



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN/2014-07

SA/CEN/EFTA/514/2014-07

«*Volatile Organic Compounds*»

Interim Report

1st INTERIM REPORT ON CEN/TC264/WG38 STATIONARY SOURCE
EMISSIONS - STANDARD METHOD TO DETERMINE FUGITIVE AND
DIFFUSE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS INTO
THE ATMOSPHERE

T Smith, F Innocenti and R A Robinson
Environment Division

© Queen's Printer and Controller of HMSO, 2017

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

This report is NPL - Commercial and must not be exposed to casual examination. It is not for general distribution and should not be cited as a reference other than in accordance with the contract.

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

CONTENTS

EXECUTIVE SUMMARY V

1 INTRODUCTION1

1.1 CONTEXT 1

2 OBJECTIVES.....1

3 WORK PACKAGES SUMMARY.....2

3.1 WP1 RESEARCH INTO PERFORMANCE OF MONITORING TECHNIQUES2

3.2 WP2 PLANNING AND COORDINATION OF THE FIELD MEASUREMENT PROGRAMME 2

3.3 WP3 SPECIFICATION OF METEOROLOGICAL MEASUREMENTS (WITH WIND SPEED AND DIRECTION)3

3.4 WP4 OPTICAL GAS IMAGING CAMERA3

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..... 3

3.6 WP6 IMPLEMENTATION OF THE REMOTE MONITORING METHODS AND ESTIMATION/CALCULATION METHODS AT THE SECOND INDUSTRIAL SITE5

3.7 WP7 SYNTHESIS AND STATISTICAL EVALUATION OF THE MONITORING DATA AVAILABLE AFTER THE FIELD TRIALS6

3.8 WP8 DEVELOP SPECIFICATIONS OF THE PERFORMANCE REQUIREMENTS FOR REMOTE MONITORING METHODS FOR USE WITH THE STANDARD6

3.9 WP9 DEVELOP SPECIFICATION OF THE PERFORMANCE REQUIREMENTS FOR REMOTE MONITORING METHODS FOR USE WITH THE STANDARD6

4 SUMMARY OF PERFORMANCE ASSESSMENT FOR AVAILABLE MONITORING TECHNIQUES6

4.1 DIFFERENTIAL ABSORPTION LIDAR (DIAL)7

4.2 SOLAR OCCULTATION FLUX (SOF)7

4.3 TRACER CORRELATION TECHNIQUES.....7

4.4 MODELLING TECHNIQUES8

4.5 RADIAL PLUME MAPPING (RPM).....8

4.6 FLUX CHAMBER MEASUREMENTS8

4.7 SNIFFING.....9

4.8 BAGGING9

4.9 OPTICAL GAS IMAGING (OGI)9

5 INITIAL CONCLUSIONS FROM THE FIRST VALIDATION STUDY10

5.1 STATUS OF THE WORK PROGRAMME..... 12

ANNEX A: PERFORMANCE CHARACTERISTICS RECOMMENDED FOR THE DRAFT STANDARD (WP1).....13

ANNEX B: PLANNING INFORMATION FOR THE FIRST FIELD CAMPAIGN (WP2).....	14
ANNEX C: METEOROLOGICAL MEASUREMENTS FROM TEST SITE 1 (WP3)	24
C1 INTRODUCTION	24
C.2 METHODOLOGY	24
C.3.1 Meteorological sensors	24
C.3.2 Wind LIDAR	25
C.5 DATA ACQUISITION AND PROCESSING	26
C.6 RESULTS	26
C.7 WIND ROSES FOR COMPARISON OF THE INERIS WIND DATA	27
C.8 COMPARISON OF TOTAL AND INERIS NORTH MET STATIONS	32
ANNEX D: OGI SELECTION AND PRELIMINARY RESULTS FROM TEST SITE 1 (WP4).....	40
D.1 DETECTION PRINCIPLE	40
D.2 DETECTABLE POLLUTANTS	40
D.3 DETECTION PROCEDURE.....	40
D.4 EQUIPMENT DEPLOYED.....	41
D.5 STAFFING.....	41
D.6 FACILITIES AND SERVICES REQUIRED	41
D.7 RESULTS FROM TEST SITE 1	41
ANNEX E: DIAL PRELIMINARY RESULTS FROM TEST SITE 1	43
E.1 MEASUREMENTS ON THE 22 ND SEPTEMBER FROM LOCATION BV02.....	44
E.2 MEASUREMENTS ON THE 23 RD SEPTEMBER FROM LOCATION BV03.....	45
E.3 MEASUREMENTS ON THE 26 TH SEPTEMBER FROM LOCATION BV04.....	46
E.4 MEASUREMENTS ON THE 26 TH SEPTEMBER FROM LOCATION BV06.....	47
E.5 MEASUREMENTS ON THE 26 TH SEPTEMBER FROM LOCATION BV09.....	48
E.6 MEASUREMENTS ON THE 27 TH SEPTEMBER FROM LOCATION BV10.....	49
E.7 MEASUREMENTS ON THE 27 TH SEPTEMBER FROM LOCATION BV11	50
E.8 MEASUREMENTS ON THE 28 TH SEPTEMBER FROM LOCATION BV13.....	51
E.9 MEASUREMENTS ON THE 29 TH SEPTEMBER FROM LOCATION BV14.....	52
E.10 SUMMARY OF DIAL VOC EMISSION RATE MEASUREMENTS	54
ANNEX F: SOF AND TRACER PRELIMINARY RESULTS FROM TEST SITE 1	55
ANNEX G: REVERSE DISPERSION MODELLING RESULTS FROM TEST SITE 1	65
G.1 PROTOCOL FOR INVERSE MODELLING TO QUANTIFY POLLUTING EMISSIONS ON A LOCAL SCALE.....	65
G.2 MONITORING STRATEGY	65
G.2.1 Measurements: Pollutants and Wind	65
G.3 DIRECT MODELLING	66
G.4 REVERSE MODELLING AND VALIDATION	66

EXECUTIVE SUMMARY

This project requires the development and validation of standardized test methods for the determination of diffuse and fugitive emissions of volatile organic compounds (VOC) 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.

A report summarising the available techniques for fugitive VOC monitoring has been completed, providing a comprehensive description of the options along with their advantages and disadvantages, suitability of particular applications and references for completed field campaigns where this is available. DIAL, OGI, SOF, tracer correlation, sniffing, flux chamber measurements, modelling, bagging and RPM are the techniques covered. The full report is included as an annex to this interim report.

A field measurement campaign was carried out at a decommissioned area of a refinery in France during September 2016. This used a controlled release facility to assess the relative strengths and weaknesses of the five techniques taking part in the testing when measuring a known quantity of VOC. OGI, DIAL, SOF, tracer and RDM were the methods tested, which achieved preliminary results according to their performance claims, demonstrating the potential to be included in the second phase of validation testing. Final data processing is currently ongoing by the instrument operators, therefore confirmed results will be released when that process is complete.

The second measurement campaign to assess the application of techniques at an active industrial site is scheduled for June 2017 in the Netherlands. The same five techniques (OGI, DIAL, SOF, tracer and RDM) will be deployed as were used in the first measurement campaign.

Overall the work is on schedule and should be successfully concluded by the projected completion date.

1 INTRODUCTION

This project requires 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".

1.1 CONTEXT

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/TC 264/WG 38.

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.

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 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.

3 WORK PACKAGES SUMMARY

3.1 WP1 RESEARCH INTO PERFORMANCE OF MONITORING TECHNIQUES

This work package is 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 present a summary of performance assessment for the available monitoring techniques and the full report is included in Annex A.

3.2 WP2 PLANNING AND COORDINATION OF THE FIELD MEASUREMENT PROGRAMME

This work package is 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.

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. Four participants participated in the tests, running a total of five instruments, covering five of the proposed techniques described in this report. Initial results and initial conclusions from the first validation study are discussed later in this report in Annexes D, E, F and G, with a full report to be completed once all results have been finalised and the statistics calculated.

A Refinery in the Netherlands has been selected for the second validation study. This testing has been scheduled for June 2017, with four participants signed up to take part in the testing deploying the five methods as used in the first validation study.

The coordinator has successfully supported the planning and organisation of the first field validation campaign. The list of tasks that have been performed to date are presented in Annex B.

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

This work package is 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 three fixed meteorological masts fitted with three ultrasonic met stations were also deployed during the first field validation test. A description of the sensors, list of parameters that were recorded and small data set examples are presented in Annex C.

3.4 WP4 OPTICAL GAS IMAGING CAMERA

This work package is 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 being selected for use at the validation site tests. This satisfies the requirements for the first task.

Initial results from the testing at Site 1 are discussed later in Annex D, with a full report to be completed once all results have been submitted and the statistics calculated.

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 is 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.

A pre-test visit to the decommissioned refinery in Southern France has been carried out by all the participants in June 2016 and the location of the controlled identified. The locations where all the participant’s meteorological stations would deployment their meteorological stations were identified. The participants also drew and agreed the implementation of a work programme. Table 3.1 lists the organisations that took part at the first validation study and their responsibilities.

Table 3.1 List of participants at the first validation study and their responsibilities.

Participating Organisations	Responsibilities
Bureau Veritas	<ul style="list-style-type: none"> • Campaign coordinator • OGI technique operator
INERIS	<ul style="list-style-type: none"> • Meteorological sensors and wind LIDAR deployment • Controlled gas release system operator
NPL	<ul style="list-style-type: none"> • Supply the controlled gas release system • DIAL technique operator
FluxSense and Chalmers University of technology	<ul style="list-style-type: none"> • SOF technique operator • Tracer technique operator
Total	<ul style="list-style-type: none"> • RDM technique operator

The field validation programme, consistent 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 (N₂O) release point for the tracer correlation method was situated in the centre of the release area.

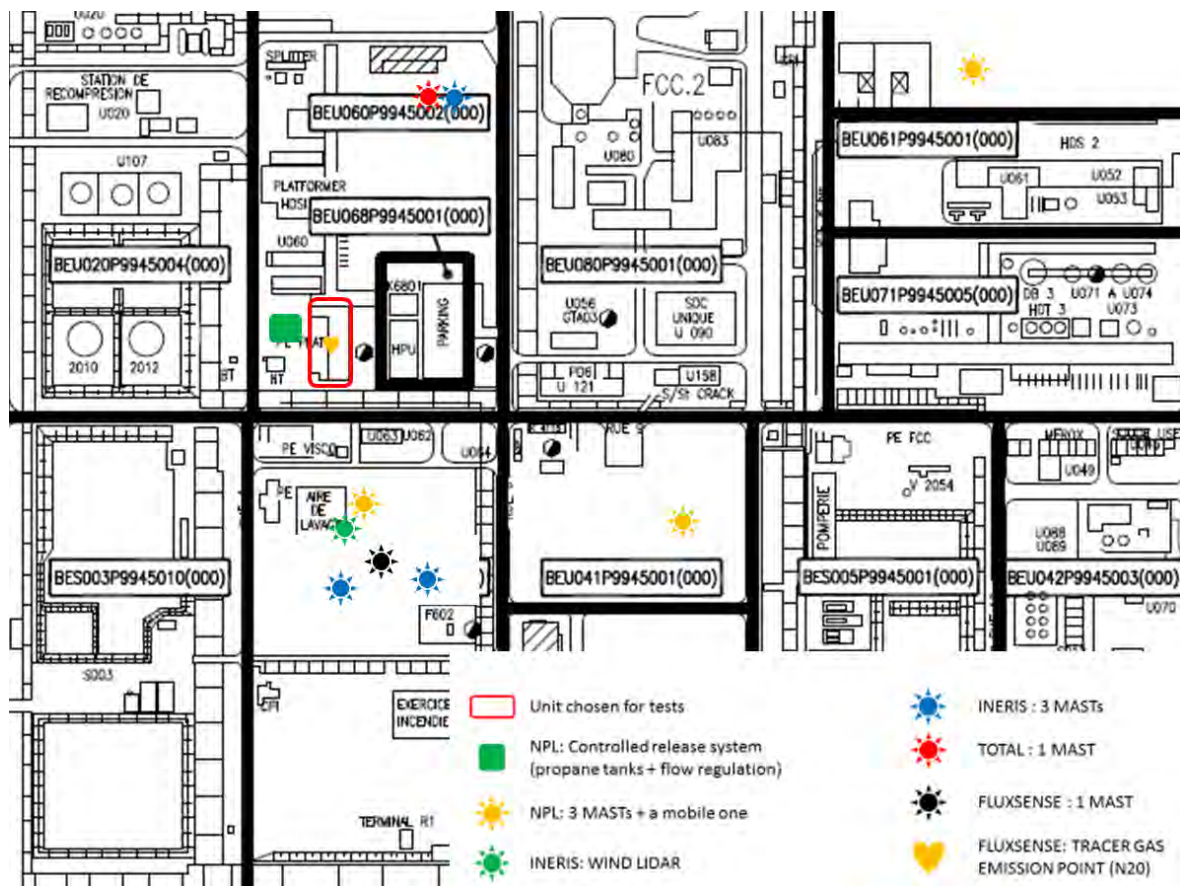


Figure 3.1 Locations of the meteorological stations

Figure 3.2 shows the locations inside the selected decommissioned unit of the five controlled release nodes. The released gas was mainly propane (about 91%) with a small percentage of propene, i-butane and n-butane. The controlled area release facility was operated by INERIS that was in charge of selecting for each test the release nodes and rates that currently are still unknown to the participants. The maximum achievable emission rate was about 30 kg/hr.

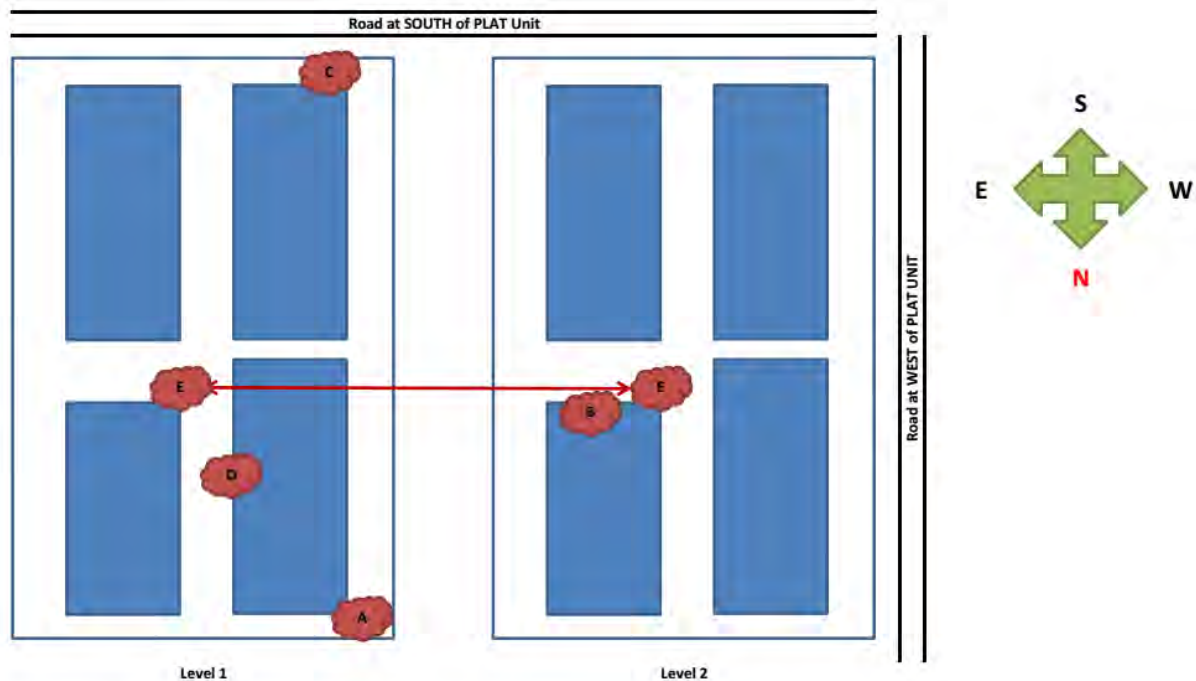


Figure 3.2 Locations of the five controlled release nodes

The FluxSense/Chalmers team using the SOF and tracer correlation methods found several interfering sources of VOC, resulting in higher background levels when the wind was in certain directions. The DIAL also measured background sources in most of the scans, but could generally isolate their plumes from the plume of the intended release.

The preliminary results were presented by the four participants at a WG38 meeting on the 11th and 12th of January 2017. These preliminary results are reported in Annexes D, E, F and G.

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

This work package is 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 site for the second field campaign has been selected in the Netherlands and, pending site's confirmation, it is due to take place in June with four participants deploying five techniques.

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

This work package is 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

Reporting on the comparisons of all the results and conclusions with proposals for consequences and inputs to the European Standard. This will be carried out once the analysis and intercomparison of the field trial data has been completed.

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

This work package is 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 recommended specifications for the techniques that have been incorporated into the most recent draft of the new standard. This will be revised once full analysis of both validation studies has been completed.

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

This report meets the requirements of the first task.

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. Eight techniques

are covered falling into three general applications. DIAL, SOF, tracer correlation, modelling techniques and RPM are used for identifying and measuring plumes and fence line or whole site surveying. Flux chamber measurement is typically used for defined area source emissions such as landfill sites or water treatment ponds, an application that can also be quantified by techniques such as DIAL. The final category is generally utilised for leak detection and/or quantification and includes sniffing, bagging and OGI. 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 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 30-40%, although a set of measurements is usually made which reduces the uncertainty typically below 30%.

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 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 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 OCCULTATION FLUX (SOF)

SOF is based on using the sun as the light source and 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 is connected to a solar tracker. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m² 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 at 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 (C₂-C₁₀), 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 CO₂ in the latter case.

4.3 TRACER CORRELATION TECHNIQUES

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. 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 MODELLING TECHNIQUES

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.

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

4.5 RADIAL PLUME MAPPING (RPM)

Radial plume mapping (RPM) uses open-path optical techniques to measure an area using multiple, non-overlapping beam paths reflecting off mirrors deployed along the ground and up a mast. 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. 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, limiting its application on larger sites.

RPM normally uses FTIR systems, but other path integrated optical remote sensing techniques like UV-DOAS or TDLAS can also be used. If FTIR is used it would detect VOC with the benefit that it can also identify the species that are present. Sensitivity will vary depending on the instrument used but will typically be in ppb range.

4.6 FLUX CHAMBER MEASUREMENTS

The flux chamber method allows quantification of VOC emissions through measurement. 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.). 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. Flux chamber measurements made with a FID analyser can measure total VOC, methane or any specific VOC. There

are a number of types of chamber based on the surface source being measured:

- Chimney chambers
- Static and accumulation chambers
- Low flux (or renewal) chambers
- Dynamic flux chambers

4.7 SNIFFING

“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. These correlation curves link the leak concentration measured (in ppmv) to a leakage rate (in g/hr).

4.8 BAGGING

“Bagging method” is a standardised method used since the early 1990s to measure the flow from a component with a pre-existing leak. This international approach is defined in the US through a standard, EPA-453/R-95-017. The method consists of enclosing (“bagging”) a leaking component like flanges, valves, pumps, compressors or plugs, to measure mass emissions of VOCs. 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.

Once the component has been bagged a known rate of carrier gas is induced through the bag. The carrier gas can be blown into the bag (blow through method) or air can be pulled through the bag using a vacuum pump (vacuum and high flow sampling methods). Blow through leads to better mixing in the bag and requires no correction for background VOC concentrations, however you require a carrier gas that is free of VOCs. The vacuum method pulling ambient air risks detecting a false background if the air contains high levels of VOCs so should not be used when screen for levels below 10ppmv.

4.9 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 areas not accessible 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 INITIAL CONCLUSIONS FROM THE FIRST VALIDATION STUDY

INERIS has received in January 2017 first results from the different contractors of WP4, WP5 and WP6. These preliminary results from the four participants to the first field validation test, running a total of five instruments, have been presented to the WG38 members in January 2017. INERIS has not yet released the actual emission rates of the twenty test releases since some parameters of the tests are not fully finalized, such as the analysis of the chemical composition of the gas released.

Figure 5.1 presents a comparison of the DIAL, SOF, Tracer and RDM preliminary results showing a general good agreement between different techniques. Figure 5.2 shows the correlation between the different methods is good and very promising a part from RDM preliminary results that are not correlated with the other techniques. Some minor changes have to be done to these first results related to the selection of which meteorological data to use before comparing them to the values of the controlled propane release. The complete analysis of the first trial results is due to the end of March 2017.

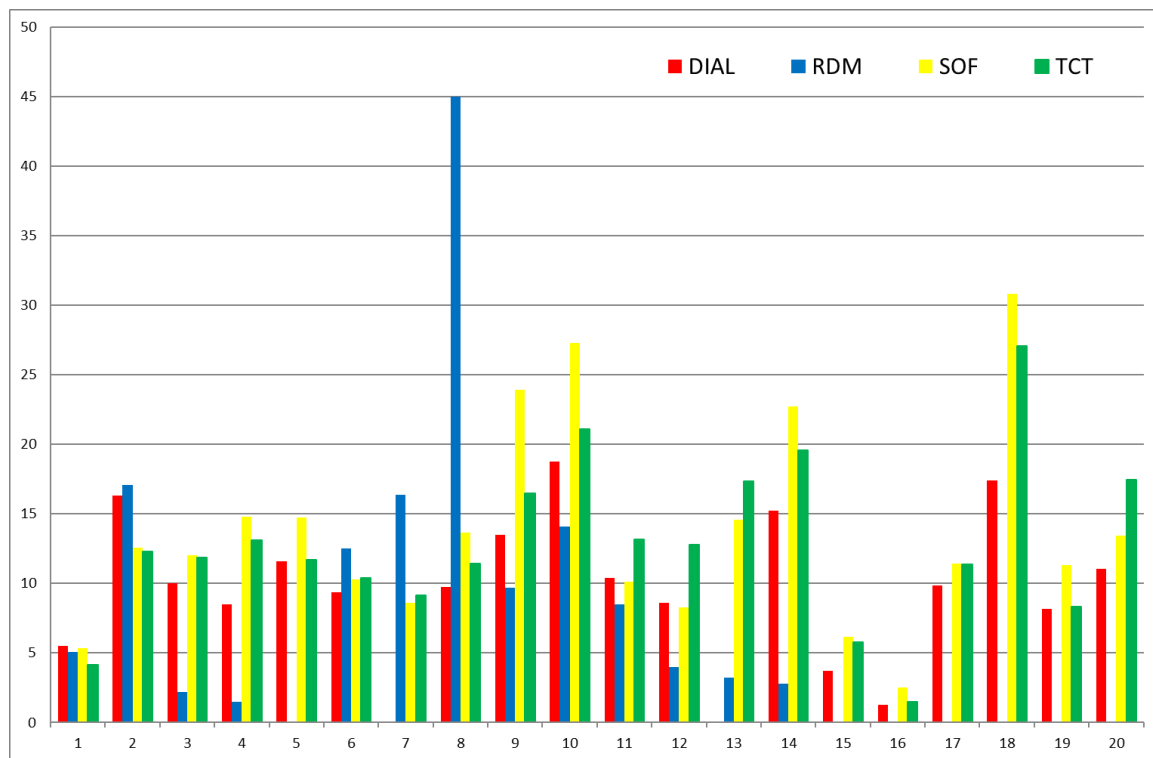


Figure 5.1 Preliminary results of DIAL, SOF, Tracer and RDM measurements

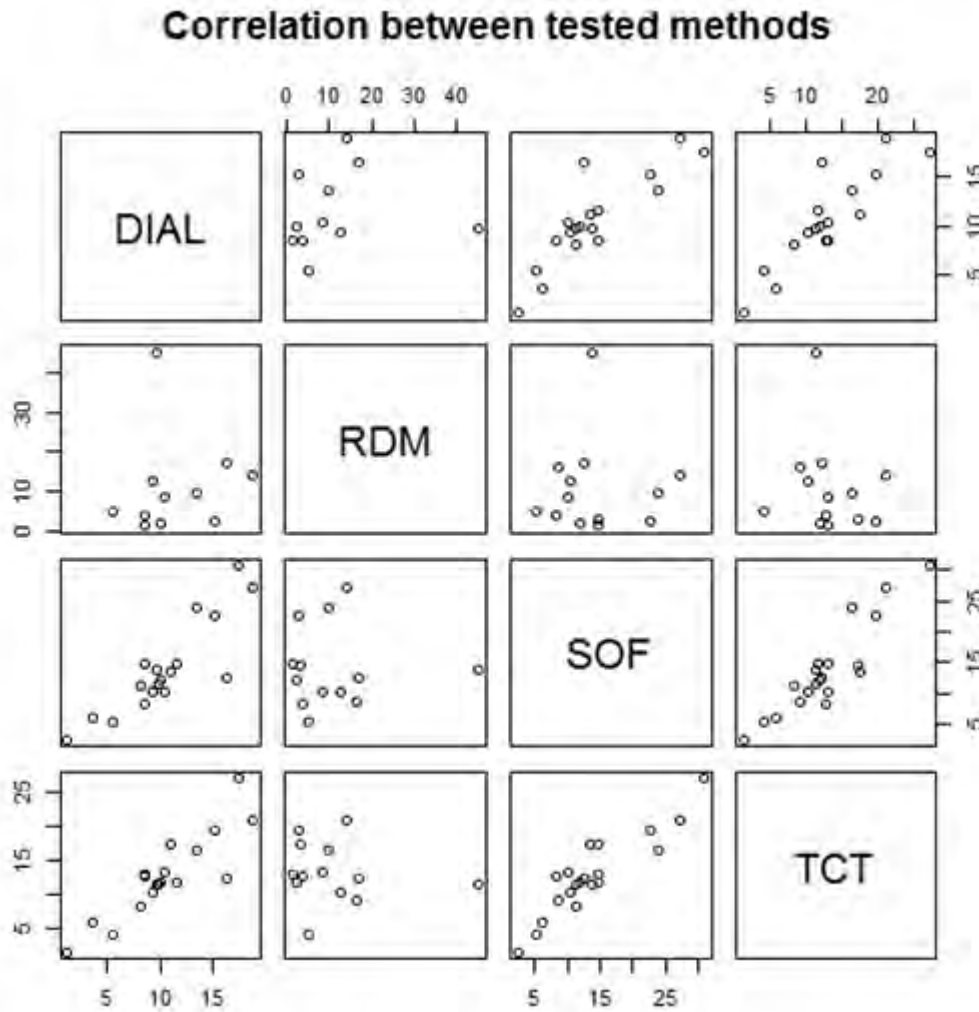


Figure 5.2 Controlled releases preliminary results correlation between DIAL, SOF, Tracer and RDM methods

All the techniques were able to produce results according to their performance claims and from the analysis of this preliminary results it is clear that all the techniques have the potential to conclude the second validation stage.

A detail analysis is currently being carried out by each participant and the results used to update the protocols that will be in place for the second validation study. These results will also provide performance data for the conclusions in WG38 European Standard.

5.1 STATUS OF THE WORK PROGRAMME

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	<p>Validation work:</p> <ul style="list-style-type: none"> • WP1: Research into performance of monitoring techniques see Annex A • WP2: First field test organised, planning of second field test See Annex B • 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 Annexes E, F, G <p>Development of the standard:</p> <ul style="list-style-type: none"> • WP9: This interim report on progress of the project 	
4/ Remaining work	<p>Validation work:</p> <ul style="list-style-type: none"> • WP2: Organise the second field validation test • WP3: Deployment of the specified sensors for the second validation test • WP5: Reports and conclusion from the first validation test • WP6: Finalise the work plan and complete the monitoring exercise at the second industrial site • WP7: Statistical evaluation of all the results and conclusions to be carried out once the field trial data is analysed <p>Development of the standard:</p> <ul style="list-style-type: none"> • WP8: Develop specifications of the performance requirements for remote monitoring methods for use with the standard once full analysis of both validation studies has been completed • WP9: Final report covering the results of the two field validation programmes with conclusions and recommendations, performance specifications for the selected methods. Reporting to the Commission on preparation of the standard <p>This project is in line with the original timeframe. In case of any unforeseen events that might influence these steps and the timeframe of the project, the Commission will be informed.</p>	<p>May/June 17 May/June 17</p> <p>May 17</p> <p>October 17</p> <p>February 18</p> <p>April 18</p> <p>June 18</p>
5/ Documents	<p>Annex A: Performance characteristics recommended for the draft standard</p> <p>Annex B: Planning information for the first field campaign</p> <p>Annex C: Meteorological measurements from test site 1</p> <p>Annex D: OGI selection and preliminary results from test site 1</p> <p>Annex E: DIAL preliminary results from test site 1</p> <p>Annex F: SOF and tracer preliminary results from test site 1</p> <p>Annex F: Reverse dispersion modelling results from test site 1</p>	

ANNEX A: PERFORMANCE CHARACTERISTICS RECOMMENDED FOR THE DRAFT STANDARD (WP1)

See separate document “Annex A Techniques Review (WP1).pdf”.

ANNEX B: PLANNING INFORMATION FOR THE FIRST FIELD CAMPAIGN (WP2)



CEN/TC 264/WG 38 - Call for tender - Work Package #2

Technical proposal

Writer: Jonathan Martinez

ECS - BUREAU VERITAS Reference 389923 / 151104-0188

Revision 0 – November 2015

Environnement Contrôle Service

SAS Capital 262 000 € - Siret 449 388 669 000 37 - RCS Aix 2003801000 - Code NAF 7120B

Numéro Intracommunautaire : FR 73 449 388 669

Siège Social : 37/39 parc du Golf CS 50515

13593 AIX EN PROVENCE cedex 3

Tél. : 33(0)4 42 54 21 96 - Fax : 33(0)4 42 54 20 15

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

Summary

GENERAL OBJECTIVES	3
SCOPE OF THE PROJECT	3
I - GENERAL STRATEGY	4
II - SERVICE DESCRIPTION AND METHODOLOGY	5
1) - Initial consultation and planning.....	6
2) - Support for validation programme at site 1	7
3) - Support for validation programme at site 2	9

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

General Objectives

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


Scope of the project

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

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

During the field measurements the coordinator will provide guidance and inputs to the field measurements.

Finally, the coordinator will provide review of reports of the field measurements and conclusions drawn.


	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

I - General Strategy

During the last 25 years, we have built a **solid experience in conducting hundreds of large-scale missions** on Oil & Gas plants, including **multidisciplinary projects** involving numerous sub-contractors coming from **different countries**.

