2013

Pilot study to quantify industrial emissions of VOCs, NO_2 and SO_2 by SOF and mobile DOAS in the Carson Area

FluxSense

FINAL REPORT

FluxSense AB

27 March 2014

Date: 2014-03-27

Title: Pilot study to quantify industrial emissions of VOCs, NO_2 and SO_2 by SOF and mobile DOAS in the Bay Area

Authors: Johan Mellqvist[1], Jerker Samuelsson[1], Brian Offerle[1], Samuel Brohede[1], Pontus Andersson[1], Marianne Ericsson[2]

[1]FluxSense AB, Hörsalsvägen 11, SE-41296 Göteborg, Sweden
[2]FluxSense Inc, 113 W G Street # 757, San Diego, CA 92101

E-mail: johan.mellqvist@fluxsense.se

FluxSense AB (www.fluxsense.se) is a spin-off company from Chalmers University of Technology in Sweden. The company has been active for 10 years and has carried out 60+ industrial site surveillances in Austria, Belgium, Denmark, France, Middle East, Netherlands, Norway, Sweden and the US.

FluxSense Inc is a subsidiary residing in San Diego.

[Cover: Visualization of alkane (blue curves) plume transects from SOF measurements taken on October 12, 2013 between 13:30 and 17:15 in Carson and Wilmington, California. Apparent graph height is proportional to the integrated vertical column concentration in mg/m^2. A white arrow indicates the approximate wind direction and speed during the measurements. Winds were light and variable from SW to NW. Image mapped on Google Earth © 2013.]

Executive summary

Overview

In October 2013, column measurements of VOCs, SO_2 and NO_2 were carried out for 2.5 weeks in Carson, California and vicinity, to study direct emissions of these air pollutants from refineries and storage facilities. Two remote sensing techniques, SOF (Solar Occultation Flux) and Mobile DOAS (Differential Optical Absorption Spectroscopy) were used on public roads and along the fence lines of several refineries to estimate facility-wide mass emissions of VOCs, SO2 and NO2. Additional measurements were made over several days by mean of meFTIR (Mobile extractive FTIR) and MW-DOAS (Mobile White cell DOAS) to map ground concentrations of alkanes and aromatic VOCs and complement the SOF data. Using this approach mass flux measurements of aromatic VOCs were demonstrated.

Objective

In this technology demonstration project the main objective was to get an initial estimate of present emission levels of VOCs from one or several refineries in the Carson area, and compare the direct measurements to current reported levels. The project also introduced and demonstrated the capabilities of the FluxSense emission monitoring concept for annual emission report validation and hot spot detection to the environmental authorities of the South Coast Air Quality Management District (SCAQMD).

Background

SOF is a proven technique employed by FluxSense in over 70 fugitive emission studies around the world. In Europe the SOF technique is considered Best Available Technology for measurements of fugitive emission of VOCs and in Sweden it is used together with tracer correlation and optical gas imaging to screen all larger refineries and petrochemical industries annually. In Scandinavia measurement is the standard for emission reporting and in Sweden FluxSense carries out annual emission surveys on most refineries and petrochemical industries, each survey corresponding to about 10 measurement days, often broken down into several periods over the different seasons to better represent mean annual conditions.

For refineries the measured emissions are typically 0.03%-0.1% of the throughput. When compared to emission estimates based on the tanks model and LDAR, the measured emissions are 3 to 10 times greater. The measurements provide the total emission coming from the whole refinery (the bubble), divided into sub parts such as process areas, crude oil storage, product storage tanks, water treatment facilities, flares and loading operations. The estimated uncertainty for the emissions is 30% for the bubble, and higher for the individual parts. The SOF measurements are complemented by tracer correlation measurements at identified hotspots; for instance at individual tanks or loading facilities measurements are made specifically during tank filling or vessel loading to improve the understanding of activity related emissions and their variability. In addition optical gas imaging is carried out on the identified hotspots (super smart LDAR), to identify the exact location of the gas leaks for further evaluation whether abatement strategies can be applied.

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 is 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.

Results

For the facilities examined in this study, measured VOC emission rates (excluding aromatics and methane) were significantly higher than rates derived from the reported annual emissions. Although this report compares a short time period (a few days to two weeks) with annualized emissions, these results are in line with the vast majority of fugitive emission measurement studies we conducted at other locations. In particular, measured inventories are generally 0.05% or more of facility throughput capacity, a factor of 3 to more than 10 times higher than reported emissions based on standard models, which may be only 0.01% of throughput. For the two Carson refineries (i.e. Tesoro and Phillips66), VOC emissions as a percent of capacity were in the lower range what is usually measured, i.e. between 0.01 – 0.04 % (See Table E1).

The typical uncertainty for SOF measurements is 20-30 % with the greatest source of uncertainty deriving from the interpretation of the wind data. In this study wind information was provided by the Tesoro refinery, in addition to wind data that was collected from two nearby monitoring stations operated by the SCAQMD. Additionally, a limited number of GPS sondes were launched to obtain vertical profiles of wind through the lower atmosphere. During the measurements winds were often weak with large spatial variability due to diurnal effects (e.g. sea-breeze). The limited wind dataset coupled with their large spatial variability makes the uncertainty of the VOC measurements higher than normal (here estimated to be between 40 and 50%). In addition measured emissions are only based on several days of measurements and are probably affected by specific operating conditions at the facilities, including possible stoppages and temporary releases. Thus, measured VOC emissions may not fully represent actual annual average emissions.

If actual throughput is at or near capacity then the facilities in Table E1 are on the low end of VOC emissions relative to throughput. Also, measurements at two other refineries were carried out, i.e. ExxonMobil in Torrance and Phillips66 in Wilmington yielding VOC emission rates of 100 and 170 kg/h, respectively, compared to reported values of 64 and 27 kg/h respectively. Since no nearby wind measurements were available and given the complexity of the wind profiles in the area, these last results are affected by large uncertainties and are only indicative. Finally, an assessment of the aromatic emissions from the Tesoro Carson refinery was carried out, yielding 2.5 and 7.5 kg/h of benzene and toluene, respectively.

Table E1. Comparison of reported and measured emissions from selected facilities.

	VOC				SO_2		NOx	NO_2
Site	Reported*		Measured		Reported*	Measured	Reported*	Measured
	kg/h	% capacity	kg/h	% capacity	kg/h	kg/h	kg/h	kg/h
Tesoro Carson	51	0.003%	204 (±32 %)	0.013%	43	40 (±58 %)	67	39 (±37 %)
Phillips66 Carson	12	0.004%	94 (±32 %)	0.033%	22	30 (±42 %)	34	21 (±43 %)

*Data from SCAQMD 2012

Outlook

The observed difference in fugitive VOC emissions between measurements and estimates appears to be a general issue for the petroleum industry worldwide, and if one would adopt the, in general, higher measured values (factor 3-5) this might create legislative challenges for the industry, for instance with permitting and potential liability issues. To avoid this, measurements and estimates could be done in parallel where the former are used for the official reporting while the latter is done as part of the proactive environmental work aimed at reducing the emissions at the site. If this is carried out for a couple of years, followed by abatement work at the dominant hotspot emissions for an industrial site, combined with adaptive improvements of the emission factors, the estimates and measurements may start to converge.

Acronyms used in this report

API	American Petroleum Institute
bbl	barrel
BPD	barrels per day
DOAS	Differential Optical Absorption Spectroscopy
FTIR	Fourier transform infrared
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory Model
MeFTIR	Mobile extractive FTIR
MW-DOAS	Mobile White cell DOAS
NO2	nitrogen dioxide
SO2	sulfur dioxide
SOF	Solar occultation flux
VOC	volatile organic compound, used interchangeably for non-methane VOC

Unit equivalents

1 kg/h = 52.9 lbs/day
1 bbl/day = 5.783 kg/h

Definitions

Alkane or Alkanes are considered to be alkane species not including methane.

Table of Contents

1. Introduction

A pilot study was carried out in Carson, California, during October 2013 to measure the gaseous emissions of VOCs, SO_2 and NO_2 from refineries in the area. The main objective of this pilot project was to get a first estimate of present emission levels of VOC from one or several refineries and to compare with current reported levels. The project also aimed at introducing and demonstrating the capabilities of SOF and mobile DOAS to the environmental authorities at the South Coast Air Quality Management District (SCAQMD). A similar project has been conducted in the San Francisco Bay Area for the Bay Area Air Quality Management District (BAAQMD).

Similar measurements conducted elsewhere in Texas (Mellqvist 2009, Johansson 2011, Johansson 2013a, Johansson 2013b., Mellqvist 2007, 2008b, 2010, Rappenglück 2008a, 2008b; De Gouw 2009; Wert 2003; Ryerson 2003) and Europe (France, Netherlands, Sweden) were 5 to 10 higher than inventory values and studies indicated that this may have an impact on the production of tropospheric ozone.

For this pilot study, measurements were conducted for about two weeks in October 2013 along the refinery fence-line at public roads, and facility-wide mass emissions of VOC, SO_2, NO_2 were obtained.

2. Methods

Several optical technologies i.e. Solar Occultation Flux (SOF), mobile DOAS, Mobile extractive FTIR (MeFTIR) and Mobile White cell DOAS (MW-DOAS) have been combined to measure and quantify facility-wide VOC emissions from the Tesoro refinery and to pin-point the potential sources, Table 1. Meteorological measurements were obtained from various wind stations and from GPS (Global Positioning System) sondes. The instruments were mounted on and inside a dedicated vehicle, with AC power provided by a small gasoline powered generator (Figures 1 and 2). An air conditioner was used to prevent overheating of some of the instruments.

Figure 1. The measurement truck used these measurements.

Figure 2 The SOF and the mobile DOAS systems. The solar tracker (front left) transmits solar light into the infrared spectrometer (mid right with a GPS on top) independent of the vehicle's position.

Table 1 The techniques used and their technical characteristics.

Parameter	SOF	Mobile DOAS	Extractive Infrared Whitecell (MeFTIR)	Mobile UV Whitecell (MW-DOAS)
Compounds	Ethene, Propene, Ammonia, Butadiene, sum of Alkanes CO	NO2 SO2 Formaldehyde	Ethene Propene Acetylene Ammonia Sum of Alkanes Methane Ethane Cyclo hexane CO / CO2 N2O	*BTEX* *SO2* *NO2*
Sensitivity	0.1-5 mg/m2	0.1-5 mg/m2	1-10 ppb	*1-5 ppb*
Flux limit	0-2-1 kg/hr	1kg/hr	0.2-2 kg/hr	*1 -2 kg/hr*
Meas. mode	Vert. Column	Vert. Column	Point Sampler	*Point Sampler*
Light Conditions	Sunny with large patches of clear sky	Daylight with patches of clear sky	24 hr Extractive instrument with internal lamp	*24 hr* *Extractive instrument with internal lamp*
Wind Speed	~2-12m/s	~2-12m/s	~2-12m/s	*~2-12m/s*
Time response/ Sampling Frequency	1-5 sec	1-5 sec	5-15 sec	*1-30 sec*
Typical driving speed while measuring	10-50 miles/hr	10-50 miles/hr	10-35 miles/hr	*10-35 miles/hr*
Complementary activity	Wind measurement from mast, balloon, or LIDAR,	Wind measurement from mast, balloon,or LIDAR,	Tracer gas releases (N2O, acetylene, SF6)	*Operated in parallel with MeFTIR.*

2.1 The SOF method

SOF measurements are carried out using an infrared spectrometer that is connected to a solar tracker (see Appendix I and Mellqvist (2010) for details). The latter is a mirror device 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) in the unit mg/m^2 of various species (for instance, propane, ethylene, propylene and ammonia) between the sun and the spectrometer. The measurement system is built into a van. In order to measure gaseous emissions from a source, the vehicle is driven in such way that the detected solar light cuts through the emission plume, Figure 3. To calculate the gas emission the wind direction and speed is also required and these parameters are usually measured from high masts, towers and GPS balloon sondes. Detection limits down to 0.5 mg/m^2 can be achieved which corresponds to measuring a point source of 0.5 kg/h at a distance of 50 m with an accuracy of better than 3%. The SO method was developed from a number of different research projects at the end of 1990's (Mellqvist 1999a, 1999b; Galle 1999). The method utilizes the sun as the light source and gas species that absorb in the infrared portion of the solar spectrum are measured from a mobile platform. The SOF method has been applied in several larger campaigns in both Europe and in the US (Mexico City 2006, Texas 2006/2009/2011/2012/2013; Le Havre 2008, Rotterdam 2008/2010 and Antwerp 2010) and in more than 60 individual plant surveys over the last 7 years. About 10 international reports and several peer reviewed scientific papers (Mellqvist 2010, Foy 2007, De Gouw 2009, Kim 2011, Parrish 2012, Johansson, 2013a, Johansson 2013b) have been written so far, applying the SOF method for various industrial measurements. The technique has been validated by comparison to other methods and tracer gas releases and it typically has an uncertainty of 30% (Table 1) mostly due to uncertainties in the wind field.

