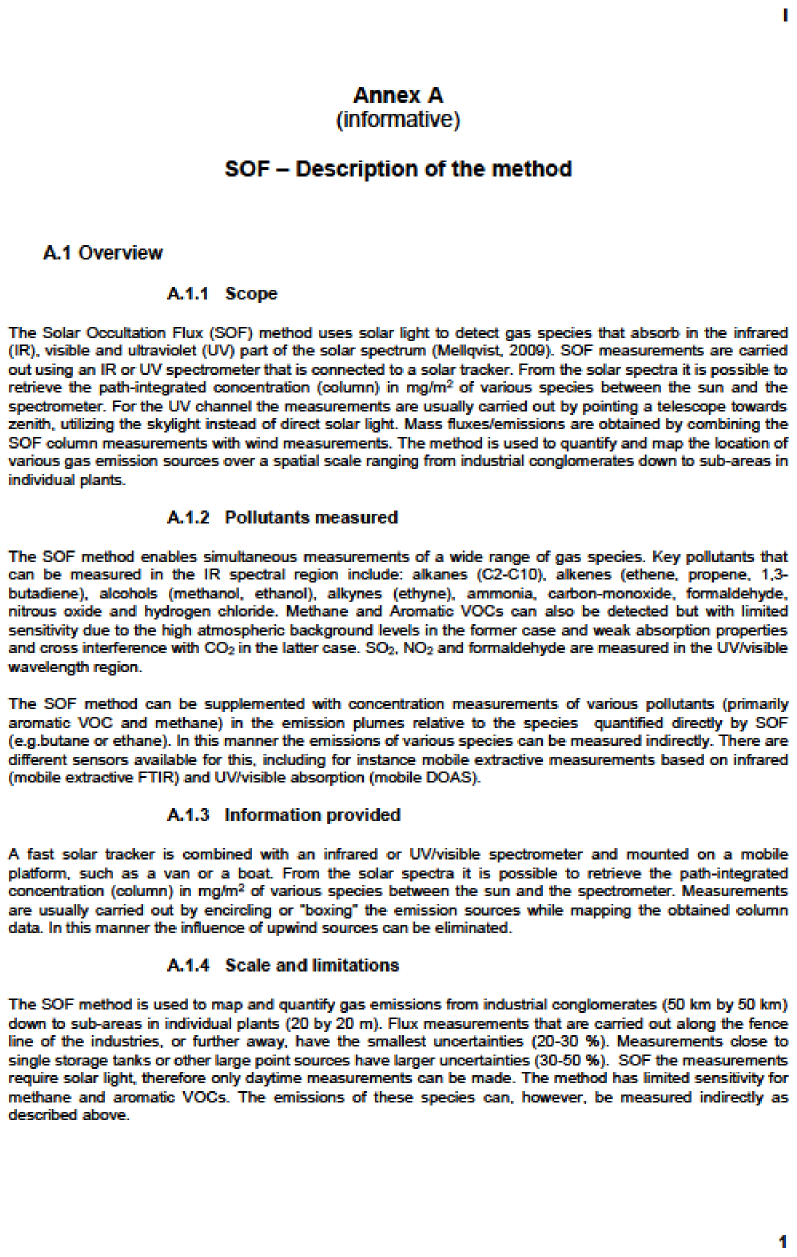
9 Appendix B: SOF Protocol v 2.0



Annex A
(informative)

SOF – Description of the method

A.1 Overview

A.1.1 Scope

The Solar Occultation Flux (SOF) method uses solar light to detect gas species that absorb in the infrared (IR), visible and ultraviolet (UV) part of the solar spectrum (Mellqvist, 2009). SOF measurements are carried out using an IR or UV spectrometer that is connected to a solar tracker. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. For the UV channel the measurements are usually carried out by pointing a telescope towards zenith, utilizing the skylight instead of direct solar light. Mass fluxes/emissions are obtained by combining the SOF column measurements with wind measurements. The method is used to quantify and map the location of various gas emission sources over a spatial scale ranging from industrial conglomerates down to sub-areas in individual plants.

A.1.2 Pollutants measured

The SOF method enables simultaneous measurements of a wide range of gas species. Key pollutants that can be measured in the IR spectral region include: alkanes (C2-C10), alkenes (ethene, propene, 1,3-butadiene), alcohols (methanol, ethanol), alkynes (ethyne), ammonia, carbon-monoxide, formaldehyde, nitrous oxide and hydrogen chloride. Methane and Aromatic VOCs can also be detected but with limited sensitivity due to the high atmospheric background levels in the former case and weak absorption properties and cross interference with CO_2 in the latter case. SO_2, NO_2 and formaldehyde are measured in the UV/visible wavelength region.

The SOF method can be supplemented with concentration measurements of various pollutants (primarily aromatic VOC and methane) in the emission plumes relative to the species quantified directly by SOF (e.g.butane or ethane). In this manner the emissions of various species can be measured indirectly. There are different sensors available for this, including for instance mobile extractive measurements based on infrared (mobile extractive FTIR) and UV/visible absorption (mobile DOAS).

A.1.3 Information provided

A fast solar tracker is combined with an infrared or UV/visible spectrometer and mounted on a mobile platform, such as a van or a boat. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m^2 of various species between the sun and the spectrometer. Measurements are usually carried out by encircling or "boxing" the emission sources while mapping the obtained column data. In this manner the influence of upwind sources can be eliminated.

A.1.4 Scale and limitations

The SOF method is used to map and quantify gas emissions from industrial conglomerates (50 km by 50 km) down to sub-areas in individual plants (20 by 20 m). Flux measurements that are carried out along the fence line of the industries, or further away, have the smallest uncertainties (20-30 %). Measurements close to single storage tanks or other large point sources have larger uncertainties (30-50 %). SOF the measurements require solar light, therefore only daytime measurements can be made. The method has limited sensitivity for methane and aromatic VOCs. The emissions of these species can, however, be measured indirectly as described above.

CEN 2017

FluxSense Report

Demonstration of tracer correlation measurements at a refinery in the Netherlands using mobile extractive FTIR as part of CEN validation, CEN WG 38 TC 264

FINAL REPORT

FluxSense AB

5 October 2019

Date: 5 October 2019

Title: Demonstration of tracer correlation measurements at a refinery in The Netherlands using mobile extractive FTIR as part of CEN validation, CEN WG 38 TC 264

Authors: Johan Mellqvist[1,2], Samuel Brohede[1,] John Johansson[1], Jerker Samuelsson[1] and Eva Emanuelsson[1]

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FluxSense started as a spin-off company from research conducted at Chalmers University of Technology in Sweden and has been active for more than 10 years. FluxSense has carried out more than 100 industrial site surveillances in Austria, Belgium, Denmark, France, Middle East, Netherlands, Norway, Sweden and the US.

[Cover:] Overview of all concentration measurements given in ppb alkane equivalents. The measurements were performed during 7 days in different wind directions. The area of the circles corresponds to the concentration while the colour corresponds to measurement day.

Summary

This report describes a validation experiment in The Netherlands 2017 as part of standardizing methods to measure fugitive VOC emissions. The work has been carried out as part of CEN WG 38 TC 264. The campaign was carried out from June 5 to June 22, at a refinery in The Netherlands. The main objective was to demonstrate different methods in a real facility and compare these if possible. The methods should follow their measurements protocol, as developed within the CEN project. This report describes concentration mapping measurements with the Mobile extractive-FTIR (MeFTIR) method which was carried out during 7 days. In addition, three emission sources were quantified using MeFTIR combined with tracer gas releases (MeFTIR/TC). This mobile remote sensing method requires steady wind, access to the emission point (for placing the trace gas) and possibility of driving around inside the industrial site.

Several VOC emission hotspots were detected at the Test Site using MeFTIR ground concentration mapping. The actual concentrations varied significantly with wind speed and distance from the source but were typically a few hundred ppb close to the hotspots. Also, mobile sources, such as vacuum trucks, had a large local and temporal influence on the concentration. The MeFTIR instrument measures ground level concentration which enhances low level sources as compared to elevated sources.

Three distinct sources (waste water treatment, vent pipe from truck loading and tank emissions from two tanks in chemical tank farm) were selected for quantification with MeFTIR/TC based on concentration mapping. The median values of the MeFTIR/TC measurements gave emissions of 9 kg/h of alkanes from the waste water treatment, 20 kg/h from the vent pipe and 44-74 kg/h from two tanks in the chemical tank farm (603/614 (no separation possible and complex source). The latter was in the form of pure cyclo-hexane. The Measurements at the vent pipe are associated with higher measurement uncertainty than in the protocol due to a misallocation in elevation of the tracer release point compared to the source gas emissions point.

Acronyms, Units and Definitions

Acronyms used in this report

FTIR	Fourier Transform InfraRed
MeFTIR	Mobile extractive FTIR
SOF	Solar Occultation Flux
TC	Tracer Correlation
SNR	Signal-to-Noise Ratio
QA	Quality Assessment
QC	Quality Control

Commonly used Gas Molecules

CH_4	Methane
NMVOC	Non-methane VOC
VOC	Volatile organic compound, used interchangeably for non-methane VOC (NMVOC)

Units

Wind direction	degrees North
Length	m
Weight	kg
Wind speed	m/s
Column	mg/m^2
Concentration	mg/m^3, 1 mg/m^3 = 1000 $\mu g/m^3$
Flux	kg/h

Table of Contents

1 Introduction and Background

This report describes a validation experiment related to standardization of methods to measure fugitive VOC emissions (CEN WG 38 TC 264). A campaign was carried out from June 5 to June 22 2017 at a refinery in The Netherlands, denoted the *Test Site* in this report. The main objective was to demonstrate different methods in a real facility and compare these if possible. The methods follow their measurements protocol, as derived within the CEN project. This report describes measurements with the Tracer Correlation method based on Mobile extractive FTIR, MeFTIR, (see Figure 2 and Annex A and B) which was carried out during four days. This mobile concentration method requires some wind (>1 m/s) and access to roads downwind and upwind the source. This report also describes the concentration mapping and leak search that was performed during the campaign to identify emission hotspots within the Test Site.

FluxSense performed controlled tracer releases at four sources during the project in order to quantify emissions. The releases were carried out at the water treatment, 2 tanks and one pipe.

Figure 1. Measurements vehicle including the mobile extractive FTIR.

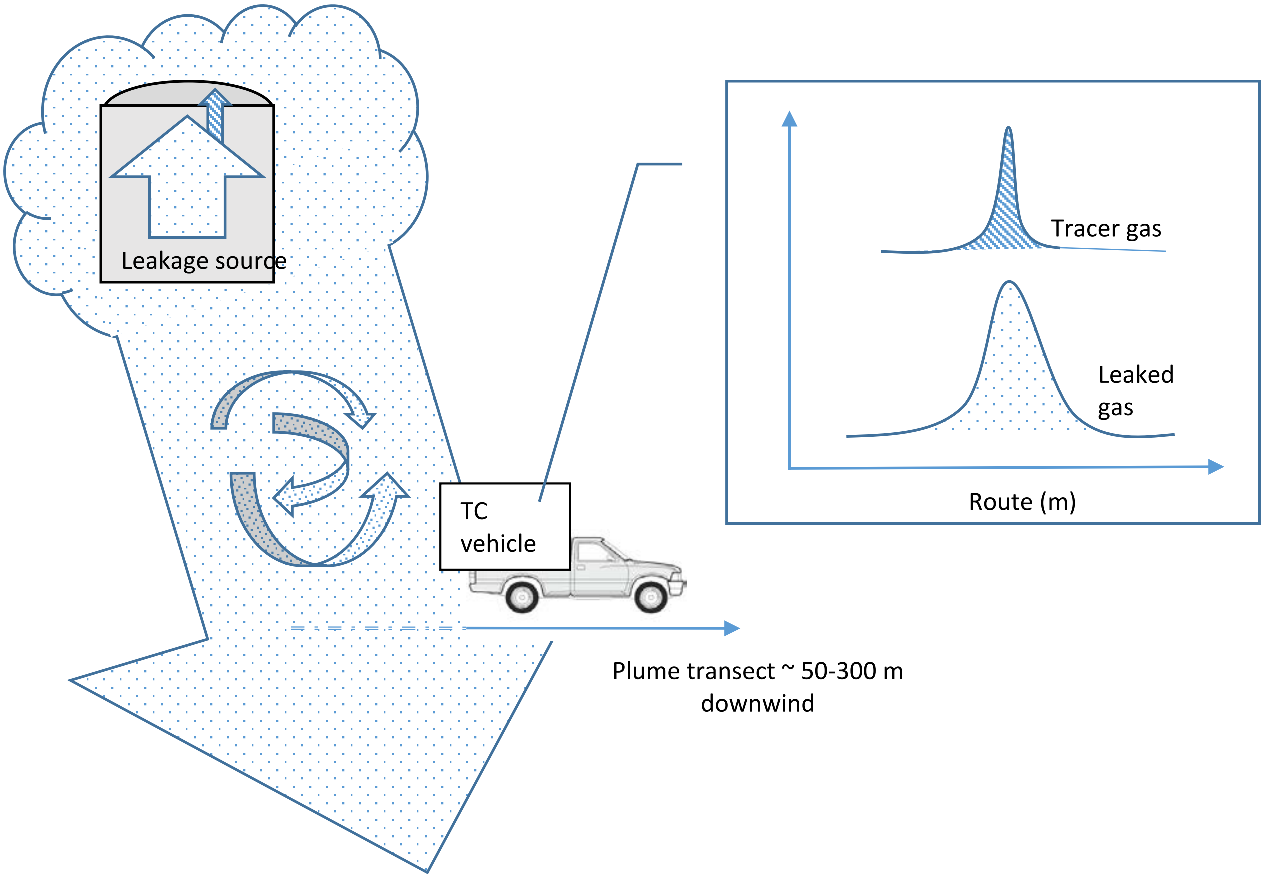


Figure 2. In the Tracer Correlation Flux method (TC) leaked gas and tracer gas are measured simultaneously by a mobile instrument with ppb sensitivity. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of leaked gas is obtained by multiplication of the plume gas/tracer quotient with the tracer release rate.

2 Measurement and Survey Setup

2.1 Concentration Mapping and Leak Search

The objective with the concentration mapping is to localize the dominant emission sources (hotspots) while measuring on accessible roads. As part of the project we performed such mapping inside the Test Site with the MeFTIR instrument during 7 days. Measurements were repeated during different times and meteorological conditions in order to study the temporal and spatial variability. The measured ground level concentrations depend on meteorological stability, wind speed and directions and distance between the source and measurements point and also on the elevation of the source. Measurements performed close to local ground sources yields the highest concentration values while elevated sources and distant sources are much more difficult to access. All concentrations are relative to a measured background level and given as concentration (ppb) of butane equivalents. Any significant and repeatable concentrations are noted as hot spots.

2.2 Emission Quantification

Tracer Correlation Measurements of VOCs and N_2O (tracer) with MeFTIR (Mobile extractive FTIR) were carried out to quantify emissions from specific local sources. In this approach, the ratio of the integrated source and tracer gas mass concentrations (kg/m^3), respectively, across plume is multiplied with tracer flow (kg/h) to obtain the gas emission mass flux (kg/h). See Annex A for details.

The tracer gas (N_2O) was released from a 10-liter gas cylinder through a ¼” tube as close as possible to the assumed leakage point. The tracer release flow rate was 1-5 kg/h based on weighing gas cylinder and a flowmeter to ensure constant flow.

Four tracer experiments were carried out during the campaign; one at the Waste Water Treatment (ground level release), two at storage tanks in the Petro-Chemical Tank Park (tank height level release) and one at a Vent Pipe west of the truck filling site (10 m level release), see locations in Figure 3:

Sources quantified with MeFTIR/TC:

- Waste Water Treatment
- Vent Pipe west of Truck Loading Area
- Tank C603/614 (in Petro-Chemical Tank Park), two separate measurements

Figure 3. Map showing the extent of the Test Site during the CEN THE NETHERLANDS 2017 survey. Also noted are local meteorological stations (white dart boards). Map from Google Earth © 2017.

Figure 4. Map showing the measured sources of the Test Site during the CEN THE NETHERLANDS 2017 survey. Local sources are denoted as white pins and area sources as shaded regions. Map from Google Earth © 2017.

2.3 Wind measurements

Wind measurements were carried out by INERIS with three portable 10 m wind masts a wind-Cube LIDAR located according to Figure 3. Note that MeFTIR/TC measurements do not require wind data directly for flux calculations (as is the case for SOF) but they are dependent on wind speed for appropriate trace gas mixing and wind direction to avoid interfering background plumes. And for the identification of the sources. For these purposes, wind information from the mast at the truck loading area was generally used.

3 Performance characteristics and measurement protocol

A summary of the performance capabilities of a typical TC system under normal conditions are given in Table 1. The values given are based on the actual levels of performance of existing TC-MeFTIR systems, determined from the typical absolute precision for concentration measurements in earlier studies. The numbers in Table 1 are applicable given that the plume concentrations of leak gas and tracer gas above background are well above detection limits.

Table 2 shows the estimated uncertainty for flux measurements in various field conditions when measuring alkane emission from refineries and petrochemical industries. This estimate is obtained as the root-sum-square of various error sources estimated from various campaigns and controlled releases. The performance will improve for small sources with less tracer mismatch uncertainty, and with longer distance to the source, given that no interfering plumes and/or too low plume concentrations are introduced as a result. The main uncertainty of the flux measurements of diffuse emission sources comes from the uncertainty in the tracer allocation relative to the emission sources.

The infrared cross sections for alkane have an uncertainty of 3–3.5 % and retrieval errors of 10 % have been estimated for the different species. This is the combined effect of instrument and retrieval stability on the integrated concentrations above background for a plume transect. For the alkane retrieval this also includes a 6 % mass retrieval uncertainty due to limited specificity. All these uncertainty sources have been combined by root-sum-square to a composite flux measurement uncertainty range for each species and study. The maximum and minimum for each range was calculated using the inherent maximum and minimum uncertainties. In most cases, the composite uncertainty is approximately 20-30 %.

Table 1— Capability of a typical TC-MeFTIR concentration measurement based on measurements in the 3 µm IR region.

Parameter	**Precision/Detection (1σ)**	**Accuracy**
Alkanes (C_2-C_8) (IR) (C_4-equivalents)	2.5 ppb	10%

(1) Precision in ppb, assuming 78 m path length and C_4 mixture.

Table 2. Typical uncertainty estimation of alkane flux measurements for diffuse emission sources (the variability of the sources not taken into account).

	Spectroscopy (cross sections) [a)]	Retrieval error [b)]	Tracer release rate	Tracer/Source allocation mismatch [c)]	Composite flux measurement uncertainty [d)]
Alkanes	3.5 %	10 %	5%	20 %	20–30 %

[a)] Includes systematic and random errors in the cross-section database.

[b)] The combined effects of instrumentation and retrieval stability on the retrieved cross-plume concentrations during the course of a plume transect and error of the TC alkane mass retrieval.

[c)] The estimated uncertainty due mismatch between tracer and leaked gas locations – depends on source size and complexity and the distance between source and plume measurement (plume dispersion time)

[d)] The composite square root sum of squares uncertainty

The main objective of this study was to demonstrate the TC technique for measurements of fugitive VOC emissions in a real measurement situation. The measurements were based on a measurement protocol developed as part of the CEN WG 38 TC 264 work, see Annex B. However, due to practical limitations of this campaign, primarily in terms of site access and restrictions in the permits to release tracer gas, the protocol could not always be followed in an optimal way, hence increasing some of the measurement uncertainties, as described in the text below.

The general methodology, as given in the TC CEN-protocol, is described here with test specific comments after each bullet:

- Drive around the site area and conduct concentration mapping to identify the location of the main source leaks, and any interfering adjacent sources.
- Carry out controlled tracer releases at the identified source areas, and make simultaneous downwind measurements of the source and tracer gas e.g. using mobile extractive FTIR.
  - For complex source areas, the major leakage points should be identified and localised. This can be done using extractive measurements, handheld devices like photo ionization detectors (PID), Optical Gas Imaging (OGI) or corresponding. *However in this campaign it was not allowed by the instrument operators to perform such measurements and this was instead by done using OGI by an independent party (ECS) to test the sensitivity of the different techniques.*

  - Position the tracer source(s) as close to the identified leak gas sources as possible so that the centre of gravity for the tracer release and leak gas sources, respectively, are close. The tracer and leak gas should disperse in the same manner. *Tracer was released as close as the sources as possible, but due to limitation in site permits it was not always possible to make optimal tracer gas releases.*

- Investigate the variability in the measurements due to tracer and source misallocation using one of the following methods:
  - Measure at far away distance, so that the area/volume source becomes more of a point source (suppression of any tracer gas and source gas location mismatch). Typically, a distance away from the source of more than 5 times the area unit dimension. *In the present test, most measurements were done somewhat closer than the ideal situation.*
  - Measure at different distances and different wind directions to assess the variability of the obtained emissions. *This was done in some cases but on different days, wherefore there was a risk that some of the actual source emissions could vary between the days due to different site operations.*
  - Utilize two different tracer gases, or move the position of the single tracer gas, to make a sensitivity study of the variation in the obtained emissions. *Not used for this test.*

For a given wind direction the area to measure should be chosen such as:

- The area under investigation is clear from strong upwind sources. Avoid areas with high inflows or where the background of VOC and tracer can't be estimated.
- It is of outmost importance to verify that no significant sources of the measured VOC or tracer gas used is located between the studied source and the measurement

location. This would interfere and offset retrieved emission results using the TC method.

-In the controlled released test concentration mapping showed background and interfering sources in nearby units of primarily hexane (C6+ alkanes) and cyclohexane, whereas the release plume was totally dominated by propane. Controlled release mass was retrieved as propane using a resolution between 0.5 – 8 cm-1. For cases where background was too strong and variable or adjacent sources seriously affected the baseline at the release plume edges, data transects were discarded.

For valid data is required a wind speed above 1 m/s (sufficient plume mixing) and at least 4 measurement transects per day downwind of each reported source. *Data was screened according to these criteria.*

4 Results

Results for Concentration Mapping and Leak Search and for Emissions Quantification and typical measurement transects are presented in the subsections below.

4.1 Concentration Mapping and Leak Search

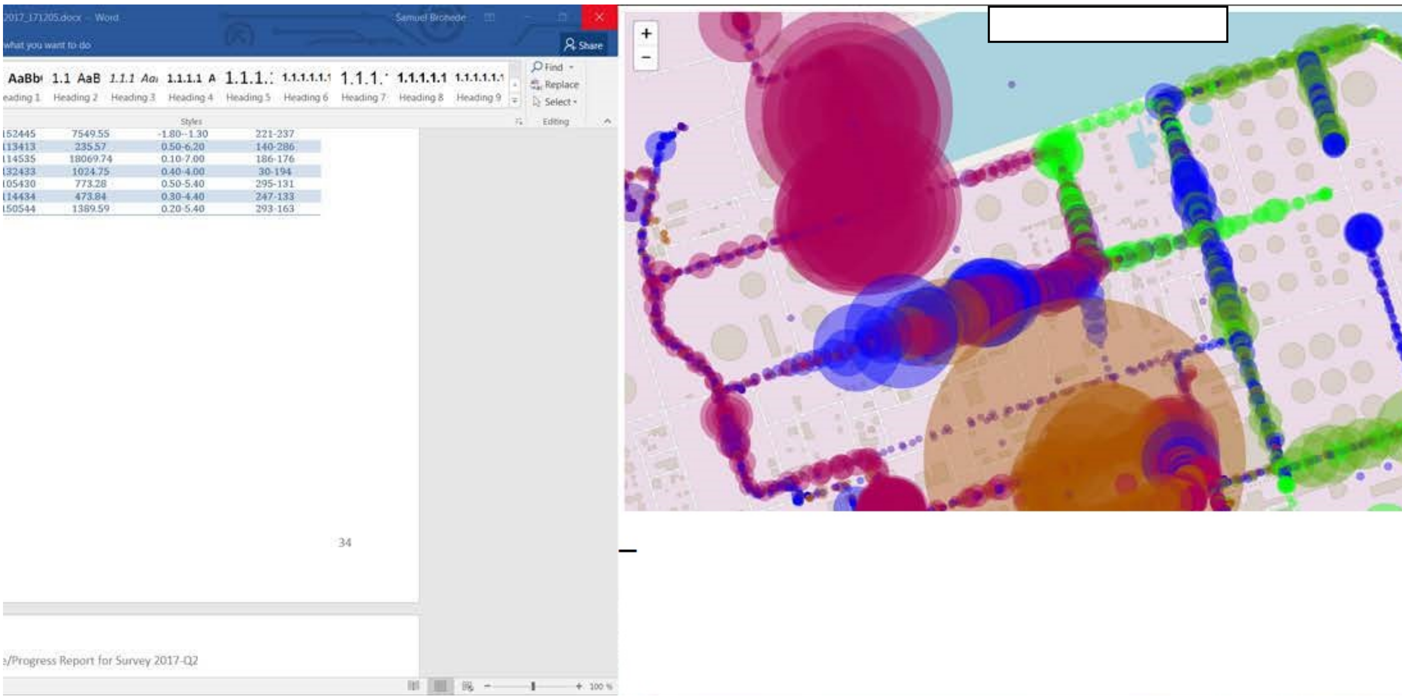
Results from concentration mapping of ground level (vehicle roof top level of 2.5 m) concentration during the CEN The Netherlands 2017 survey are presented in this section. Note that the concentrations are given as butane equivalents in ppb above background levels. The measurements were performed during 7 days with 14 measurement series, see Table 3.

Table 3 Maximum measured ground concentrations (ppb) of butane equivalents above background levels during concentration mapping of the Test Site. Each row corresponds to a measurement series. * On 170616 a vacuum truck was in operation at the Petro-Chemical Tank Park resulting in temporal high concentrations in its proximity.

Day	Time span [hhmmss]	Max Conc [ppb]
170609	115836-141509	2275.43
170609	103103-115525	439.35
170609	100623-102718	470.90
170612	101002-104534	1170.42
170612	133754-161219	204.25
170612	104854-112824	86.13
170613	100034-121105	408.40
170613	133852-152445	7549.55
170615	105029-113413	235.57
170616*	105748-114535	18069.74
170619	113709-132433	1024.75
170620	101239-105430	773.28
170620	112030-114434	473.84
170620	135750-150544	1389.59

A visualization of the concentration mapping measurements, where each color corresponds to a separate day, is found in Figure 5. Individual measurements are printed as coloured dots in OSM-maps (Open Streetmap™) where the radius is proportional to the concentration and the smallest area corresponds to the detection limit. Note that the wind speed and direction changes between days. Also, mobile sources appeared in the measurements that was not the focus of the study. On 170616, a vacuum truck was in operation in the Petro-Chemical Tank Park, resulting in local temporarily concentrations.

Still a clear pattern of local/stationary hot spots emerges from the measurements as pointed out in Figure 6. Tank 112 in the Middle Tank Park, Tank 603/614 in the east part of the Petro-Chemical Tank Park and the Vent Pipe west of the Truck loading area clearly stands out, but there are also other local sources for example individual tanks in the East Tank Park. Many of these sources are also recognized in the SOF column mapping (See separate report).



152445	7549.55	-1.80--1.30	221-237
113413	235.57	0.50-6.20	140-286
114535	18069.74	0.10-7.00	186-176
132433	1024.75	0.40-4.00	30-194
105430	773.28	0.50-5.40	295-131
114434	473.84	0.30-4.40	247-133
150544	1389.59	0.20-5.40	293-163

Figure 5. Overview of all concentration measurements given in ppb butane equivalents for seven different days in different wind directions. The area of the circles is proportional to the concentration. Each colour series corresponds to measurement during one day. On 170616, a vacuum truck (mobile source) was in operation in the Petro-Chemical Tank Park, resulting in local temporarily concentrations there.

Figure 6. Local hotspots found during real-time concentration measurements using the mobile extractive FTIR, based on data in Figure 5.

4.2 Emission Quantification

VOC emissions were quantified from 4 different sources with MeFTIR/TC during the CEN THE NETHERLANDS 2017 campaign as presented in Table 3 and indicated in Figure 4. Results in the subsections below are presented as different statistical measures such as averages, standard deviations and medians. Median values are less sensitivity to outliers while the averages more closely resemble the actual emissions during the measurements.

Table 4. Summary of **MeFTIR/TC** emission flux measurements during the CEN The Netherlands 2017 survey. Results are reported here as median values of all quality assured transects to reduce sensitivity to outliers, 1-Q=1st quartile, 3-Q=3rd quartile. SD= 1-σ Standard Deviation. 95% CI= 95% Confidence Interval for the mean. *These measurements were outside the MeFTIR/TC protocol due to trace gas release mismatch.

CEN The Netherlands 2017 Quantified Sources with MeFTIR/TC	**Counts**		**MeFTIR/TC Alkane Mass Flux Results**						**Comment**
	Days	**No**	**Median** Flux [kg/h]	**1-Q** Flux [kg/h]	**3-Q** Flux [kg/h]	**Mean** Flux [kg/h]	**SD** Flux [kg/h]	**95%CI** Flux [kg/h]	
Sources									See Figure 4
WWT	1	11	9.0	6.9	12	9.2	2.6	1.8	Complex source
*Vent Pipe**	*1*	*13*	*20*	*9.7*	*31*	*30*	*31*	*19*	*Release Mismatch*
Tank 603/614 (tracer@614)	1	11	44	16	65	43	23	16	Complex Source
Tank 603/614 (tracer@603)	1	10	74	24	117	77	52	37	Complex Source

4.2.1 Waste Water Treatment

The Waste Water Treatment (WWT) is located northeast of the Main Process and east of the Middle Tank Park, see Figure 4. The measurements were done during northerly winds. The trace gas was released between the two tanks as indicated by the yellow dot in Figure 4.

Quantification of this source was based on 11 quality assured MeFTIR/TC transects 20 June between 11:36 and 12:22 as presented in Table 5. The mean value was 9.2 kg/h and the median value 9.0 kg/h. See example of a typical measurement transect in Figure 6.

As discussed in section 3 it was not allowed to carry out independent leak search inside the area, due to the setup of the campaign, but it was later found out in the OGI data by ECS that there were actually three main leakage sources in the WWT area. The tracer gas was released close to one of the three sources, but for the actual wind direction during the TC measurements the sources overlapped and the controlled gas release therefore simulated the emissions from all three sources relatively good. In addition, the sources were relatively far away from the measurement point wherefore we estimate that the uncertainty of the TC measurement is within the normal uncertainty range of the TC method as given in section 3 and the annexes. This is strengthened by a relatively small standard deviation in the emission measurements and the fair spatial correlation between tracer and source gas plume

Table 5. MeFTIR/TC alkane measurements of **Waste Water Treatment** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 4 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170620	113658-122211	11	9.2	2.5	2.4-5.9	14-343
Average		**11**	**9.2**	**2.5**		
Median			**9.0**			

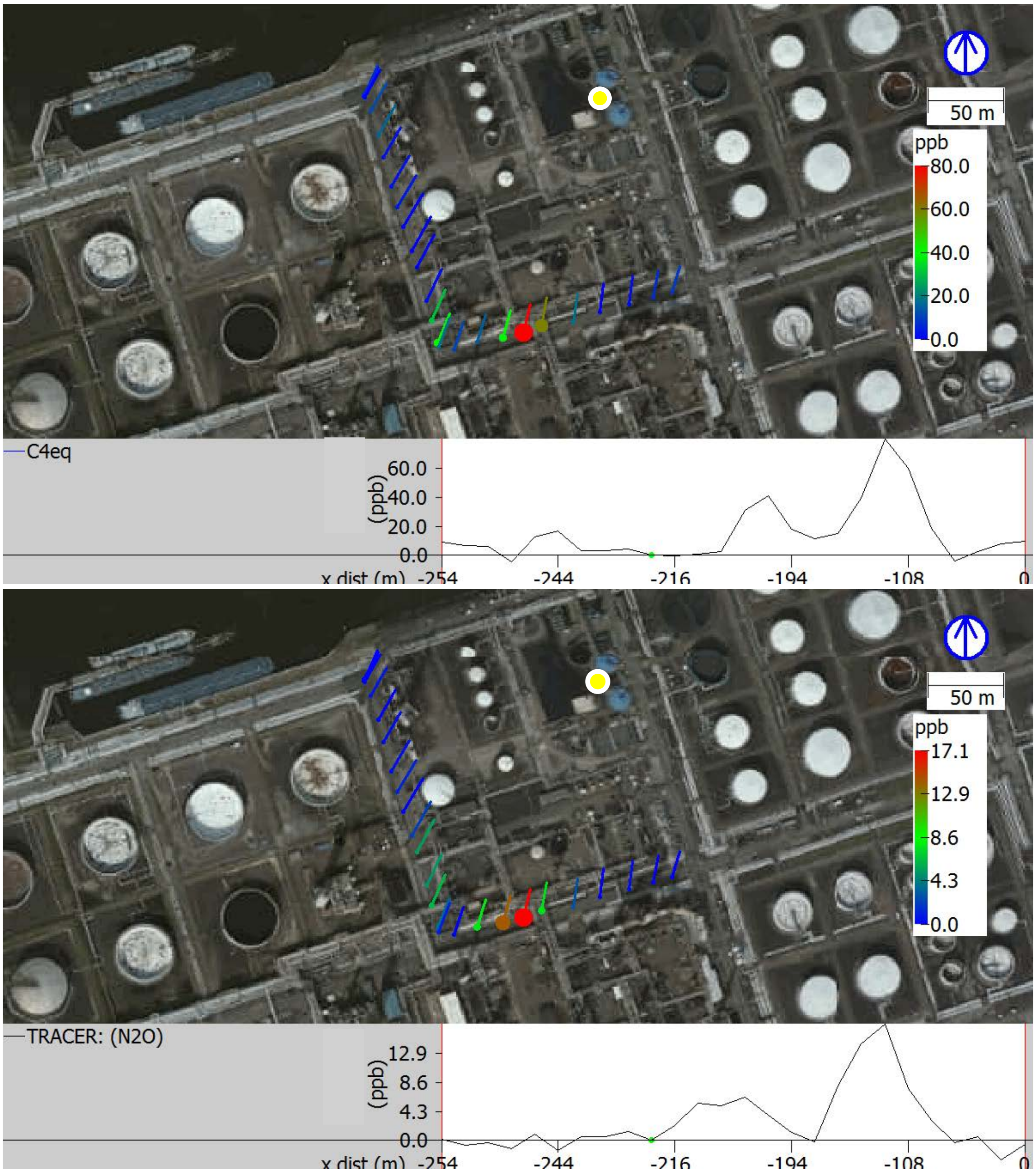


Figure 7 Example of MeFTIR/TC measurements of the Waste Water Treatment, 2017-06-20 at 11:19. Ground level concentrations of butane equivalents (C4eq) in upper figure and trace gas (N_2O) in the lower figure. The dots show the trace of the vehicle and the colour indicate the local concentration (ppb) according to the colour bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the concentrations as a function of distance from the start. The yellow dot indicates the trace release point.

4.2.2 Vent Pipe

The Vent Pipe is located west of the Truck Loading area (see Figure 4) and it is approximately 10 m high. The measurements were done during northerly winds. The tracer gas was released below the pipe at ground level (1 m).

The leakage rate from this source was obtained from 13 quality assured MeFTIR/TC transects 20 June between 14:51 and 15:27 as presented in Table 6. The mean value was 30 kg/h and the median value 20 kg/h. See example of a typical measurement transect in Figure 8. The measurements were carried out relatively far from the release points, 100-200 m, compared to the dimensions of the source.

The reason for not releasing the tracer gas from the top of the pipe was due to diffulties in acquiring and modifying the permit for the tracer gas release (originally it was planned to release the gas from a nearby structure at the ground). The mismatch in release altitude of the tracer and the source gas was evident from the large relative standard deviation (100%, see Table 6) of the individual measurements and distinct spatial separation between the source and tracer gas plumes, on many occasions. Part of the large standard variation in emissions could be caused by real emission variations but other measurements in this study by the SOF technique indicates a much smaller variability (30%, see separate report). All in all, we estimate that the misallocation in height between the tracer and source gas may have caused higher measurement uncertainties than reported in sections 3.

Table 6. MeFTIR/TC alkane measurements of **Vent Pipe** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 4 for area localizations. *This measurement was outside the MeFTIR/TC protocol due to trace gas release mismatch.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170620*	*145139-152719*	*13*	*29.6*	*30.0*	*3.3-8.3*	*6-354*
Average		**13**	**29.6**	**30.0**		
Median			**19.8**			

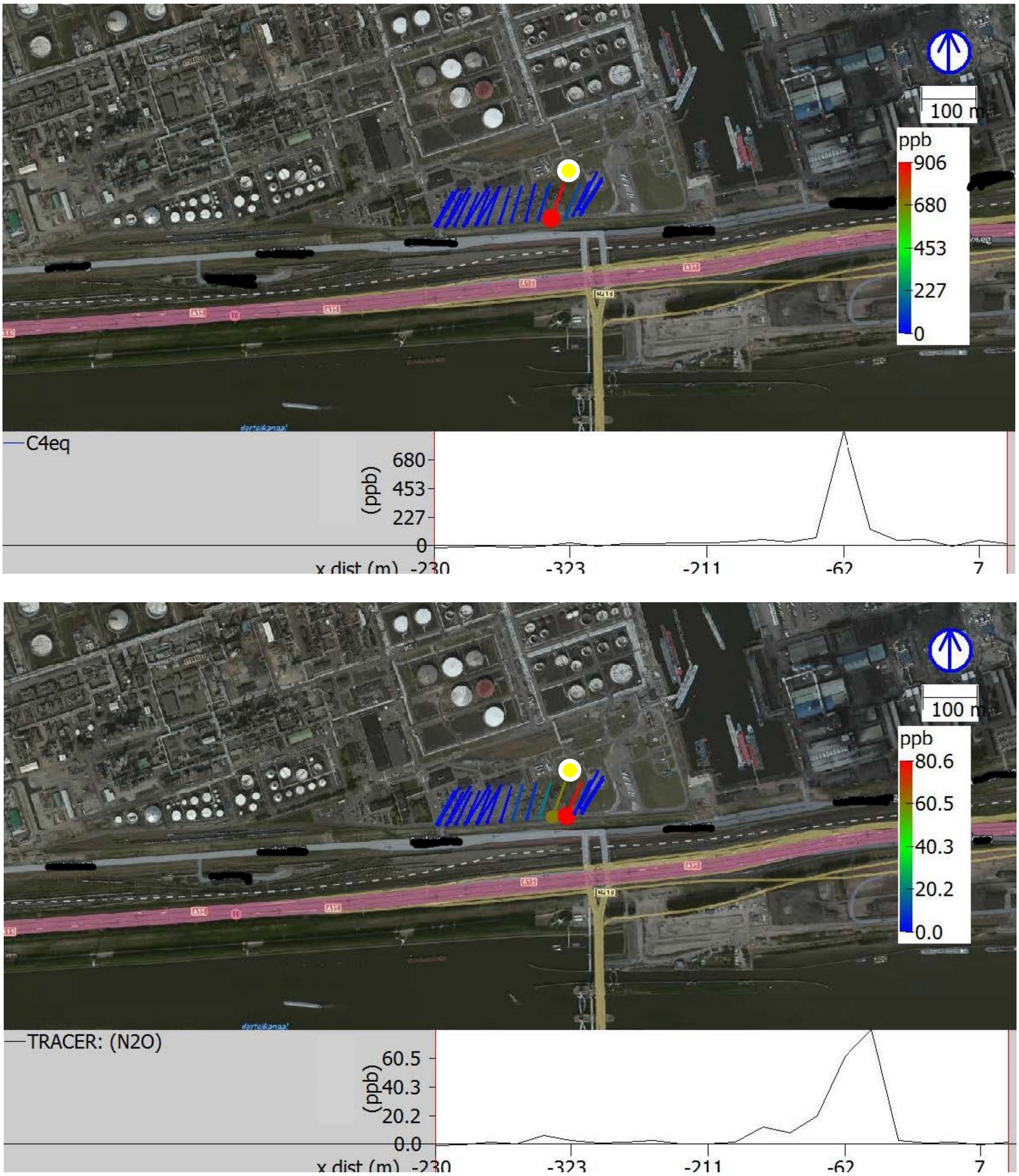


Figure 8 Example of MeFTIR/TC measurements of the Vent Pipe, 2017-06-20 at 14:59. Ground level concentrations of butane equivalents (C4eq) in upper figure and trace gas (N_2O) in the lower figure. The dots show the trace of the vehicle and the colour indicate the local concentration (ppb) according to the colour bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the concentrations as a function of distance from the start. The yellow dot indicates the trace release point.

Figure 9 Alternative visualization of MeFTIR/TC measurements of the Vent Pipe, 2017-06-20 at 15:00. The height of the blue line is proportional to the ground level concentration of Butane equivalents (1 m is equivalent to 1 ppb; max measured value was 906 mg/m^2) and the red line is proportional to the ground level trace gas concentration (1 m is equivalent to 1 ppb; max measured value was 81 mg/m^2). Different areas of the test site are shown as colored fields. The wind direction is indicated by the white arrow. Map from Google Earth™ 2018.

4.2.3 Tank 603/614

Concentration mapping was carried out around the Petro-Chemical Tank Park, see Figure 4, and significant VOC emissions were observed at the eastern part of the tank farm, pointing mostly towards the two tanks 603 and 614. From the spectral analysis it was identified that the emission was in the form of pure cyclo-hexane. According to the MeFTIR/TC-protocol, the spectroscopic mixture was changed from normal alkanes to pure cyclohexane.

Two independent tracer release measurements were carried out during two days with westerly and northerly winds, with tracer positioned on tank 614 and 603, respectively. The trace gas was released from different positions at the ceiling of the tanks on the upwind side. It was not possible to separate between the emission from the two tanks with the current wind conditions and the plume distributions indicated emissions from both tanks during both episodes.

On June 13 the tracer gas was released from tank 603 and 10 good transects were carried out with MeFTIR/TC between 12:14 and 13:10 as presented in Table 7. The mean value was 77 kg/h and the median value 74 kg/h. On June 16 the tracer was instead released on tank 614 and then 11 quality assured MeFTIR/TC transects could be carried out between 11:20 and 12:17 as presented in Table 8. The mean value was 43 kg/h and the median value 44 kg/h. See example of a typical measurement transect in Figure 10.

Normally, following the protocol, a leakage detection to identify the source should have been done but as discussed in section 3 this was instead carried out by the independent contractor ECS and revealed first afterwards at the time of reporting. The OGI measurements on June 13 showing that tank 603 was the main source on this day but that also tank 614 was leaking. It is not known what the situation was on June 16.

Table 7. MeFTIR/TC alkane (cyclo-hexane) measurement of **Tank 603/614 – Tracer on 603** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 4 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170613	121457-131035	10	77.2	48.9	3.1-5.7	228-266
Average		**10**	**77.2**	**48.9**		
Median			**74.3**			

Table 8. MeFTIR/TC alkane (cyclo-hexane) measurement of **Tank 603/614 – Tracer on 614** during the CEN The Netherlands 2017 survey presented as daily averages and standard deviations (SD) and survey Average and Median. See Figure 4 for area localizations.

Day [yymmdd]	Time span [hhmmss-hhmmss]	Num Meas	Emission avg [kg/h]	Emission SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Span [deg]
170616	112000-121714	11	42.9	22.2	3.4-6.3	293-326
Average		**11**	**42.9**	**22.2**		
Median			**43.5**			

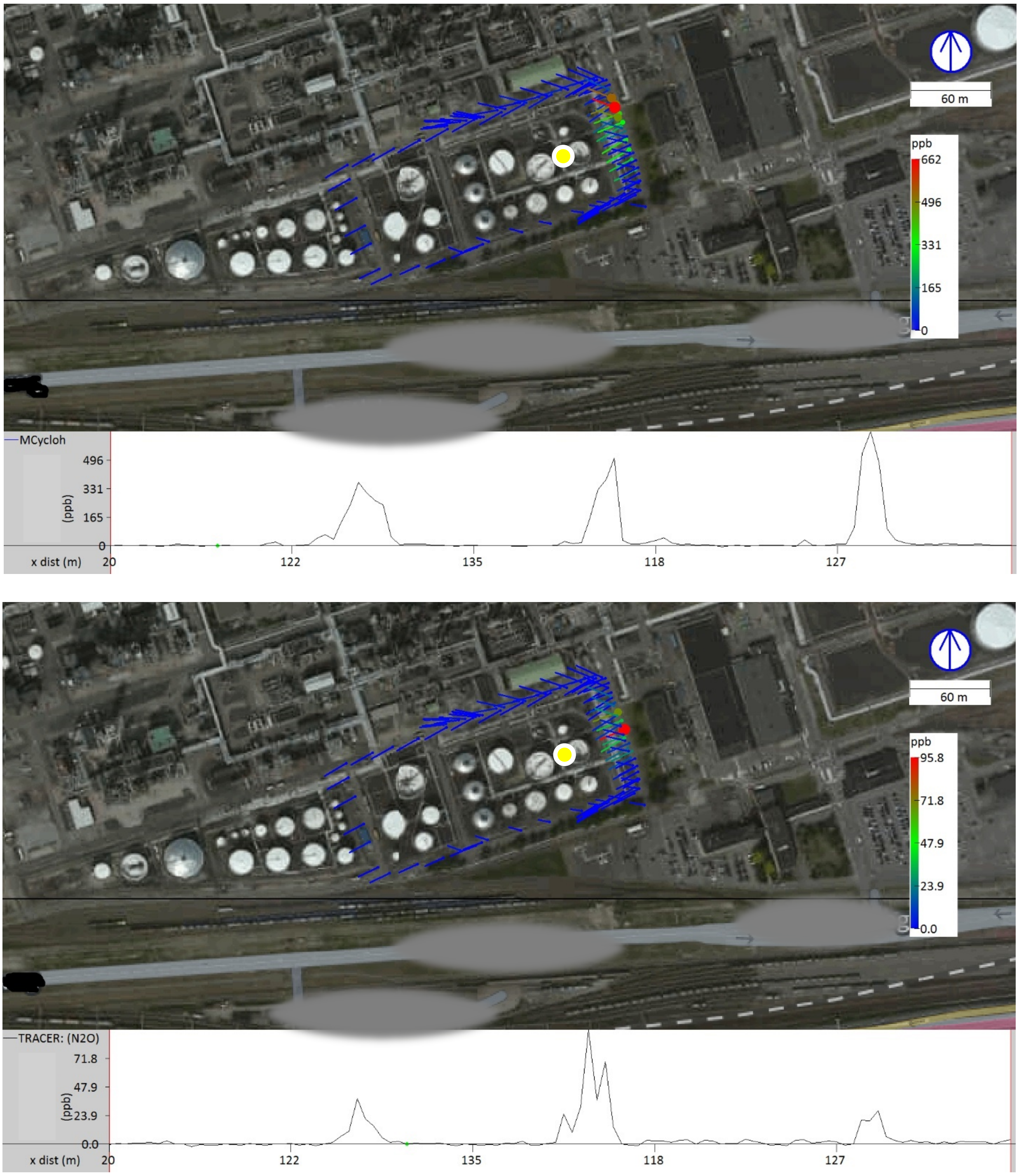


Figure 10 Example of MeFTIR/TC measurements of C603/614 (Petro-Chemical Tank Park), 2017-06-13 at 12:24. Ground level concentrations of butane equivalents in upper figure and trace gas (N_2O) in the lower figure. The dots show the trace of the vehicle and the colour indicate the local concentration (ppb) according to the colour bar scale. The lines connected to the dots point in the direction of the wind. The lower panel shows the concentrations as a function of distance from the start. The yellow dot indicates the trace release point.

5 Discussion and Conclusion

Several VOC emission hotspots were detected at the Test Site using MeFTIR ground concentration mapping. The actual concentration varied significantly with wind speed, height of, and distance from the source. Also, mobile sources, such as vacuum trucks, has a large local and temporal influence on the concentration. MeFTIR measures ground level concentrations and this enhances low level sources as compared to elevated sources, such as flares or highly placed process equipment. The result from the MeFTIR mapping is, on the other hand, more representative of the typical exposure levels of the facility staff.

The overall measurement period for the campaign was unfavorable for MeFTIR concentration mapping since there were many obstacles and closed roads due to a large construction project and it was therefore difficult to make boxes around the sources or measuring the upwind contribution. An additional problem was that one of the sources, (Tank 112) had so high emissions that it interfered with the measurements from the smaller emission sources.

Three sources were selected for quantification with MeFTIR/TC based on the concentration mapping. The measurement uncertainty at the Vent Pipe were probably higher than normal due to misallocation of the tracer compared to the source gas while the corresponding value at the water treatment was normal. The measurements at the chemical tank farm showed emissions from either of two tanks, with an emission range of 44-77 kg/h on two different days at different wind conditions and placement of tracer. It is not clear how much of this range that corresponds to changes in the actual emissions of the tanks or measurements errors due to tracer/source misallocation.

The measurement results at the chemical tank farm shows the importance of assessing the relevant gas species in the MeFTIR spectral evaluation. The standard protocol states that information about the typical gas-mixture in the emissions must be obtained or complementary measurements made. Since SOF measures broadband infrared spectra, significant absorption by an atypical plume composition of species not included in the standard spectral fit can be detected in the residual of the fit. In such a case, the species included in the evaluation routine are updated to match the observed absorption signal. Plumes from tank 603/614 of the Petro-Chemical Tank Park contained pure cyclo-hexane which is not included in the standard alkane evaluation. A sensitivity study of Tank603/614 showed that the emission increased with 20% when replacing the standard evaluation with a cyclohexane evaluation. Also, the cyclohexane evaluation helped identifying the real plume against a background of other emissions in the post processing.

The campaign was in general successful, with MeFTIR concentration mapping over most of the site and three different sources quantified with MeFTIR/TC, although the measurement planning and set-up was not optimal. A standard survey would, for example, be planned based on the weather forecast so that measurements were done during optimal wind directions. Also, the road access and work permits would have been set up to assure access to all areas and thus avoiding periods of major construction work. Finally, periods with non-typical operations, such as the maintenance of Tank112 (which gave extreme emissions), would have been avoided, unless these emissions were of particular interest. Ironically, Tank 112 could not be quantified with MeFTIR/TC during this campaign due to safety reasons (extreme emissions) and construction work that precluded tank access for trace gas release.

6 Acknowledgment

This work is a part (WP6) of the CEN WG 38 TC 264 standardization project, funded by the European Commission/EFTA. The measurement campaign was administrated by INERIS. Special thanks to the staff of the Test Site in The Netherlands for cooperation and to the other measurement teams for fruitful collaboration.

Annex A (informative), Tracer Correlation (TC) – Description of the Method

A.1 Overview

A.1.1 Scope

The Tracer Correlation (TC) method is based on using a tracer gas release to represent the atmospheric dispersion of a gaseous release from the source location to the observation point downwind the source. The concentrations and correlation of the leaked gas and the tracer gas are measured with high sensitivity through the plume cross section at an appropriate downwind distance from the source. Since the tracer mass flow rate is known, the leaked gas to tracer gas concentration ratio can be used to derive the mass emission rate of the leaked gas from the source. In this way mass fluxes/emissions are obtained combining sensitive gas plume concentration measurements with a known tracer release rate from single or multiple tracer sources, or even multiple tracer gases, without requirements for a wind profile measurement to assess the source gas emission rate.

The TC method is used to quantify and map the location of various gas emission sources over a spatial scale ranging from large area sources (for instance landfills) down to unit level in individual plants (for instance flares, vents, water treatment units, individual tanks, loading operations, tanker trucks, compressors etc.).

A.1.2 Pollutants measured

The applicability of the TC method in terms of measurable pollutants is restricted only by the capability of the analysis instrumentation. The deployed instrumentation is required to measure leaked gas and tracer gas down to low ppbv levels (<1-10 ppbv) in ambient air conditions in order to be able to detect dispersed plume concentrations far downwind the source location using only a limited, cost effective, safe and practical tracer release rate. Real time continuous concentration data with fast time resolution (~1-10 s) are required in order to monitor the plume location and any interfering sources on site and integrate through the plume cross section at a sufficient pace. At a minimum, the TC instrumentation is required to analyse two gases simultaneously (tracer gas and leaked gas), but multiple gas capabilities are useful for efficiency and uncertainty assessment purposes.