The recurrence of our missions and the extremely high quality of our services allowed us to **establish excellent long-term relations** with most of European majors' industrial sites.

We propose to associate the **strength of this experience** to the **territorial coverage of Bureau Veritas' network** in order to **approach and facilitate negotiations** with the most important number of candidate sites for the two validation studies.

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

II - Service description and methodology

The proposed services include 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 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 - Review of reports and conclusions drawn


3/ - Support for validation programme at site 2

- 3A - Preparation: Logistic organisation - Coordination
 - 3B - Existing data recovering and reviewing of LDAR programmes in place
 - 3C - Drawing up of a tests plan
 - 3D - Site visit
 - 3E - Presence at site 1 during trials
 - 3F - Review of reports and conclusions drawn
-

All deliverables generated for the purpose of this project will be written in English.

For all these phases, ECS - BUREAU VERITAS has developed:

- Fifty procedures over a 25-year period
- Tens of registration documents to collect and summarise data
- Advanced scheduling tools
- Clients' and prospects' database

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

1) - INITIAL CONSULTATION AND PLANNING

PHASE 1A - Candidate sites selection

The very first step of this phase will be to appoint from our resources, the coordinator for the field measurement programme.

(Deliverable 2a of the tender)

The second step of this phase will be to generate selection criteria for sites for the 2 campaigns (taking into account results from WP1). This work will be 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 will then present the project to potential candidate sites, corresponding to defined criteria.

Upon completion of this step, we will generate a short list of candidate site(s) for the two validation studies identified and then submit it to CEN/TC 264/WG 38.


(Deliverables 2b and 2c of the tender)

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

During this phase, our coordinator will manage the **draft scheduling** of all sub-phases on the two field validation tests.

To perform this task, he will **collect the needs** of each player (involved in the execution of WP3, WP4, WP5 and WP6) and **ensure their coordination** in line with the constraints of the sites hosting the tests.

It will also take care of driving everyone to **meet the established deadline**.

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

2) - SUPPORT FOR VALIDATION PROGRAMME AT SITE 1

PHASE 2A - Preparation: Logistic organisation - Coordination

Coordinator will provide assistance to coordinate contracts signing between CEN and site.

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

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

(Deliverable 2d of the tender)

The coordinator will play 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...

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

The coordinator will be in charge of "data recovering" regarding LDAR programmes in place on the site. He will review and evaluate its credibility (equipment, calibration, frequency, applicable regulation...).

This evaluation will be submitted to CEN/TC 264/WG 38 for being assessed.

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 will draw up a test plan for the first validation study.

This will, among others things, define 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 will take care about requirements of all techniques, especially spatial constraints.

This test plan will take into account the defined duration of the tests.

It is 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 is anticipated that the complete field campaign will have a duration of one to two weeks.

(Deliverable 2e of the tender)

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

PHASE 2D - Site visit

Coordinator will organise and lead a pre-study visit to the industrial site.

This visit will notably permit 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 will participate to this visit.

PHASE 2E - Presence at site 1 during trials

Coordinator will lead the opening of the project with the site representative and provide assistance for logistic aspects regarding all players.

The first role of the coordinator during the trials will be 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 will permanently be the focal point for exchanges with the site representative.

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

He will also check if every expected raw data is recorded, and ensure a backup of these.

Coordinator will manage the closing of the project with the site representative and provide assistance for logistic aspects regarding all players.


(Deliverable 2f of the tender)

PHASE 2F - Review of reports and conclusions drawn

Coordinator will review the reports of the field measurements and the conclusions drawn.

He will submit the report of his review to CEN/TC 264/WG 38.

(Deliverable 2g of the tender)

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
---	------------------------------------	-----------------

3) - SUPPORT FOR VALIDATION PROGRAMME AT SITE 2

PHASE 3A - Preparation: Logistic organisation - Coordination

Coordinator will provide assistance to coordinate contracts signing between CEN and site.

Together with the site representative, the coordinator will be in charge of the delimitation of the "testing area" on the first selected industrial site.

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

(Deliverable 2h of the tender)

The coordinator will play 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...

PHASE 3B - Existing data recovering and reviewing of LDAR programmes in place

The coordinator will be in charge of "data recovering" regarding LDAR programmes in place on the site. He will review and evaluate its credibility (equipment, calibration, frequency, applicable regulation...).

This evaluation will be submitted to CEN/TC 264/WG 38 for being assessed.

PHASE 3C - 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 will draw up a test plan for the first validation study.

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

This test plan will take into account the defined duration of the tests.

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

(Deliverable 2i of the tender)

	CEN/TC 264/WG 38 - Call for tender	Work Package #2
--	------------------------------------	-----------------

PHASE 3D - Site visit

Coordinator will organise and lead a pre-study visit to the industrial site.

This visit will notably permit 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 will participate to this visit.

PHASE 3E - Presence at site 1 during trials

Coordinator will lead the opening of the project with the site representative and provide assistance for logistic aspects regarding all players.

The first role of the coordinator during the trials will be 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 will permanently be the focal point for exchanges with the site representative.

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

He will also check if every expected raw data is recorded, and ensure a backup of these.

Coordinator will manage the closing of the project with the site representative and provide assistance for logistic aspects regarding all players.

(Deliverable 2j of the tender)

PHASE 3F - Review of reports and conclusions drawn

Coordinator will review the reports of the field measurements and the conclusions drawn.

He will submit the report of his review to CEN/TC 264/WG 38.

(Deliverable 2k of the tender)

ANNEX C: METEOROLOGICAL MEASUREMENTS FROM TEST SITE 1 (WP3)

C1 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.

C.2 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.

C.3 EQUIPMENT

INERIS has deployed the following equipment:

C.3.1 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.

C.3.2 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

C.4 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

C.5 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.

C.6 RESULTS

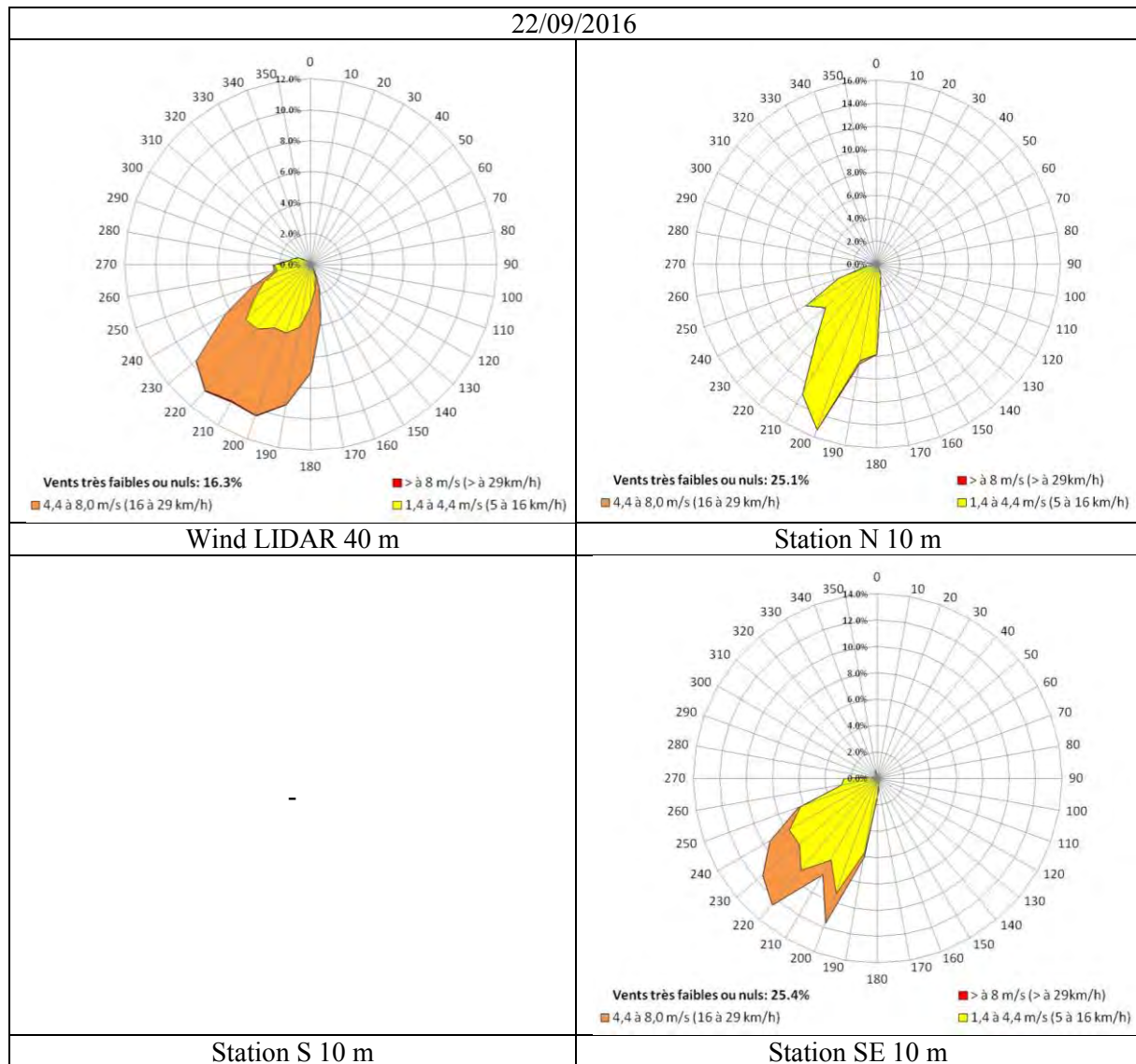
All instruments except the met station “Station S” have been running without any problem during the test releases. Only the station “Station S” has faced some acquisition problems, causing the loss of three days of data, out of six.

	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	Red	Green	Green	Red	Red	Green	Green	Green	Green	Red
Station_S	Red	Red	Red	Red	Red	Green	Green	Green	Green	Red
Station_SE	Red	Green	Green	Red	Red	Green	Green	Green	Green	Red
Wind LIDAR	Red	Green	Green	Red	Red	Green	Green	Green	Green	Red

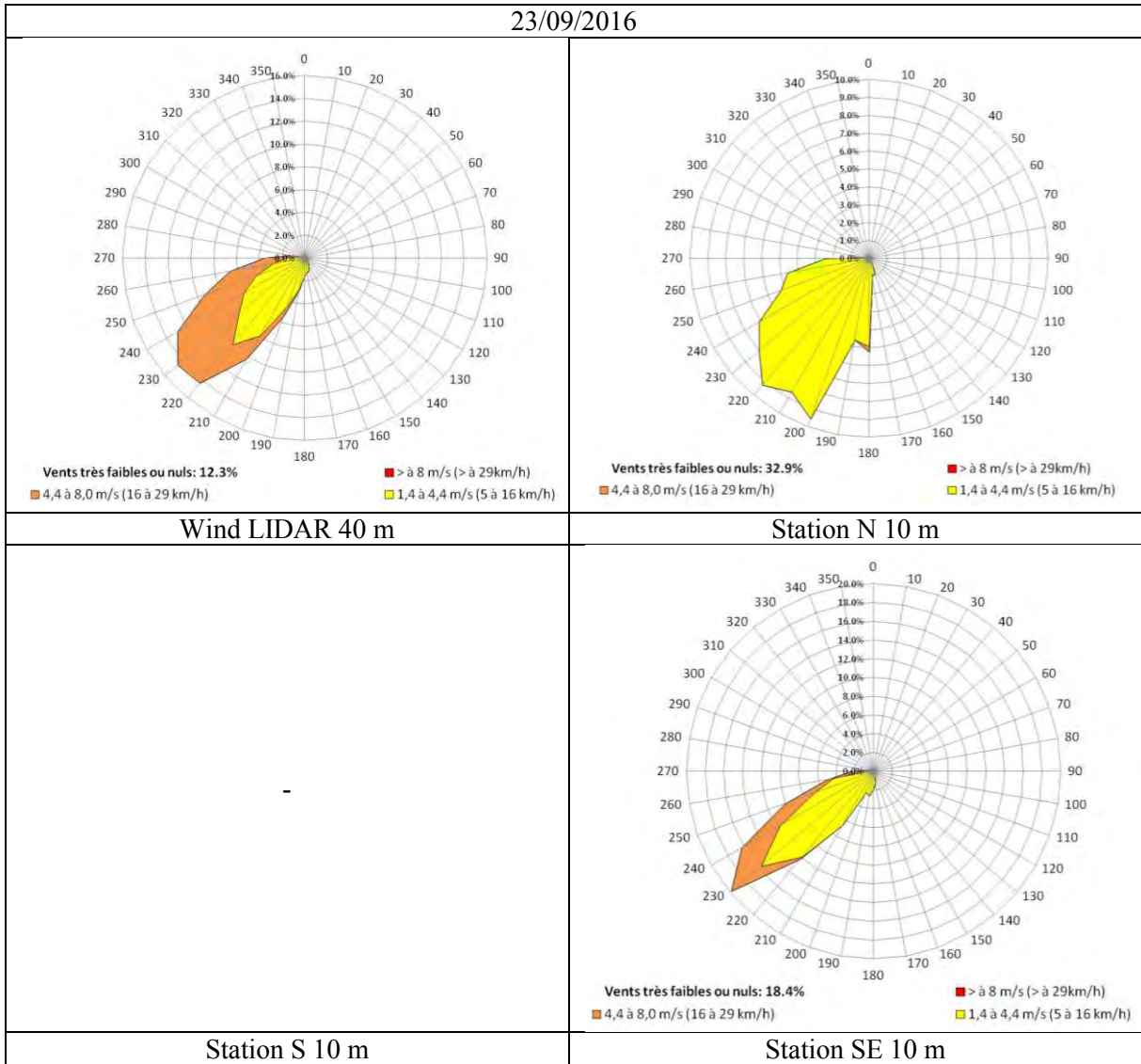
Figure C.1 Gantt diagram – met data acquisition

C.7 WIND ROSES FOR COMPARISON OF THE INERIS WIND DATA

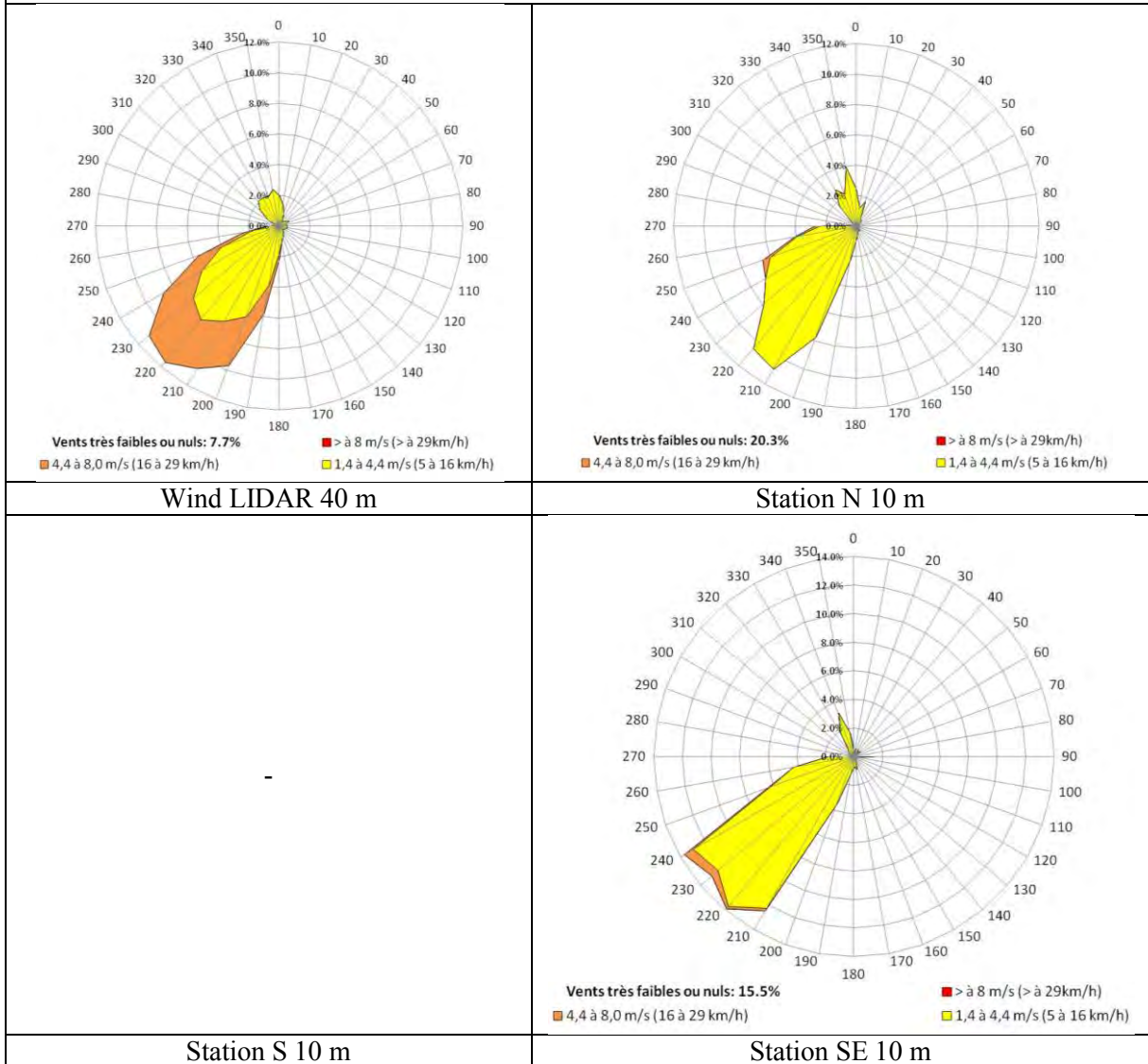
Wind roses have been prepared by INERIS to compare the wind data from each of their instruments on a daily basis for the duration of measurement at Test Site 1.