In previous campaign studies it has been found that measured emissions obtained with SOF are 3–10 times higher than those from emission inventory calculations. For instance, during TexAQS 2006, it was shown that industrial releases of alkenes for the Houston Galveston area were, on average, 10 times higher than what was reported by industry (Mellqvist 2010). These results were supported by airborne measurements (De Gouw 2009). For alkanes the discrepancy factor was about 8 (Mellqvist 2007). During similar SOF studies in Rotterdam (Netherlands) in 2008 and 2010 (Mellqvist 2009a), Le Havre 2008 and Antwerp 2011 showed overall discrepancies of 4.2, 4.4 and 7.7, respectively. For Swedish refineries the VOC emissions typically correspond to 0.03–0.09 % of the throughput of oil, compared to a typical value of 0.01% obtained with API estimations. Modelers in the USA have responded to the observed discrepancies by increasing the modeled VOC emissions; for instance TCEQ (Texas Commission on Environmental Quality) increases industrial VOCs by ~6 times in ozone modeling (SIP model) and scientists at the US weather service (NOAA-National Oceanographic Atmospheric Administration) (Kim, 2011) have upscaled VOC emissions based on 2006 SOF data in Texas. This improved the agreement with airborne measurements for both VOCs and ozone significantly.

In Europe the SOF technique is considered as Best Available Technology for measurements of fugitive emission of VOCs (besides DIAL) and in Sweden it is used together with trace correlation and optical gas imaging to screen all larger refineries and petrochemical industries annually, over a time period of about 10 days. The data are used for the annual emission reporting and to follow up on abatement strategies, such as new tank sealings, flare efficiency etc.

Figure 3 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, see http://www.youtube.com/watch?v=6cre9q8YAzE

2.2 Mobile DOAS

Mobile DOAS (Differential Optical Absorption Spectroscopy) measurements of scattered solar light in zenith direction were carried out in parallel with the SOF measurements in order to measure formaldehyde, NO2 and SO2. DOAS works in the ultraviolet (UV) and visible wavelength region while SOF works in the infrared region and hence there are large differences in spectroscopy and in the used spectrum evaluation methods. However, both methods measure vertical columns which are integrated along the measurement transect and multiplied by the wind to obtain the flux. The principle of flux-measurements using Mobile DOAS is hence the same as for SOF, although it is not necessary to compensate for any slant angle observations since the telescope is always pointing towards zenith. The DOAS system also works under cloudy conditions in contrast to SOF, although the most precise measurements are conducted under clear sky. The system is explained in appendix I and elsewhere (Johansson, 2013b).

The DOAS method was introduced in the 1970's (Platt 1979) and has since then become an increasingly important tool in atmospheric research and monitoring both with artificial light sources and in passive mode utilizing the scattered solar light. In recent time the multi axis DOAS method (scanning passive DOAS) has been applied in tropospheric research for instance measuring formaldehyde (Heckel 2005). Passive DOAS spectroscopy from mobile platforms has also been quite extensively applied in volcanic gas monitoring (Galle et al., 2002) for SO_2 flux measurements and for mapping of formaldehyde flux measurements in megacities (Johansson 2009). Mobile DOAS has only been used to a limited extent for measurements of industrial emissions. For example, Rivera et al. (2009c) performed SO_2 measurements on a power plant in Spain for validation purposes showing an average agreement of 7 % with continuous emission measurements. The same research group also deployed a mobile DOAS to study emissions from an industrial conglomerate in Tula in Mexico (Rivera 2009d) and measured SO_2, NO_2 and HCHO during the 2006 TexAQS campaign (Rivera 2009a, 2009b). There are other groups in both China and Spain working with mobile mini DOAS systems.

2.3. Mobile extractive FTIR

A Mobile extractive FTIR (MeFTIR) system, (Samuelsson 2005a; Galle 2001), was used to measure ground concentrations of alkanes (including methane). The extractive FTIR system contains a spectrometer of the same type as the one being used for SOF measurements (Bruker IRCube) but utilizes an internal light source (glowbar) instead of the sun. The spectrometer is connected to an optical multi-pass cell (Infrared Analysis Inc.) with 40 m path-length, Figure 4. Atmospheric air is continuously pumped with high flow through the optical cell from the outside, taking the air in from the roof of the van through a Teflon tube. See appendix I for details.

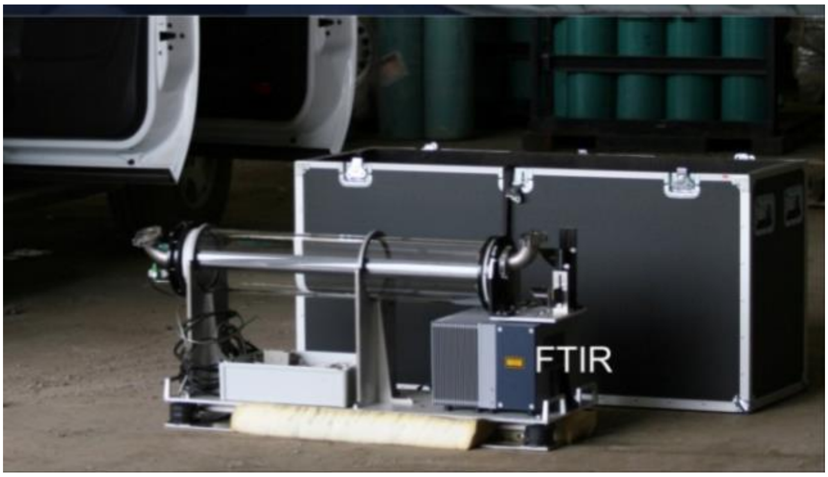


Figure 4 The MeFTIR instrument used in parallel with the SOF system during the campaign. The gas is extracted into the White-cell where it is analyzed by infrared absorption measurements. The residence time in the gas cell and, hence, the measurements time resolution is just a few seconds.

2.4 Mobile White Cell DOAS (MW-DOAS)

A multi-reflection UV system was used to measure ground concentrations of aromatic VOCs including benzene, toluene, and xylenes). In a validation test conducteed in Houston in October 2013 this system was tested against PTR-MS (Proton Transfer Reaction Mass Spectrometer), showing good agreement and sub-ppb sensitivity for benzene and other species (Johansson 2013c). The measurements of aromatic VOCs were carried out using a custom built multi-reflection cell (so called White cell) connected to an ultraviolet lamp and a grating spectrometer (Andor) using optical fibers. The open White cell on the roof of the car is shown in Figure 5, and through 84 reflections an effective optical path of 210 m is obtained yielding good sensitivity for measuring low concentrations of aromatic VOCs.

Measurements are carried out in the wavelength region 250-285 nm and analyzed using the DOAS (Differential Optical Absorption Spectroscopy) retrieval principle using custom software and QDOAS (Fayt 2001). Several aromatic compounds exhibit strong absorption lines in the measured wavelength region. The calibration cross sections for benzene, toluene and p-xylene were obtained from Fally (2009) and the cross sections for styrene and trimethylbenzene from Etzkorn (1999). See appendix I for details.

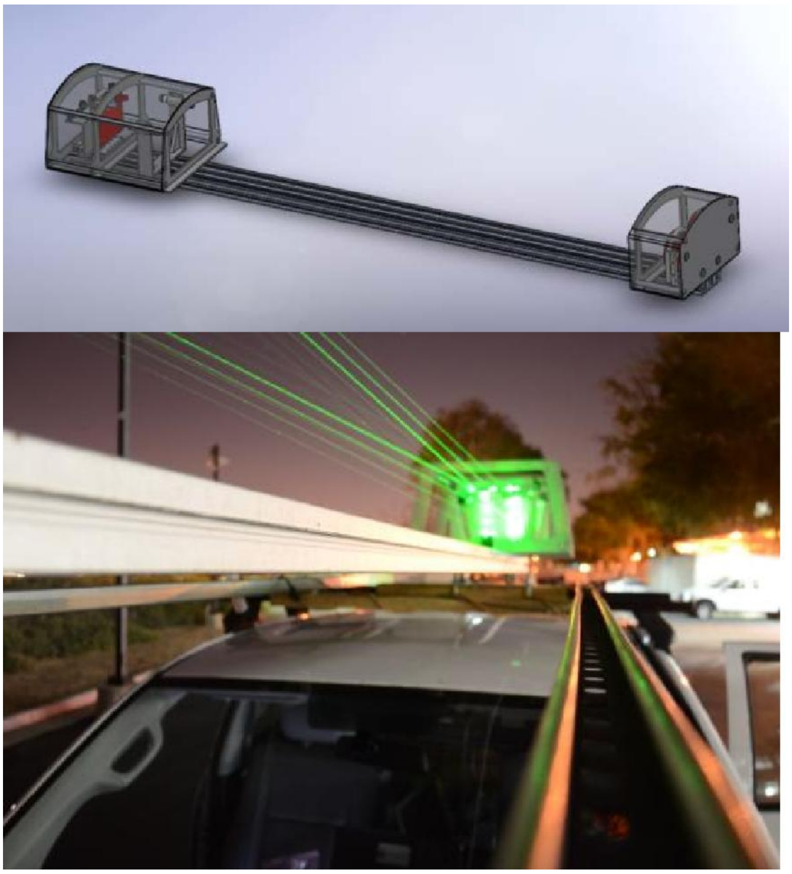


Figure 5 Measurements of aromatic VOCs were carried using a UV multi-reflection cell (White cell) connected to a DOAS spectrometer (MW-DOAS).

3. Measurements

This measurement study was carried out in the Carson area from October 5 to October 16, 2013, Figure 6. Column measurements of VOCs, SO_2 and NO_2 were taken to quantify direct emissions of the above-mentioned species from specific refineries and petrochemical industries. The primary methods used were SOF and Mobile DOAS. Two additional instruments, i.e. meFTIR and MW-DOAS were added to the project to map ground concentrations of alkanes and aromatic VOCs.

The main objective of this pilot study was to demonstrate and carry out flux measurements of VOCs, NO_2 and SO_2 around a refinery operated by Tesoro in the city of Carson. Other refineries were studied, such as Conoco Phillips in Carson and Wilmington. The ExxonMobil refinery in Torrance was also examined.

Accurately gauging the plume speed is typically the greatest source of error in SOF and mobile DOAS measurements. Continuous wind profiles, for instance from a Wind LIDAR, radar wind profiler or, at least, a number of tall masts at each site at the height of tanks, provide the most reliable and useful wind data. The SOF measurements obtained during this pilot project are particularly uncertain due to the lack of adequate wind data.

In this study vertical wind profiles were obtained with GPS meteorological sondes launched from a park just north of the Tesoro Refinery. The main complication, as shown by these profiles (See Appendix), is the gradients within the mixing boundary layer (turning winds versus height). Unfortunately, only a few GPS sondes launches were possible (see Appendix for details) and only limited vertical wind information were obtained. Thus, in most cases only data from three wind masts (one located at the Tesoro site, and two others operated nearby by the SCAQMD) were used for data analysis and interpretation.

The weather conditions for the first 3 days were clear with easterly winds and then the remaining days had low wind speeds with clouds in the mornings and afternoon sea breeze conditions. Due to sea breeze conditions the wind sometimes turned at midday causing high and varying backgrounds of VOCs or NO_2. In one case the wind direction at 300 m was opposite to the ground level wind.

To minimize the problem with varying background values, box measurements of the sites were made, measuring what goes in versus what comes out from the bubble constituting the refinery. In cases with large variability in the background it is however difficult to remove the upwind influence from the downwind measurements making the emission determination more uncertain. In these cases the measurements were omitted.