Example of instrumentations that fulfil the stated performance criteria (for certain species) and are applied for TC measurements are:

- Mobile extractive (or in situ open path cell) Fourier Transform Infrared (MeFTIR)
- Cavity Ring-Down Spectroscopy (CRDS)
- Mobile (extractive or in situ open path cell) Whitecell Differential Optical Absorption Spectroscopy (MWDOAS)
- Proton Transfer Mass Spectrometry (PTr-MS)

A.1.3 Information provided

The measurements provide mapped concentrations, hot spot identification, and continuous fluxes in real time for single or multiple point sources. For area sources the measurements provide real time hot spot mapping while plume integrated concentrations and fluxes are typically assessed after measuring unless there are separate operators for the vehicle and measurements.

A.1.4 Scale and limitations

The TC method is used to map and quantify gas emissions from isolated large area sources (km) down to unit level in individual plants (for instance flares, vents, water treatment units, individual tanks, loading operations, tanker trucks, compressors etcetera). The scale is only limited by instrument detectivity and source interference.

The accuracy of the measurements is dependent on how well the tracer can replicate the source dispersion. Therefore, the tracer must be released near the leak source, requiring the source to be known or that the measurement be made at a sufficient distance downwind so that adequate mixing is achieved. This may be difficult for highly placed sources both due to accessibility and interference.

A.2 Tracer Correlation Measuring principle

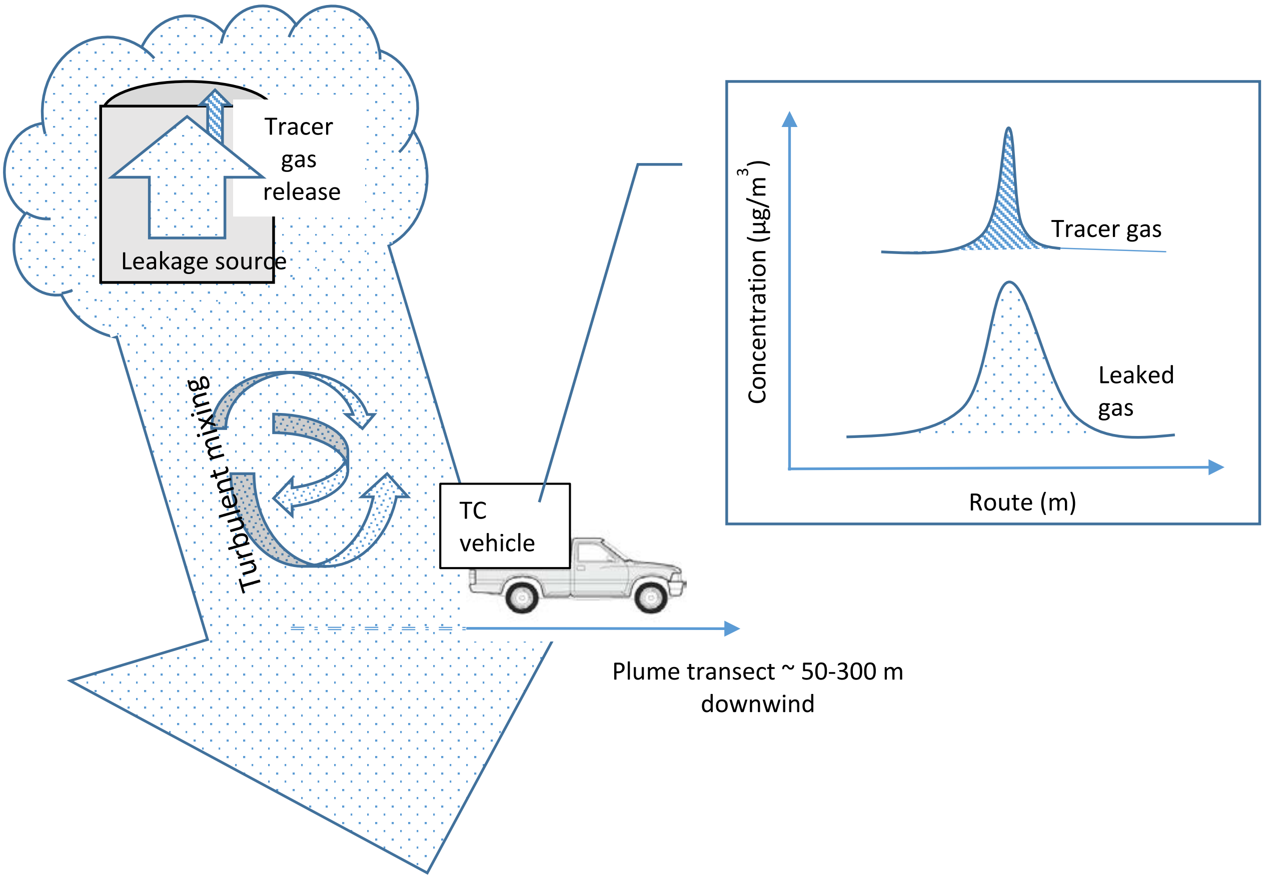


Figure A 1. In the Tracer Correlation Flux method (TC) leaked gas and tracer gas are measured simultaneously by a mobile instrument with ppb sensitivity. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of leaked gas is obtained by multiplication of the plume gas/tracer quotient with the tracer release rate.

A.2.1 Typical mobile measurement systems

A.2.1.1 Mobile extractive FTIR (MeFTIR)

Mobile Extractive FTIR (MeFTIR) (Galle 2001, Börjesson 2009) is a typical instrumentation setup to the tracer correlation method. MeFTIR in combination with TC has been used to quantify VOC emissions from refinery and petrochemical sources in Europe and in USA (Mellqvist 2016; 2017). Alkanes and alkenes are typically measured, but also methane (CH_4), ammonia (NH_3), nitrous oxide (N_2O) and other climate gases can be retrieved. MeFTIR is an optical technique capable of monitoring gas concentrations at ppb-sensitivity in mobile field operations. It is used both independently for concentration mapping and flux measurements, but often combined together with simultaneous Solar Occultation Flux (SOF) flux measurements to provide more detailed VOC speciation of plumes and for plume height assessments (Johansson et. al. 2014). The plume height can be estimated by dividing measured columns (mg/m^2) with ground concentrations (mg/m^3), assuming that the plume is evenly distributed up to the plume height.

The MeFTIR system consists of a mid-infrared spectrometer with medium resolution (0.5 cm^{-1}). It utilizes an internal glow bar as an infrared radiation source, and by customized optics this light is transmitted through an optical multi-pass measurement cell with long path-length of 50-120 meters. The system is mounted on a vibration dampening platform to allow for real time plume mapping from a mobile platform, such as a vehicle or boat, see Figure A 2.

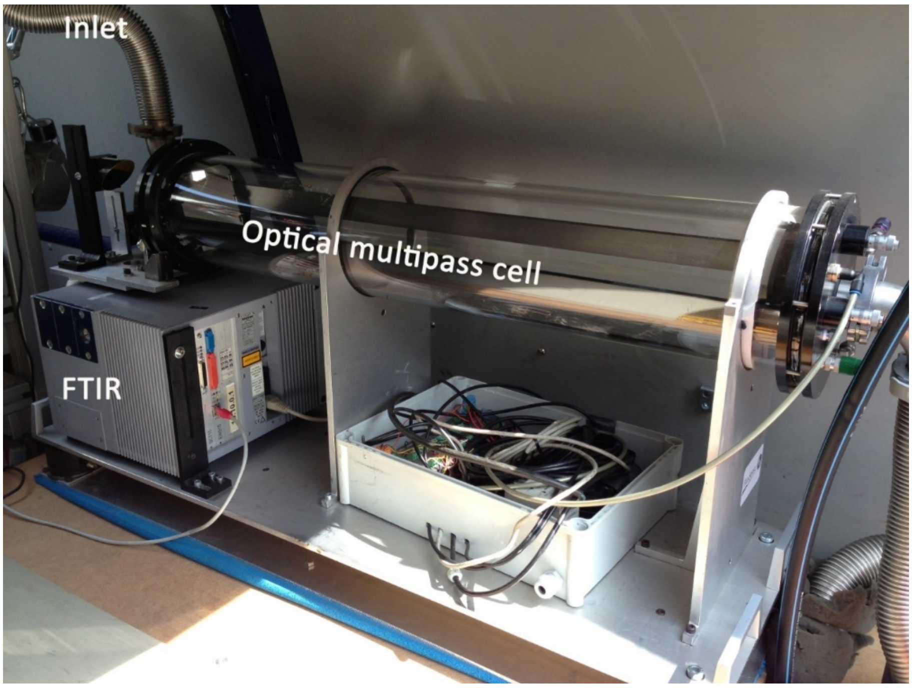


Figure A 2. The MeFTIR instrumentation consisting of a Bruker FTIR spectrometer connected to an optical multi-pass cell.

The transmitted light is detected simultaneously with an InSb-detector (Indium Antimonide) in the 2.5–5.5 µm (1800–4000 cm^{-1}) region and an MCT (Mercury Cadmium Telluride) detector in the 8.3–14.3 µm (700–1200 cm^{-1}) region. Temperature and pressure in the cell are averaged over the duration of each measurement. Atmospheric air is continuously pumped at high flow rate through the optical cell from the outside, taking in plume air from the roof of the vehicle (2 m height) through a Teflon tube. A high flow pump is used to ensure that the gas volume in the cell is fully replaced within a few seconds. Spectra are typically recorded with an integration time of 10 seconds. A GPS-receiver is used to register the position of the vehicle every second. The concentration in the spectra is analyzed in real time by fitting a set of calibrated spectra from the HITRAN infrared database (Rothman 2003) and the PNL database (Sharpe 2004) in a least-squares fitting procedure. Compounds being analyzed include ethylene, propylene, total alkane mass (based on fitting cross sections of ethane, propane, n-butane, i-pentane, n-octane), water, methane, CO, CO_2 and N_2O. The analysis routines are very similar to the ones for SOF, but less complex because strong absorption by atmospheric trace gases (water, methane, CO_2) has less consequence at the shorter path length in the MeFTIR measurement cell.

Concentration measurement by FTIR is a widely used procedure (Griffith 1996), and the main uncertainties are associated with the absorption cross sections (typically < 3.5%) and spectral retrieval, with an aggregate uncertainty better than 10% in the analysis. Concentrations are monitored in real time in order to detect emission plumes and to judge whether any interfering sources are being sampled. Unwanted signals from local traffic exhaust or from the measurement vehicle itself could be filtered out by looking at the carbon monoxide (typical exhaust compound) concentrations. A stationary source is, on the contrary to any local traffic plumes, characterized by recurrent downwind plumes. Transient and non- repeatable observations are therefore excluded from the results. Furthermore, measurements of ambient concentrations of methane, nitrous oxide and carbon dioxide (with known atmospheric concentrations) are used for consistency check.

A.2.1.2 Mobile White cell DOAS (MWDOAS)

The ground level mass concentration of benzene, toluene, ethylbenzene, meta- and para-xylene (BTEX) can be measured using a mobile real-time system: mobile Whitecell DOAS (Differential optical absorption spectroscopy). The MWDOAS system consists either of an open, 2.5 m long optical White cell that is mounted on the roof of the measurement vehicle (see Figure A 3) or by extractive gas cell connected to a pump. By multiple reflections in the White cell mirror system an overall path length of 120-210 m is obtained, resulting in low detection limits (ppb). The light signal from the internal lamp is transmitted through the White cell and then analyzed in a DOAS spectrometer, using the ultraviolet (UV) wavelength region 255 - 285 nm.

A measurement begins by acquiring a reference spectrum outside the plume, usually upwind of the facility. Spectra are then sampled and averaged continuously while driving through emission plumes. The averaging time is set to around 4-8 seconds in order to achieve acceptable SNR (see below). This is the lower limit of the temporal sampling between independent measurements, but the spatial sampling is also dependent by the vehicle’s velocity. A typical driving speed for MWDOAS measurements is 10-20 km/h for sufficient plume sampling.

Figure A 3. The open path MWDOAS cell having an overall optical path-length of 210 m.

The spectra are geo-tagged and evaluated in real-time using the standard DOAS technique, giving information of plume locations and constituents. The data is later post evaluated and often merged with the corresponding MeFTIR data to produce a plume specific BTEX/Alkane mass ratio. The mass ratio of BTEX/Alkanes is then used to calculate the aromatic flux from individual sub areas where alkane fluxes have been measured by SOF or MeFTIR-TC.

The MWDOAS system has been used in previous campaigns in USA during 2013 with good results. During the 2013 DISCOVER-AQ (Johansson et.al. 2013) campaign in Houston, Texas, the system was run in parallel to a mobile Proton Transfer Mass spectrometer (PTr-MS) lab as a validation check. The results of benzene, toluene and styrene was compared and showed good agreement, with the PTr-MS showing slightly elevated benzene concentrations compared to the MWDOAS. The sensitivity of MWDOAS is less than 1 ppb for benzene, less than 3 ppb for toluene, ethylbenzene and m-xylene and 0.5 ppb for p-xylene.

A.2.2 Flux measurement

Applying the TC method, the source flux is retrieved by integrating the cross-plume mass concentrations (above background baseline) of the source gas and tracer gas respectively. The mass concentration ratio together with the known tracer gas release rate gives the source emission, see Equation A.1. (Units in grey brackets):

$$Q_N^{Leak\ gas}[\mathrm{kg/h}] = Q_N^{tracer}[\mathrm{kg/h}]\,\frac{\int_{Plume\ start}^{Plume\ end}(C_l^{Leak\ gas} - C_{background}^{Leak\ gas})[\mathrm{\mu g/m^3}]\ dl[\mathrm{m}]}{\int_{Plume\ start}^{Plume\ end}(C_l^{tracer} - C_{background}^{Tracer})[\mathrm{\mu g/m^3}]\ dl[\mathrm{m}]} \qquad \text{(Equation A.1)}$$

$Q_N^{Leak\ gas}$ = the flux of the leak gas obtained for plume transect N,
Q_N^{Tracer} = the average (stable) release rate of the tracer gas for all plume transects N
$C_l^{Leak\ gas}$ = the measured mass concentration of the leak gas for transect N,
$C_l^{Tracer\ gas}$ = the measured mass concentration of the tracer gas for transect N,
$C_{background}^{Leak\ gas}$ = the measured background mass concentration of the leak gas for transect N,
$C_{background}^{Tracer\ gas}$ = the measured background mass concentration of the tracer gas for transect N,
dl = the driving distance across the plume

To isolate emissions from a specific source, the incoming/upwind background flux must be either insignificant or subtracted. Note that tracer gas correlation fluxes do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume and the tracer gas is well mixed at the sampling distance. Complete plume transects are, however, strongly recommended since the tracer gas and source gas release point might not completely match at the sampling distance and complete plume integration suppress mismatch errors in the direction perpendicular to the wind direction.

A.2.3 Overall Measurement methodology

The TC method is used to quantify emissions from distinct sources of various sizes, from point sources to large area sources such as land-fills. Single or multiple trace gas releases are combined with in-plume sampling of trace gas and source gas concentrations using a mobile measurement system. Naturally occurring turbulent mixing of the air is utilized where the trace gas and the source gas are dispersed in a similar way. Gas ratios are samples downwind of the source but upwind measurements must also be performed to assure no interfering background sources. Plume concentrations are usually sampled with gas inlet tubes of the measurement platform at ground-level (1-2 m), away from any vehicle exhaust that may interfere. Other ways of plume sampling can also be applied, such as using long tubes or open path cells.

A.2.4 Advantages and constraints

The TC provides real-time information about the location and magnitude of VOC sources for known or suspected leaks and can be used for diffuse emissions monitoring for suitably isolated sources of various sizes and magnitudes. Fluxes can be safely measured from a distance (non-invasive) and monitored and followed over time to study temporal variations. The method has a large dynamic range and can be operated any time of day or season, given sufficient plume dispersion (wind) and that plume access is granted. The method does not rely on wind data measurements, since the tracer release simulates the atmospheric dispersion.

The TC technique is constrained by meteorological conditions, source geometry and interfering emissions from upwind sources or a source located in between the source release and the plume sample location. In a complex environment with many interfering sources, the risk of biasing obtained emissions are significant, and care need to be taken to rule out such effects. The same applies for highly placed sources which are usually difficult to access for tracer placement or for interference screening. A tracer-source allocation mis-match in the vertical can significantly bias obtained results, although the tracer-source-plumes seem correlated in space.

The TC method requires good dispersion and mixing of the source and tracer gas release, and plume access at appropriate downwind distance from the source. This means measurements have to be coordinated with suitable meteorological conditions, and long-term measurements (12-24+ hours) can be challenging to complete, due changing conditions.

The method also involves handling and safe placement of tracer gases, which can be logistically challenging, especially for long term studies. In the case of strong wind and sunny conditions with effective dispersion both in the horizontal and vertical, the plume might raise rapidly aloft and be inaccessible or at too low concentration levels at the required plume sample location (distant). Cases with strong dispersion might also require large tracer release rates in order for the tracer to be detectable far downwind.

A.2.5 Uncertainty

The TC flux is determined by multiplying the quotient of plume integrated mass of leaked gas to tracer with the tracer mass flow. The main uncertainty for flux measurements in the TC method comes from how well the tracer dispersion replicates the leaked gas dispersion. For a complex and distributed source, care need to be taken in matching the source release with tracer as good as possible, and center of gravity of source release and tracer release should be close. Tracer-source allocation mismatch in the direction along the wind direction, or in the vertical as in the case of a process unit for instance, is more severe compared to mismatch in the direction orthogonal to the wind direction. This is because the source and tracer plumes then will have had differing plume transport times and/or dispersion conditions to the sampling location, and that will bias the source-tracer gas quotient. Mismatch in the orthogonal wind direction is usually not as problematic, given that dispersion conditions do not change dramatically along this direction. Integrating the full source and tracer plumes cross-wind from edge to edge would still give a credible ratio, since the two plumes have had comparable plume transport times and dispersion, even if they are somewhat shifted in the cross-wind direction.

Tracer and source gas mismatch can be overcome somewhat by sampling the plume at a far downwind distance. In practice, sampling distance is usually limited by instrumentation detection limits and present dispersion conditions, and available roads to intersect the emission plume. Typically, a sampling distance of more than five times the dimension radius of the source area should be used, to limit mismatch effects.

Care need to be taken to avoid bias by any sources feeding into the studied emission plume in between the source area and plume measurement location. A strong source at a considerable closer distance to the sample location could severely bias the retrieved TC flux. Ideally the area between the source and the plume measurement location is screened for additional sources. Measuring in different wind directions can also help identifying possible interfering sources. Sharper concentration peaks on a dispersed Gaussian emission plume at a far downwind distance can be an indication of an interfering adjacent source.

The uncertainty of the TC measurements can be better understood by measuring the same source in different wind directions and at different distances. Significant changes in obtained fluxes would flag a risk for tracer-source mismatch and/or interfering sources. The tracer-source mismatch effect can be confined by operating additional tracer gas(es) located at the upwind/downwind border of the source release area, or by relocating the single tracer gas correspondingly, and compare obtained fluxes with the “best guess tracer allocation”-result.

A.2.6 Validation and comparisons

The tracer correlation approach using MeFTIR has been tested in controlled gas release tests in several experiments. Concentration measurement by FTIR is a widely used procedure, and the main uncertainties are associated with the absorption cross sections (typically < 3.5%) and spectral retrieval, with an aggregate uncertainty better than 10% in the analysis.

In a so-called “blind test” together with other techniques in USA (Babilotte, EREF 2011), methane was released from an area-distributed source in four different configurations and flow rates ranging from 1.1-3.3 g/s. At a downwind distance of 400 meters TC-MeFTIR retrieved the fluxes within 6% in 3 cases and 19% in the fourth. This is consistent with other validation experiments, showing a flux estimate accuracy within 20%.

In an experiment at Nynas AB refinery in Sweden, tracer gas was released from a crude oil tank. In this case, plume measurements in the disturbed wind field at a downwind distance of about 5 tank heights, (Samuelsson 2005b). The actual VOC release was measured by an independent vendor (ÅF) using FID (flame ionization detector) in a controlled fan vent attached to the tank. The FID rate uncertainty given was ±30%. TC compared to FID was in the range -21% to -49% for four release tests (VOC emission rates 4-8 kg/h). At a similar test at a coupled Bitumen tank system vent, TC compared to FID was in the range -12% to +23% for two tests with emission rates about 1 kg/h.

Another TC validation study involving three different teams, was conducted at a sewage treatment plant (Delre 2018). Two teams operated TC-CRDS (cavity ring-down spectroscopy) instruments and one team operated TC-MeFTIR. Four different tracer gases were released at various positions in the plant in order to study source-tracer allocation mismatch effects. The methane emission from the treatment plant was assessed by the various methods and tracer combinations to on average 8 kg/h in the first test and 10 kg/h in the second. Overall, the various methane emission estimates ranged from -18% to +11% compared to average measured emission rate among the methods. A deliberate sideward misplacement of tracer in the cross-wind direction showed that the retrieved emission was not affected by more than 12%, when the full source and tracer plumes were integrated. A corresponding deliberate tracer misplacement 150m in the upwind direction introduced a deviation of +49% in the retrieved emission rate.

A.3 Technical performance / Performance requirements

A.3.1 Performance characteristics

A summary of the performance capabilities of a typical TC system under normal conditions are given in Table A.3. The values provided are based on the actual levels of performance of existing TC systems, determined from the typical absolute precision for concentration measurements.

The accuracy of the TC is estimated as the square root sum of the precision and the systematic spectroscopic uncertainties and is typically 20-30%, Table A.4.

The typical precision and accuracy of the complementary measurements which are used to derive the flux rates is shown in Table A.5.

Table A.3 — Capability of a typical TC measurement (MeFTIR and MWDOAS)

Parameter	Detection Limit[1] (ppb)	Concentration Accuracy
Alkanes (C_2-C_{10}) (IR), (C_4-equivalents)	2.5	10%
Ethene (IR)	3.5	5%

Propene (IR)	7.5	5%
N_2O (IR)	1	5%
Acetylene (IR)	1.5	5%
SF_6 (IR)	1	5%
SO_2 (UV)	2	5%
Benzene (UV)	1	5%
p-xylene (UV)	0.5	5 %
BTEX (UV)	3	10%

(1) 1-σ-precision in ppb assuming 78 m path length (IR) or 210 m (UV).

Table A.4 Typical uncertainty estimation of TC alkane flux measurements for diffuse emission sources (the variability of the sources not taken into account).

	Spectroscopy (cross sections) a)	**Retrieval error b)**	**Tracer release rate**	**Tracer/Source allocation mismatch c)**	**Composite flux measurement uncertainty d)**
Alkanes	3.5 %	10 %	5%	15-25 %	20–30 %

a) Includes systematic and random errors in the cross-section database.

b) The combined effects of instrumentation and retrieval stability on the retrieved cross-plume concentrations during the course of a plume transect and error of the TC alkane mass retrieval.

c) The estimated uncertainty due mismatch between tracer and leaked gas locations – depends on source size and complexity and the distance between source and plume measurement (plume dispersion time)

d) The composite square root sum of squares uncertainty

Table A.5 — Requirements of complementary measurement devices to the TC method

Parameter	Precision/Detection Limit (1σ)	Accuracy
Wind direction (for plume location interpretation purposes only)	2°	±2 degrees
Wind speed (for plume dispersion assessment only)	0.5 m/s	±0.5 m/s for winds 0-5 m/s ±1 m/s for winds 5-40 m/s
Tracer release rate	n/a	±5 %

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Annex B
(normative)

Tracer Correlation (TC) – Performance Requirements and QA/QC

B.1 Performance requirements

For practical applications in order to be able to monitor general VOC emissions from an industrial scale site, the system shall be:

- firmly mounted on a mobile platform, with access to the outside air.
- equipped with sensors that can either measure single VOC gas species or measure the sum of VOC gas species (alkanes, alkenes, alcohols, aromatics) and simultaneously one or several tracer gas species.
- able to measure the tracer gas with a detection limit of 1-10 ppb and the target gas better than 10 ppb.
- able to perform fast measurements (time response of about 1-10 s) while moving up to 50 km/h.
- equipped with a global positioning system.
- capable of showing real time concentration data of tracer gas and VOC, projected on a map.

B.2 Application of the method

B.2.1 Measurements planning

It is necessary to clearly define the measurements to carry out. This includes the species to be measured, experimental arrangements (field setup) and likely interfering species:

- Campaign logistics: this includes pre-site visits (if required) and checklists for ensuring the site is aware of the logistics of TC measurements and that the site is operating in a normal manner. A method statement covering the TC method may be provided if required.
- Selection of measurement roads.
- Identification of likely emission sources: this requires information from the site, usually including site plans and existing emissions information. Potential sources off-site (both for VOC and tracer gas) should also be considered.
- Identification of potential interfering species: for complex sites this may require process information or air-sample analysis taken as part of the campaign measurements.

- Assessment of wind field: pre-site planning includes an assessment of the likely wind conditions and what existing meteorological data are available.

B.2.2 Selection of gas species to be measured

- Obtain information about the typical gas species being emitted and make decisions whether complementary composition measurements are needed.

B.2.3 Selection of tracer gas species

- Use an appropriate tracer gas which is not emitted from the site to be studied.

- The tracer gas should have as small health and environmental impact as possible on the surrounding. The tracer gas must with margin be stable in atmospheric conditions over the time frame covering the plume transport from the source to the measurement location. The tracer gas purity should be 99.9% or better.

- The tracer gas and positions chosen must be sanctioned by the site and marked off, in order not to put working personnel or installations at risk (for example if a flammable, oxidising, toxic or suffocating tracer gas is used).

- The sensors used should have high sensitivity to the tracer gas, better than 1-10 ppbv detection limit in order to be able to release only small amounts of tracer gas (typically 0.5-2 kg/h per tracer bottle).

B.2.4 Measurement strategy

Installation of a meteorological mast location in a clear area.

Identification of ideal wind conditions and TC measurement roads to use for measurements at each different site area. This and the weather forecast during the measurements period would help to plan when to measure a specific site area and from which location. This in turn would help to:

a) Communicate each day to the site the possible TC locations facilitating the work permit.

b) Quickly react if the actual wind direction during the day is not as forecasted.

c) Interpret and understand the origin of observed plumes and any interfering sources.

For a given wind direction the area to measure should be chosen such as:

a) The area under investigation is clear from strong upwind sources. Avoid areas with high inflows or where the background of VOC and tracer can’t be estimated.

b) It is of outmost importance to verify that no significant sources of the measured VOC or tracer gas used is located between the studied source and the measurement location. This would interfere and offset retrieved emission results using the TC method.

In order to make an appropriate tracer correlation measurement it is necessary to know the location of the main leaks to be investigated. This is done by concentration mapping, driving around the site on all available roads measuring the concentrations.

- The tracer gas should then be positioned in such a way that it disperses in the same manner as the leakage gas. For a single leakage source, the tracer gas should be released in close proximity to the source gas leakage.

For area sources or more complex volume sources an assessment of the main leakage points inside the areas needs to be made and then tracer gas is released from one or multiple distributed points. In order to estimate the performance of the measurements it is necessary to either:

- measure at far away distance, so that the area/volume source becomes more of a point source (suppression of any tracer gas and source gas location mismatch) (typically a distance away from the source of more than 5 times the area unit dimension),
- measure at different distances and different wind directions to assess the variability of the obtained emissions,
- utilize two tracer gases, or move the position of the single tracer gas, to make a sensitivity study of the variation in the obtained emissions. Typically, the tracer gas should be relocated from the estimated “best match” location, to an offset location with respect to the upwind/downwind direction of the unit in study, in order to observe the impact on the retrieved emission rate. In the case of two different tracer gases this can be accomplished simultaneously.

B.2.5 Set-up and initial tasks

General:

☐ Site specific requirements such as safety inspection and introduction course.
☐ Agree the procedure for changing TC location with site operators and possible use of special permits to drive in ATEX areas with a safety guard.
☐ Ascertain safe measurements. For measurements inside industrial areas the equipment should be equipped with a single safety switch by which all instruments can be turned off, in case of emergency.

TC vehicle or platform:

☐ Check TC vehicle/platform status according to safety and performance and ascertain safe measurements
☐ Mount warning lights and signs
☐ Make sure that car or mobile platform battery pack in is fully charged
☐ Make sure any loose items are stowed away securely

Instruments:

☐ Turn on instruments.
☐ Check that sensors are fully operational, according to the operations manual and other instructions.
☐ Check the time synchronization of all instruments and computers against GPS, Tol. 1s.

GPS:

☐ Check that the GPS information is available and reasonable.

Wind:

☐ Set-up the meteorological sensors at the agreed locations and check the functionality.

☐ Direct sensor correctly (toward magnetic north) using a compass. Tolerance: ±5°.

☐ Erect the wind mast vertically and secure it firmly

☐ Check that wind information is available and reasonable.

☐ Check the time of the data logger versus standard. Tolerance 1 s.

Tracer gas:

☐ Once the emission sources have been chosen apply for permit to release tracer gas in the vicinity of the sources.

☐ At the tracer gas release point, make appropriate safety arrangements by marking off several meters around the release point depending on the health impact of the tracer gas.

B.2.6 Measurements

Before start to measure ensure:

☐ Staff is signed in on site (if required).

☐ If necessary, apply for a work permit.

☐ Ensure that staff is familiar with local safety protocols.

☐ Logging of the meteorological data is started.

☐ Determine the measurement plan.

Measurement procedure:

☐ Measure the concentrations on the full site by driving on the accessible roads measuring the road side concentrations of the gas species of interest.

☐ Take notes and photos on interesting findings and events.

☐ Repeat the measurements during different times and meteorological conditions in order to study the temporal and spatial variability.

☐ Plot the measured concentrations on a 2D map for trace back of observed plumes and identification of "hot spots". Note that since the measurements are usually performed on the ground, the measurements are comparably more sensitive to sources which are close to the measurement vehicle and at low elevation level.

☐ Make additional concentration measurements at the hot spot areas using the TC sensors, OGIs, and sniffers. Scan upwind and downwind the sources to investigate whether the hotspot corresponds to one or several interfering sources.

☐ Discuss the finding of potential emission sources at the hotspot locations with site personnel, to understand the reason for the leaks and how frequent they could occur.

☐ Apply for permit to emit tracer gas at the source locations. See description in section B 2.4.

- ☐ Carry out controlled tracer gas releases according to the description in section B 2.4. Keep track of tracer gas release rates by weighing released amounts, usage of stable regulators and/or mass flow controllers and register the accumulated tracer release time.
- ☐ Measure both upwind and downwind the source at various distances to investigate whether the emissions correspond to one or several interfering sources. The measurements should be carried out according to the description in section B 2.4. Make sure the VOC and tracer gas plumes are entirely traversed. Make sure no significant interfering sources (concentrations) of the studied VOC compound or tracer gas are observed in between the studied source area and the plume measurement location. Any such source having a different plume transport (dispersion) time than the studied source emission, can severely offset the retrieved emission result.
- ☐ The emission plume in study should be entirely traversed for complex areas/volume sources with a driving speed corresponding to 5-50 km/h, depending on distance to the source and the time resolution of the analysis instrumentation. Sampling speed should be chosen so that significant under-sampling is avoided, and so that different parts of the plume are given equal sample time in the plume integration. For simple isolated sources, fixed measurements can also be carried out.
- ☐ The cross section of the plume should be probed at comparable plume transport times from the source, e.g. typically at the same distance to the source on a transect perpendicular to the wind direction.
- ☐ Check the wind meter and tracer gas release sources on a regular basis to make sure that it is operational.
- ☐ Check that wind speed stays above 1 m/s in order to assure appropriate mixing conditions during the experiment.
- ☐ Check the GPS sensor on a regular basis to make sure that it is operational.

At the end of the measurement day ensure that:

- ☐ All the sensor data is saved and backed up.
- ☐ All the met data is downloaded, saved and backed up.
- ☐ Dismount wind mast and move out tracer bottles, if not in a safe location and according to work permit.
- ☐ Update survey documents. If feasible, discuss measurements results with the industrial site and collect complementary data such as tank product levels, flaring activity, etc.
- ☐ Turn off instruments.
- ☐ Charge measurement vehicle, and data logger batteries overnight.
- ☐ Make sure that instruments are well protected from rain/moisture.

B.3 Quality control

B.3.1 General

Quality checks and quality assurance and measures are performed at several levels. In general, most checks are done prior to measurement, including powering up the equipment, checking operating parameters, and test the instruments. The purpose is to run operational checks to catch problems prior to field deployment and repair all malfunctioning equipment in order to avoid bad data during survey.

B.3.2 Calibration of gas sensors

The gas sensors need to be calibrated according requirements in the instrument manuals. When using instruments based on optical spectroscopic absorption measurements one can generally rely on published line parameters or absorption cross sections. This is appropriate as long as the instruments are well aligned and its spectral response is well characterized. A response check versus atmospheric background levels, tracer gas and/or a known reference is recommended to assure valid performance prior to commencing with the measurements.

B.3.3 Meteorological sensors calibration

The meteorological sensor should be calibrated regularly by the manufacturer or by a reference wind meter.

B 3.4 Tracer release equipment calibration

The gas regulators and mass flow controllers used for the tracer release need to be properly calibrated to assure correct tracer rates for the given application conditions (tracer gas, pressure, temperature). The tracer gas bottles should be gravimetrically weighed on a calibrated scale before and after the tracer release study to obtain the total mass released. The accumulated time of the tracer release need to be noted, and a constant release rate during the experiment assured.

B.3.5 Required QC checks in the field

☐ The gas sensors need to be quality controlled according requirements in the instrument manuals.

☐ Check that the tracer release rate is constant over the duration of the measurement.

☐ Check that GPS is running ok and that instrumentation time stamps are synchronized.

☐ Observe real time concentration data and assure no abnormal drifts or performance deterioration, interfering source or tracer plumes are observed – make notes and take action in case.

☐ Check that wind speed stays above 1 m/s in order to assure appropriate mixing conditions during the experiment.

B.4 Data analysis

B.4.1 Calculation of gas fluxes

Applying the TC method, the source flux is retrieved by integrating the cross-plume mass concentrations (above background baseline) of the source gas and tracer gas respectively. The mass concentration ratio together with the known tracer gas release rate gives the source emission in kg/h, see equation B.1. These fluxes are given for each transect (*j*) by:

$$Q_{VOC}^{j}[\mathrm{kg/h}] = Q_{tracer}^{j}[\mathrm{kg/h}]\,\frac{\int_{Plume\,start}^{Plume\,end} C_{VOC}^{j}[\mathrm{\mu g/m^3}]\,dl[\mathrm{m}]}{\int_{Plume\,start}^{Plume\,end} C_{tracer}^{j}[\mathrm{\mu g/m^3}]\,dl[\mathrm{m}]} \qquad \text{(Equation B.1)}$$

Where,

Q_{tracer}^{j} = the tracer gas release mass flux for plume transect j (should be constant over all transects j),

C_{tracer}^{j} = the tracer gas mass concentration above background baseline, integrated across the plume cross section.

C_{VOC}^{j} = the VOC (or source gas in study) gas mass concentration above background baseline, integrated across the plume cross section

l = distance across the emission plume, ideally across the full plume cross section perpendicular to the wind direction (e.g. the measurements should probe the plume at comparable plume transport time throughout the whole plume transect).

Note that tracer gas correlation fluxes do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume and the tracer gas is well mixed at the sampling distance. Complete plume transects are, however, strongly recommended since the tracer gas and source gas release point might not completely match at the sampling distance and complete plume integration suppress mismatch errors in the direction perpendicular to the wind direction.

In the gas flux calculation, the background baselines of tracer gas and VOC respectively, need to be assessed and withdrawn for each plume transect. Any significant offset/drift in the baselines as observed comparing concentrations at the plume edges should flag the transect, see section B.4.3.

B.4.2 Estimation and localization of emission sources

From spatial mapping of the flux measurements together with wind measurements, the source areas causing the measured gas fluxes can be interpreted. Depending on the site or application, it is important to measure over appropriate time duration and ideally in different wind directions to be able to pinpoint the sources. If applicable, it is also recommended to make leak search at the source unit with the TC instrumentation and attached tubing and/or handheld OGI or sniffer devices to allocate sources of emissions as good as possible within the identified source units.

In order to better characterize and understand the source emission distribution over time, it’s recommended to gain statistics on the emission by multiple measurements over a time frame suitable for the survey objective. Since emissions may vary both on a short and long timescale, and meteorological dispersion effects also may induce some noise (variability) in observed emissions, averaging of at least 4 measurement transects on each measurement occasion is recommended.

Industrial sites, such as refineries are complex and include both continuous emissions from tanks and process areas as well as intermittent ones from various activities such as cleaning and repair, ship and truck loading and flaring. The obtained data from various areas should be analysed in a statistical manner. The best estimate of the continuous emissions is the median value, given that intermittent emissions only have occurred infrequently during the measurement study, while the average emissions is the best estimate for the total emissions during the period. However, since intermittent emissions can be very high, it is important to understand the origin of these before including these in any emission assessment. Once the source of the intermittent emission is understood one should assess, if possible together with the industrial site, how frequent such emissions occur during the year. The TC method can preferably be used to study emissions related to a complete cycle in the production, such as filling of a tank, product loading to trucks or vessels etcetera. By obtaining an emission factor for the activity, the resulting emission can then be extrapolated by the number of operations. Obviously, any seasonal change in the emission factor need to be measured or assessed in this extrapolation.

B.4.3 Data validation procedures

One shall maintain records that include sufficient information to reconstruct the measurement from the variables originally gathered in the measurement process. This includes, but is not limited to, information (raw data, electronic files, and/or hard copy printouts) related to sampler calibration, sample collection, measurement instrument calibration, quality control checks of sampling or measurement equipment, "as collected" or “raw” measurement values, an audit trail for any modifications made to the "as collected" or “raw” measurement values, and traceability documentation for reference standards. Difficulties encountered during sampling or analysis, such as interference between adjacent plumes, large upwind fluxes or highly variable wind fields should be documented.

To ensure high quality data an internal audit procedure of the data shall be carried out. In the audit procedure the completed TC measurements shall be reviewed by an experienced TC-operator that has not been involved in the actual data evaluation. It is preferred that at least one of the persons involved in the data processing have been present while the actual measurements were made.

The final emission data should be presented as the hourly emission rate and its variability.

The criteria below shall be used to flag uncertain TC measurement data and these data should either be discarded, tagged with higher uncertainty, as requiring complementary information or new spectroscopic retrieval:

1. Abnormal noise levels, tolerance less than 3 times the standard detection limit.

2. Leak search to identify the leaking sources should be performed. (Y/N)

3. Quantification based on at least 4 measurement transects per source. (Y/N)

4. Leak gas and tracer gas concentration above 3 times the detection limit. (Y/N)

5. Assess the variability of the emissions results due to poor overlap (correlation) of tracer gas and leakage gas by using at least one of several methods as explained in section B 2.4: dual tracer gas releases, multiple release positions of tracer gas, different wind directions and distances or measurements at a far-away distance (without introducing interfering adjacent sources of studied VOC or tracer gas).

6. If complex area/volume source the plume should to be traversed entirely and at different distances. (Y/N)
7. Risk for a significant mismatch between tracer gas and source gas in the vertical orientation due to unknown sources or inaccessible unit parts for leak search and verification. (Y/N)
8. Leak gas and tracer gas should “correlate” in the spatial regime, and the cross section of the plume should be probed at comparable plume transport times from the source. (Y/N)
9. Scan upwind and downwind for interfering sources, especially important to avoid VOC sources very close to the sampling point relative the distance to the tracer gas/main VOC source location. (Y/N)
10. The background baseline concentration of VOC and tracer gas respectively differ significantly comparing concentrations at the plume edges. Should be similar, or an indication of instrument drift or interfering sources.
11. Keep track of tracer gas release rates by weighing released amounts and usage of stable regulators or mass flow controllers.
12. Wind criteria, 1-12 m/s.

B.5 Reporting

The report should include the following:

☐ Overview and description of measurement method.
☐ Description of emission quantification procedure.
☐ Measurement objectives.
☐ Factors influencing detection limit and accuracy. A response to whether any flags according to section B.4.3. were raised and in case, how issues were resolved.
☐ Emission for each area measured.
☐ Meteorological and other data collected pertaining to the TC measurement:
  - date, time and duration of measurement
  - wind velocity and direction
  - Tracer release rates, times and total tracer amounts released
  - geographic location (GPS coordinates)
  - description of areas observed

☐ Two-dimensional concentration data for the measurements overlaid on a site plan (2D plot) to aid visualization of the plume and to identify emission sources.

☐ Conclusion: which areas were measured and total emission rate. Emission rates should be presented as statistical data (daily means, standard deviations, median).

TOTAL
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Raffinage-Chimie
Direction R&D
Laboratoire Qualité de l'Air

MEMO

Destinataire : CEN WG38 group *To* :		Expéditeur : Olivier DUCLAUX.... *From* Guillaume VINCENT ....
Copie : Equipe LQA .... *Copy* Sylvie SUTTER................		Date : 12/05/2018 ....
Object : *Subject*	**RESULTATS RDM in CEN campaign #2 : real site emission**	

Reference CEDRE : HSE -2018- ENV –025

Sommaire / Summary

1. Contexte

In the framework of CEN WG38, an emission quantification campaign has been carried out in Holland in an operational refinery.
The emission quantification was conducted using several technics, including macroscale optical tools (Lidar from NPL, SOF from Fluxsense), mobile FTIR using tracer operated by Fluxsense and Reverse Dispersion Modeling operated by TOTAL LQA.
The study was conducted on TOTAL funding for a participation in the first two weeks.
The TOTAL team focus the work on the quantification of the Waste Water Treatment area.

All the emission estimates by RDM were sent to INERIS & CEN before knowing the estimated emissions from other team, with a presentation of the results in Powerpoint format.

This report summarizes the emission estimates originally submitted, modifications related to protocol adaptation, and a comparison with other technics for the WWT area.

The report is in three parts:

- Preparatory work and measurement campaign
- RDM methodology : Direct Modeling and Reverse dispersion estimation
- Results of RDM and comparison with other technics.

2. Preparatory work and measurement campaign

- The preparatory work was done in march – June 2017 :
    - Meetings
    - Send of protocol and equipment description to refinery.
    - Safety training.
    - Retrieval of geometry information (Map of the installation, pictures, measurement of height with laser …)
    - Retrieval process information (water/ oil circuit of the WWT)

- During the measurement campaign, the means use for emission estimation were :
    - Staff :
        - 2 persons from TOTAL for Met Mast installation
        - Measurements : 2 persons
    - On-site material
        - Weather station Gill sonic 3 D measurement, installed on mast 3.7 meters (see picture). To obtain an estimation of turbulence, a solar measurement was installed (pyrometer). The change of met station was due to a problem of availability (the METEK USA-1 - 3 D with turbulence was in maintenance).
        - Portable Foxboro Analyzer (FID / PID) (see picture).
        - 6 PID VOC micro sensor (but not working well, not enough sensibility), measurement not use.
        - 1 vehicle for transport (a van)
        - Gas for calibration (Methane + Air zero)
        - Computer
        - Personal protective equipment

- Off-site material :
    - Hydrogen bottle for FID refueling.

Measurement Protocol:

The defined area was the Waste Water Treatment of the refinery.

Mobile VOC Measurement:

- Before measurement, a calibration of FID detector was done with methane standard.
- The number of measurement point was variable for each test according to meteorological conditions.
- The location of measurement point were choice :
    - first, a up wind measurement is done for background
    - in the WWT area or in downwind to be in the plume of each source for quantification
    - not to close for safety reasons (max concentration accepted 1 000 ppm)
    - not to close for representativeness of dispersion model reasons (minimum 2 meters)
    - Following the path, the strategy is to obtain a transversal section of each plume (with the objective to have 7 significative points in each plume)
    - Measurement at a specific location: minimum 30 seconds.

Meteo data :

- For CEN campaign 1 : measurement of stability (Lmo) with sonic 3D METEK
- For CEN campaign 2 : calculation of U* for each station according to ADMS module using solar radiation (Total) for turbulence and wind speed (each station).
- First evaluation with TOTAL met station.
- Sensitivity test with all meteo station (only influence of wind direction) and some days (Wind Speed & Direction)
-

Fixed VOC Measurement with microsensors:

Not use for RDM, due to sensor not adapted to low concentration

Figure 1 : views of Waste Water Treatment area

Figure 2 : views of FID Measurements and Meteo Station

Exact measurement locations and timing were recorded.

The minimum measurement duration at a point was 30 seconds for FID measurements. According to the wind variability, the duration could reach several minutes in the same point. All measurement locations are reported in annexe for each measuring period.
An example of a path with measurement point is reported in next Figure.

Figure 3 : Measurement points (colored cross according to FID measurment) during a path

From the 22/06/2016 to the 28/09/2016 14 :00, the TOTAL team participated in 13 Tests. For all the tests in which TOTAL RDM participated, an RDM estimation was performed and sent to INERIS.

	Start time (local)	End time (local)	TOTAL Measurements	TOTAL estimation by RDM
14/06 PM	14/06/2017 13:52:57	14/06/2017 15:11:27	yes	yes
15/06 AM	15/06/2017 11:23:27	15/06/2017 12:35:57	yes	yes
15/06 PM	15/06/2017 14:03:10	15/06/2017 15:21:30	yes	yes
20/06 AM	20/06/2017 09:58:34	20/06/2017 11:18:04	yes	yes
20/06 PM	20/06/2017 14:36:33	20/06/2017 15:42:03	yes	yes
21/06 AM	21/06/2017 09:02:31	21/06/2017 10:23:31	yes	yes
21/06 PM	21/06/2017 13:00:29	21/06/2017 13:50:59	yes	yes
22/06 AM	22/06/2017 08:51:01	22/06/2017 11:04:31	yes	yes

Table 1 : list of tests with participation of TOTAL team, and sources

Conversion factor :

All the FID measurement were done in methane equivalent, converted to –CH2 equivalent to represent average mass of hydrocarbon (* 14/16). This first approximation was use for the RDM, with first emission estimation in equivalent –CH2.
For the report, a final conversion using the VOC speciation done by NPL the 22/06, was use after first emission estimation.

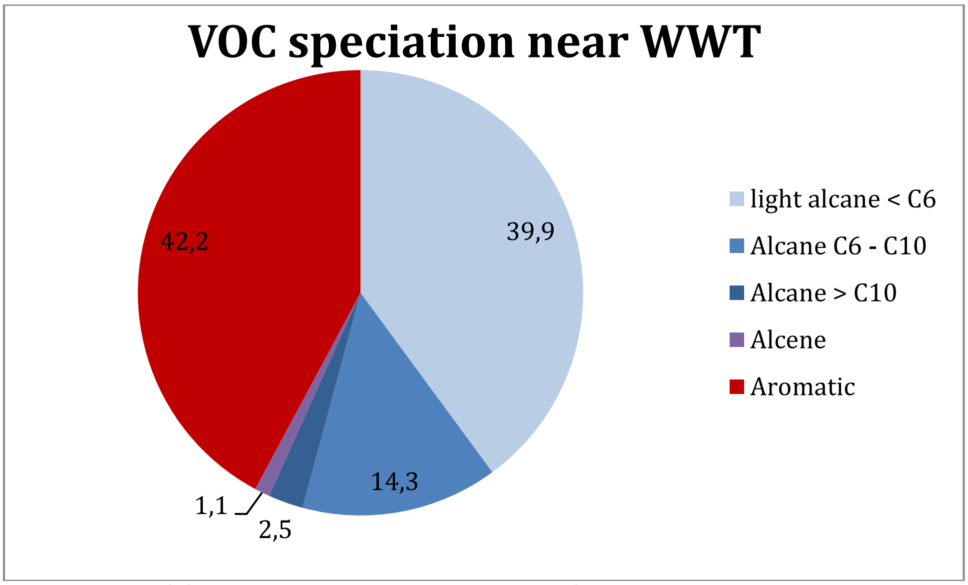


Figure 4 : VOC speciation near WWT the 22/06 (from NPL sampling and analysis) in mass percentage.

- Use of EPA conversion factor for each VOC (87 % of VOC mass identified) in equivalent CH4
- Conversion factor from FID equi CH2 to VOC "real" mass : 2.05 * (16 / 14) = 2.34

3. RDM methodology : Direct Modeling and Reverse dispersion estimation

The RDM methodology was applied after the measurement campaign. To reproduce dispersion conditions specific of the measurement period, direct dispersion calculation was performed with unitary emission.

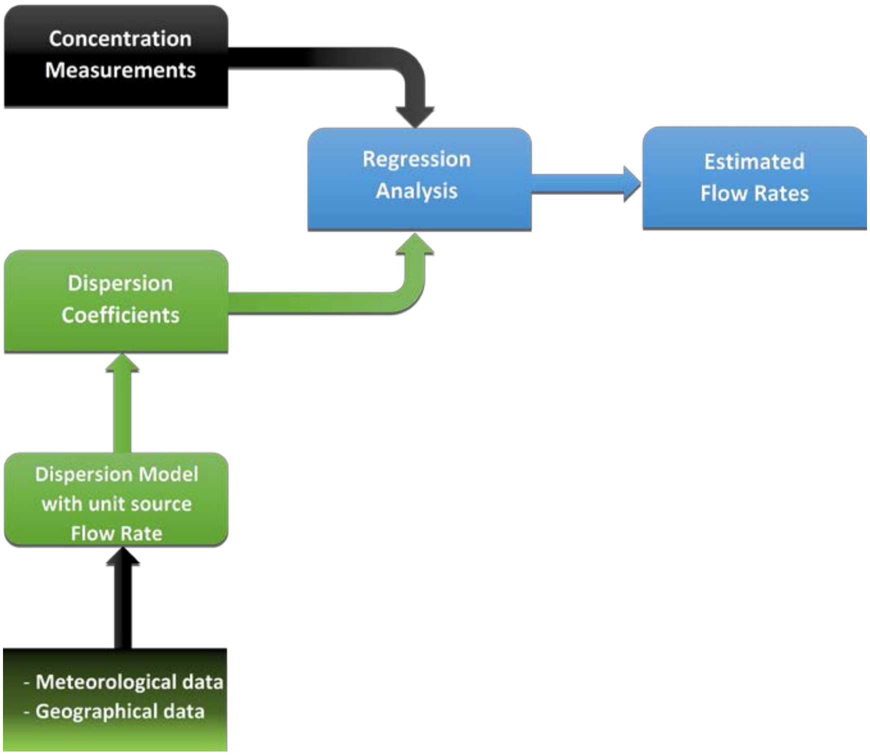


Figure 5 : Reverse Dispersion Methodology

Direct model description :

Following RDM standard, the model must be adapted to the situation. In presence of obstacles (building, tanks, industrial units …), the selected model must be able to reproduce effects of obstacles in the wind field.

The model selected for the CEN campaign is a combination of a CFD model and a Lagrangian dispersion model.

CFD calculation :

In complex area, CFD model is a solution to reproduce wind fields and turbulence variability. The model requires parameterizations adapted to studied atmospheric turbulences, and uses the meteorological parameters (wind direction, speed and turbulence) to construct a 3D wind field data base. This database is used for dispersion calculation to obtain unstationnary evolution of meteorological conditions.

A specific domain was defined to represent the WWT and the main obstacles around, which could influence the local wind field. The domain is represented in the next pictures, as the satellite view, modeled structure and meshing (all domain and a zoom). An example of CFD model results for 2 meters above ground wind is also reported.