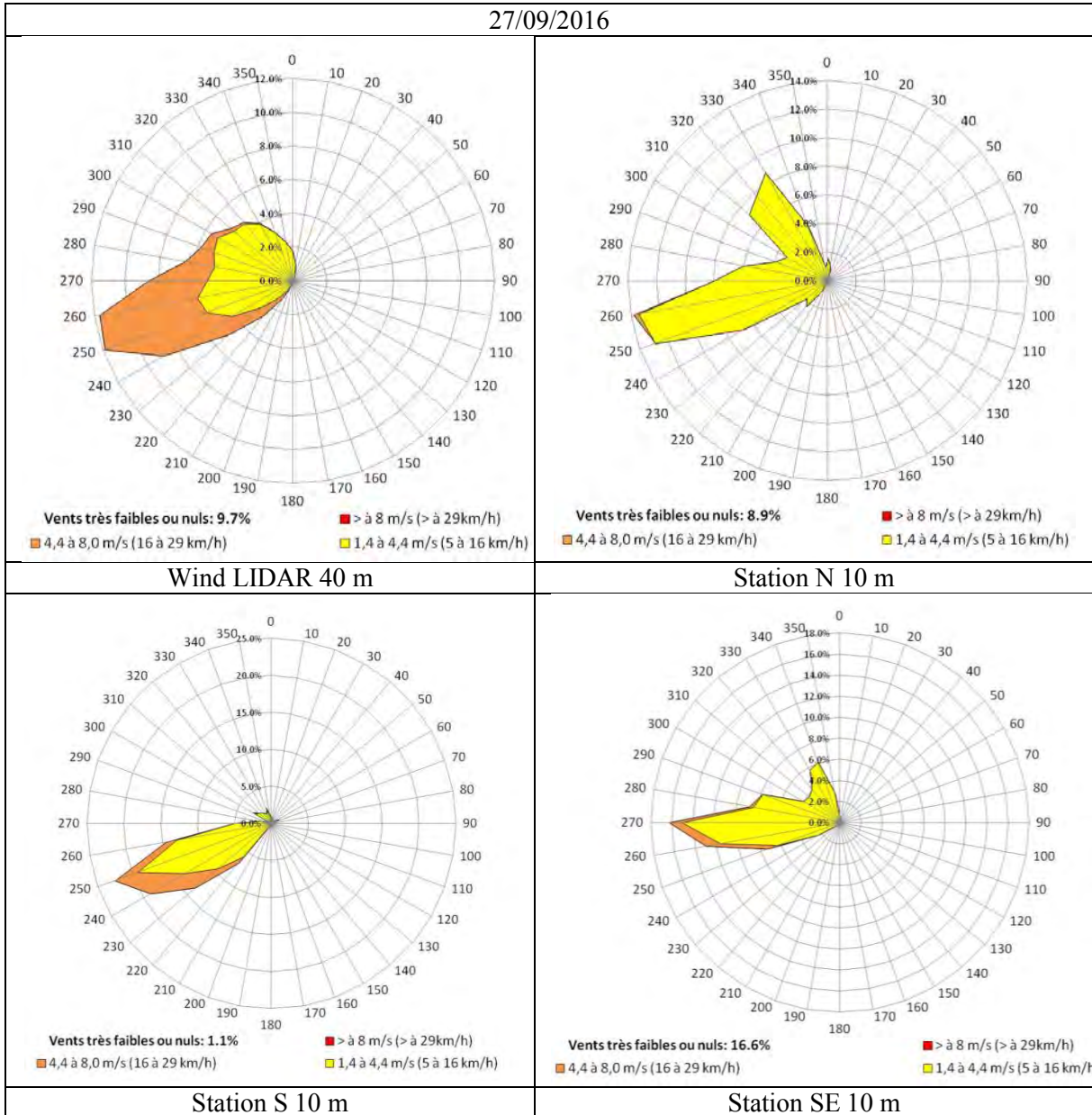
23/09/2016



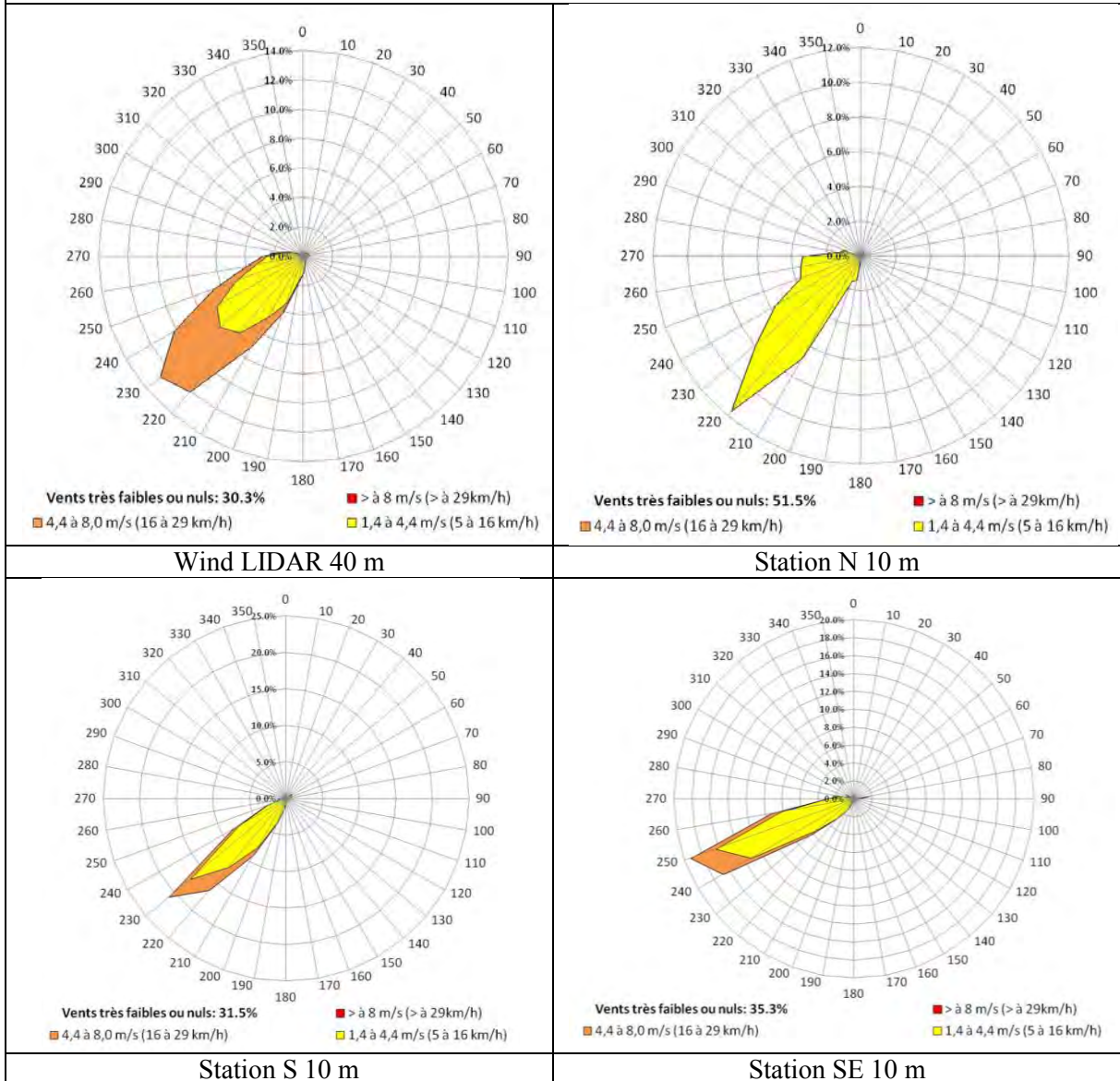
26/09/2016



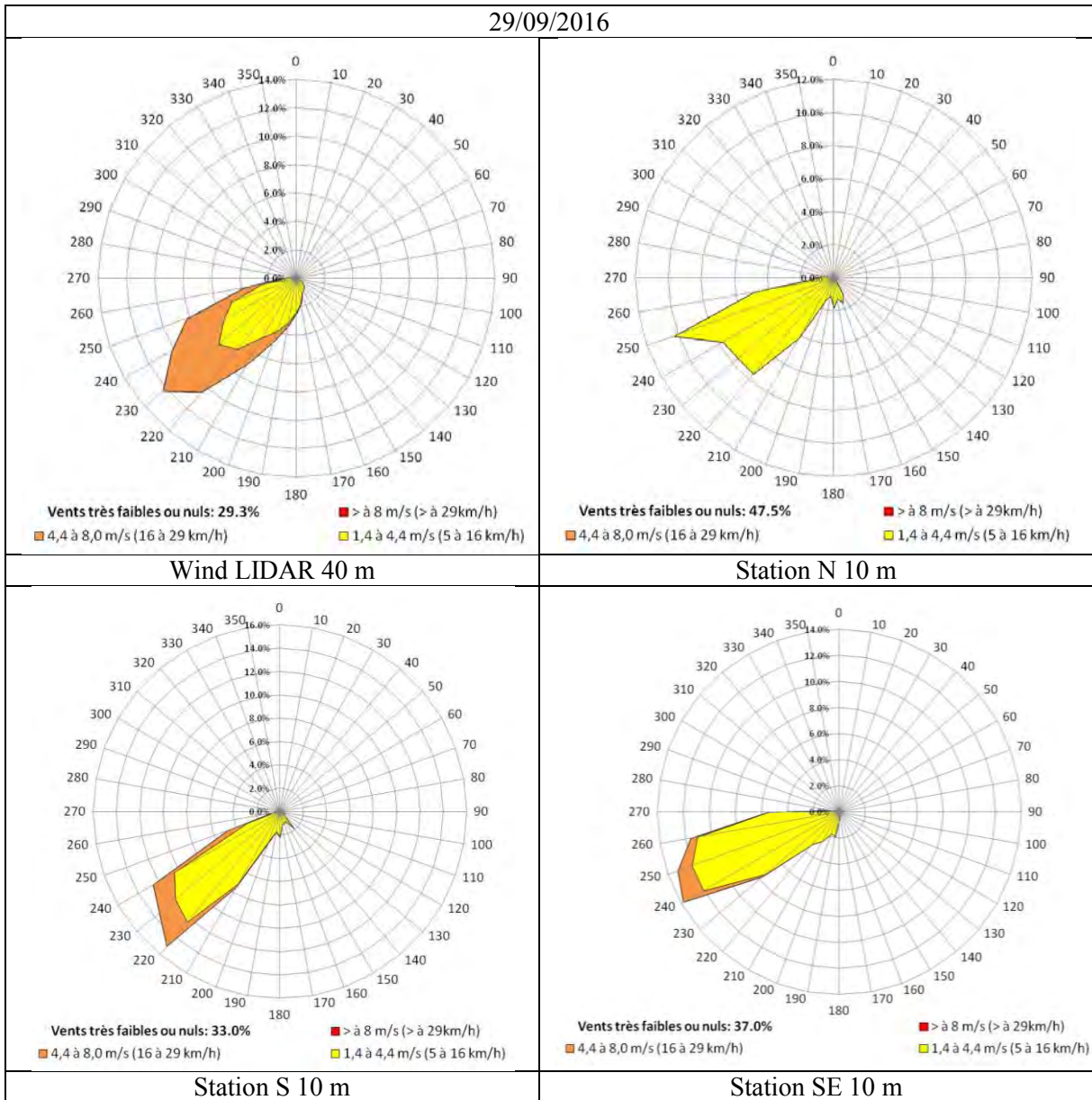
27/09/2016



28/09/2016



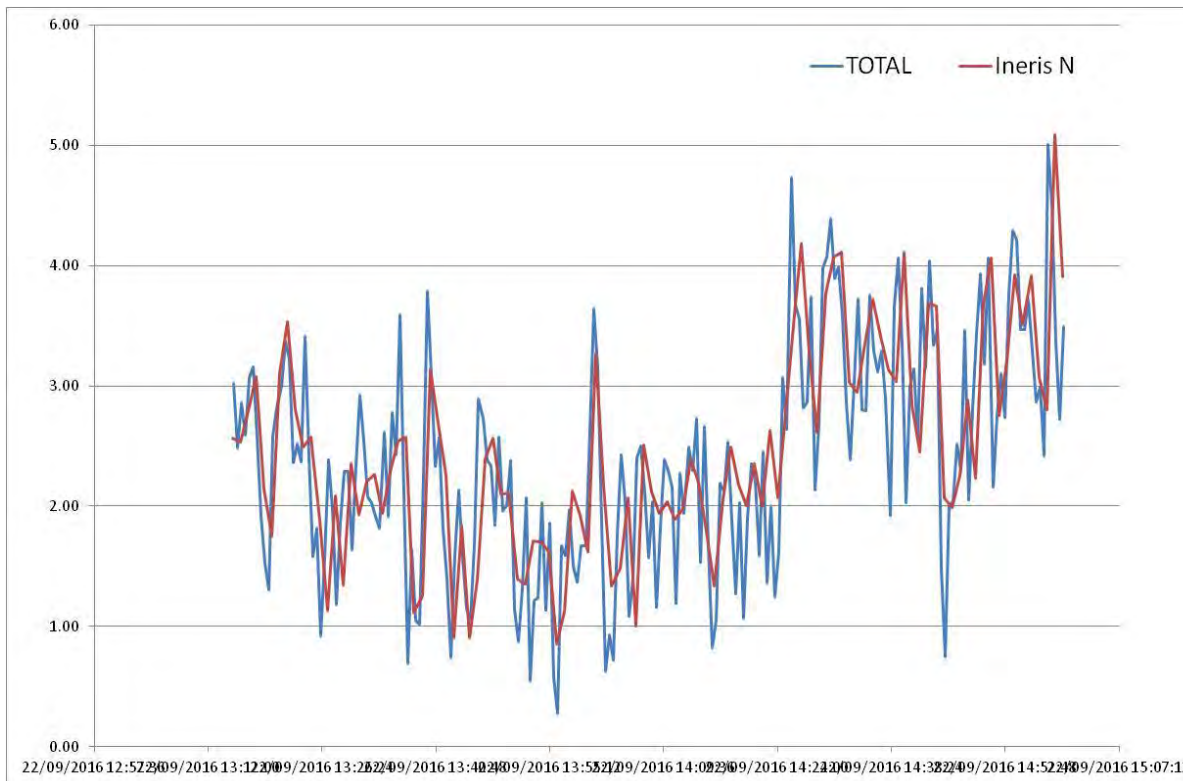
29/09/2016



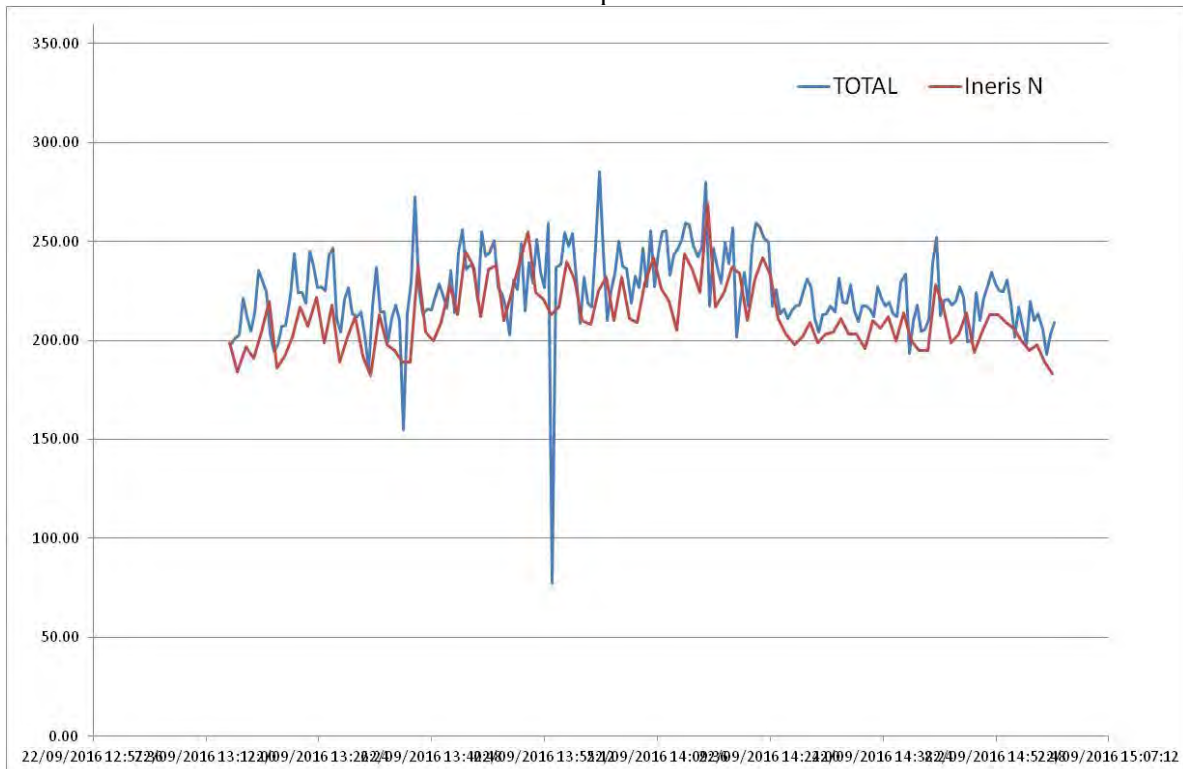
C.8 COMPARISON OF TOTAL AND INERIS NORTH MET STATIONS