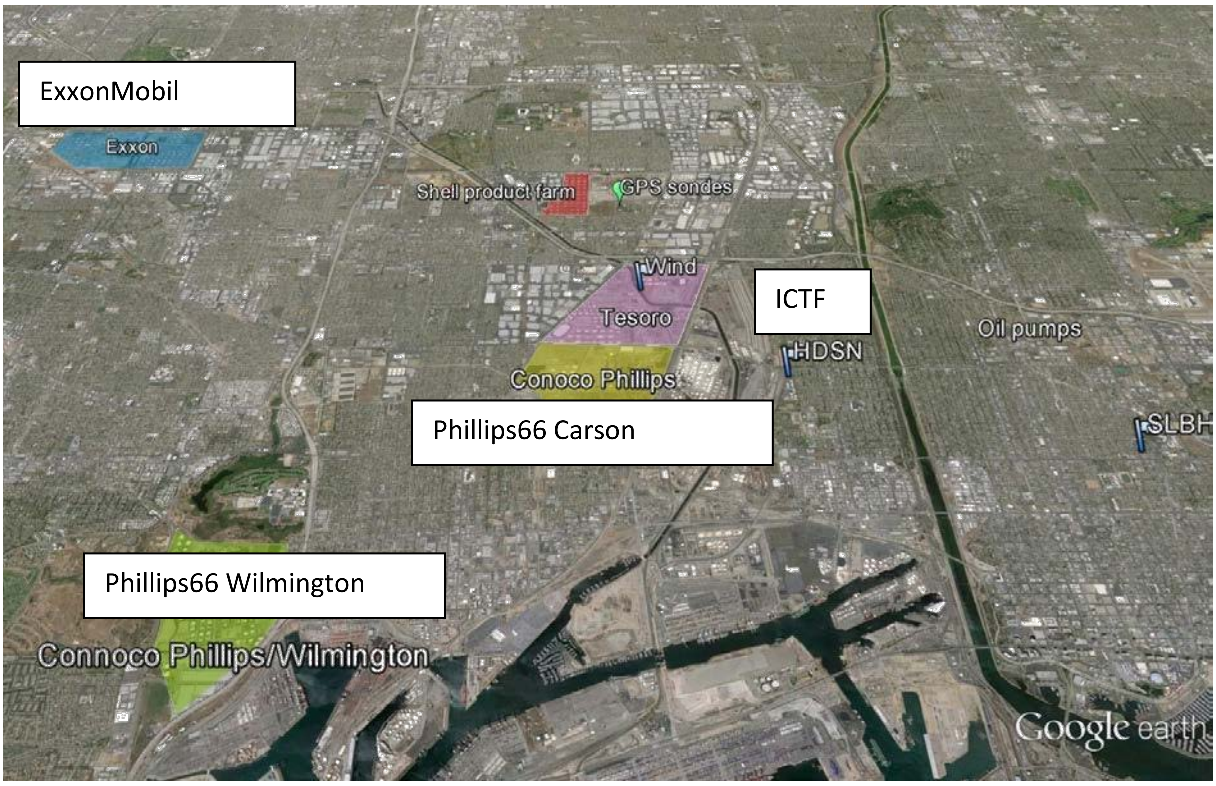


Figure 6 The sites studied are indicated here. The position for the meteorological soundings are indicated as well as the three wind stations (Tesoro, Hudson (HDSN) and South Long Beach (SLBH); the latter two locations are part of the SCAQMD monitoring network). North is towards the top of the image.

3.1 Wind measurements

Wind station data (15 minute averages) collected inside the Tesoro site from a 10 m high mast was used as primary wind information. Two nearby SCAQMD sites (Hudson and South Long Beach stations; here referred to as HSDN and SLBH respectively) were used to provide supporting wind data (also collected using 10 m high wind masts). The latter data were provided as 1 minute values and were compared with the Tesoro site data. In addition, 4 meteorological sondes were launched. The normally accepted height for wind measurements is at least at tank height or higher, since the fugitive emissions downwind a refinery are typically distributed from ground up to 200 m and since the wind field is rather disturbed at below tank height. The wind speeds used in this study are possibly too low, yielding conservative emission figures.

Figure 7 Sounding of the wind height profile by launching a weather balloon (I-met) during the campaign. The balloon drifts with the wind and sends its position measured with a GPS to a receiver.

Figures A7.1 and A7.2 in the Appendix compare the wind data measured at the Tesoro refinery with that collected at the South Long Beach (SLBH) and Hudson (HDSN) stations. The wind speed at Tesoro is approximately 30% higher than that at Hudson. There is also a slightly directional offset, with Tesoro being around 15 degrees less than HDSN. There is no apparent offset in either speed or direction between SLBH and HDSN.

Measured winds were also compared to data obtained from a number of meteorological GPS radiosondes launched from an open location nearby the Tesoro Carson refinery, Figure 7 and 8. These sondes were used to determine instantaneous vertical wind profiles as well as boundary layer heights. A comparison between the sondes and mast measured winds is shown in Figure 9.

Because the location of the Tesoro wind measurements more closely approximates the location of the plume emitted by the refinery, the wind directions measured at the Tesoro plant, corrected for the observed directional offset (15 degrees), were used to calculate fluxes for the two Carson refineries and the Phillips66 Wilmington plant. The Tesoro wind data was not suitable to determine the emission fluxes at the ExxonMobil refinery in Torrance and a fixed wind data recorded at the Torrance Airport (2.6 m/s, 240 degrees plume determined) was used instead.

Because of the short duration of this study and also because wind data was mostly provided by a third party, FluxSense cannot guarantee the accuracy of the wind data nor that the reported wind measurements accurately represent the speed and direction of the measured emission plumes.

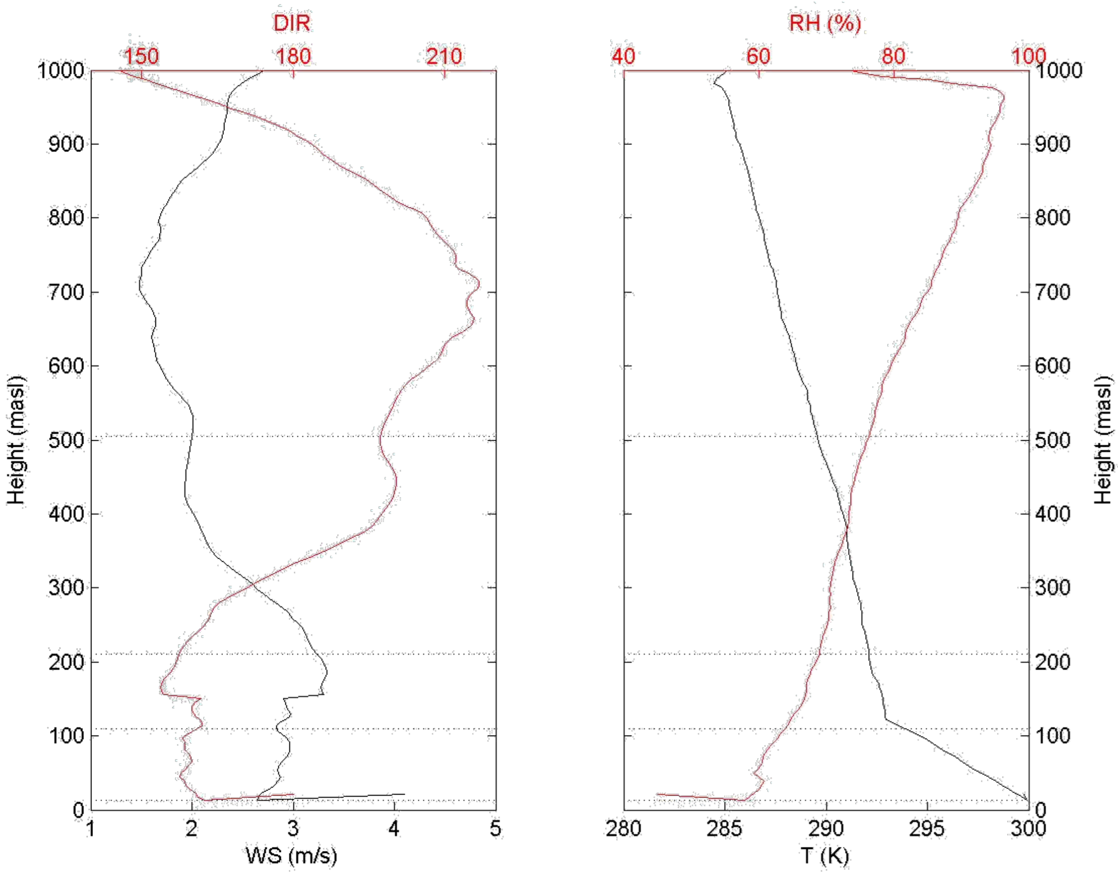


Figure 8 Wind, temperature and relative humidity profiles from radiosonde on 8 October, 13:38.

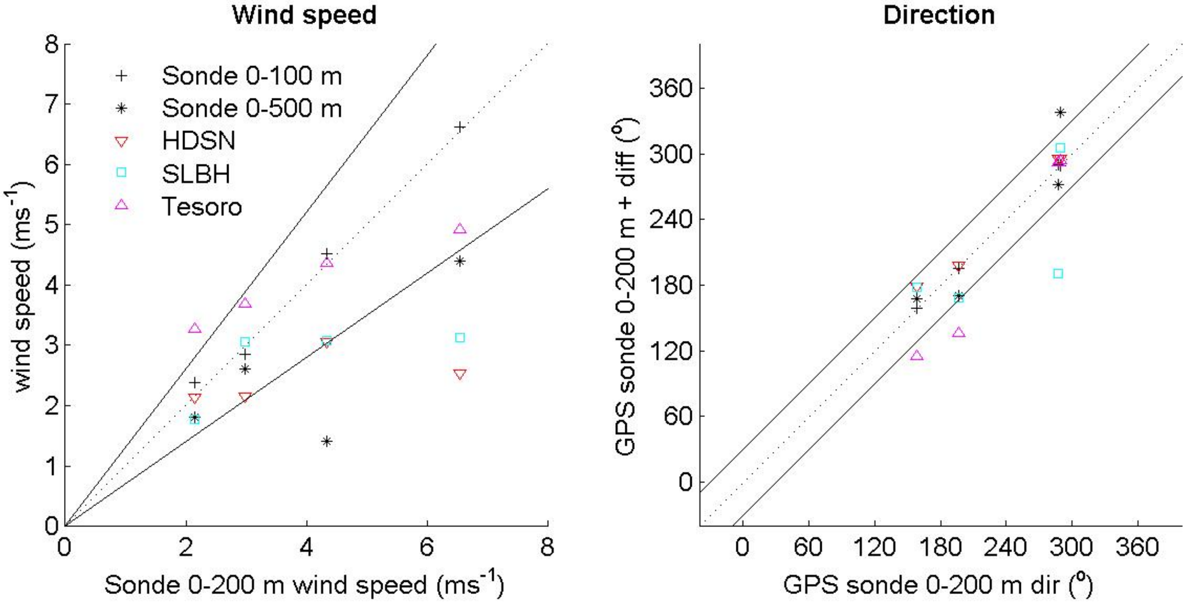


Figure 9 Comparison among vertically average winds and ground based measurements in and around. For wind speed solid lines indicate ± 30% of the 1:1 line (dashed) and for wind direction the solid lines represent ± 30° of the 1:1 line (dashed).

4. Results

Results are presented by area, with primary focus on the two refineries in Carson (i.e. Tesoro and Phillips66). Additionally a few measurements conducted in Wilmington and Torrance (at the Phillips66 and ExxonMobil refinery, respectively) are presented.

4.1 Large scale measurements

Large scale measurements were carried out to investigate the major sources of VOC emissions in the study areas. These measurements, together with the wind soundings and trajectory modeling show that the flow patterns in the Carson area were rather complex with sea breeze circulation occasionally causing reversed flow direction during the middle of the day.

For instance, on October 16 at noon the wind turned from a northerly to a southerly direction during the measurements. Polluted air drifted back and we saw very high columns of VOCs, NO_2 and HCHO while measuring. This is shown in Figure 10 for two times, 10:30 am and 1:30 pm local time on October 16. The same figure shows data from the HYSPLIT dispersion model as contours (Draxler and Rolph 2013) and the SOF data, as blue curves. The simulated source was located on Tesoro.

Another example of a large-scale measurement is shown in Figure 11. This measurement was conducted on October 12 and began by ExxonMobil in Torrance and took approximately 50 minutes to complete.

All in all these measurements shows that flow patterns can be complex in the Carson area and that it is important to carry out measurements both upwind and downwind of the refineries (box measurements).