Figure 6 : View of the real site

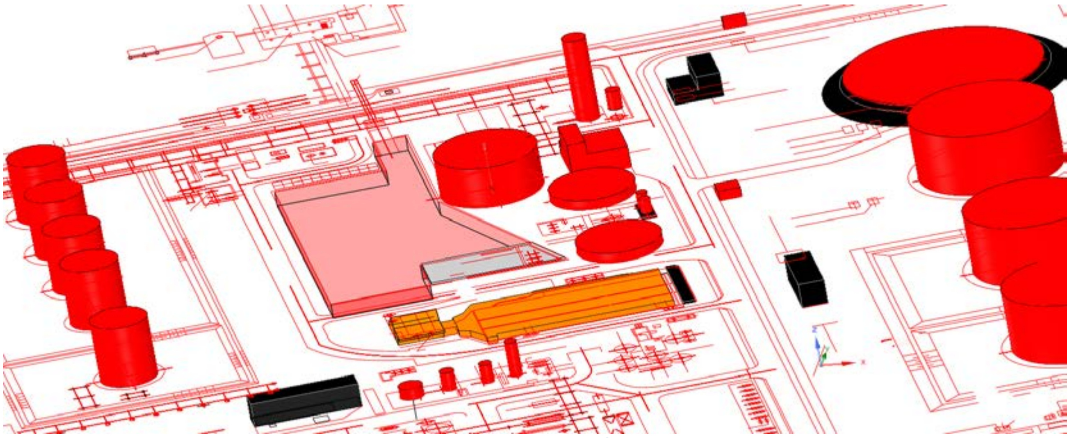


Figure 7 : View of the modeled site

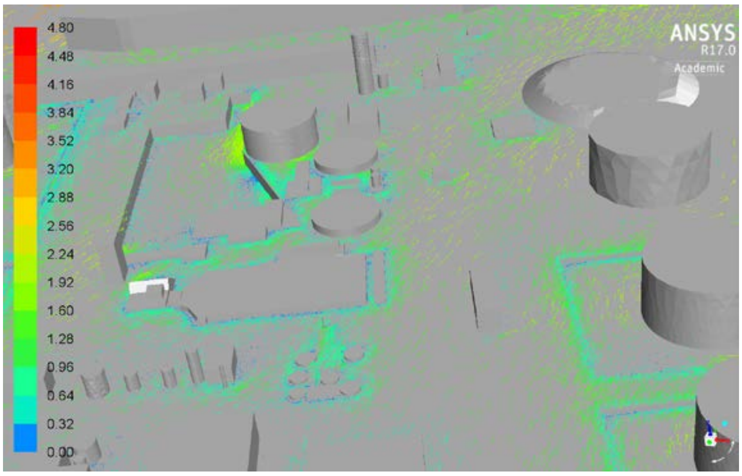


Figure 8 : View of wind field calculate by CFD model (Fluent)

- The combination of the data base with measured real meteorological conditions allows to construct a variable wind field.

- The next work is the dispersion. The dispersion is based on the recombined 3d wind field and the use of a lagrangian model (SLAM). The emission sources are represented by volume, point or area sources. Classical direct dispersion is performed with a theoretical unitary emission flux set at 1 g/s for each source, in order to obtain the dispersion factor matrix at each monitoring point.

Dispersion :

- The emission sources are used in the dispersion model (SLAM) with the combination of CFD wind and turbulence fields corresponding to a specific meteorological condition (station measurement).

- **Representation of emission sources :**
    - 6 emissions sources are presented in the next figure.
    - An example of instantaneous dispersion with three sources is reported.

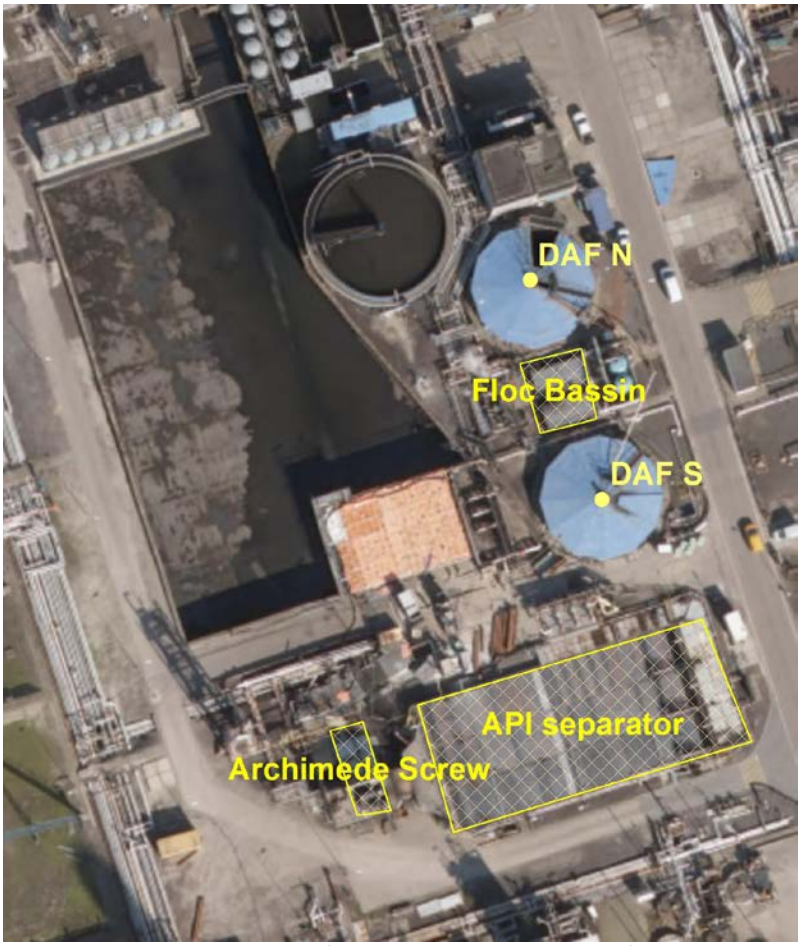


Figure 9 : View of emissions sources identified

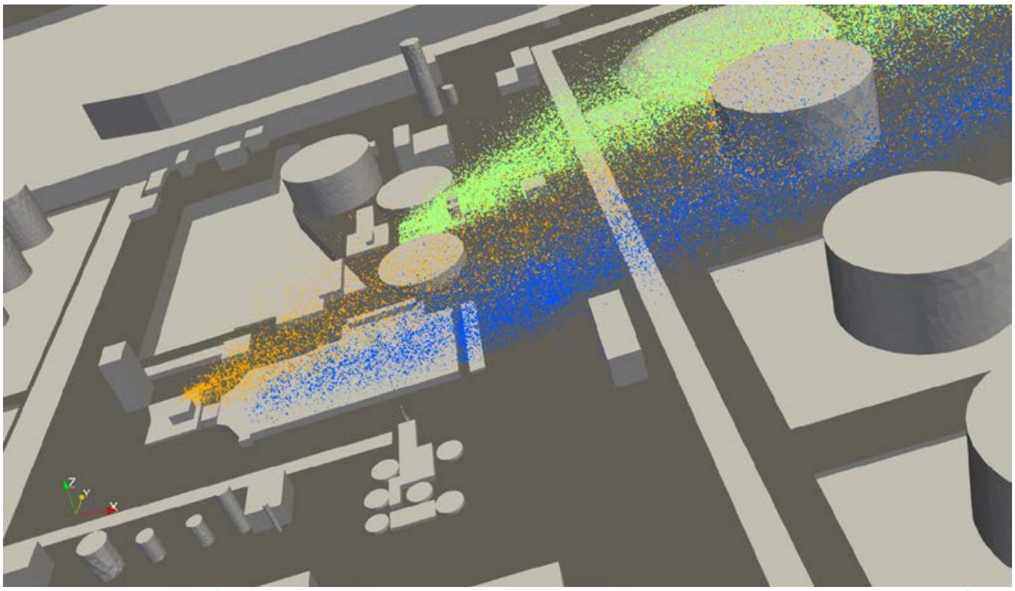


Figure 10 : View of Lagrangian dispersion with three sources (unitary emission) : VIS : orange, API : blue, Bassin : green

RDM :
The dispersion coefficients (defined as the concentrations simulated with an unitary emission per source, ex : 1 g/s), are specific at each time and measurement location point.

Multilinear regression is applied to the dataset (Measured concentrations = function of simulated concentrations). Result of RDM is reported according to different meteorological station information and measurement integration times (30 seconds and 2 minutes). For size reasons, only 2 minutes averaged measurements are reported in annex.

Validation of RDM is describe by comparison against validation criteria defined in CEN campaign#1 (see next part).

4. Results of RDM and sensibility study

For each period, main data are in annex.
The results obtain with RDM sended to INERIS are summarized in the table and figures below.

Several different RDM tests were done :

- using the Total meteo station (for wind direction and speed, and turbulence estimated from solar radiation).
- using one INERIS or NPL Stations for wind (direction and/or speed) and turbulence from solar radiation estimation.

Estimation with the Total's meteo Station:

The TOTAL's meteo station is the closest of WWT area. The estimation with the TOTAL meteo Station is reported in the next table, including all the sources identified (API, VIS, Bassin, DAF). In comparison of data send to INERIS, the RDM emission estimation was corrected:

- the DAF was added
- Emission are in "real" VOC, correction based on NPL VOC speciation.

The measurement data selection exclude value below 2 ms^{-1} of wind speed.
The RDM quality criteria was determined as the slope of measurement concentration vs average modeling concentration. A negative slope is noted as Low quality, but emission are reported

For 14/06 and 15/06 am, measured point don't permit to quantify correctly DAF and basin contribution. The criteria of validity is negative the 14/06, 15/06 PM and 22/06 AM, but value are reported with an indication of low quality.

Debit (kg VOC/h) Date	WWT sum	API	Bassin	Archimede's screw	DAF	Meteo Station	Wind Speed averaged	Wind Speed	wind direction	RDM quality criteria
14/06pm		2.0		0.9		TOTAL	2.78	1.4	SE	Low
15/06am		0.6		3.9		TOTAL	3.7	2.35	WS	Medium
15/06pm	14.1	6.0	3.4	1.5	3.2	TOTAL	4.45	2.48	E-SE	Low
20/06am	10.7	2.4	1.5	3.2	3.53	TOTAL	3.55	2.48	NE	Good
20/06pm	7.4	2.8	0.7	1.8	2.07	TOTAL	4.32	2.765	N-NE	Good
21/06am	5.3	1.8	0.6	1.9	1.017	TOTAL	2.9	1.49	E-SE	Medium
21/06pm	11.3	4.5	0.5	3.2	3.146	TOTAL	2.96	1.75	E-NE	Good
22/06 am	11.9	0.3	4.3	2.1	5.18	TOTAL	3.5	1.684	W-SW	Low
Average	**10.1**	**2.6**	**1.8**	**2.3**	**3.0**					

Table 1 : estimation of emission by RDM with TOTAL met station (gray : not validated emission; blue : lack of source in the global flux sum).

A final correction was applied to correct two mistakes in the dispersion model calculation:

- A bug in VIS estimation was corrected (initial calculation was done with unitary emission fixed at 0.9 instead of 1 g/s, a simple factor 1.11 is use).
- The ejection velocity of the DAF was not take in account. The plume rise was applied with a 10 ms^{-1} ejection speed (estimated). The result of the modification correspond to an average increase of 1.44 of DAF emission source.

Debit (kg VOC/h) Date	WWT sum	API	Bassin	Archimede's screw (* 1.11)	DAF (*1.44)	Meteo Station	Wind averaged	Wind Min	wind direction	RDM quality criteria
14/06pm		2.0		0.9		TOTAL	2.78	1.4	SE	Low
15/06am		0.6		4.3		TOTAL	3.7	2.35	WS	Medium
15/06pm	15.7	6.0	3.4	1.7	4.6	TOTAL	4.45	2.48	E-SE	Low
20/06am	12.5	2.4	1.5	3.5	5.1	TOTAL	3.55	2.48	NE	Good
20/06pm	8.5	2.8	0.7	2.0	3.0	TOTAL	4.32	2.765	N-NE	Good
21/06am	6.0	1.8	0.6	2.2	1.5	TOTAL	2.9	1.49	E-SE	Medium
21/06pm	13.1	4.5	0.5	3.5	4.5	TOTAL	2.96	1.75	E-NE	Good
22/06 am	14.4	0.3	4.3	2.3	7.5	TOTAL	3.5	1.684	W-SW	Low
Average	**11.7**	**2.6**	**1.8**	**2.6**	**4.4**					

Table 2 : estimation of emission by RDM with TOTAL met station with corrections in dispersion calculation (gray : not validated emission; blue : lack of source in the global flux sum).

The RDM estimation of WWT emission is around 10 kg/h, and with correction of mistakes in dispersion model, the average estimated emission is 11,7 kg/h of VOC.

Sensibility study with different meteo Station:

The influence of meteorology is a sensibility test, the simulations were done with only three emissions sources (API, VIS, Bassin), the DAF contribution was not take in account.

For all the RDM's period, an emission estimation is done using the wind direction specific of each station, but with wind speed and turbulence estimation from Total's station.

For the second week (20 to 22/06), RDM calculation were done for each met station wind (speed and direction) and the turbulence estimation from Total's station
In comparison of the emission estimation variation, we can conclude on the homogeneity of wind field.

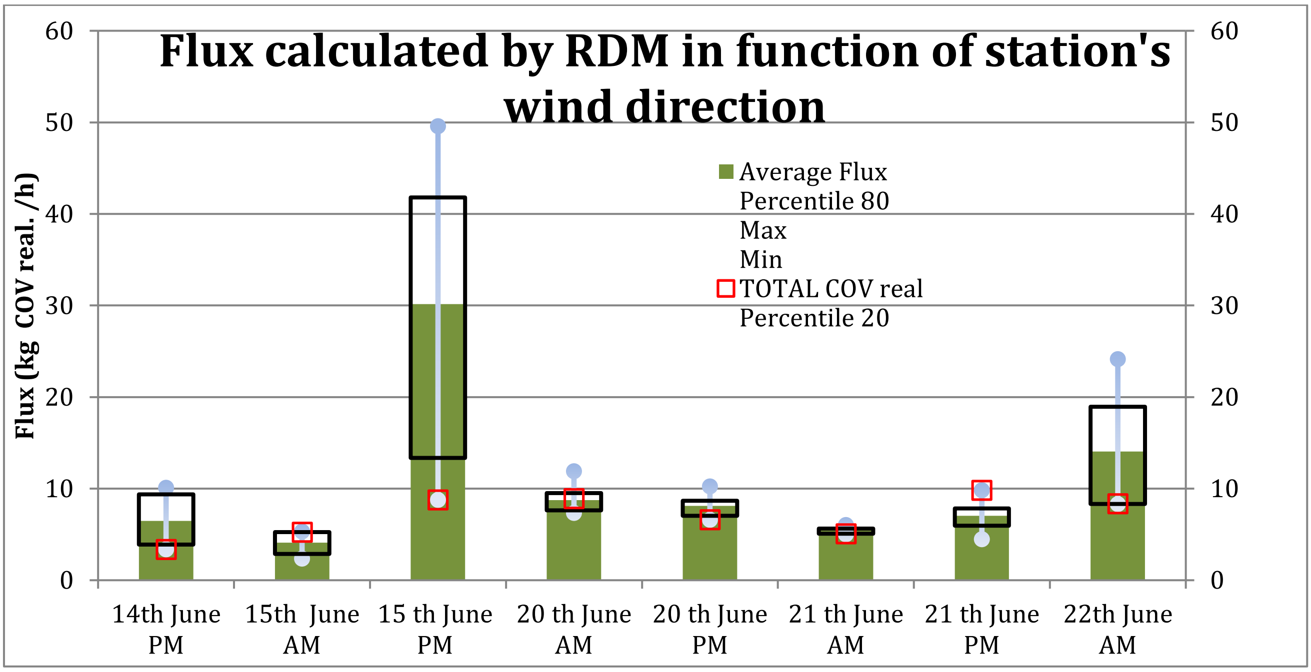


Figure 11 : Sensitivity test with all met station direction as input of RDM,

We can highlight two different typologies according to the choice of meteo station direction:

- Periods with high variation according to meteo station choice : 15th June PM and 22th June AM.
- Periods with no significant differences with the met stations directions.

To improve the comparison for specific period with no influence of wind direction, we calculate the effect of wind direction specific and wind direction and speed for each station.
There is no constant effect, using the wind direction is the most important parameter, difference due to wind speed is a second order except for the 21th June PM. It's difficile to conclude or extrapolate a tendency, it seems to be only representative of the Rotterdam site during the period. Further investigations are needed.

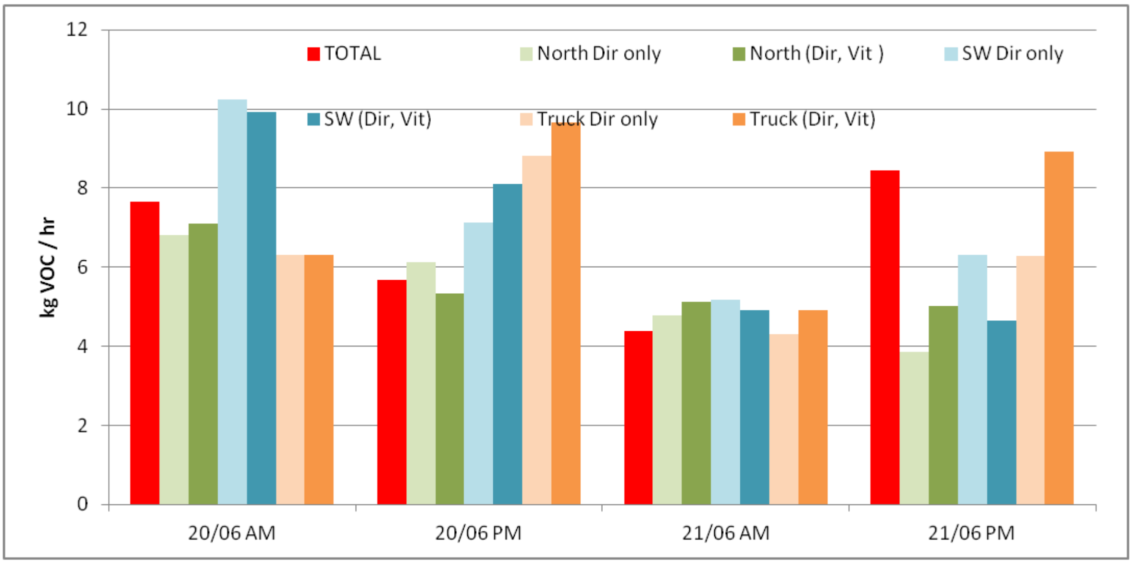


Figure 12 : Sensitivity test with all met station wind direction or wind direction and speed as input of RDM,

The preferred MET station is noted, and the choice was done based data consistency (best fit between measurement and model).

5. Comparison with other technics

Each technic have done a measurement of the WWT area, but not at the same time. For the WWT area, the other technics operate:

- Tracer TCT one time (20/06 AM) :
- SOF two time 15/06 PM and 22/06 AM
- Lidar 22/06 AM

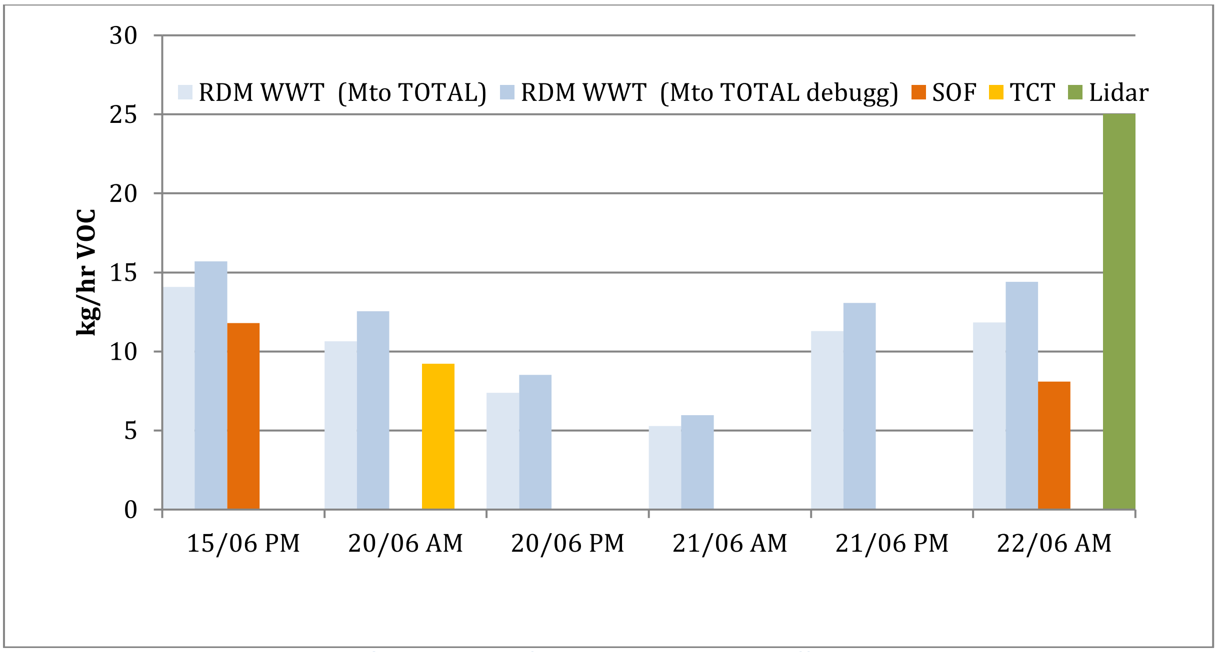


Figure 13 : Comparison of WWT emission with different technics.

The 22/06, in principle all technics must quantify the WWT area, but TCT didn't.
The SOF for this period have done only one measure, not representative (high uncertainty).
The Lidar have the highest emission (25 kg/h). To compare with RDM, we calculate emission based on Lidar scan in the same period, so the emission estimated by Lidar is (23,5 kg/h).
As the 22/06, RDM estimated with TOTAL met station have a low quality, a new calculation was done using NPL portable met station. The estimation with RDM is around 18,9 kg/h.

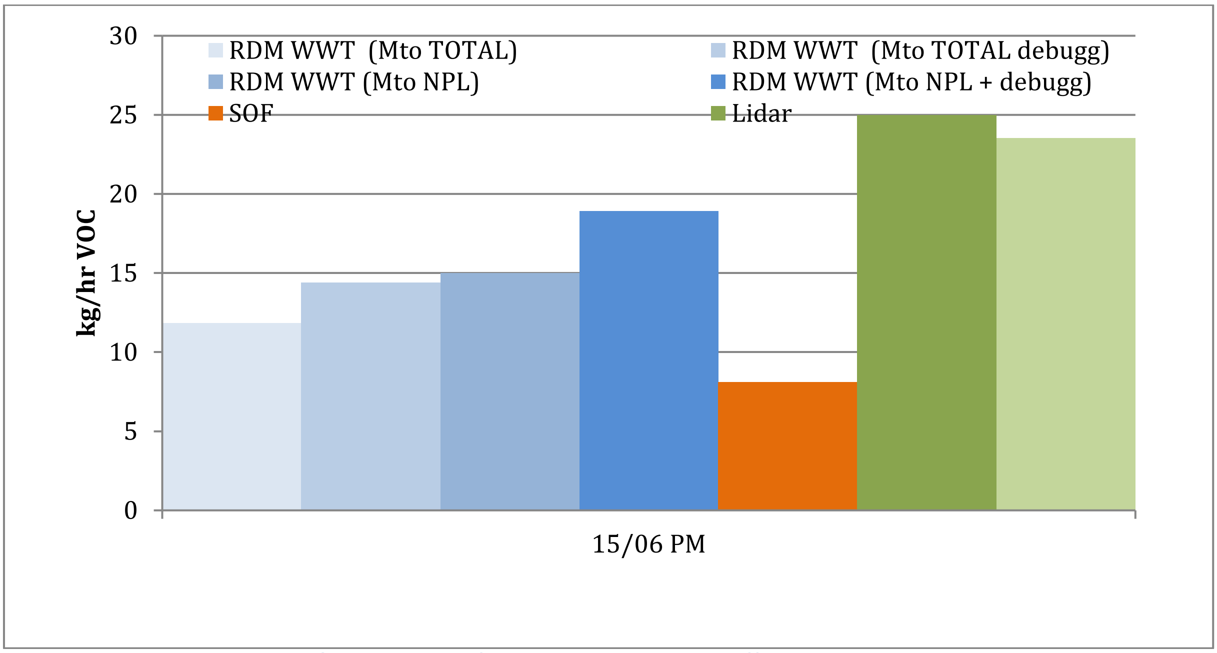


Figure 14 : Comparison of WWT emission with different technics the 22/06

6. Assessment of the method protocol:

The main changes in comparison of the fisrt CEN campaign were :

- Use FID calibrate with CH4 instead of Propane. A specific correction factor was applied according to VOC speciation.
- The meteo station was a 3 D wind sensor, but no turbulence quantification. Turbulence was estimated from solar radiation.
- For direct dispersion calculation, there is a need to have better estimation of ejection parameter. Need to be measure in case of “canalized” emission like for DAF.
- Use of a portable mast installed in the measurement area could improve the estimation in some specific meteorological variability

7. ANNEXES

Annexe : CFD description

Description of modeling choices retained for the specific campaign:

The CFD calculations are done with the ANSYS FLUENT code, using preprocessor Space Claim for meshing.

MESHING :

For the present case, we retains the strategy to obtain a good meshing quality:

- Layout of the unit with as much precision as possible

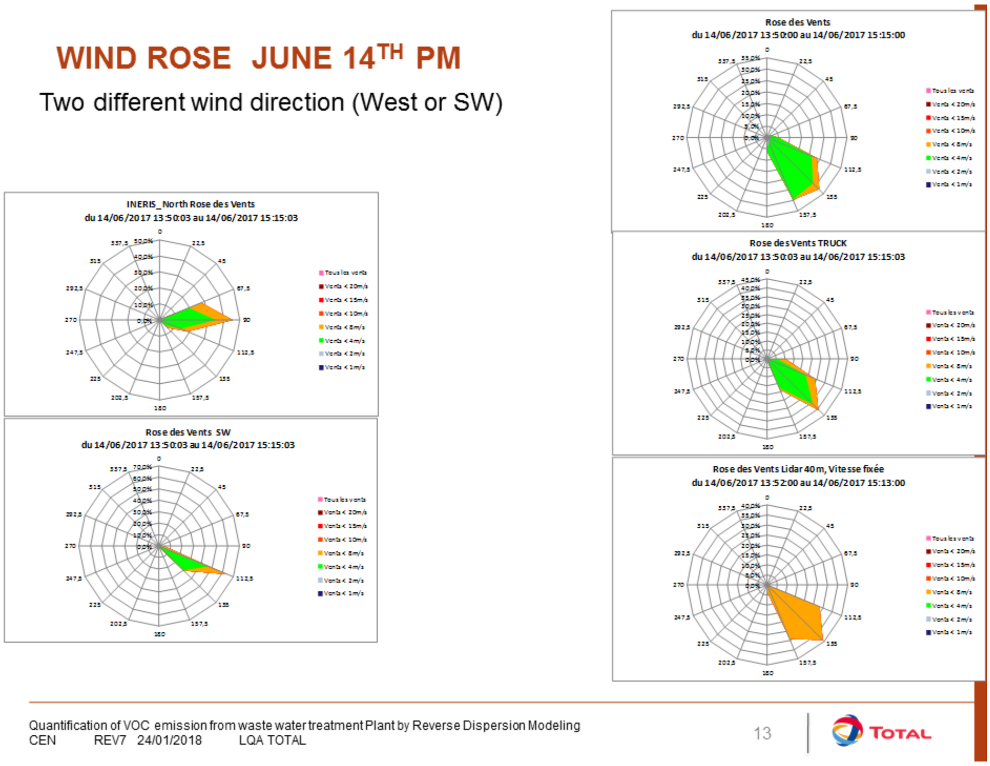
- Management of fine detail levels (like pipes) via porous volumes

- Size function: Proximity and curvature
- Directed design at ground level (2m)
- Result: ~ 5 million meshes with precise refinement in the WWT areas.

CFD calculation

- Establishment of profiles based on observed weather data
- Launch of test calculations and validation of the vertical wind profiles at the end of the domain in comparison with the profiles measured by LiDAR wind (see INERIS)
- Bibliography carried out to evaluate the coefficients of resistance law in the Gryning model. (see French GT3D “good practice guide”)
- Retention: Vachat model (gives formulation according to k, u *, f and LMO.
- One pair (A, B) per stability class

Annexe :14/06/2017 PM



WIND ROSE JUNE 14TH PM

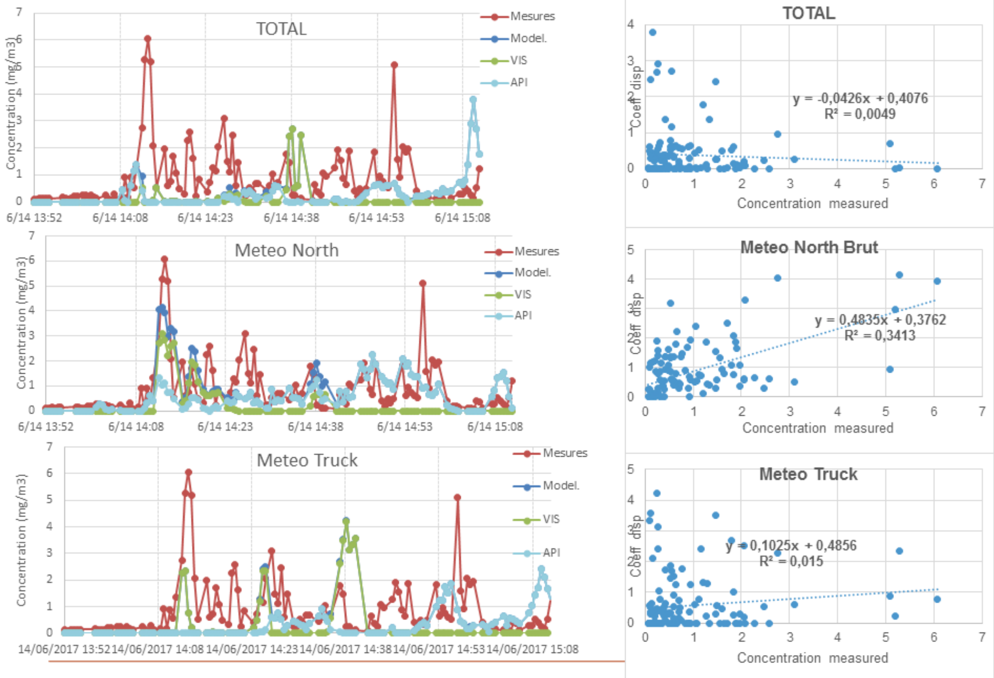
Two different wind direction (West or SW)

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

13

TOTAL

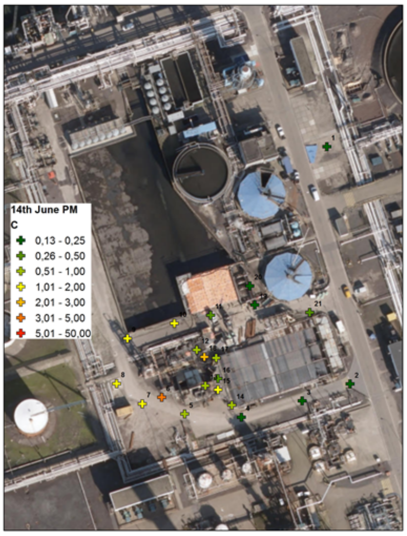
JUNE 14th :RDM with different wind direction



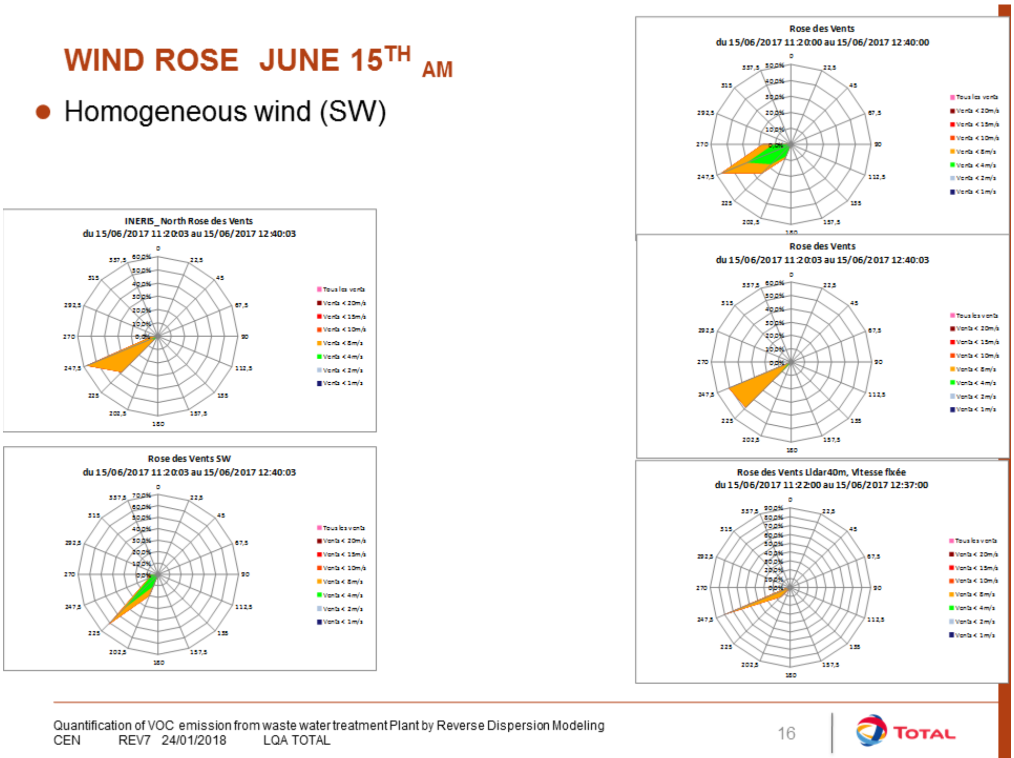
14 JUNE EMISSION

- According to criteria of « data consistency » :
  - TOTAL station low quality (negativ slope), wind measurement not representativ of local wind
  - Best fit with North Station
  - No evaluation of Activation bassin

RDM	Global	API	Bassins	VIS
TOTAL	2.9	2.0		0.9
Truck	7.9	3.1		4.8
North	4.9	3.1		1.7
SW	8.7	3.5		5.2
Lidar 40m	3.5	1.7		1.8



Annexe : 15/06/2017 AM

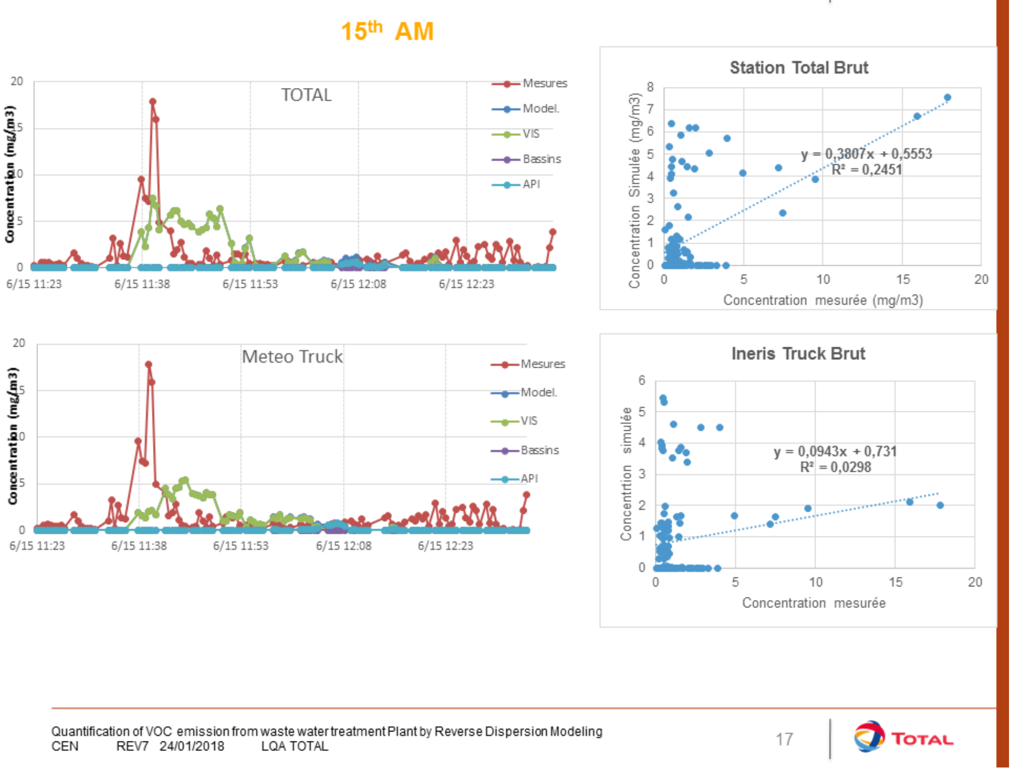


WIND ROSE JUNE 15TH AM

- Homogeneous wind (SW)

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

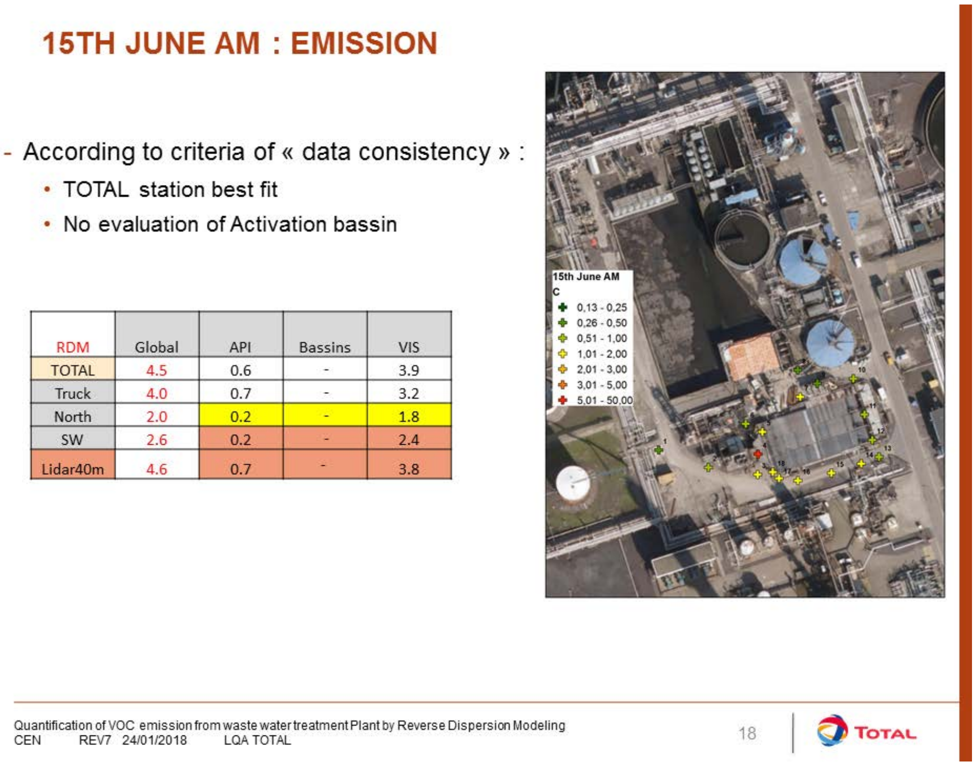
16 TOTAL



15th AM

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

17 TOTAL



15TH JUNE AM : EMISSION

- According to criteria of « data consistency » :
  - TOTAL station best fit
  - No evaluation of Activation bassin

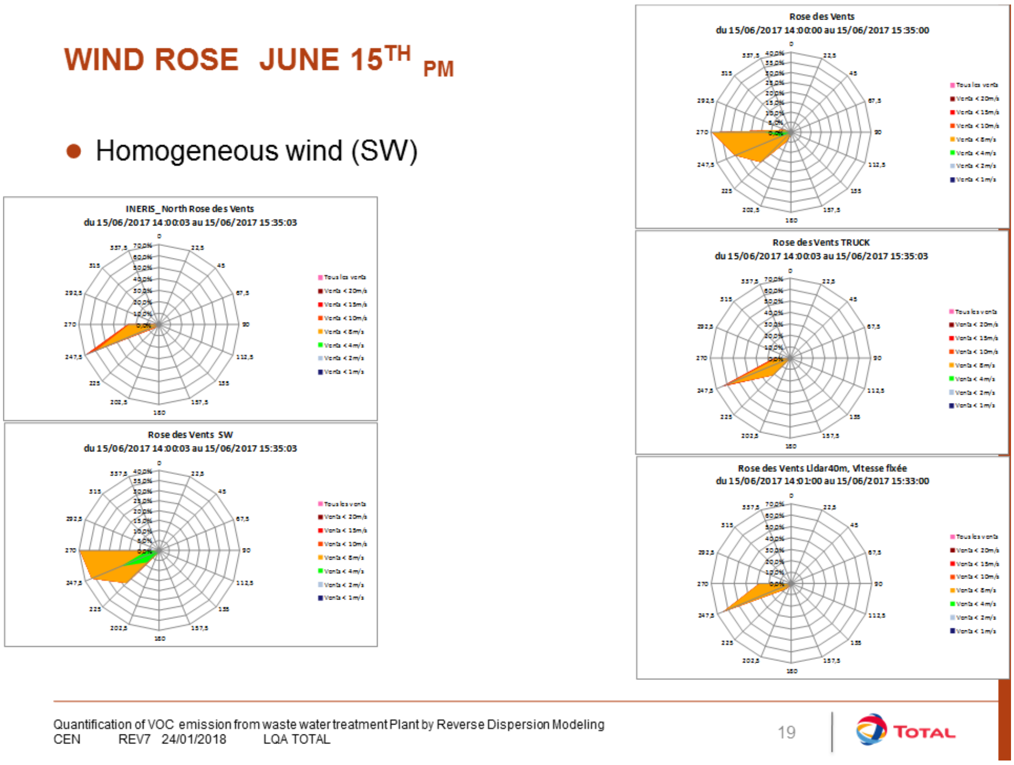
RDM	Global	API	Bassins	VIS
TOTAL	4.5	0.6	-	3.9
Truck	4.0	0.7	-	3.2
North	2.0	0.2	-	1.8
SW	2.6	0.2	-	2.4
Lidar40m	4.6	0.7	-	3.8

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

18

TOTAL

Annexe : 15/06/2017 PM



WIND ROSE JUNE 15TH PM

- Homogeneous wind (SW)

INERIS_North Rose des Vents
du 15/06/2017 14:00:03 au 15/06/2017 15:35:03

Rose des Vents SW
du 15/06/2017 14:00:03 au 15/06/2017 15:35:03

Rose des Vents
du 15/06/2017 14:00:00 au 15/06/2017 15:35:00

Rose des Vents TRUCK
du 15/06/2017 14:00:03 au 15/06/2017 15:35:03

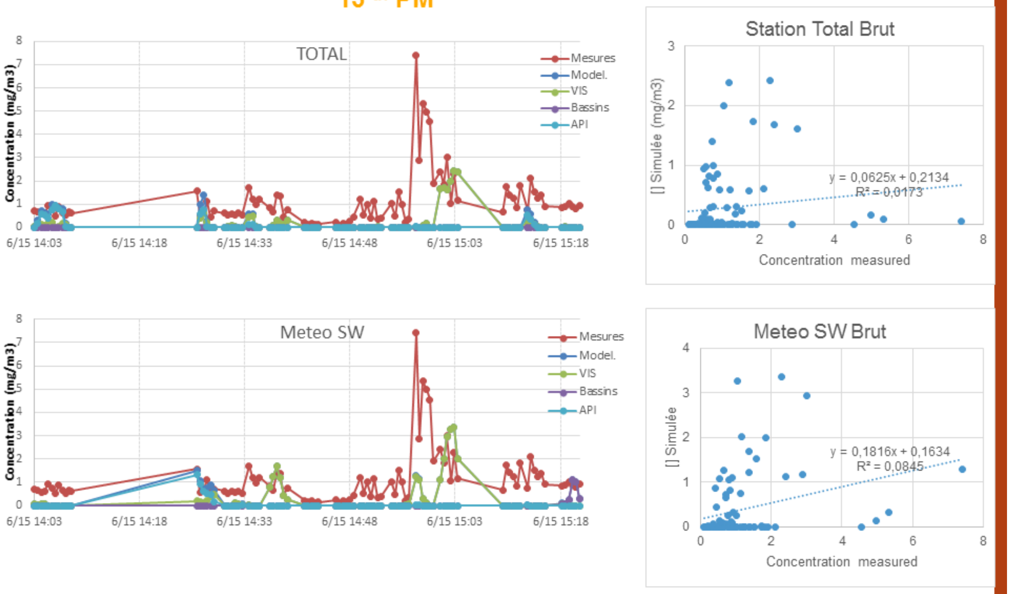
Rose des Vents Lidar40m, Vitesse fixée
du 15/06/2017 14:01:00 au 15/06/2017 15:33:00

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

19

TOTAL

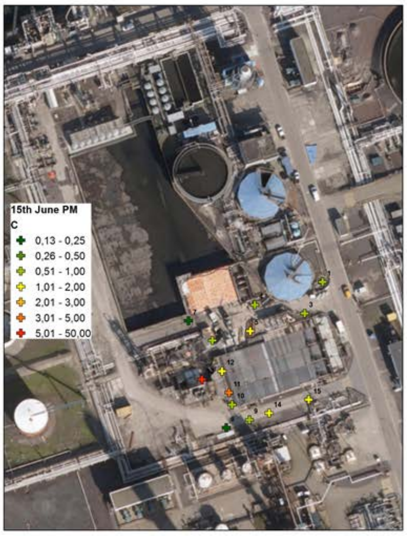
15 th PM



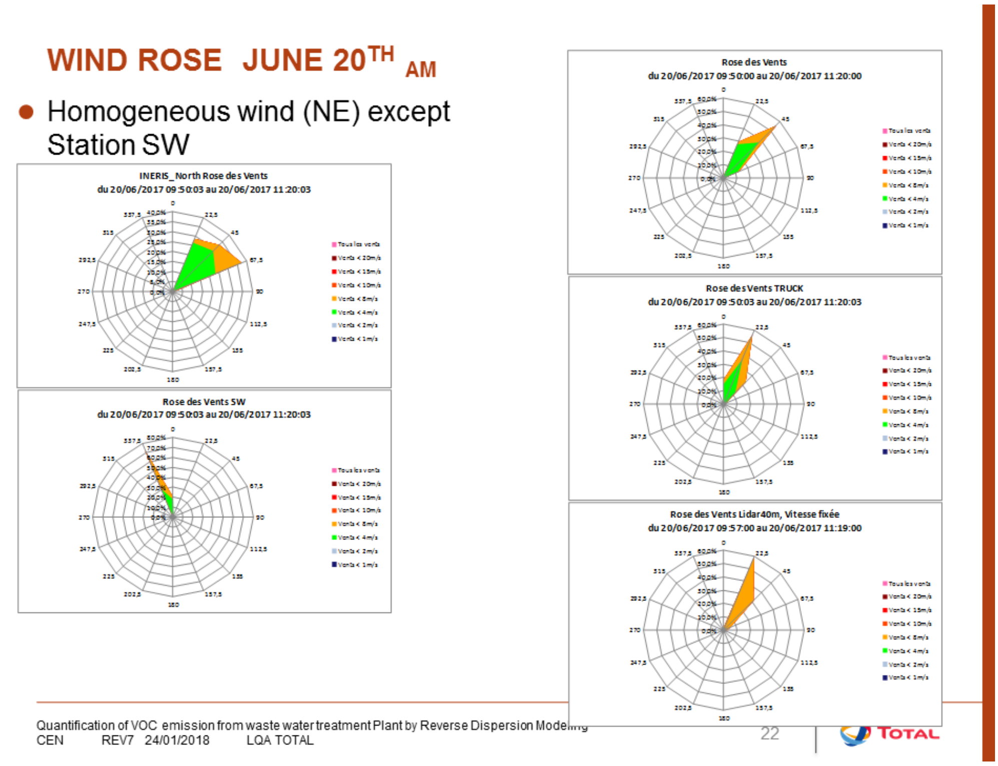
15TH JUNE PM : EMISSION

- According to criteria of « data consistency » :
  - SW station best fit, but very low quality
  - Some estimation of Activation bassin

RDM	Global	API	Bassins	VIS
TOTAL	7.6	6.0	0.0	1.5
Truck	42.7	21.5	19.6	1.6
North	32.8	24.7	6.9	1.2
SW	12.5	2.3	8.4	1.8
Lidar40m	34.3	22.4	10.7	1.2



Annexe : 20/06/2017 AM



WIND ROSE JUNE 20TH AM

- Homogeneous wind (NE) except Station SW

INERIS_North Rose des Vents
du 20/06/2017 09:50:03 au 20/06/2017 11:20:03

Rose des Vents SW
du 20/06/2017 09:50:03 au 20/06/2017 11:20:03

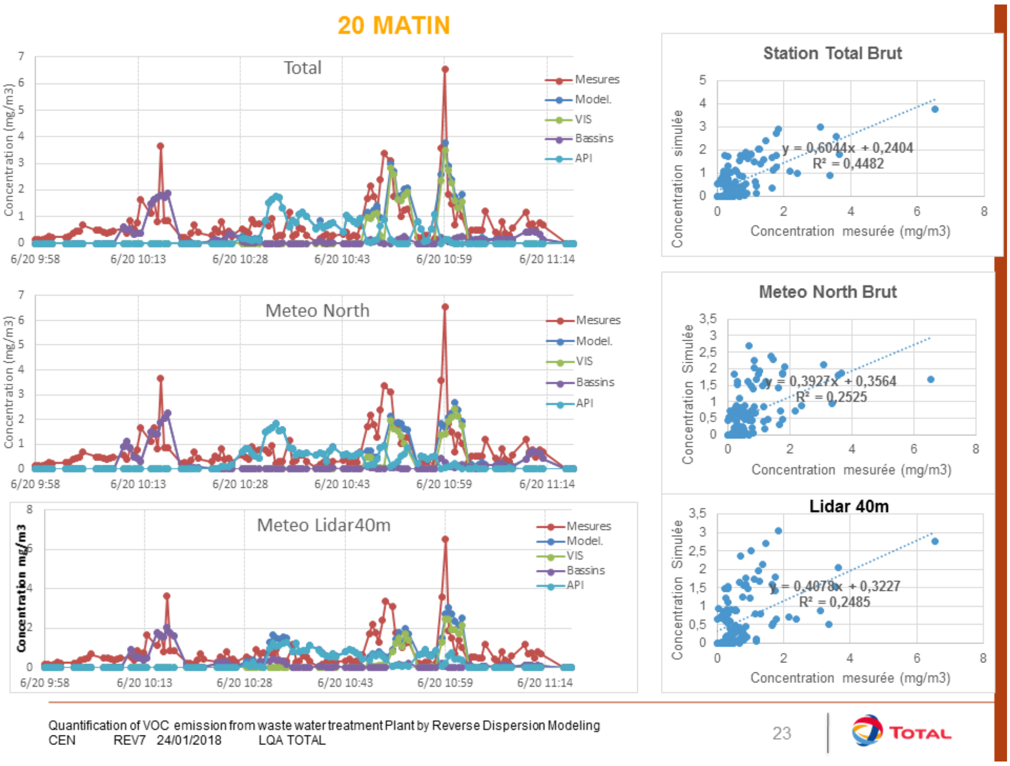
Rose des Vents
du 20/06/2017 09:50:00 au 20/06/2017 11:20:00

Rose des Vents TRUCK
du 20/06/2017 09:50:03 au 20/06/2017 11:20:03

Rose des Vents Lidar40m, Vitesse fixée
du 20/06/2017 09:57:00 au 20/06/2017 11:19:00