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

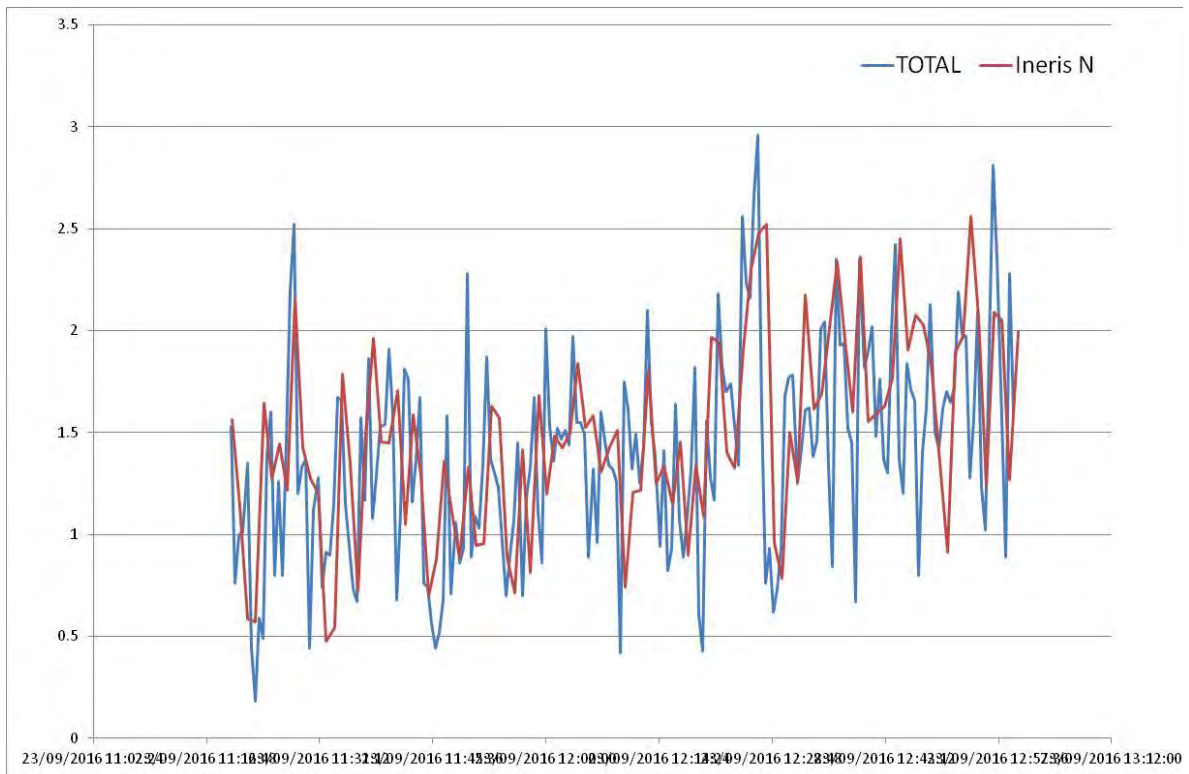


Wind speed

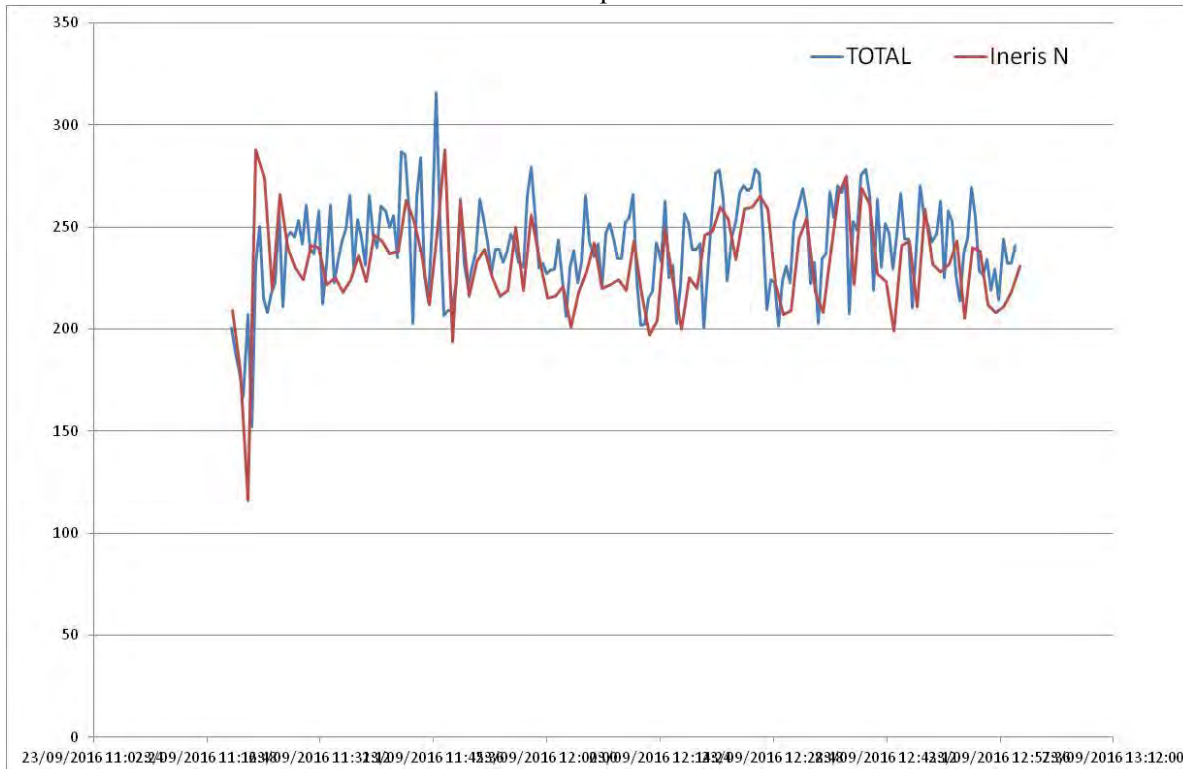


Wind direction

Test # 3 – 23/09 11h20 13h00

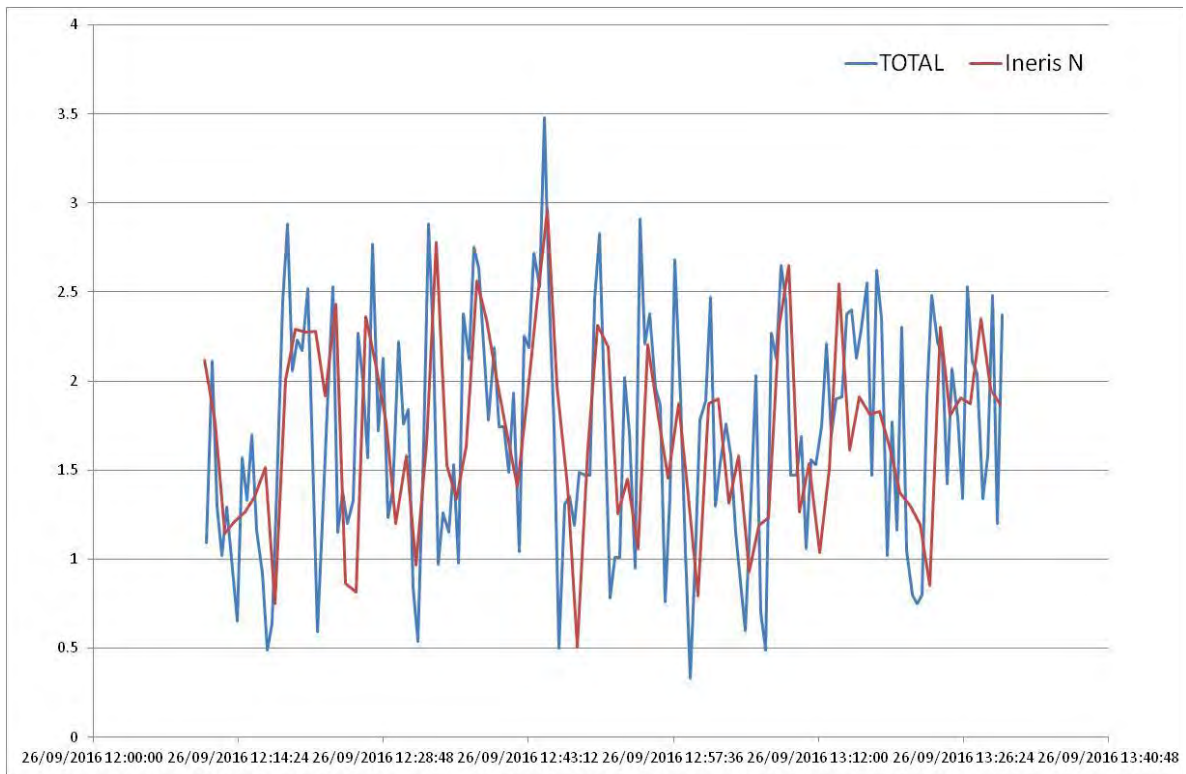


Wind speed

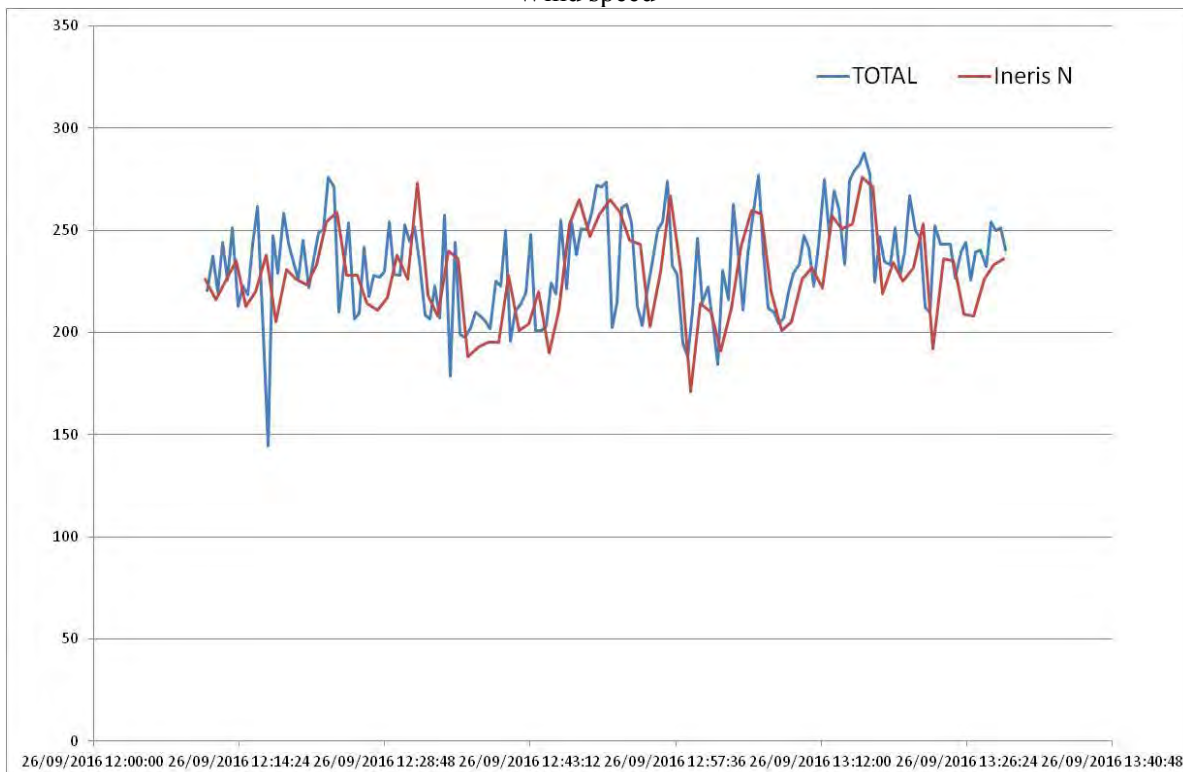


Wind direction

Test # 6 – 26/09 12h11 13h30

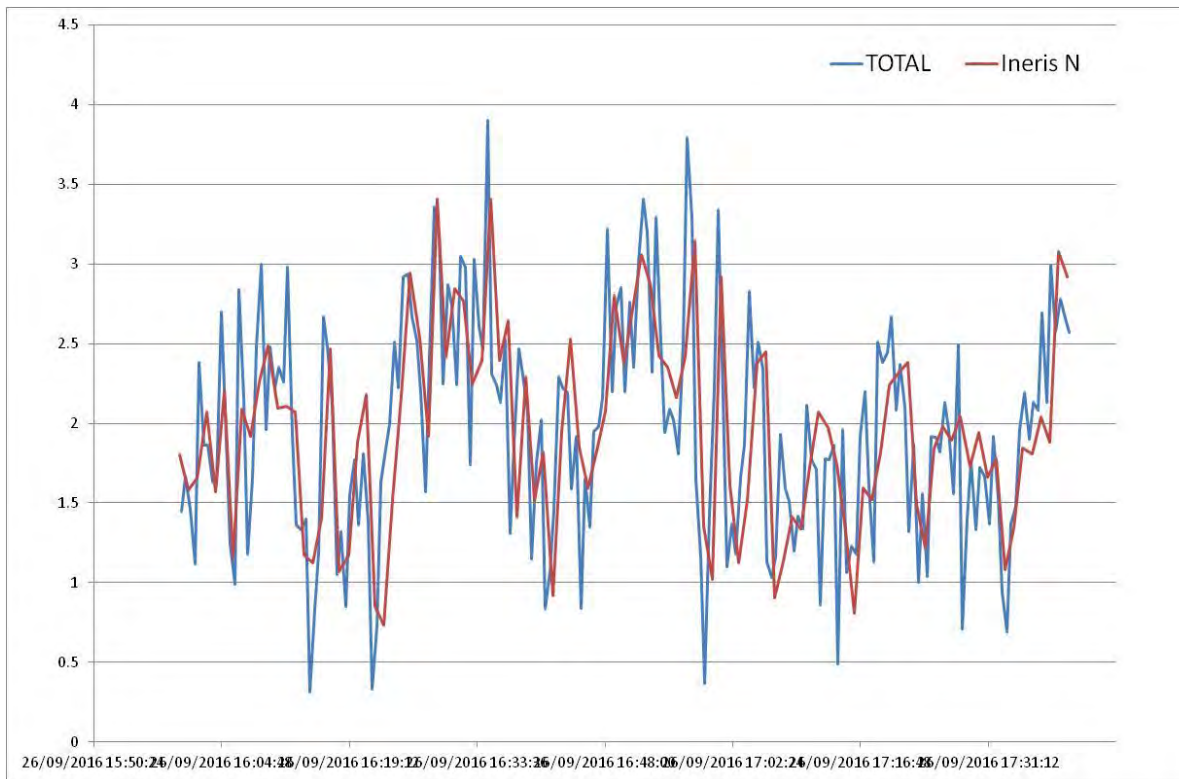


Wind speed

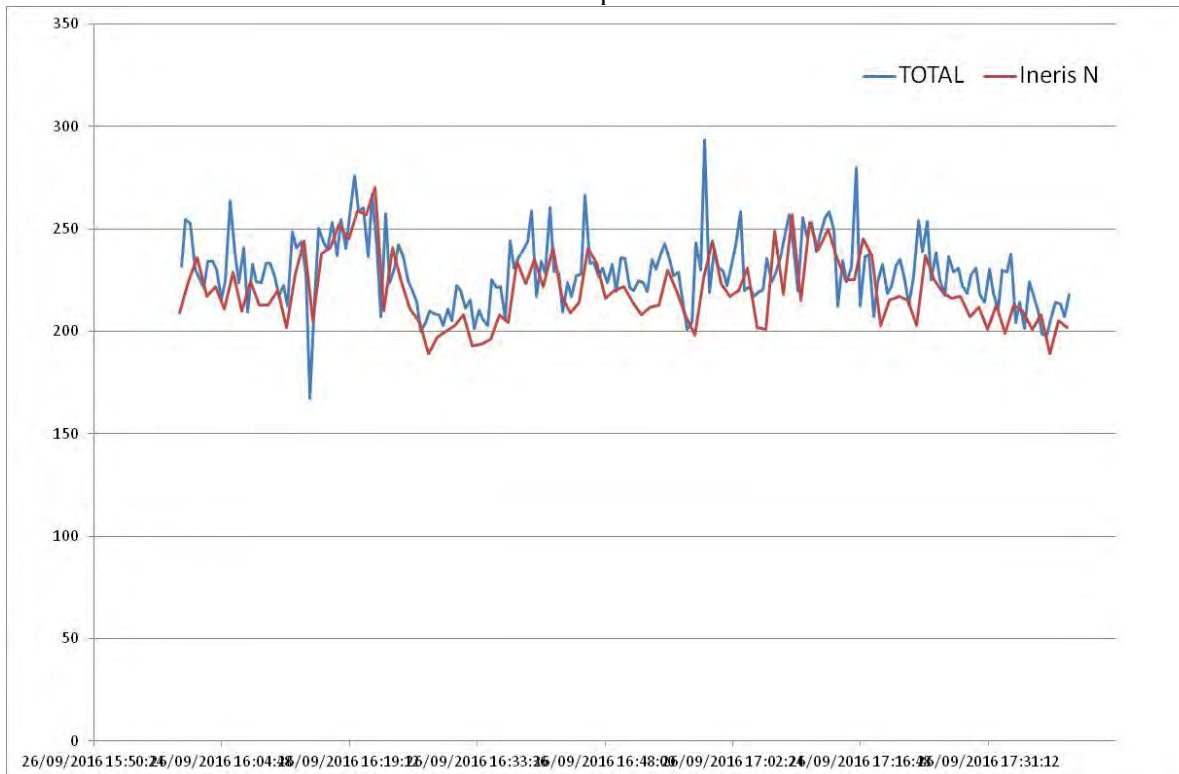


Wind direction

Test # 8 – 26/09 16h00 17h40

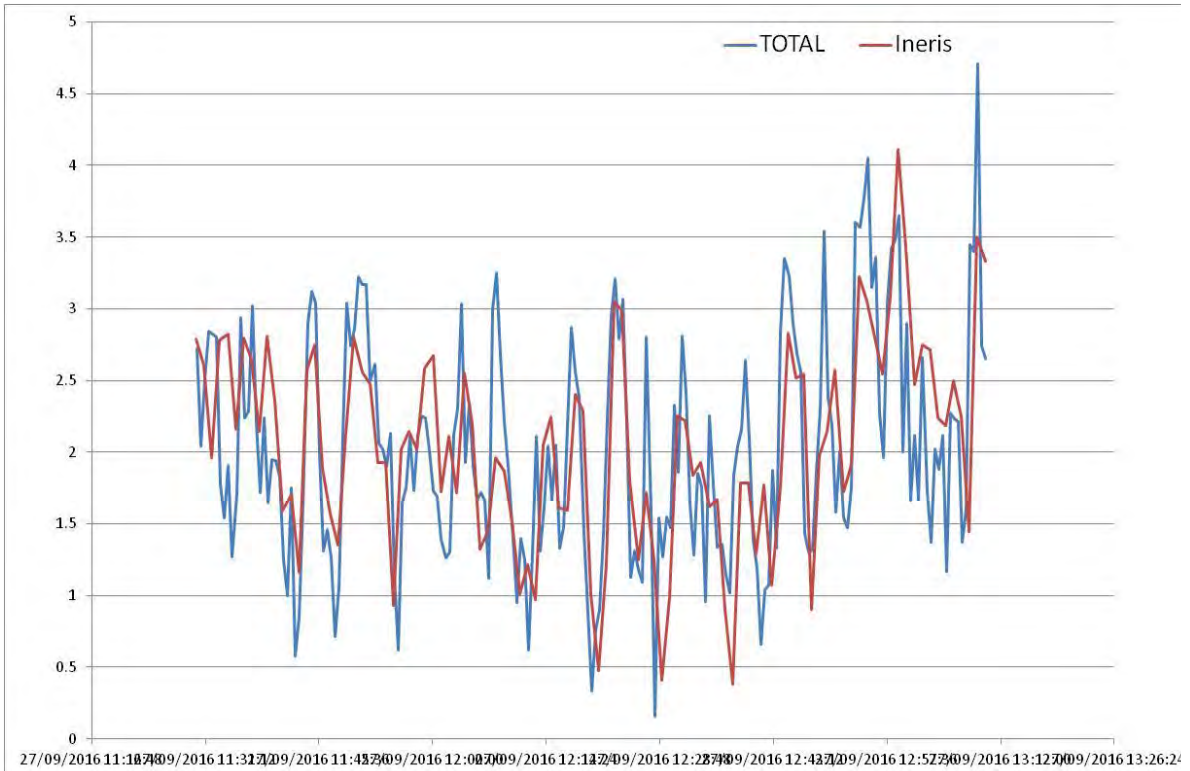


Wind speed

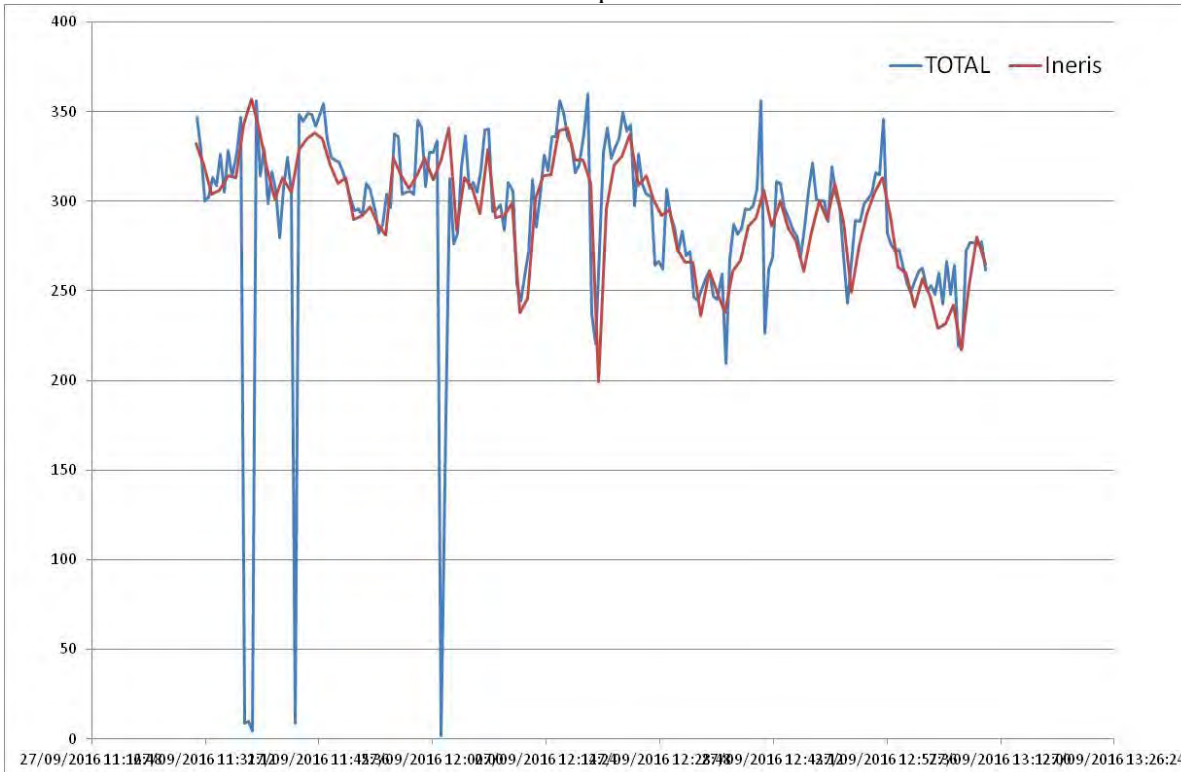


Wind direction

Test # 10 – 27/09 11h30 13h10

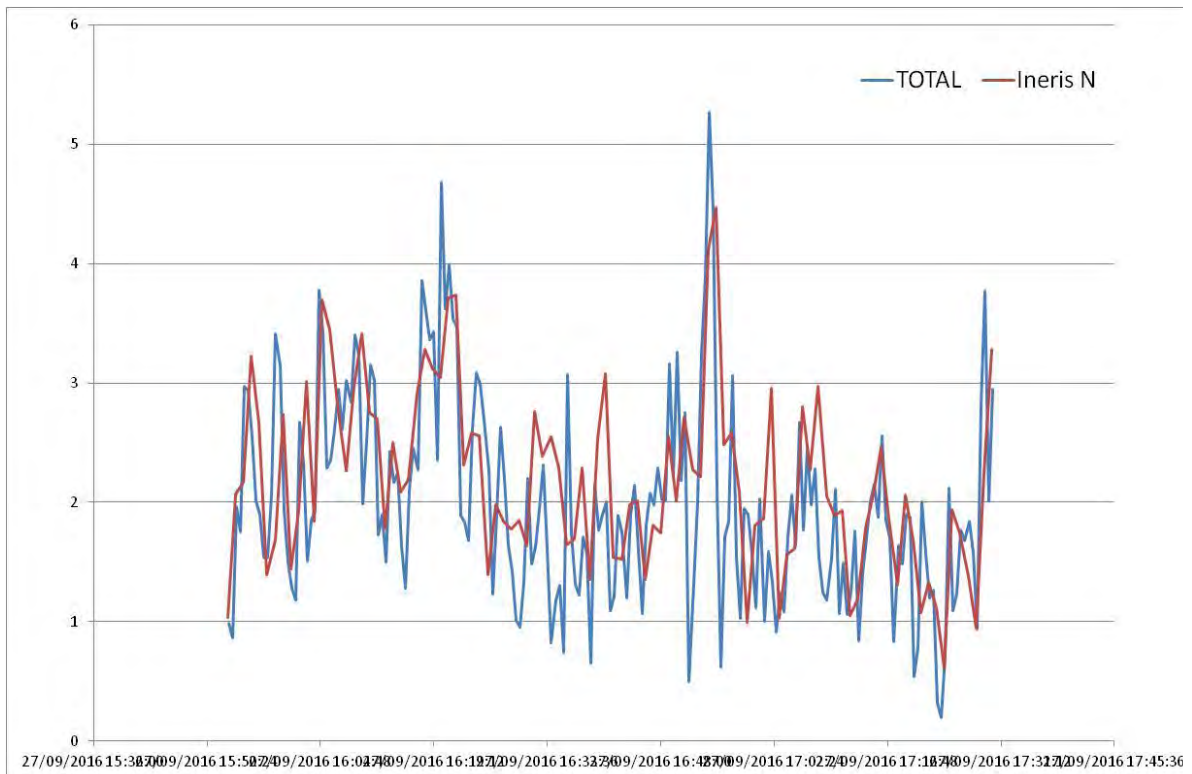


Wind speed

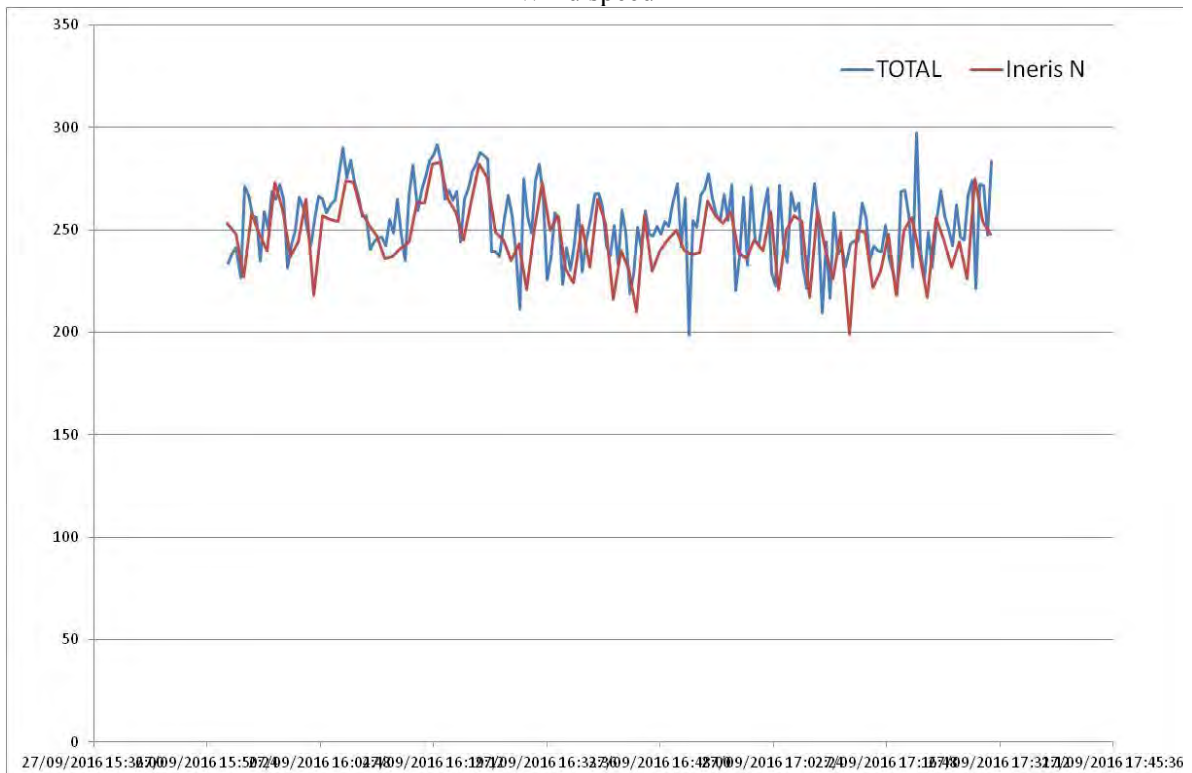


Wind direction

Test # 12 – 27/09 15h53 17h30

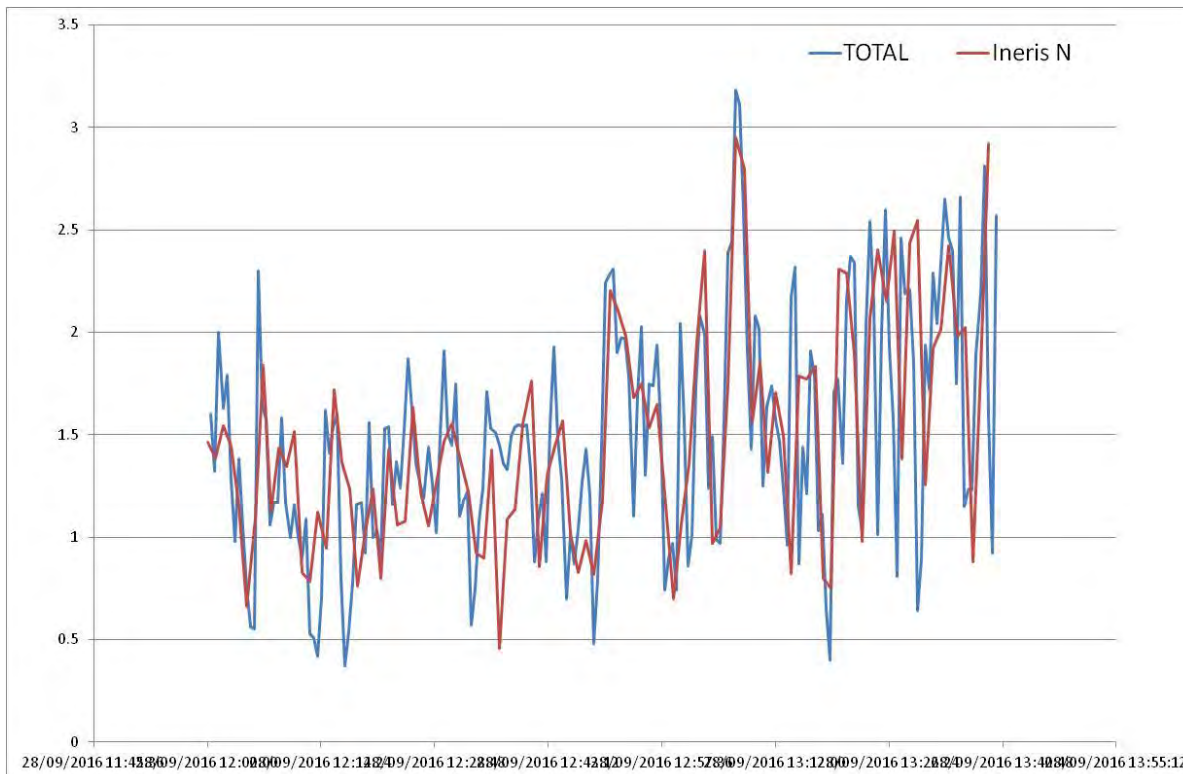


Wind speed

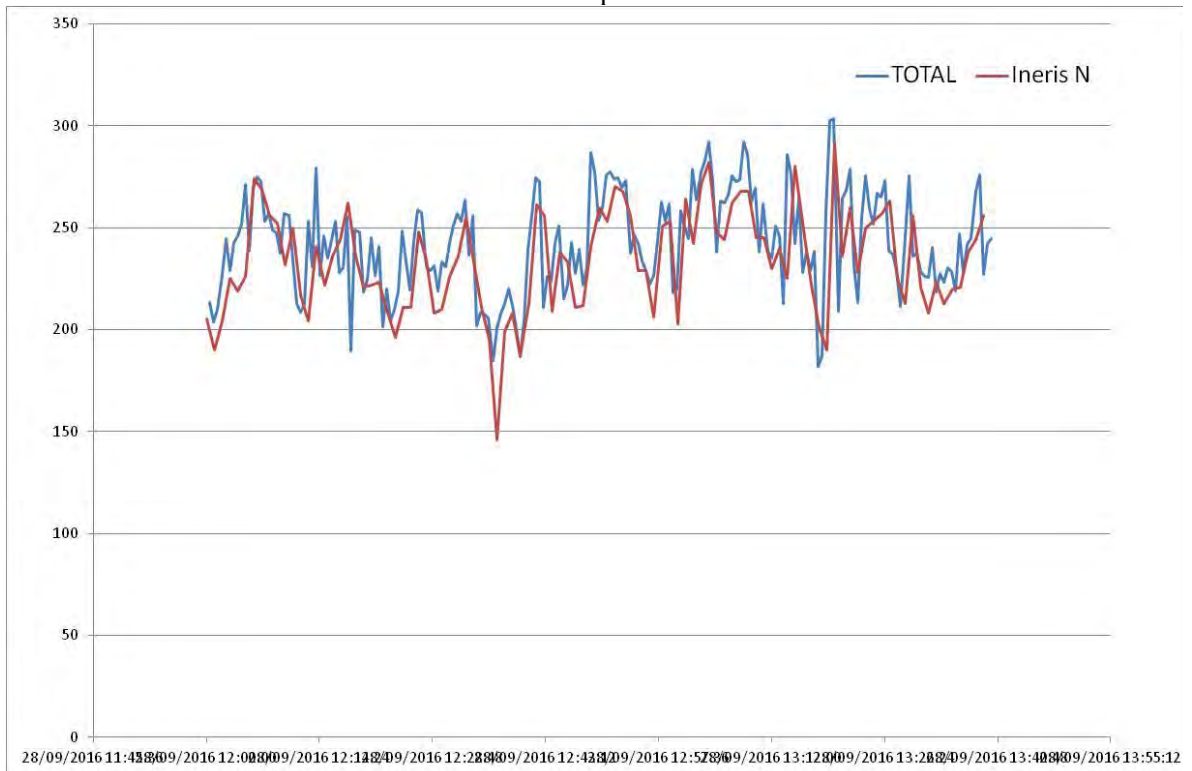


Wind direction

Test # 14 – 28/09 12h15 13h39



Wind speed



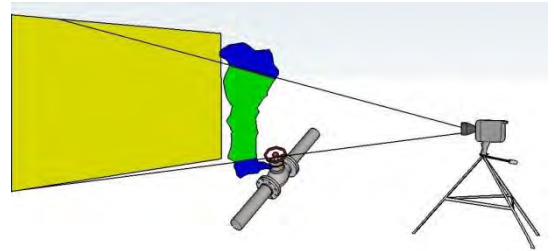
Wind direction

ANNEX D: OGI SELECTION AND PRELIMINARY RESULTS FROM TEST SITE 1 (WP4)

This technique uses an infrared thermal imaging camera, fitted with optical filter, which is sensitive to IR absorption by certain VOCs. The camera enables plumes of VOCs to be visualised, appearing as clouds of vapour on the video screen of the camera. This method can be used to locate certain emission sources located in Oil and Gas industries. Some ATEX certified models exist, however non-ATEX models are frequently used together with explosimeters and dedicated hot work permits

D.1 DETECTION PRINCIPLE

Passive Optical Gas Imaging cameras 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.

The basic principle is that an IR recording will be made only if an emission is detected.

D.2 DETECTABLE POLLUTANTS

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.

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.

D.3 DETECTION PROCEDURE

Before starting the detection, a test procedure is carried out in order to ensure the ability of the instrument to visualise emissions of the targeted VOCs.

Following a pre-determined detection plan, the leak detection round is carried out by qualified experts continuously taking care of keeping the OGI settings to the most appropriate ones. When available, a High Sensitivity Mode is preferred.

Before accessing the detection zone, a quick safety scan from an ample distance for very large and potentially hazardous leaks is performed. The average detection distance in "normal" conditions is around 2 to 4 meters. This distance can be extended when watching for huge emissions and/or using specific lenses. As the background of a visualisation scene is crucial for detecting an emission, the cameraman takes continuously care of its selection.

D.4 EQUIPMENT DEPLOYED

The deployed OGI will be a FLIR GF320 IR Camera.

Its main characteristics are:

- High Sensitivity mode
- GPS
- Thermal Sensitivity <15 mK @ +30°C
- Temperature Range -20°C to 350°C
- Spectral Response 3.2 – 3.4 μm
- Standard lens 24° × 18°
- Non-ATEX
- Transportable
- Camera weight, including lens and battery 2,48 kg
- Internal memory (SD cards)
- Battery-powered
- Encapsulation IP 54 (IEC 60529)



D.5 STAFFING

The detection staff team will consist of a single qualified expert watching thru each OGI. He will be guided and supported by the field test coordinator and others members of the WG38.

D.6 FACILITIES AND SERVICES REQUIRED

A place for storage of "calibrations" tanks will be required. A secured office with 200V supply will be required for charging the batteries, and for storing the equipment during the nights.

D.7 RESULTS FROM TEST SITE 1

The OGI camera was deployed at the test site 1 and the observations from the twenty controlled releases are reported in Table D.1.

Table D.1 Summary of the OGI controlled release measurements.

Date	Time	Test #	Source A/B/C/D/E	Vidéo reference	Camerman location when detecting the leak	Detection distance	Detection mode	Remarks
22-Sep	13:17	1	D	5587 to 5495	LvL 1	7m	HSM	
22-Sep	15:40	2	B	5500 to 5511	LvL 0	5m	HSM	
23-Sep	11:30	3	A	5519 to 5525	LvL 0	5m	HSM	Several minuts for TOTAL to detect the leak using AUTO mode
23-Sep	14:00	4	E	5527 to 5534	LvL 0	5m	HSM	
26-Sep	09:40	5	A and D	5535 to 5537	LvL 0 for A and 1 for D	5m and 2m	HSM	NPL was not able to detect leaks using OGI (John was not trained)
26-Sep	12:00	6	A and C	5543 to 5545	LvL 0 for A and C	5m and 5m	HSM	Flow C seems > Flow A
26-Sep	14:30	7	A B C D	5549 to 5553	LvL 0 for A and C LvL 1 for D LvL 2 for B	5m and 2m and 5m	HSM	Flow C and B seem > A and D
26-Sep	16:10	8	C	5555 to 5557	LvL 0	5m and more	HSM	Very High Flow !!!!
27-Sep	09:30	9	E	5559 to 5563	LvL 0 and 1	5m and more	HSM	Nothing to report
27-Sep	11:30	10	A B C D	5564 to 5567	LvL 0 for A and C LvL 1 for D LvL 2 for D	5m and 2m and 5m	HSM	Flow C and B seem > A and D
27-Sep	14:00	11	A and B	5568 to 5571	LvL 0 for A LvL 0 for B	A from 5m B from 10m and more	HSM	Flow B > Flow A (widely)
27-Sep	16:00	12	B	5576 to 5577	LvL 1	10m	HSM	Flow B seems < to Flow B from test #11
28-Sep	10:10	13	E	5581 to 5587	LvL 0	20m	HSM	Visible even in MANUAL mode / Important Flow
28-Sep	11:30	14	E	5588 to 5592	LvL 0	20m	HSM	Flow seems > to test #13
28-Sep	14:45	15	E	5593 to 5598	LvL 1 and LvL 0	20m	HSM	Flow seems < to test #14
28-Sep	16:55	16	E	5600 to 5601	LvL 1 and intermediate	4m	HSM	Low Flow, not visible at LvL 2 because exposed to wind
29-Sep	10:55	17	A D	5605 to 5611	LvL 0 for A LvL 2 for D	A 3m D 4m	HSM	A, Gas swept by the small wind D, Flow less important that leak A, gas stays on the ground as wind is poor
29-Sep	13:00	18	A	5612, 5614, 5617, 5618, 5619, 5620	LvL 0	6m and a lot more	HSM	Flow > to leak A from test #17, visible even from 300m at the angle of streets 6 and 7
29-Sep	14:15	19	A B C D	5621 to 5628	LvL 0 for A and C LvL 1 for D LvL2 for B	A 6m B 4m C 2m D 4m	HSM	A Flow seems > to all leaks from test #19 B and C seems to have the same Flow D Flow seems to be the smaller of tests #19
29-Sep	15:45	20	A B C D	5629 to 5638	LvL 0 for A and C LvL 1 for D LvL2 for B	A 5m B 3m C 6m D 6m	HSM	A = low Flow, seems to be the lowest fo test #20 B Flow > to leaks A C and D of test #20 C Flow > to leak C of test #19, seems equal to leak B of test #20 D Flow < to C but > to A

ANNEX E: DIAL PRELIMINARY RESULTS FROM TEST SITE 1

The DIAL was able to measure 18 of the 20 controlled releases as shown in Table E.1. Tests 7 and 13 were not measured as the DIAL was parked in non-ideal locations as consequence of the low wind speed and variable wind direction.

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 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 Table E.1 are after the subtraction of the background contribution from the test scans and the standard deviation 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 and it should not be used.

Table E.1 Summary of the DIAL controlled release test results

Emission Area	Average	Standard
	Emission Rate	Deviation
	kg/hr	kg/hr
Test 1	5.41	1.83
Test 2	16.06	1.95
Test 3	9.83	2.33
Test 4	8.36	2.61
Test 5 *	11.42	1.86
Test 6	9.18	1.43
Test 8	9.56	1.13
Test 9	13.27	4.37
Test 10	18.47	5.60
Test 11	10.23	4.46
Test 12	8.46	4.47
Test 14	14.96	3.66
Test 15	3.68	2.52
Test 16	1.22	3.05
Test 17	9.68	1.14
Test 18	17.09	5.46
Test 19	8.01	4.55
Test 20	10.89	5.13

E.1 MEASUREMENTS ON THE 22ND SEPTEMBER FROM LOCATION BV02

Table E.2 VOC emission rates determined from BV02 on 22nd September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

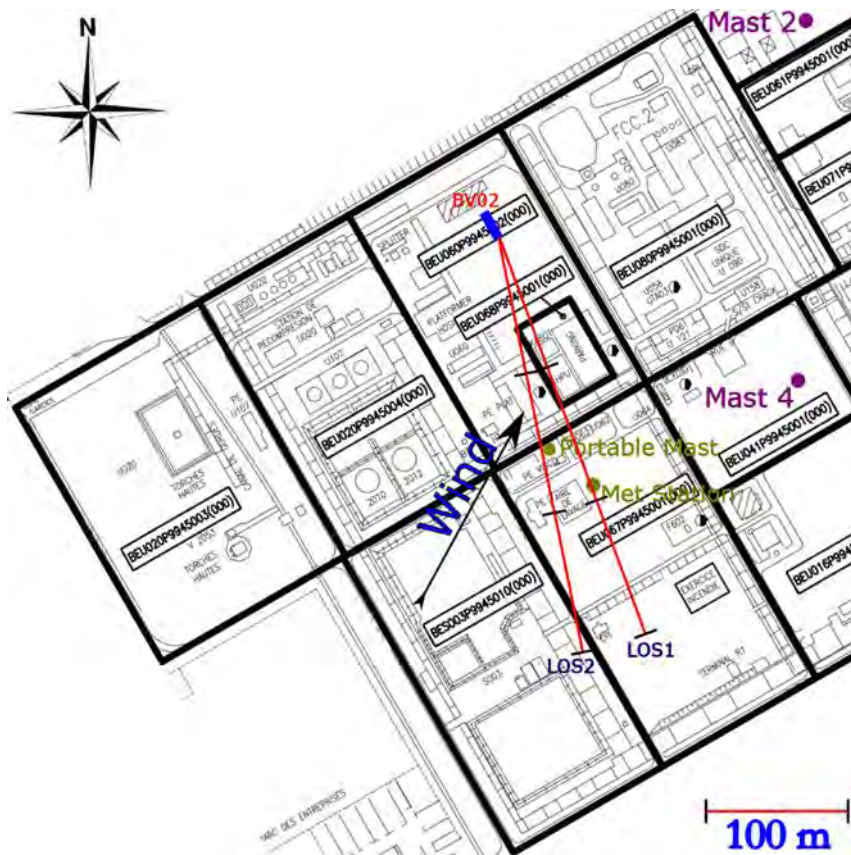


Figure E.1 Measurement configuration for location BV02 on 22nd September.

Test 1: plume probably from the South end of the unit rather than the north end.
 Test 2: similar to Test 1.

E.2 MEASUREMENTS ON THE 23RD SEPTEMBER FROM LOCATION BV03

Table E.3 VOC emission rates determined from BV03 on 23rd September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

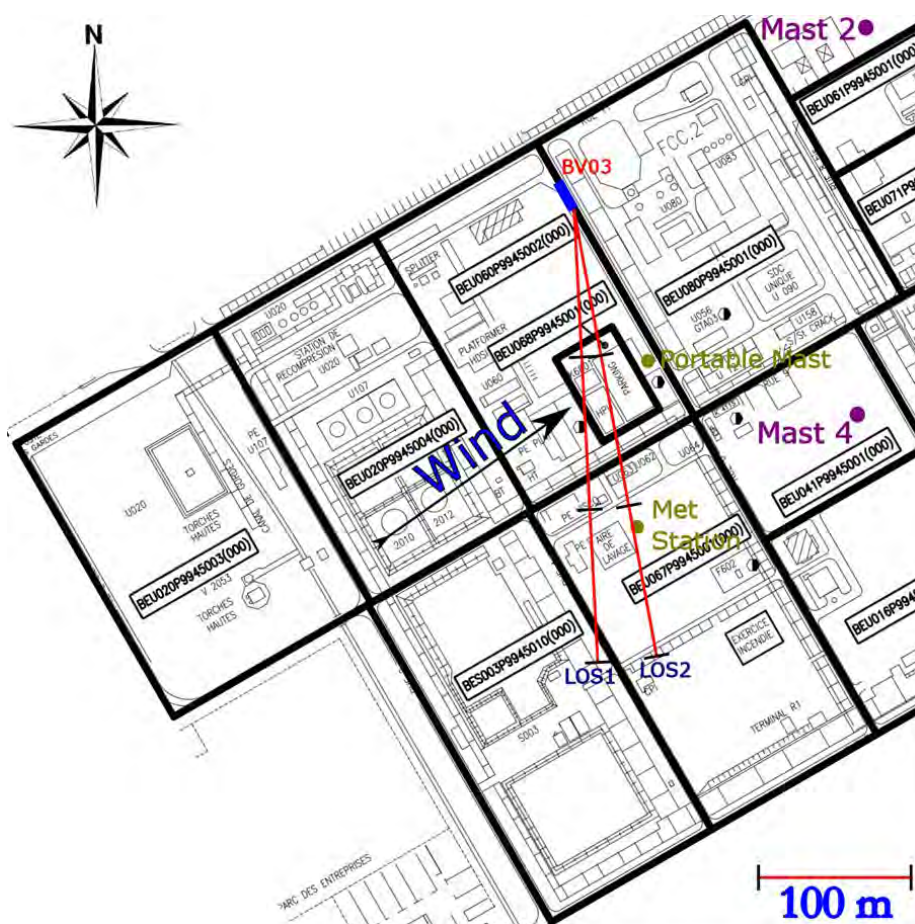


Figure E.2 Measurement configuration for location BV03 on 23rd September.

Test 3: plume probably from the South end of the unit rather than the north end.

Test 4: compared to Test 3 the plume seems to be more northerly. North-Middle node/s?

E.3 MEASUREMENTS ON THE 26TH SEPTEMBER FROM LOCATION BV04

Table E.4 VOC emission rates determined from BV04 on 26th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

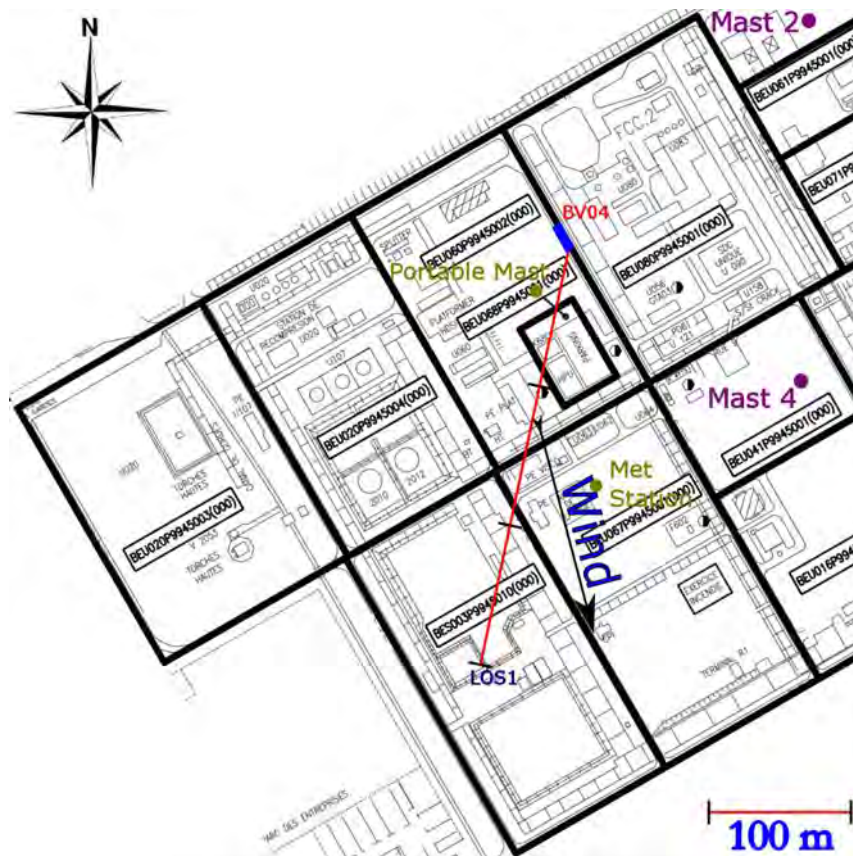


Figure E.3 Measurement configuration for location BV04 on 26th September.

Test 5: no background scans - at least few kg/hr overestimated and it shouldn't be used. Because of the northerly wind direction it is impossible to say from which node the release was from.

E.4 MEASUREMENTS ON THE 26TH SEPTEMBER FROM LOCATION BV06

Table E.5 VOC emission rates determined from BV06 on 26th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

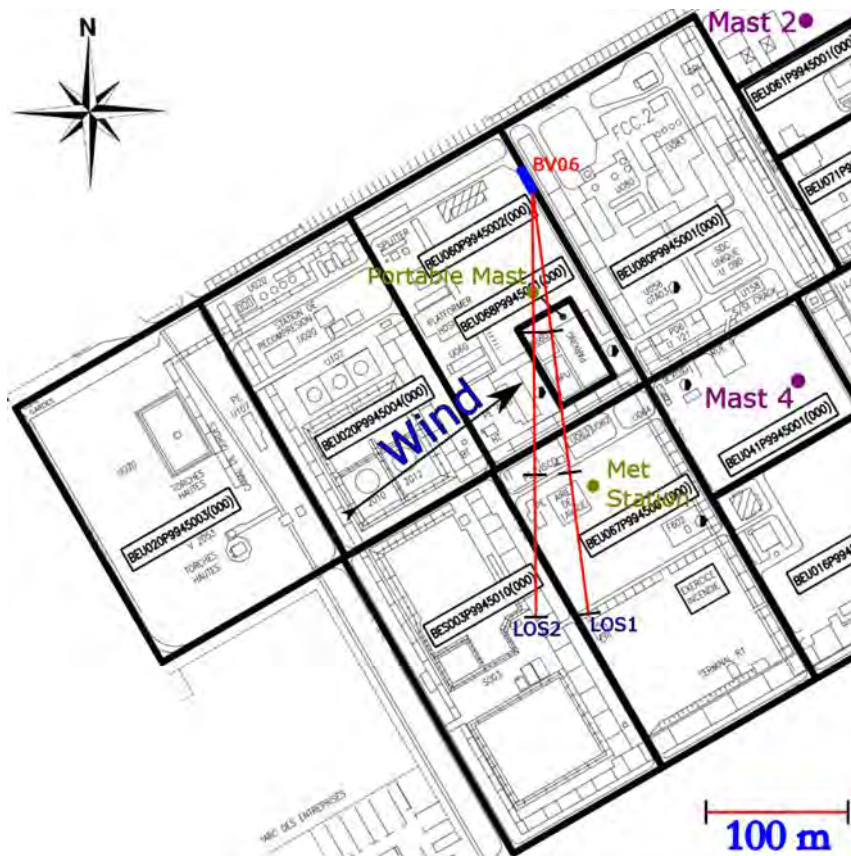


Figure E.4 Measurement configuration for location BV06 on 26th September.

Test 6: relatively wide plume, but centred on the south end of the unit. South-Middle nodes.

E.5 MEASUREMENTS ON THE 26TH SEPTEMBER FROM LOCATION BV09

Table E.6 VOC emission rates determined from BV09 on 26th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

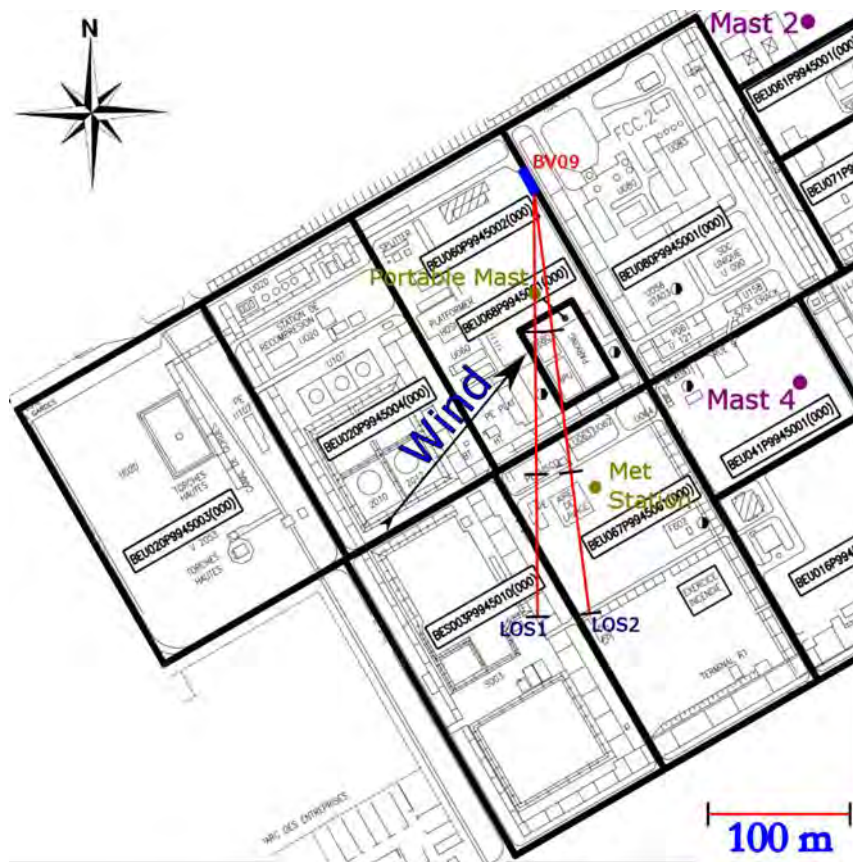


Figure E.5 Measurement configuration for location BV09 on 26th September.