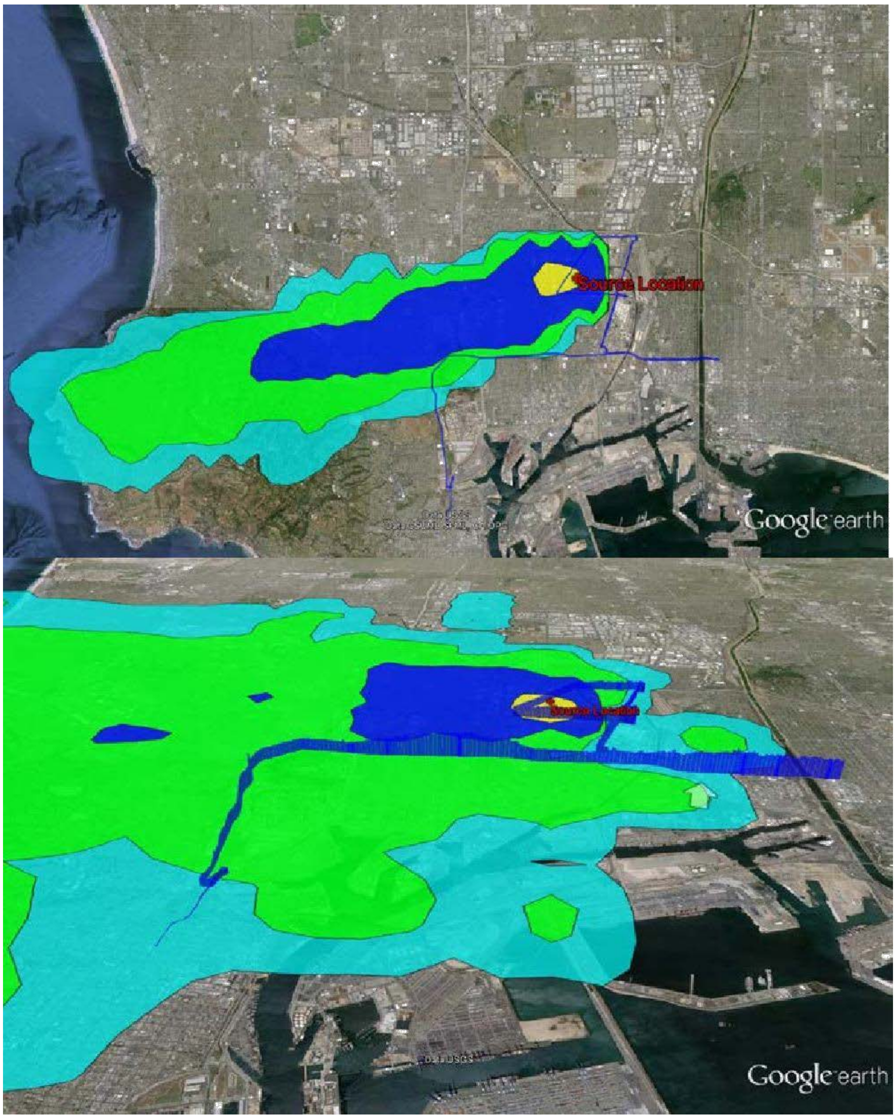


Figure 10 HYSPLIT dispersion model results (contours) for source located in Carson between 10:30 am and 13:30, on October 16, 2013. Also shown are SOF alkane measurements (blue curves). North is towards the top of the figure.

Figure 11 Large scale measurement of Carson-Wilmington-Torrance performed on October 12, 2013 along with smaller box measurements around the Carson refineries. North is towards the right of the figure

4.2 Emissions from refineries and storage facilities in Carson

4.2.1 Tesoro

The main focus of this study was to carry out fugitive emission measurements from the Carson refinery (former BP), which is the refinery with the highest throughput in the Los Angeles Basin, with a capacity of 265 thousand barrels per day (265 kBPD). Measurements were taken for ten days with a variety of winds. A typical box measurement taken on October 8 with easterly winds is shown in Figure 12. In this case the inflow of VOCs is rather insignificant. Total emissions for Tesoro on this traverse were 112 kg/h. Also seen in the Figure is the one recurring 'hot spot' in the southwest corner of the facility. Figure 13 shows a box measurement with westerly winds and almost insignificant inflow. Results for these measurements are summarized in Table 2. Alkane emissions averaged 204 kg/h over the 10 days and 40 plus measurements performed. A histogram of all measurements is shown in Figure 14.

Figure 12 SOF 'box' measurement of the Tesoro Carson refinery on October 8 at 11:55 am. The shaded area in brown delineates the refinery area while measurements encompass a slightly larger area. Alkane column is shown as a blue curve with the apparent height being proportional to the gas column (5 m equivalent to 1 mg/m^2, max 160 mg/m^2). Wind directions during the measurement are indicated by white arrows. North is to the upper right of the figure.

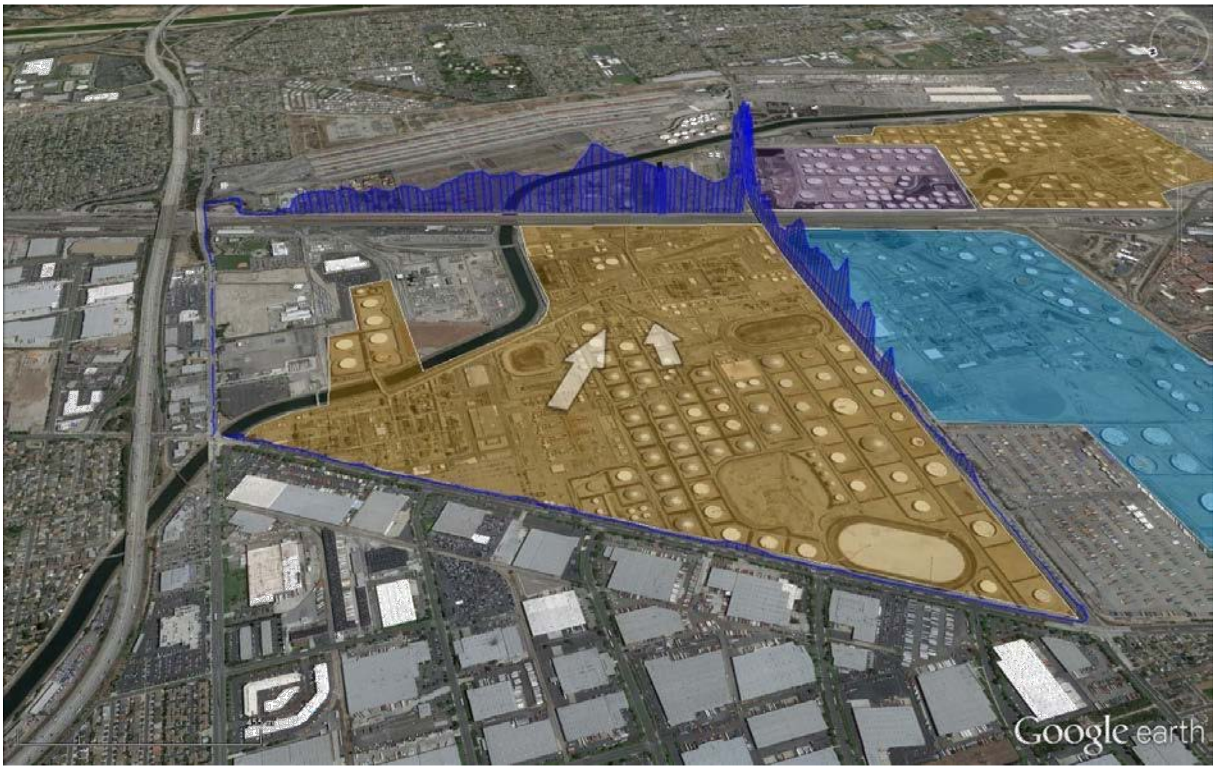


Figure 13 SOF box measurement of the Tesoro Carson refinery on October 7, at 13:55. Alkane column is shown as a blue curve with the apparent height being proportional to the gas column (5 m equivalent to 1 mg/m^2, max 81 mg/m^2). Wind directions during the measurement are indicated by white arrows. North is to the lower left of the figure.

Table 2 Summary of SOF alkane measurements of Tesoro Carson

Date (mm/dd)	Time Span Start-stop (hhmmss)	Number of Measurements	Alkane Emission±SD (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
10/05	102720 -144904	5	155.8±63.7	1.9-6.4	40-93
10/06	104136 -162424	9	174.4±55.7	1.8-3.9	1-359
10/07	141759 -162318	5	287.3±60.6	4.1-5.7	285-320
10/08	112251 -155724	9	165.8±64.1	1.8-3.3	92-196
10/10	155539 -160356	1	78.7	3.8	195
10/11	132146 -155251	5	257.5±75.1	4.5-5.4	285-311
10/13	150959 -154650	2	175.1±7.6	2.5-2.6	174-179
10/14	111503 -145422	5	285.6±124.5	3.3-4.5	289-332
10/15	154739 -163124	2	162.5±67.2	4.1-4.5	297-300
10/16	141205 -151008	3	210.1±93.6	2.3-4.5	262-309
Average	**-**	**(total 46)**	**204±86 (42%)**	**3.6**	**-**

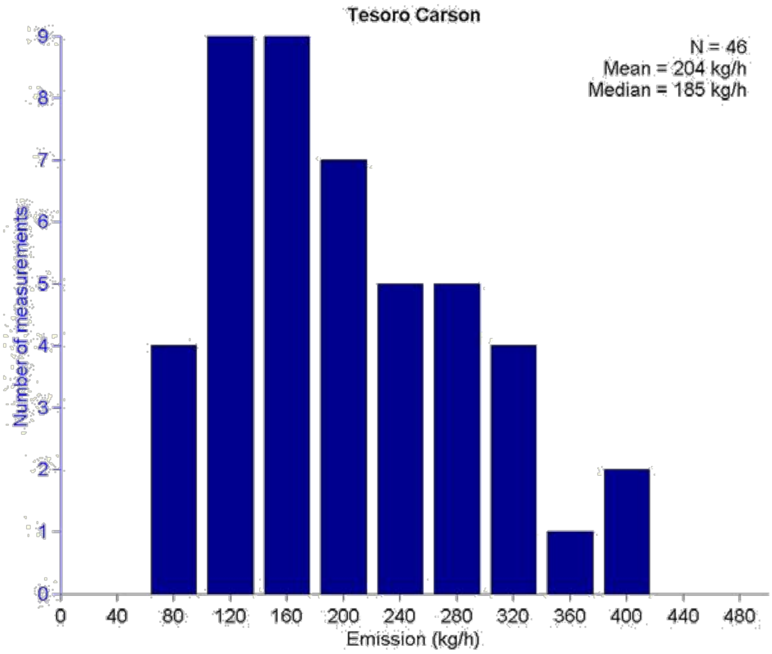


Figure 14 Histogram of SOF measurements.

Quantifying SO_2 and NO_2 emissions from these facilities during the same measurement period is more uncertain due to the shifting of winds with height and the lack of measured vertical wind profiles. As these plumes are from combustion sources and presumably stack releases, the plumes are expected to be at a higher altitude than the VOC plume when measuring near the facility in nearly all the measurements. An example of a measurement from the area is shown in Figure 15. Summaries of DOAS emission measurements are presented in Table 3 and Table 4. Similarly to the alkane measurements, emissions are determined using wind data from the Tesoro refinery except when a sonde launch was made within the hour. Typically, baselines were corrected for background emissions (e.g. from motor-vehicles and other sources for NO_2) thus setting inflow to zero. NO_2 emissions are also affected by plume travel time since source NO is rapidly converted to NO_2 when reacting with ozone. Thus emissions may vary based on the wind speed and distance between the measurement and the source, a distance which is dependent on the wind direction. Emissions averaged approximately 40 kg/h for both NO_2 and SO_2.

Figure 15 DOAS box measurements at Tesoro showing the NO_2 (brown) and SO_2 (pink) plumes. These measurements were taken on October 7, at 13:30. North is to the lower left of the figure.