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

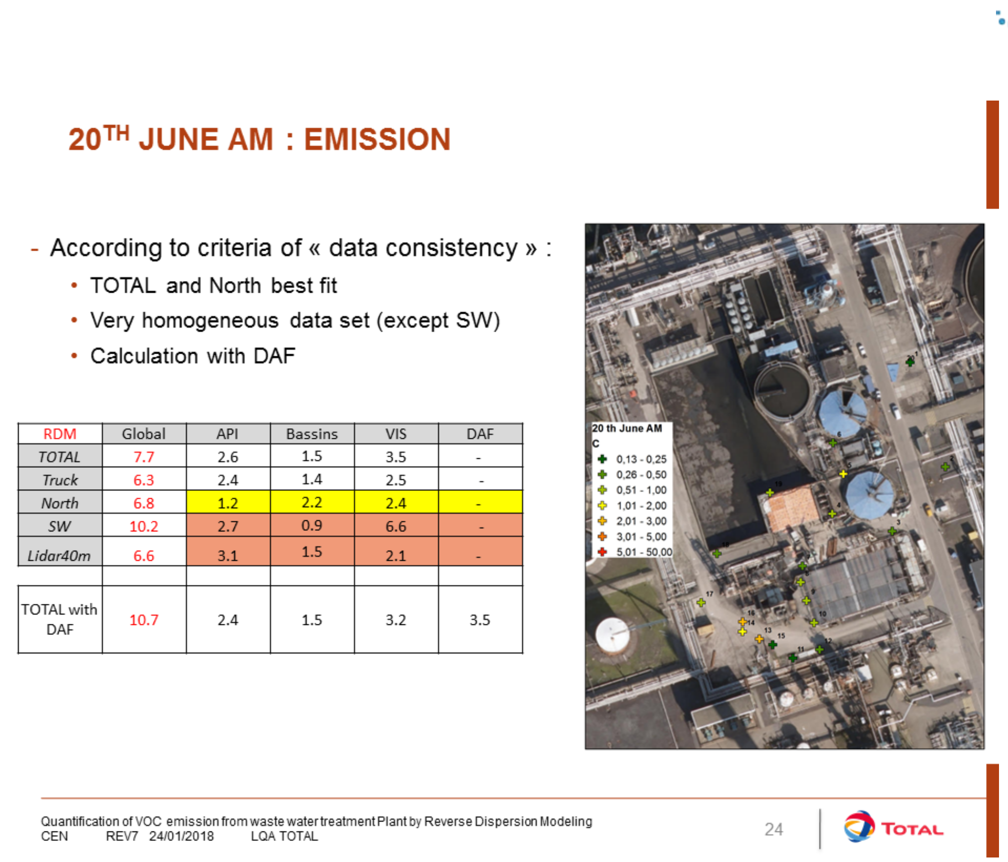
22 TOTAL



20 MATIN

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

23 TOTAL



20TH JUNE AM : EMISSION

- According to criteria of « data consistency » :
  - TOTAL and North best fit
  - Very homogeneous data set (except SW)
  - Calculation with DAF

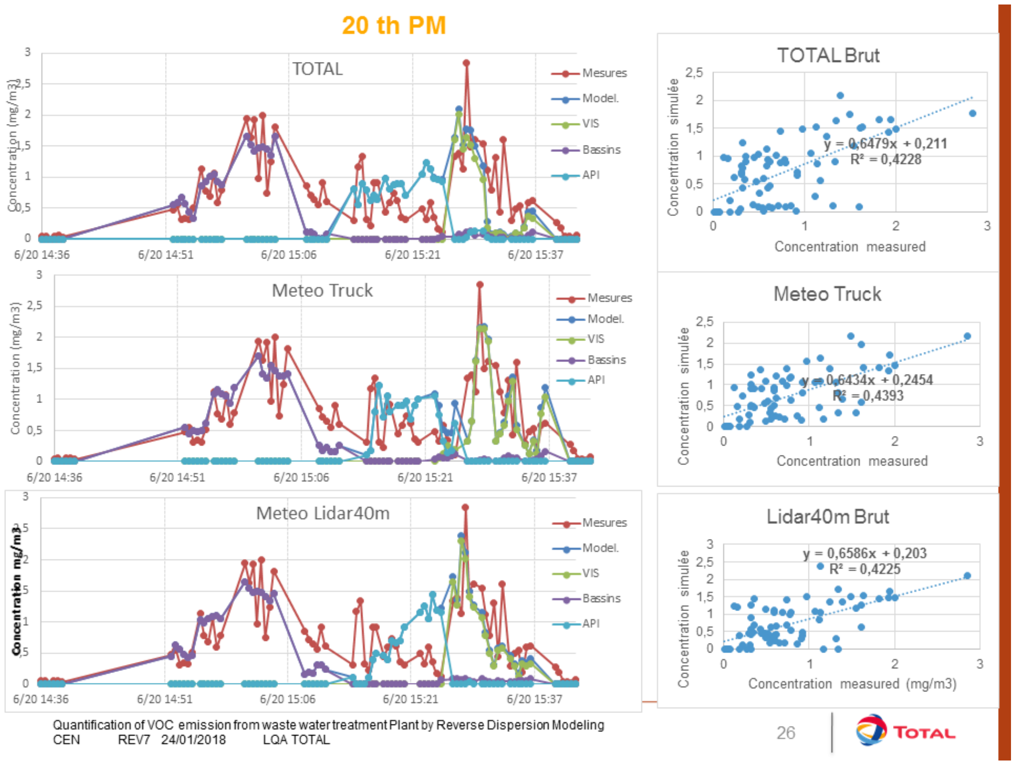
RDM	Global	API	Bassins	VIS	DAF
TOTAL	7.7	2.6	1.5	3.5	-
Truck	6.3	2.4	1.4	2.5	-
North	6.8	1.2	2.2	2.4	-
SW	10.2	2.7	0.9	6.6	-
Lidar40m	6.6	3.1	1.5	2.1	-
TOTAL with DAF	10.7	2.4	1.5	3.2	3.5

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

24

TOTAL

Annexe : 20/06/2017 PM



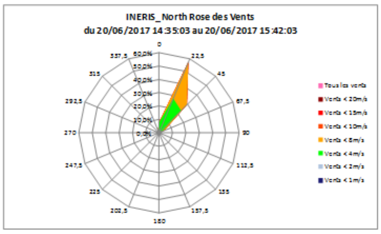
Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

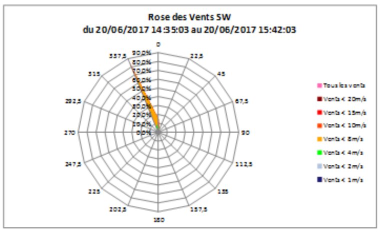
26

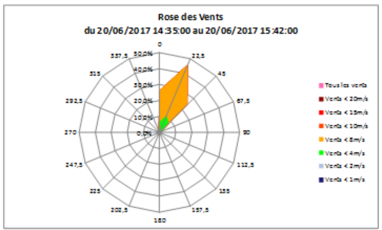
TOTAL

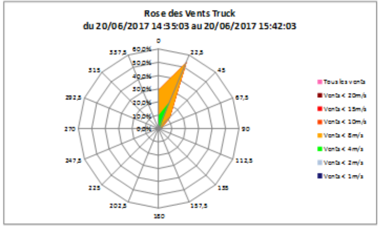
WIND ROSE JUNE 20TH PM

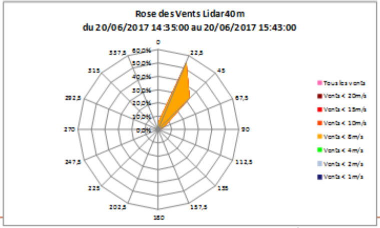
- Homogeneous wind (NE) except Station SW







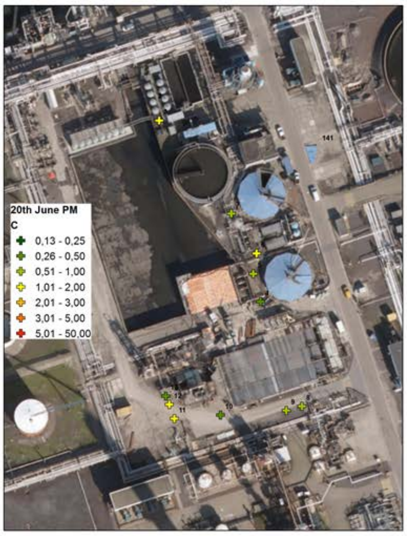




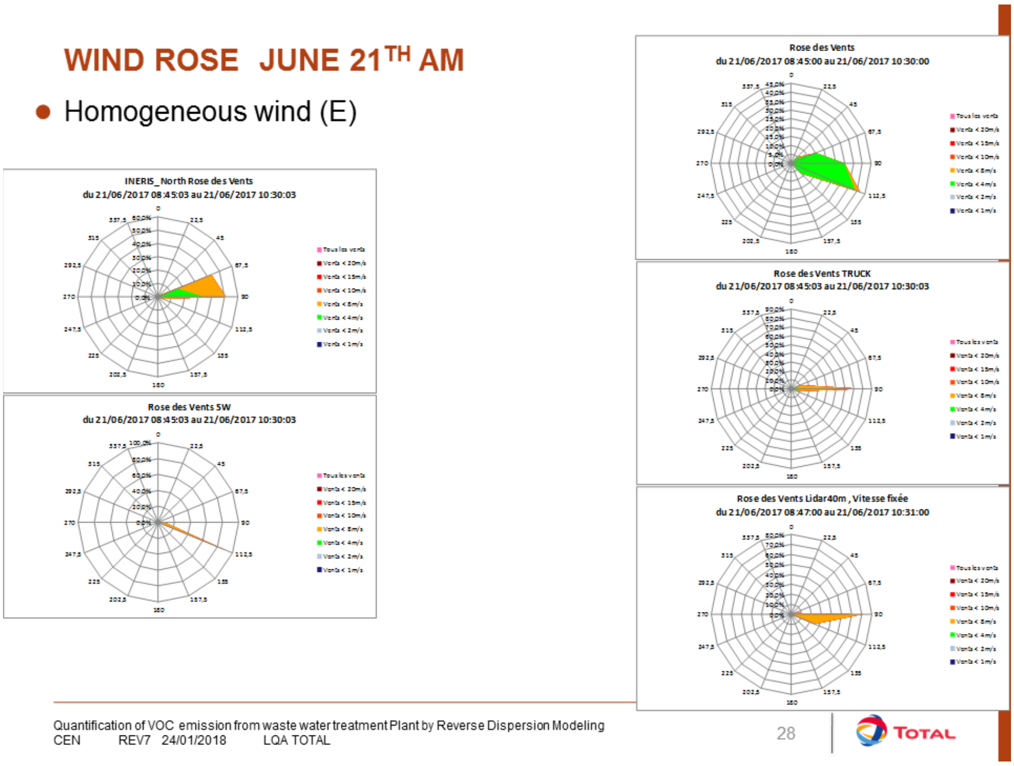
20TH JUNE PM : EMISSION

- According to criteria of « data consistency » :
  - TOTAL & Lidar 40m best fit
  - Very homogeneous data set (except SW)
  - Estimation of DAF emission

RDM	Global	API	Bassins	VIS	DAF
TOTAL	5.7	2.8	0.8	2.1	-
Truck	8.8	3.7	0.8	4.4	-
North	6.1	4.3	0.8	1.1	-
SW	7.1	3.3	1.7	2.1	-
Lidar40m	7.1	3.5	0.8	2.8	-
TOTAL avec Flotatteurs	7.4	2.8	0.7	1.8	2.1



Annexe : 21/06/2017 AM

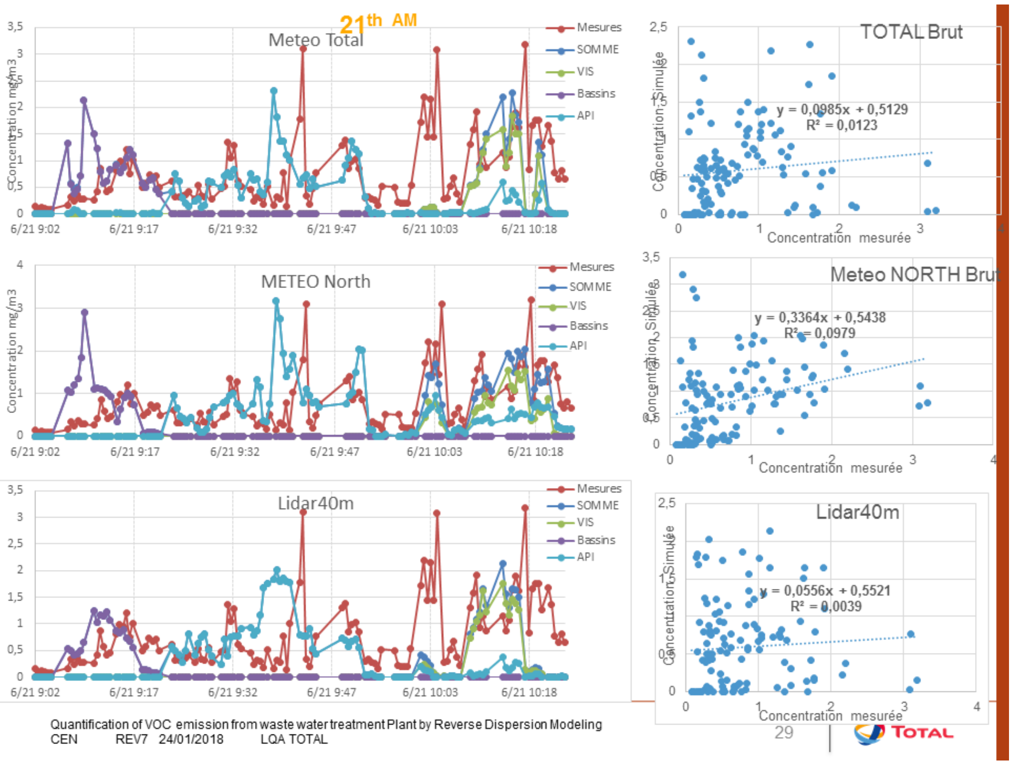


WIND ROSE JUNE 21TH AM

- Homogeneous wind (E)

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

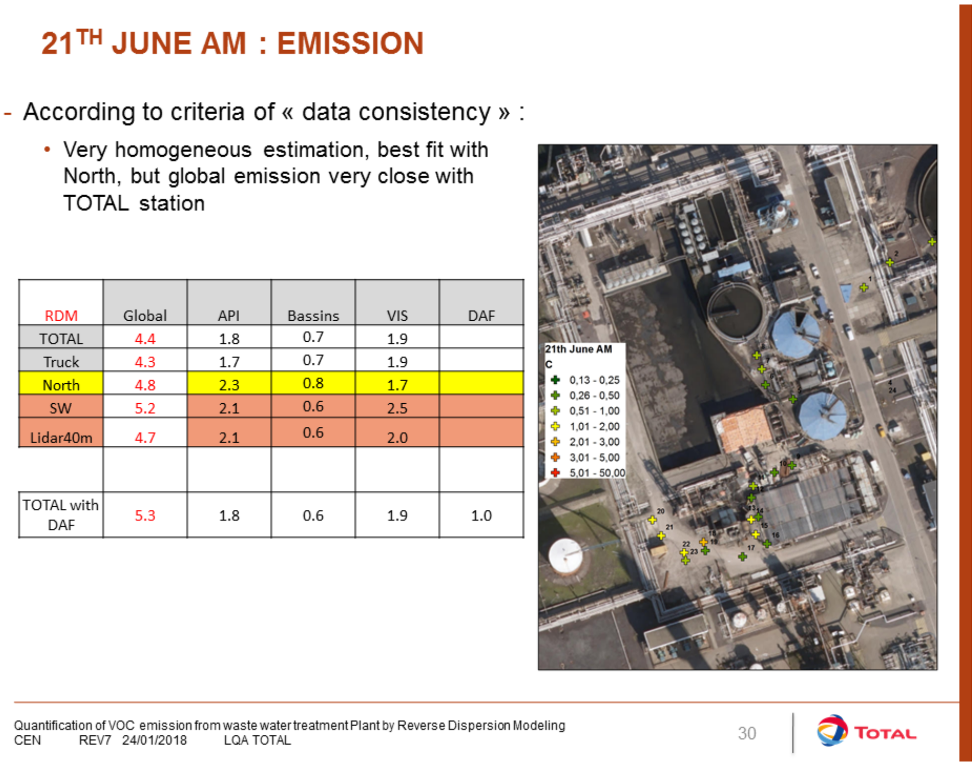
28 TOTAL



21th AM

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV7 24/01/2018 LQA TOTAL

29 TOTAL

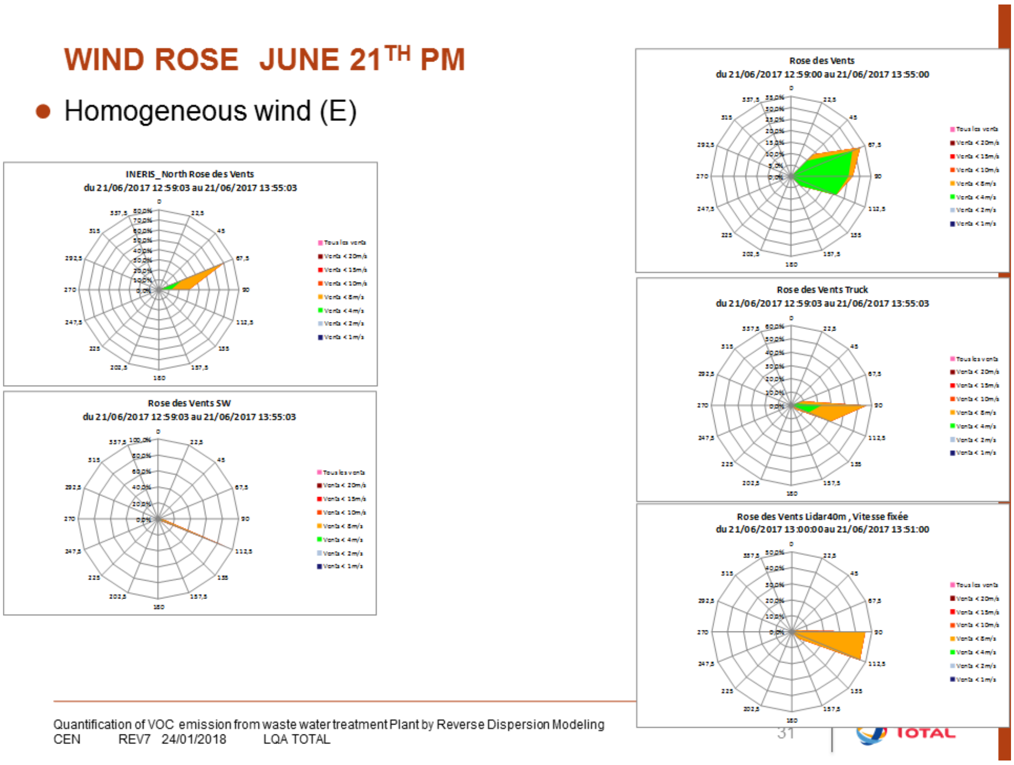


21TH JUNE AM : EMISSION

- According to criteria of « data consistency » :
  - Very homogeneous estimation, best fit with North, but global emission very close with TOTAL station

RDM	Global	API	Bassins	VIS	DAF
TOTAL	4.4	1.8	0.7	1.9	
Truck	4.3	1.7	0.7	1.9	
North	4.8	2.3	0.8	1.7	
SW	5.2	2.1	0.6	2.5	
Lidar40m	4.7	2.1	0.6	2.0	
TOTAL with DAF	5.3	1.8	0.6	1.9	1.0

Annexe : 21/06/2017 PM



WIND ROSE JUNE 21TH PM

- Homogeneous wind (E)

INERIS_North Rose des Vents
du 21/06/2017 12:59:03 au 21/06/2017 13:55:03

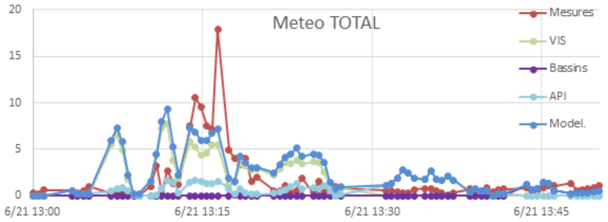
Rose des Vents SW
du 21/06/2017 12:59:03 au 21/06/2017 13:55:03

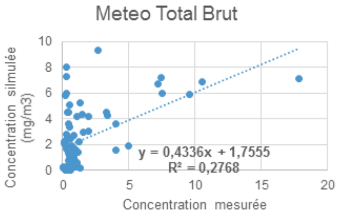
Rose des Vents
du 21/06/2017 12:59:00 au 21/06/2017 13:55:00

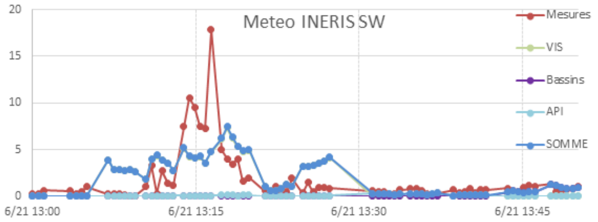
Rose des Vents Truck
du 21/06/2017 12:59:03 au 21/06/2017 13:55:03

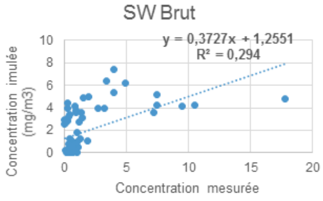
Rose des Vents Lidar40m , Vitesse fixée
du 21/06/2017 13:00:00 au 21/06/2017 13:51:00

21^{TH} PM





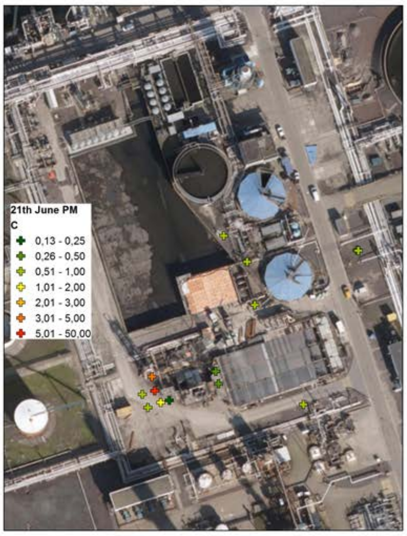




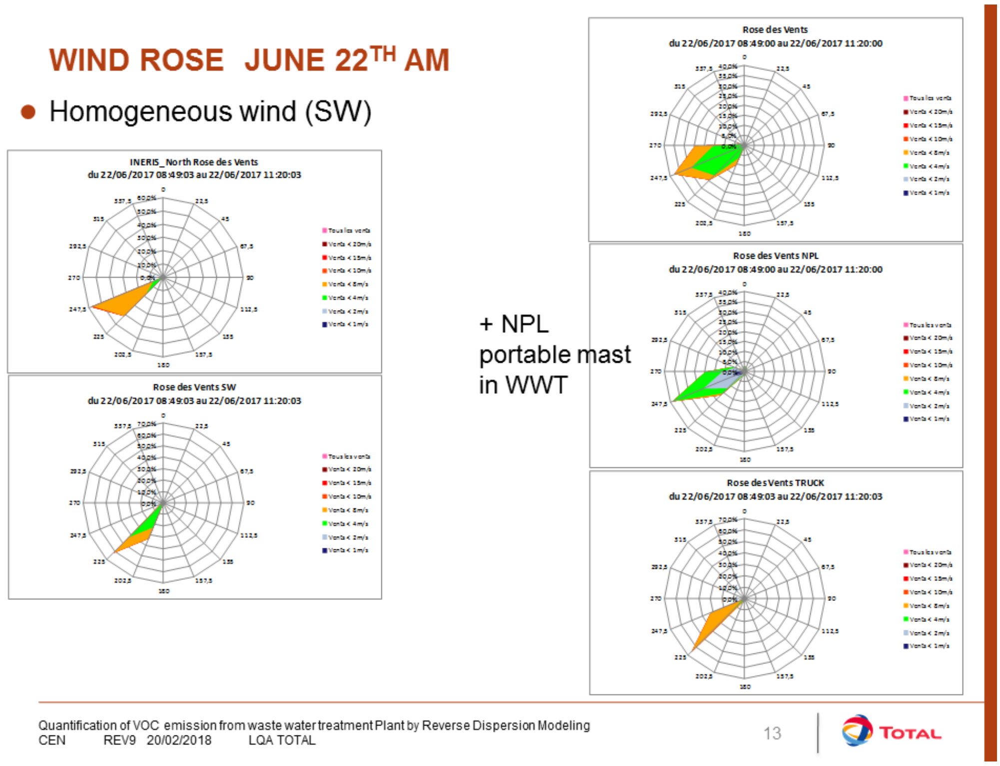
21^{TH} JUNE PM : EMISSION

- According to criteria of « data consistency » :
  - TOTAL best fit

RDM	Global	API	Bassins	VIS	DAF
TOTAL	8.5	4.6	0.7	3.2	
Truck	6.3	3.0	1.2	2.1	
North	3.9	1.4	0.4	2.0	
SW	6.3	0.8	1.6	3.9	
Lidar40m	5.4	1.6	0.9	2.9	
TOTAL with DAF	11.3	4.5	0.5	3.2	3.1



Annexe : 22/06/2017 AM



WIND ROSE JUNE 22TH AM

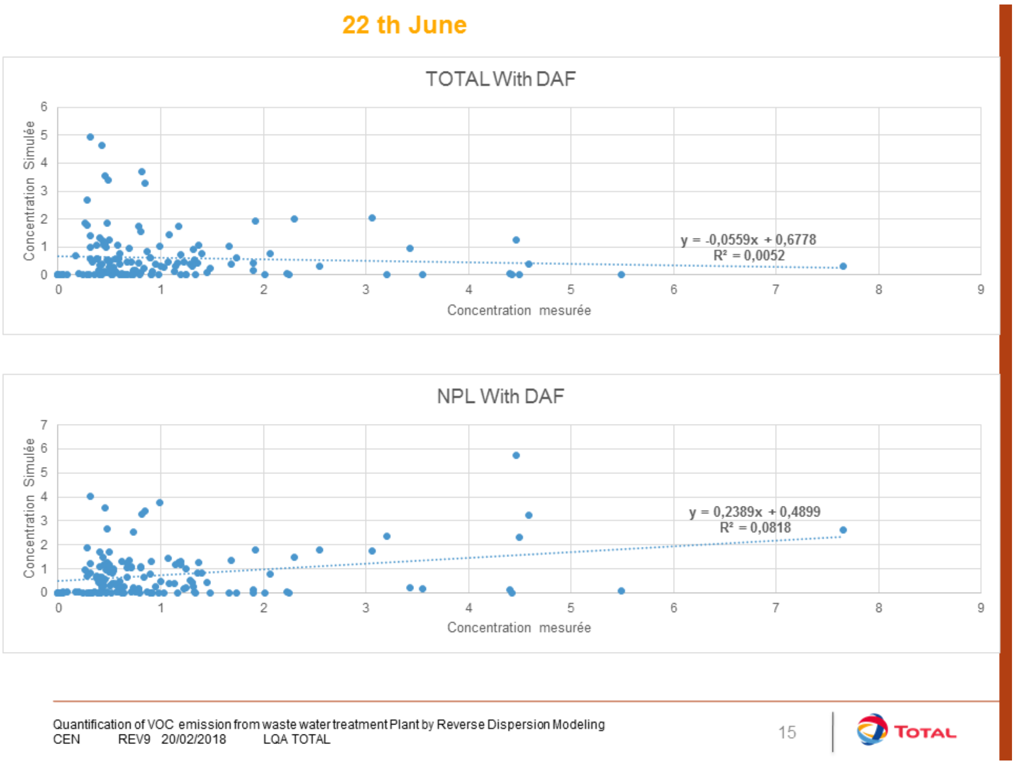
- Homogeneous wind (SW)

+ NPL portable mast in WWT

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV9 20/02/2018 LQA TOTAL

13

TOTAL

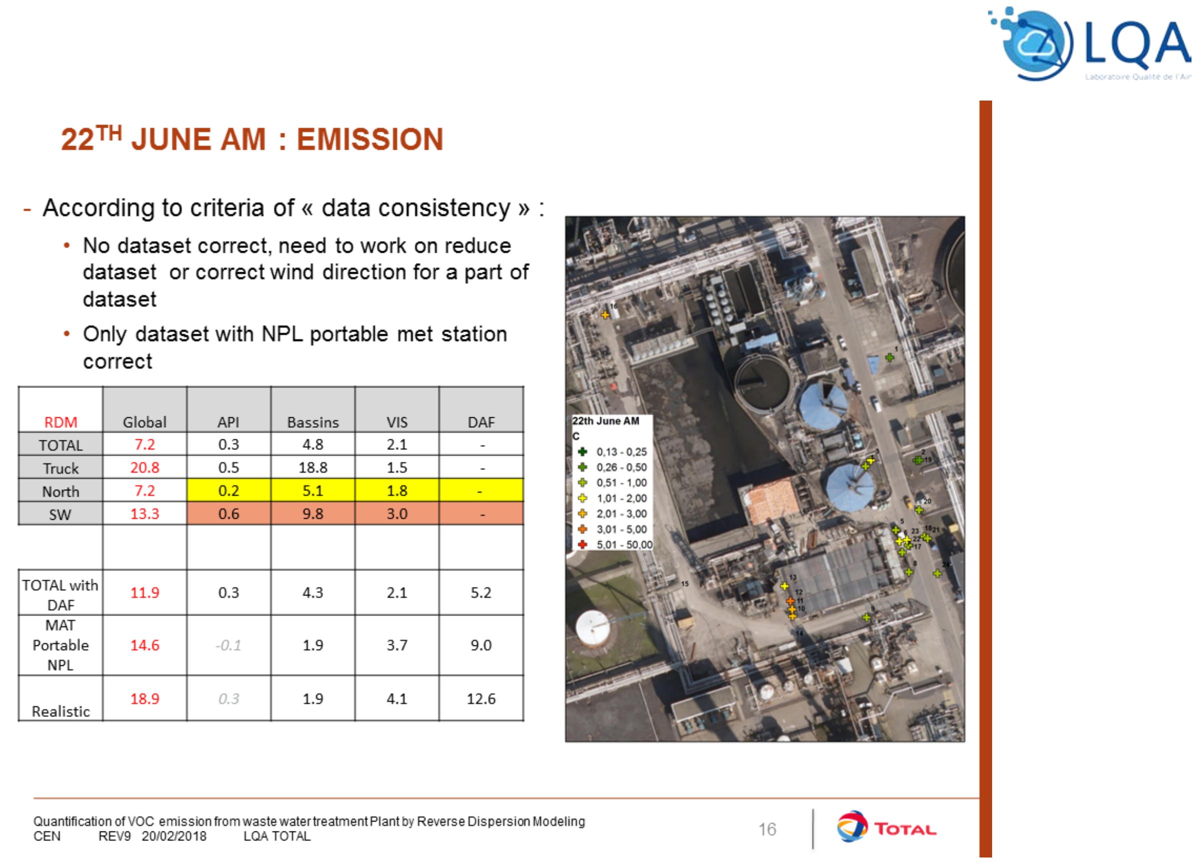


22 th June

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV9 20/02/2018 LQA TOTAL

15

TOTAL



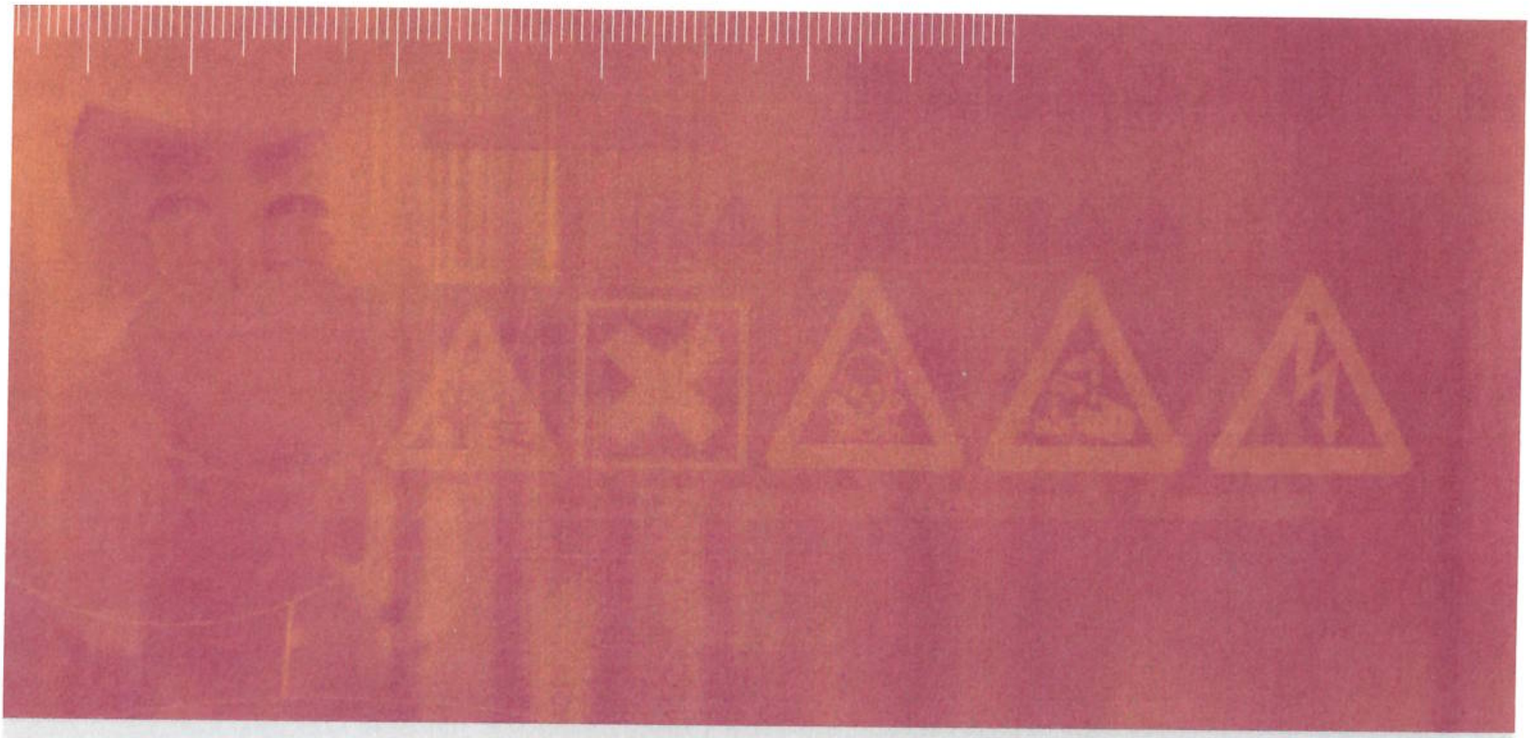
22TH JUNE AM : EMISSION

- According to criteria of « data consistency » :
  - No dataset correct, need to work on reduce dataset or correct wind direction for a part of dataset
  - Only dataset with NPL portable met station correct

RDM	Global	API	Bassins	VIS	DAF
TOTAL	7.2	0.3	4.8	2.1	-
Truck	20.8	0.5	18.8	1.5	-
North	7.2	0.2	5.1	1.8	-
SW	13.3	0.6	9.8	3.0	-
TOTAL with DAF	11.9	0.3	4.3	2.1	5.2
MAT Portable NPL	14.6	-0.1	1.9	3.7	9.0
Realistic	18.9	0.3	1.9	4.1	12.6

Quantification of VOC emission from waste water treatment Plant by Reverse Dispersion Modeling
CEN REV9 20/02/2018 LQA TOTAL

16



RAPPORT D'ÉTUDE
N° - DRC-18-157219-04456A

09/07/2018

CEN / TC 264 / WG 38

WP7 – Synthesis and statistical evaluation of the monitoring data available after the field trials

INERIS

controlling risks
for sustainable development

CEN / TC 264 / WG 38

WP7 – Synthesis and statistical evaluation of the monitoring data available after the field trials

VDI

PRÉAMBULE

Le présent rapport a été établi sur la base des informations fournies à l'INERIS, des données (scientifiques ou techniques) disponibles et objectives et de la réglementation en vigueur.

La responsabilité de l'INERIS ne pourra être engagée si les informations qui lui ont été communiquées sont incomplètes ou erronées.

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	Rédaction	**Vérification**	**Approbation**
NOM	François GAUTIER	Jean POULLEAU	Marc DURIF
Qualité	Ingénieur à l'Unité « Caractérisation du milieu air en PROXimité de source » Direction des Risques Chroniques	Ingénieur à l'Unité « Caractérisations des EMISsions atmosphériques et aqueuses » Direction des Risques Chroniques	Responsable de Pôle « Caractérisation de l'Environnement » Direction des Risques Chroniques
Visa	Fo		

TABLE DES MATIÈRES

1. SUMMARY

Through mandate M/514, 3rd December 2012, the European Commission requested the European standardisation bodies to develop a standard method to determine fugitive and diffuse emissions of volatile organic compounds (VOC) from certain industrial sectors. As part of this work two field campaigns were to be carried out, firstly to provide information relative to the standard and secondly to demonstrate the draft standard method in application.

This report describes the output of work package (WP) 7 of contract <insert contract reference> which aims to provide a synthesis and statistical evaluation of the monitoring data from the two field campaigns. It draws upon individual contractor reports prepared under the work-packages:

WP 3 - Specification of meteorological measurements (with wind speed and direction)
WP 4 - Optical gas imaging camera
WP 5 - Implementation of the remote monitoring methods at a site where a controlled emission source of VOCs can be located and operated in the field.
WP 6 - Implementation of the remote monitoring methods and estimation/calculation methods at the second industrial site.

This report does not provide a detailed assessment of all the necessary planning, health and safety, work permit and client discussions required by the draft standard. All work was carried out in due accordance with site rules, appropriate induction training was taken, and the campaigns were managed in full co-operation with site personnel.

The first field campaign involved the controlled release of propane gas in several different source arrangements within the process area of a disused refinery site. The releases were conducted "blind" and the remote sensing techniques used to identify the source location and estimate the release rates. Participating teams submitted their estimates before the release rates were published. The release rates used ranged from 0.8 to 18 kg/h. These values are representative of the smaller emission sources that the standard method should detect. Under the meteorological conditions of the campaign, and with the limitations on measurement access posed by a real site, the techniques DIAL, SOF and TC were able to detect this full range and provide emission estimates that were consistent with the releases. Similarly, the OGI operators were able to detect and make a qualitative assessment of each emission test. The technique RDM was not able to resolve emissions smaller than 5 kg/h.

The campaign demonstrated some inherent limitations in the planning of field measurements. The weather (wind direction and wind speed) was significantly different to the historic record for the location. The need for the standard to embrace flexibility in its requirements is thus underlined. Secondly the results of the field trial were obtained after correcting for external sources. A need to improve the protocols with respect to how such corrections are made and the contribution to uncertainty analysis was demonstrated.

The second field campaign was carried out on an operating refinery and timed to best fit the refinery operations. The campaign was purposed to allow the draft standard to be applied, with each participant following their specific protocol. The individual techniques were applied independently, and draft reports submitted to this assessment. Once all of the results were gathered they were shared between all the working groups for discussion and learning.

This exchange led to only one significant adjustment in conclusions when the composition of one single VOC source was established as cyclo-hexane rather than a straight chain alkane requiring a significant adjustment of DIAL results. Although the second campaign did not include any reference sources, i.e. sources of known emission rate, there were emissions from two tanks that enabled rate calculation methods to be compared.

All techniques were deployed to good effect, with broad correspondence of the emission estimates for the quantitative techniques. The detection of sources by OGI mapped well to those found by other techniques. Generally missing from the reports is a quantitative discussion of how background concentrations were accounted for in determining emission fluxes. Qualitatively, the presence of background was described as significant and problematic.

A more detailed analysis of data generated should follow this basic assessment and inform the refinement of the protocols. Specific regard needs to be paid to the analysis of uncertainty in the derivation of emission fluxes, especially with respect to the number and timing of measurements to be made.

2. TABLES AND FIGURES LIST

3. INTRODUCTION

In 2012 the European Commission requested the European standardisation bodies to develop and validate a European standard for the determination of fugitive and diffuse emissions of VOCs to the atmosphere from certain industrial sectors. The mandate M/514, made with reference to Directive 2010/75/EU on industrial emissions was accepted by CEN/BT, and a working group (WG 38) convened. WG 38 reports to CEN technical committee (TC) 264.

WG 38 prepared a technical proposal in response to the mandate. The mandate called for the development of standard backed by evidence from two field campaigns. The first to provide information to aid the development of the standard and establish normative criteria relating to sensitivity and uncertainty. The second to demonstrate the use of the standard and assess sufficiency and applicability. Not all elements of the mandate were able to be incorporated into the proposal. For example, no work on adaption of flux chambers for assessing emissions from water was proposed. The first field campaign was purposed to use controlled releases rather than practically occurring emissions, so as better to establish detection limits and measure the performance of emission flux estimation calculations.

The technical proposal was accepted, and participants sought using a tender process. Contracts were awarded for a total of 8 work packages (WP) which are independently reported.

This report describes WP 7 - Synthesis and statistical evaluation of the monitoring data available after the field trials, which draws upon individual contractor reports prepared under the work-packages:

WP 3 - Specification of meteorological measurements (with wind speed and direction)
WP 4 - Optical gas imaging camera
WP 5 - Implementation of the remote monitoring methods at a site where a controlled emission source of VOCs can be located and operated in the field.
WP-6 - Implementation of the remote monitoring methods and estimation/calculation methods at the second industrial site.

This report aims to collate and summarise results obtained during the two field campaigns, to assess the advantages and limitations of each technique and to assess the how the techniques perform against the requirements of their individual protocols. Information was taken from draft reports. There may be small differences in detail between this account and the final reports of the individual work packages.

4. FIRST CAMPAIGN: CONTROLLED RELEASE TEST

4.1 DESCRIPTION

The objective of the first field campaign was to provide a sequence of controlled releases against which the VOC detection/assessment techniques could be applied. With the release rates unknown to the users of the techniques, the capacity of each technique to detect / estimate the released flux could be independently assessed.

To simulate industrial conditions the tests were carried out on a refinery process unit that is shutdown. The unit was in a remote part of a site still in use for chemicals manufacture. Propane was used as the test gas. This is typical of the VOC sought by the techniques. A controlled release facility developed by NPL was located within the process unit. The unit has been designed to simulate different release types ranging from diffuse to point sources. A total of five emission sources were used in several combinations:

Source A: First floor, north west corner

Source B: Second floor, middle of unit

Source C: First floor, south west corner

Source D: First floor, middle of unit

Source E: Diffuse source, middle of unit, between floors 1 and 2.

Propane could be released from these points independently or in combination. A map of the sources positions is presented in Figure 1.

Although the test could not be completely "blind" to the participants because the use of the unit was known, the combinations of source points and quantity of propane released was kept confidential until all participants had submitted their assessments.

4.2 CAMPAIGN CONDITIONS

As called for by the draft standard the campaign was planned and conducted in due consultation with the site operator and with full regard to safety processes and permissions. This aspect of the protocol compliance will not be described further.

To prepare for the measurement campaigns a statistical assessment of the climatology for the measurement period was prepared to determine the likelihood of wind-direction, wind speed, precipitation patterns etc. Wind statistics were provided by the national meteorological institute and confirmed locally by the industrial site. The expectation was for a consistent strong north to north-west wind with the propane releases dispersing in a south to south east direction into a mostly clear and open field area with good access for measurement.

During the campaign these conditions were only partially realised. The wind was light and variable between the west-southwest and northwest. This difference in wind direction, and less steady wind behaviour than expected, tested the flexibility of the protocols. The monitoring strategies had to become adaptive, especially for SOF where access is constrained by the presence of roads. Further, the wind-directions during the trial introduced interference from upwind sources that was not anticipated, and which was significant. Nevertheless, it was possible to carry out measurements using the intended number of releases and range of release rates. That the meteorological conditions were less favourable than expected is an aspect of field work that cannot be avoided.

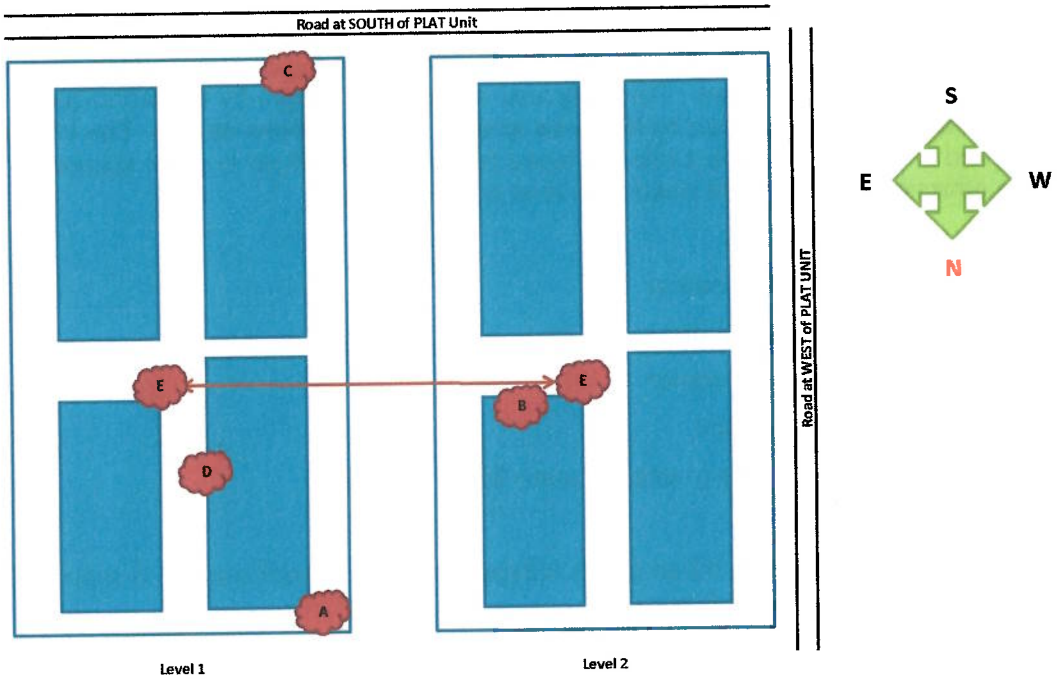


Figure 1 : experimental set up for controlled release of gas inside the industrial unit

4.3 CONTROLLED RELEASES

Twenty controlled releases of propane (91% purity) were made, each release lasting up to 90 minutes in duration. The maximum release rate achieved was 18.9 kg/h against a target of 25 kg/h. This was due to a technical problem. The minimum release rate was 0.78 kg/h. This range is representative of emission sources that would need to be found during a leak detection and repair campaign.

The matrix of release position and release rate is given in Table 1. Tests 5, 6, 7, 10, 11, 17, 19 and 20 involved simultaneous releases from more than one-point position. Tests 7,10, 19, 20 used all the points and a flux range of 6.6 – 18.8 kg/h. Tests 13, 14, 15 and 16 simulated a diffuse source with strength ranging from 0.78 – 16.6 kg/h. A total release rate of ~10 kg/h was realised on eight occasions across 5 days of testing. This was incorporated in the plan to assess the effect of wind condition variation on detection. In the event the wind speed variation was not large.

Table 1 : propane fluxes (kg/h) – controlled releases

	Test 1	**Test 2**	**Test 3**	**Test 4**	**Test 5**	**Test 6**	**Test 7**	**Test 8**	**Test 9**	**Test 10**
A			8.87		7.39	1.80	1.65			4.63
B		14.85					1.65			4.63
C						7.21	1.65	8.87		4.63
D	5.07				1.85		1.65			4.63
E				9.75					11.62	
Total:	5.07	14.85	8.87	9.75	9.24	9.01	6.59	8.87	11.62	18.51
	Test 11	**Test 12**	**Test 13**	**Test 14**	**Test 15**	**Test 16**	**Test 17**	**Test 18**	**Test 19**	**Test 20**
A	1.93						7.39	18.86	1.65	3.14
B	7.71	9.75							1.65	3.14
C									1.65	3.14
D							1.85		1.65	3.14
E			14.74	16.61	4.77	0.78				
Total:	9.64	9.75	14.74	16.61	4.77	0.78	9.24	18.86	6.59	12.55

4.4 DIAL RESULTS

DIAL uses a scanning technique to build up a time-averaged concentration field in a plane that can be angled approximately normal to the direction of wind-flow. The measurements are mapped onto a Cartesian grid with spatial resolution of ~ 3 m and multiplied by a wind profile that is horizontally uniform and increasing with height. The dimensions of the plume cross-section are determined so the plume centroid height and area are known. The mass flux passing normal to the sampling plane in the wind direction is averaged over a measurement time which is typically of order 5 minutes. Measurements are repeated according to the protocol so that an average flux and its variation can be calculated. The assumptions are that the wind vector and concentration field are uncorrelated so that the flux is given by the product of the average values of wind speed and correlation.

The flux obtained must be corrected for background concentrations. This is normally done by effecting a measurement upwind of the target source and evaluating the average concentration across the reference scan. A necessary assumption is that background concentrations are unchanging between scans.

If there is spatial structure in the reference scan the correction becomes an adjustment of flux rather than concentration. The principle difference being necessary assumptions of overlap of the mapped area.

The conditions of the controlled release experiments of low wind and variable wind direction increase the uncertainty of flux methods because dispersion behaviour becomes more complex and concentration fluctuations increase. This is true of all methods. Two controlled releases occurred when wind-speeds were less than 1 m/s at the reference anemometer position.

During the field campaign, interference from background sources was described as a major concern. The background fluxes determined by DIAL are shown in Figure 2. During September 27th fluxes of over 20 kg/h as well as negligible fluxes were seen. On the 28th they were between 10-15 kg/h and on the 29th above 30 kg/h. Considering that the controlled releases were at most 19 kg/h this interference from unexpected sources was a big challenge affecting all deployed techniques.

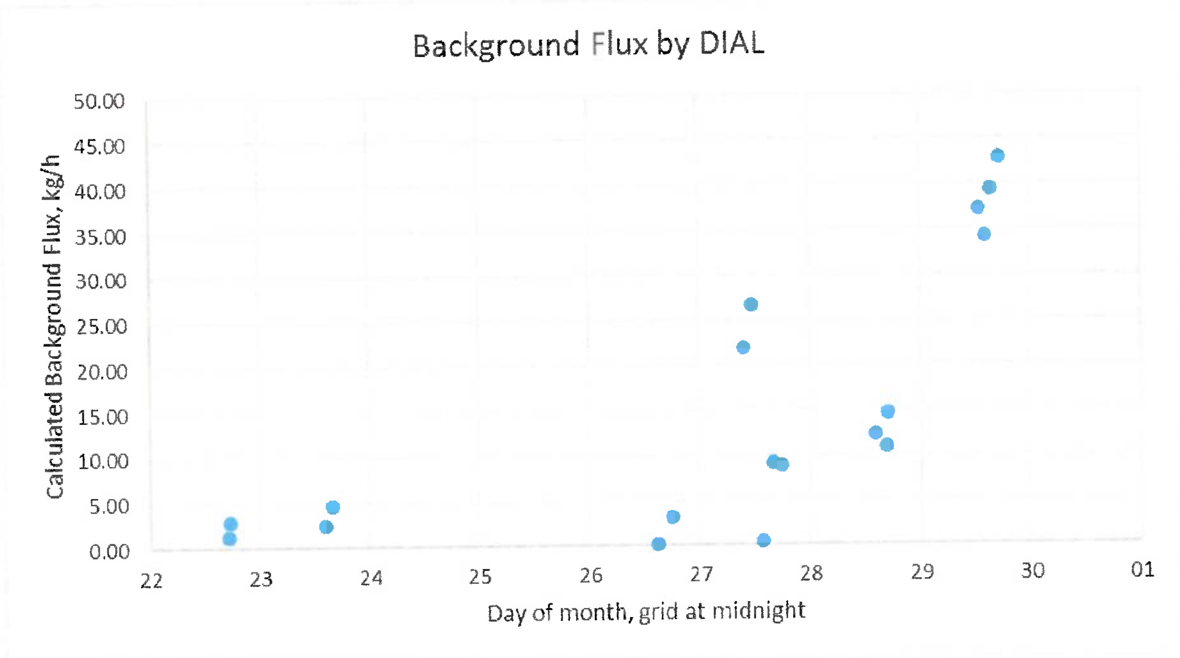


Figure 2 Variation in Background VOC flux during the trial

These high background fluxes were not associated with a fixed wind direction as shown in Figure 3 where both highest and lowest background fluxes were associated with similar wind directions. They therefore reflect time-varying emissions.