Test 8: quite wide plume because of wind direction, probably south or middle node or combination of the two.

E.6 MEASUREMENTS ON THE 27TH SEPTEMBER FROM LOCATION BV10

Table E.7 VOC emission rates determined from BV10 on 27th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

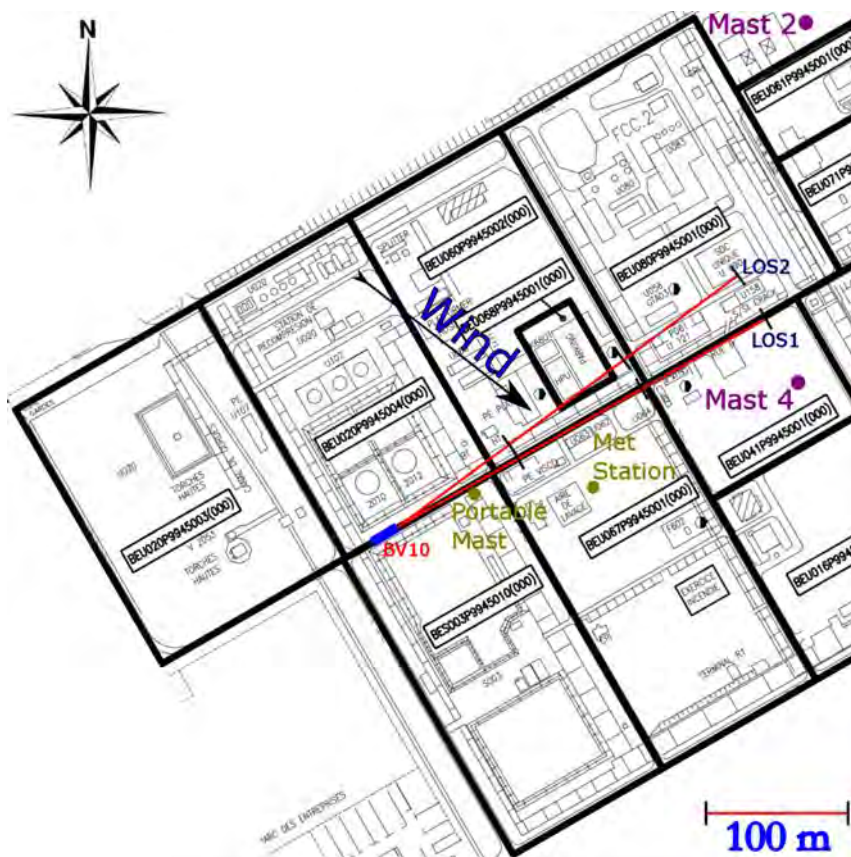


Figure E.6 Measurement configuration for location BV10 on 27th September.

Test 9: because of the wind direction it is impossible to say from which node the release was from. Complex plume, high background emission rate and therefore high uncertainty in the emission rate.
 Test 10: same as Test 9 plus variable background due to change in wind direction.

E.7 MEASUREMENTS ON THE 27TH SEPTEMBER FROM LOCATION BV11

Table E.8 VOC emission rates determined from BV11 on 27th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

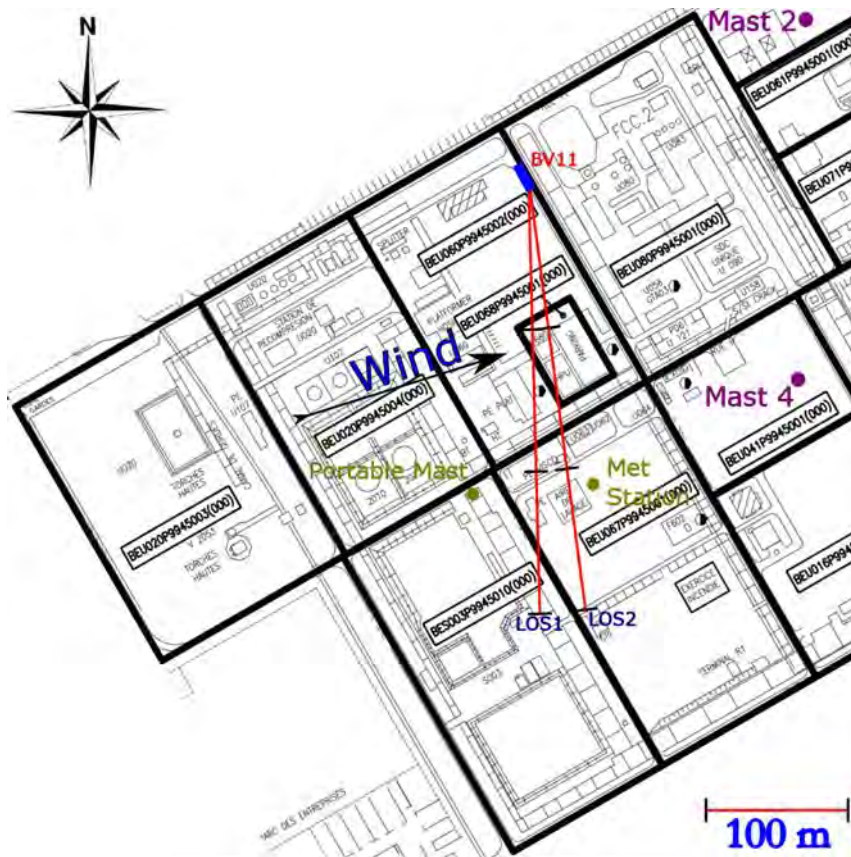


Figure E.7 Measurement configuration for location BV11 on 27th September.

Test 11: elongated plume shape indicating emission sources from both south and north end of the unit. Probably several release nodes used.

Test 12: smaller plume compared to Test 11, emission probably from middle-north of unit. Possibly just one node.

E.8 MEASUREMENTS ON THE 28TH SEPTEMBER FROM LOCATION BV13

Table E.9 VOC emission rates determined from BV13 on 28th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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

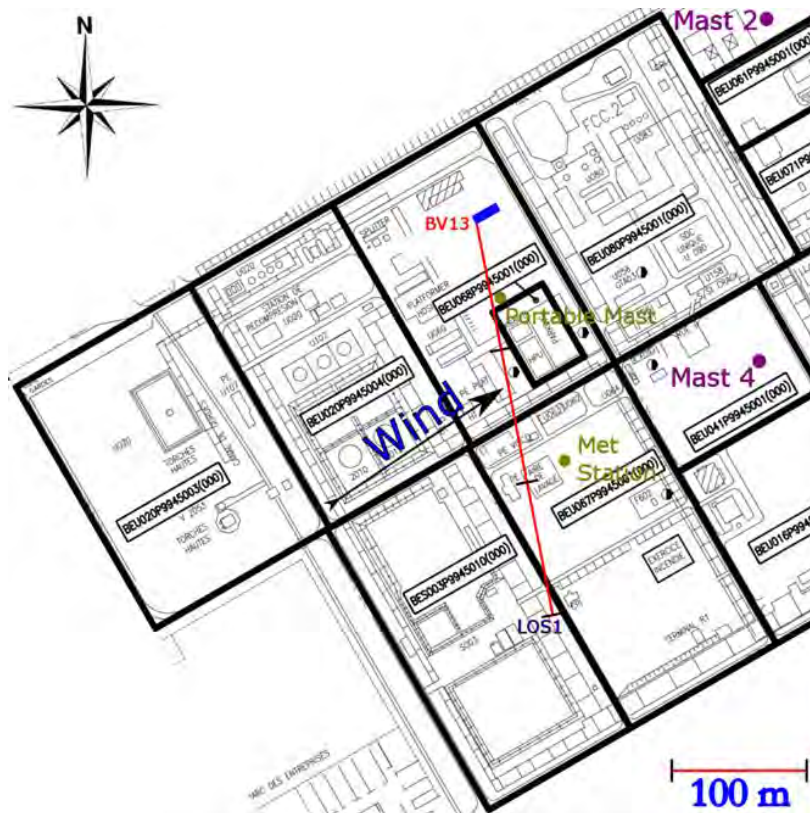


Figure E.8 Measurement configuration for location BV13 on 28th September.

Test 14: difficult to tell, plume centred at about 120m from the DIAL (i.e. about middle of the unit) but relatively wide. Possibly just one node but it could be from any node apart from the north one.
 Tests 15 and 16: same as test 1.

E.9 MEASUREMENTS ON THE 29TH SEPTEMBER FROM LOCATION BV14Table E.10 VOC emission rates determined from BV14 on 29th September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
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	37.47	Background
122	BV14/LOS2	12:40	12:56	2.3	238.8	58.71	Downwind Test 18
123	BV14/LOS1	12:57	13:09	2.2	234.3	54.05	Downwind Test 18
124	BV14/LOS2	13:11	13:24	2.3	226.2	58.46	Downwind Test 18
125	BV14/LOS1	13:25	13:37	1.9	210.2	58.15	Downwind Test 18
126	BV14/LOS1	13:38	13:50	1.8	214.5	49.40	Downwind Test 18
128	BV14/LOS1	13:56	14:10	2.7	233.3	34.39	Background
129	BV14/LOS1	14:11	14:24	3.4	233.6	44.98	Downwind Test 19
130	BV14/LOS1	14:25	14:38	3.7	233.3	50.09	Downwind Test 19
131	BV14/LOS1	14:38	14:52	3.1	235.4	44.21	Downwind Test 19
132	BV14/LOS1	14:52	15:05	3.2	240.4	49.03	Downwind Test 19
133	BV14/LOS1	15:06	15:13	3.3	251.3	45.03	Downwind Test 19
134	BV14/LOS1	15:13	15:27	3.1	235.7	39.66	Background
135	BV14/LOS1	15:33	15:46	3.1	235.9	52.25	Downwind Test 20
136	BV14/LOS1	15:47	16:02	2.8	237.7	54.36	Downwind Test 20
137	BV14/LOS1	16:03	16:18	2.8	230.8	50.82	Downwind Test 20
138	BV14/LOS1	16:18	16:34	2.5	242.0	48.31	Downwind Test 20
139	BV14/LOS1	16:34	16:49	2.8	231.1	44.80	Downwind Test 20
140	BV14/LOS1	16:50	17:05	2.8	238.5	46.73	Downwind Test 20
141	BV14/LOS1	17:05	17:21	2.7	238.5	43.11	Background

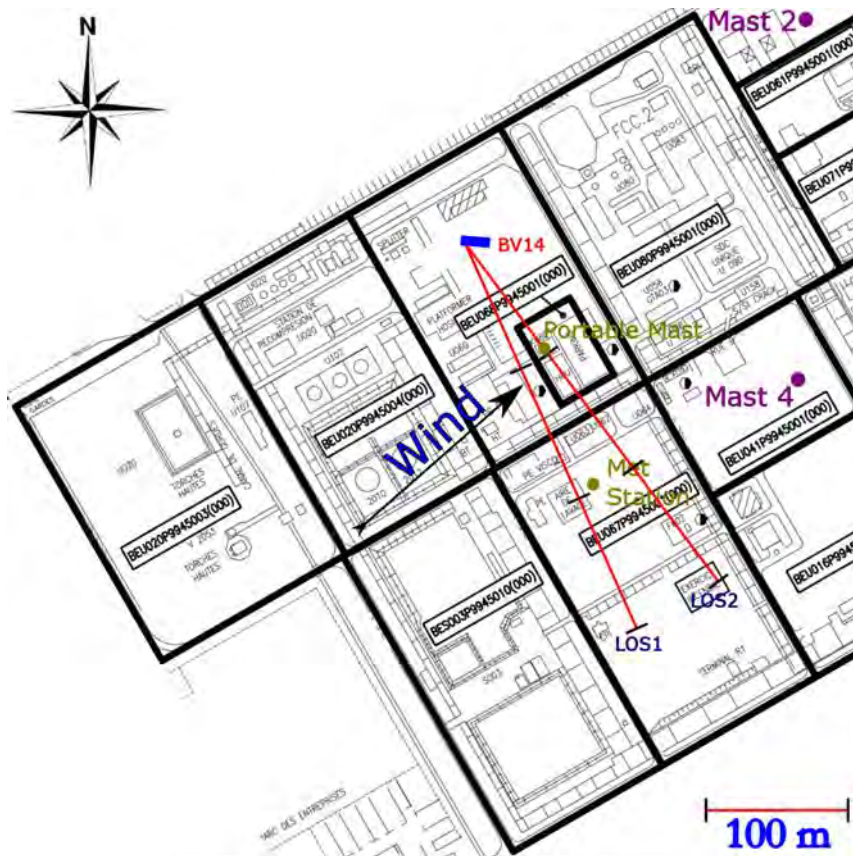


Figure E.9 Measurement configuration for location BV14 on 29th September.

Test 17: because of the south wind it is difficult to say from which node the release was from, although the plume is centred at about 100m indicating more north of the unit.

Test 18: plume centred at about 100m from DIAL and quite wide indicating it should come from north node and maybe contribution from middle nodes.

Test 19 and 20: complex broad plume in the 100-130m region from the DIAL indicating more nodes were used.

E.10 SUMMARY OF DIAL VOC EMISSION RATE MEASUREMENTS

Table E.11 Summary of VOC emission rate measurements

Date	Location/	Notes	Average Emission Rate	Standard Deviation	Scans
			kg/hr	kg/hr	#
22-Sep	BV02/LOS1	Downwind Test 1	7.7	1.4	6
22-Sep	BV02/LOS1,2	Downwind Test 2	18.4	1.6	6
22-Sep	BV02/LOS2	Background	2.3	1.2	2
23-Sep	BV03/LOS1,2	Downwind Test 3	13.7	1.7	6
23-Sep	BV03/LOS1,2	Downwind Test 4	12.2	2.1	5
23-Sep	BV03/LOS2	Background	3.9	1.6	2
26-Sep	BV04/LOS1	Downwind Test 5	11.4	1.6	4
26-Sep	BV06/LOS1,2	Downwind Test 6	9.6	1.0	4
26-Sep	BV06/LOS2	Background	0.4	1.0	1
26-Sep	BV09/LOS1,2	Downwind Test 8	13.0	0.5	5
26-Sep	BV09/LOS2	Background	3.4	1.0	1
27-Sep	BV10/LOS1	Downwind Test 9	37.9	2.9	5
27-Sep	BV10/LOS1	Downwind Test 10 a	42.9	5.8	4
27-Sep	BV10/LOS1,2	Downwind Test 10 b	19.5	1.2	2
27-Sep	BV10/LOS1	Background a	24.6	3.3	2
27-Sep	BV10/LOS1	Background b	0.7	1.0	1
27-Sep	BV11/LOS1,2	Downwind Test 11	19.5	4.4	4
27-Sep	BV11/LOS1	Downwind Test 12	17.7	4.5	6
27-Sep	BV11/LOS1	Background	9.3	0.3	2
28-Sep	BV13/LOS1	Downwind Test 14	27.8	3.2	6
28-Sep	BV13/LOS1	Downwind Test 15	16.5	1.8	5
28-Sep	BV13/LOS1	Downwind Test 16	14.1	2.5	4
28-Sep	BV13/LOS1	Background	12.9	1.8	3
29-Sep	BV14/LOS1	Downwind Test 17	9.7	0.5	3
29-Sep	BV14/LOS1,2	Downwind Test 18	55.8	4.0	5
29-Sep	BV14/LOS1	Downwind Test 19	46.7	2.7	5
29-Sep	BV14/LOS1	Downwind Test 20	49.5	3.6	6
29-Sep	BV14/LOS1	Background	38.7	3.7	4

ANNEX F: SOF AND TRACER PRELIMINARY RESULTS FROM TEST SITE 1

SOF and tracer correlation at the validation campaign

¹Johan Mellqvist, ²Jerker Samuelsson and
²Samuel Brohede

¹ Chalmers University of technology
² FluxSense AB

Validation campaign Marseille

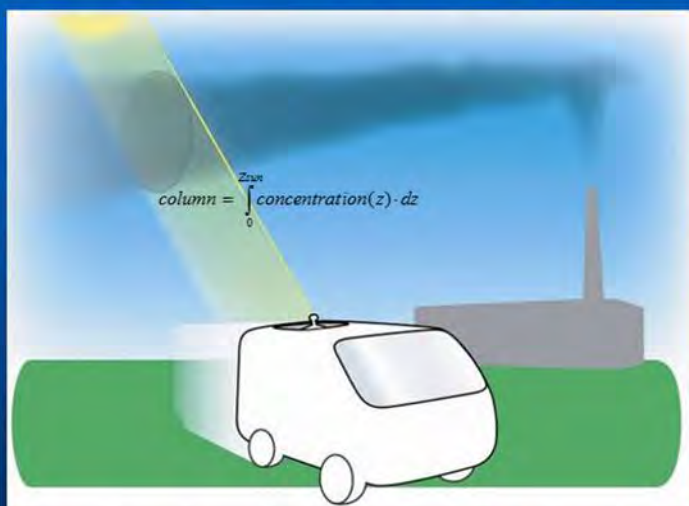
- Monday Sep 19-Thursday sep 30 2016
- 20 release experiments of butane (1-+25 kg/h) from 4 nodes at a decommissioned refinery.
- SOF and tracer correlation measurements were carried out at the site by FluxSense AB with funding from CEN TC264 WG 38 .
- Measurement planning and data interpretation coupled to CEN standard and measurements the last week was done by Chalmers as part of IMPRESS.
- Final data based on standard approach sent in to [Ineris](#) on Jan 10, 2017.
- 15 out of 20 experiments fulfilled criteria for SOF and 18 out of 20 for tracer correlation

Technique

The Solar Occultation Flux method (SOF): mobile direct infrared solar measurements for retrieval of VOCs, CO and NH₃



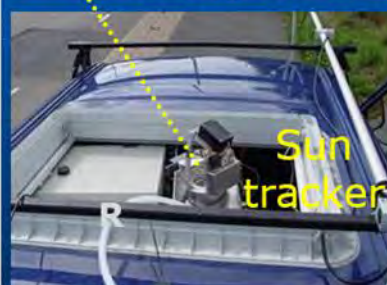
<http://www.youtube.com/watch?v=6cre9n8YAzE>



Mellqvist

$$\text{flux} = F \cdot u'_{\text{average}} \int_{x1}^{x2} \text{column}(x) dx$$

u' = mass averaged wind



3

Mobile extractive FTIR (MeFTIR)



- FTIR coupled to a 60 m multi-reflection cell
- Real time concentration measurements of alkanes, alkenes, methane, CO, CO₂ and NH₃ with 1-15 s response time and 1-10 ppb detection limit
- Tracer correlation measurements using N₂O or C₂H₂ as source gas.

4

Methods

Method	Solar Occultation Flux	Tracer Correlation using Mobile Extractive FTIR
Compounds	Alkane, C ₂ H ₄ , C ₃ H ₆ , C ₄ H ₈ , NH ₃ , CO	Alkane, CH ₄ , C ₂ H ₄ , C ₃ H ₆ , C ₄ H ₈ , NH ₃ , CO, CO ₂ , N ₂ O
Comment	Requires wind field measurements for flux calculation	N ₂ O or C ₂ H ₄ used as tracer gas (0-5-4 kg/h)
Measured unit	Vert. Column	Concentration
Sensitivity	0.1-5 mg/m ²	1-10 ppb
Flux limit	0.2-1 kg/hr	0.2-2 kg/hr
Wind Speed	1.5-12m/s	1-12m/s
Time response	1-5 sec	5-15 sec
Uncertainty	20-30%	15-30%



SOF details

- A mast measuring a relatively undisturbed flow at 10 m was used as main wind. We generally used Ineris SE until sep 28 and then INERIS S
- The alkane composition for the background sources and source was identified as propane, hexane and cyclohexane from SOF spectra. This mixture gives 5% higher values than the standard combination of propane, butane and octane.
- Main measurement criteria are: average windspeed above 1.5 m/s (1.3 m/s for individual scan), at least 4 scans and a solar elevation above 20°. If the shadows cover less than 25% of the plume for a scan the neighbouring datapoints are interpolated otherwise the scan is discarded. This results in approx 10% higher values.

7

SOF details

- A mast measuring a relatively undisturbed flow at 10 m was used as main wind. We generally used Ineris SE until sep 28 and then INERIS S
- The alkane composition for the background sources and source was identified as propane, hexane and cyclohexane from SOF spectra. This mixture gives 5% higher values than the standard combination of propane, butane and octane.
- Main measurement criteria are: average windspeed above 1.5 m/s (1.3 m/s for individual scan), at least 4 scans and a solar elevation above 20°. If the shadows cover less than 25% of the plume for a scan the neighbouring datapoints are interpolated otherwise the scan is discarded. This results in approx 10% higher values.

7

Estimated uncertainty for SOF

Baseline error	5%
Spectroscopy	10%
Shadow Interpolation error	5%
Wind uncertainty	30%
Overall Uncertainty	32%

9

Tracer correlation methodology

- Tracer Correlation Measurements of VOCs and N₂O (tracer) with MeFTIR (Mobile extractive FTIR)
- The ratio of the integrated source and tracer gas, respectively, across plume is multiplied with tracer flow to obtain gas flux.
- Tracer gas (N₂O) was released on the first floor, in the middle of the studied process unit. No complementary information about the location of the leakages was used to position tracer (untypical). An underestimation is anticipated for the high releases.
- The tracer release rate was 1-5 kg/h based on weighing gas cylinder and a flowmeter to ensure constant flow.
- The uncertainty of the method is 20-30% but it depends on proximity of tracer gas to the leakages

Example of tracer correlation measurements



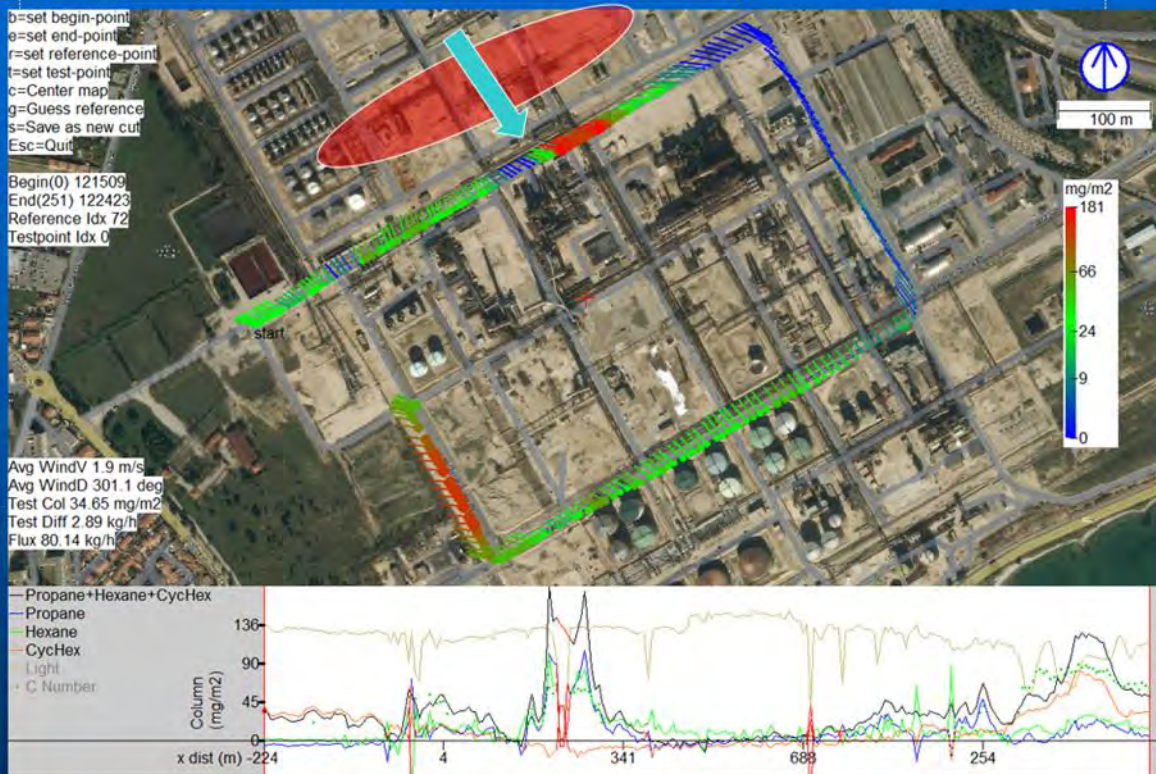
From wind statistics it was expected that most measurements would be carried out here!

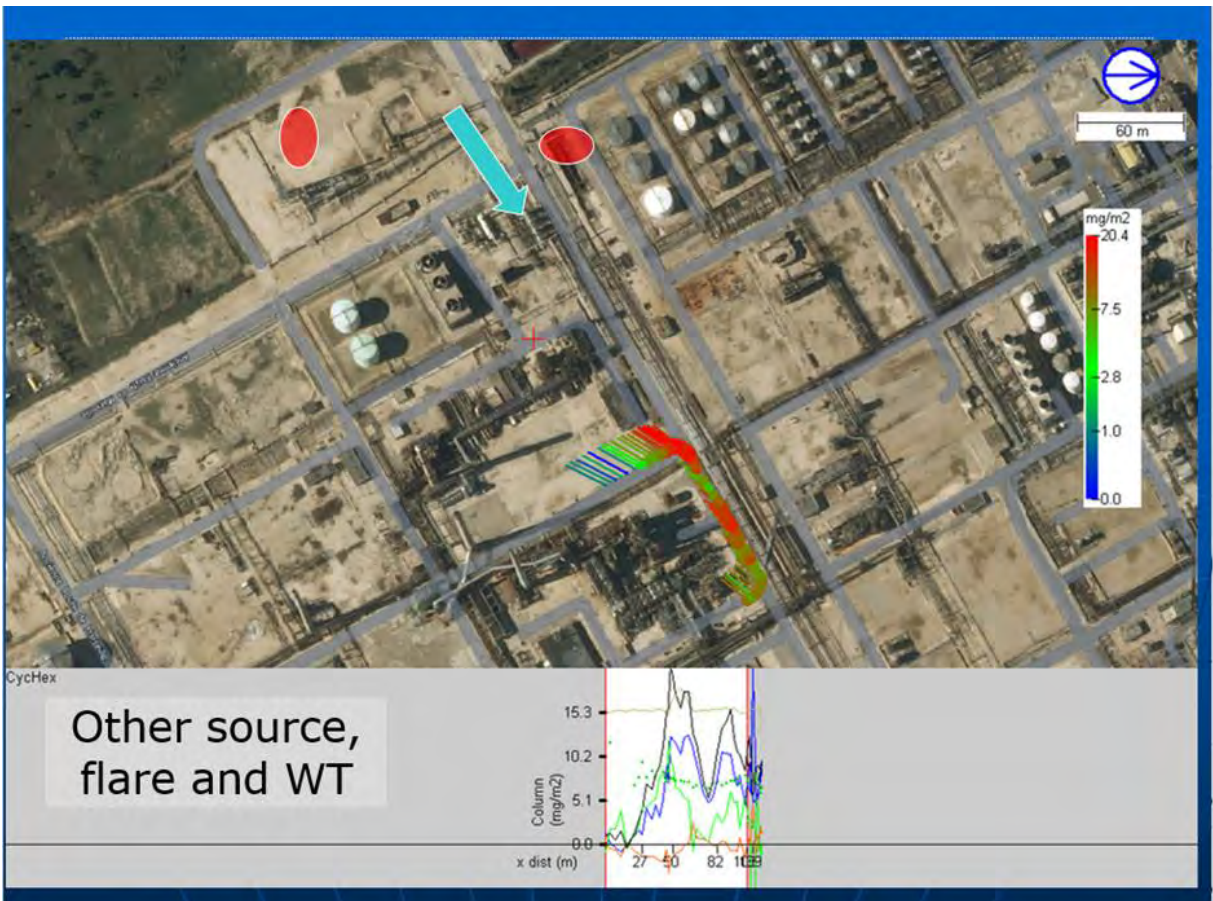
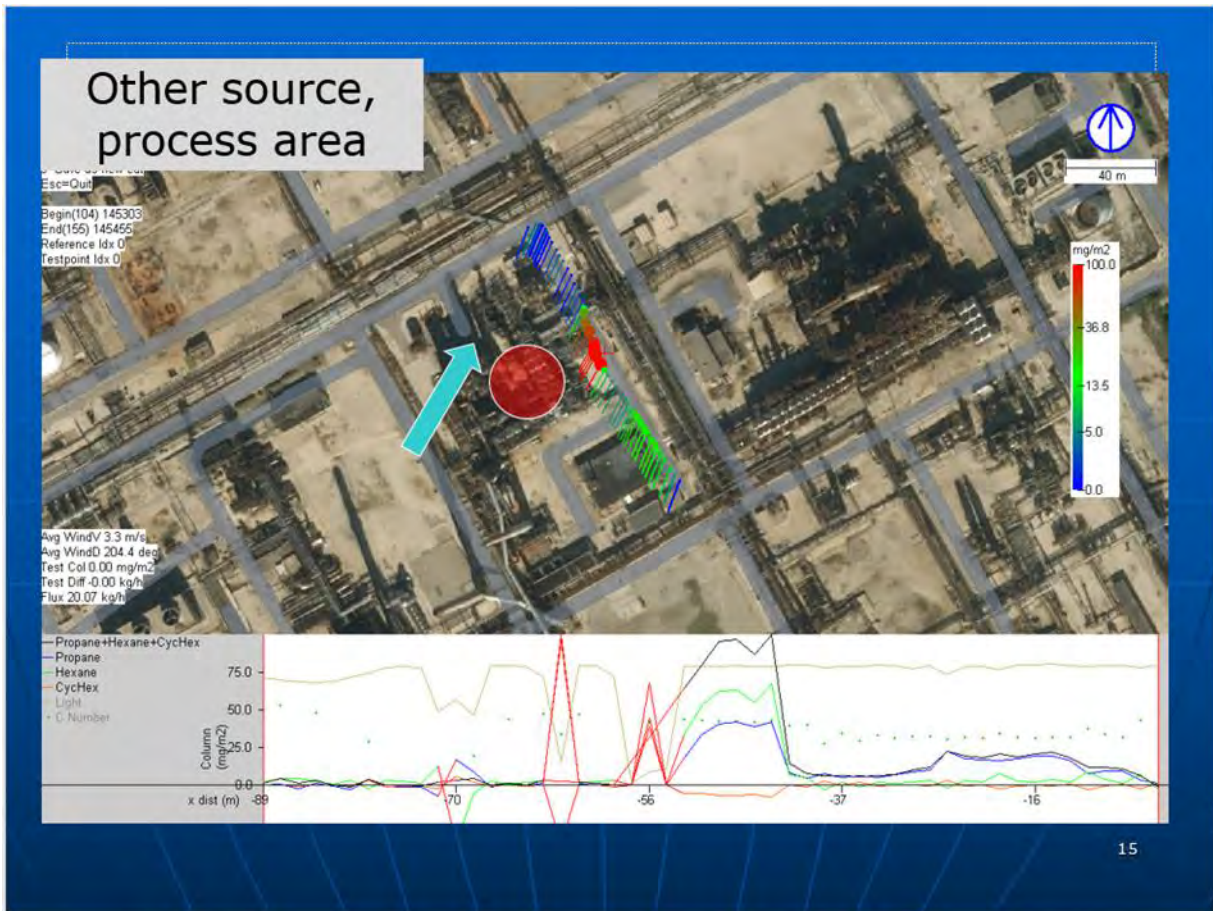