Table 3 Summary of Tesoro NO_2 measurements

Date (mm/dd)	Time Span Start-stop (hhmmss)	Number of traverses	Emission±SD (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
10/06	120831 -160326	5	38.5±11.3	1.8-2.9	36-356
10/07	141736 -161746	5	55.4±11.9	4.1-5.8	292-317
10/11	161003 -161121	1	18.4	4.9	292
10/12	145254 -145431	1	26.7	3.5	311
10/14	125938 -163027	4	29.0±7.4	4.1-5.3	301-317
10/16	145837 -163738	4	37.5±11.7	2.1-4.9	2-298
Average	**-**	**(total 20)**	**39.0±14.5 (37 %)**	**3.6**	**-**

Table 4 Summary of Tesoro SO_2 measurements

Date (mm/dd)	Time Span Start-stop (hhmmss)	Number of traverses	Emission±SD (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
10/05	115132 -145148	4	29.7±8.0	1.9-5.1	79-92
10/06	104205 -141606	6	26.5±4.0	1.8-3.6	8-360
10/07	135921 -153512	6	72.4±36.0	4.0-5.1	292-320
10/11	132232 -145346	4	38.5±17.0	4.5-4.9	287-311
10/14	105135 -161213	6	36.7±9.6	3.1-4.6	295-332
10/15	124745 -132215	2	35.8±1.9	1.8-1.8	28-347
10/16	145837 -163738	4	28.1±7.5	2.1-4.9	2-298
Average	**-**	**(total 33)**	**40±23 (58 %)**	**3.4**	**-**

4.2.2 Phillips 66

The Phillips 66 Refinery in Carson is located just south of the Tesoro refinery and has a capacity of 50 kBPD. This site was frequently measured in combination with the adjacent Tesoro facility, see Figure 16. However, due to the proximity of the Kinder Morgan tank farm and the Tesoro Wilmington facility located east of the Phillips 66 refinery, there is an increased possibility of interference depending on wind direction, and thus there were fewer acceptable emissions measurements. Additionally, no on-site wind measurements were available so all emissions are determined using Tesoro wind or sondes. One of the measurements on October 8 is shown in Figure 16, corresponding to an average VOC emission of 68 kg/h. A summary of all measurements is presented in Table 5.

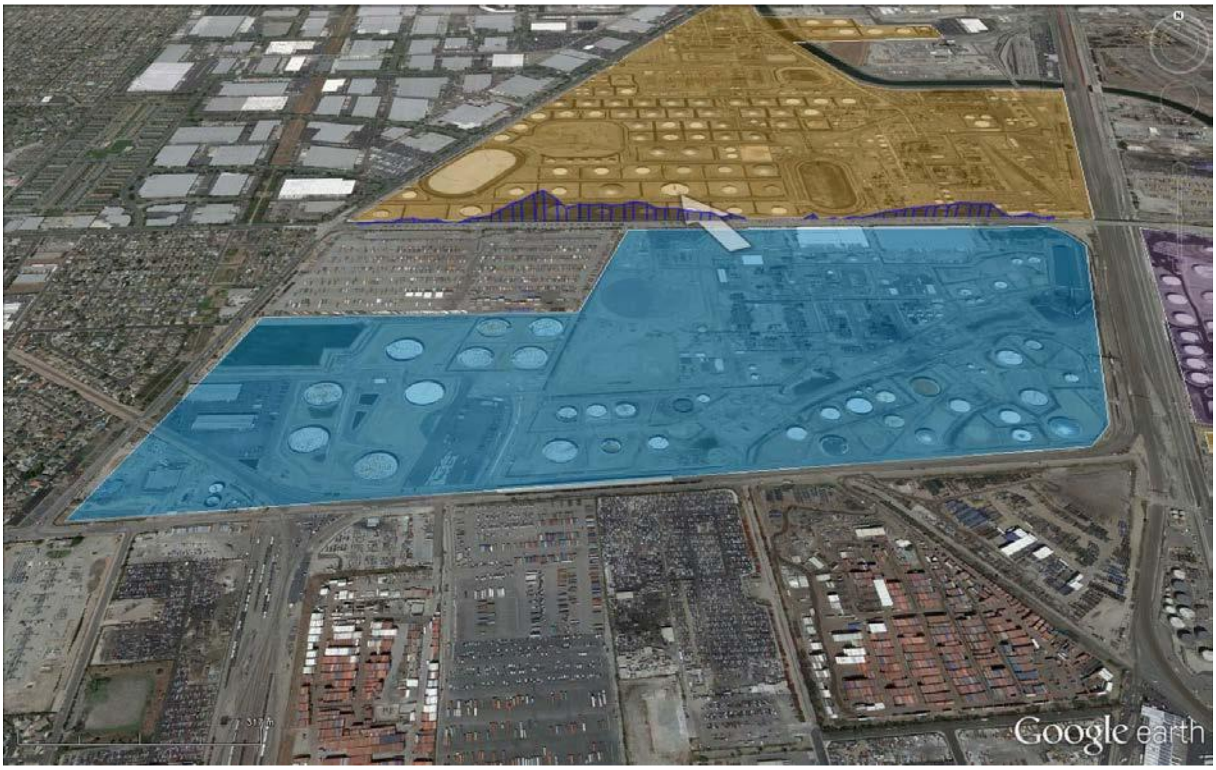


Figure 16 Example of SOF measurements at the Phillips66 Carson refinery (blue shading) on October 8 at about 14:30. The alkane column is shown as a blue curve with the apparent height proportional to the gas column (5 m equivalent to 1 mg/m^2, max 24 mg/m^2). Wind direction during these measurements is indicated by a white arrow. North is to the top of the figure.

Table 5 Summary of SOF alkane measurements of Phillips Carson

Date (mm/dd)	Timespan Start-stop (hhmmss)	Number of Measurements	Emission±SD (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
10/08	111912 -145227	4	62.8±10.2	2.4-3.0	117-196
10/10	155152 -155532	1	101.4	3.3	194
10/11	132402 -163308	4	121.5±15.0	4.1-4.5	294-311
10/16	140857 -141033	1	100.7	3.4	308
Average	-	**(total 10)**	**94±30 (32%)**	**3.5**	-

Emissions of NO_2 and SO_2 from Phillips were also measured on several days. Figure 17 shows one transect measured on October 15. All other measurement data are summarized in Table 6 and Table 7.

Figure 17 DOAS measurements taken at the Phillips refinery showing NO_2 (brown) and SO_2 (pink) emissions plumes (October 15, 16:10). North is to the upper left of the figure.

Table 6 Summary of NO_2 measurements taken at the Phillips 66 refinery in Carson

Date (mm/dd)	Timespan Start-stop (hhmmss)	Number of Measurements	Emission±SD (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
10/07	154748 -154853	1	35.7	5.7	311
10/08	111829 -123259	4	25.1±11.0	1.8-2.8	118-199
10/11	141004 -161303	2	20.0±6.0	3.1-4.9	291-292
10/13	150620 -150715	1	13.3	3.2	158
10/14	122544 -163138	6	20.1±6.2	3.4-5.4	300-327
10/15	160708 -172323	2	27.6±9.8	3.6-5.6	293-296
10/16	155901 -160218	2	8.9±4.8	1.9-2.0	242-250
Average	**-**	**(total 18)**	**21.0±9.0 (43 %)**	**-**	**-**

Table 7 Summary of Phillips SO_2 measurements

Date (mm/dd)	Timespan Start-stop (hhmmss)	Number of Measurements	Emission±SD (kg/h)	Wind Speed (m/s)	Wind Dir (deg)
10/07	153527 -154837	2	43.1±17.2	5.5-5.7	311-317
10/08	111829 -123323	4	24.1±14.2	1.5-2.8	118-199
10/11	132416 -141102	2	36.7±5.2	4.1-4.6	301-311
10/13	135043 -150717	3	26.2±8.7	3.2-4.4	138-158
10/14	105332 -160910	5	32.5±13.4	2.8-5.4	307-328
10/15	161055 -161141	1	40.3	3.8	296
10/16	155901 -160218	2	17.9±5.1	1.9-2.0	242-250
Average	**-**	**(total 19)**	**30.2±12.6 (42 %)**	**3.7**	**-**

In addition to the measurements taken at the Tesoro and Phillips66 facilities, upwind measurement allowed for the assessment of emissions from other facilities in the area including Tesoro Wilmington and Kinder Morgan (Figure 18) and a tank farm to the north of Tesoro (Figure 19).

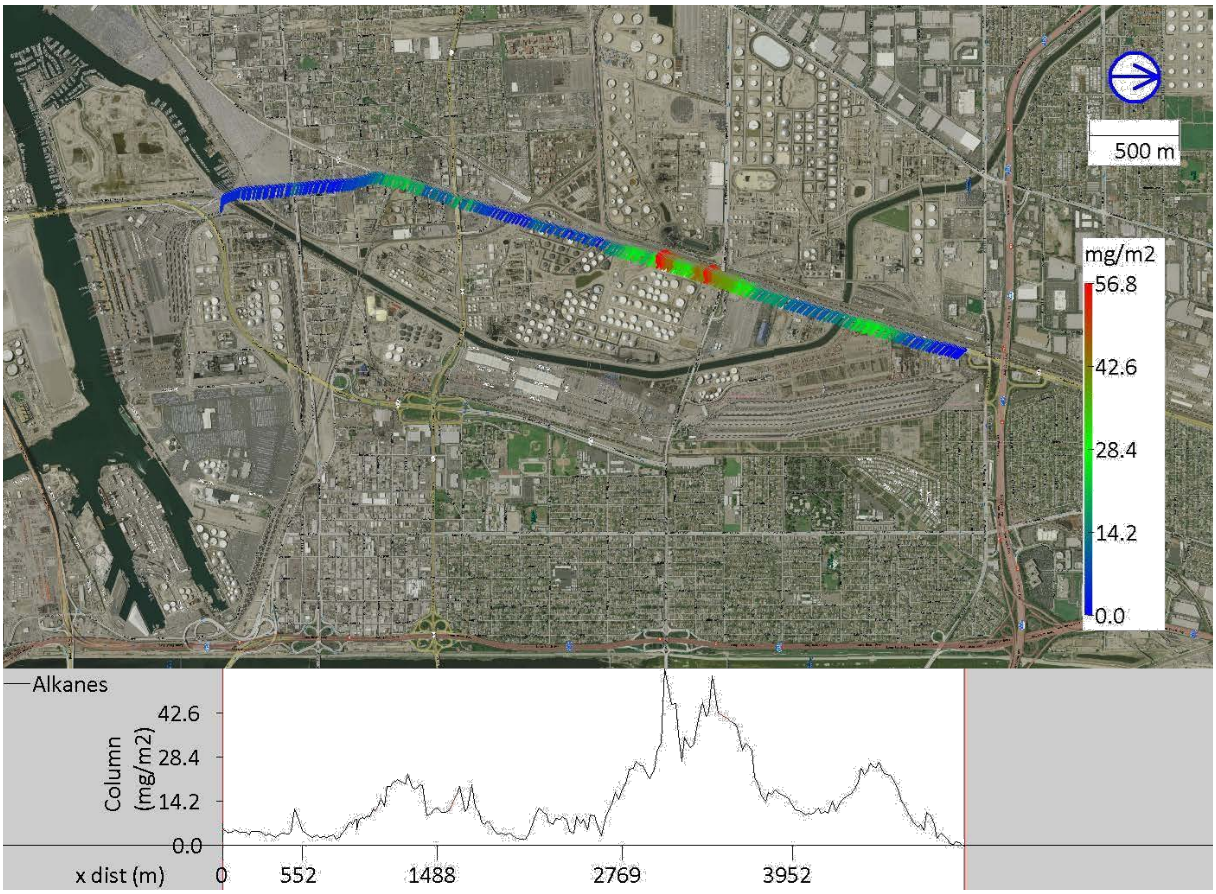


Figure 18 SOF measurements showing plumes from facilities to the east of Alameda Street. Color scale and point size correspond to the plot below the image and indicate alkane column in mg/m^2. The lines point against the wind, i.e. towards the source of the VOC emissions.. In this case HDSN wind is shown. North is to the right in the image.