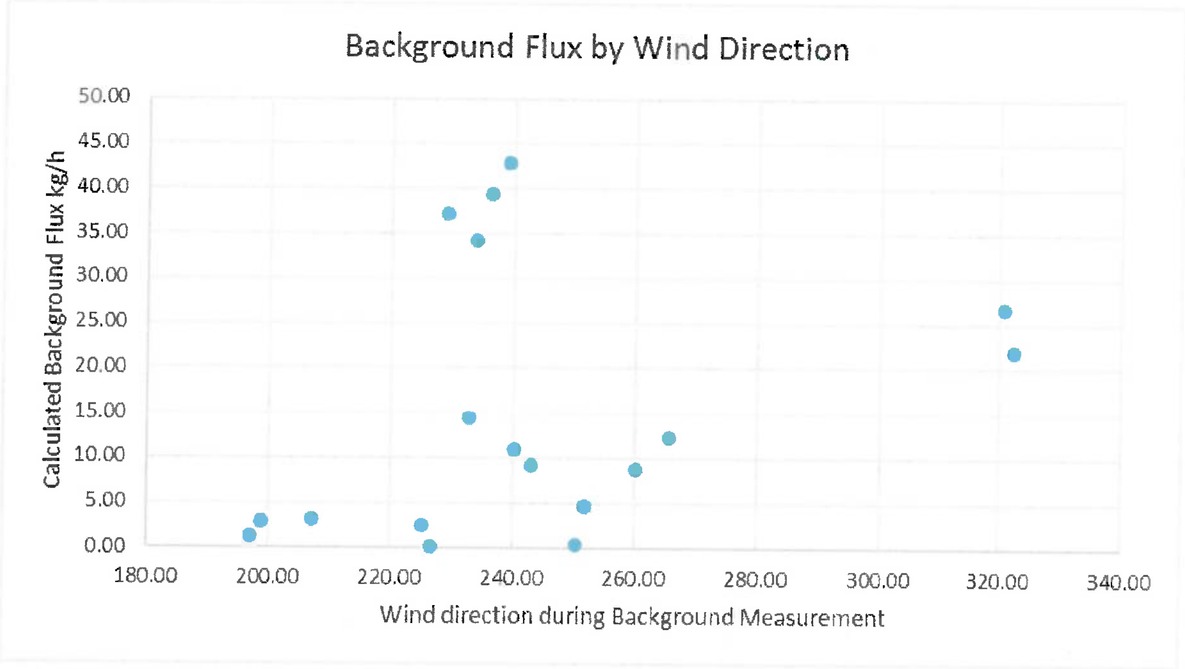


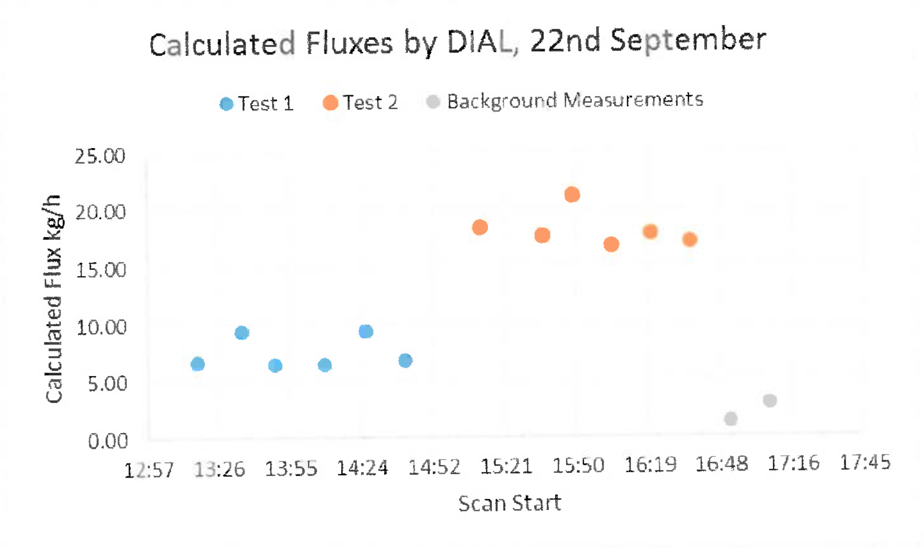
Figure 3. Change in background flux with wind-direction

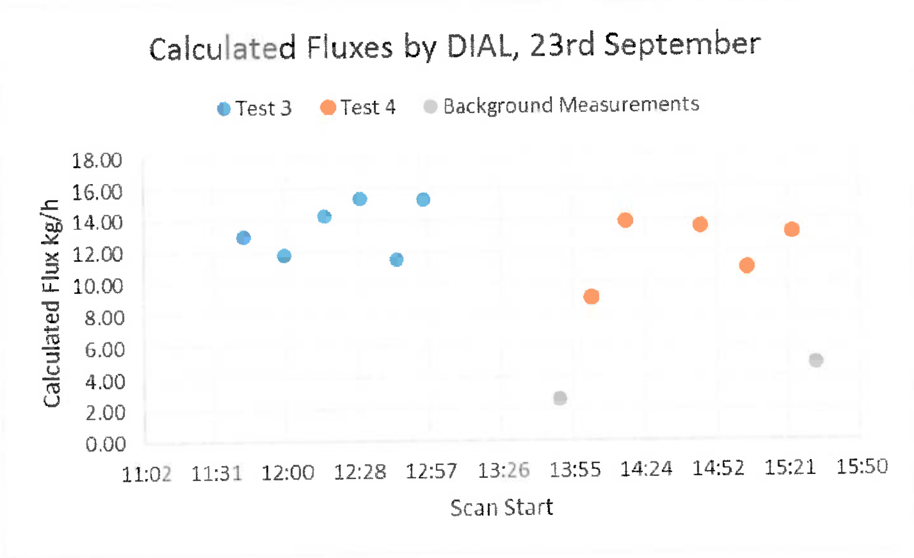
A consequence of the variable background is that the determination of flux from the source depends on the treatment of the background during the period of each controlled release. The derived upwind (background) and downwind (release + background) fluxes for each individual trial are shown in time sequence below.

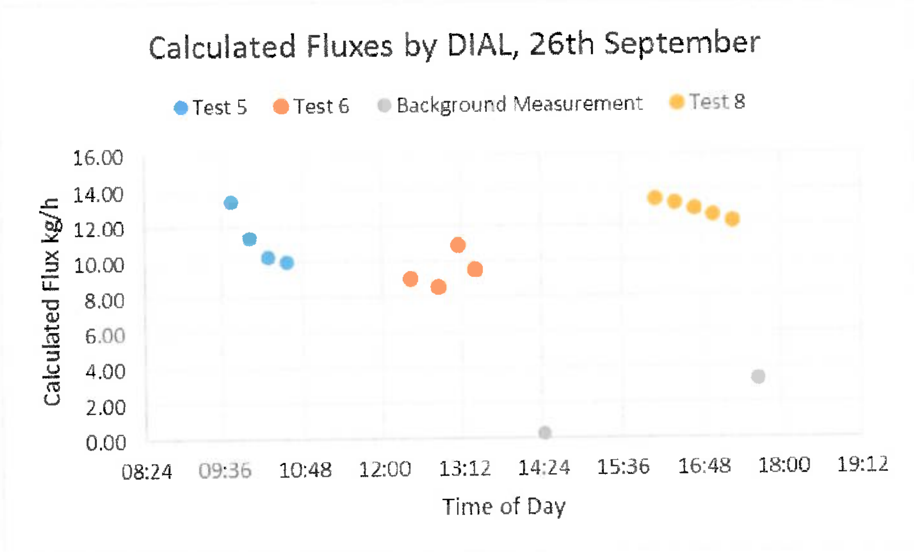
It is clear that, overall, there is reasonable reproducibility between DIAL scans for the duration of the releases. In the examples of, say, Test 1 and Test 2 averaging over the sequence will give a sensible indication of the average flux detected. This data supports the assumption in the DIAL protocol that variability has a random behaviour and that averaging over several scans will reduce uncertainty.

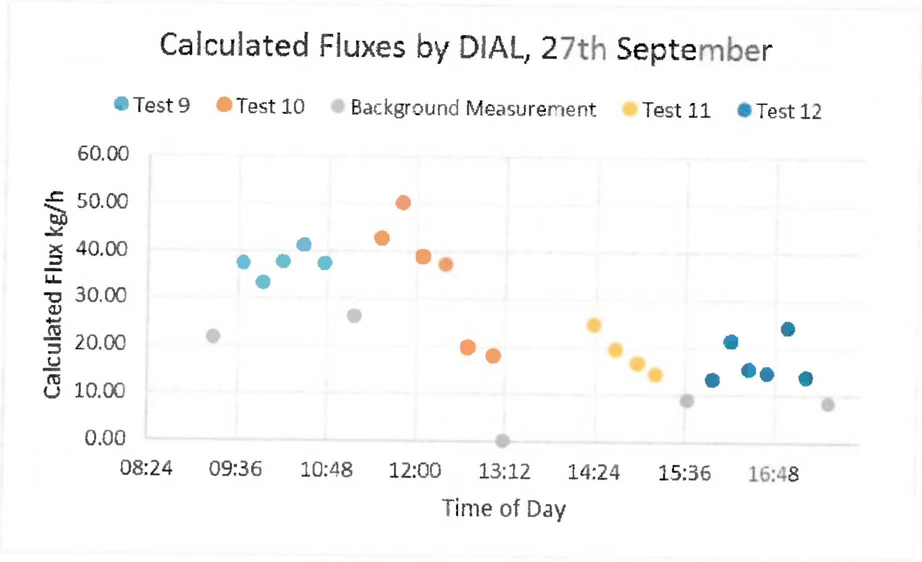
However, for Test 10 it is clear that the background concentration has changed significantly over the course of the release. The determined downwind fluxes reduce by ~30 kg/h over the scan sequence. This is consistent with the decreased in background measurements before and after the release. Estimates of the source flux contribution depend on how this change in background is assumed to take place:

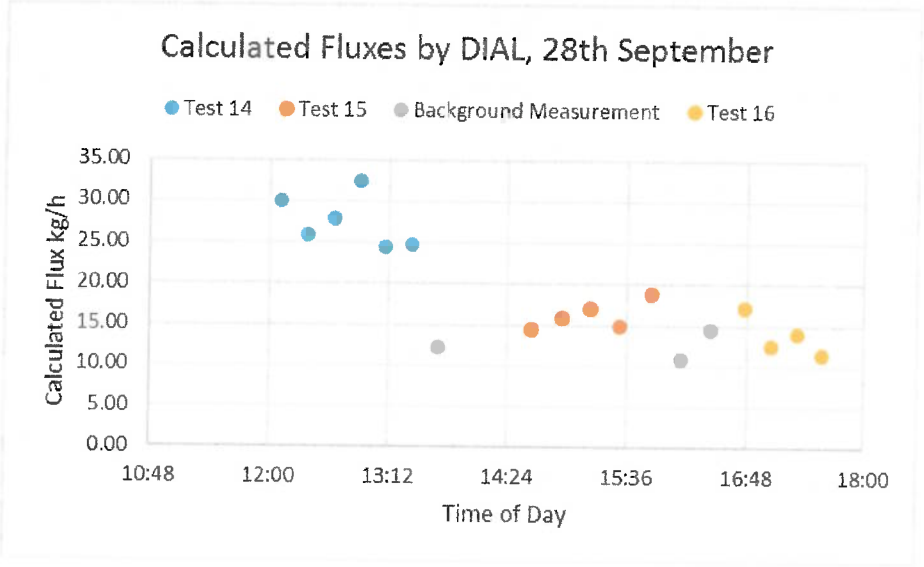
Calculated Source Flux for Test 10	Assumption
21.3 kg/h	Background changes linearly between measurements made before and after Test 10.
16.96 kg/h	Step change in background, using the background before test 10 value if the calculated flux is greater than background and the background value after test 10 otherwise.
18.47 kg/hr	Step change as above but using the average of the two background values obtained on the day before the start of Test 10. This was the value reported by the DIAL team.

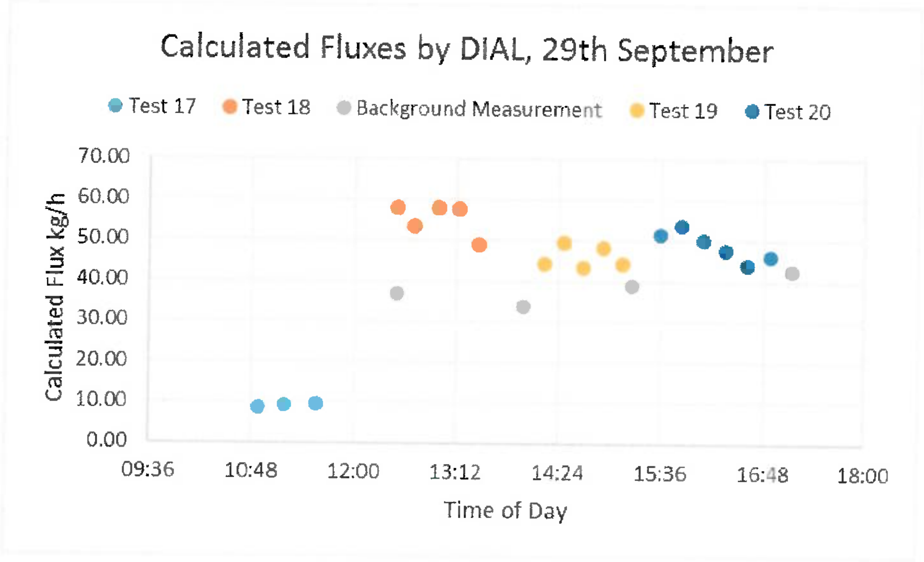

Calculated Fluxes by DIAL, 22nd September


Calculated Fluxes by DIAL, 23rd September


Calculated Fluxes by DIAL, 26th September


Calculated Fluxes by DIAL, 27th September
● Test 9
● Test 10
● Background Measurement
● Test 11
● Test 12
Calculated Flux kg/h
60.00
50.00
40.00
30.00
20.00
10.00
0.00
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
Time of Day


Calculated Fluxes by DIAL, 28th September
● Test 14
● Test 15
● Background Measurement
● Test 16
Calculated Flux kg/h
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
10:48
12:00
13:12
14:24
15:36
16:48
18:00
Time of Day


Calculated Fluxes by DIAL, 29th September
● Test 17
● Test 18
● Background Measurement
● Test 19
● Test 20
Calculated Flux kg/h
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
09:36
10:48
12:00
13:12
14:24
15:36
16:48
18:00
Time of Day

4.4.1 COMPARISON WITH RELEASE DATA

DIAL was used to detect and quantify 18 out of 20 controlled releases of propane following protocol criteria.

According to the DIAL protocol an average of at least four DIAL scans taken in succession should achieve an overall uncertainty of 20-30% for emission flux. This assumes that the correction for background is straightforward and the sources of uncertainty in each individual DIAL quantification a random behaviour and that the measured concentrations are above the detection limit. The background itself was determined using relatively few scans intermediate with controlled releases.

Despite the significant background concentration for later test runs the agreement between reported DIAL flux assessment and the control release emission rates was very good over the full range. As shown in Figure 4 there was no net bias and, when averaged over 4 or more consecutive DIAL scans the deviation was significantly less than the 30% set out in the protocol. This is shown in Table 2.

It is clear from the data that for some of the tests the way the background was compensated for could influence the results and generally the background measurement set could have been more complete. The example of test 10 has been described where the reported value could lie between 16.96 and 21.3 kg/h depending on the choice of background correction. For the lowest released rate of 0.8 kg/h in test 16 the background flux was some 16 times greater and so the recovery of an estimate of 1.2 kg/h for the emission flux should be regarded as fortuitous. Nevertheless, the presence of high background fluxes did not seem to affect the estimation of release flux.

An analysis that could be developed is the sensitivity of the results to assumptions about the wind speed and wind-direction made in converting the measurement made to a mass-flux. The flux estimate is linear in wind-speed and becomes increasingly sensitive to wind-direction as the angle of intersection with the measurement plane becomes oblique.

The ability of the DIAL to detect and quantify the emitted flux did not depend on the origin of the release as indicated in Figure 5. There was no noticeable effect of release location on the degree of correlation between DIAL assessed flux and release rate. It was possible from the observed concentration distributions and wind directions to infer where on the unit the release was coming from and this is discussed in the next section.

Table 2 : controlled release tests - DIAL results

Test	Source configuration	average emission rate	Number of Scans	Wind speed	Average Emission Rate	Standard Deviation	95% Confidence limit on mean	Difference between Dial and Release	Relative difference (DIAL - CR)/CR
		kg/hr		m/s	kg/h	kg/h	kg/h	kg/h	%
1	D	5.1	6	3.0	5.4	1.8	1.9	0.3	7%
2	B	14.9	6	3.1	16.1	2.0	2.1	1.2	8%
3	A	8.9	6	2.3	9.8	2.3	2.4	1.0	11%
4	E	9.8	5	3.7	8.4	2.6	3.2	-1.4	-14%
5	A+D	9.2	4	1.9	11.4	1.6	2.5	2.2	24%
6	A+C	9.0	4	2.4	9.2	1.4	2.2	0.2	2%
7	A+B+C+D	6.6							
8	C	8.9	5	2.5	9.6	1.1	1.4	0.7	8%
9	E	11.6	5	2.1	13.3	4.4	5.5	1.6	14%
10	A+B+C+D	18.5	6	1.7	18.5	5.6	5.9	0.0	0%
11	A+B	9.6	4	2.7	10.2	4.5	7.2	0.6	6%
12	B	9.8	6	2.8	8.5	4.5	4.7	-1.3	-13%
13	E	14.7							
14	E	16.6	6	1.9	15.0	3.7	3.9	-1.6	-10%
15	E	4.8	5	2.7	3.7	2.5	3.1	-1.1	-23%
16	E	0.8	4	2.9	1.2	3.0	4.8	0.4	56%
17	A+D	9.2	3	1.1	9.7	0.5	1.2	0.4	5%
18	A	18.9	5	2.1	14.9	8.3	10.3	-4.0	-21%
19	A+B+C+D	6.6	5	3.4	8.5	4.7	5.8	1.9	29%
20	A+B+C+D	12.6	4	2.8	11.5	5.3	8.4	-1.1	-8%

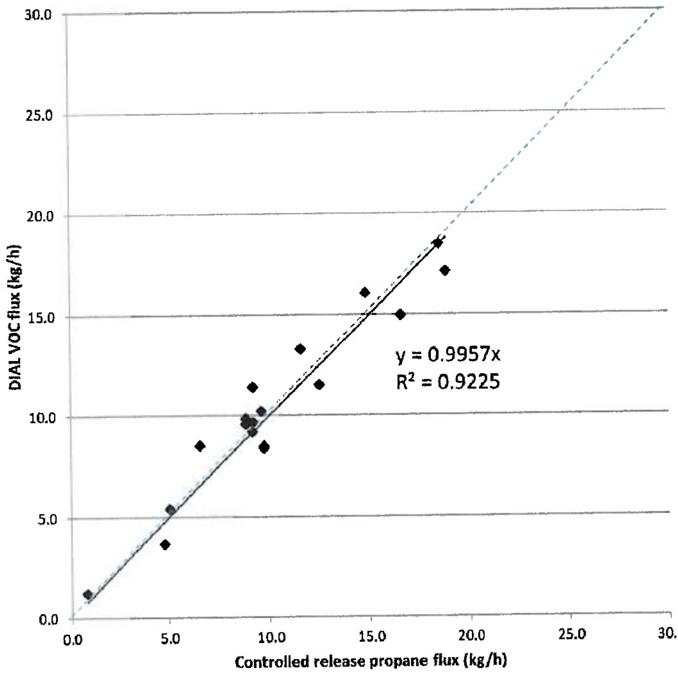


Figure 4 : correlation between DIAL and controlled release fluxes

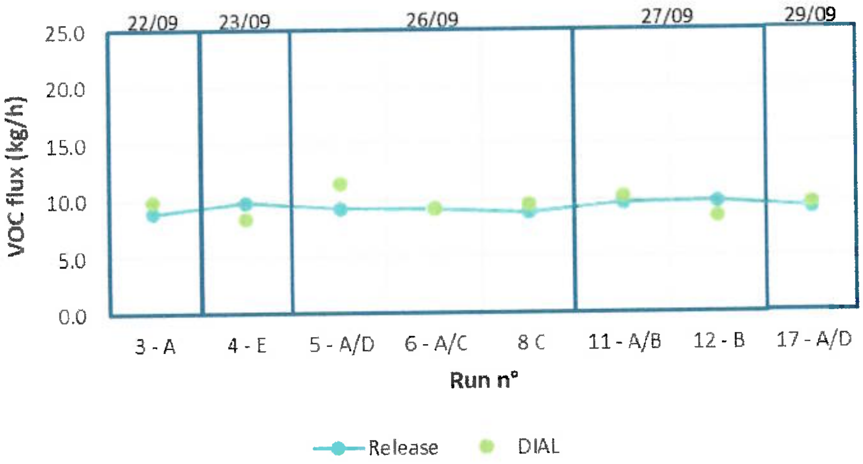


Figure 5 : results obtained with repeating 10kg/h flux for different source configuration and wind conditions – DIAL

4.4.3 ABILITY TO LOCATE SOURCES

The cross-wind concentration distributions observed in the trials allowed the following observations to be made about the likely position of the release points on the process unit.

Table 3 : field observations regarding sources locations – DIAL (1/2)

Test n°	Sources configuration	DIAL observations	Real configuration
1	D	Plume probably from the South end of the unit rather than the north end.	plume in the South end of the unit, but source located in the middle of the unit
2	B	Similar to Test 1.	plume in the South end of the unit, but source located in the middle of the unit
3	A	Plume probably from the South end of the unit rather than the north end.	plume in the South end of the unit, but source located in the North of the unit
4	E	Compared to Test 3 the plume seems to more northerly. North-Middle node/s? Possibility to miss part of the plume?	plume in the South end of the unit, but source located in the middle of the unit (diffusion tube)
5	D	Overestimated - it shouldn't be used. Because of the wind direction is also impossible to say from which node the release was from.	
6	A+C	Relatively wide plume, but centred on the South end of the unit. South-Middle nodes.	Two sources located at both North and South side of the unit
7	A+B+C+D		
8	C	Quite wide plume because of wind direction, probably south or middle node or combination of the two.	One source on South side of the unit
9	E	Because of the wind direction is also impossible to say from which node the release was from. Complex plume, high background emission rate and therefore high uncertainty in the emission rate.	
10	A+B+C+D	Same as Test 9	

Table 4 : field observations regarding sources locations – DIAL (2/2)

Test n°	Sources configuration	DIAL observations	Real configuration
11	A+B	Elongated plume shape indicating emission sources from both south and north end of the unit. Probably more release nodes used.	Two sources, on south side and middle
12	B	Smaller plume compared to Test 11, emission probably from middle-north of unit. Possibly just one node.	One source, in the middle of the unit
13	E	-	-
14	E	Difficult to tell, plume centred at about 120m from the DIAL (i.e. about middle of the unit) but relatively wide. More likely to be from one node but it could be from any mode apart from the north node	One source but diffused in the middle of the unit
15	E	Same as test 15.	One source but diffused in the middle of the unit
16	E	Same as tests 15 and 16.	One source but diffused in the middle of the unit
17	A+D	Because of the south wind direction it is difficult to say from which node the release was from, although the plume is centred at about 100m indicating more north of unit.	Two sources, more on the North side of the unit
18	A	Plume centred at about 100m from DIAL indicating it should come from north node. But the plume is also quite wide so it could also come from middle nodes or have some contribution from them. High background emission rate and therefore high uncertainty in the emission rate.	One source on the North side of the unit
19	A+B+C+D	Complex broad plume in the 100-130m region from the DIAL indicating more nodes were probably used, at least both south and north nodes. High background emission rate and therefore high uncertainty in the emission rate.	All sources on
20	A+B+C+D	Compared to Test 19 the plume seems slightly smaller and centred at around 120 m. Very difficult to tell if only south and/or middle nodes were releasing or also the north node.	All sources on

4.5 OGI RESULTS

A FLIR GF320 IR camera was used by a trained operator to perform the optical gas imaging (OGI) survey. Two operators were used during the test period. The camera was used in high sensitivity mode (HSM) from distances of up to 20m from the source. The cameraman was able to enter the unit and survey up to the release points to determine which were in action and which were not. This would be typical survey behaviour as part of a LDAR program. Each video measurement was recorded.

The commentary of findings is summarised in the table below. Importantly, all of the controlled releases were detected, including the smallest release although a close approach had to be made. The low wind speed conditions during the trials favour the detection of smaller releases.

Although the purpose of the OGI camera is to detect the emission source, the experienced operator can make some judgement as to the nature and strength of release according to the behaviour of the viewed plume. The judgement is not absolute and different operators may have different views. The apparent size of release can be affected by several parameters including the favourability of conditions for OGI (viewing background, temperature) and the presence of background concentrations. In this trial the background concentrations which affect the flux calculations do not impact the OGI camera applied directly to the release where concentrations are high.

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Table 5 : field observations - OGI

	Control unit configuration		OGI detection and observations			
Test #	Nod #	Controlled release Flux (kg/h)	Active Nod #	Detection distance (m)	Detection mode	Observations and comments
1	A		A		HSM	
	B		B			
	C		C			
	D	5.07	**D**	7		
	E		E			
2	A		A		HSM	
	B	14.85	**B**	5		
	C		C			
	D		D			
	E		E			
3	A	8.87	**A**	5	HSM	
	B		B			
	C		C			
	D		D			
	E		E			
4	A		A		HSM	
	B		B			
	C		C			
	D		D			
	E	9.75	**E**	5		
5	A	7.39	**A**	5	HSM	Emission rate A seems > emission rate D
	B		B			
	C		C			
	D	1.85	**D**	2		
	E		E			
6	A	1.80	**A**	5	HSM	Emission rate C seems > emission rate A
	B		B			
	C	7.21	**C**	5		
	D		D			
	E		E			
7	A	1.65	**A**	5	HSM	Emission rate C or B seem > emission rate A or D
	B	1.65	**B**	2		
	C	1.65	**C**	5		
	D	1.65	**D**	5		
	E		E			
8	A		A		HSM	very huge emission
	B		B			
	C	8.87	**C**	5+		
	D		D			
	E		E			
9	A		A		HSM	
	B		B			
	C		C			
	D		D			
	E	11.62	**E**	5+		
10	A	4.63	**A**	5	HSM	Emission rate C or B seem > emission rate A or D
	B	4.63	**B**	2		
	C	4.63	**C**	5		
	D	4.63	**D**	5		
	E		E			

	Control unit configuration		OGI detection and observations			
Test #	Nod #	Controlled release Flux (kg/h)	Active Nod #	Detection distance (m)	Detection mode	Observations and comments
11	A	1.93	**A**	5	HSM	Emission rate B >> Emission rate A
	B	7.71	**B**	10 +		
	C		C			
	D		D			
	E		E			
12	A		A		HSM	Emission rate B seems < emission rate B test 11
	B	9.75	**B**	10		
	C		C			
	D		D			
	E		E			
13	A		A		Manuel / HSM	Visible in manual mode - huge emission rate
	B		B			
	C		C			
	D		D			
	E	14.74	**E**	20		
14	A		A		HSM	Emission rate > emission rate test 13
	B		B			
	C		C			
	D		D			
	E	16.61	**E**	20		
15	A		A		HSM	Emission rate seems < emisison rate test 14
	B		B			
	C		C			
	D		D			
	E	4.77	**E**	20		
16	A		A		HSM	Low emission rate, not detectable at long distance
	B		B			
	C		C			
	D		D			
	E	0.78	**E**	4		
17	A	7.39	**A**	3	HSM	Emission rate A > emission rate D
	B		B			
	C		C			
	D	1.85	**D**	4		
	E		E			
18	A	18.86	**A**	6	HSM	Emission rate > Emission rate A test 17
	B		B			
	C		C			
	D		D			
	E		E			
19	A	1.65	**A**	6	HSM	Emission rate A seems > emission rate B, C or D Emission rate B = emission rate C Emission rate D < emission rate A, B or C
	B	1.65	**B**	4		
	C	1.65	**C**	2		
	D	1.65	**D**	4		
	E		E			
20	A	3.14	**A**	5	HSM	Emission rate B seems > emission rate A, C or D Emission rate B = emission rate C Emission rate A < Emission rate D < Emission rate C
	B	3.14	**B**	3		
	C	3.14	**C**	6		
	D	3.14	**D**	6		
	E		E			

4.6 RDM RESULTS

Reverse Dispersion Modelling (RDM) relies on pre-calculating the downwind concentration field from potential sources and then inferring the strength of a source from the spatial distribution of concentrations determined by sampling. The wind patterns created by flow around the process units is calculated using computational fluid mechanic methods and a lagrangian dispersion model used to calculate concentrations. Thus, RDM aims to account for complex wind flows characteristic of industrial sites. Assumption are for quasi-steady flow. The main constraint on application, as for other methods, is that the method will not return results in very low and unsteady wind speed conditions.

To use the method a geometric model of the plant is constructed, and the flow fields are calculated for a set of wind conditions using standard wind profiles and a range of incident wind-directions. Concentration fields corresponding to unit strength sources are also calculated. In the field, gas concentrations are mapped using a hand-held portable detector. Wind measurements are used to re-scale the flow fields for speed and a mathematical solver used to estimate the source strength and location.

RDM was applied to 13 test releases according to the availability of staff.

	Date	Start time (local)	End time (local)	Participation TOTAL RDM
Test 1	22/09/2016	13:18:00	14:48:00	yes
Test 2	22/09/2016	15:10:00	16:46:00	yes
Test 3	23/09/2016	11:27:00	12:57:00	yes
Test 4	23/09/2016	14:00:00	15:30:00	yes
Test 5	26/09/2016	09:41:00	11:11:00	no
Test 6	26/09/2016	12:00:00	13:30:00	yes
Test 7	26/09/2016	14:30:00	16:00:00	yes
Test 8	26/09/2016	16:05:00	17:35:00	yes
Test 9	27/09/2016	09:35:00	11:04:00	yes
Test 10	27/09/2016	11:30:00	13:05:00	yes
Test 11	27/09/2016	14:00:00	15:30:00	yes
Test 12	27/09/2016	15:55:00	17:25:00	yes
Test 13	28/09/2016	10:07:00	11:37:00	yes
Test 14	28/09/2016	12:05:00	13:35:00	yes
Test 15	28/09/2016	14:35:00	16:00:00	no
Test 16	28/09/2016	16:45:00	17:52:00	no
Test 17	29/09/2016	10:50:00	12:15:00	no
Test 18	29/09/2016	12:38:00	13:52:00	no
Test 19	29/09/2016	14:10:00	15:10:00	no
Test 20	29/09/2016	15:30:00	17:00:00	no

4.6.2 UNCERTAINTIES

The uncertainty budget reported is comprising contributions from:

- Concentration measurement,
- Wind measurement,
- Dispersion model forward calculation,
- Inversion modelling.

It would seem probable that there is additional uncertainty arising from the flow-field calculation that is not included in this budget. It is unclear how the method would account for significant spatial or temporal variation in background concentration due to upwind sources. The management of a high background was not reported although most of the RDM experiments were done early in the trial period where background was less.

Table 6 : controlled release tests - RDM results

Test	Source configuration	average emission rate	Number of measurement points	Wind speed	Average Emission Rate	Standard Deviation	95% Confidence limit on mean	Difference between RDM and Release	Relative difference (RDM - CR)/CR
		kg/hr		m/s	kg/h	kg/h	kg/h	kg/h	%
1	D	5.1	16	2.4	7.2	n/a	n/a	2.1	42%
2	B	14.9	15	2.8	17.5	n/a	n/a	2.6	18%
3	A	8.9	24	1.4	3.1	n/a	n/a	-5.8	-65%
4	E	9.8	27	2.4	3.0	n/a	n/a	-6.8	-69%
5	A+D	9.2							
6	A+C	9.0	22	1.7	5.6	n/a	n/a	-3.4	-38%
7	A+B+C+D	6.6	32	1.9	26.8	n/a	n/a	20.2	306%
8	C	8.9	28	2.0	23.7	n/a	n/a	14.8	167%
9	E	11.6	32	2.4	9.9	n/a	n/a	-1.7	-15%
10	A+B+C+D	18.5	37	2.0	14.5	n/a	n/a	-4.0	-22%
11	A+B	9.6	33	2.6	8.7	n/a	n/a	-0.9	-10%
12	B	9.8	29	2.0	4.1	n/a	n/a	-5.7	-58%
13	E	14.7	32	0.9	3.3	n/a	n/a	-11.4	-78%
14	E	16.6	29	1.5	2.9	n/a	n/a	-13.7	-83%

4.6.1 RESULTS

RDM was applied to 3 controlled releases of propane according to the availability of staff. The results are tabulated in Table 6 and all results are plotted below including those for wind-speeds outside of the validity range specified in the protocol. Of the tests simulated the lowest emission rate was 5.1 kg/h so the ability to detect lower release rates was not tested.

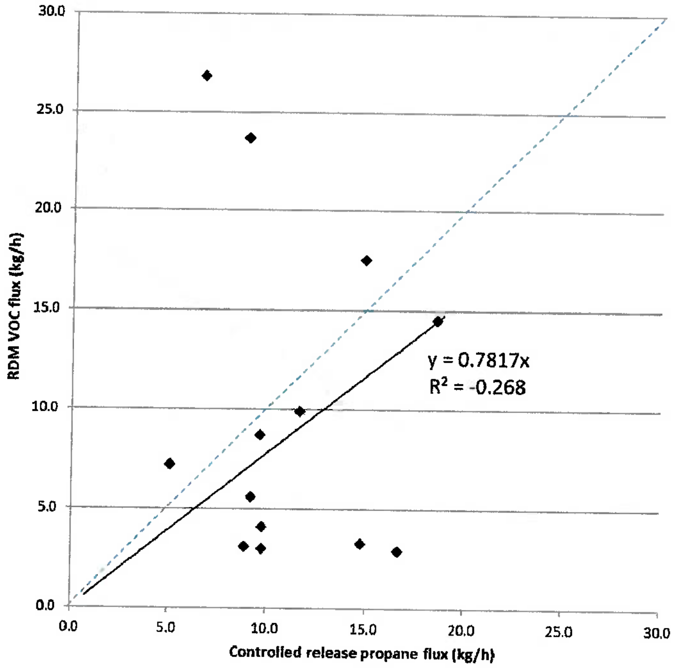
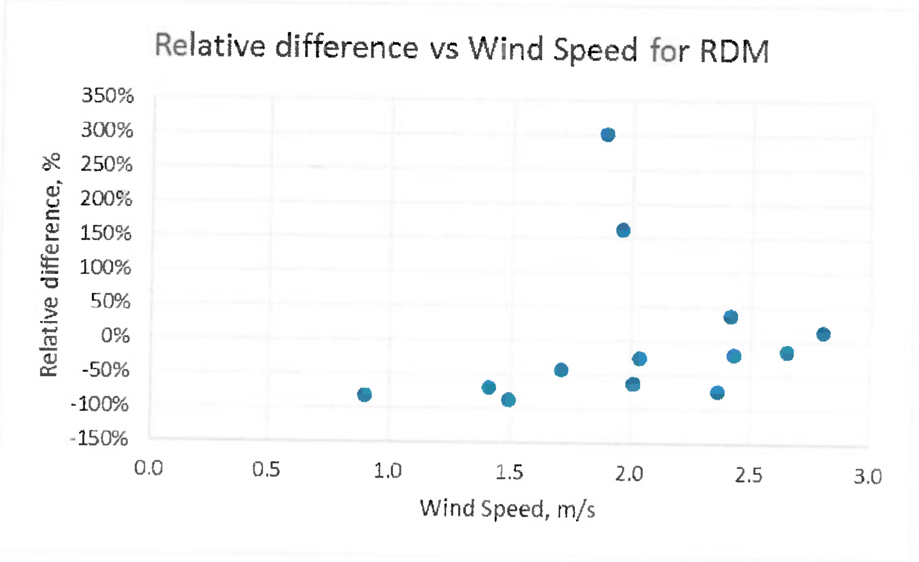


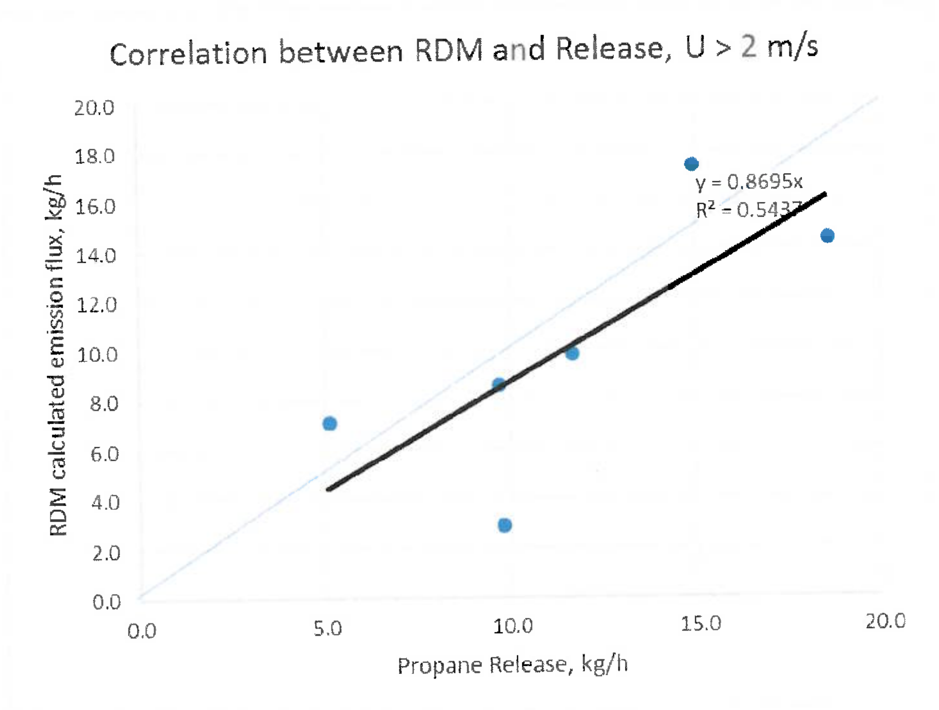
Figure 6 : correlation between controlled release and RDM

The correlation between all RDM results and controlled release fluxes is poor, with no apparent trend. However, if the relative difference is plotted against wind-speed it can be seen that there is a general trend from underprediction at low wind speed toward agreement at higher wind speed. The two points of significant over-prediction appear as outliers when the data is presented in this way. They correspond to Test 7, results for which were not reported for DIAL and Test 8, results for which were not reported for SOF as not meeting performance criteria.

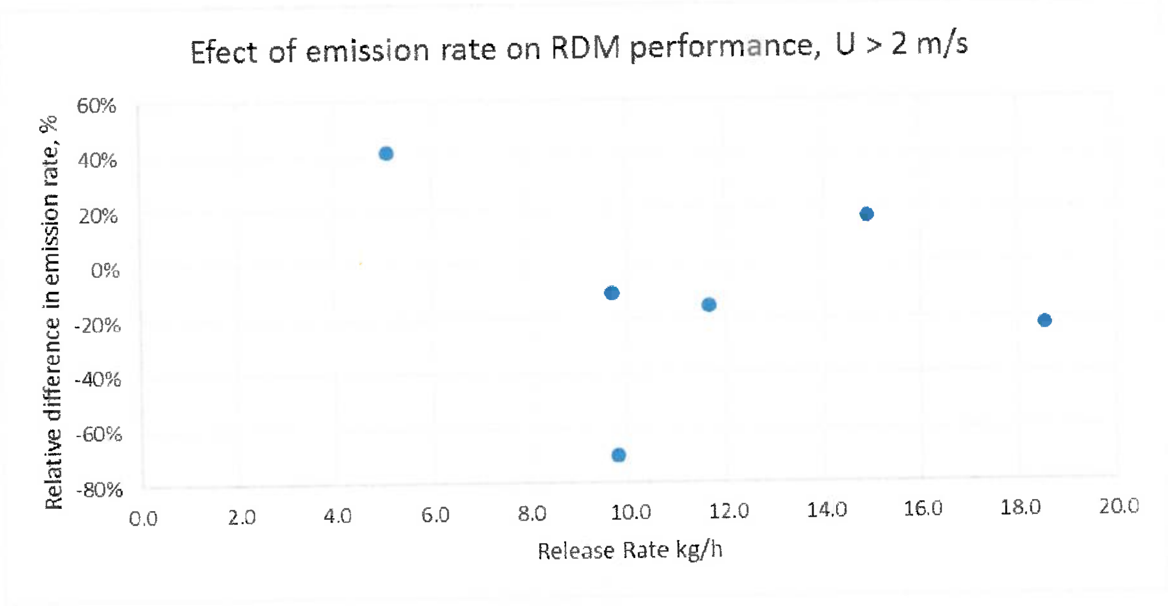


If the RDM protocol limit on wind-speed is applied, i.e. technique should not be used below 2 m/s then the performance improves as shown in Figure 7. The technique has generally underestimated emissions as first applied which implies that the dispersion model is underestimating dispersion.

Figure 7 : correlation between controlled release and RDM (revised dataset)



With this reduced data set it is not possible to say whether the performance was substantially different for the different locations and types of release.



4.6.2 ABILITY TO LOCATE SOURCES

Table 7 : sources configurations – RDM

Test n°	Sources configuration	RDM sources configuration modelled
1	D	D
2	B	B
3	A	A
4	E	E
5	D	
6	A+C	A+C
7	A+B+C+D	A+B+C+D
8	C	C
9	E	E
10	A+B+C+D	A+B+C+D
11	A+B	A+B
12	B	B
13	E	E
14	E	E

The ability to identify sources through the RDM measurement was not tested and the model was configured using the actual release locations. The technique is intended to be used to quantify leaks from pre-identified sources.

4.6.3 DISCUSSION

There are number of sensitivity studies that could be carried out to investigate how the performance of the RDM methodology depends on inputs. The first would be to investigate how the source position affects the results. For example, by replicating the TC method test whereby a physical tracer source was placed at separately to the release points. The other aspect is the sensitivity to the wind input. No detailed analysis has been carried out to evaluate differences in meteorological data recorded by the stations around the release point, but it is known that there are differences between stations. This is something to be evaluated in order to finalise the protocol for this and other methods.

It is probable that non-negligible background concentrations occurred during one or more of the tests where RDM was applied. There is no data to assess but the effect would be to increase predicted emissions. The degree to which this would be significant depends on where the background occurs (uniform or spatially varying) and the weighting given to different concentrations, especially low concentrations, in the inversion process.

4.7 SOLAR OCCULTATION FLUX RESULTS

The solar occultation Flux (SOF) method determines column integrated concentrations of VOC using spectral absorption data with the sun as the light source. Mounted on a vehicle the instrument is continuously driven to provide a swept area with path-integrated concentrations determined approximately every 10 m distance @ a vehicle speed of ~30 km/h. Flux is calculated using the wind-component normal to the driven path and the swept-plane area projection to the vertical. The advection velocity is evaluated at a reference height that depends on context as set out in the protocol.

A measurement set comprises a sequence of short duration measurements of flux both downwind and upwind of a source in normal operation. In these controlled release tests, lasting at most 90 mins, these short duration measurements are sequential and provide a time-series of concentrations.

The SOF spectral analysis provides speciated hydrocarbon information. This allows for detection of species that would otherwise confound reported alkane concentrations. During these experiments targeting the propane tracer, instances of hexane and cyclohexane contamination were encountered.

Interference from background sources was a considerable concern. Unfortunately, no data on background concentrations was available to assess the level of background interference in the same way as was plotted in the DIAL results. The qualitative feedback given was that the background was a significant problem.

The protocol requirements for a SOF emission estimate were met for 15 out of the 20 test releases. The limiting criteria were wind speed greater than 1.5 m/s, a solar elevation above 20° and a minimum 75% coverage of the target area per scan. A minimum of 4 scans meeting criteria to be used to derive a flux. Here a scan is the sweeping of a target area.

The uncertainty in evaluating a scan according to the SOF protocol, must take into account:

- Baseline error,
- Spectroscopy,
- Shadow interpolation,
- Wind uncertainty.

The uncertainty budget generally corresponds to fenceline measurements at some distance from the source. With measurements performed closer to the source (controlled release configuration), the uncertainty will be greater.

4.7.1 RESULTS

A comparison of SOF results with the controlled release results is given in Table 8 and plotted in Figure 8. As presented in the figure below, SOF was able to detect and quantify 15 out of 20 controlled releases of propane in a way consistent with the protocol.

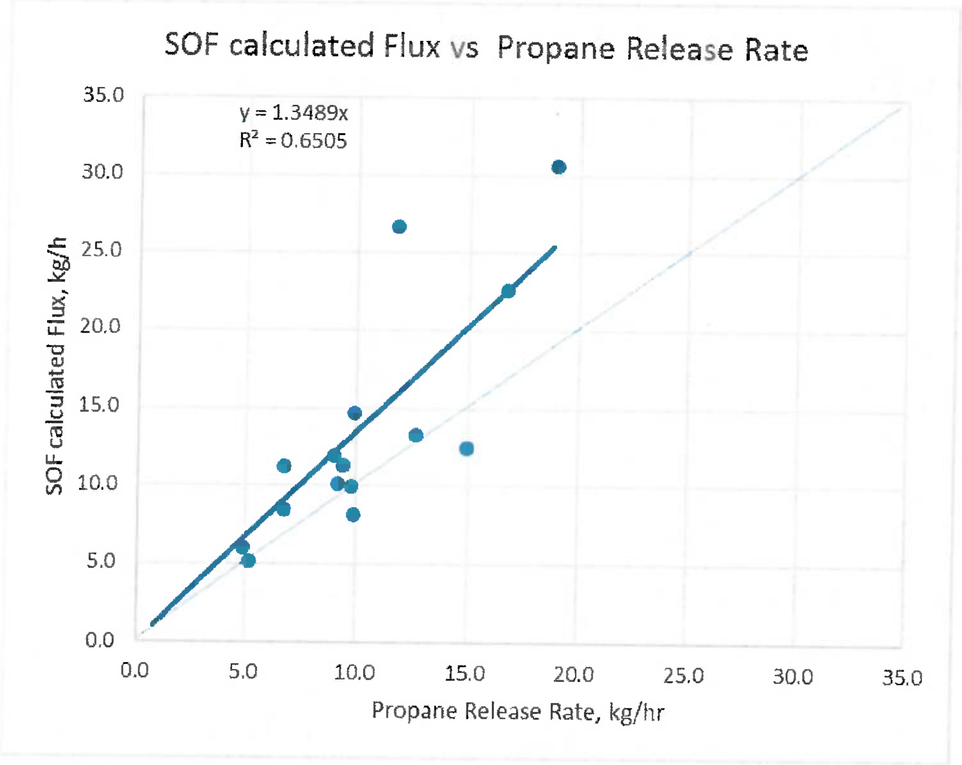


Figure 8 : correlation between controlled release and SOF

The minimum rate quantified was 5 kg/h. Correlation between SOF results and controlled release fluxes is influenced by some high results. Giving a net bias toward over prediction of 35%. This is representative of previous comparisons between SOF and controlled release data. The bias is reduced to 27% if the results from trial 9 is removed. This is one of the releases on the 27th where high background concentrations were reported by DIAL. A more complete understanding of the results would be possible if the basis of the background corrections were provided.

Table 8 : controlled release tests – SOF results

Test	Source configuration	average emission rate	Number of Scans	Wind speed	Average Emission Rate	Standard Deviation	95% Confidence limit on mean	Difference between SOF and Release	Relative difference (SOF - CR)/CR
		kg/hr		m/s	kg/h	kg/h	kg/h	kg/h	%
1	D	5.1	8	4.2	5.3	0.8	0.7	0.3	5%
2	B	14.9	16	3.4	12.6	4.0	2.1	-2.3	-15%
3	A	8.9	8	2.7	12.0	1.5	1.3	3.2	36%
4	E	9.8	13	4.6	14.8	5.8	3.5	5.0	52%
5	A+D	9.2							
6	A+C	9.0	10	3.0	10.3	4.9	3.5	1.3	14%
7	A+B+C+D	6.6	6	3.5	8.6	2.2	2.3	2.0	
8	C	8.9							
9	E	11.6	4	2.4	26.8	2.8	4.5	15.2	131%
10	A+B+C+D	18.5							
11	A+B	9.6	14	3.5	10.1	2.9	1.7	0.5	5%
12	B	9.8	11	3.1	8.3	2.1	1.4	-1.5	-15%
13	E	14.7							
14	E	16.6	11	2.1	22.7	11.4	7.7	6.1	37%
15	E	4.8	13	3.7	6.2	2.3	1.4	1.4	29%
16	E	0.8							
17	A+D	9.2	11	1.5	11.4	5.7	3.8	2.2	24%
18	A	18.9	16	3.1	30.8	9.7	5.2	11.9	63%
19	A+B+C+D	6.6	12	3.8	11.3	4.5	2.9	4.7	71%
20	A+B+C+D	12.6	12.7	3.3	13.4	4.0	2.5	0.9	7%

4.7.1 RESULTS OBTAINED WITH REPEATING 10KG/H FLUX

SOF results from the six releases at ~10 kg/h are presented below.

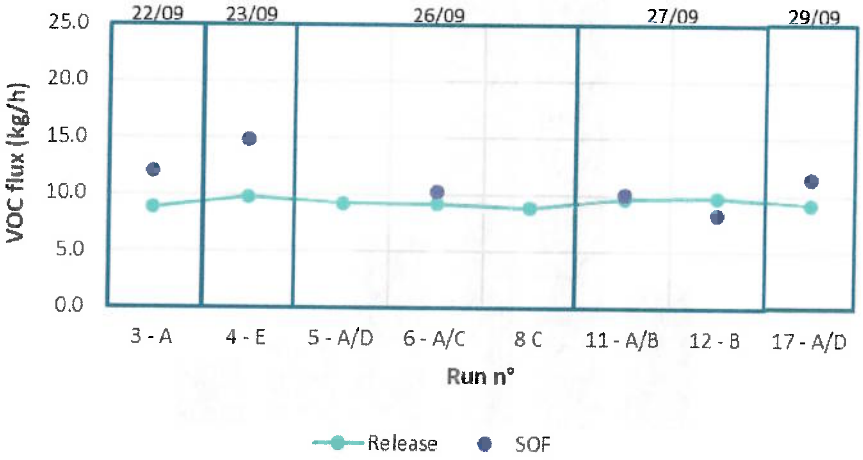


Figure 9 : results obtained with repeating 10kg/h flux for different source configuration and wind conditions - SOF

SOF variability is good and results are close to the true emission rate. There is overprediction for the tests 3 and 4 which were conducted before the background interference became a problem.

Table 9 : statistics for results obtained with repeating 10kg/h flux for different source configuration and wind conditions - SOF

	Release	SOF
Mean (kg/h)	9.3	11.2
Median (kg/h)	9.2	10.9
Standard deviation (kg/h)	0.4	2.2

Individual scan results can vary widely. A histogram of the 67 individual flux measurement transects from the variability tests is shown in the figure below, grouped into 4 kg/h bins. This illustrates that the variation between individual flux measurements is significantly larger than the stated uncertainty of the SOF method. Further, these results are after correction for background interference, determination of which will be similarly distributed. Note that the distribution is typically skew as fluxes are required to be positive.