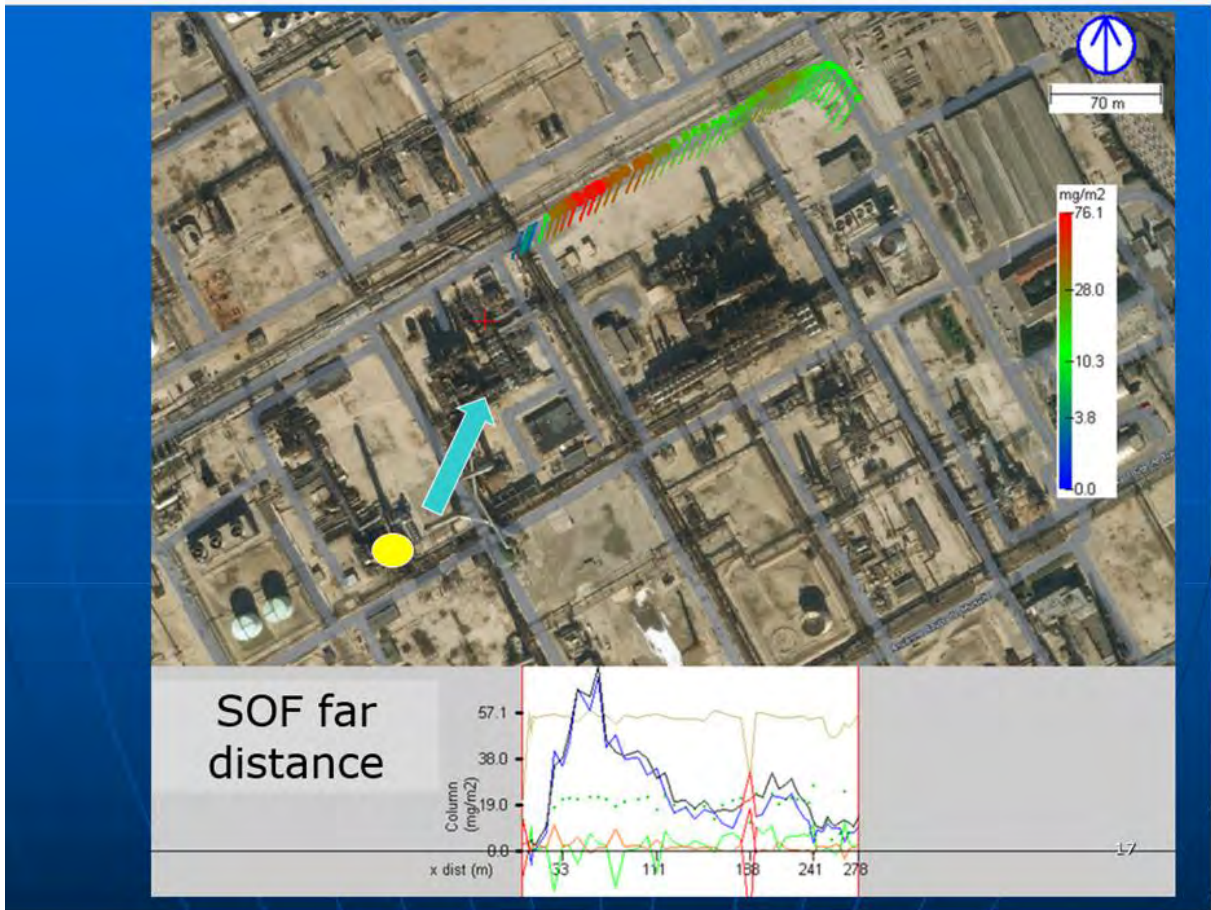


We ended up measuring on this road most of the time (source to the left). This was not ideal since the wind was disturbed, many shadows and there was a distinct leakage source in the end of the road in the process unit, and two additional sources in the north west (traetment facility and flare)

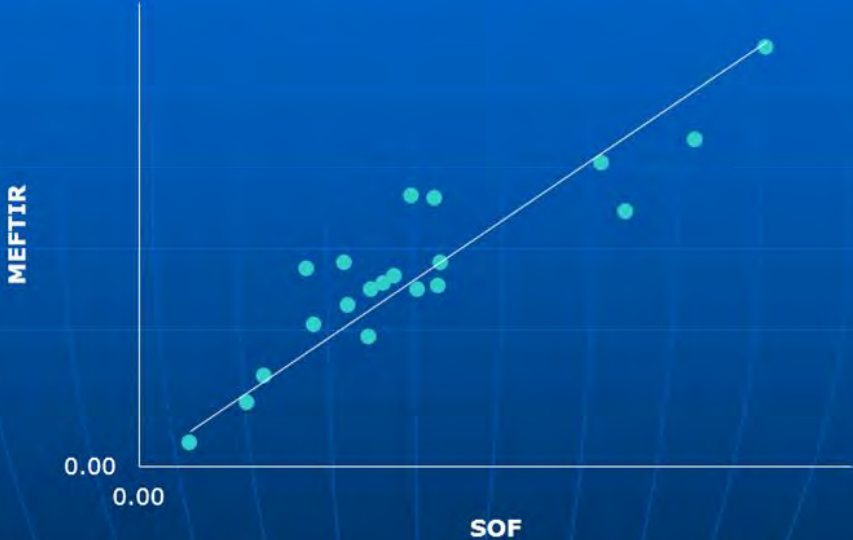
Other background sources







SOF and MEFTIR results for the different experiments



ANNEX G: REVERSE DISPERSION MODELLING RESULTS FROM TEST SITE 1

G.1 PROTOCOL FOR INVERSE MODELLING TO QUANTIFY POLLUTING EMISSIONS ON A LOCAL SCALE

The research for volatile organic compounds (VOC) diffuse emissions sources in an industrial site requires implementing a methodology of inverse modelling on a local scale:

Step one: monitoring strategy

Step two: direct modelling

Step three: reverse modelling

G.2 MONITORING STRATEGY

The global tools will have to raise two challenges: the localization of the sources (discrimination of the issuer among a large number of potential sources) and the flow of the source. To obtain these results, the monitoring strategy needs to provide enough information.

G.2.1 Measurements: Pollutants and Wind

Pollutant Measurements need to have a lot of data to correctly describe the inhomogeneous area (several ponds, units, tanks, etc.). Uses of a multitude of analysers or optical techniques could be applied, but for economic reason, the choice has been made to use a combination of mobile and fixed analysers with a meteorological station:

- A meteorological station installed in an undisturbed place near the emitting area, monitors wind and stability changes at high frequency (30 s). The met station is installed on a 10 m mast and must ideally be installed upstream of the emission zone. In practice, the use of a single meteorological station cannot be representative of all wind fields in complex, cluttered industrial site like a refinery. So, the installation of a second meteorological mast could be an improvement if the localization of the first mast is not perfect.
- One mobile analyser (portable FID / PID / GC-Ms according to the pollutant) 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. The mobile analyser could be portable by a person, using a telescopic rod or install in a drone.
 - The first step is a rapid screening around the emission area with several points to identify hot spot.
 - The second step is the real measurement, with at least seven points in each main plume. For each point, the record time is at least one minute (according to analysers responds and wind variability). The points must be at several meters (> 2 m) from the sources in the objective to have a more homogeneous plume. A background correction of concentrations is done with upstream wind concentration.
- An improvement for long term estimation is the installation of a limited number of fixed analysers (in our case 3 FID or PID) records the concentration during a representative period of 2 weeks with a frequency of 15 minutes. Their localizations 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.

G.3 DIRECT MODELLING

- Like in RDM standard, the model must be adapted to the situation. In presence of obstacles (building, tanks, industrial unit ...), the selected model must be able to reproduce effects of obstacles in the wind field.
- For the majority of case, the use of a CFD model is a solution. The model requires an adaptation of atmospheric turbulence, and uses the meteorological parameters (wind direction, speed and turbulence) to construct a 3D wind field data base.
- The combination of data base with evolution of the real meteorological measurement permits 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 emissions sources are represented by volume or area sources. Classical direct dispersion is done with a theoretical emission flux set at 1 g/s for each source, to obtain the matrix of dispersion factor at each monitoring point.

G.4 REVERSE MODELLING AND VALIDATION

- Concentrations measured are corrected by the background concentration.
- Concentrations simulated in each point are adjusted to mobile measured concentrations corrected with background at the same time using the “reverse model”, i.e. a linear regression as shown in Figure G.1. Thus conducting to the emission flux estimates for each source.

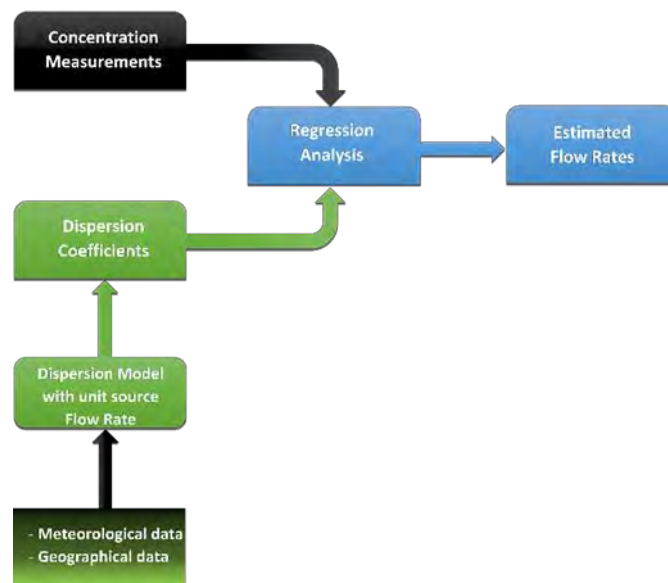


Figure G.1 RDM principle

- 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.
- For long term measurements, the work is the same with the fixed analyzers.



EUROPEAN COMMITTEE FOR STANDARDIZATION

VOC EMISSION QUANTIFICATION BY REVERSE DISPERSION MODELLING

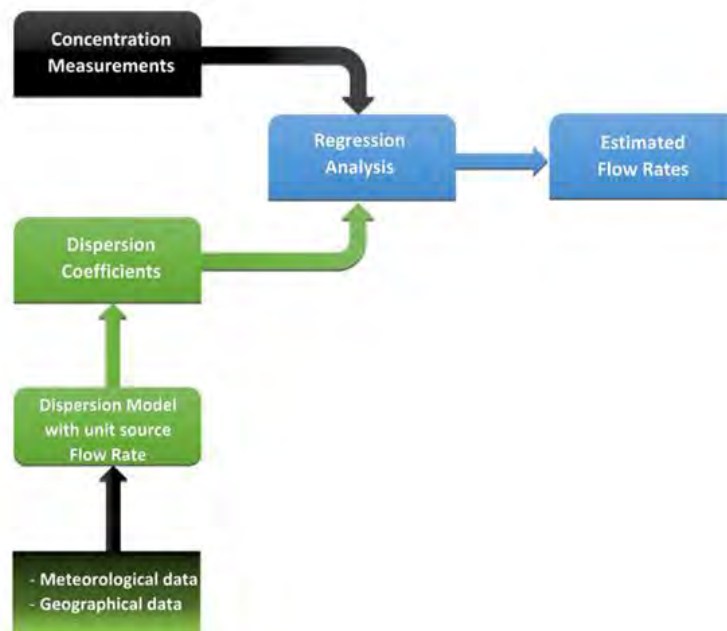
Olivier DUCLAUX

Jonathan LEMUS

Pierre MANGEON

LQA – TOTAL

REVERSE DISPERSION MODELLING (RDM)



CONCENTRATION MEASUREMENTS ON SITE

- Propane concentration measured with FID (Flame Ionisation Detector), on different points in and around the unit. 5 minutes measurement per points.



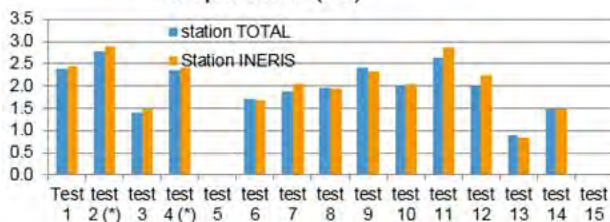
VOC Emission Quantification by Reverse Dispersion Modelling – January 11th 2017

3



METEOROLOGICAL MEASUREMENTS ON SITE

- 3-dimensionnal weather station
 - Altitude: 10m
 - Position: North from the unit
 - Measurements (30s averaging):
 - Wind direction (°)
 - Wind speed (m/s)
 - Turbulence parameters
 - Temperature (°C)



Colonne1	station TOTAL	Station INERIS	% ecart
Test 1	2.39	2.46	-2.73
test 2 (*)	2.79	2.90	-3.98
test 3	1.40	1.47	-5.06
test 4 (*)	2.35	2.42	-2.84
test 5	1.70	1.69	0.69
test 6	1.88	2.05	-8.21
test 7	1.95	1.94	0.86
test 8	2.42	2.32	3.94
test 9	2.03	2.05	-0.88
test 10	2.64	2.87	-8.00
test 11	2.00	2.25	-11.45
test 12	0.89	0.86	3.79
test 13	1.48	1.47	0.52
test 14	1.47	1.47	0.52
test 15	1.47	1.47	0.52

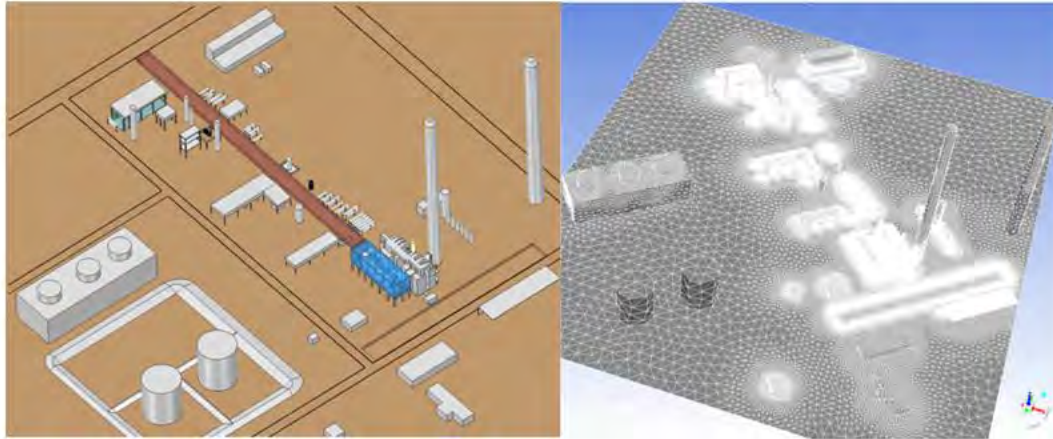
VOC Emission Quantification by Reverse Dispersion Modelling – January 11th 2017

4



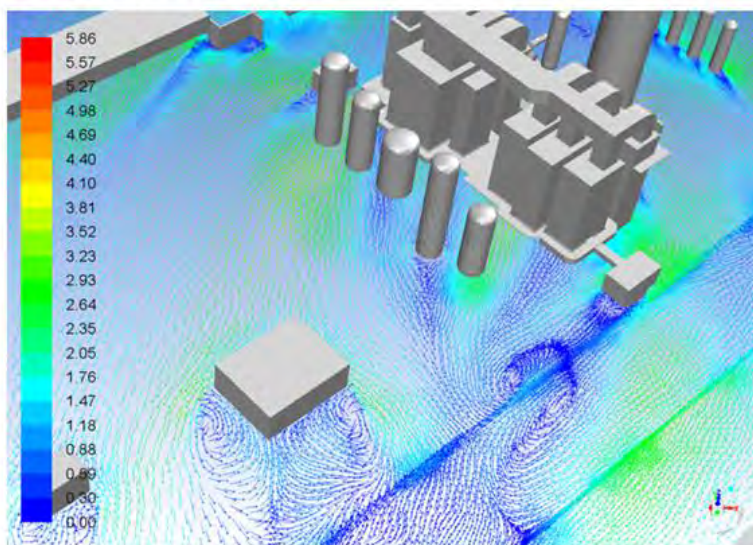
MODELLING – DIFFERENT STEPS

1) Representative digital model construction and meshing



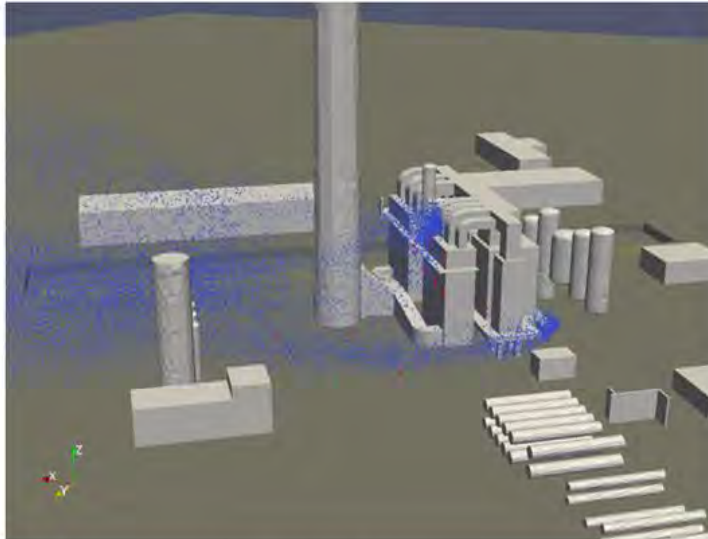
MODELLING – DIFFERENT STEPS

2) Air flow calculation through the digital model for multiple meteorological conditions



MODELLING – DIFFERENT STEPS

- 3) Dispersion calculation from the different sources with unitary flow rate for each source. Propane concentration calculated at each measurements points



VOC Emission Quantification by Reverse Dispersion Modelling – January 11th 2017

7



MODELLING – DIFFERENT STEPS

- 4) Regression analysis in order to estimate the real sources flow rates in accordance with the law:

$$C_r(t) = \sum_i (\alpha_{ir}(t) \cdot \dot{M}_i)$$

where:

- $C_r(t)$ is the measured concentration at each point
- $\alpha_{ir}(t)$ are the dispersion coefficient at the point r for the source i
- \dot{M}_i is the flow rate of the source i .

Remark: in fact, the dispersion coefficient $\alpha_{ir}(t)$ is the calculated concentration at the point r by the dispersion model, with a unitary flow rate for each source.

VOC Emission Quantification by Reverse Dispersion Modelling – January 11th 2017

8



FLOW RATE ESTIMATIONS BY RDM

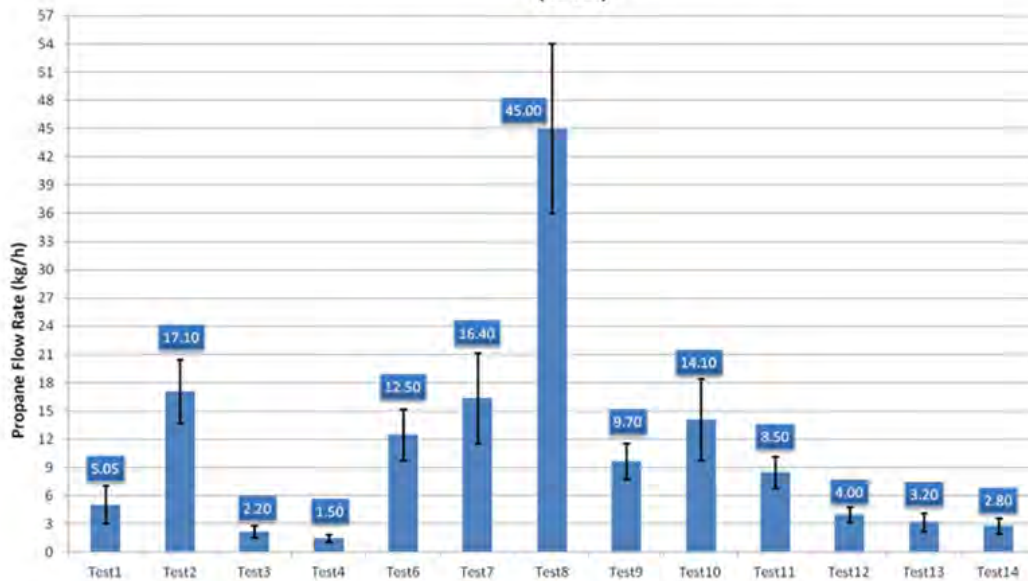
- Lvl1N : the source at the north side of the unit, first level
- Lvl1M: the source at the middle of the unit, first level
- Lvl1S: the source at the south side of the unit, first level
- Lvl2 : the source at the middle of the unit, second level
- Tube : the tube source at the middle of the unit

The results are given in kilograms per hour (kg/h)

Global Uncertainties and RDM validation : see Annexes

FLOW RATE ESTIMATIONS BY RDM (NEED TO BE IMPROVED BY 2,5 % ACCORDING TO VOC COMPOSITION)

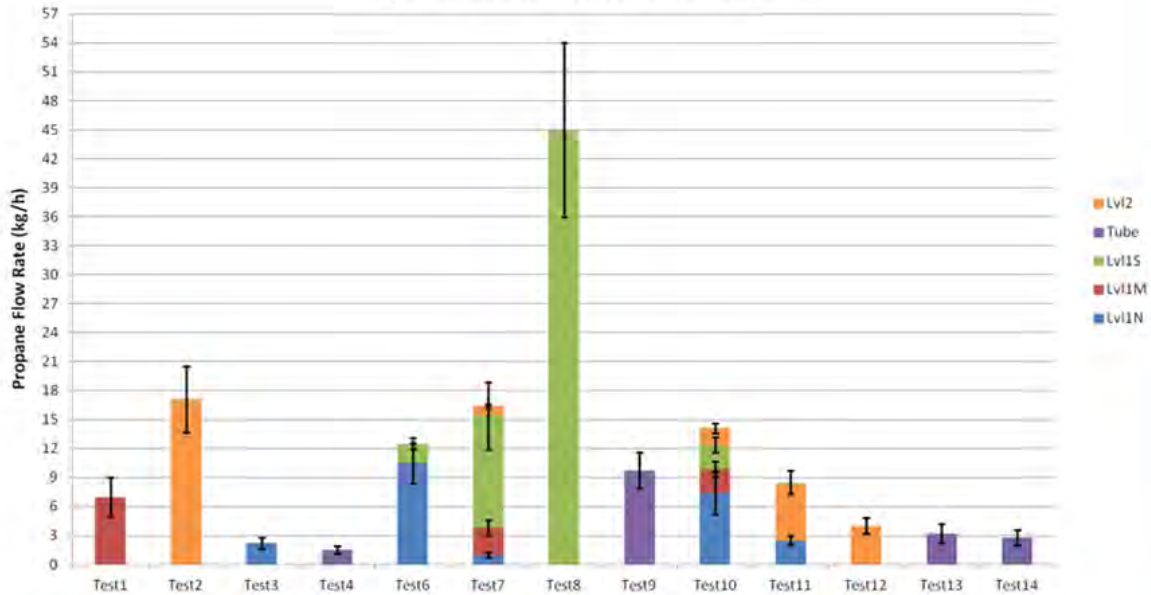
Estimation results with the RDM method
(total)



FLOW RATE ESTIMATIONS BY RDM

(NEED TO BE IMPROVED BY 2,5 % ACCORDING TO VOC COMPOSITION)

Estimation results with the RDM method
(with each source contribution)



FLOW RATE ESTIMATIONS BY RDM

(NEED TO BE IMPROVED BY 2,5 % ACCORDING TO VOC COMPOSITION)

	Lvl1N	Incert	Lvl1M	Incert	Lvl1S	Incert	Tube	Incert	Lvl2	Incert	Total	Incert	Wind Speed
Test1			7	2							7.0	2.0	2.2
Test2									17.1	3.4	17.1	3.4	2.8
Test3	2.2	0.6									2.2	0.6	1.4
Test4							1.5	0.4			1.5	0.4	2.4
Test6	10.5	2.1			2.0	0.6					12.5	2.7	1.7
Test7	1.0	0.3	2.8	0.8	11.6	3.5			1.0	0.2	16.4	4.8	1.9
Test8					45	9					45.0	9.0	1.9
Test9							9.7	1.9			9.7	1.9	2.4
Test10	7.4	2.2	2.5	0.8	2.5	0.8			1.7	0.5	14.1	4.3	2.0
Test11	2.5	0.5							6.0	1.2	8.5	1.7	2.6
Test12									4	0.8	4.0	0.8	2.0
Test13							3.2	1.0			3.2	1.0	0.9
Test14							2.8	0.8			2.8	0.8	1.5

Remark : the values in the last column represent the average wind speed measured by the weather station (alt. 10m)

OUTLOOKS

- New runs with improved turbulence parameterizations.
- Comparison and integration of Wind LiDAR profiles.
- Possibility to compare modelling results with SOF or DIAL measurements.
- Development of a method taking account unit shadows effect on surface thermal fluxes.

ANNEXES

- Evaluation of RDM efficiency with the most complex dataset (Test 10 with 4 sources):

Source	Lvl1S	Lvl1M	Lvl1N	Lvl2
Synthetic Flow rate (kg/h)	7.2	7.2	14.4	10.8
Estimated Flow rate (kg/h)	7.0	7.1	13.7	10.9
Relative Error (%)	2.7	1.2	4.9	0.5

ANNEXES

- Calculation of the global error on flow rate estimation by RDM
 - Error on the propane concentration measurement : $E_1=10\%$
 - Error on the wind measurement: $E_2=10\%$
 - Error on the dispersion model calculation: $E_3=10\%$
 - Error on the data processing: $E_4=10-20\%$ (depending on the regression analysis convergence)

→ Global error = $(E_1^2 + E_2^2 + E_3^2 + E_4^2)^{0.5}$

We took a global error included in **[20-30%]** interval

NPL REPORT ENV (RES) 026

CEN/TC264/WG38 – WP 1 – TECHNIQUE REVIEW

**T SMITH
F INNOCENTI
R A ROBINSON**

NPLML - COMMERCIAL

JUNE 2016

CEN/TC264/WG38 - WP 1 - TECHNIQUE REVIEW

T Smith, F Innocenti, R A Robinson
Environment Division

© NPL Management Limited, 2017

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

This report is NPL - Commercial and must not be exposed to casual examination. It is not for general distribution and should not be cited as a reference other than in accordance with the contract.