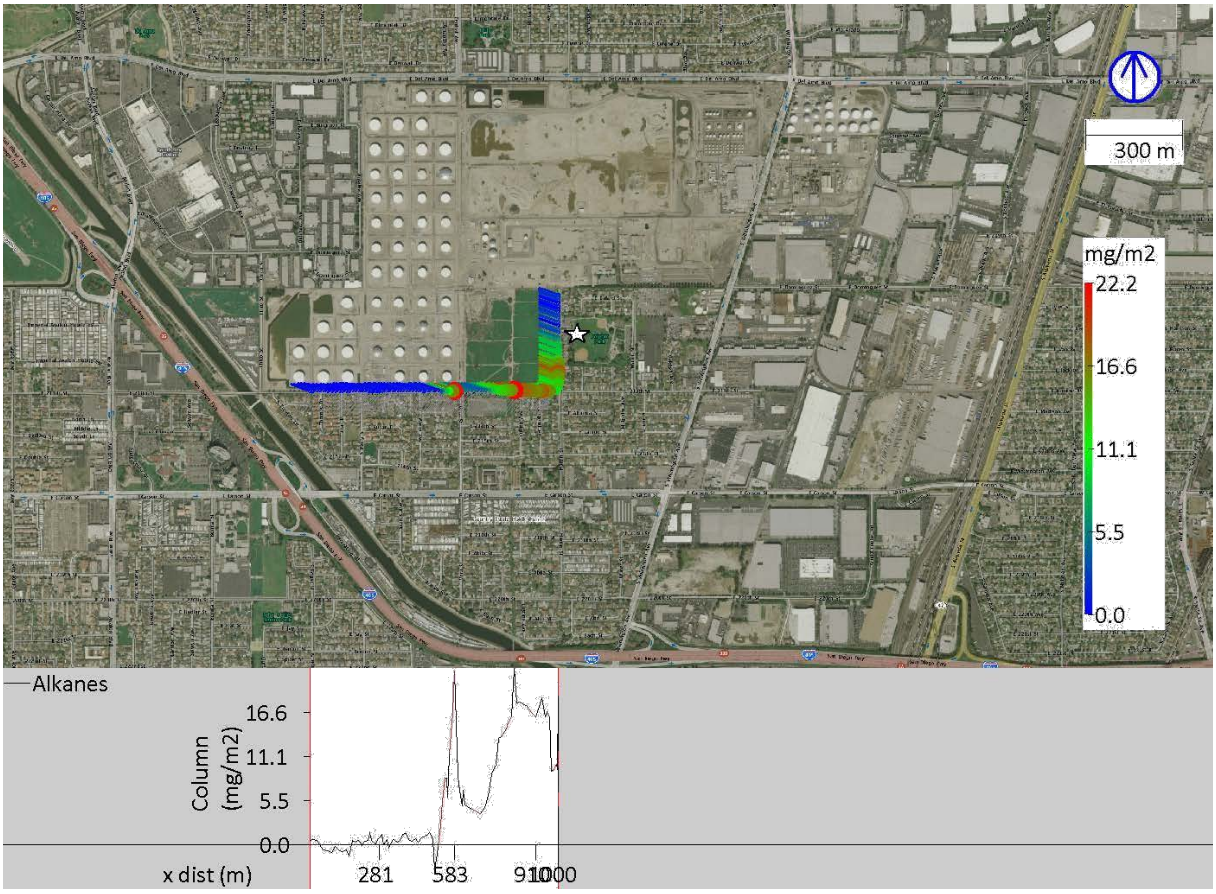


Figure 19 Measurements taken near the tank farm (Shell) to the north of Tesoro (October 14, 14:20). Color scale and point size correspond to the plot below the image and indicate the alkane column in mg/m^2. The lines point against the wind, i.e. towards the source of the VOC emissions.. The wind used was from GPS sonde launched in park just to the right of the measurement (white star).

4.3 Other Areas

During the campaign a few SOF measurements were also carried out at other facilities. However, since no nearby wind measurements were available outside of the Carson area, the following results are only indicative and are based on wind measurements from the Tesoro wind mast and from the two SCAQMD wind stations.

4.3.1 ExxonMobil Torrance

SOF measurements at ExxonMobil were conducted on one Date (mm/dd) with weak west-south-westerly winds. Measurements were conducted of both the total facility and isolating the western portion, indicating VOC emissions of around 100 kg/h for four transect scans, when using wind measurements from Carson. Examples of measurements are shown in Figure 20.

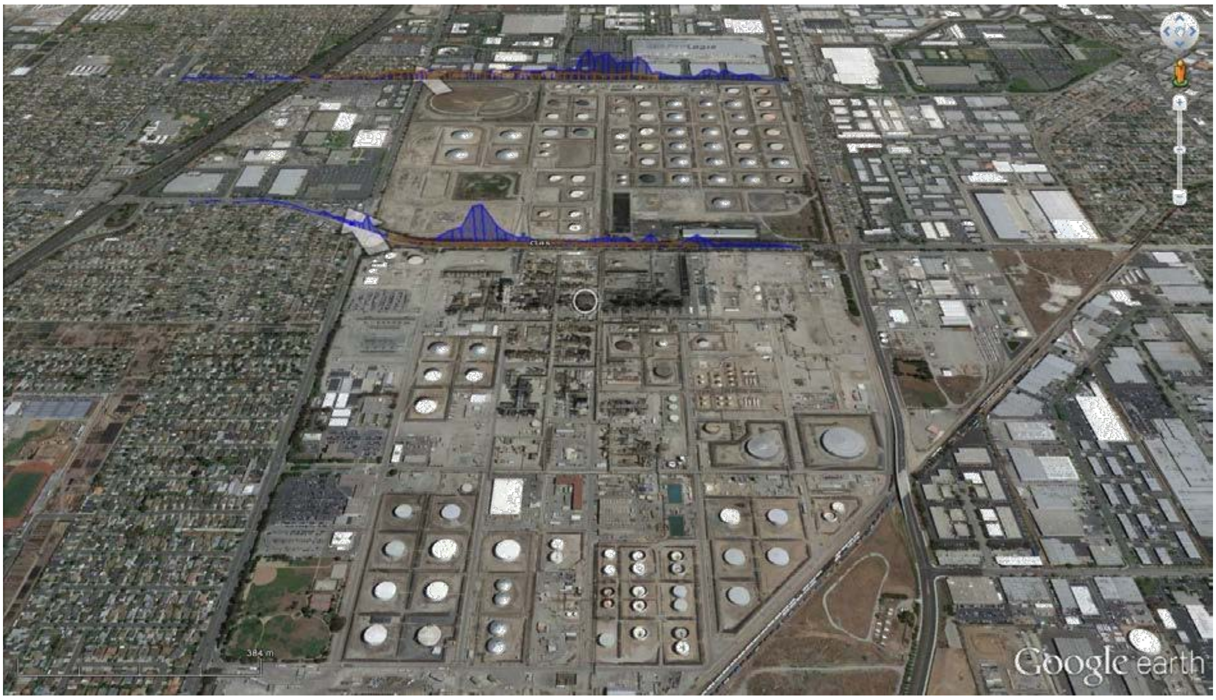


Figure 20 SOF and DOAS measurements made at the Exxon Torrance plant showing alkane (blue) and NO_2 (brown) plumes (October 12, 13:20). North is to the left in the image.

4.3.2 Phillips 66 Willmington

Emissions from the Phillips 66 Wilmington facility were measured more frequently, on three separate days in total (an example is shown in Figure 21). The results indicate VOC emissions of around 170 kg/h, estimated using wind data from the Tesoro Carson wind site.

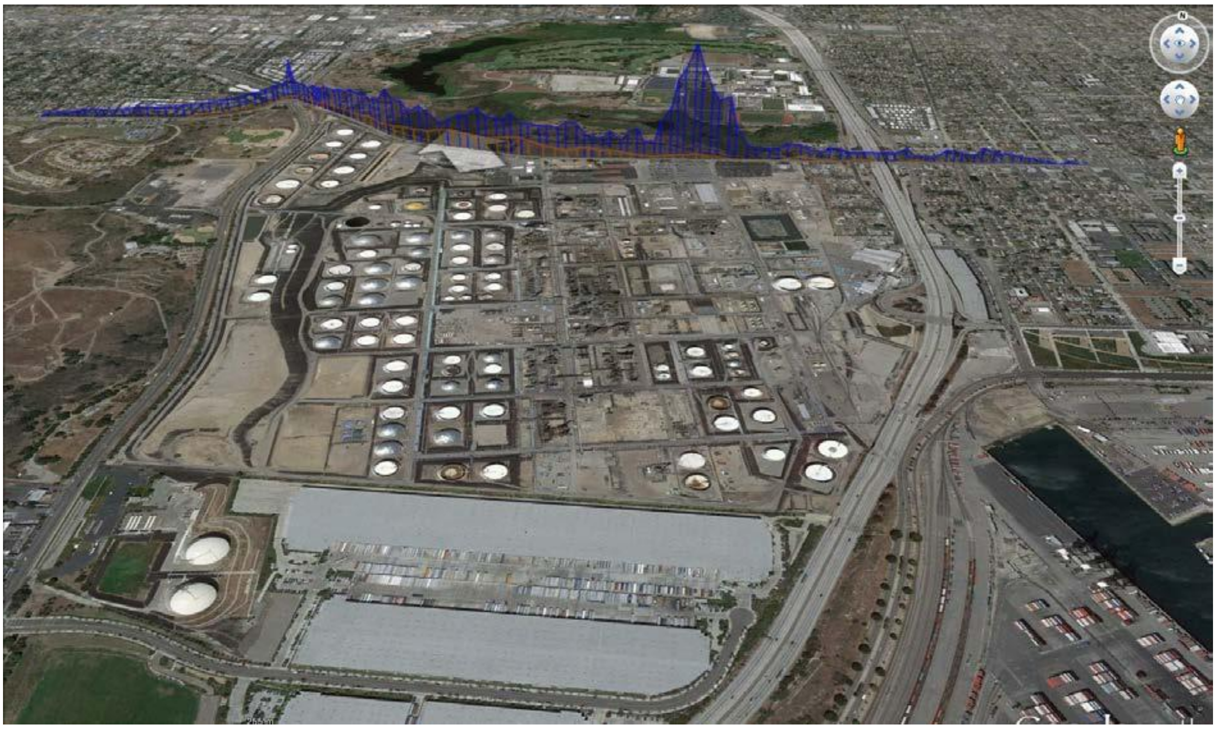


Figure 21 SOF and DOAS measurements of Phillips 66 Wilmington showing alkane (blue) and NO2 (brown) plumes (October 10, 12:50 pm). North is to the top in the image

4.4. Aromatic emissions

The ratio of the concentration of benzene or toluene to the total alkane concentration can be used in combination with alkane flux measurements to estimate the aromatic emissions for a given site. The ratio of aromatics (e.g. benzene and toluene) to the total concentration of non-methane alkanes was measured on several evenings during the study. Aromatic concentrations of several species were directly measured using the MW-DOAS system. The MeFTIR technique was used to quantify the level of alkanes.

In order to get an accurate measurement it is important to avoid the short peak concentrations (> 15 ppb) of ground based point sources, which would not give a fair ratio compared to the flux measured using the SOF method. Aromatics originating from car exhausts (from the measurement vehicle and in particular the generator, and other traffic sources) must also be avoided. Care has been taken to remove these sources of error when calculating the total out flux from the chosen sites.

4.4.1 Tesoro plant

The Tesoro site was considered for the purpose of this report due to the availability of data from SOF measurements and the possibility of fence- line measurements. Concentrations of alkanes and several aromatic species were measured downwind of the facility on several transects. The upwind perimeter of the plant was also measured to control for possible inflow of gases. Measurements were made during two evenings, October 12 and 13. The wind was from a north-westerly direction and the highest concentrations were measured close to the storage tanks in the southern part of the facility. An example is shown in Figure 22.

Presumably (at least partly due to low wind speed) the levels of aromatics here were high, well above 10 ppb, yet still judged to be representative for the aromatic/alkane mixing found in plumes measured by SOF flux measurements.. The possible inflow of both aromatics and alkanes was measured upwind from the region which resulted in a lowering of the toluene value by 25 %. This adjustment has a larger inherent uncertainty as the levels and the statistics were low. The results from Tesoro facility are presented in Table 8.

Table 8. The results of the aromatic/alkane ratio measurements at the Tesoro plant, 12 and 13 October.