There are many possible reasons for this variation which deserve to be explored. The protocol, like that of the other techniques, seeks to reduce variability by requiring that several measurements are averaged. The protocol proposal was that at least 4 scans need to be averaged to reduce the uncertainty in the mean to the level proposed in the draft standard.

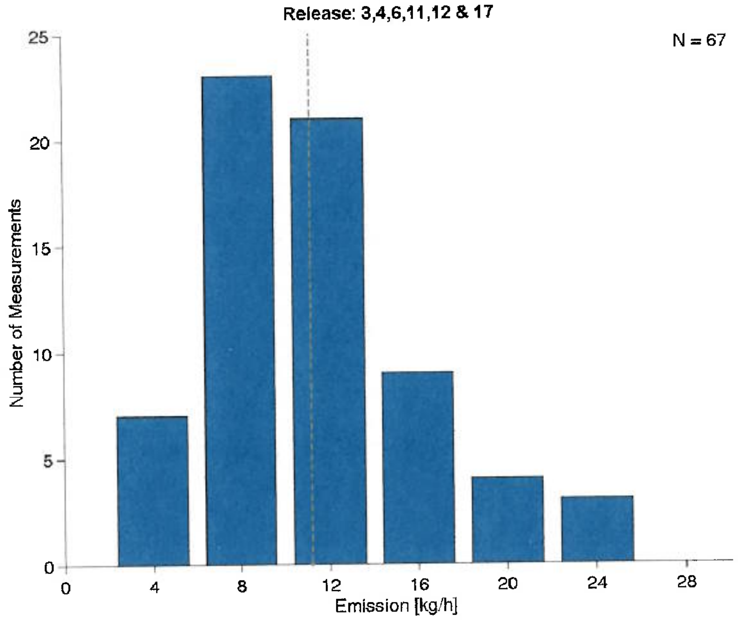


Figure 10 : An histogram of the variability test for 67 individual SOF measurements. Here the mean corresponds to 11.2 kg/h, the median to 10.3 and the standard deviation to 4.6 kg/h.

To estimate the effect of increasing sample number on variability FluxSense proposed a simulation based on a bootstrap analysis. It is assumed that the population of 67 runs from the 8 tests is representative of the full set of possible measurements and flux estimation outcomes. Using resampling, populations of progressively larger data sets were drawn. The statistics of these data-sets (mean, standard deviation etc.) were then evaluated.

Figure 11 shows how the median, 5th, 10th, 90th and 95th percentiles, mean and standard deviations of the sample distributions varies with the sample size N. The graph is complicated because the SOF data set is positively biased compared to the target release of 10 kg/h. The graph shows that a sample size of ~16 runs is needed to reach the 95% confidence level that the mean of this set would be no greater than 13.2 kg/h (mean + 32% from the SOF draft protocol). When the sample distribution is generated using 6 measurements per set, then the mean will be in the range with confidence ~73%.

This has important considerations for the SOF protocol. To identify a practical way forward a better understanding is needed of the measurements made, both with and without release, the sensitivity of the flux calculation to the choice of wind speed and direction as well as the statistical processing.

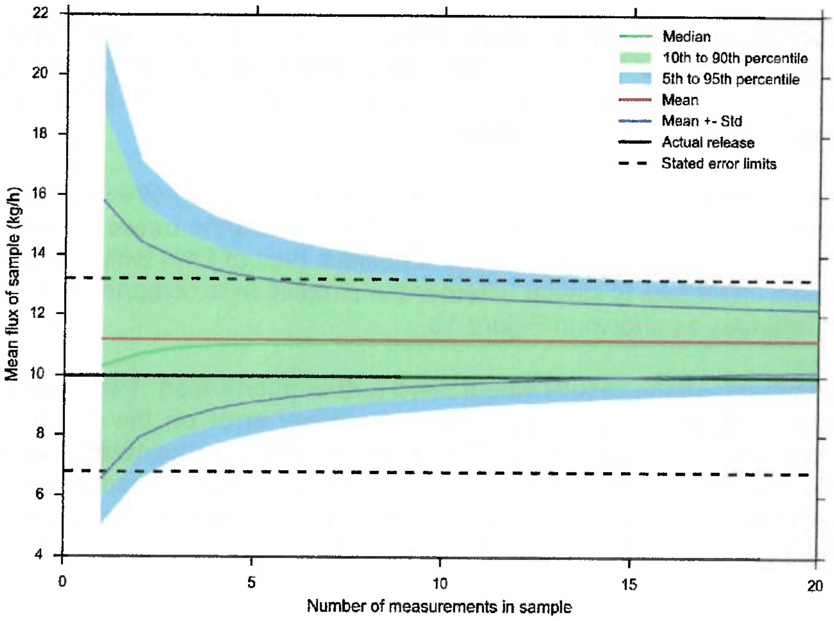


Figure 11 : A bootstrap analysis for all variability measurements

4.8 TRACER CORRELATION RESULTS

The Tracer Correlation (TC) method aims to co-locate a tracer gas source with an emission source so that the tracer and emitted gas disperse in a common way. The emission source rate is obtained from the concentration ratio between VOC and the tracer gas at a downwind point and the known tracer gas flow. This method is independent of wind conditions and uses wind measurements to locate downwind locations for sampling.

In the absence of background concentrations, the principle uncertainty in using the method is in accurately co-locating the tracer source. Other error sources relate to the measurement of concentration. As deployed in these trials spectroscopic analysis is used for both hydrocarbon and tracer. The uncertainty is based upon:

- Baseline error,
- Spectroscopy,
- Tracer/Source co-location mismatch.

In general, the effect of the uncertainty term on the concentration ratio will go through a maximum at some [close] distance to the source and then decrease with distance.

In the presence of background concentrations, the interpretation of tracer data depends on the nature of the interference. A constant background can be subtracted but a varying background requires complex analysis.

The uncertainty budget should be an error component for control of the tracer release rate. The protocol should clarify if the errors on baseline and on spectroscopy should apply independently to tracer and the VOC measurement.

In these controlled release experiments a perfectly co-located tracer is redundant other than to test measurement uncertainty. Although this would be a useful control it was not done. The tracer was released in the centre of the unit and differences between tracer and propane indicate how separation affects the dispersion of the two species.

The TC method was applied to all releases. In two cases (Test 8 and Test 13) protocol criteria were not met and results not included. The measurement process is not well described. It is assumed that the concentration ratios are measured at a number of points using a moving sensor. Averaging times for the concentrations are not known.

Results for the estimated release rates are given in Table 10 and plotted in Figure 12. Results were obtained for the full range of release rates. The correlation between the TC results and the release data is a straight line and shows a positive bias of 24% which is unexpected for a tracer experiment. The bias is similar whether the simulation is compared with single point or multiple point releases as shown in Figure 13.

To more fully understand the results would need further information. Two possible reasons for a positive bias would be a systematic flow proportional error on the tracer gas rate or an influence of background concentration. The latter depends on the weighting given to tracer ratios where hydrocarbon concentrations are low. The two tests results that stand out from the trend are Test 1 and Test 2 where the TC flux is an underestimated. These are tests less likely to be conducted with a large background concentration.

Table 10 : controlled release tests - TC results

Test	Source configuration	average emission rate	Number of Scans	Wind speed	Average Emission Rate	Standard Deviation	95% Confidence limit on mean	Difference between TC and Release	Relative difference (TC - CR)/CR
		kg/hr		m/s	kg/h	kg/h	kg/h	kg/h	%
1	D	5.1	10	4.2	4.1	2.2	1.6	-1.0	-19%
2	B	14.9	6	3.4	12.3	1.4	1.5	-2.6	-17%
3	A	8.9	7	2.7	11.8	1.3	1.2	2.9	33%
4	E	9.8	13	4.6	13.1	2.0	1.2	3.3	34%
5	A+D	9.2	4	1.5	11.7	2.4	3.8	2.5	27%
6	A+C	9.0	13	3.0	10.4	1.1	0.7	1.4	15%
7	A+B+C+D	6.6	12	3.5	9.1	2.4	1.5	2.5	0
8	C	8.9							
9	E	11.6	7	2.4	16.5	4.5	4.2	4.9	42%
10	A+B+C+D	18.5	12	1.8	21.1	4.0	2.5	2.6	14%
11	A+B	9.6	16	3.5	13.2	2.8	1.5	3.6	37%
12	B	9.8	19	3.1	12.8	2.8	1.3	3.0	31%
13	E	14.7							
14	E	16.6	10	2.1	19.6	4.0	2.9	3.0	18%
15	E	4.8	13	3.7	5.8	1.3	0.8	1.0	22%
16	E	0.8	7	4.6	1.5	0.6	0.6	0.7	91%
17	A+D	9.2	14	1.5	11.4	4.3	2.5	2.2	23%
18	A	18.9	12	3.1	27.1	7.8	5.0	8.2	44%
19	A+B+C+D	6.6	11	3.8	8.3	1.8	1.2	1.7	26%
20	A+B+C+D	12.6	18	3.3	17.4	6.1	3.0	4.8	39%

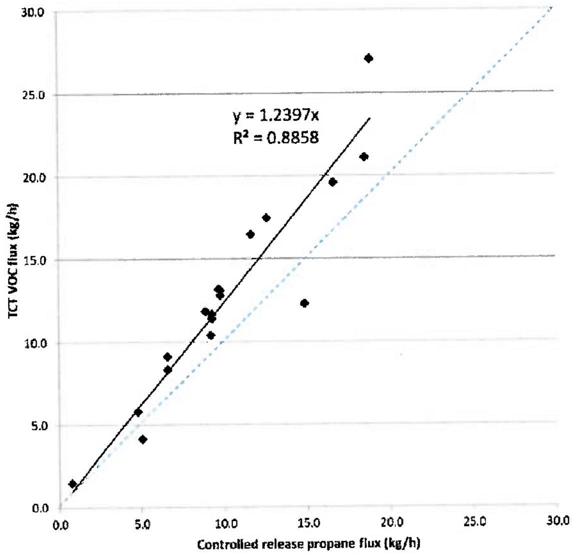


Figure 12 : correlation between controlled release and TC

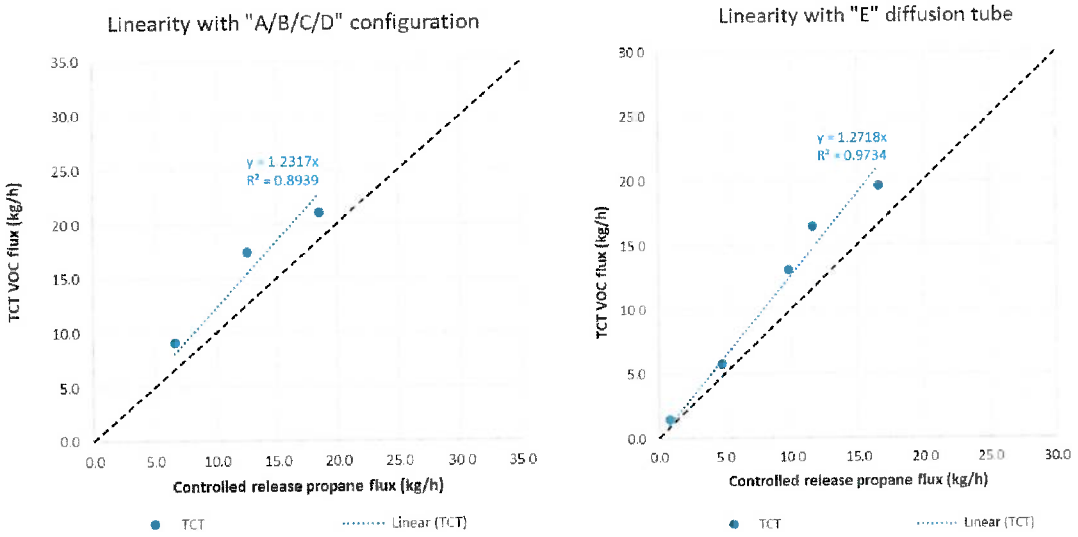


Figure 13 : Effect of release configuration - TC

4.8.2 RESULTS OBTAINED WITH REPEATING 10KG/H FLUX

TC results from the seven releases at ca. 10 kg/h are presented below.

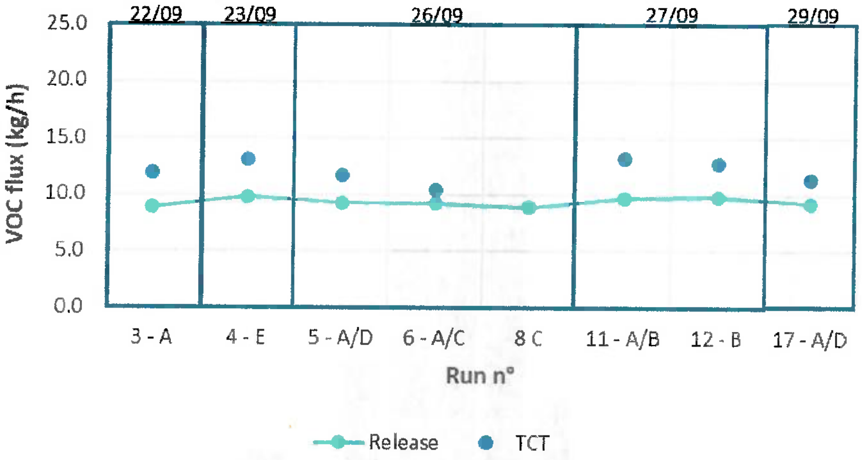


Figure 14 : results obtained with repeating 10kg/h flux for different source configuration and wind conditions - TC

The variability of TC is very good across the series with a consistent bias to over-estimation as found for SOF. Over this set of tests, the average bias was 30%, and the variation across the set was low with a standard deviation of 1 kg/h.

Table 11 : statistics for results obtained with repeating 10kg/h flux for different source configuration and wind conditions - TC

	Release	**TC**
Mean (kg/h)	9.3	12.1
Median (kg/h)	9.2	11.8
Standard deviation (kg/h)	0.4	1.0

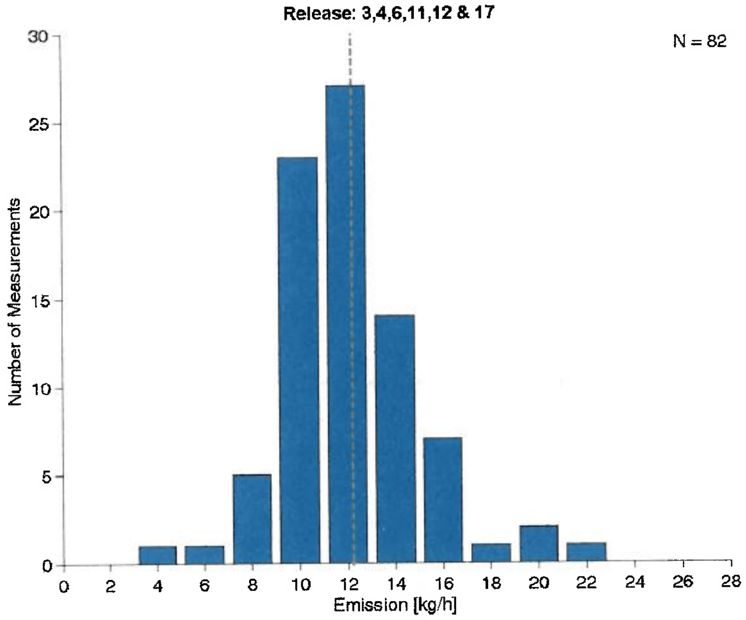


Figure 15 : Histogram of the variability test for 82 individual tracer correlation measurements using MeFTIR. Here the mean corresponds to 12.2 kg/h, the median to 11.8 and the standard deviation to 2.9 kg/h.

The FluxSense team repeated the SOF exercise to investigate the number of scans that would be needed to for the mean to be within the desired uncertainty. Again, this was based on a bootstrap analysis with replacement. Taking the 83 individual measurements across the 7 trials to be representative of the variability population statistics for samples of size N were calculated. The frequency histogram is shown in Figure 15 and the sample population range as a function of sample size in Figure 16.

The exercise shows that the effect of bias dominates the performance of the technique and no matter how many samples are taken the mean of the sample population will always have a significant probability of exceeding the target flux by more than the required uncertainty.

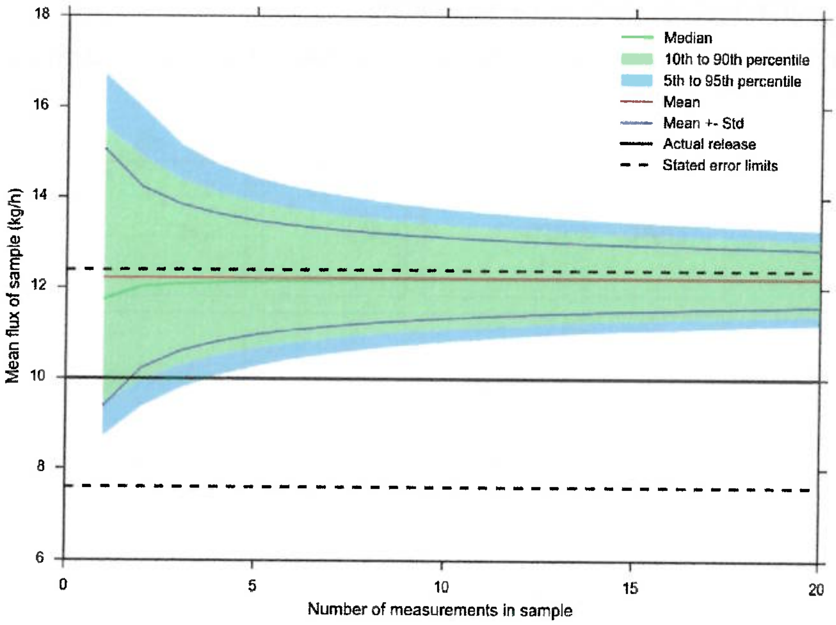


Figure 16 : A bootstrap analysis for all variability measurements by the TC method, showing how the statistical distribution is related to the number of samples.

4.9 INTERCOMPARISON OF METHODS

Four different methods have been tested during this experiment. Correlations between those methods are presented below.

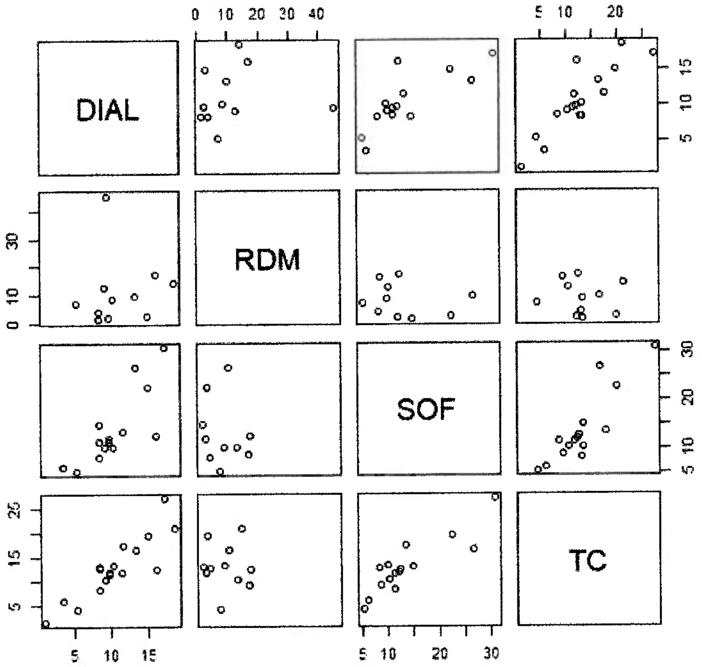


Figure 17 : correlation between the four different methods

Correlation between DIAL, SOF and TC looks good. RDM results are correlated with none of the other techniques. Using the additional validation criteria on wind speed for RDM, the correlation looks a bit better.

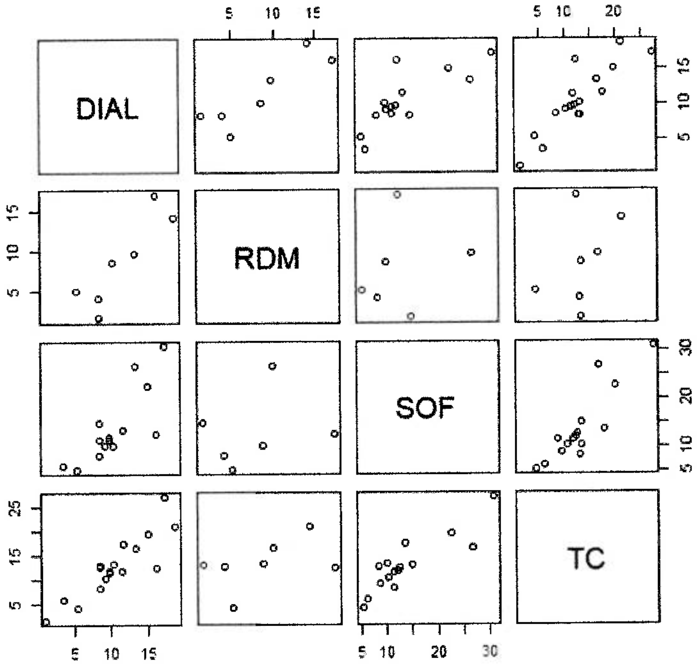


Figure 18 : correlation between the four different methods (RDM revised dataset)

5. SECOND CAMPAIGN: REAL INDUSTRIAL CONDITIONS

5.1 INTRODUCTION

The objective of the second campaign was to test and validate the protocol of each technique on a real industrial site. The campaign was planned in close association with the company operating the site. The planning and permitting aspects of the protocols is not assessed here. The important consideration was that the date window for the campaign was fixed to lie between June 8th and June 22nd 2017. Part of the site was off-limits due to construction work and this posed some access constraints because roads were closed. The closed off section was to the edge of the refinery and did not materially affect the trial.

The refinery was divided into 9 nominal sections for emissions assessment. These were surveyed using SOF and DIAL techniques. Two other areas not accessible to DIAL were surveyed by SOF. The DIAL emission flux totals for each section were composites of targeted measurements of specific equipment. SOF also utilised fenceline measurements to estimate global emissions. OGI was applied at identified emission sources from the remote sensing techniques. The Tracer Correlation Method was restricted to 4 sources. The RDM method was only applied to the waste-water treatment plant. Each technique has been run independently, with the common objective to get the best assessment of site VOC sources locations and corresponding VOC emissions quantification.

Three meteorological stations were installed in the refinery (North West, South West, South East) together with a wind-lidar (South East). Individual WP reports describe how the meteorological data were used. Supplementary data on wind conditions within the refinery and away from the reference stations was obtained during DIAL and RDM measurements. The wind conditions were representative of those expected from the analysis of historic records.

This section describes the results of the application of the protocols as reported by the teams. These primarily focus on end results and summary statistics. Further analysis of the results and investigation of questions arising will need to take place before the protocol is finalised.

5.2 DIAL RESULTS

5.2.1 MEASUREMENT STRATEGY

Following the DIAL measurement protocol, a reference wind mast was erected in an open area the South East corner of the site. The mast was close to the 10 m mast and wind Lidar instrument installed as part of Work Package 3. The mast was fitted with anemometers at four heights (12, 9, 6 and 3 m) which were used to derive vertical profiles of wind-speed though fitting a standard wind-profile. During measurements local wind data was gathered using a 10m mast mounted on the DIAL truck. A portable anemometer, measuring at 2 m height, was deployed in the field to determine whether there was a large impact on wind-speed and direction due to flow around buildings. A concern of flux measurements is ensure that the plane of measurement does not cut through a recirculation zone marked by very low or reverse flow near ground-level.

A plot plan of the industrial site was used to select measurement targets in the 9 zones delimited in the planning process. The objective of the DIAL survey being to survey individual plant components for emissions. This is most clearly done for isolated units such as tanks.

Over the 10 days of DIAL measurements the DIAL van was located in 34 positions to carry out the targeted surveys. The order in which the measurements were carried out was determined by the wind-conditions arising and predicted for the day and taking account of site activities and activities of the other measurement teams. Precise alignment of the scanning plane was fine-tuned at the time of measurement taking account of the local wind data.

5.2.2 QUALITY CONTROL

The DIAL protocol, imposes conditions on measurements that have to be fulfilled for a specific measurement to be considered compliant with the protocol. The key criteria are listed below with commentary. The QA conditions were fulfilled.

Table 12 : QA/QC - DIAL

QA/QC criteria	This campaign
Carry out a set of at least four DIAL scans for each line-of-sight to quantify variability and hence reduce the uncertainty that accompanies a single measurement.	Done for 96 % of the sources. The main exception was position P3 in survey area 6. The main process area, and this was because the wind was variable. However, the main emission source within zone 6 was covered by 4 scans. A temporary source was found in area T10 and reported separately
Repeat one or two extra sets of measurements of the same area along different scan lines or from different locations or on a different day as set out in the measurement objectives.	The measurement objectives [customer input] did not define specific needs but some measurements were repeated to provide timely data comparisons with other techniques
Measure upwind sources if present	Fulfilled
Carry out all the necessary quality assurance measurements	Fulfilled
Take air samples at locations which would provide an indication of the actual speciation of the emission sources sampled by the DIAL	Carried out for the emission sources most likely to be complex mixtures (WWT) and/or not straight-chain alkanes (petrochemical tank farm)

All protocols could improve their reporting requirements in regard to species composition, management of information depending on composition and the implications for uncertainty. DIAL includes compositional uncertainty into its uncertainty balance, but this is not clearly identified.

5.2.3 RESULTS

DIAL results were reported as averages over the number of scans made. Each scan providing the average of concentrations over ~5 minutes period. During DIAL measurements the light-absorption data on a C-H line is mapped using a pre-calibration factor to give a mass concentration equivalent to gasoline vapour. This needs to be adjusted in post-processing to better account for hydrocarbon speciation. For example, an oxygenated hydrocarbon will give a different absorption per mass than a straight chain alkane and a dominance of pure compounds will give a different absorption per mass than the assumed generic mix. The data for speciation is gained by taking gas canister samples of ambient air at different locations and subjecting them to chemical analysis. The corrections that are applied are mostly small as indicated in Figure 20 which shows the default and speciated mass-flux rates. However, in one case, where the hydrocarbon was found to be cyclohexane, the correction is large (x10).

The results presented as mass-flux crossing the measurement plane after correction for speciation are given in Table 13 for the areas delimited by DIAL scans and also aggregated to to provide section totals. These latter are shown proportionally in in Figure 19.

Table 13 : VOC emission assessment - DIAL

Source		Time period	Validated scans	VOC mass flux (average)		95% level of confidence
		(days)	(number)	kg (VOC)/h		kg (VOC)/h
1. East Tank Park	T1	1	4	3.5	41.7	0.8
	T2 & T3	1	4	9.3		1.9
	T4 & T5	1	4	9.4		3.3
	T6	1	4	8.2		2.3
	T7	1	5	6.9		1.6
	T8	1	4	4.4		3.1
5. PetroChemical Tank Park	T9 West	1	4	2.8	7.1	0.8
	T10	1	3	3.3		1.6
	T11	1	4	1.0		0.6
3. Middle Tank Park	T12	1	4	1.4	150.0	0.4
	T13	1	6	11.2		1.6
	T14 - Temp Source	1	4	130.0		59.9
	T15	1	4	7.5		2.5
2. West Tank Park	T16	1	4	0.0	10.2	1.8
	T17	1	4	10.3		2.0
6. Main Process	P1	1	4	20.2	54.5	9.8
	P2	1	4	16.2		4.8
	P3	1	1	18.0		2.2
7. PetroChemical Process	P4	1	4	25.7	48.0	7.7
	P5	1	4	9.8		7.1
	P6	1	4	12.4		5.3
8. WWT	WT	2	19	25.9	25.9	5.9
10. Vent Pipe	Stack SE Site Area - Temp Source	1	6	6.7	6.7	1.9
11. Truck Loading Area	Truck Loading - Temp Source	1	5	11.2	11.2	2.4
	T9 Est - T603 & T614 Cyclohexane *	1	4	101.1	101.1	79.7
	Flare - Temp Source	1	4	10.7	10.7	1.4
	Coker - Temp Source	1	4	29.1	29.1	7.3
			Total, no temp sources :	**207.4**		**15.2**
			Total, including temp sources :	**395.1**		**64.0**
			Total, including cyclohexane estimate :	**496.2**		**88.5**

* This is only an estimate and it should be treated as maximum values if all the VOC assigned to the T9 east area is from the two cycloexane tanks. 1/2 to 1 kg difference in VOC is about 15 to 30 kg difference of cyclohexane

During the campaign there were non-routine emissions from two sources. The first was a tank in the middle tank farm (area 3) that was under repair. It was a significant source of emissions at the beginning of the campaign. The second was a leak from a tank containing cyclo-hexane in the petrochemical tank farm (area 5). In Table 13 this latter is indicated separately as a temporary source but should be added to the total for Area 5 to give emissions during the test. This has been done in Figure 19.

The aggregate emission expressed as hydrocarbons of carbon number 3 and above (C3+) was 207.4 kg/h without the two non-routine sources and 395.1 kg/h with. Some sources such as the flare and truck-loading are likely to be variable during the day, and from day-to-day through the measurement period.

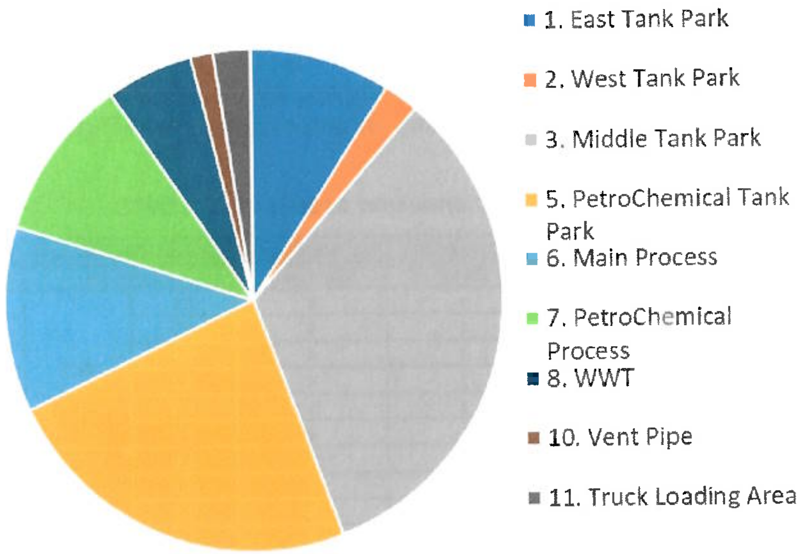


Figure 19 : VOC sources apportionment - DIAL

5.2.4 DISCUSSION

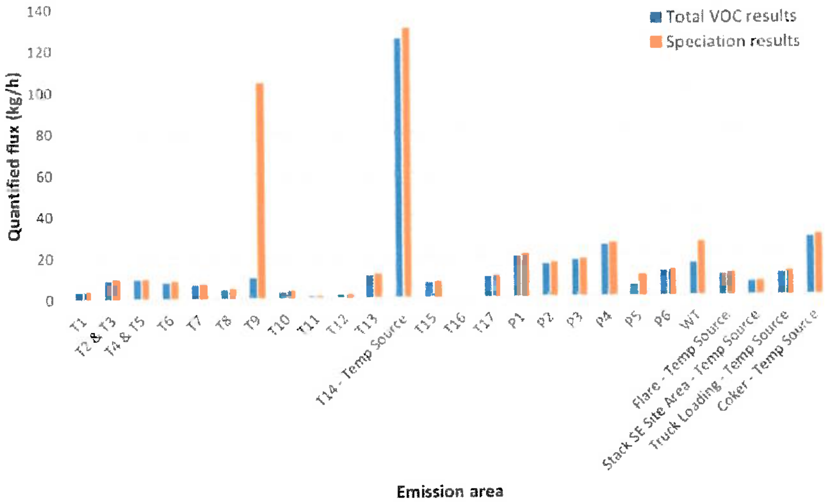


Figure 20 : quantified VOC flux by source - DIAL

DIAL measurements were carried out according to plan and, with the exception of the cyclohexane source, the correction to flux for speciation was modest. Therefore, DIAL was successful, in all but one case, of identifying emissions as the survey proceeded. The presence of cyclohexane was not anticipated. It was toward the end of the survey confirmation was received that the chemical was stored in two tanks in area T9. The presence of cyclohexane was first detected by the SOF survey. It was also detected by MeFTIR (see TC section) and by canister sample. Without this information, confirmed with the site, a lower emission rate would have been reported for Area 5. This underlines the importance in the initial planning process of identifying if, and where, pure components are stored.

Because the presence of cyclohexane was accounted for in post-processing the emission flux estimate is less certain than it might have been. The measurements use a weakly absorbing line then combined with a large weight factor. If the presence of had been suspected a more accurate measurement using a different absorption line could have been made.

The DIAL measurements are obtained using, for the most part, 4 to 6 consecutive scans over a period of up to 1 hour. Therefore, DIAL measurements are well time-averaged and are expected to be representative of both the average and the variability of emission flux over this time period provided wind-conditions (windspeed, direction) remain consistent.

The DIAL has the potential to investigate temporally varying sources by extending the number of scans. The effectiveness depends on the consistency of wind conditions and lack, or invariance of, upstream sources. Where possible the time series of scan results should be shown to identify trends. A key example of this was seen in the first field campaign, test 10.

The segregation of downwind and upwind measurements for determining background needs to be made clearer in the protocol and in the reporting of results, especially where the background is significant.

There is some flexibility in choice of the meteorological data source in making flux calculations. A full sensitivity analysis of the calculated fluxes to inputs should be carried out and the wind direction and wind speed, as well as the vertical wind profile, are important variables. Calculated flux has a linear dependence on wind speed. Sensitivity to direction is small if the beam crossed normal to the flow but increases as the angle of intersection increases. Limited results from a test to examine the effect of using wind data from different wind masts is shown in Table 14. The example is for Tank 14 emissions where the tank and the reference wind mast are more than 1 km apart. In this case the changes in mean flux arising from the wind-speed choices are not significant with respect to uncertainty in the mean flux.

Table 14 : wind data sensitivity test - DIAL

	Wind speed (WS) and direction (WD) sensors used for emission rate calculation			
	WS: Mast 4 WD: DIAL	WS: Mast 4 WD: Mast 4	WS:Mast 4 WD: Portable	WS: Portable + Mast 4 WD: DIAL
VOC emission rate (kg/h)	124.8	128.8	123.3	121.3
Standard deviation (kg/h)	38.3	40.1	37.2	37.6

5.3 OGI

The optical gas imaging camera was used to detect and identify sources where the remote sensing techniques (DIAL, SOF and MeFTIR used as part of the TC method) indicated the presence of hydrocarbons and requested an OGI survey.

5.3.1 QUALITY CONTROL

The OGI protocol was followed. The operators were experienced staff, trained in OGI and familiar with the specific equipment used. The specific quality assurance measures are listed in Table 15.

Table 15 : QA/QC - OGI

QA/QC criteria	This campaign
Perform a functional test at least one time per day	The test was carried out once a day, at a distance of 6 meters and under representative wind conditions. This included verification of the camera operation in both normal and high sensitivity modes, check that conditions were appropriate for OGI use, detection test against a known source.
Record a video for each detected leak	A thorough and systematic approach to recording data was put in place. Video and still records were made, archived and indexed for all the leak investigations carried out. Including negative results.

5.3.2 RESULTS

OGI surveys were carried out after being directed to the presence of gas concentrations by the other teams. A total of 44 independent survey requests was made, in 2 cases by both SOF and MeFTIR, leading to 42 surveys. OGI located 40 emission sources across the survey areas. Some sources were observed from more than one position and provided more than one record. Some survey areas contained more than one potential source, for one area indicated by DIAL four tanks were screened but no source found.

All but one of the emission sources detected with the OGI camera would not normally be scheduled for inspection in a LDAR program for fugitive emissions. Although this was a natural consequence of the experimental design it provides confirmation that OGI can detect emissions from other equipment. The main sources were tank seals (especially on the known problem tank), vents and traps. The detection range was good from 20m to over 50 m (62% of records were made from 50m or more distance). Tank roof emission could be seen looking across the roof and also looking up toward the tank rim from below.

The operator was able to give a judgement on the relative size of the emission source using a grading small, big, huge. Of the recordings made 1 was counted small, 26 big and 16 huge (4 videos the known tank fault across 3 days).

The search pattern depended on the information given to the OGI team. It was faster to survey areas marked as high concentration areas when the potential sources were few. The SOF and MeFTIR surveys pick up high concentration points next to roads and it was very effective to search near these areas. The DIAL informed on potential upwind sources from locations not necessarily adjacent to the beam. The process for screening for leaks was therefore more elaborate due to the area to cover. There was no standardised trigger point for requesting a survey. DIAL requested 36 investigations while SOF and MeFTIR requested 5 independent (2 requests were for the same area) even though the techniques were used to screen the same areas of the refinery.

Table 16 : summary of interactions between OGI and other techniques

Method	Number of interactions with other technique	Precision on emission height given? (% of time)	Mean OGI working hours	Leak found by OGI? (% of time)
DIAL	36	72%	5.2	86%
SOF	3	100%	1.2	100%
MeFTIR(TC)	4	100%	1.5	100%
RDM	1	100%	0.5	100%

5.3.3 DISCUSSION

Deployment of the OGI camera showed that a number of leaks, that would not be sought in an fugitive emission oriented LDAR of point emission sources, could be detected and ranked. Furthermore, for the environmental conditions of the campaign, the detection distance was large (≥ 50 m) for the biggest leaks. This allowed observation from the ground of elevated emissions such as those from tanks.

Methodical searching of the plant for leaks is time-consuming and a clear benefit was experienced when the OGI was steered by initial rapid screening using the SOF and MeFTIR vehicles. These drive around the site and can locate concentration hotspots on refinery roads which can act as a search starting point. In this trial there were a small number of these.

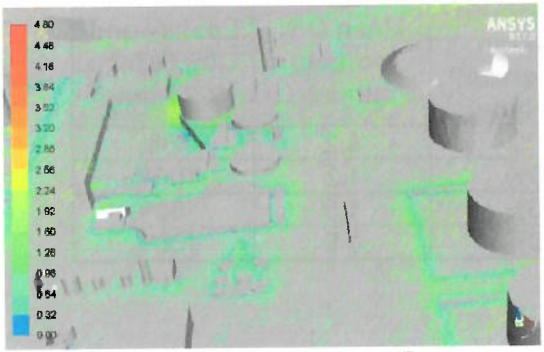
Many more areas were flagged for screening by DIAL which can detect the presence of likely upwind sources. The search for these was more time-consuming in this case. This could reflect that smaller sources were being sought or that information from the DIAL scan which can inform on height, strength and upwind distance, was not fully used.

The viable application of OGI to diffuse emission sources was well demonstrated in this field trial. Although the deployment here was guided using other techniques OGI could be used alone to survey sources such as tanks.

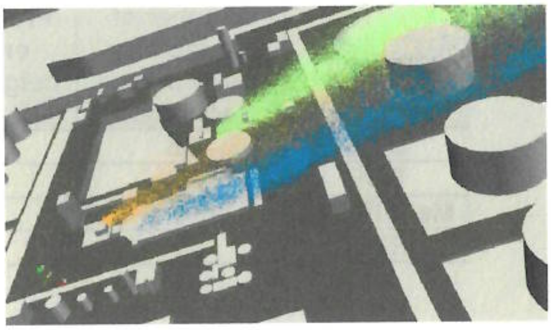
5.4 RDM RESULTS

The reverse dispersion modelling technique was applied to the waste water treatment plant (WWT) which comprises five main emitting components, an Archimedean screw water lift, an API design oil-water separator, a flocculation basin and two dissolved air flocculation (DAF) units. Each of these units was confirmed as an emission source using the OGI camera visualisation.

The dispersion of emissions has been calculated using the Fluent CFD model for the flow-field calculation and the SLAM Lagrangian particle model to simulate dispersion. The geometric inputs to the model were obtained from site plans. A schematic of the wind-vector field and dispersion from three of the sources for one incident wind direction is given below.



Wind field vector – CFD



Three sources dispersion - SLAM

Measurements of total VOC were carried out at using a portable flame ionisation detector (FID) to move between a set of reference points. The FID was calibrated against a methane reference and these measurements were later corrected to a representative mixture composition using a factor of 2.34. The duration of the sample taken at each point was at least 30 seconds. A supplementary system of fixed microsensor detectors was also deployed but concentrations were everywhere below their detection limit.

To provide information on local wind-speeds a 3D sonic meteorological station was set up close to the WWT area and at height t 3.7 meters.

Incident wind direction and speed was taken from a 10 m mast equipped with a radiometer to measure incident solar radiation flux. This was used as input to the dispersion mode and was located in a remote area west of the water treatment plant.

5.4.1 QUALITY CONTROL

The RDM protocol was respected. The method requires at least a minimum wind speed, determined at 10 m height and that concentrations to be used in reverse modelling are above detection limits. These were fulfilled. An internal modelling criterion, which is related to the choice of solution to the inverse problem was used as set out in the draft protocol but is still under development and is expected to be improved. The tests are summarised in the table below.

Table 17 : QA/QC - RDM

QA/QC criteria	This campaign
Wind speed > 2 m/s	Mean wind speed respected for the validated calculations
FID measurement > 0.5 mg/m^3 eq. CH_4	Fulfilled
Slope of the regression line between measured and modelled concentrations.	The slope of the regression line represents the emission rate. The best slope by least squares regression is chosen. Work to develop exclusion criteria for outlier points is in progress

5.4.2 RESULTS

Two sets of emission reconstruction were made. The first calculation assumed emissions from three sources: the Archimedean screw, the API separator and the flocculation basin. The second set included the two covered DAF units. The reconstructions covered two periods of time. In the first time period wind conditions were such that DAF emissions were expected not to make a contribution to concentrations across the measurement grid. Results are summarized in Table 18.

Table 18 : VOC emission modelling results - RDM

Calculations parameters	Time period	Validated cal.	VOC mass flux (mean)	Standard deviation
	(days)	(number)	kg (VOC)/h	kg (VOC)/h
Three sources / TOTAL met station	2	4	7.6	2.2
Five sources / TOTAL met station	4	6	11.7	3.7

In the reconstruction for the five sources the DAF units were calculated to have an average emission of 4.37 kg/h and the other three sources 7.33 kg/h so there is consistency between the two calculations.

A sensitivity calculation was carried out to see if the choice of reference wind mast affected the reconstructions. The results above used the reference wind mast for the technique (labelled TOTAL in Figure 21). The permutations were then to use the North wind mast, sited next to the technique reference) for direction, then for direction and wind speed. This was repeated for the SW mast and for the SE mast located in the Truck loading area.

Results are shown in Figure 21 for the three sources reconstruction. It can be seen that the choice of wind data does not have a straightforward effect on the reconstructions. During the third measurement set the calculated emission rate is indifferent to the wind data source. During the first reconstruction period using the wind direction at the SW station gives a higher calculated emission rate. During the second and final reconstruction the wind speed and direction at the Truck loading station, which is the reference station for other techniques, gives the largest calculated emission. Note that the calculated emission varies between measurement periods irrespective of the choice of measurement station.

5.4.3 DISCUSSION

The RDM method has been applied to estimate emissions from the water treatment area which is a challenging source to assess using other methods. Emissions are area source emissions and that can originate at, or below, ground level whereas remote measurement techniques focus on elevated plumes. The method relies on realistic simulation of flow and dispersion around often complex geometry. It is therefore important to accurately place the reference wind mast. For protocol development it would be useful to have some measure of how well the wind-field is predicted in addition to the concentration results. This would provide important insight also to guide the use of other techniques where coverage of the downwind concentration field with height is an unknown.

Supplementary data on VOC composition is important to the results which are proportional to the scaling factor used. The reconstructions based on sampling data appear internally consistent. It would be useful to establish any dependence on sampling strategy and the extent to which the concentration fields are steady over the measurement period. In this demonstration it was unfortunate that the fixed sensor array did not yield results because time-series at even a few positions would inform on this greatly.

Presentation of results should include 95% confidence limits on the calculated emission rate and inform on the goodness of fit of the modelled emission to the measured concentrations with respect to the developments taking place to account for outlier points.

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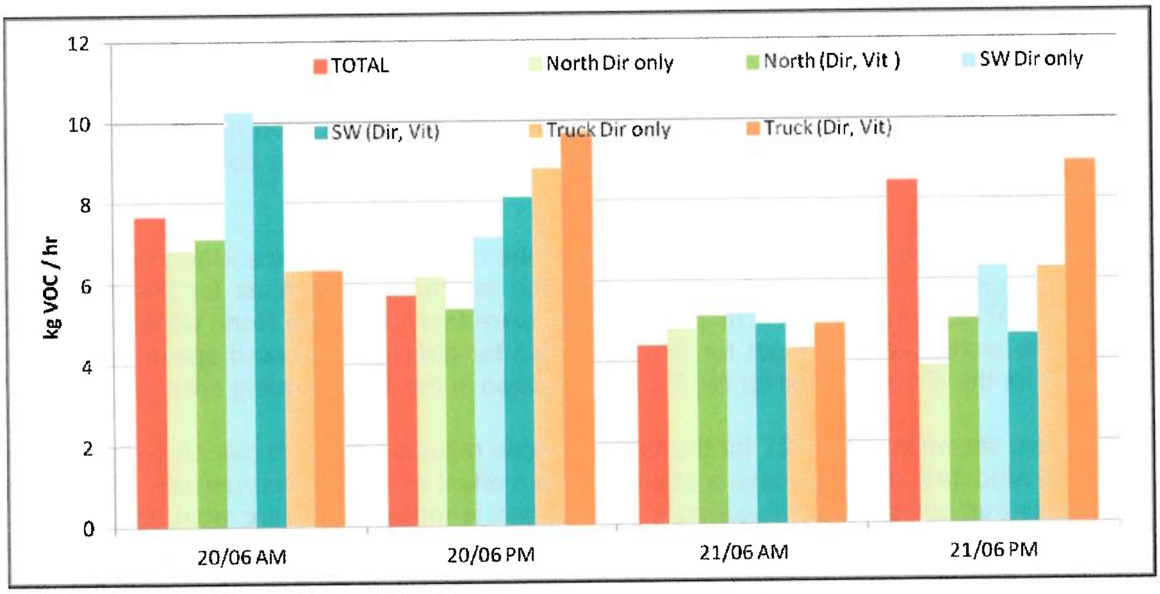


Figure 21 : wind data sensitivity test - RDM

5.5 SOLAR OCCULTATION FLUX (SOF) RESULTS

The SOF survey was planned in accordance with the protocol. The mapping of the refinery into areas for survey took account of the layout of the road structure. Additionally, SOF could access two zones to the north of the site unavailable to DIAL. Boundary measurements were also undertaken to delimit emissions from neighbouring facilities.

Two measurement sets were obtained: a mapping of the individual areas ("bottom up") and a mapping from the boundary ("top down").

The wind data was taken from one of the three masts, measuring the wind at 10 meters height, set up for the campaign and described previously. For the "bottom" up analysis this was the mast in the SE of the refinery near the truck-loading area. For the "top down" study assumptions about plume height were made to give wind-speeds and directions using data from this SE wind mast and from the wind lidar set up near to it. The wind lidar provides information on the variation of horizontal wind-speed and direction with height. Assumptions about the height of the plume were made to choose a reference speed and direction. The procedure for doing this is not very clear and the description of how wind-speed and directions are derived could be improved.

5.5.1 QUALITY CONTROL

The SOF protocol includes several conditions that must be met to satisfy the normative requirements. These are summarised in Table 19, however, in the light of these two field campaigns some improvements in these criteria should be made with respect to the number and timing of the scans.

Table 19 : QA/QC - SOF

QA/QC criteria	This campaign
Quantification based on at least 4 measurement transects per area source and per day	Quantifications based on more than 4 measurements per area (except E1). This was generally done but this criterion needs to be revisited to define the number and period of the measurements needed.
Solar angle higher than 20°	Reported data is for periods where the sun is more than 20° above the horizon. This criterion defines the available daytime hours available for measurement.
Wind speed between 1.5 and 12 m/s	Reported data is for 10 m wind speed on the reference mast between 1.5 and 12 m/s
For each source area the inflow from the background is determined	Generally performed, except for the WWT, but not reported. The protocol should be clear as to the relative importance of upwind and downwind flux.

Some other important information should be provided. SOF uses spectroscopic methods to quantify path-integrated concentrations by providing speciation information. In comparing mass-fluxes, or subtracting mass-fluxes the speciation, or a measure such as mean molecular weight, should be given. An example in this study was that an important source of cyclo-hexane was detected. This was (presumably) determined as part of a QA procedure to evaluate errors in the deconvolution of the measured spectrum. This procedure was not clear in the draft reporting.

It would be useful, for comparison purposes between SOF and DIAL to know if there are significant differences in speciation.

5.5.2 RESULTS

The summary results from the SOF surveys are given in Table 20 and Table 21. The four areas (4. North Tank Park, 9. Oil Pit, and the external facilities 1 and 2) have to be subtracted from the total. To estimate the total site emission the western boundary measurement is supplemented by 3 other area measurements to complete coverage of the site. These comprise another tank farm on the east side of the refinery, a point source identified as a vent and the main loading area for trucks.