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

CONTENTS

GLOSSARY/ABBREVIATIONS

EXECUTIVE SUMMARY

1	INTRODUCTION	1
2	DIAL	2
2.1	OVERVIEW	2
2.1.1	Scope	2
2.1.2	Compounds measured.....	2
2.1.3	Information provided.....	2
2.1.4	Scale and limitations.....	2
2.2	DIAL MEASURING PRINCIPLE	2
2.2.1	Description of the technique.....	2
2.2.2	Advantages and constraints	5
2.2.3	Uncertainty	6
2.3	PERFORMANCE CHARACTERISTICS.....	7
2.4	QUALITY CONTROL	7
2.4.1	General	7
2.4.2	Spectroscopic calibration procedures	8
2.4.3	Calibration gases.....	8
2.4.4	Calibration cell	8
2.4.5	Spectral scans	8
2.4.6	Continuous spectral monitoring.....	8
2.4.7	Detection and acquisition system checks	8
2.4.8	Meteorological sensor calibration.....	9
2.5	DATA ANALYSIS.....	9
2.5.1	General	9
2.5.2	Background subtraction.....	9
2.5.3	Normalisation for variation in transmitted energy.....	9
2.5.4	Calculation of path-integrated concentration.....	9
2.5.5	Derivation of range-resolved Concentrations.....	9
2.5.6	Calculation of emission fluxes	9
2.6	REFERENCES.....	10
3	OGI	12
3.1	OVERVIEW	12
3.1.1	Scope	12
3.1.2	Detectable pollutants	12

- 3.1.3 Information provided..... 12
- 3.1.4 Scale and limitations..... 13
- 3.2 OGI DETECTION PRINCIPLE 14
 - 3.2.1 Advantages and constraints 14
 - 3.2.2 Uncertainty 14
- 3.3 QUALITY CONTROL 15
 - 3.3.1 Test procedures..... 15
 - 3.3.2 Basic requirements 15
 - 3.3.3 Frequency 15
 - 3.3.4 Operating mode 15
- 3.4 DATA ANALYSIS 15
 - 3.4.1 Database Management..... 15
 - 3.4.2 Mass flux calculation / quantification..... 16
- 3.5 REFERENCES..... 16
- 4 SOF 17**
 - 4.1 OVERVIEW 17
 - 4.1.1 Scope 17
 - 4.1.2 Pollutants measured..... 17
 - 4.1.3 Information provided..... 17
 - 4.1.4 Scale and limitations..... 17
 - 4.2 SOF MEASURING PRINCIPLE 18
 - 4.2.1 Spectroscopy..... 18
 - 4.2.1.1 Infrared measurements 18
 - 4.2.1.2 Ultraviolet measurements 19
 - 4.3 FLUX MEASUREMENT..... 20
 - 4.4 MEASUREMENT METHODOLOGY 20
 - 4.5 ADVANTAGES AND CONSTRAINTS 22
 - 4.6 UNCERTAINTY 23
 - 4.7 PERFORMANCE CHARACTERISTICS..... 23
 - 4.8 QUALITY CONTROL 24
 - 4.8.1 Calibration 24
 - 4.9 DATA ANALYSIS..... 25
 - 4.9.1 Spectroscopy..... 25
 - 4.9.2 Wind field..... 25
 - 4.10 REFERENCES..... 25
- 5 TRACER CORRELATION TECHNIQUES 28**
 - 5.1 OVERVIEW 28

5.1.1	Scope	28
5.1.2	Compounds measured.....	28
5.1.3	Information provided.....	28
5.1.4	Scale and limitations.....	28
5.2	MEASURING PRINCIPLE.....	28
5.2.1	Tracer correlation techniques	28
5.2.1.1	General description.....	29
5.2.2	Advantages and constraints	29
5.2.3	Uncertainty	30
5.3	PERFORMANCE CHARACTERISTICS.....	30
5.4	QUALITY CONTROL	31
5.5	DATA ANALYSIS.....	31
5.6	REFERENCES.....	31
6	 SNIFFING.....	33
6.1	OVERVIEW	33
6.1.1	Scope	33
6.1.2	Pollutants measured.....	33
6.1.3	Information provided.....	33
6.1.4	Scale and limitations.....	33
6.2	MEASURING PRINCIPLE.....	34
6.2.1	Sniffing.....	34
6.2.2	Advantages and constraints	34
6.2.3	Uncertainty	34
6.3	TECHNICAL PERFORMANCE/REQUIREMENTS.....	34
6.4	QUALITY CONTROL	35
6.4.1	Calibration procedures.....	35
6.5	DATA ANALYSIS.....	35
6.5.1	Database management	35
6.5.2	Mass fluxes calculation / quantification	35
6.5.3	Software validation.....	35
6.6	REFERENCES.....	35
7	 FLUX CHAMBER MEASUREMENTS	37
7.1	OVERVIEW	37
7.1.1	Scope	37
7.1.2	Pollutants measured.....	37
7.1.3	Information provided.....	37
7.1.4	Scale and limitations.....	37

7.2	DETECTION PRINCIPLE	37
7.2.1	Flux chamber detection	37
7.2.2	Advantages and constraints	37
7.2.3	Uncertainty	37
7.3	TECHNICAL PERFORMANCE/REQUIREMENTS.....	38
7.4	QUALITY CONTROL	38
7.4.1	Calibration procedures.....	38
7.5	DATA ANALYSIS	38
7.5.1	Database Management.....	38
7.5.2	Mass fluxes calculation / quantification	38
7.6	REFERENCES.....	38
8	MODELLING TOOLS TO QUANTIFY POLLUTING EMISSIONS ON A LOCAL SCALE.....	40
8.1	GENERAL	40
8.2	OVERVIEW	40
8.2.1	Compounds measured.....	40
8.2.2	Scale and limitations.....	40
8.3	RDM MEASURING AND MODELLING PRINCIPLE	40
8.4	REVERSE DISPERSION MODELLING	41
8.4.1	General	41
8.4.2	Reverse dispersion modelling in the case of a homogeneous source structure	41
8.4.3	Reverse dispersion modelling in the case of an inhomogeneous source structure	44
8.4.4	Practical procedure	46
8.5	EXAMPLE OF RDM APPLICATION IN QUANTIFICATION OF VOC IN REFINERY	48
8.6	TECHNICAL PERFORMANCE.....	50
8.6.1	Performance characteristics.....	50
8.6.2	Advantages and constrains	50
8.6.3	Uncertainty	50
8.7	QUALITY CONTROL	50
8.7.1	Calibration procedures.....	51
8.7.2	Calibration gases.....	51
8.7.3	Meteorological sensors calibration.....	51
8.8	DATA ANALYSIS	51
8.8.1	Background subtraction.....	51
8.8.2	Calculation of emission fluxes	51
8.9	REFERENCES.....	51
9	BAGGING METHOD.....	52
9.1	OVERVIEW	52

9.1.1	Scope	52
9.1.2	Pollutants measured.....	52
9.1.3	Information provided.....	52
9.1.4	Scale and limitations.....	52
9.2	MEASURING PRINCIPLE.....	52
9.2.1	Bagging technical description	52
9.2.2	Advantages and Constraints	53
9.2.3	Uncertainty	53
9.3	TECHNICAL PERFORMANCE/REQUIREMENTS.....	54
9.3.1	Blow through method requirements	54
9.3.2	Vacuum method requirements.....	54
9.3.3	Common requirements	54
9.4	QUALITY CONTROL	54
9.4.1	Calibration procedures.....	54
9.5	DATA ANALYSIS.....	54
9.5.1	Mass flux calculation / Quantification.....	54
9.6	REFERENCES.....	54
10	RPM.....	55
10.1	OVERVIEW	55
10.1.1	Scope	55
10.1.2	Compounds measured.....	55
10.1.3	Information provided.....	55
10.1.4	Scale and limitations.....	55
10.2	MEASURING PRINCIPLE OF RPM	55
10.2.1	Description of technique.....	55
10.2.2	Advantages and constraints	57
10.2.3	Uncertainty	57
10.3	PERFORMANCE CHARACTERISTICS.....	57
10.4	QUALITY CONTROL	57
10.5	DATA ANALYSIS.....	58
10.5.1	Overview	58
10.5.2	HRPM Methodology	58
10.5.3	HRPM Theory	58
10.5.4	HRPM Algorithm	58
10.5.5	Check for Reasonableness of Surface Concentration Plot Results.....	59
10.5.6	Qualitative check.....	59
10.5.7	Quantitative checks.....	59

- 10.5.8 Hot spot location determination 59
- 10.5.9 VRPM Methodology 59
- 10.5.10 VPRM Theory and Algorithms 59
- 10.5.11 Check for reasonableness of the calculated flux..... 62
- 10.5.12 1D-RPM Methodology 63
- 10.5.13 1D-RPM Theory and Algorithms 63
- 10.5.14 Check for reasonableness of the concentration profile..... 64
- 10.5.15 Qualitative checks..... 64
- 10.5.16 Quantitative checks..... 64
- 10.6 REFERENCES..... 65

1 INTRODUCTION

This review looks at the available monitoring techniques for Benzene 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.

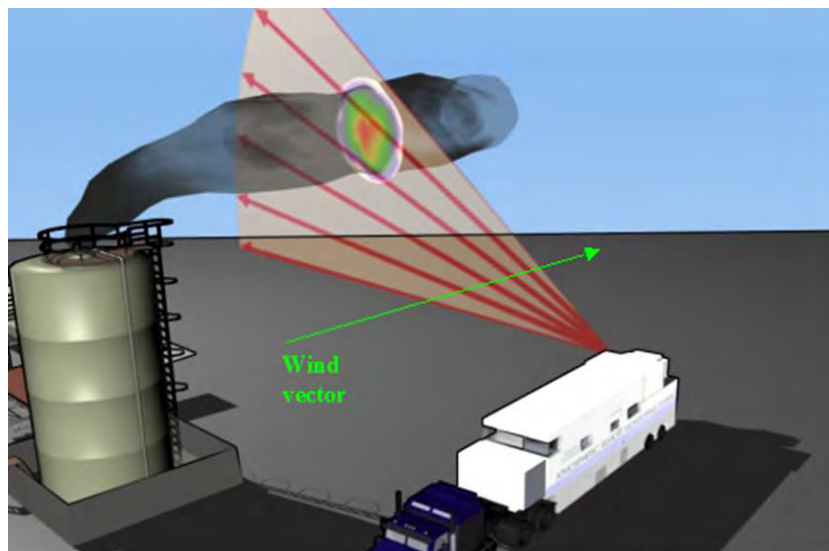


Figure 1.1 — DIAL Measurement Configuration

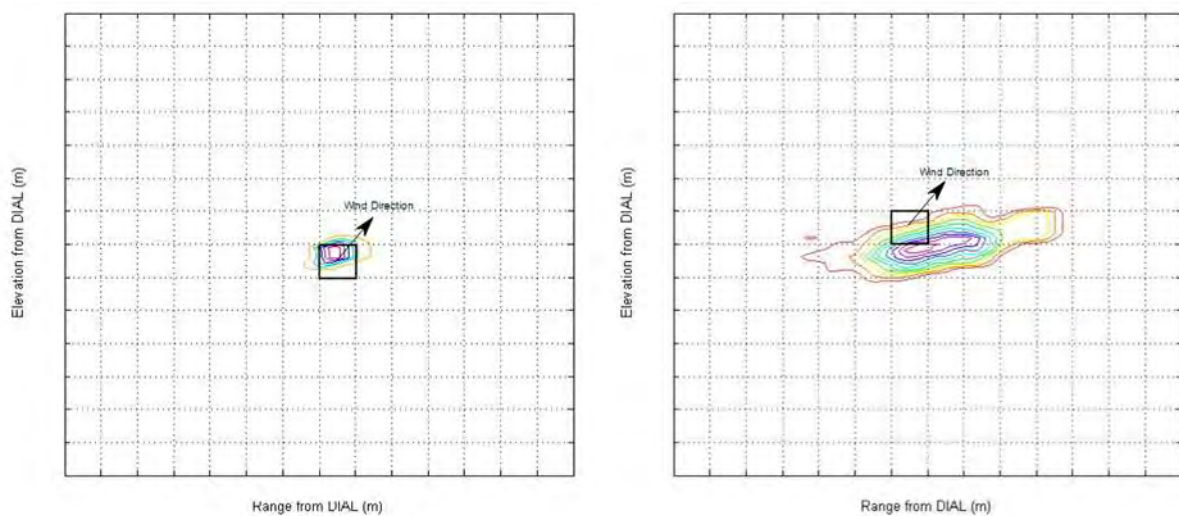


Figure 1.2 — Illustration of the emission rate calculation approach

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.

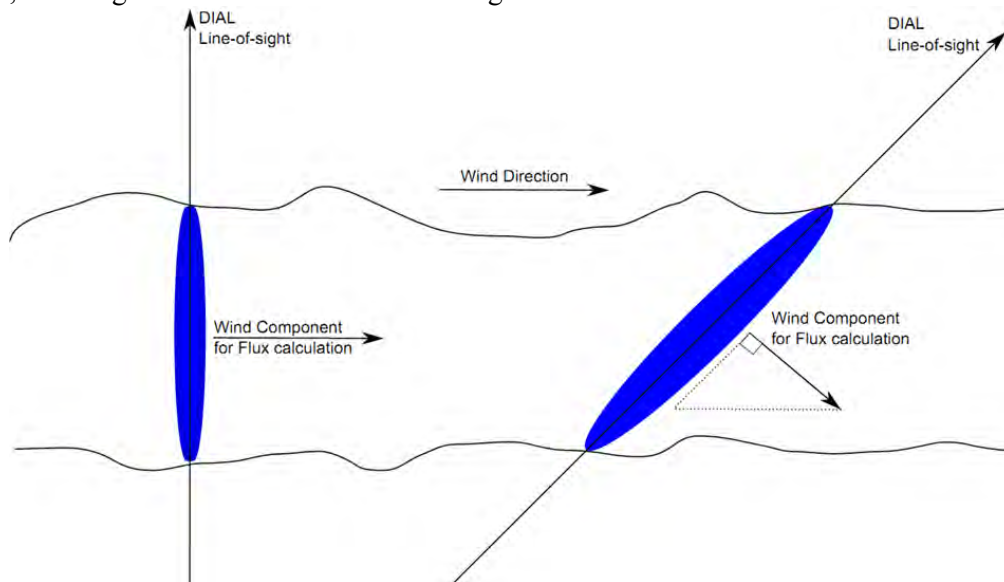


Figure 1.3 — Schematic showing relationship between emission rate and wind direction

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 be 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).

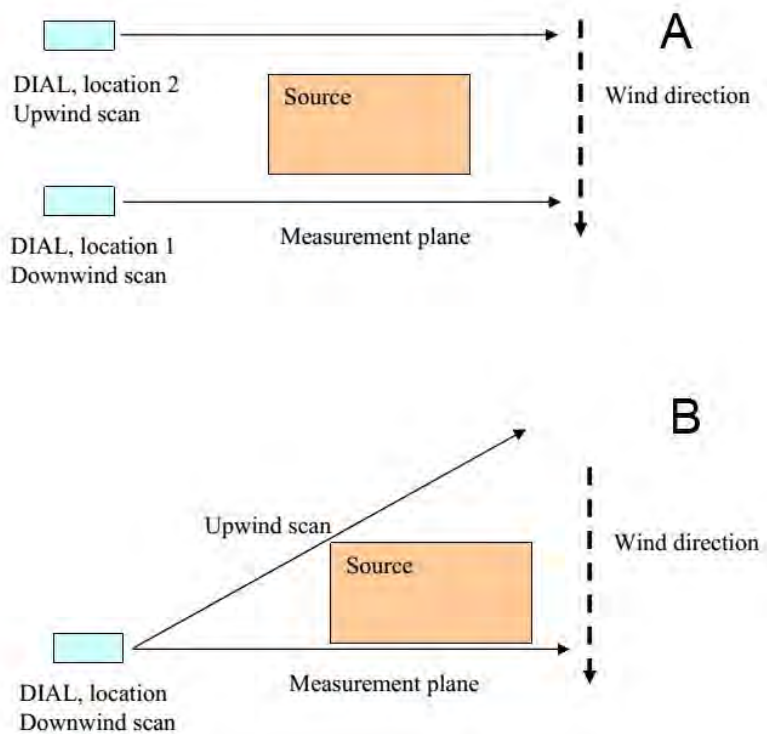


Figure 1.4 — Measurements of upwind and downwind emissions from one (B) or two (A) DIAL locations

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, it is advisable to use more wind speed sensors at different heights in order to calculate 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.

2.6 REFERENCES

Hoyt, D., & Raun, L. H. (2015). Measured and estimated benzene and volatile organic carbon (VOC) emissions at a major U.S. refinery/chemical plant: Comparison and prioritization. *Journal of the Air & Waste Management Association*, 65(8), 1020-1031. doi:10.1080/10962247.2015.1058304

Robinson, R., Gardiner, T., Innocenti, F., Woods, P., & Coleman, M. (2011). Infrared differential absorption Lidar (DIAL) measurements of hydrocarbon emissions. *Journal of Environmental Monitoring*, 13(8), 2213-2220. doi:10.1039/c0em00312c

Babilotte, A., Lagier, T., Fiani, E., & Taramini, V. (2010, August). Fugitive Methane Emissions from Landfills: Field Comparison of Five Methods on a French Landfill. *Journal of Environmental Engineering*, 136(8), 777-784. doi:10.1061/(ASCE)EE.1943-7870.0000260

Texas Commission on Environmental Quality. (2010). *Differential Absorption Lidar Study Final Report*. Houston: TCEQ. Retrieved August 2, 2016, from https://www3.epa.gov/ttn/chief/old/ap42/ch13/s05/reference/ref_09c13s05_2014.pdf

Robinson, R. A., Andrews, A. S., Gardiner, T. D., Uprichard, I. J., & Woods, P. T. (1998). *Differential Absorption Lidar Measurements of VOC Emissions from Wytch Farm Crude Oil Gathering Station*.

National Physical Laboratory, COEM. London: NPL. Retrieved August 2, 2016, from <https://uk-air.defra.gov.uk/assets/documents/reports/cat07/NPLreportCOEM13.pdf>

Innocenti, F., Robinson, R. A., Gardiner, T. D., & Wang, J. (2010). *Differential Absorption Lidar (DIAL) Measurements of VOC and Benzene Emissions from a Refinery Site in Houston, TX, US, January/February/March 2010*. National Physical Laboratory, AS. London: NPL. Retrieved August 2, 2016, from https://www3.epa.gov/ttnamti1/files/20072008csatam/Houston_dial_appendixa.pdf

Innocenti, F., Robinson, R. A., Gardiner, T. D., Finlayson, A. J., Connor, A., Lowry, D., & Fisher, R. (2013). *WR1125 - Measurement Of Methane Emissions And Surface Methane Oxidation at Landfills: A Supplementary Survey*. National Physical Laboratory, AS. London: NPL. Retrieved August 2, 2016, from http://www.google.co.uk/urlhttp://randd.defra.gov.uk/Document.aspx?Document=12437_WR1906SupplementarySurveyReport.pdf

De Caluwe, G., Smithers, B., Leotoing, F., Duclaux, O., Ribeiro, N., Leventos, D., . . . Gonzalez, L. (2014). *Towards the establishment of a protocol for the quantification of VOC diffuse emissions using open-path remote monitoring techniques: DIAL monitoring of a VOC source of known emission flux*. Brussels: Concawe. Retrieved August 2, 2016, from https://www.concawe.eu/uploads/Modules/Publications/rpt_12-14-2014-03534-01-e.pdf

US EPA. (2011). *EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux*. Guidance document, US Environmental Protection Agency, Office of Air Quality Planning and Standards. Retrieved August 5, 2016, from <https://www3.epa.gov/ttn/emc/guidlnd/gd-052.pdf>

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)

3.5 REFERENCES

Robinson, D. R., Luke-Boone, R., Aggarwal, W., Harris, B., Anderson, E., Ranum, D., . . . Smylie, M. (2007, July). Refinery Evaluation of Optical Imaging to Locate Fugitive Emissions. *Journal of the Air & Waste Management Association*, 57(7), 803-810. doi:10.3155/1047-3289.57.7.803

Benassy, M.-F., Bilinska, K., De Caluwe, G., Ekstrom, L., Leotoing, F., Mares, I., . . . Post, L. (2008). *Optical methods for remote measurement of diffuse VOCs: their role in the quantification of annual refinery emissions*. Brussels: Concawe. Retrieved August 2, 2016, from https://www.concawe.eu/uploads/Modules/Publications/rpt_08-6-2008-02481-01-e.pdf

Gonzalez, L., Juery, C., Kangas, P., Negroni, J., Roberts, P., Tupper, P., . . . Lawson, C. (2015, July). Abating Fugitive VOC Emissions More Efficiently. *Petro Industry News*, 22-23. Retrieved August 2, 2016, from https://www.petro-online.com/article_read/1882/

Lev-On, M., Epperson, D., Siegell, J., & Ritter, K. (2007, September). Derivation of New Emission Factors for Quantification of Mass Emissions When Using Optical Gas Imaging for Detecting Leaks. *Journal of the Air & Waste Management Association*, 57(9), 1061-1070. doi:10.3155/1047-3289.57.9.1061

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 CO₂ in the latter case. In the ultraviolet and visible wavelength region the species SO₂, NO₂ 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

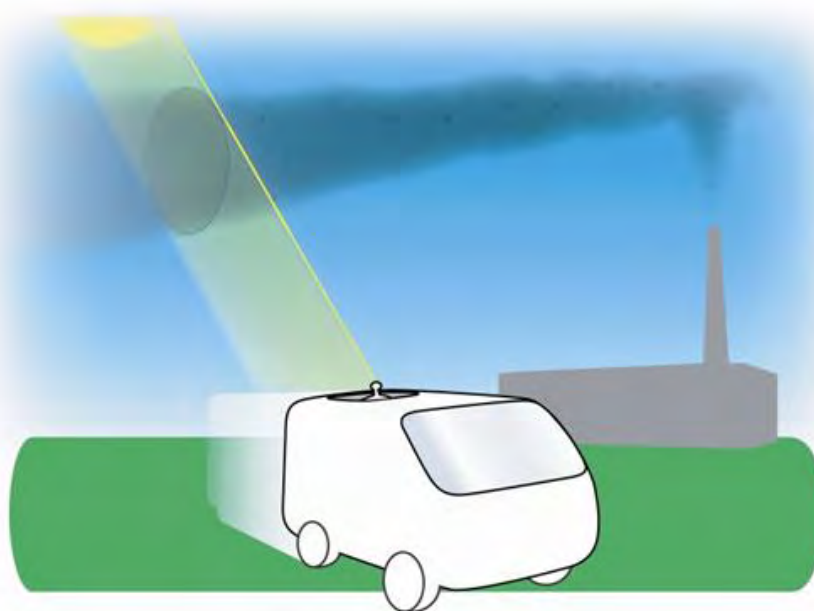


Figure 3.1 — In the Solar Occultation Flux method (SOF) gases are measured by observing solar light in the infrared portion of the solar spectrum. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of gas is obtained by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

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

Here $I(\nu)$ corresponds to the measured light intensity as a function of frequency ν , $I_{o,j}$ 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 SO₂ and NO₂ (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 NO₂ are retrieved between 324 to 350 nm, together with the interfering species O₃, O₄ and SO₂. SO₂ and O₃ is instead retrieved between 310 to 324 nm together with the NO₂ 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.

$$flux = \int_{x1}^{x2} \left(\int_0^{H_{mix}} conc(z) \cdot u'(z) \cdot dz \right) dx = u'_{mw} \int_{x1}^{x2} column(x)$$

(Eq.2)

$$\text{Where: } u'_{mw} = \frac{\int_0^{H_{mix}} conc(z)u'(z) \cdot dz}{\int_0^{H_{mix}} conc(z)dz} \quad \text{and} \quad column = \int_0^{H_{mix}} conc(z) \cdot dz$$

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 fence line 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 fence line, 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.

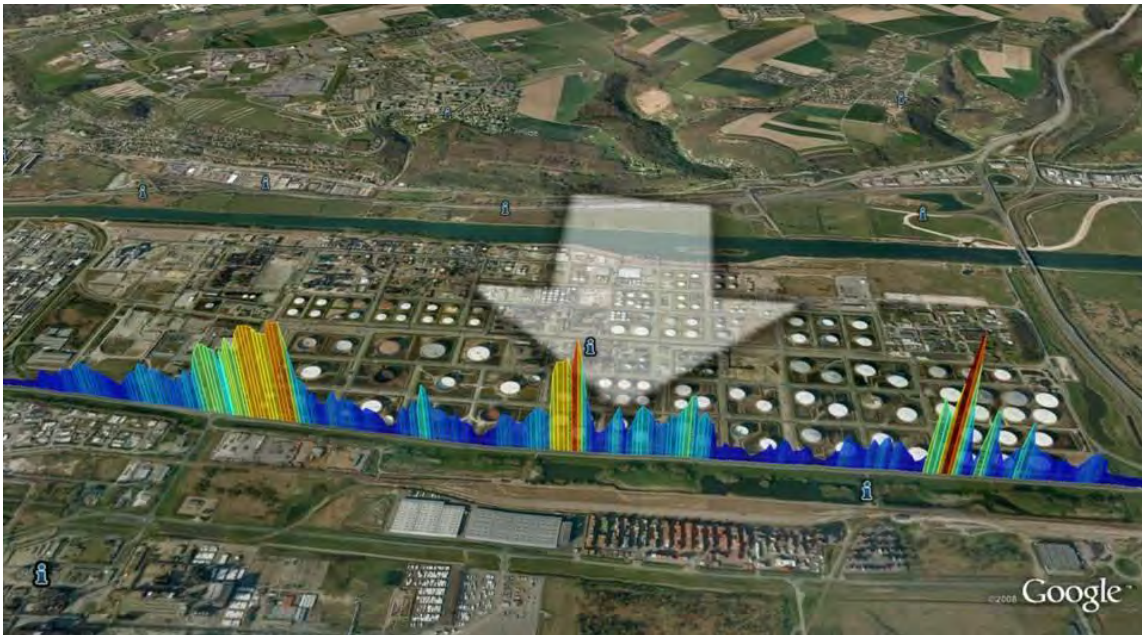


Figure 3.2 — A SOF transect past a refinery. The staples and colours shows the integrated amount of butane, as retrieved from the solar spectra. After multiplication with the wind velocity the mass flux is obtained.

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 fence line 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).

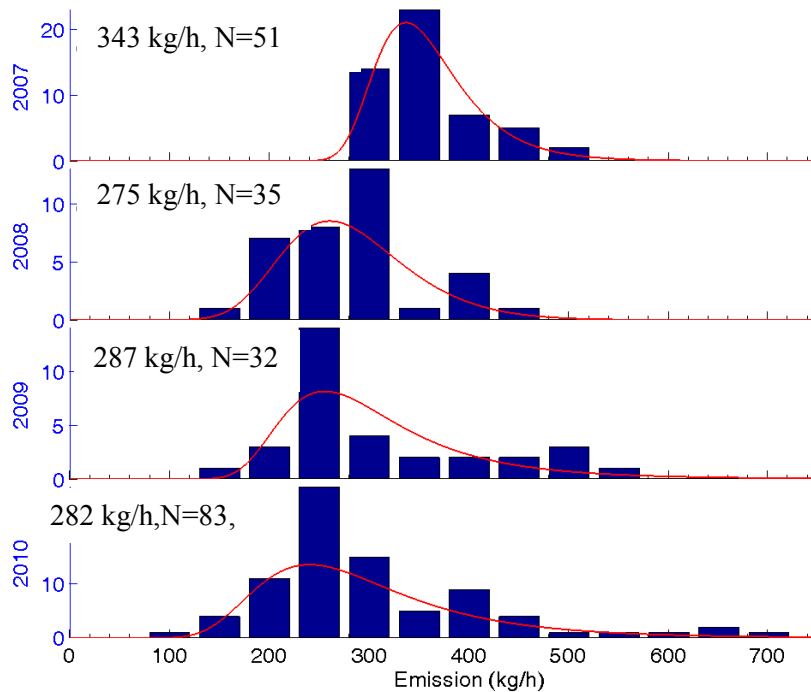


Figure 3.3 — Total VOC emission from a Swedish refinery over several years. The average emission is given, calculated as weighted average. Days with large variability are less weighted to minimize the influence of intermittent emissions, weight factor $1/\text{standard deviation}$ of daily emission values. 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 fence-line 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 $\pm 30\%$, while wind direction is typically recorded to within $\pm 15^\circ$, 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 (1 σ)	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], NO₂ [Vandaele 1998], SO₂ [Bogumil 2003], O₃ [Burrows 1999] and O₄ [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.

4.10 REFERENCES

Benassy, M.-F., Bilinska, K., De Caluwe, G., Ekstrom, L., Leotoing, F., Mares, I., . . . Post, L. (2008). *Optical methods for remote measurement of diffuse VOCs: their role in the quantification of annual refinery emissions*. Brussels: Concawe. Retrieved August 2, 2016, from https://www.concawe.eu/uploads/Modules/Publications/rpt_08-6-2008-02481-01-e.pdf

Sharpe, S. W., Johnson, T. J., Sams, R. L., Chu, P. M., Rhoderick, G. C., & Johnson, P. A. (2004, December). Gas-Phase Database for Quantitative Infrared Spectroscopy. *Applied Spectroscopy*, 58(12), 1452-1461. doi:10.1366/0003702042641281

Rinsland, C. P., Zander, R., & Demoulin, P. (1991, May 20). Ground-based infrared measurements of HNO₃ total abundances: Long-term trend and variability. *Journal of Geophysical Research: Atmospheres*, 96(D5), 9379-9389. doi:10.1029/91JD00609

Griffith, D. W. (1996, January). Synthetic Calibration and Quantitative Analysis of Gas-Phase FT-IR Spectra. *Applied Spectroscopy*, 50(1), 59-70. doi:10.1366/0003702963906627

Mellqvist, J., Samuelsson, J., Johansson, J., Rivera, C., Lefer, B., Alvarez, S., & Jolly, J. (2010, March 13). Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method. *Journal of Geophysical Research*, *115*, D00F17. doi:10.1029/2008JD011682

Mellqvist, J., Samuelsson, J., Johansson, J., Rivera, C., Lefer, B., Alvarez, S., & Jolly, J. (2010, April 16). Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method. *Journal of Geophysical Research: Atmospheres*, *115*(D7), 2156-2202. doi:10.1029/2008JD011682

Johansson, J. K., Mellqvist, J., Samuelsson, J., Offerle, B., Lefer, B., Rappenglueck, B., . . . Yarwood, G. (2014, February 27). Emission measurements of alkenes, alkanes, SO₂, and NO₂ from stationary sources in Southeast Texas over a 5 year period using SOF and mobile DOAS. *Journal of Geophysical Research: Atmospheres*, *119*(4), 1973-1991. doi:10.1002/2013JD020485

Johansson, J. K., Mellqvist, J., Samuelsson, J., Offerle, B., Moldanova, J., Rappengluck, B., . . . Flynn, J. (2014, April 16). Quantitative measurements and modeling of industrial formaldehyde emissions in the Greater Houston area during campaigns in 2009 and 2011. *Journal of Geophysical Research: Atmospheres*, *119*(7), 4303-4322. doi:10.1002/2013JD020159

Rivera, C., Mellqvist, J., Samuelsson, J., Lefer, B., Alvarez, S., & Patel, M. R. (2010, April 27). Quantification of NO₂ and SO₂ emissions from the Houston Ship Channel and Texas City industrial areas during the 2006 Texas Air Quality Study. *Journal of Geophysical Research: Atmospheres*, *115*(D8), D08301. doi:10.1029/2009JD012675

US EPA. (2011). *EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux*. Guidance document, US Environmental Protection Agency, Office of Air Quality Planning and Standards. Retrieved August 5, 2016, from <https://www3.epa.gov/ttn/emc/guidInd/gd-052.pdf>

Kihlman, M. (2005). *Application of solar FTIR spectroscopy for quantifying gas emissions*. Chalmers University of Technology, Department of Radio and Space Science. Goteborg: Chalmers University of Technology. Retrieved August 3, 2016, from <http://www.fluxsense.se/wp-content/uploads/ftp-uploads/pdf/SOF%20Licenciate%20thesis%20Kihlman%202005.pdf>

Rothman, L., Barbe, A., Benner, D., Brown, L., Camy-Peyret, C., Carleer, M., . . . Smith, K. (2003). The HITRAN molecular spectroscopic database: edition of 2000 including updates through 2001. *Journal of Quantitative Spectroscopy & Radiative Transfer*, *82*, 5-44. doi:10.1016/S0022-4073(03)00146-8

Fayt, C., & Van Roozendaal, M. (2001, February). WinDOAS 2.1 Software User Manual. Retrieved August 4, 2016, from <http://uv-vis.aeronomie.be/software/WinDOAS/WinDOAS-SUM-210b.pdf>

Cantrell, C. A., Davidson, J. A., McDaniel, A. H., Shetter, R. E., & Calvert, J. G. (1990, May). Temperature-dependent formaldehyde cross sections in the near-ultraviolet spectral region. *Journal of Physical Chemistry*, *94*(10), 3902-3908. doi:10.1021/j100373a008

Vandaele, A. C., Hermans, C., Simon, P. C., Carleer, M., Colin, R., Fally, S., . . . Coquart, B. (1998, May). Measurements of the NO₂ absorption cross-section from 42000 cm⁻¹ to 10000 cm⁻¹ (238-1000 nm) at 220 K and 294 K. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *59*(3-5), 171-184. doi:10.1016/S0022-4073(97)00168-4

Burrows, J. P., Richter, A., Dehn, A., Deters, B., Himmelmann, S., Voigt, S., & Orphal, J. (1999, March). Atmospheric remote-sensing reference data from GOME-2. Temperature-dependant absorption cross sections of O₃ in the 231-794 nm range. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *61*(4), 509-517. doi:10.1016/S0022-4073(98)00037-5

Fish, D. J., & Jones, R. L. (1995, April 1). Rotational Raman-Scattering and the Ring Effect in Zenith-Sky Spectra. *Geophysical Research Letters*, *22*(7), 811-814. doi:10.1029/95GL00392

Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O. C., . . . Burrows, J. P. (2003, May 5). Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and reference data for atmospheric remote-sensing in the 230-2380 nm

region. *Journal of Photochemistry and Photobiology A: Chemistry*, 157(2-3), 167-184. doi:10.1016/S1010-6030(03)00062-5

Hermans, C., Vandaele, A. C., Carleer, M., Fally, S., Colin, R., Jenouvrier, A., . . . Merienne, M.-F. (1999, September). Absorption cross-sections of atmospheric constituents: NO₂, O₂, and H₂O. *Environmental Science and Pollution Research*, 6(3), 151-158. doi:10.1007/BF02987620

Kraus, S. (2009, November 2). *DOASIS - DOAS Intelligent System*. Retrieved August 3, 2016, from <https://doasis.iup.uni-heidelberg.de/bugtracker/projects/doasis/index.php>

US EPA. (2014). *Geospatial Measurement of Air Pollution, Remote Emissions Quantification*. Draft Other Test Method. Retrieved August 5, 2016, from <https://www3.epa.gov/ttnemc01/prelim/otm33.pdf>

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 SO₂, NO₂ 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 SF₆, 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 (SF₆) in combination with HC/SF₆ analysis with gas chromatography in a number of points downwind the plant (so called conventional SF₆ 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 fluxes 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

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

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.