Gas	Ratio % of Alkane	SOF Alkane emissions (kg/h)	Inferred Aromatic emissions (kg/h)
Benzene	1.2 %	204	2.5 (± 50 %)
Toluene	3.7%	204	7.5 (± 50 %)

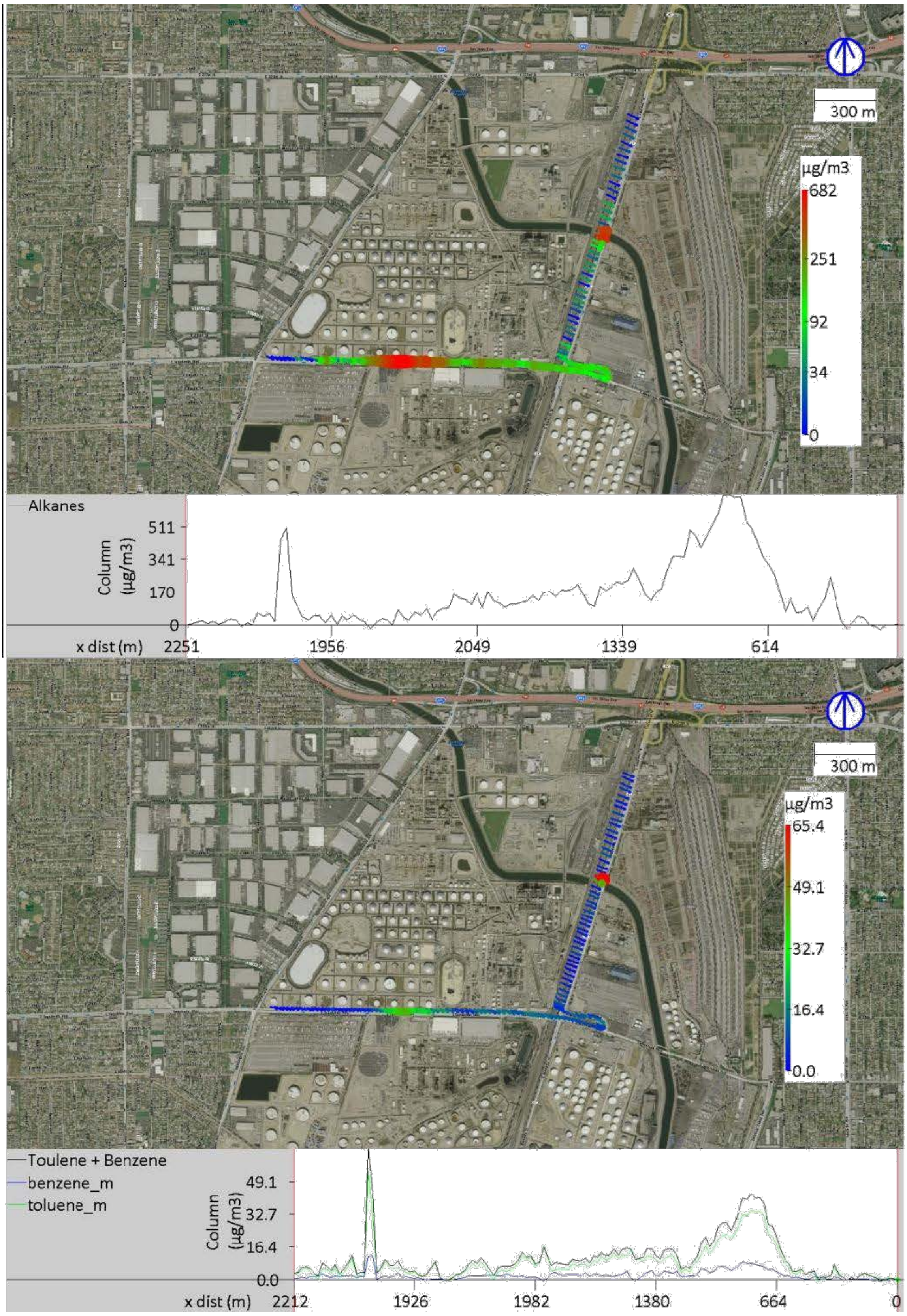


Figure 22 Mobile measurements of the ground concentration of alkanes (upper) and aromatics (lower) downwind of the Tesoro plant in Carson, obtained with MeFTIR and MW-DOAS, respectively (October 13, 19:25).

4.4.2 Oil wells

Mobile concentration measurements of aromatic VOCs and alkanes downwind of oil wells in Signal Hill, Figure 23, were measured by MeFTIR and MW-DOAS, to demonstrate and test the capabilities of these two extractive measurements. The errors are lower for this measurement since the plumes are more local and have higher concentration, making the baseline positioning both easier and less sensitive.

The results are illustrated in Figure 24 and Figure 25, and show that the most abundant gas species in the emission plume from the oil well is butane (about 1000 µg/m3) and that the mass fraction of benzene and toluene to alkanes is 0.7 % and 1.5 %, respectively. The objective was also to quantify the alkane emission from this well by SOF, but since we prioritized measurements in Carson the sun got too low before the measurements could be carried out. However, given the large number of such wells we believe it could be very interesting to estimate the emissions from these sources in the Los Angeles Basin.

Figure 23 Oil well in Signal Hill

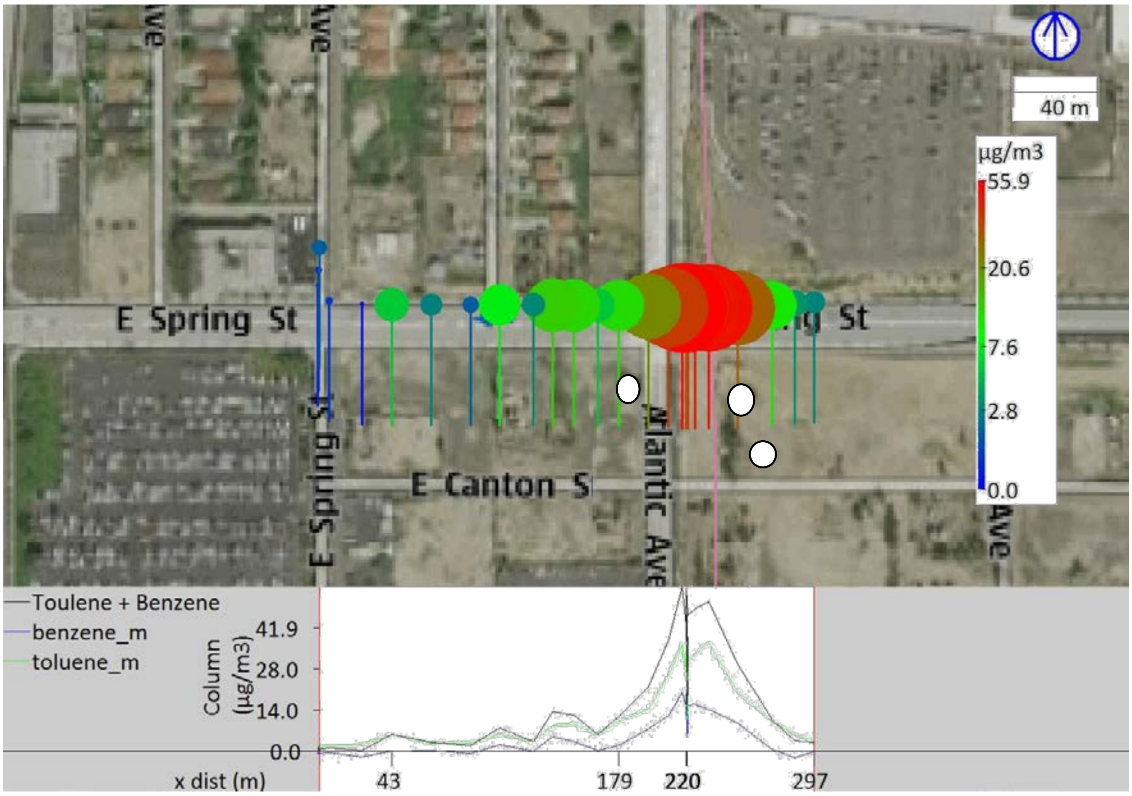


Figure 24 Concentration measurements of aromatic VOCs downwind an oil well in Signal Hill (measurements were conducted on October 13, at 6 pm). The locations of the closest wells are indicated with white circles, (33°48' 40.73'', 118° 11' 06.79'').

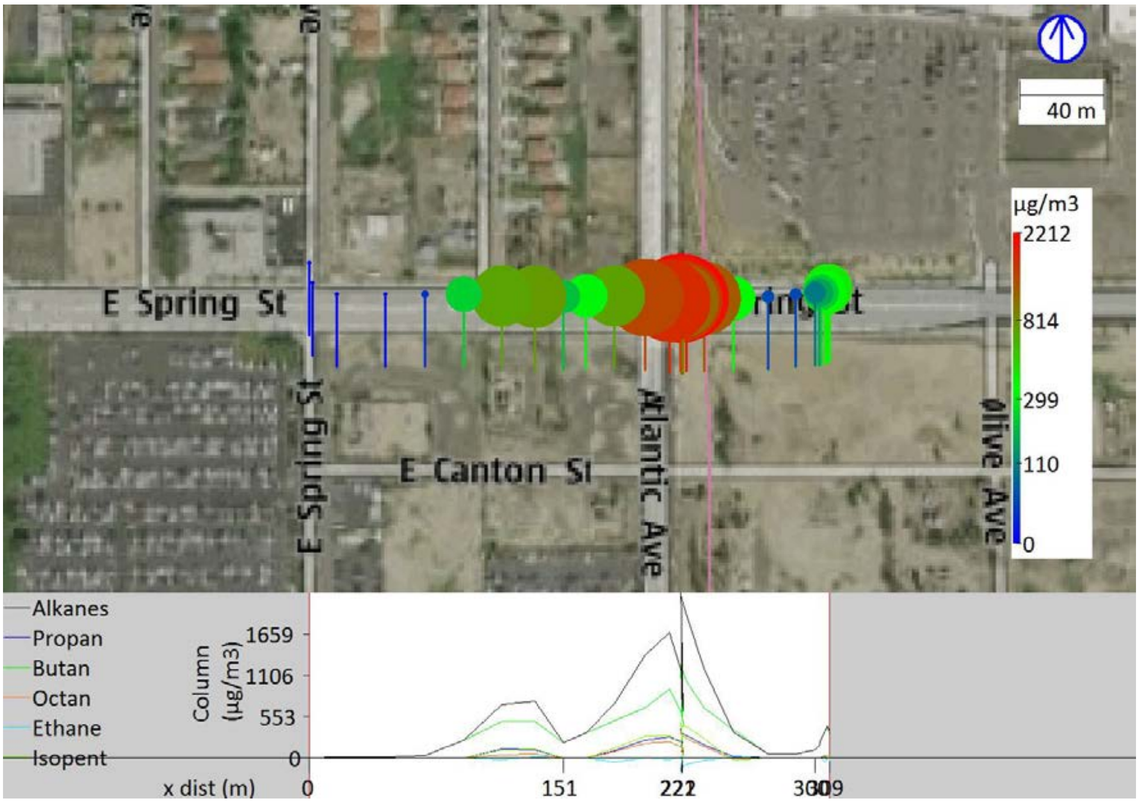


Figure 25 Concentration measurements of alkanes downwind an oil well in Signal Hill (measurements were conducted on October 13, at 6 pm).

5. Discussion and conclusion

The main scope of this work was to demonstrate that optical column measurements can be used to quantify fugitive emissions from refineries of the South Coast Air Basin and to investigate whether these measurements indicate large discrepancies from the reported values based on emission inventories, as observed previous in studies conducted in other part of the United States and abroad (Mellqvist, 2009).

In Table 9 VOC, SO_2, and NO_2 emissions measured over a period of about 10 days are shown for the various study sites. Note that the main focus of our measurements was the Tesoro refinery in Carson, and only limited emission data were collected at the refineries in Wilmington and Torrance, where no detailed wind information was available. Therefore, the emissions estimated at the latter two facilities (100 and 170 kg/h for the Wilmington and Torrance refineries, respectively) are only indicative and are probably affected by high uncertainty. For comparison with the measurements and among sites, the reported annual emissions are shown as hourly figures and as a percent of capacity. It should be noted that the reported emissions are based on annual average values and may not be representative of emissions measured over a shorter timeframe. In addition because SOF measurements can only be made during daylight hours there may be a slight bias in measured VOC emissions. According to a recent study (Johansson 2013b) based on the TANKS model, developed by the US API and EPA, an upper estimate of the effects is 30-40% maximum overestimation in the emissions for an external floating roof EFRT crude oil tank (Mellqvist 2009a), compared to the annual average.

For the facilities examined in this study, measured VOC emission rates were greater than rates derived from the reported annual emissions. This result is not surprising and in some regards may be considered positive. Measured fugitive VOC emissions are often a factor 4 to 10 times higher than reported emissions (Mellqvist 2009a, Johansson 2014). Additionally, measured as a percent of throughput or capacity, VOC emissions are generally at least 0.05% of throughput and often much more (Cuclis 2012). In the current study all facilities are below this level.

Although measured VOC emissions at the Tesoro Carson refinery were 3.5 times higher than reported, this can still be considered as a well maintained site since emissions are only 0.013 % of capacity. Phillips66 Carson, on the basis of fewer measurements and, therefore, less certain statistics had much higher emissions than reported, but even here fugitive VOC emissions were only 0.033 % of capacity, which is a relatively low value with respect to the majority of facilities studied in North America and Europe.