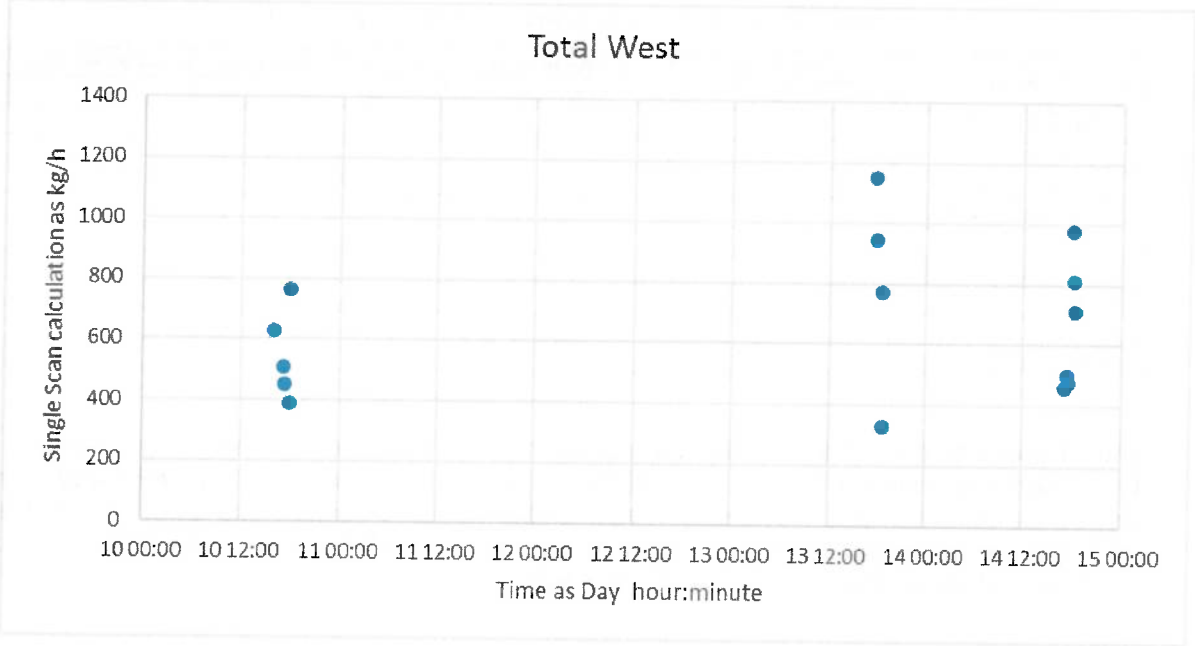
Table 20 : quantification results (top-down) - SOF

Source	Time period	Validated scans	VOC mass flux (median)	Standard deviation
	(days)	(number)	kg (VOC)/h	kg (VOC)/h
West part	3	15	634	242
1. East Tank Park	3	15	76	51
10. Vent Pipe	4	55	21	8
11. Truck Loading Area	3	13	5	12
External sources (to be subtracted)				
4. North Tank Park	2	11	12	4
9. Oil Pit	3	6	14	14
E1 External Facility 1	4	6	9	5
E1 External Facility 2	2	2	7	1
		Total:	694	

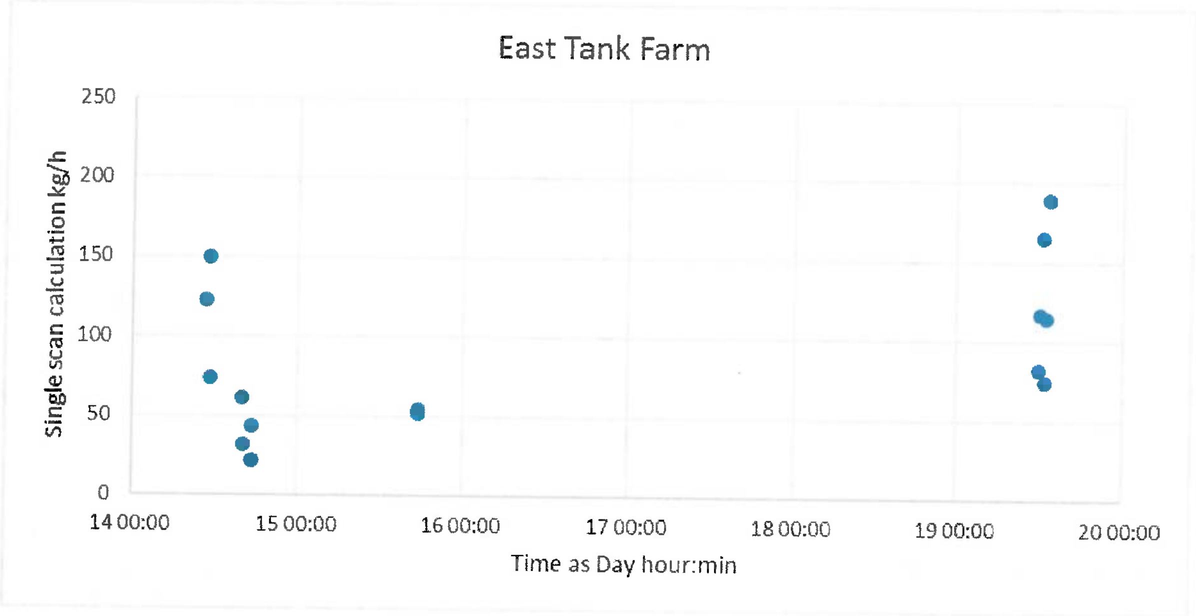
Using this top-down approach, the VOC flux for the whole site reported according to the SOF protocol was 694 kg/h, taken to the sum of the median values of the 4 measured areas less the sum of the median for the external sources.

The protocol selects the median, rather than the mean, of the combined data set of all validated (i.e. satisfying protocol requirements) runs because of the high variability between individual SOF scans generally leads to a skew distribution of results.

Measurements along the west part path provided the largest contribution to the flux estimate for the whole site. Individual results for the west part scans are shown as a time series below. The 15 scans were taken on 3 days (10th, 12th, 14th) and on each day the individual flux calculations showed a wide and broadly overlapping range. The median was 634 kg/h, mean 667 kg/h and the 95% confidence interval on the mean was 134 kg/h if all points were to have equal weighting. The external sources were small in comparison.



The second contributor, the east tank farm was also subjected to 15 scan measurements but with a greater number of repeats, on the 14th and 19th. Two scans on the 15th returned very similar results. The reported median flux was 76 kg/h, the mean 92 kg/h and the 95% confidence interval on the mean 28 kg/h if all points are weighted equally.

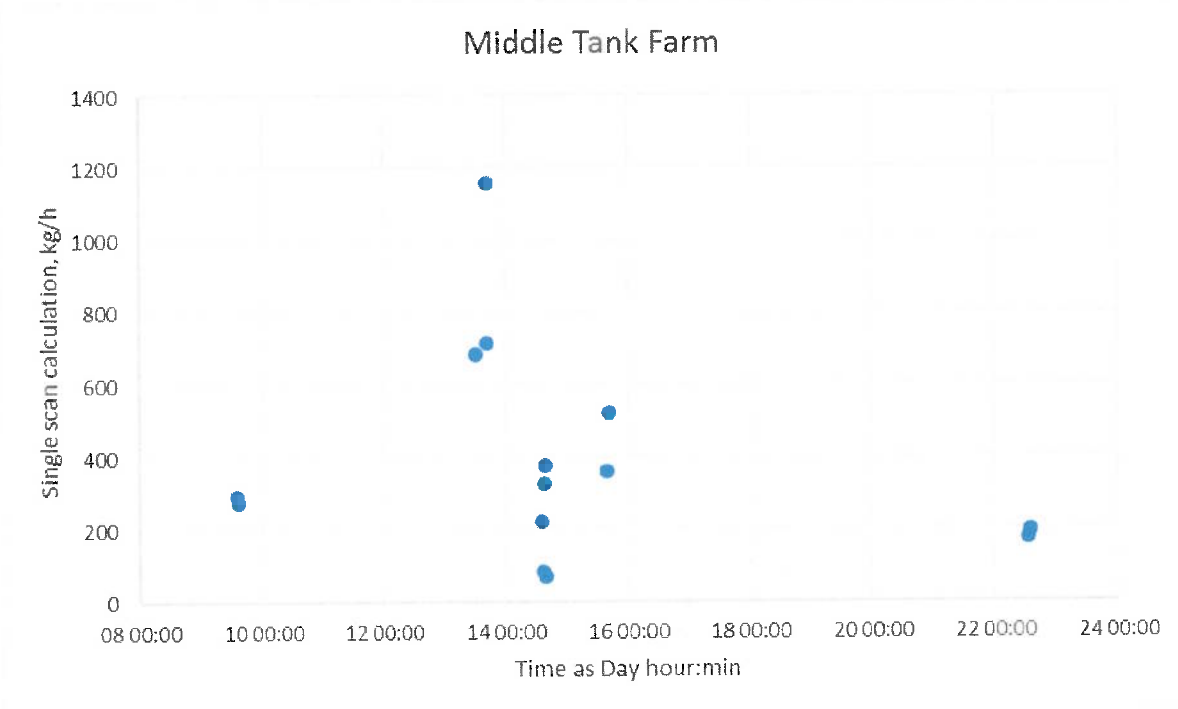


Using the "bottom up" approach the sum of the median fluxes for each of the 9 areas was 599 kg/h. The largest fluxes were seen at area 3, the Middle Tank Park where there was a known issue with a tank before the measurement survey began.

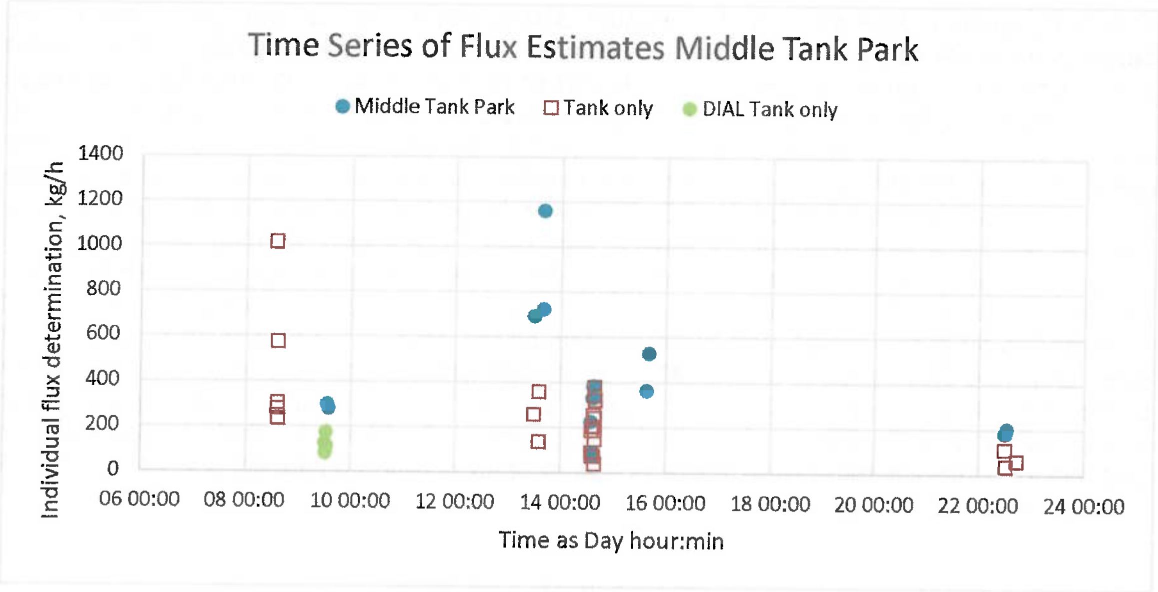
Table 21 : quantification results (bottom - up) - SOF

Source	Time period	Validated scans	VOC mass flux (median)	Standard deviation
	(days)	(number)	kg (VOC)/h	kg (VOC)/h
1. East Tank Park	3	15	76	51
2. West Tank Park	1	4	30	11
3. Middle Tank Park	5	14	316	296
5. PetroChemical Tank Park	6	50	61	30
6. Main Process	2	4	40	24
7. PetroChemical Process	3	7	37	25
8. WWT	2	6	13	3
10. Vent Pipe	4	55	21	8
11. Truck Loading Area	3	13	5	12
		Total:	599	

The 14 scans on the middle tank farm are shown below. The scan flux results were variable. There were few scans on the 9th, 13th and 22nd. The 13th saw a high scan value here and on also on the West side pass. The scan results on the 14th were variable and lower than on the 13th. If all the scans were of equal weight the median was 316 kg/h, the mean 396 kg/h and the 95% confidence interval on the mean 164 kg/h.



The very high median flux value for "3. Middle Tank Park" was attributed to a known issue with a tank which was strongly emitting. No other significant sources were found. This tank was investigated independently by SOF and also by DIAL, which gives an average flux of 125 kg/h on the 9th. The composite results are shown below. The statistics for the tank alone based on SOF runs are: mean (247 kg/h, median 219 kg/h, standard deviation 209 kg/h, 95% confidence limit on the mean 88 kg/h: Looking at the at the measurements overall, if the emissions from the middle tank park come essentially from one tank then the range of individual flux determinations on the 13th is from 136 to 1163 kg/h which seems too great to be a realistic change in an emission rate from a large source.



The apportionment of emissions is shown graphically below. :

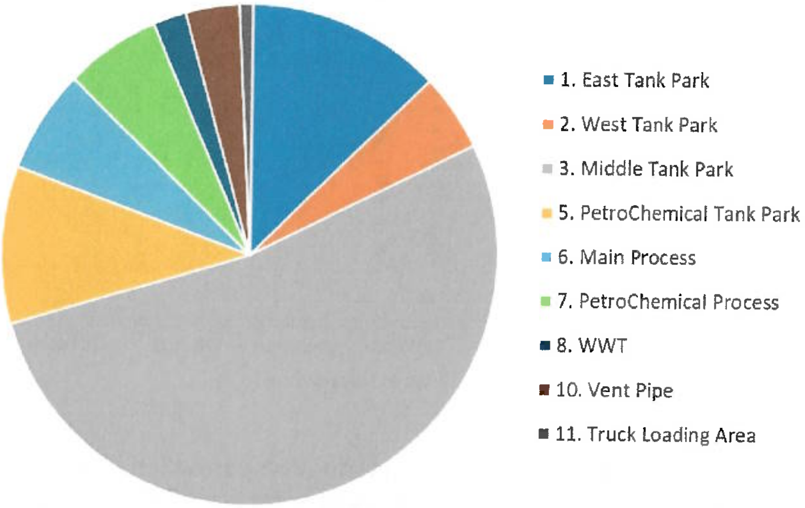
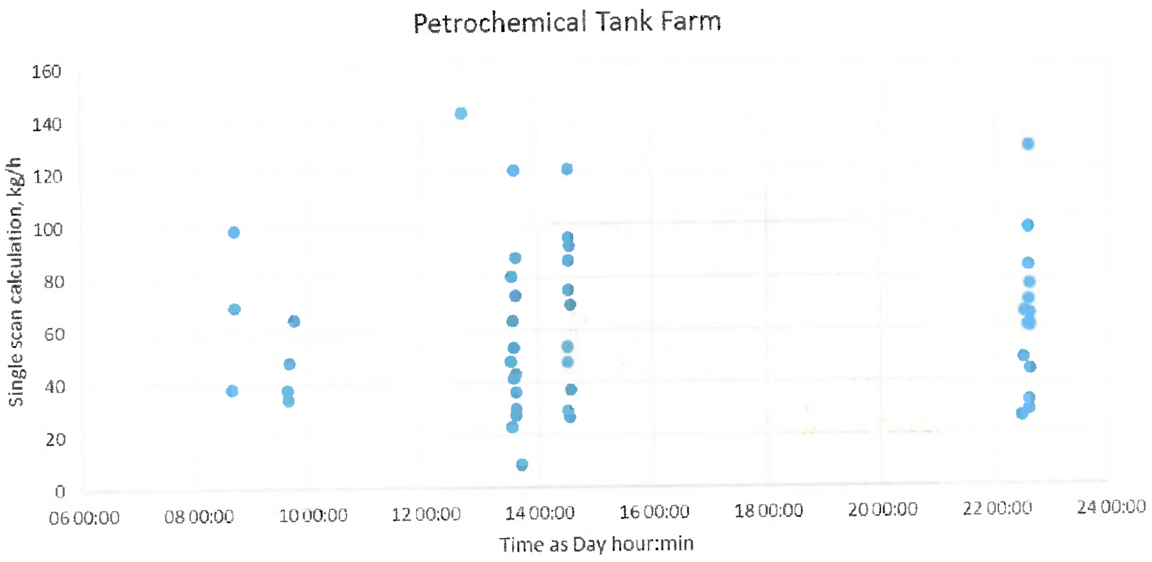


Figure 22 : emission sources apportionment - SOF

5.5.3 DISCUSSION

The "top down" and "bottom up" approaches for the SOF quantification assessed as sums of median values of individual SOF flux determinations were in reasonable agreement (differed by 100 kg/h) if the 95% confidence interval on mean for the west side scan path of 134 kg/h is taken as characteristic of confidence in the sum of the median emissions.

The SOF method does show that individual determinations of flux can vary dramatically between measurements taken at short time periods. This touches the question of cause and sufficiency in the number of measurements raised by FluxSense in the first field campaign which suggested that a larger number of scans should be used to improve confidence in the sample statistics. The timing of scans should also be addressed to evaluate this A key question is why should the individual flux determinations show such variation? It is worthwhile to examine one source, identified by SO. This was the emission of cyclohexane, tracked to a physical fault on a tank in the petrochemical tank park. There were no other known sources of cyclohexane so the correction for background concentrations is likely to be small. The median of the SOF flux determinations was 61 kg/h so this was a substantial source and subjected to 50 scans overall, with many repeats on the days 13th, 14th and 22nd. On each of those days the distribution of individual fluxes determinations was very similar, being evenly distributed between 2- and 120 kg/h. It seems unlikely that emissions are changing, or that this could be entirely due to changes in wind-speed, direction etc. that go into the flux calculation. It seems more likely that it is due to short duration fluctuations in concentration due to atmospheric turbulence.



In this case there is little or no background concentration correction. More generally it must be assumed that there is similar variability in the determination of background. It is therefore desirable to see some further work in the protocol to address the implications of variability of measurements for inferring source emissions. Also, to extend the presentation of results to look for evidence of changing background concentration vs changing emission strength. From the above examples the cyclo-hexane source seems likely invariant over the period of the trials whereas the emission from the tank in the Middle Tank Park is decreasing over the period.

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5.6 TRACER CORRELATION RESULTS

The Tracer Correlation (TC) technique was applied to four sources during the campaign. The scope for using the technique was limited on this site. The areas investigated were the water treatment area, the source referred to above as the vent pipe and releases from two tanks. The tracer used was N_2O. Following the protocol, the rate of release was measured (range 1-5 kg/h) and at a downwind position the ratio of VOC to N_2O measured using an intra-red spectrometer (FTIR). The emission rate of VOC is then estimated from the product of the concentration ratio and the N_2O release rate.

The location of the source must be known to use the TC method and the TC protocol calls for a leakage search and concentration mapping. Because the TC method is essentially ground based a means of searching for leaks that confirms the presence of ground-level concentrations increases the success rate.

The FTIR instrument was mounted in a van together with a sampling system drawing air at a height of 2.5 m. The resulting mobile system (Mobile extractive FTIR) was used on site between June 5th and June 22nd to map "hot spots". The results can be speciated to provide composition data. This screening technique was an effective companion to OGI, used to more precisely search for leaks, and to SOF which does not distinguish the height above ground. The survey has been useful to uncover emissions sources not found by other methods including a vacuum truck used for draining clearing. More generally the pattern of ground level concentration hot spots was a good fit with the understanding of the site emissions from the other techniques. Both the middle tank farm and the petrochemical tank farm cyclohexane source were detected.

The TC protocol requires that the tracer gas should then be positioned in such a way that it disperses in the same manner as the leakage gas. For a single leakage source, the tracer gas should be release in close proximity to the source gas leakage. For area sources or more complex volume source an assessment of the main leakage points inside the areas needs to be made and then tracer gas is released from one or multiple points. In order to estimate the performance of this measurements it is necessary to either: The draft report does not describe how the placement of the tracer was assessed or achieved.

he TC protocol requires that concentration measurements are made sufficiently far away to avoid building specific effects. Typically, at a separation of 5-10 times the structure characteristic dimension, so that the area/volume source has the dispersion characteristics of a point source,
- or measure at different distances and different wind directions to assess the variability of the obtained emissions,
- or use two different tracer gas sources, or move the position of the tracer gas, to make a sensitivity study of the variation in the obtained emissions.

In this campaign the tracer gas was measured using the MeFTIR, i.e. the tracer position was fixed, and the mobile unit used to map ground level concentrations of tracer and VOC. There is no discussion in the draft report of the distances over which the tracer could be a considered a unique marker of the specific source or how interference (background) concentrations of hydrocarbons are accounted or of the measurement averaging times used.

5.6.1 QUALITY CONTROL

According to the TC protocol, some validation criteria have to be fulfilled. Respect of these criteria during this campaign are summarized in the Table 22.

Table 22 : QA/QC - TC

QA/QC criteria	This campaign
Leak search to identify the leaking sources should be performed (Y/N)	Fulfilled part of the time, using OGI. The sources used for TC were all known from the other techniques.
Quantification based on at least 6 measurement transects per source and per day. (Y/N)	Fulfilled but only summary statistics reported, no information on spatial relationship.
Leak gas and tracer gas concentration above 3 σ detection limit (Y/N)	Fulfilled but not explicitly reported.
If complex area/volume source the plume should to be traversed entirely and at different distances. (Y/N)	Fulfilled but only summary statistics reported, no information on spatial relationship.
Leak gas and tracer gas should “correlate” in the spatial regime (Y/N)	Not demonstrated
Scan upwind and downwind for interfering sources, especially important to avoid VOC sources very close to the sampling point relative the distance to the tracer/main VOC source location. (Y/N)	Not reported.
Keep track of tracer release rates by weighing released amounts and usage of stable regulators or mass flow controllers.	Fulfilled but release rates not provided in draft report.
Wind criteria, 0.5-12 m/s	Fulfilled

5.6.2 RESULTS

The location of leaks using the mobile extractive FTIR (MeFTIR) system was consistent with the known emission pattern on the refinery. The selection of sources where the TC method could be used was constrained by the permitted use of tracer gas.

Only summary results were provided in the draft report and it is difficult to draw conclusions. As the distance from the source increases and tracer gas concentration decreases the effect of background or other source contribution will be to increase the hydrocarbon to tracer concentration ratio and hence the inferred release rate. Without knowing the relationship between measurement position and release it is difficult to assess errors. The tracer for cyclohexane should be less affected than the other sources because there are not expected to be other sources of cyclohexane.

The summary results are given below. The mean and median values are similar for all but the vent pipe suggesting symmetric distributions. The variance is quite high for the vent and tank sources, the cyclo-hexane source was identified on tank 614 which is consistent with the poorer performance of the TC method with the tracer on tank 603.

				VOC mass-flux				
		Time Period	Number of validated scans	Median	Mean	Sdev	95% confidence on mean	
		(days)		kg/h	kg/h	kg/h	kg/h	
WWT		1	11	9	9.2	2.6	1.7	
Vent Pipe		1	13	20	30	31	18.7	
Tank 603/614 (tracer on 614)		1	11	44	43	23	15.5	cyclohexane
Tank 603/614 (tracer on 603)		1	10	74	77	52	37.2	cyclohexane

Table 23 : VOC quantification results - TC

5.6.3 DISCUSSION

The tracer technique is an effective way to estimate release rates if the source is known and properly marked. The presentation of the results in the draft report is missing a lot of information that would assist the interpretation. The results of individual scan results with the absolute concentrations and ratios together with background concentrations would be useful.

For the cyclohexane tank the corresponding SOF assessment assuming all determinations have equal weight compare as:

Statistic	SOF	TC
Median, kg/h	61.26	44.00
Mean, kg/h	62.01	43.00
Standard Deviation, kg/h	29.50	23.00
95% confidence interval, kg/h	8.38	15.5

6. VALIDATED MEASUREMENT CRITERIA

Measurement criteria tested and validated during the two campaigns are summarized in the table below.

Table 24 : tested and validated measurement criteria (part 1)

Method	**DIAL**	**OGI**	**RDM**	**SOF**	**TC**
Tested emission sources size and applicability					
Site	👍	👎	Not tested	👍	👎
Section	👍	👎	👍	👍	👍
Main equipment	👍	👍	👍	👍	👍
Component	👎	👍	Not tested	👎	👎
Quantification of site emissions (>300 m x 300 m)					
Time period to achieve required uncertainty	2 to 3 weeks	Not applicable	Not tested	2 to 3 weeks	Not applicable
Uncertainty	undefined	Not applicable	Not tested	undefined	Not applicable
Limit of quantification	undefined	Not applicable	Not tested	undefined	Not applicable
Quantification of section emissions (50 m x 200 m)					
Time period to achieve required uncertainty	1 hour but measurements has to be repeated on different days / or different operating conditions	Not applicable	A few days, with winds > 2 m/s. Quantification only. Needs a perfect assessment of source	1 hour but measurements has to be repeated on different days / or different operating conditions	A few hours, with winds > 0.5 m/s. Quantification only.
Uncertainty	undefined	Not applicable	undefined	undefined	Undefined
Limit of quantification	undefined	Not applicable	undefined	undefined	undefined

Table 25 : tested and validated measurement criteria (part 2)

Method	**DIAL**	**OGI**	**RDM**	**SOF**	**TC**
Main equipment (1 – 30m) emission source identification and quantification					
Time period to achieve required uncertainty	1 hour but measurements has to be repeated on different days / or different operating conditions	1 hour. Identification only	A few days, with winds > 2 m/s. Quantification only but identification during measurement path. Needs a perfect assessment of source	1 hour but measurements has to be repeated on different days / or different operating conditions	A few hours, with winds > 0.5 m/s. Quantification only.
Uncertainty	10 – 20 %	Not applicable	30 - 40 % with winds > 2,0 m/s	30 – 40 % depending on obstruction and with winds > 1.5 m/s	30 %, need to well know the source
Limit of quantification	1 kg/h	Not applicable	5 kg/h	1 kg/h	1 kg/h
Characterisation of component emissions					
Time period to achieve required uncertainty	Not applicable	Few minutes. Identification only. Needs a few different scans from different location and skilled operator	Not tested	Not applicable	Not applicable
Uncertainty	Not applicable	Not applicable	Not tested	Not applicable	Not applicable
Limit of quantification	Not applicable	Not applicable	Not tested	Not applicable	Not applicable

7. DISCUSSION AND CONCLUSIONS

Two field campaigns have been carried out in accordance with M/514 and the objectives to provide information for the development of protocols for remote sensing and to test protocols in action under realistic conditions have been broadly met.

Campaign 1

Applying the techniques to the controlled releases under difficult conditions of high background concentration revealed several areas of development improvement for the protocols. Most significantly there is no discussion or presentation in the standardised results of how background concentrations are identified, and flux estimates calculated. The background signal was very significant for some of the trials to the degree that the treatment of background would influence the results.

The results as presented showed overall good agreement with the controlled release experiments. DIAL predicted fluxes were in-line with the release rates with uncertainty close to the proposed protocol value. SOF predicted fluxes were proportional to the release rates with a positive bias and much scatter in the individual results and uncertainty greater than the proposed protocol value. An example calculation to simulate the effect of increasing sample size suggested that increasing the number of scans to be averaged from 4 (or 6) to 16 would bring the difference between calculated flux and release rate @10 kg/h within the 95% confidence limit on the sample mean. The tracer correlation method with mobile sampling predicted fluxes proportional to the release rates and also with a positive bias. The variability was less, and the bias was less but analysis similar to that used for SOF showed that no increase in the number of samples taken would overcome the bias @10 kg/h. These latter exercises do not address the possibility that a different treatment of the background would have produced a different outcome but do highlight a need to understand why the short time measurement (not given for the TC with MeFTIR) techniques produced positive bias (over prediction). The RDM method underpredicted the release rates and this is likely due to the dispersion model over-predicting concentrations. Again, there was no discussion of the role of background concentrations on the results. Two tests where the RDM method gave far too high a flux could be eliminated on the grounds that the wind-speeds were too low. It seems more likely that these are outliers for unknown reasons. DIAL didn't report one of these and SOF didn't report the other.

The application of OGI as a detection method in the first campaign was successful.

Campaign 2

All the techniques were successfully applied at a cooperating industrial site (refinery) according to a test plan prepared and executed according to the draft standard protocol. The logistic aspects have not been reviewed.

A summary is given below of the results given by the techniques, rounded to whole numbers. The total for the chemical tank park for DIAL includes the dominating emission for the cyclo-hexane tank which, as is upscaled by a large factor due to post measurement correction for speciation.

The bottom up totals for SOF is greater than that for DIAL by 38% (which by numerical coincidence is close to the bias noted in the controlled release experiment) but the extent of the uncertainty on the flux estimates for the largest emitters is too great to draw conclusions on this difference. Sufficient to note that a wide range of emission values are assigned to the refinery areas.

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Table 26 Summary of results (rounded)

Refinery Area	SOF		DIAL		TC (MeFTIR)		RDM	
	median	stdev	mean	stdev	mean	stdev	mean	stdev
	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h
1. East Tank Park	76	51	42					
2. West Tank park	30	11	10					
3. Middle Tank Park	316	296	150	60				
5. Petrochemical Tank park	61	30	108	80	43	23		
6. Main Process Area	40	24	55					
7. Petrochemical Process Area	37	25	48					
8. Waste Water Treatment	13	3	7		9	3	12	4
10. Vent Pipe	21	8	7	2	30	31		
11. Truck Loading Area	11	12	11					
Total (bottom up)	605		437					
Total (top down)	694							

The OGI campaign was very successful. Where the other techniques indicated the probability of an emission source and emission was nearly always found. Detection from a range of ≥50m was typical of the largest releases and emissions from tanks could be detected from both across the tank roof and from the ground. The combination of a rapid scouting for high concentrations using a mobile sensor (here SOF and MeFTIR) followed by OGI was felt to be very efficient. Follow up from DIAL scans, the majority of cases, was more thorough. The campaign supports the use of OGI for detecting diffuse as well as fugitive sources.

The main learning points from the campaign is that there should be some standardisation of reporting across the protocols to make the assumptions and uncertainty budgets more transparent. It was not possible to follow and assess the importance of background concentrations and how their correction affected the reported results. There is generally a high commentary that background correction is difficult and significant, but this needs to be quantified.

The question of how to reduce uncertainty by increasing the number of scans using SOF, and TC (with MeFTIR), was raised. It is clear that there is a very high variability in individual flux assessments and that building a larger ensemble across several days of measurement risks confusing the variability due to flux determination with structural differences in emission rates with time. It does not seem a safe assumption that the variability in flux equates to variability in source emission rate in all cases.

There are many factors that go into the individual flux assessment that could influence the result. Sensitivity analysis needs to be developed on an even basis with clear identification of assumptions made with respect, for example, to wind direction and wind speed. There was much meteorological information gathered within both field campaigns, with multiple instrumentation. Little analysis has been done on the effect of changing the parameters in the calculations. The RDM model is shown to be sensitive to its inputs, which is not surprising for a model that is simulating detailed flow. DIAL has made some robustness tests to add to the uncertainty budget.

Speciation is not fully addressed in the protocols on reporting. No information is generally given on scaling factors applied due to the light absorption measurements to convert to mass-flux. This can have a large effect on result as was evidenced by the upscaling mass flow rates by a factor of 10 in the case of the cyclo-hexane work.

This assessment of the campaign results concludes that the objectives were met. The campaigns were very productive of data and showed that a real site could be surveyed and key messages on emissions developed using the principles.

It is recommended that the observations made above are followed through, especially formalising the treatment of background concentrations and incorporation of sensitivity assessments into the uncertainty budget. The initial thoughts provided by Fluxsense on managing variability between individual flux measurements and developing robust sampling rules for SOF and TC+MeFTIR should be developed. A goal would be to understand why the methods should evidence positive bias.

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FINALISED PROTOCOLS FOR VOC MONITORING TECHNIQUES USED AS PART OF CEN/TC264/WG38

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FINALISED PROTOCOLS FOR VOC MONITORING TECHNIQUES USED AS PART OF CEN/TC264/WG38

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CONTENTS

EXECUTIVE SUMMARY

This document contains the final test protocols for the all of the different VOC monitoring techniques selected as part of the WG38 standard. These techniques are: differential absorption lidar (DIAL), solar occultation flux (SOF), time correlation tracer (TCT) and reverse dispersion modelling (RDM). The protocols for each technique were tested during two field campaigns and revised according to the findings of these studies.

1 DIAL PROTOCOL

1.1 PERFORMANCE REQUIREMENTS

For practical applications in order to be able to monitor hydrocarbons, specifically VOCs, the DIAL shall be able to operate in the 3 µm region. To monitor aromatic specific compounds like benzene and toluene, the measurements shall be made in the UV region.

In order to characterise emissions from an industrial scale site, the DIAL system shall:

- Be mobile/transportable
- Transmit an eye safe beam, according to IEC 60825-1 ed3.0.
- Able to scan in the vertical and horizontal plane with an absolute pointing accuracy better than one degree. The relative movement precision in a vertical and horizontal scan shall be better than 0.1°.
- Able to record all the relevant information needed for the data analysis and quality controls.
- Able to perform the required calibrations and quality checks.
- Able to produce a narrow optical bandwidth in order to maximise sensitivity and reduce cross interference. The optical bandwidth should be equal or less than the gas absorption line. In the near infrared this is approximately 0,1 cm^{-1}.
- Able to ensure pulsed laser wavelength stability to avoid the selected differential absorption to drift. This can be achieved with stability better than the laser optical bandwidth that in the near infrared is approximately 0.1 cm^{-1}.
- Able to tune and control the on and off wavelengths.
- Able to ensure fast switching (>10 Hz) between on and off wavelengths to avoid atmospheric backscatter variation between the on and off return signals.
- Able to achieve a spatial resolution of 10-30 metres. This places a requirement on the laser pulse length (< 10 ns) and detector bandwidth (>2 MHz).
- The transmitted beam energy shall be such that the system is able to record a vertical scan in 10 min - 20 min with an acceptable signal to noise ratio.
- Able to deploy several wind sensors at different elevations.

As an example, these requirements would be meet by a DIAL system with the following characteristics:

- Transient digitizer with a 10 MHz - 20 MHz bandwidth.
- Infrared detector with 2 MHz - 10 MHz bandwidth.
- 0,5 m diameter light collection system.
- Laser power output greater than 1 mJ per pulse.

Some aspects of health and safety for specific applications may have implications on the design of the DIAL system. For example, for use on refineries the DIAL system should have a fire prevention system, which is maintained and tested (EN 54), and all electrical equipment should be routinely tested accordingly to IEC 60364.

1.2 APPLICATION OF THE METHOD

1.2.1 Before Campaign:

It is necessary to clearly define the measurements to be carried out. This includes the species to be measured, experimental arrangements (field setup) and likely interfering species. The following pre campaign activity should be carried out:

- Campaign logistics: this includes pre-site visits (if required) and checklists for ensuring the site are aware of the logistics of a DIAL measurement. A method statement covering the DIAL may be provided if required.

- Health and safety: this covers requirements for site specific health and safety, for example safety inductions or hot work permit systems. It also requires a risk assessment for site specific hazards and for example the provision of suitable PPE.

- List and identification of all the areas to be measured as specified by the customer on a site map (see measurement objective Section). Create a checklist of the areas to be measured and note:

    a) Ideal wind direction/s to measure each area considering available DIAL parking locations and potential upwind sources.

    b) Identify areas that can only be measured with a specific wind direction.

    c) Any information or requirement the customer may provide such as level of uncertainty or spatial resolution required.

- Selection of measuring locations: identification of suitable measurement locations from a technical viewpoint (measurement range, upwind sources etc.) and also from a site logistics (parking and potential obstructions etc.).

- Identification of likely emission sources: this requires information from the site, usually including site plans and existing emissions information. Potential sources off-site should also be considered.

- Identification of potential interfering species: for complex sites this may require process information or preliminary air-sample analysis taken as part of the pre-site visit in order to identify species with potentially interfering absorption features. With this information it is also possible to advice the site if ethane measurements are necessary in order to improve VOC measurements accuracy.

- Assessment of wind field: pre-site planning includes an assessment of the likely wind conditions, and what existing meteorological data are available.

- Identification of the meteorological mast location in a clear area. If site topography is complex, evaluate the possibility to deploy a second meteorological station.

- Check the site magnetic declination angle during the measurement period.

1.2.2 Set-up and initial tasks:

The following should be carried out on site at the start of the campaign:

- Site specific requirements such as safety inspection and induction course.
- Site visit if a pre-site visit was not carried out, check/agree with site personnel all the suitable measurement locations and update the checklist of the areas to be measured accordingly.
- Agree the procedure for changing DIAL location with site operators, e.g. permit requirement, identify contact, communication protocol.
- Agree what to do in an emergency/ evacuation i.e. shutdown procedure.
- Set-up the meteorological sensors at the agreed locations and check the functionality.
- Assure that all the instruments and logger clocks are at the same time reference.
- Set-up the lasers; for each species to be measured, the on and off DIAL wavelengths shall be selected such that:

a) The differential absorption between the wavelengths is of an appropriate level to achieve the required sensitivity. This requires pre-assessment of the likely emission rate and the system performance.

b) There are no absorption features from interference species, this requires knowledge of likely emission sources. As minimal the wavelengths shall be checked for common atmospheric species interference. This can be achieved with an appropriate spectral database such as HITRAN.

c) The on and off wavelengths should be as close as possible to minimize possible interferences.

d) A protocol shall be in place to ensure that the laser is tuned to the corrected wavelength and that the wavelength doesn’t drift.

- Set-up the detector and perform acquisition test.
- Check long-term weather forecast for the measurement period. This in, combination with the checklist of the areas to be measured under certain wind condition, allows a measurement plan to be defined. The plan should be updated daily with short-term weather forecast. This in turn will include:

    a) Communication each day to the site of the possible DIAL locations facilitating the work permit.

    b) Identification in advance possible locations for the portable wind sensor facilitating the site work permit.

    c) Identification in advance the necessity to perform upwind scans for certain site areas.

    d) Quick reaction if the actual wind direction during the day is not as forecast.

1.2.3 Daily Tasks:

At the beginning of the measurement period ensure:

- Staff complied with local rules, i.e. signed in on site register.
- If necessary, apply for a work permit.
- Ensure that staff are familiar with local safety protocols.
- Logging of the met data is started.
- Optical source is set-up at the correct wavelength accordingly to the spectral scan test procedure.

The following should be carried out for each measurement location

- Determine the measurement plan and move the DIAL to a location with clearest possible field of view.
- If possible, deploy a portable wind sensor along the DIAL measuring line-of-sight to assess local wind at a relatively low elevation.
- Work place safety assessment for the planned measurement location.

While measuring record the following information:

- Measurement locations, met location and lines-of-sight on site map.
- File name, time, scanner azimuth and elevation, other specific information of the scan.
- Site information
- The time when periodically measurements to check the detection and acquisition system response are made.
- Update the notes on the checklist of areas to be measured, record:
  a) If the measurement of a specific area is completed.
  b) If the measurement should be repeated because it was made in a non-ideal condition or if more measurements are needed to achieve the required uncertainty.
  c) If the upwind source is measured, to be measured or not required.
  d) If an air sample has been taken.

At the end of the measurement period ensure that:

- All the met data is downloaded.
- All the data is saved and backed up.

1.2.4 Measurement strategy:

The selection of the area(s) to be measured depends on several factors driven by wind conditions, available parking locations and line-of-sight:

- For a given wind direction the area to be measured should be chosen in order of priority such as:

  a) The areas that can only be measured with that specific wind direction are prioritised.

  b) At low wind speed it is preferable to measure, if possible, a relatively open area rather than an area with potentially more complex wind profile.

  c) Considering the range resolution of the DIAL system, depending upon the current meteorological conditions and the system sensitivity, a DIAL location is available to measure the area of interest.

  d) The area under investigation is clear from upwind sources.

  e) If upwind sources are present, they can either be measured from the same location or from a different DIAL location under similar wind conditions.

  f) When moving to a new location the measurement of the upwind contribution to the area that was just measured should be prioritised if such measurement is needed and possible.

  g) If the site layout is such that several areas are downwind of each other, the first area to be measured should be (if possible) the one that has no upwind contribution from the rest of the site. The second area to be measure should be the one directly downwind of the first area and so on. In this way for each area the upwind contribution would be measured just before the area itself is measured.

- The choice of the scan line-of-sight should consider that:
  a) At close distance from the emission source the wind field could potentially have a complex behaviour due to the presence of buildings. If possible, a portable wind sensor should be deployed along the DIAL measuring line-of-sight.

  b) The higher the wind speed the faster the emissions are diluted leading to a reduction in ambient concentration. Higher concentrations are therefore obtained closer to the emission area.

  c) The DIAL method usually cannot measure in the first 50 m to 100 m from the DIAL as consequence of the optical assembly.

A scan should be setup in a way that:

- The measuring line-of-sight is as clear as possible from obstacles.

- The highest elevation angle is high enough to enclose a plume emitted from the highest point of the area under investigation. Such elevation can be estimated based on the convective conditions and observing the behaviour of other visible plumes on site.

- If a plume is observed from the last elevation angle, extra lines should be added in the following scan to capture the whole plume.

- If a broad slope above background is observed in the last elevation line, this could be due to a diffuse upwind source/background or to a diffuse source from the area under investigation. In the latter case, extra lines should be added in the following scan to capture the whole source. In the former case, there is no need to add extra lines and the slope above background can be used at the analysis stage to estimate the upwind background contribution in the measuring plane when a specific upwind measurement is not available. Which of the two cases is the most likely scenario should be assessed based on site layout and knowledge of potential upwind sources.

- The selected DIAL scan rate is as fast as possible within the limit imposed by the detection limit (signal to noise) at the range where a plume from the area under investigation is expected and/or observed.
- The scan total acquisition time is less than 20 minutes, if possible.
- The step-size between two consecutive lines is not be bigger than two degrees.
- Considering the above restrictions, the number of measuring lines capturing a plume should be maximised.
- If during the measurements the signal to noise drop below an acceptable level for the required range either increase the averaging time or select a different measurement area where a shorter range is required.

In order to achieve the quality requirements of the measurement objective these procedures should be followed:

- Carry out a set of at least four DIAL scans for each line-of-sight to minimise the uncertainty.
- Repeat one or two extra sets of measurements of the same area along different scan lines or from different locations or on a different day to decrease the uncertainty associated with that area if specified by the measurement objective.
- Measure upwind sources if present.
- Carry out all the necessary quality assurance measurements.
- If the detector bandwidth can be varied, select the most appropriate value. Higher the bandwidth (i.e. higher spatial resolution) greater is the noise. Higher spatial resolution can therefore be selected in favourable atmospheric conditions. In unfavourable conditions when the DIAL signal to noise ratio is low, smaller bandwidth may be selected.
- Take air samples at locations which would provide an indication of the actual speciation of the emission sources sampled by the DIAL.

1.3 QUALITY CONTROL

1.3.1 General

Quality assurance of the emission measurements is necessary. These procedures require detailed project planning and progress monitoring with project subject to regular internal reviews and quality audits at measurement institutions.

Care should be taken when measurements are made with wind speeds outside the 1- 15 m/s range and with variable wind direction.

1.3.2 Spectroscopic calibration procedures

1.3.2.1 *General*

A crucial requirement for high quality DIAL measurements is accurate knowledge of the actual differential absorption coefficients that are appropriate for a particular measurement. The following calibration procedures should be employed to ensure the spectroscopic quality, and therefore the accuracy of the differential absorption measurement. The three key elements that need to be verified through these checks are that:

- A suitable calibration reference cell prepared with a known (concentration∗pathlength) parameter.
- The laser source is operating with a suitably narrow linewidth to properly resolve the spectral feature of interest.
- The wavelength of the laser source is fixed and stable on the appropriate on and off resonant wavelengths.

1.3.2.2 *Calibration gases*

A standard gas mixture of the target gas (or an appropriate proxy - e.g., propane or pentane for the total hydrocarbon measurements) should be used to provide the reference for the spectroscopic measurements. These standards should be, where possible, gravimetrically prepared, internationally-traceable reference gas mixtures with absolute volume mixing ratio (VMR) accuracies of 0,5 % or better.

1.3.2.3 *Calibration cell*

Direct measure of the transmission through a calibration cell filled to atmospheric pressure with the reference gas. This ensures that the pressure broadening, and therefore the linewidth, is the same for the calibration gas as in the ambient environment.

1.3.2.4 *Spectral scans*

A spectral scan of the relevant absorption feature should be carried out on a daily basis. The measured absorption feature is compared to the expected one. This provides confirmation that the cell has been filled correctly and that the laser source linewidth is correct. If the measured width of the absorption features differs significantly (typically by more than 0.2 cm^{-1}) from the expected widths then this indicates an issue with the laser source bandwidth and a number of laser checks should be carried out.

1.3.2.5 *Continuous spectral monitoring*

Having established that a suitable reference cell is available and the laser source linewidth is correct, the on- and off-resonant wavelengths are set to their chosen values for the DIAL measurements. A system to check the wavelengths do not drift from the expected value should be in place and logged continuously.

1.3.2.6 *Check of system performance*

In addition to verifying the spectroscopic performance of the laser source, a check that the full system is measuring correctly should be carried out at least once a day using a standard gas.
These checks should be carried out periodically and if they exceed more than 20% of the expected value the system should be adjusted to bring it back to normal compliance.

1.3.3 Meteorological sensors calibration

The meteorological sensor should be calibrated once a year by the manufacturer. The calibration certificates may provide a calibration factor for the wind speed and wind direction readings. If data

loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.
In addition, the different sensors should be compared side-by-side in the field to provide a further check on their correct function.

1.4 DATA ANALYSIS

1.4.1 General

The data acquired has to be analysed to give the range-resolved concentration along each line-of-sight. The data analysis process consists of the following steps:

1.4.1.1 *Background subtraction*

Any DC background value is subtracted from the signals. This measured background takes account of any DC signal offset which may be present due to electronic offsets and from incident background radiation. The background level is derived from the average value of the far field of the returned Lidar signal where no significant levels of backscattered light is present.

1.4.1.2 *Normalization for variation in transmitted energy*

The two signal returns are normalized using the monitored values of the transmitted energy for the on and off resonant wavelength pulses. The mean transmitted energy is used to normalize the averaged return signal. For this application, this has been shown to be equivalent to normalizing individual shots against transmitted energy and then averaging the normalized values.

1.4.1.3 *Calculation of path-integrated concentration*

The path-integrated concentration of the target species, out to the range r, is calculated. The absorption coefficients used in this calculation is derived from high-resolution spectroscopy.

1.4.1.4 *Derivation of range-resolved concentrations*

The integrated concentration profiles are piecewise differentiated with a selectable range resolution, to give the range-resolved concentration along the line-of-sight.

1.4.1.5 *Calculation of emission fluxes*

Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile. Care should be taken to reduce artefacts due to the difference in data density at different ranges, due to the polar scanning format of the data. The emission flux is then determined using the concentration profile together with meteorological data.
The emitted flux is calculated using the following mathematical steps:

- The product is formed of the gas concentration measured with the DIAL technique at a given point in space and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.

- This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.

- This array of flux results is then integrated over the complete concentration profile to produce a value for the total emitted flux.

A logarithmic wind profile can be used to describe the vertical distribution of the wind by using at least two wind speed sensors at different heights. Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large spatial variations since, for example, errors in the wind speed in regions where large concentrations are present will significantly affect the accuracy of the results. In such cases, is advisable to use more wind speed sensors at different heights in order to calculates the variation of wind speed with height, as a function of various parameters (such as the roughness of the terrain). At close distance from the emission source the wind field could potentially have a complex behaviour due to the presence of buildings increasing the uncertainty in the determination of the emitted flux. This can be reduced by deploying a portable wind sensor along the DIAL measuring line-of-sight to either use the wind speed for the wind profile determination or to scale the wind profile derived from the fixed mast sensors to match the portable wind speed at the portable elevation. Local terrain effect can be important and introduce systematic bias in flux determinations. The ground elevation where the wind measurement system is located needs to be checked to establish if it is similar to the ground level downwind of the source; if not, the ground elevation along the scan line where the plume is detected should be used as the reference point for establishing the wind profile. The calculated wind field is then combined with the measured gas concentration profile using the procedure described above.

The spatial averaging applied to the DIAL data can be adjusted in post processing, to take account of low signals due to atmospheric backscatter. This primarily affects the production of concentration plots. These are a secondary data product used to provide visual indications of plume location and as an aid to source identification. The averaging used has minimal effect on calculation of the emission fluxes, which are the main data product.

2 SOF PROTOCOL

2.1 B.1 PERFORMANCE REQUIREMENTS

For practical applications in order to be able to monitor gas emissions from an industrial scale site, the SOF (both IR and UV) system shall be:

– firmly mounted on a mobile platform that enables direct infrared solar measurements for IR-SOF, direct UV solar measurements or zenith sky measurements for UV-SOF.

– equipped with a global positioning system with at least 1 s temporal sampling time.

– able to perform high temporal sampling (< 5 s) and vibrational noise levels below the specified criteria while moving up to 70 km/h.

– capable of showing real time column data and platform position on a map.

– used together with continuous wind measurements (unobstructed wind at 10 m) and frequent vertical profiling of the wind.

For practical applications in order to be able to monitor general VOC emissions (alkanes, alcohol, alkenes) and other species (e.g. NH3), from an industrial scale site, the SOF system shall be:

– equipped with a fast infrared spectrometer (typically FTIR) with spectral resolution of 1 cm_{-1} or better covering the spectral region 800 cm_{-1} to 3100 cm_{-1} (3.2-12.5 µm).

– equipped with fast response solar tracker with a precision of 1 mrad while moving.

For practical applications in order to be able to monitor SO_2, NO_2 and HCHO emissions from an industrial scale site, the system shall be:

– equipped with a fast UV/visible spectrometer with a spectral resolution of 1 nm or better covering the spectral region 305 to 365 nm.

– equipped with an optical fibre and a zenith viewing telescope.

2.2 APPLICATION OF THE METHOD

2.2.1 Measurements planning

It is critical to thoroughly plan the survey before carrying out the measurements. This includes the following:

☐ Campaign logistics: this includes site pre-visit meeting (if required) or checklists for ensuring the site are aware of the logistics of the measurements. A SOF methodology description may be provided if required. Also make sure that the site is operating normally during the time of the measurements. Periods of major plant revisions should be avoided. Ask staff for a detailed site map/overview. Site orientation: Identifying site areas and measurement roads considering different wind directions and solar paths (to predict where shadows exists during the course of the day). Ask site staff about how to get access to roads in any ATEX-areas. Extract, based on this information, ideal wind conditions for measurements of the site and areas.

☐ Identification of likely emission sources: this requires information from the site, usually including site plans and existing emissions information. Potential background sources off-site should also be considered.

☐ Potential interfering species: for complex sites this may require process information or preliminary air sample analysis taken as part of the campaign measurements.

☐ Meteorology assessment: get information on typical wind directions and solar conditions and other relevant meteorological data. Try to access data from any nearby meteorological stations.

2.2.2 Selection of gas species to be measured

Selection of optical channels for SOF:
- Obtain information about the typical gas-mixture in the emissions and handled products of the site de Make complementary composition measurements, such as canister analysis or high-resolution MeFTIR, if needed.
- Decide on the time sharing between the different optical channels (alkanes, alkenes or other species).

2.2.3 Measurement strategy

Identify an optimal meteorological mast location, preferably a clear and flat area on the upwind side of the facility. If site topography is complex and different wind directions are anticipated, deploy a second and possibly third meteorological station to ascertain that the unobscured wind is always available. The unobscured (main) wind should be measured at 10 m altitude. Optionally deploy or use an available on-site mast with a height of +30 m to get above tank height. Combine with wind profiler or frequent balloon wind soundings.

Figure out ideal SOF measurement transects for each site area based on the weather forecast for the actual measurements period. Use the following daily strategy:

a) Communicate each day to the site the possible SOF locations facilitating the work permit.

b) Quickly react if the actual wind direction during the day deviates from the forecast.

For a given wind direction, the area to measure should be chosen such as:

a) The area under investigation is clear from strong upwind/background sources. Avoid areas with high inflows or where the background cannot be estimated.

b) When measuring at close distance from the emission source, i.e. close to low level sources, such as water treatment ponds and sewers, a ground level wind sensor should be deployed close to the SOF measurement transect.

2.2.4 Set-up and initial tasks

General:

- Site specific requirements such as safety inspection and introduction course.

- Agree on the procedure for changing SOF location with site operators and prepare any special permits to drive in ATEX areas (with a safety guard).

- Assure safe operation of the SOF vehicle.

Vehicle:

- Check SOF vehicle status according to safety and performance.
- Check that warning lights and signage are mounted and operational.
- For measurements inside industrial areas the equipment should be equipped with a single safety switch by which all instruments can be turned off, in case of emergency.
- Make sure that car battery pack is fully charged.
- Make sure any loose items are stowed away securely.

Instruments:

- Turn on instruments and make sure that detectors are properly cooled.
- Optimize signals by optical alignment.
- Clean mirrors and optics if necessary
- Make a rotational alignment test and determine the resulting column. Tolerance: ±2 mg/m^2 in any direction while standing still.
- Check spectral resolution and intensity response. Check that the width of narrowest absorption lines in the measured solar spectra are within the set spectral resolution. Tolerance within 20%.
- For the UV/visible spectrometer run a daily line shape test to calibrate the wavelength and to convert the absorption cross sections to the appropriate special resolution.
- Check the time synchronization of all instruments and computers against GPS-time, Tolerance 1s.

GPS:

- Check that the GPS data are available and correct.

Wind:

- Set-up the meteorological sensors at the agreed locations and check the functionality.
- Align sensor correctly (toward magnetic north) using a compass. Tolerance: ±5^o.
- Erect the wind mast vertically and secure it firmly.
- Check that wind information is available and reasonable.
- Check the time difference of logger and computer. Tolerance 1 s.

2.2.5 Measurements

Before starting the measurements, ensure:

- Staff is signed in on site register (if required).
- If necessary, apply for a work permit.

- Ensure that staff is familiar with local safety protocols.
- Logging of the meteorological data is started.

- Determine the measurement plan/strategy for the day.

Measurement procedure:

- During the measurements check that the retrieved columns change less than 5 mg/m$_2$ when turning in different directions. If the changes are larger a recalibration of the rotational alignment should be done or a note to account for this in the uncertainty evaluation during post analysis. Note that this effect usually depends on the solar angle and the offset is usually worse for low solar angles.