Equation 4.2

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

Where: u(z) is the wind velocity, u* is the friction velocity, k is the von Karman constant, d is the displacement height and z₀ 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.

5.6 REFERENCES

- Lamb, B. K., McManus, J. B., Shorter, J. H., Kolb, C. E., Mosher, B., Harriss, R. C., . . . Zimmerman, P. (1995). Development of Atmospheric Tracer Methods To Measure Methane Emissions from Natural Gas Facilities and Urban Areas. *Environmental Science & Technology*, 29(6), 1468-1479. doi:10.1021/es00006a007
- Scheutz, C., Samuelsson, J., Fredenslund, A. M., & Kjeldsen, P. (2011, May). Quantification of multiple methane emission sources at landfills using a double tracer technique. *Waste Management*, 31(5), 1009-1017. doi:10.1016/j.wasman.2011.01.015
- Monster, J. G., Samuelsson, J., Kjeldsen, P., Rella, C. W., & Scheutz, C. (2014, August). Quantifying methane emission from fugitive sources by combining tracer release and downwind measurements - A sensitivity analysis based on multiple field surveys. *Waste Management*, 34(8), 1416-1428. doi:10.1016/j.wasman.2014.03.025
- Galle, B., Samuelsson, J., Svensson, B. H., & Borjesson, G. (2001). Measurements of Methane Emissions from Landfills Using a Time Correlation Tracer Method Based on FTIR Absorption Spectroscopy. *Environmental Science & Technology*, 35(1), 21-25. doi:10.1021/es0011008
- Babilotte, A., Lagier, T., Fiani, E., & Taramini, V. (2010, August). Fugitive Methane Emissions from Landfills: Field Comparison of Five Methods on a French Landfill. *Journal of Environmental Engineering*, 136(8), 777-784. doi:10.1061/(ASCE)EE.1943-7870.0000260
- Samuelsson, J., Borjesson, G., Galle, B., & Svensson, B. (2001). *The Swedish landfill methane emission project*.
- Roscioli, J. R., Yacovitch, T. I., Floerchinger, C., Mitchell, A. L., Tkacik, D. S., Subramanian, R., . . . Marchese, A. J. (2015, May 7). Measurements of methane emissions from natural gas gathering facilities and processing plants: measurement methods. *Atmospheric Measurement Techniques*, 8, 2017-2035. doi:10.5194/amt-8-2017-2015
- Rella, C. W., Crosson, E. R., Dayton, D., Green, R., Hater, G., Lafleur, R., . . . Thoma, E. (n.d.). An Acetylene Tracer-Based Approach to Quantifying Methane Emissions from Distributed Sources Using Cavity Ring-Down Spectroscopy. Retrieved August 5, 2016, from <https://picarro.app.box.com/shared/l7a72vp74u/1/85919254/755512092/1>

Yver Kwok, C. E., Muller, D., Caldow, C., Lebegue, B., Monster, J. G., Rella, C. W., . . . Ciais, P. (2015, July 17). Methane emission estimates using chamber and tracer release experiments for a municipal waste water treatment plant. *Atmospheric Measurement Techniques*, 8(7), 2853-2867. doi:10.5194/amt-8-2853-2015

Mellqvist, J., Arlinder, B., Galle, B., & Berqvist, B. (1996). *Measurements of Industrial Fugitive Emissions by the FTIR Tracer Method (FTM)*. Goteborg: Swedish Environmental Research Institute. Retrieved August 5, 2016, from http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/27/053/27053343.pdf

Foster-Wittig, T. A., Thoma, E. D., Green, R. B., Hater, G. R., Swan, N. D., & Chanton, J. P. (2015). Development of a mobile tracer correlation method for assessment of air emissions from landfills and other area sources. *Atmospheric Environment*, 102, 323-330. doi:10.1016/j.atmosenv.2014.12.008

US EPA. (2011). *EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux*. Guidance document, US Environmental Protection Agency, Office of Air Quality Planning and Standards. Retrieved August 5, 2016, from <https://www3.epa.gov/ttn/emc/guidInd/gd-052.pdf>

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) = $2.29\text{E-}06 \times (\text{SV})^{0.746}$
Pump seals/all	Leak rate (kg/hr) = $5.03\text{E-}05 \times (\text{SV})^{0.610}$
Others ^d	Leak rate (kg/hr) = $1.36\text{E-}05 \times (\text{SV})^{0.589}$
Connectors/all	Leak rate (kg/hr) = $1.53\text{E-}06 \times (\text{SV})^{0.735}$
Flanges/all	Leak rate (kg/hr) = $4.61\text{E-}06 \times (\text{SV})^{0.703}$
Open-ended lines/all	Leak rate (kg/hr) = $2.20\text{E-}06 \times (\text{SV})^{0.704}$

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.

6.6 REFERENCES

Benassy, M.-F., Bilinska, K., De Caluwe, G., Ekstrom, L., Leotoing, F., Mares, I., . . . Post, L. (2008). *Optical methods for remote measurement of diffuse VOCs: their role in the quantification of annual refinery emissions*. Brussels: Concawe. Retrieved August 2, 2016, from https://www.concawe.eu/uploads/Modules/Publications/rpt_08-6-2008-02481-01-e.pdf

Gonzalez, L., Juery, C., Kangas, P., Negrone, J., Roberts, P., Tupper, P., . . . Lawson, C. (2015, July). Abating Fugitive VOC Emissions More Efficiently. *Petro Industry News*, 22-23. Retrieved August 2, 2016, from https://www.petro-online.com/article_read/1882/

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, CH₄, or any specific VOC when connected to FID analyser. NH₃ 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, CH₄, 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)

7.6 REFERENCES

Parker, D., Ham, J., Woodbury, B., Cai, L., Spiehs, M., Rhoades, M., . . . Cole, A. (2013, February). Standardization of flux chamber and wind tunnel flux measurements for quantifying volatile organic compound and ammonia emissions from area sources at animal feeding operations. *Atmospheric Environment*, 66, 72-83. doi:10.1016/j.atmosenv.2012.03.068

Yver Kwok, C. E., Muller, D., Caldow, C., Lebeque, B., Monster, J. G., Rella, C. W., . . . Ciais, P. (2015, July 17). Methane emission estimates using chamber and tracer release experiments for a municipal waste water treatment plant. *Atmospheric Measurement Techniques*, 8(7), 2853-2867. doi:10.5194/amt-8-2853-2015

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 CH₄, CO, CO₂) [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.

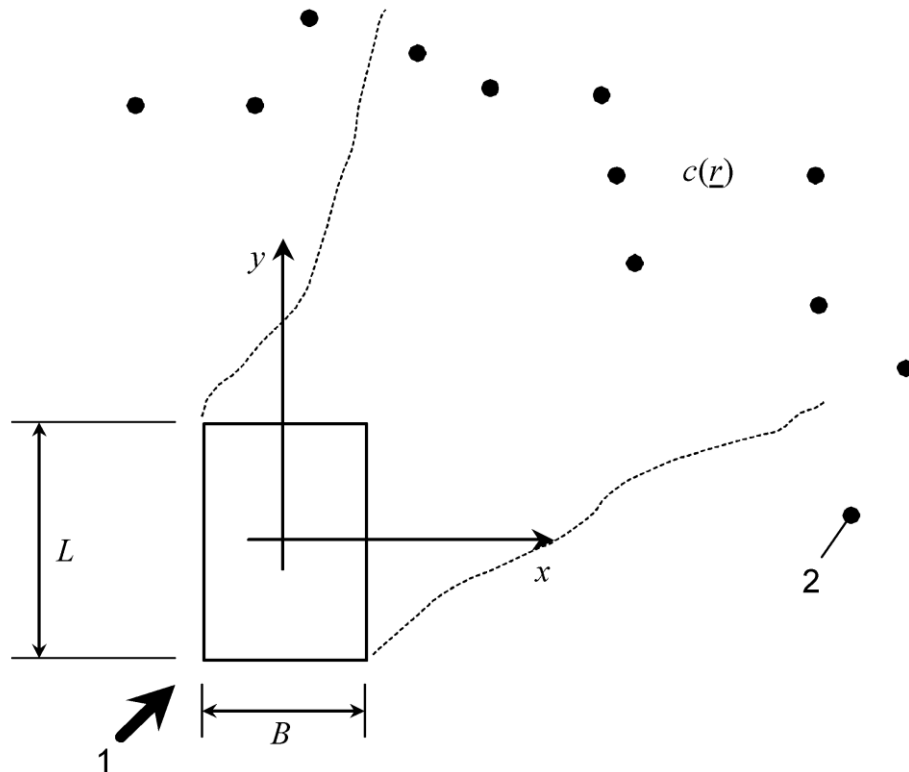
The methods to be used for the reverse dispersion modelling essentially depend on the fundamental properties of the source to be analysed. The respective procedure especially depends on the spatial structure of the source and the temporal emission behaviour over time. The development of a suitable source 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 $c_Q(\vec{r})$ and the background pollution c_∞ :

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

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 $c_Q(\vec{r})$ 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}
$c_Q(\vec{r})$	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:

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

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):

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

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):

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

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):

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

NOTE The superscript „ \sim ” 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:

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

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 :

$$Q = \sum_{j=1}^M Q_j \quad (11)$$

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} :

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

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

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:

$$\vec{c} = \mathbf{F} \cdot \vec{q} + \vec{c}_{\infty} \quad (13)$$

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}_∞ 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:

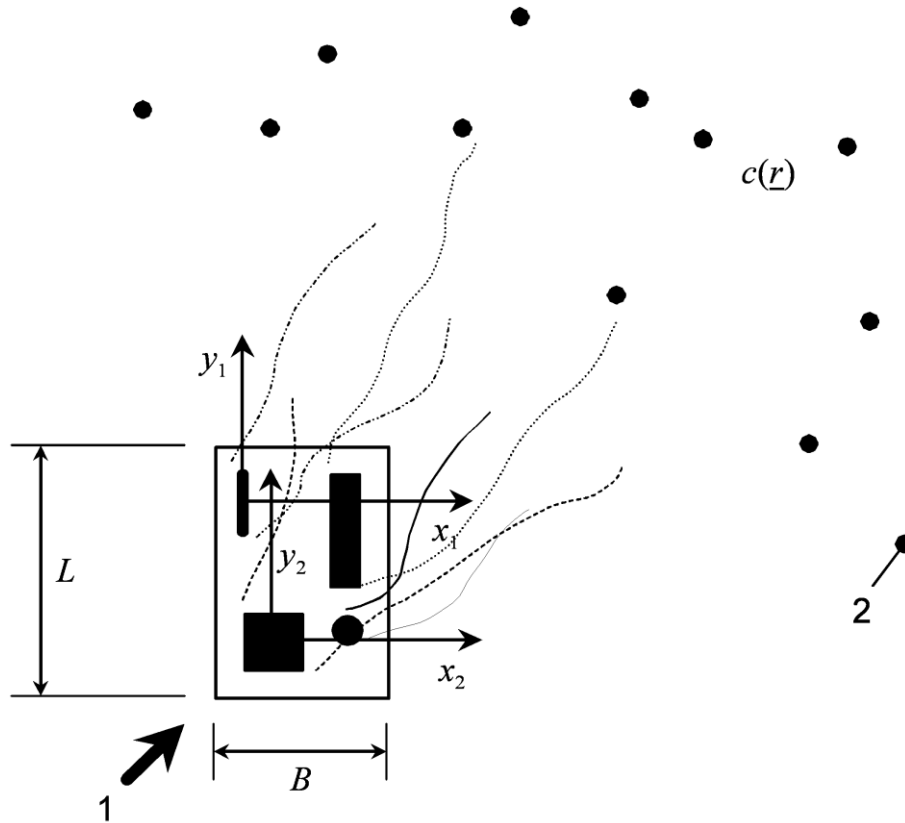
- a) Due to the local conditions, the whole source area can be divided into individual, homogeneous sources that are independent of one another. Under favourable meteorological conditions, the emission dispersion of each individual source is spatially separate, and there is no significant overlap with 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:

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

For the total emission rate the following applies:

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

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):

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

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 characteristic dimensions of the source. Using the mass flow density $\dot{m}_{d,j}$, the emission rate Q_j is related to the size of the transitional area A_j of the emissions, $\dot{m}_{d,j} = Q_j / A_j$. 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:

$$c(\vec{r}) = \hat{m}_d \sum_{j=1}^M A_j f_j(\vec{r} - \vec{q}_j) + c_\infty \quad (19)$$

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

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

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

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

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 (\bar{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 (\bar{c}_∞ 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 (\bar{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.

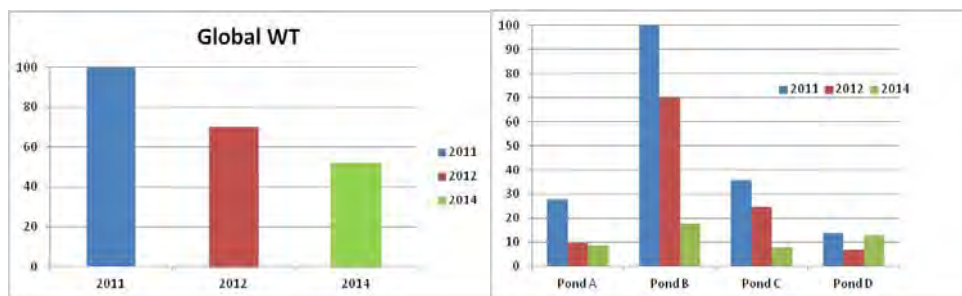


Figure E.4 : Emissions estimated with RDM for the water treatment area and for each pond (normalized to 100 for the highest) from 2011 to 2014

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

Babilotte, A., Lagier, T., Fiani, E., & Taramini, V. (2010, August). Fugitive Methane Emissions from Landfills: Field Comparison of Five Methods on a French Landfill. *Journal of Environmental Engineering*, 136(8), 777-784. doi:10.1061/(ASCE)EE.1943-7870.0000260

US EPA. (2011). *EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux*. Guidance document, US Environmental Protection Agency, Office of Air Quality Planning and Standards. Retrieved August 5, 2016, from <https://www3.epa.gov/ttn/emc/guidInd/gd-052.pdf>

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.

9.6 REFERENCES

Kangas, P., Roberts, P., Smithers, B., Vaskinen, K., Caico, C., Tupper, P., . . . Lawson, C. (2015). *Techniques for detecting and quantifying fugitive emissions - results of comparative field studies*. Brussels: Concawe. Retrieved August 2, 2016, from https://www.concawe.eu/uploads/Modules/Publications/rpt_15-6.pdf

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.

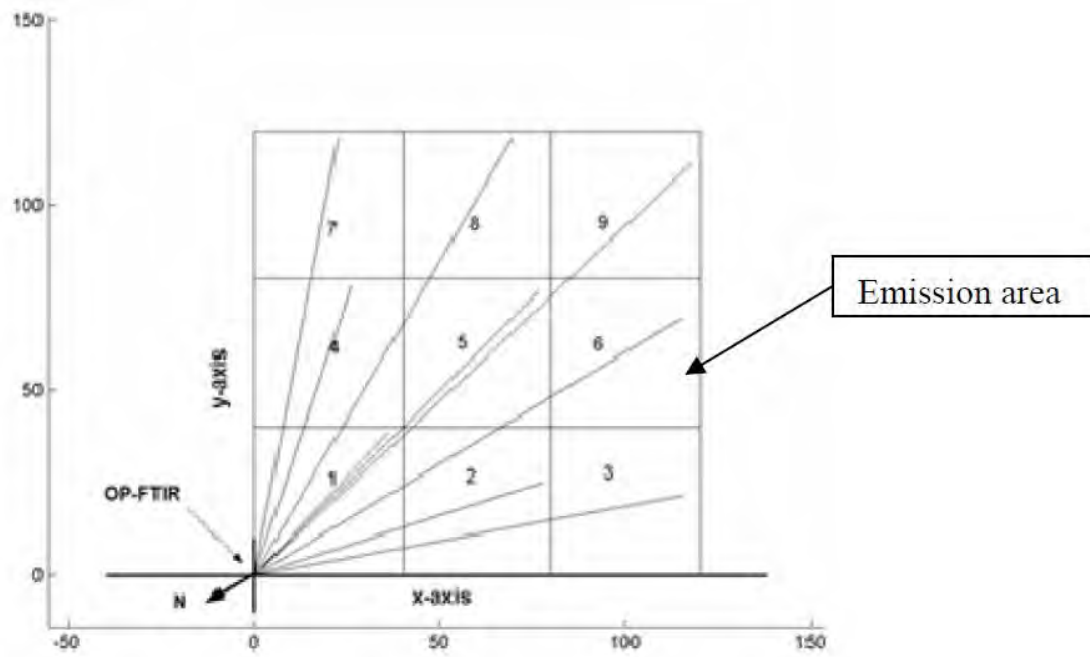


Figure 9.1: Typical HRPM measurement configuration (Modrak 2006)

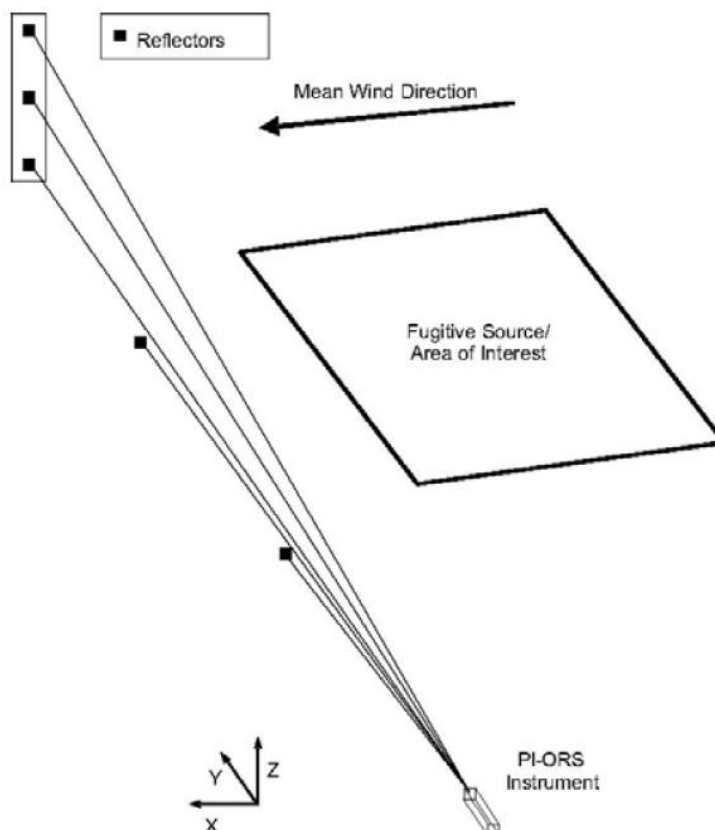


Figure 9.2: Typical VRPM measurement configuration (Modrak 2006)

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.

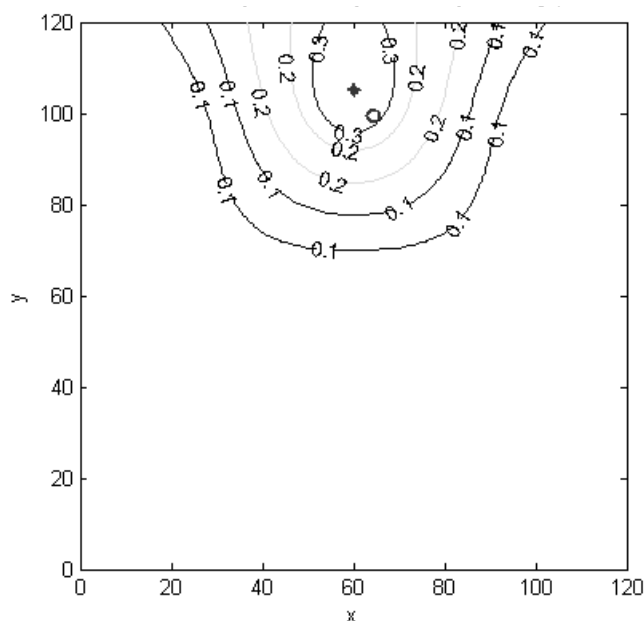


Figure 9.3: Example emission source location map, with the circle representing the controlled release point and the cross representing the detected centre of the plume.

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 be 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.

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

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 i^{th} beam
- m_y = the mean (peak location)
- σ_y = the standard deviation of the j^{th} Gaussian function
- PIC_i = the measured PIC value of the i^{th} 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 ($\rho_{12}=0$ 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:

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

Equation 9.5

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

m_{y-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:

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:

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/m³), 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:

$$CCF = rA \tag{Equation 9.8}$$

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:

$$\tag{Equation 9.9}$$

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:

$$\begin{aligned}
 B &= \text{area under the Gaussian distribution} \\
 r_i &= \text{path length of the } i\text{th beam} \\
 A &= \left[\frac{1}{2} \left(\frac{\sigma_{PIC_P}}{\sigma_{PIC_M}} + \frac{\sigma_{PIC_M}}{\sigma_{PIC_P}} + \left(\frac{PIC_P - PIC_M}{\sqrt{\sigma_{PIC_P} \sigma_{PIC_M}}} \right)^2 \right) \right]^{-1} \\
 m_y &= \text{the mean (peak location)} \\
 \sigma_y &= \text{standard deviation of the } j\text{th Gaussian function} \\
 PIC_i &= \text{measured path-integrated concentration value of the } i\text{th path}
 \end{aligned}$$

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.

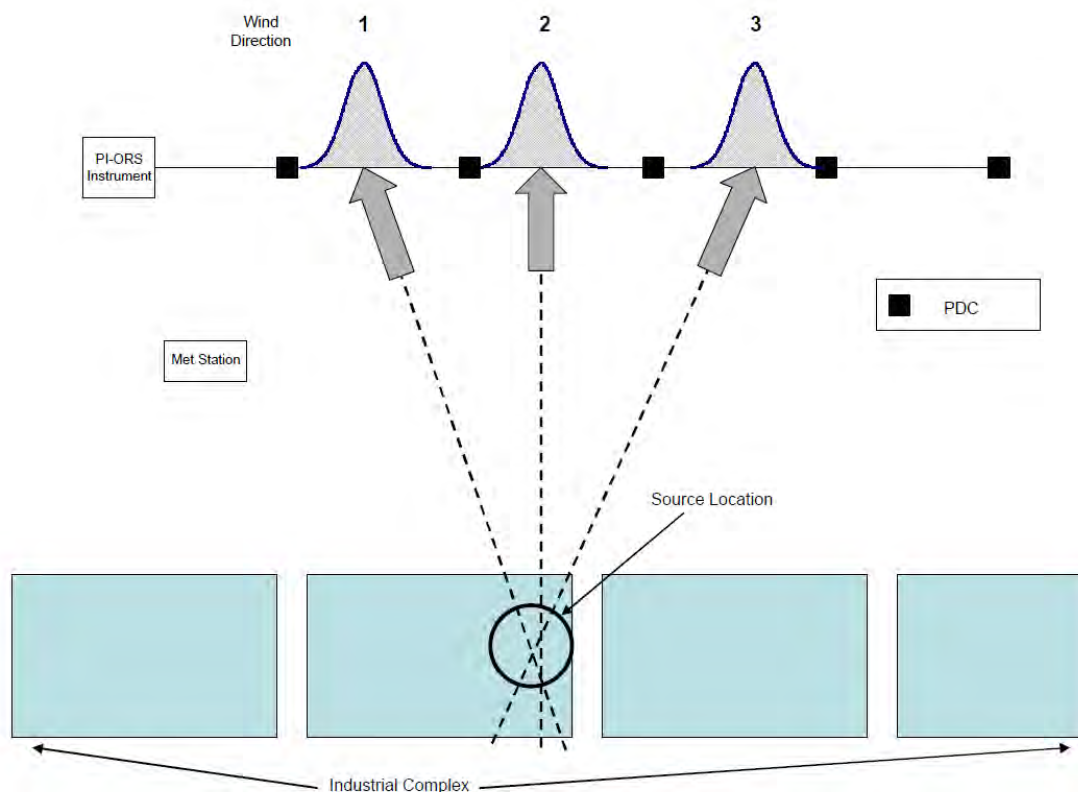


Figure 9.4: 1D-RPM set up with multiple peaks recorded over time due to shifting winds used to triangulate the source of the detected plume

10.6 REFERENCES

- Babilotte, A., Lagier, T., Fiani, E., & Taramini, V. (2010, August). Fugitive Methane Emissions from Landfills: Field Comparison of Five Methods on a French Landfill. *Journal of Environmental Engineering*, 136(8), 777-784. doi:10.1061/(ASCE)EE.1943-7870.0000260
- Modrak, M., Hashmonay, R., & Keagan, R. (2004). *Measurement of Fugitive Emissions at a Region I Landfill*. National Risk Management Research Laboratory, Air Pollution Prevention and Control . Washington: US Environmental Protection Agency.
- Hashmonay, R. A., & Yost, M. G. (1999). Innovative Approach for Estimating Fugitive Gaseous Fluxes Using Computed Tomography and Remote Optical Sensing Techniques. *Journal of the Air & Waste Management Association*, 49(8), 966-972. doi:10.1080/10473289.1999.10463862
- Modrak, M., D'Amato, V., Doorn, M., Hashmonay, R., Vergara, W., Deeb, A., . . . Cuevas, M. (2006). *Characterization of fugitive emissions of greenhouse gases from a wastewater treatment plant using the radial plume mapping technique*. Warwe Environment Foundation.
- Ro, K. S., Johnson, M. H., Hunt, P. G., & Flesch, T. K. (2011, September 23). Measuring Trace Gas Emission from Multi-Distributed Sources Using Vertical Radial Plume Mapping (VRPM) and Backward Lagrangian Stochastic (bLS) Techniques. *Atmosphere*, 2, 553-566. doi:10.3390/atmos2030553
- Viguria, M., Ro, K. S., Stone, K. C., & Johnson, M. H. (2015). Accuracy of vertical radial plume mapping technique in measuring lagoon gas emissions. *Journal of the Air & Waste Management Association*, 65(4), 395-403. doi:10.1080/10962247.2014.996267
- Wu, C.-F., Wu, T.-g., Hashmonay, R. A., Chang, S.-Y., Wu, Y.-S., Chao, C.-P., . . . Kagann, R. H. (2014). Measurement of fugitive volatile organic compound emissions from a petrochemical tank farm using

open-path Fourier transform infrared spectrometry. *Atmospheric Environment*, 82, 335-342. doi:10.1016/j.atmosenv.2013.10.036

Wu, C.-f., & Chang, S.-y. (2011). Comparisons of radial plume mapping algorithms for locating gaseous emission sources. *Atmospheric Environment*, 45, 1476-1482. doi:10.1016/j.atmosenv.2010.12.016

US EPA. (2006). *Optical Remote Sensing for Emissions Characterization from Non-point Sources*. Preliminary Method. Retrieved August 5, 2016, from <https://www3.epa.gov/ttnemc01/prelim/otm10.pdf>

US EPA. (2011). *EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux*. Guidance document, US Environmental Protection Agency, Office of Air Quality Planning and Standards. Retrieved August 5, 2016, from <https://www3.epa.gov/ttn/emc/guidlnd/gd-052.pdf>