- For each source multiple measurement transects per day are required with accepted quality. The solar angle above horizon should be sufficiently high and the average wind during the transects within the required wind speed.

- For each area source, the inflow from the background should be determined, this should be done by measuring in a “box” around the source area for at least half of the measurements. In a dense industrial area it is necessary to make box measurements while for more isolated sources the background levels can also be determined from the baseline of the downwind SOF measurements, if upwind roads are not available. Extra care should be taken if there is large source upwind the area source. Such sources can meander in and out of the area source relatively quickly and this effect is more pronounced the bigger source and the further away it is located. If such a source is identified it is important to localize and quantify it, in order to be able to discard its effect in later measurements.

- The measurements should be done at highest driving speed possible, taking into account speed limits and the noise of the retrieved columns, in order to “freeze” horizontal movement of the plume during the scan. Higher speed causes vibrational noise, depending on the quality of the road, and it also increases the influence of shadows. For instance one should adapt the speed to minimize the effect from periodically occurring shadows, such as light posts.

- Avoid measurement situations when the observed sun cuts through the emission plume from the upwind side, and when it goes below high emitting objects, such as flares. This is usually a problem when measuring too close to high structures or process area with plume lift, in combination with low solar angles.

- Keep track of wind directions and measured columns/concentrations so that the entire plume from a facility is captured.

- Always try to start new measurements outside the plume. Although this can be fixed in the post analysis, it significantly improves the real time interpretation and analysis.

- When measuring in the alkene channel around 10 μm, one should measure dark spectra that will be subtracted from all other spectra. Such measurements, carried out by pointing the solar tracker away from the sun toward typical sky, should be carried out frequently, at least every hour, with the same settings as the solar measurements.

- Take notes and photos on interesting findings and events.

- If unexpected measurement results are obtained, such as high emissions or higher than previously experienced, try to check in real time whether these could be explained by for instance intermittent emissions due to for instance maintenance activity such as tank cleaning operation or ship or truck loading. If feasible, take contact with the industrial site and discuss whether the emissions can be explained by some known activity.

- Check the wind meter on a regular basis to make sure that it is operational.
- Check the GPS sensor on a regular basis to make sure that it is operational.

At the end of the measurement day ensure that:

- All SOF data are saved and backed up.
- All met data are downloaded, saved and backed up.
- Demount the wind mast if it is not in a secure location
- Update survey documents. If feasible discuss measurements results with the industrial site and collect complementary data such as tank height level, flaring activity, etc.
- Turn off instruments.
- Charge measurement vehicle, and data logger batteries.
- Make sure that instruments are well protected inside the vehicle from rain/moisture.

2.3 QUALITY CONTROL

2.3.1 General

Quality checks and quality assurance and measures are performed at several levels. In general most checks are done prior to measurement, including powering up the equipment, checking operating parameters, and test the instruments. The purpose is to run operational checks to catch problems prior to field deployment and repair all malfunctioning equipment.

2.3.2 Spectroscopic calibration procedures

2.3.2.1 *General*

The SOF instrument does not need calibration prior to the measurements and instead one relies on published line parameters or absorption cross sections from the literature available in data bases. This is appropriate as long as the instrument is well aligned and its spectral response is well characterized. It should have the same response in all pointing directions relative to the sun.

2.3.2.2 *Calibration*

Published line parameters, for instance from the HITRAN database (Rothman 2003) should be used to simulate absorption spectra for atmospheric background species (H_2O, HDO, CO_2, CH_4) at the actual pressure, temperature and instrumental resolution of the measurements. For the retrievals of the VOC species, high resolution calibration spectra can be obtained from data bases, such as the PNL (Pacific Northwest Laboratory) database (Sharpe, 2004). The uncertainty in the absorption strength of the calibration spectra is here about 4 %. To use these cross sections they have to be degraded to the spectral resolution of the instrument by convolution with the instrument line-shape. The advantage with this approach is the traceability since it does not require calibration. However, the actual line shape of the instrument is not measured and instead one relies on the accuracy of the theoretical line shape in the retrieval. An optional way to obtain calibration spectra of VOCs is to measure absorbance spectra directly by using a calibration cell containing calibration mixtures of VOCs in the solar beam.

2.3.3 Meteorological sensors calibration

The meteorological sensor should be calibrated once a year by the manufacturer or by a reference wind meter.

The calibration certificates may provide a calibration factor for the wind speed and wind direction readings. If data loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.

In addition, the different sensors should be compared side-by-side in the field to provide a further check on their correct function. For instance if mechanical anemometers are being used the bearings can be worn causing lower apparent wind speeds which is difficult to identify afterwards. This must therefore be checked by relatively short term comparisons in the field or lab to a reference anemometer once per year.

2.3.4 Required QC checks in the field

For the SOF instrument several QC procedures should be carried out prior to conducting the spectral measurements on each day. This includes checking that the instruments work in general and that the spectral response is appropriate and independent on the positioning of the instrument, relative to the sun.

This should be done by measuring solar spectra at the highest resolution and investigate the m maximum intensity and width and line position of narrow absorption lines which have an apparent linewidth which is similar to the spectral resolution of the instruments. There are many such narrow lines. For instance the solar absorption line at around 2158 cm^{-1} at high solar angles is suitable for this purpose, corresponding to the atmospheric absorption of CO. Note that the width of the atmospheric lines is usually dependent on the solar angle. In the QC procedure it should be checked that the width of the measured narrow absorption lines is not more than 20 % wider than the nominal theoretical width of the instrument and that the line position is not shifted more than 0.2 cm^{-1} towards lower wavenumbers. If this is not the case, a realignment of the SOF instrument is required. If the linewidth and line position is acceptable, the next step is to make sure that the same line shape is achieved when the SOF system is directed in four 90^{o} directions relative to the sun. If the linewidth is within 5 % and the position is not shifted more than 0.2 cm^{-1} and intensity is within 10 % for all four directions then the quality is acceptable. If not, the instruments should be rotationally aligned. The above mentioned procedure should be performed on each measurement day.

The next step in the QC procedure is to run the instrument with the actual resolution used for measuring the VOCs, typically 8 cm^{-1}. Measurements are again carried out with the instrument positioned in four 90^{o} directions relative to the sun and then the columns (path integrated concentration) of VOCs should be retrieved. These should change less than 2 mg/m^2 in the different directions. The same test should be carried out several times every measurement day to be used for the error estimation in the reporting.

During the measurements it should be checked in the real time data that the precision of the instruments is normal, and whether upwind emission sources or other short term activities influence the measurements.

Prior to each SOF transect it should be checked that the spectra have an intensity which is less than 25 % from saturation. If one uses an FTIR, saturation effects can also be seen as baseline effects in dark spectral regions.

For the UV/visible spectrometer run a daily line-shape test by holding a low pressure mercury lamp in front of the zenith viewing telescope. The emission lines should be used for wavelength calibration and to convert the cross section to the appropriate special resolution of the instrument.

2.4 DATA ANALYSIS

2.4.1 General

General data analysis is based on the following:

– Retrieve the path average concentration (column) of VOCs from the solar spectra

☐ Retrieve gas fluxes

☐ Identify source emission areas and make statistics over their emissions over multiple days for the different source areas.

2.4.2 Calculation of path-integrated concentration

The retrieval of the path integrated concentration (column) from the infrared spectra should be performed by spectral fitting of calibration spectra to the measured SOF spectra. In addition to the fitting of VOC spectra, one should also fit background species such as H_2O CO_2 and CH_4.

In the spectral retrieval a reference spectrum should be chosen from a region of the measurement transect where it can be assumed that the target gas concentration is near zero and which corresponds to the lowest column value measured, i.e. typically and upwind spectrum.

The spectral retrieval shall be based on the Beer-Lambert law, which states that the logarithm of the intensity ratio for the light which is absorbed by the gas is proportional to the path averaged concentration. The retrieval algorithm can be implemented in different ways, but usually some kind of nonlinear fitting scheme is required. One solution is to work directly in the logarithmic space. Here the logarithm of the reference spectrum is fitted to the measured spectrum together with absorption cross sections of the gas species to be retrieved. This approach makes it possible to account for wavelength shifts in the spectra and also to include several reference spectra in the fit, which results in efficient removal of the influence of the upper atmosphere. However, such a scheme is suitable only for small absorbers.

For measurements of alkenes, alkadienes and ammonia the spectral region between 750cm^{-1} and 1000 cm^{-1} should be used with a spectral resolution corresponding to 1 cm^{-1} or better, for sufficient specificity. In the spectral evaluation routine it is required that background species, such as H_2O and CO_2, are fitted with good precision together with the main absorbing VOC species in the spectral region, e.g. ethene, propene, 1-butene, butadiene and ammonia. A thermal background spectrum should be recorded at regular intervals by measuring with the solar tracker pointed to the cold sky. The background thermal spectrum should be subtracted from each recorded solar spectrum.

For measurements of alkanes, the spectral region between 2700 cm^{-1} and 3005 cm^{-1} (CH- stretch region) should be used with a resolution of 4 cm^{-1} to 8 cm^{-1}, for improved signal to noise. The absorption features of the different alkanes are similar and interfere with each other and specificity is therefore poor. However, since the number of absorbing C-H-bonds is directly related to the molecular mass, the total alkane mass can be retrieved with good accuracy despite the interference. In addition, since the absorption structures of the different alkane species change systematically with the number of carbon atoms, it is possible in the spectral retrieval to evaluate also the average carbon number in the measured VOC plume. The VOC's that are emitted from a typical refinery correspond mostly to light alkanes (90%). The composition of the alkanes is however usually complex and it may consist of many tenths of species. Even so, to obtain the total alkane mass and average number, it is in the spectral retrieval sufficient to fit only a few VOC calibration spectra (ethane, propane, n-butane, and n-octane) together with the atmospheric background species of CO_2, HDO, H_2O and CH_4. For other industries it is necessary to obtain complementary information about the general VOC composition at the source before choosing the calibration mixture to use in the spectral evaluation since also aromatic VOCs, alcohols and alkenes have absorption features in the CH-stretch region.

For measurements of SO_2, NO_2 and HCHO in the UV/visible the spectral region between 305 and 365 nm should be used with a resolution better than 1 nm. In the retrieval it is also necessary to take into account absorption features of O_3, O_4 (O_2-O_2 weak complex) and "ring spectra", the latter corresponding to spectral structures coming from inelastic atmospheric scattering [Fish 1995]. In the data retrieval it is preferable to use published cross sections.

2.4.3 Calculation of gas fluxes

The flux should be obtained as the product of the SOF column measurements integrated across the plume and the average wind speed for the VOC plume.

For inside refinery measurements the wind used should be obtained from the non-obscured 10 minute wind at the plant. For special cases the ground wind speed downwind the source should instead be used, i.e. from the water treatment area.

For measurement beyond the fence-line of the site or on site measurements covering a larger area such as tank farm, the plume wind speed should be obtained as the average wind speed from the ground to the upper mixing height of the plume. The upper mixing height is obtained as the product of the assumed vertical mixing speed (0.5 m/s) and the time it takes for an air parcel to travel between the main source and measurement position. The latter is obtained as the ratio between distance to source and the wind speed. For a tank area the position of the source is assumed to be in the middle of the tank farm. The mixing height can optionally be measured indirectly, by making use of complementary alkane concentration measurements on the ground. From the ratio between the measured column by SOF and the measured ground concentration, an estimate of the upper mixing height of the plume is obtained, assuming a well-mixed plume from ground and upward.

The wind height profile is needed to calculate the average wind speed from ground to upper mixing height. The profile should either be obtained directly from (a) a wind profiler running continuously, (b) a combination of the 10 m measurement wind from a mast and statistical scaling factors obtained from wind balloon soundings or wind profiler measurements, (c) mast measurements at different heights and logarithmic extrapolation or d) equivalent methods. If variant b is chosen the balloon sounding should be taken over several full measurements days, with 3 -6 sounding per day. The days should be chosen so that they cover the different wind conditions occurring during the SOF measurements.

2.4.4 Estimation and localization of emission sources

From spatial mapping of the flux measurements together with wind measurements, the source areas causing the measured gas fluxes can be interpreted. It is important to measure over several days and ideally in different wind directions to be able to pinpoint the sources.

The SOF measurements has the smallest uncertainty when carrying out measurements outside the fenceline of the refinery, since the wind field is then less disturbed and most of the emissions plume has had time to distribute itself over several hundred metres in height. For the subarea measurements performed close to the source inside the refinery, the wind field is more complex and using an unobscured 10 m wind risks overestimating the emissions. . The emission values obtained by SOF inside the refinery should therefore be rescaled to the appropriate plume speed, so that their sum matches the emission value measured at the fenceline. In this manner the uncertainty of the wind field close to tanks etc. is minimized.

The SOF measurements are influenced by turbulence in the wind field, causing apparent horizontal shifts in the position of the plume in the measurement plane. One shall therefore average over at least 4 measurements during the same day to mitigate this effect.

Industrial sites, such as refineries are complex and include both continuous emissions from tanks and process areas as well as intermittent ones from various activities such as cleaning and repair, ship and truck loading and flaring. To get an understanding of the emissions at a site one should measure over 5-10 days, depending on the size of the site, for varying wind directions. The obtained data from various areas should be analysed in a statistical manner. The wind turbulence normally causes an emission curve that follows a normal distribution while a skew shape of these curves is due to intermittent emissions due to tank cleaning etc. The best estimate of the continuous emissions is the median value, given that intermittent emissions only have occurred infrequently during the measurement study, while the average emissions is the best estimate for the total emissions during the period. However, since intermittent emissions can be very high, it is important to understand the origin of these before including them in any emission assessment. Once the source of the intermittent emission is understood one should assess, if possible together with the industrial site, how frequent such emissions occur during the year.

Indirect flux measurements of aromatics, methane and other gases not measured solely by SOF are also possible. By combining SOF measurements with complementary concentration measurement techniques based on optical (infrared and ultraviolet) absorption in multi-reflection cells in the same measurement vehicle fluxes of the gases are obtained. The measured ratio of the gas (aromatic species, methane, etc.) concentration to total alkane concentration is multiplied with the measured alkane flux to indirectly measure the gas emissions. The ratio of the column and the concentration measurements also provides an estimate of the average plume height for well mixed plumes as mentioned above.

If the total emission values obtained at the fence line of the industry differs to the total estimated emissions in the refinery of sub areas and tanks, the inside measurements should be rescaled to match the outside. The rational for this is that the fenceline measurements are considered more accurate since the wind field is then less disturbed compared to on site measurements, caused primarily by the fact that the plume has had time to rise to higher altitudes where the wind field is more stable.

2.4.5 Data validation procedures

One shall maintain records that include sufficient information to reconstruct measurement from the variables originally gathered in the measurement process. This includes, but is not limited to, information (raw data, electronic files, and/or hard copy printouts) related to sampler calibration, sample collection, measurement instrument calibration, quality control checks of sampling or measurement equipment, "as collected" or “raw” measurement values, an audit trail for any modifications made to the "as collected" or “raw” measurement values, and traceability documentation for reference standards. Difficulties encountered during sampling or analysis, such as interference between adjacent plumes, large upwind fluxes or highly variable wind fields should be documented.

To ensure high quality data an internal audit procedure of the data shall be carried out. In this procedure, the completed SOF measurements shall be reviewed by an experienced SOF-operator that has not been involved in the actual data evaluation. At least one of the persons involved in the data processing must have been present while the actual measurements were made.

The final emission data should be presented as daily means and standard deviations for each measured source. Histograms, showing all individual measurements of a source, may also be presented to analyse the emission distributions.

Extreme outliers should generally not be excluded, unless non-typical conditions/operations at the facility are reported. In this case, the outliers should be reported separately so that these conditions/operations can be followed up. However since the median is used as the best estimate of the continuous emissions, the outliers will generally not include this value.

The criteria below shall be used to flag uncertain SOF measurement data and these data should either be discarded, tagged with higher uncertainty, as requiring complementary information or new spectroscopic retrieval:

1. For each reported source emission, at least 4 measurement transects are required per day.
2. Noise levels above the detection limits, tolerance less than 3×detection limit.
3. Significant baseline variations, tolerance <10 mg/m^2.
4. Significant data gaps in the plume, tolerance < 20 % of the spatial extent of emission plume.
5. Extended vehicle stops, tolerance < 20% of the of the time extent of emission plume measurement.
6. Nearby upwind plumes are of significant magnitude, tolerance < 90% of downwind emissions
7. Average wind speed during the transects included in the average emission value, tolerance 1.5 m/s to 12 m/s.
8. Highly varying wind directions, tolerance < 30^o in standard deviation of 10 min wind direction.
9. Low solar angle, tolerance > 20^o above horizon.
10. Upwind measurements close to high structures, or process area, for which the solar beam cuts through the gas plume from the upwind side or goes below the emission plume, such as a flare.
11. Data corresponding to significant systematic residual in the spectral fitting, tolerance 2× typical spectral residual noise.

2.5 REPORTING

The report should include the following:

Overview and description of measurement method.

Description of emission quantification procedure.

Measurements objectives.

Factors influencing detection limit and accuracy.

Emission for each area measured.

Meteorological and other data collected pertaining to the SOF measurement:

- date, time and duration of measurement
- wind velocity and direction
- geographic location (GPS coordinates)
- description of areas observed

Two-dimensional column data for the measurements.

Display of the data overlaid on a site plan (2D plot) to aid visualization of the plume and to identify emission sources.

Conclusion: which areas were measured and total emission rate.

The emission rates should be presented as statistical data (daily means, standard deviations, median)

3 TIME CORRELATED TRACER PROTOCOL

3.1 PERFORMANCE REQUIREMENTS

For practical applications in order to be able to monitor general VOC emissions from an industrial scale site, the system shall be:

- Firmly mounted on a mobile platform, with access to the outside air.
- Equipped with sensors that can either measure single VOC gas species or measure the sum of VOC gas species (alkanes, alkenes, alcohols, aromatics) and simultaneously one or several tracer gas species.
- Able to measure the tracer gas with a detection limit of 1-10 ppb and the target gas better than 10 ppb.
- Able to perform fast measurements (time response of about 1-10 s) while moving up to 50 km/h.
- Equipped with a global positioning system.
- Capable of showing real time concentration data of tracer gas and VOC, projected on a map.

3.2 APPLICATION OF THE METHOD

3.2.1 Measurements planning

It is necessary to clearly define the measurements to carry out. This includes the species to be measured, experimental arrangements (field setup) and likely interfering species:

- Campaign logistics: this includes pre-site visits (if required) and checklists for ensuring the site is aware of the logistics of TC measurements and that the site is operating in a normal manner. A method statement covering the TC method may be provided if required.
- Selection of measurement roads.
- Identification of likely emission sources: this requires information from the site, usually including site plans and existing emissions information. Potential sources off-site (both for VOC and tracer gas) should also be considered.
- Identification of potential interfering species: for complex sites this may require process information or air-sample analysis taken as part of the campaign measurements.
- Assessment of wind field: pre site planning includes an assessment of the likely wind conditions and what existing meteorological data are available.

3.2.2 Selection of gas species to be measured

- Obtain information about the typical gas species being emitted and make decisions whether complementary composition measurements are needed.

3.2.3 Selection of tracer gas species

- Use an appropriate tracer gas which is not emitted from the site to be studied.
- The tracer gas should have as small health and environmental impact as possible on the surrounding. The tracer gas must with margin be stable in atmospheric conditions over the time frame covering the plume transport from the source to the measurement location. The tracer gas purity should be 99.9% or better.
- The tracer gas and positions chosen must be sanctioned by the site and marked off, in order not to put working personnel or installations at risk (for example if a flammable, oxidising, toxic or suffocating tracer gas is used).
- The sensors used should have high sensitivity to the tracer gas, better than 1-10 ppbv detection limit in order to be able to release only small amounts of tracer gas (typically 0.5-2 kg/h per tracer bottle).

3.2.4 Measurement strategy

Installation of a meteorological mast location in a clear area.

Identification of ideal wind conditions and TC measurement roads to use for measurements at each different site area. This and the weather forecast during the measurements period would help to plan when to measure a specific site area and from which location. This in turn would help to:

a) Communicate each day to the site the possible TC locations facilitating the work permit.

b) Quickly react if the actual wind direction during the day is not as forecasted.

c) Interpret and understand the origin of observed plumes and any interfering sources.

For a given wind direction the area to measure should be chosen such as:

a) The area under investigation is clear from strong upwind sources. Avoid areas with high inflows or where the background of VOC and tracer can’t be estimated.

b) It is of outmost importance to verify that no significant sources of the measured VOC or tracer gas used is located between the studied source and the measurement location. This would interfere and offset retrieved emission results using the TC method.

In order to make an appropriate tracer correlation measurement it is necessary to know the location of the main leaks to be investigated. This is done by concentration mapping, driving around the site on all available roads measuring the concentrations.

- The tracer gas should then be positioned in such a way that it disperses in the same manner as the leakage gas. For a single leakage source the tracer gas should be released in close proximity to the source gas leakage.

For area sources or more complex volume sources an assessment of the main leakage points inside the areas needs to be made and then tracer gas is released from one or multiple distributed points. In order to estimate the performance of the measurements it is necessary to either:

- measure at far away distance, so that the area/volume source becomes more of a point source (suppression of any tracer gas and source gas location mismatch) (typically a distance away from the source of more than 5 times the area unit dimension),

- measure at different distances and different wind directions to assess the variability of the obtained emissions,

- utilize two tracer gases, or move the position of the single tracer gas, to make a sensitivity study of the variation in the obtained emissions. Typically, the tracer gas should be relocated from the estimated “best match” location, to an offset location with respect to the upwind/downwind direction of the unit in study, in order to observe the impact on the retrieved emission rate. In the case of two different tracer gases this can be accomplished simultaneously.

3.2.5 Set-up and initial tasks

General:

- Site specific requirements such as safety inspection and introduction course.

- Agree the procedure for changing TC location with site operators and possible use of special permits to drive in ATEX areas with a safety guard.

- Ascertain safe measurements. For measurements inside industrial areas the equipment should be equipped with a single safety switch by which all instruments can be turned off, in case of emergency.

TC vehicle or platform:

- Check TC vehicle/platform status according to safety and performance and ascertain safe measurements

- Mount warning lights and signs

- Make sure that car or mobile platform battery pack in is fully charged

- Make sure any loose items are stowed away securely

Instruments:

- Turn on instruments.

- Check that sensors are fully operational, according to the operations manual and other instructions.

- Check the time synchronization of all instruments and computers against GPS, Tolerance 1s.

GPS:
- Check that the GPS information is available and reasonable.

Wind:

- Set-up the meteorological sensors at the agreed locations and check the functionality.

- Direct sensor correctly (toward magnetic north) using a compass. Tolerance: ±5°.

- Erect the wind mast vertically and secure it firmly
- Check that wind information is available and reasonable.
- Check the time of the data logger versus standard. Tolerance 1 s.

Tracer gas:

- Once the emission sources have been chosen apply for permit to release tracer gas in the vicinity of the sources.
- At the tracer gas release point, make appropriate safety arrangements by marking off several meters around the release point depending on the health impact of the tracer gas.

3.2.6 Measurements

Before start to measure ensure:

- Staff is signed in on site (if required).
- If necessary, apply for a work permit.
- Ensure that staff is familiar with local safety protocols.
- Logging of the meteorological data is started.
- Determine the measurement plan.

Measurement procedure:

- Measure the concentrations on the full site by driving on the accessible roads measuring the road side concentrations of the gas species of interest.
- Take notes and photos on interesting findings and events.
- Repeat the measurements during different times and meteorological conditions in order to study the temporal and spatial variability.
- Plot the measured concentrations on a 2D map for trace back of observed plumes and identification of “hot spots”. Note that since the measurements are usually performed on the ground, the measurements are comparably more sensitive to sources which are close to the measurement vehicle and at low elevation level.
- Make additional concentration measurements at the hot spot areas using the TC sensors, OGIs, and sniffers. Scan upwind and downwind the sources to investigate whether the hotspot corresponds to one or several interfering sources.
- Discuss the finding of potential emission sources at the hotspot locations with site personnel, to understand the reason for the leaks and how frequent they could occur.
- Apply for permit to emit tracer gas at the source locations. See description in section 3.2.4.

- Carry out controlled tracer gas releases according to the description in section 3.2.4. Keep track of tracer gas release rates by weighing released amounts, usage of stable regulators and/or mass flow controllers and register the accumulated tracer release time.

- Measure both upwind and downwind the source at various distances to investigate whether the emissions correspond to one or several interfering sources. The measurements should be carried out according to the description in section 3.4.3. Make sure the VOC and tracer gas plumes are entirely traversed. Make sure no significant interfering sources (concentrations) of the studied VOC compound or tracer gas are observed in between the studied source area and the plume measurement location. Any such source having a different plume transport (dispersion) time than the studied source emission, can severely offset the retrieved emission result.

- The emission plume in study should be entirely traversed for complex areas/volume sources with a driving speed corresponding to 5-50 km/h, depending on distance to the source and the time resolution of the analysis instrumentation. Sampling speed should be chosen so that significant under-sampling is avoided, and so that different parts of the plume are given equal sample time in the plume integration. For simple isolated sources, fixed measurements can also be carried out.

- The cross section of the plume should be probed at comparable plume transport times from the source, e.g. typically at the same distance to the source on a transect perpendicular to the wind direction.

- Check the wind meter and tracer gas release sources on a regular basis to make sure that it is operational.

- Check that wind speed stays above 1 m/s in order to assure appropriate mixing conditions during the experiment.

- Check the GPS sensor on a regular basis to make sure that it is operational.

At the end of the measurement day ensure that:

- All the sensor data is saved and backed up.

- All the met data is downloaded, saved and backed up.

- Dismount wind mast and move out tracer bottles, if not in a safe location and according to work permit.

- Update survey documents. If feasible, discuss measurements results with the industrial site and collect complementary data such as tank product levels, flaring activity, etc.

- Turn off instruments.

- Charge measurement vehicle, and data logger batteries overnight.

- Make sure that instruments are well protected from rain/moisture.

3.3 QUALITY CONTROL

3.3.1 General

Quality checks and quality assurance and measures are performed at several levels. In general most checks are done prior to measurement, including powering up the equipment, checking operating parameters, and test the instruments. The purpose is to run operational checks to catch problems prior to field deployment and repair all malfunctioning equipment in order to avoid bad data during survey.

3.3.2 Calibration of gas sensors

The gas sensors need to be calibrated according requirements in the instrument manuals. When using instruments based on optical spectroscopic absorption measurements one can generally rely on published line parameters or absorption cross sections. This is appropriate as long as the instruments are well aligned and its spectral response is well characterized. A response check versus atmospheric background levels, tracer gas and/or a known reference is recommended to assure valid performance prior to commencing with the measurements.

3.3.3 Meteorological sensors calibration

The meteorological sensor should be calibrated regularly by the manufacturer or by a reference wind meter.

3.3.4 Tracer release equipment calibration

The gas regulators and mass flow controllers used for the tracer release need to be properly calibrated to assure correct tracer rates for the given application conditions (tracer gas, pressure, temperature). As a backup the tracer gas bottles should be gravimetrically weighed on a calibrated scale before and after the tracer release study. The accumulated time of the tracer release need to be noted, and a constant release rate during the experiment assured.

3.3.5 Required QC checks in the field

The gas sensors need to be quality controlled according requirements in the instrument manuals.

- Check that the tracer release rate is constant over the duration of the measurement.
- Check that GPS is running ok and that instrumentation time stamps are synchronized.
- Observe real time concentration data and assure no abnormal drifts or performance deterioration, interfering source or tracer plumes are observed – make notes and take action in case.
- Check that wind speed stays above 1 m/s in order to assure appropriate mixing conditions during the experiment.

3.4 DATA ANALYSIS

3.4.1 Calculation of gas fluxes

Applying the TC method, the source flux is retrieved by integrating the cross-plume mass concentrations (above background baseline) of the source gas and tracer gas respectively. The mass concentration ratio together with the known tracer gas release rate gives the source emission in kg/h, see equation below. These fluxes are given for each transect (j) by:

$$Q_{VOC}^{j}[kg/h] = Q_{tracer}^{j}[kg/h]\,\frac{\int_{Plume\ start}^{Plume\ end} C_{VOC}^{j}[\mu g/m^3]\,dl[m]}{\int_{Plume\ start}^{Plume\ end} C_{tracer}^{j}[\mu g/m^3]\,dl[m]}$$

Where,

Q^{j}_{tracer}= the tracer gas release mass flux for plume transect j (should be constant over all transects j),

C^{j}_{tracer} = the tracer gas mass concentration above background baseline, integrated across the plume cross section.

C^{j}_{VOC}= the VOC (or source gas in study) gas mass concentration above background baseline, integrated across the plume cross section.

l = distance across the emission plume, ideally across the full plume cross section perpendicular to the wind direction (e.g. the measurements should probe the plume at comparable plume transport time throughout the whole plume transect)

Note that tracer gas correlation fluxes do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume and the tracer gas is well mixed at the sampling distance. Complete plume transects are, however, strongly recommended since the tracer gas and source gas release point might not completely match at the sampling distance and complete plume integration suppress mismatch errors in the direction perpendicular to the wind direction.
In the gas flux calculation, the background baselines of tracer gas and VOC respectively, need to be assessed and withdrawn for each plume transect. Any significant offset/drift in the baselines as observed comparing concentrations at the plume edges should flag the transect, see section 3.4.3.

3.4.2 Estimation and localization of emission sources

From spatial mapping of the flux measurements together with wind measurements, the source areas causing the measured gas fluxes can be interpreted. Depending on the site or application, it is important to measure over appropriate time duration and ideally in different wind directions to be able to pinpoint the sources. If applicable, it is also recommended to make leak search at the source unit with the TC instrumentation and attached tubing and/or handheld OGI or sniffer devices to allocate sources of emissions as good as possible within the identified source units.

In order to better characterize and understand the source emission distribution over time, it’s recommended to gain statistics on the emission by multiple measurements over a time frame suitable for the survey objective. Since emissions may vary both on a short and long timescale, and meteorological dispersion effects also may induce some noise (variability) in observed emissions, averaging of at least 6 measurement transects on each measurement occasion is recommended.

Industrial sites, such as refineries are complex and include both continuous emissions from tanks and process areas as well as intermittent ones from various activities such as cleaning and repair, ship and truck loading and flaring. The obtained data from various areas should be analysed in a statistical manner. The best estimate of the continuous emissions is the median value, given that intermittent emissions only have occurred infrequently during the measurement study, while the average emissions is the best estimate for the total emissions during the period. However, since intermittent emissions can be very high, it is important to understand the origin of these before including these in any emission assessment. Once the source of the intermittent emission is understood one should assess, if possible together with the industrial site, how frequent such emissions occur during the year. The TC method can preferably be used to study emissions related to a complete cycle in the production, such as filling of a tank, product loading to trucks or vessels etcetera. By obtaining an emission factor for the activity, the resulting emission can then be extrapolated by the number of operations. Obviously, any seasonal change in the emission factor need to be measured or assessed in this extrapolation.

3.4.3 Data validation procedures

One shall maintain records that include sufficient information to reconstruct the measurement from the variables originally gathered in the measurement process. This includes, but is not limited to, information (raw data, electronic files, and/or hard copy printouts) related to sampler calibration, sample collection, measurement instrument calibration, quality control checks of sampling or measurement equipment, "as collected" or “raw” measurement values, an audit trail for any modifications made to the "as collected" or “raw” measurement values, and traceability documentation for reference standards. Difficulties encountered during sampling or analysis, such as interference between adjacent plumes, large upwind fluxes or highly variable wind fields should be documented.

To ensure high quality data an internal audit procedure of the data shall be carried out. In the audit procedure the completed TC measurements shall be reviewed by an experienced TC-operator that has not been involved in the actual data evaluation. It is preferred that at least one of the persons involved in the data processing have been present while the actual measurements were made.

The final emission data should be presented as the hourly emission rate and its variability.

The criteria below shall be used to flag uncertain TC measurement data and these data should either be discarded, tagged with higher uncertainty, as requiring complementary information or new spectroscopic retrieval:

1. Noise levels above the detection limits, tolerance less than 3×detection limit

2. Leak search to identify the leaking sources should be performed (Y/N)

3. Quantification based on at least 6 measurement transects per source. (Y/N)

4. Leak gas and tracer gas concentration above 3 times the detection limit (Y/N)

5. Assess the variability of the emissions results due to poor overlap (correlation) of tracer gas and leakage gas by using at least one of several methods as explained in section 3.4.3: dual tracer gas releases, multiple release positions of tracer gas, different wind directions and distances or measurements at a far-away distance (without introducing interfering adjacent sources of studied VOC or tracer gas)

6. If complex area/volume source the plume should to be traversed entirely and at different distances. (Y/N)

7. Risk for a significant mismatch between tracer gas and source gas in the vertical orientation due to unknown sources or inaccessible unit parts for leak search and verification (Y/N)

8. Leak gas and tracer gas should “correlate” in the spatial regime, and the cross section of the plume should be probed at comparable plume transport times from the source (Y/N)

9. Scan upwind and downwind for interfering sources, especially important to avoid VOC sources very close to the sampling point relative the distance to the tracer gas/main VOC source location. (Y/N)

10. The background baseline concentration of VOC and tracer gas respectively differ significantly comparing concentrations at the plume edges. Should be similar, or an indication of instrument drift or interfering sources.

11. Keep track of tracer gas release rates by weighing released amounts and usage of stable regulators or mass flow controllers.

12. Wind criteria, 1-12 m/s

3.5 REPORTING

The report should include the following:

Overview and description of measurement method.

Description of emission quantification procedure.

Measurement objectives.

Factors influencing detection limit and accuracy. A response to whether any flags according to section 3.4.3. were raised and in case, how issues were resolved.

Emission for each area measured.

Meteorological and other data collected pertaining to the TC measurement:

- date, time and duration of measurement
- wind velocity and direction
- Tracer release rates, times and total tracer amounts released
- geographic location (GPS coordinates)
- description of areas observed

Two-dimensional concentration data for the measurements overlaid on a site plan (2D plot) to aid visualization of the plume and to identify emission sources.

Conclusion: which areas were measured and total emission rate.

4 REVERSE DISPERSION MODELLING PROTOCOL

The protocol of Reverse Dispersion Modeling (RDM) is fully described in Norm EN15445 for fugitive dust quantification. The present protocol is an adaptation of RDM methodology for quantification of others pollutants in the context of complex industrial site. The scope of the present document focuses on volatile organic compounds (VOC) diffuse emissions in an industrial site which requires to implement a methodology of inverse modeling at local scale.

The calculation of emission flux needs two elements: a knowledge of concentration in the plume and meteorological information to extrapolate an emission flux from the concentration measurements.

Optical technologies like Lidar and SOF need to measure a full transect of the full plume to calculate the emission flux. With RDM, the measurement strategy is to have concentration information in several points of the plume, and a dispersion model reconstruct the full plume.

4.1 PERFORMANCE REQUIREMENTS

The global tools will have to raise 2 challenges: the identification of the sources (localization and estimation of ejection parameters) and the pollutant flux of the sources. To obtain these results, the monitoring strategy needs to provide enough information.

For practical applications in order to be able to monitor hydrocarbons, the analyser used for RDM methodology must be adapted to the pollutant to be quantified. For VOC a portable FID / PID is enough, but other techniques could be used (like IR / FTIR / DOAS …) according to the pollutant.

The portable analyzer is used to quantify specific points in the perimeter of the sources. The objective is to cover a representative part of the space to identify the heterogeneity of emission sources.

In order to characterise emissions from an industrial scale site, the measurement system shall be:

- Mobile/transportable portable by a person or in a vehicle, using a telescopic rod or install on a drone.
- Able to record all the relevant information needed for the data analysis and quality controls.
- Able to perform the required calibrations and quality checks.
- Able to give concentration variation at least of 1 minute.
- Able to deploy a meteorological station at a location near the study area, with wind sensor and measurement of parameters required to calculate atmospheric turbulence (direct turbulence measurement or solar radiation)

As an example, these requirements would be meet by:

- a FID system with the following characteristics:
  - Stability of the detector must be obtain after at least one heating hour.
  - Sensitivity of detector must be able to quantify a variation of 0.1 mg/m^3 VOC equivalent above the background concentration.
- a 10 m mast with a wind station METEK ultrasonic with turbulence measurement

In complement, the direct dispersion model shall be able to:

- Reproduce the situation like in RDM standard. The choice of the direct dispersion model is the responsibility of the user and driven by the respect of physics:
  - If the presence of obstacles (building, tanks, industrial unit …) influenced the pollutant dispersion in the measurement area, the selected model must be able to reproduce effects of obstacles in the wind field
  - The time scale of the model must be adapted to the concentration measurement.
  - The spatial resolution of the model must be adapted to the concentration measurement.
- Take into account emission's source geometry and ejection parameters.
- Transport a mass of emitted pollutants taking into account weather changes along the plume trajectory (space & time variations)

4.2 APPLICATION OF THE METHOD

4.2.1 Before Campaign

It is necessary to clearly define the measurements to be carried out. This includes the species to be measured, experimental arrangements (field setup) and likely interfering species. The following pre-campaign activities should be carried out:

- Campaign logistics: this includes pre-site visits (if required) and checklists for ensuring the site are aware of the logistics of a VOC measurement. A method statement covering the analyser and met station may be provided if required.
- Health and safety: this covers requirements for site specific health and safety, for example safety inductions or hot work permit systems. It also requires a risk assessment for site specific hazards and for example the provision of suitable PPE.
- List and identification of all the areas to be measured as specified by the customer on a site map (see measurement objective Section). Create a checklist of the areas to be measured and note:
  a) Ideal path for mobile analyser measurement to turned around emissions sources.
  b) Identify areas that can only be measured with a specific access authorization
  c) Any information or requirement the customer may provide such as level of uncertainty or process information.
  d) Structure in the area (tanks, building …) and obtain height information. If not available, must be measured.
- Identification of likely emission sources: this requires information from the site, usually including site drawings and existing emissions information. Potential sources off-site should also be considered.
- Identification of potential interfering species: for complex sites this may requires process information or preliminary air-sample analysis taken as part of the pre-site visit in order to identify species with potentially detector response (FID: H_2S, Hydrogen …).
- Assessment of wind field: pre-site planning includes an assessment of the likely wind conditions, and what existing meteorological data are available.

- Identification of the meteorological mast location in a clear area near the studied area. If site topography is complex, evaluate the possibility to deploy a second meteorological station.

4.2.2 Set-up and initial tasks

The following should be carried out on site at the start of the campaign:

- Site specific requirements such as safety inspection and induction course.
- Site visit if a pre-site visit was not carried out, check/agree with site personnel all the suitable measurement locations and update the checklist of the areas to be measured accordingly.
- Agree what to do in an emergency/ evacuation i.e. shutdown procedure.
- Set-up the meteorological sensors at the agreed locations and check the functionality.
- Set-up the analyser, respect stabilization period and perform calibration test.
- Assure that all the instruments and logger clocks are at the same time reference.

4.2.3 Daily Tasks

At the beginning of the measurement period ensure:

- Staff complied with local rules, i.e. signed in on site register.
- If necessary, apply for a work permit.
- Ensure that staff is familiar with local safety protocols.
- Logging of the met data is started.
- Analyser is set-up and recording.
- Follow a path in the study area to have point up wind and downwind of the sources.

The following should be carried out for each measurement location along the path:

- Work place safety assessment for the planned measurement location.
- Determine the exact localization and timing of each measurement.

While measuring record the following information:

- Measurement locations and met location.
- File name, start time, end time, location, measured concentration, other specific information.
- Site information
- Update the notes on the checklist of areas to be measured, record:
  a) If the measurement of a specific area is completed.

b) If the measurement should be repeated because it was made in a non-ideal condition or if more measurements are needed to achieve the required uncertainty.

c) If the upwind source is measured, to be measured or not required.

d) If an air sample has been taken.

At the end of the measurement period ensure that:

- All the met data is downloaded.
- All the data is saved and backed up.

4.2.4 Measurement strategy

The selection of the area(s) to be measured depends on several factors driven by wind conditions, path accessibility around the sources and obstacles.

The first step is a rapid screening in the emission area with the mobile apparatus to identify hot spots and source characteristics. The knowledge of process information or IR optical camera could be useful, but not essential.

The second step is the real measurement period: The measurement points are done during a path around the emissions sources, at least five points are needed in the main plume.

For a given wind direction the points to be measured should be chosen in order of priority such as:

a) At low wind speed (below 2 metres per second at 10 metres), it is preferable to not measure.

b) The areas that can only be measured with that specific wind direction are prioritised, but the measurement path must go around the sources to obtain upwind and downwind measurement points.

c) Considering the sensibility of the FID system, depending upon the current dispersion conditions and emission, the measurement points need to be localised at distance from the sources where a downwind response is recorded but not too close from sources (not below 2 metres) .

d) If several sources are emitting in the area, the path must be done to obtain measurement around each source if possible.

e) The area under investigation is cleared from upwind sources.

f) If upwind sources are present, they can either be measured in a different path specific to identify it.

g) If the site layout is such that several areas are downwind of each other, the first area to be measured should be (if possible) the one that has no upwind contribution from the rest of the site. The second area to be measure should be the one directly downwind of the first area and so on. In this way for each area the upwind contribution would be measured just before the area itself is measured.

The measurement point should consider that:

a) The higher the wind speed the faster the emissions are diluted leading to a reduction in ambient concentration. Higher concentrations are therefore obtained closer to the emission area.
b) At close distance from the emission source the wind field could potentially have a complex behaviour due to the presence of obstacles. It's not recommended to measure at least above 2 metres from an obstacle.

c) The acquisition time for a point location is at least 1 minute for an FID, but could be lower for faster measuring technics.

d) The distance between two consecutive points is variable :
   a. in the downwind plume, the objective is to maximised the number of points to have a transect of the plume.
   b. In upwind location, if no significant concentrations are recorded, the distance could be spaced

e) Considering the above restrictions, the number of measuring points in the plume should be maximised.

In order to achieve the quality requirements of the measurement objectives these procedures should be followed:

- Carry out a set of at least seven measurement points in the plume for each path to minimise the uncertainty.

- Repeat one or two extra sets of measurements of the same area along different path or from different points locations or on a different day to decrease the uncertainty associated with that area if specified by the measurement objective.

- Measure upwind sources if present.

- Carry out all the necessary quality assurance measurements.

- Take air samples at locations which would provide an indication of the actual speciation of the emission sources sampled by the analyser.

4.3 QUALITY CONTROL

4.3.1 General

Quality assurance of the emission measurements is necessary. These procedures require detailed project planning and progress monitoring with project subject to regular internal reviews and quality audits at measurement institutions.

Care should be taken when measurements are made with wind speeds outside the 2- 10 m/s range and with variable wind direction.

4.3.2 Analyser calibration procedures

4.3.2.1 *General*

A crucial requirement for high quality VOC measurements is accurate knowledge of the actual differential absorption coefficients that are appropriate for a particular measurement. The following calibration procedures should be employed to ensure the measurement quality. The two key elements that need to be verified through these checks are that:

- A suitable calibration with reference bottles (VOC standard and pure air standard). For FID, a calibration is done each day, and before and after each path, a control with the VOC standard is done to assure that the analyser is stable.
- The analyser need to be clean and stable (heating period is respected).

4.3.2.2 *Calibration gases*

A standard gas adapted of the target gas is selected (e.g., propane or methane for the total hydrocarbon measurements with FID, isobutylene for PID). These standards should be, where possible, gravimetrically prepared, internationally-traceable reference gas mixtures with absolute volume mixing ratio (VMR) accuracies of 0,5 % or better.

4.3.2.3 *Calibration bag*

A bag is fuelled with the standard gas or air zero. The FID/ PID is connected to the bag, and calibration procedure is applied.

4.3.2.4 *Continuous monitoring*

During measurement, there is no specific requirement except to check that the analyser works (e.g. FID: no shut down of the flame, PID: lamp active ….) and data are recorded.

4.3.2.5 *Check of system performance*

In addition to verifying the stability of the analyser, a check that the full system is measuring correctly should be carried out at least twice a day using a standard gas.

These checks should be carried out periodically and if they exceed more than 20% of the expected value the system should be adjusted to bring it back to normal compliance.

4.3.3 Meteorological sensors calibration

The meteorological sensor should be calibrated. The calibration certificates may provide a calibration factor for the wind speed, wind direction and turbulence or solar flux readings.

If data loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.

In addition, if there is different sensors, they should be compared side-by-side in the field to provide a further check on their correct function.

4.4 DATA ANALYSIS

4.4.1 General

The data acquired has to be analysed to give the concentration in each location. The data analysis process consists of the following steps:

4.4.1.1 *Background subtraction*

For each path period, background value is subtracted from the signals. For FID, background is mainly atmospheric methane. The measured background is derived from the average value of the upwind points without impact of significate sources.

4.4.1.2 *Concentration conversion according to speciation*

Based on speciation analysis and / or process information, a conversion factor is applied to the analyser measurement to obtain concentration of real VOC. The final VOC concentration is expired in mass/m^3.

4.4.1.3 *Calculation of emission fluxes*

Concentration measurements in different points represent contains only a partial information of the plume. To reconstruct a complete plume information, the RDM procedure need two steps to obtain the emitted flux:

- A direct dispersion calculation, to take in account of emission sources characteristics, meteorology and atmospheric dispersion :
    - The emissions sources are represented by volume, point or area sources. An estimation of ejection parameters is needed to take in account exit velocity or high temperature of emission.
    - Classical direct dispersion is done with a theoretical emission flux set at 1 g/s for each source independently, to obtain the matrices of dispersion factor at each monitoring point (x,y,z,t).
- A reverse modelling to combine modelled results with real concentration measurement permit to obtain the emission flux :
    - In the case of a single source, the estimation is obtain by linear regression for a single source, and multi linear regression for non-independent multi sources plume.
    - The quality of the flux estimation is dependant of the parameter of the linear regression.

5 OPTICAL GAS IMAGING PROTOCOL

5.1 APPLICATION OF THE METHOD

5.1.1 General

OGI as described in this document is used to:

- Detect leaks on inaccessible components (in a LDAR programme)
- Detect leaks on irregular components
- Detect leaks on tanks roofs
- Detect leaks while loading operations
- Detect important leaks at safer distance (using different lenses)
- Perform qualitative inspection after maintenance actions

5.1.2 Set-up and initial tasks / detection planning

When starting an OGI project the following steps should be taken:

- Establish the purpose of the detection. As a minimum, the purpose of the detection covers the following aspects:
- Description of what is to be controlled (areas, streams…)
- Nature of the location where detection will take place, (tank farm, handlings…)
- Relevant operating conditions of the controlled facility,
- The types of components to be controlled
- The envisaged detection period,
- Requirements for the detection method,
- Relevance of permit requirements, and
- Competence of the personnel to be employed.
- Kick of meeting with all parties involved
- Process Review in order to determine the lines or equipment to be inspected, their VOC compositions, and the IR spectrums to be covered
- Safety Review in order to determine onsite risks
- Leak detection of all equipment defined in the preliminary scope of work

- List of leaking equipment / Maintenance assistance
- Establish the detection plan on the basis of the defined purpose of the detection
- Reporting

5.1.3 Detection

Take the following steps to prepare the detection:

- Ensure that a map or similar information stating the detection locations is available. Record the progress of the detection on it;
- Ensure that a database or similar information with a summary of the potential sources of emission is available. Record the progress of the detection in it;
- If necessary, apply for a work permit for the activities;
- Ensure that means are available to record the time, the leak location and identification code of the emission source, picture and video references, specifics, etc.;
- Ensure a realistic time planning;
- Ensure regular switch of operators behind the IR camera (every 1 hour maximum)
- Ensure that there is sufficient capacity and/or spare capacity to store the data;
- Ensure there is sufficient battery capacity;
- Ensure that personal safety equipment is available;
- Ensure that you are familiar with the local safety protocols;
- Ensure that an explosion meter is available in case of non ATEX tool;
- Ensure that the date and time settings of the IR camera are correct;
- Carry out a functional test of the IR camera;
- Camera is working properly
- Cameras can detect the researched streams

Start the detection after:

- Determining the detection plan,
- Making the preparations mentioned above and
- Carrying out the test procedure for the use of the IR camera.
- The basic principle is that an IR recording will be made only if an emission is detected.

- Only make IR recordings of all emission sources if laid down specifically in the detection plan.
- Before accessing the detection zone, first do a quick safety scan from an ample distance for very large and potentially hazardous leaks. If there are no such leaks, continue with the following steps:
- Inspectors follow detection procedures in order to control some uncertainties
- Perform an accurate and systematic round of detection on the basis of the measuring plan, while preventing exposure to released VOC emissions as much as possible.
- Record a continuously emitting source for at least 20 s
- Record a fluctuating emission source for at least 20 s or for as much longer as is necessary to make its fluctuating character visible
- If possible, film around the emitting source.
- Make a visible picture (non-IR) of the emission source. The visual recording of the source shall also make the surroundings of the source visible, so that the reason for the leak becomes as clear as possible.

Record the following for every recording:

- Leak number of the emitting source
- time of the recording,
- file name of the recording,
- name of the emitting source, and
- Unit / Area / Drawing number / Stream number / Equipment / Source / Phase / Accessibility / Precise location / Remarks / Picture of leaking component / IR video of the leak

Base your choice of sensitivity settings for the IR camera on what is being detected and the detection strategy.

Maintain a distance from the source of emission that:

- is practical and safe,
- is compliant with the daily functional test results,
- generates the most information,
- relates to what is being controlled.
- After detection ensure:
- Database is backed up.

5.2 QUALITY CONTROL

5.2.1 Test procedures

5.2.2 General

No calibration (from provider) is required for OGI used in "gas detection". On the other hand, a functional test is required. This functional test consists of validating the ability of the IR Camera to detect a certain determined flow rate of a certain substance, from a certain distance, under certain weather conditions.

5.2.2.1 *Basic requirements*

As weather conditions have an impact on OGI sensitivity, this test must be performed under real weather conditions (outside).

As substances have an impact on OGI sensitivity, this test must be performed using substances representative of the main streams to control.

As background has an impact on OGI sensitivity, this test must be performed using a heterogeneous background, representative to the background of the real place of work.

If the IR camera will be used in HSM mode (or equivalent) during the detection, the functional test can be performed using the IR camera will be used in HSM mode (or equivalent).

5.2.2.2 *Frequency*

This functional test must be performed at least one time per day, before starting the detection.

In case of major weather conditions change during a detection period, the test must be repeated. (wind and humidity are known to be the most impacting factors)

5.2.3 Operating mode

An artificial leak, of two different representative VOC substances, with a determined constant flow rate is generated under real weather conditions (outside).

As far as possible, the background should be representative to the background of the real place of work.

After the IR camera's detector cooling period, the operator shall determine the maximum distance from which one the IR Camera is able to detect the artificial leak. This maximum distance can be limited to the maximum necessary detection distance for the day work.

This distance shall not be exceeded during the detection period.

Record the tests results for each substance:

- Date and time of the test
- Artificial leak flow rate (6 g/h is recommended)
- Wind speeds

- Maximum detection distance allowed

5.3 DATA ANALYSIS

5.3.1 General

All gathered pieces of information on site are recorded in a database.

5.3.2 Database Management

Information recorded during the identification allows:

- Creation of a list of leaks with exact location

5.3.3 Mass fluxes calculation / quantification

The direct mass flow quantification using OGI technology is not - yet - possible.

In order to quantify leaks, several methods can be implemented:

- FID measurement and quantification using specific correlations
- Bagging

5.4 REPORTING

5.4.1 Customer requirements

The main goal of an OGI project is to reduce VOC’s emissions, so customers need others deliverables in order to help them in the maintenance preparation.

Other deliverables can be:

- List of residual leaks
- Analysis per leaking sources, units, compounds, …

In addition to that, a picture and a movie of the leaking sources plus a transfer of leaking sources on PIDs for an efficient maintenance preparation.