For SO_2 and NO_x the reported emissions were in closer agreement with measured emissions i.e. within 30 % agreement for SO_2 while within 40 % when comparing the measured NO_2 with reported NO_x, consistent with studies elsewhere (Johansson, 2014). The latter discrepancy is expected since the measurements are carried out in proximity of the emission sources and the fact that NO_x is released primarily as NO which is then converted to NO_2 through reaction with ozone.

It is difficult to assess the total uncertainty of the measured emissions due to the complex wind patterns, sea breeze circulation and limited wind measurement sites. Even though these effects were detected and corrected for by measuring in a box around the sites, subtracting downwind and upwind fluxes, the uncertainty increases, especially for weak sources that may become hidden in the high background signals. The typical uncertainty is 30% for the optical column measurements (see Appendix I) but in this case we estimate higher uncertainties, 40-50%.. We recommend that future campaigns include more detailed wind data with additional mast measurements and, if possible, continuous wind profiling (e.g. using IR LIDAR). Overall, these results demonstrate that the SOF method is a suitable remote sensing method for validating refinery emissions and for identifying hot spot locations.

Table 9 Comparison of reported and measured emissions from selected facilities.

	VOC				SO_2		NOx	NO_2
	Reported*		Measured		Reported*	Measured	Reported*	Measured
Site	kg/h	% capacity	kg/h	% capacity	kg/h	kg/h	kg/h	kg/h
Tesoro Carson	51	0.003%	204 (±32 %)	0.013%	43	40 (±58 %)	67	39 (±37 %)
Phillips66 Carson	12	0.004%	94 (±32 %)	0.033%	22	30 (±42 %)	34	21 (±43 %)
Phillips66 Wilmington	27	0.005%						
ExxonMobil Torrance	64	0.007%						

*Data from SCAQMD 2012

The measurements carried out here indicate that the emissions from the South coast refineries are within the expected range when relating to throughput. But there is a significant difference between actual and reported emissions, indicating that the conventional API method of estimating the emissions does not provide reliable values. The problem with under estimation of fugitive emissions by the API model has been admitted publicly by the US EPA on several occasions in the press (Washington post, April 22, 2010) and they claim they are working to resolve this issue.

We believe that the results demonstrate the value of carrying out measurements instead of relying on estimation methods only. In the estimation methods the fugitive emissions from tanks are estimated using the API-model under the assumption that tanks are leak free (well maintained) and to our experience, running measurements elsewhere, this is seldom the case for a whole tank farm. Since the emissions from non-ideal tanks with distinct leakages often are one to several orders of magnitude higher than the modeled leakage rate through the tank sealing, a few malfunctioning tanks will easily increase the total emissions from a tank farm by an order of magnitude.

The SOF measurements demonstrated here can rapidly identify the relevant leaking tanks in a tank farm and then optical gas imaging cameras can be used to find the leakage points, (super smart LDAR). Other source areas for fugitive emissions which are difficult to estimate and instead should be measured are: anomalous emissions from process areas (especially after maintenance stops), flares, loading operations, tank cleaning and drainage operation and water treatment areas.

The observed difference in fugitive VOC emissions between measurements and estimates appears to be a general problem for the industry worldwide, and if one would adopt the, in general, higher measured values (factor 3-5) this would create legislative problems for the industry, for instance with permitting and potential liability issues. To avoid this, measurements and estimates could be done in parallel where the former are used for the official reporting while the latter is done as part of the proactive environmental work aimed at reducing the emissions at the site. If this is carried out for a couple of years, followed by abatement work at the dominant hotspot emissions for an industrial site, combined with adaptive improvements of the emission factors, the estimates and measurements may start to converge.

A significant value of carrying out measurements is the possibility to establish baseline emission for a site and its various subareas and by frequent (annual) measurements the trends can be followed and anomalous emissions can further be reacted upon by abatement measures.

6. Acknowledgements

This work was funded by the South Coast Air quality Management District (SCAQMD).

7. References

California Air Resources Board (CARB), 2009. Recommended Area Designations For The 2010 Federal Sulfur Dioxide (So2) Standard. California Environmental Protection Agency

De Gouw, J.A., et. al. (2009), Airborne Measurements of Ethene from Industrial Sources Using Laser Photo-Acoustic Spectroscopy, Environmental Science and Technology, 43, 2437–2442.

Draxler, R.R. and Rolph, G.D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD.

Etzkorn, T., B. Klotz, S. Sørensen, I.V. Patroescu, I. Barnes, K.H. Becker, and U. Platt, "Gas-phase absorption cross sections of 24 monocyclic aromatic hydrocarbons in the UV and IR spectral ranges," Atmos. Environ. 33, 525-540 (1999).

Fally, S., M. Carleer, and A. C. Vandaele, "UV Fourier transform absorption cross sections of benzene, toluene, meta-, ortho-, and para-xylene", J. Quant. Spectrosc. Radiat. Transfer 110, 766-782 (2009).

Fayt, C. and Van Roozendael, M., 2001. QDOAS 1.00 Software User Manual, BIRA-IASB.

Foy, B., ... Mellqvist, J., et al., Modeling constraints on the emission inventory and on vertical dispersion for CO and SO2 in the Mexico City Metropolitan Are using Solar FTIR and zenith sky UV spectroscopy, Atmos. Chem. Phys., 7, 781–801, 2007

Galle, B.; Mellqvist, J., et al., Ground Based FTIR Measurements of Stratospheric Trace Species from Harestua, Norway during Sesame and Comparison with a 3-D Model, JAC, 1999, 32, no. 1, 147–164.

Galle, B., J. Samuelsson, B.H. Svensson, G. Börjesson, "Measurements of methane emissions from landfills using a time correlation tracer method based on FTIR absorption spectroscopy." Environ. Sci. Technol. 35: 21–25. 2001.

Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A.J.S., Edmonds, M. and Horrocks, L., (2002), A miniaturised ultraviolet spectrometer for remote sensing of SO $_2$ fluxes: A new tool for volcano surveillance, Journal of Volcanology and Geothermal Research, 119 241–254

Heckel, A., A. Richter, T. Tarsu, F. Wittrock, C. Hak, I. Pundt, W. Junkermann, and J.P. Burrows, MAX-DOAS measurements of formaldehyde in the Po-Valley, Atmospheric Chemistry and Physics, 5, 909–918, 2005.

Johansson, M., C. et al, 2009, Mobile mini-DOAS measurement of the outflow of NO_2 and HCHO from Mexico City, Atmos. Chem. Phys., 9, 5647–5653

Johansson, J., et al., 2013a, Quantitative Measurements and Modeling of Industrial Formaldehyde Emissions in the Greater Houston Area during Campaigns in 2009 and 2011, accepted by Journal of Geophysical Research – Atmospheres, 2013JD020159R.

Johansson, J., et al., 2013b, Emission Measurements of Alkenes, Alkanes, SO_2 and NO_2 from Stationary Sources in Southeast Texas over a 5-year-period Using SOF and Mobile DOAS, which has been submitted for possible publication in Journal of Geophysical Research - Atmospheres. accepted by Journal of Geophysical Research – Atmospheres,, 2013JD020485.

Johansson, J., Mellqvist, J., et al., Quantification of industrial emissions of VOCs, NO2 and SO2 by SOF and Mobile DOAS during DISCOVER-AQ, AQRP project 13-0051, AQRP report, Dec 7 2013c

S.-W. Kim,..Mellqvist, J., et al., Evaluations of NOx and highly reactive VOC emission inventories in Texas and their implications for ozone plume simulations during the Texas Air Quality Study 2006S, Atmos. Chem. Phys., 11, 11361–11386, 2011, www.atmos-chem-phys.net/11/11361/ 2011/doi:10.5194/acp-11-11361-2011

Mellqvist, J., Application of infrared and UV-visible remote sensing techniques for studying the stratosphere and for estimating anthropogenic emissions, doktorsavhandling, Chalmers tekniska högskola, Göteborg, Sweden, 1999a

Mellqvist, J och Galle, B., Utveckling av ett IR absorptionssystem användande solljus för mätning av diffusa kolväteemissioner, Rapport till Preems miljöstiftelse juli 1999b.

Mellqvist, J., Arlander, D. W., Galle, B. and Bergqvist, B., Measurements of Industrial Fugitive Emissions by the FTIR-Tracer Method (FTM), IVL report, 1995, B 1214.

Mellqvist, J., Flare testing using the SOF method at Borealis Polyethylene in the summer of 2000. 2001, Chalmers University of Technology. (Available at www.fluxsense.se)

Mellqvist, J., J. Samuelsson, C. Rivera, B. Lefer, and M. Patel (2007), Measurements of industrial emissions of VOCs, NH_3, NO_2 and SO_2 in Texas using the Solar Occultation Flux method and mobile DOAS, Project H053.2005, Texas Environmental Research Consortium., Texas. (http://www.harc.edu/projects/airquality/Projects/Projects/H053.2005)

Mellqvist, J., Johansson, J.,Samuelsson, J., Rivera, C., Lefer, B. and S. Alvarez (2008b), Comparison of Solar Occultation Flux Measurements to the 2006 TCEQ Emission Inventory and Airborne Measurements for the TexAQS II, Project No. 582-5-64594-FY08-06 , TCEQ report., Texas. (available at http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/20081108-comparison_solar_occultation_flux_measurements.pdf)

Mellqvist, J., et al. (2009a), Emission Measurements of Volatile Organic Compounds with the SOF method in the Rotterdam Harbor 2008, available at www.fluxsense.se

Mellqvist, J., J. Samuelsson, J. Johansson, C. Rivera, B. Lefer, S. Alvarez, and J. Jolly(2010), Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method,J. Geophys. Res.,115, D00F17, doi:10.1029/2008JD011682.

Parrish, D.D., Ryerson, T.B., Mellqvist, J. et al., Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region, Atmos. Chem. Phys., 12, 3273-3288, 2012:

Platt, U., D. Perner, and H.W. Pätz, Simultaneous Measurement of Atmospheric CH_2O, O_3 and NO_2 by Differential Optical Absorption, Journal of Geophysical Research, 84 (C10), 6329–6335, 1979.

Rivera, C. et al., (2010), Quantification of NO_2 and SO_2 emissions from the Houston Ship Channel and Texas City during the 2006 Texas Air Quality Study, J. Geophys. Res., 115, D08301, doi:10.1029/2009JD012675

Rivera , C., Application of Passive DOAS using Scattered Sunlight for quantification of gas emission from anthropogenic and volcanic sources (2009a), Dissertation, ISBN 978-91-7385-317-0, ISSN 0346

Rivera, C., J.A. Garcia, B. Galle, L. Alonso, Y. Zhang, M. Johansson, M. Matabuena, and G. Gangoiti (2009b), Validation of optical remote sensing measurement strategies applied to industrial gas emissions, Int. J. Remote Sens., vol 30, no 12, p3191–3204.

Rivera, C., et al. (2009c),Tula industrial complex (Mexico) emissions of SO_2 and NO_2 during the MCMA 2006 field campaign using a mobile mini_DOAS system, Atmos. Chem. Phys., 9, 6351–6361, 2009.

Samuelsson, J., Börjesson, G., Svensson, B., Galle, B., Metan från avfallsupplag i Sverige (Methane from landfills in Sweden), final report to the Swedish Energy Agency, projekt nr P10856-4, December 2005a. In Swedish (www.stem.se), can be ordered from Studsviksbiblioteket, 611 82 Nyköping, Sweden, www.lib.kth.se/SB/service/stemavf.html.

Samuelsson, J., et. al., VOC measurements of VOCs at Nynas Refinery in Nynäshamn 2005b *(Utsläppsmätningar av flyktiga organiska kolväten vid Nynas Raffinaderi i Nynäshamn 2005, in Swedish*), Bitumen refinery official report to provincial government 2005, Available at: http://www.fluxsense.se

Appendix

A1 The SOF method

A1.1. Introduction

The Solar Occultation Flux (SOF) method utilizes the sun as the light source and gas species that absorb in the infrared portion of the solar spectrum are measured from a mobile platform, Figure A1.1. The method is used to screen and quantify VOC emissions from industrial conglomerates down to sub-areas in individual plants, such as a few tank process area or water treatment areas. The SOF method is usually combined with an extractive FTIR instrument in the same measurement vehicle, by which it is possible to carry out complementary measurements by tracer correlation (Galle 2001), 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 analyzing the gas concentrations by infrared spectroscopy.

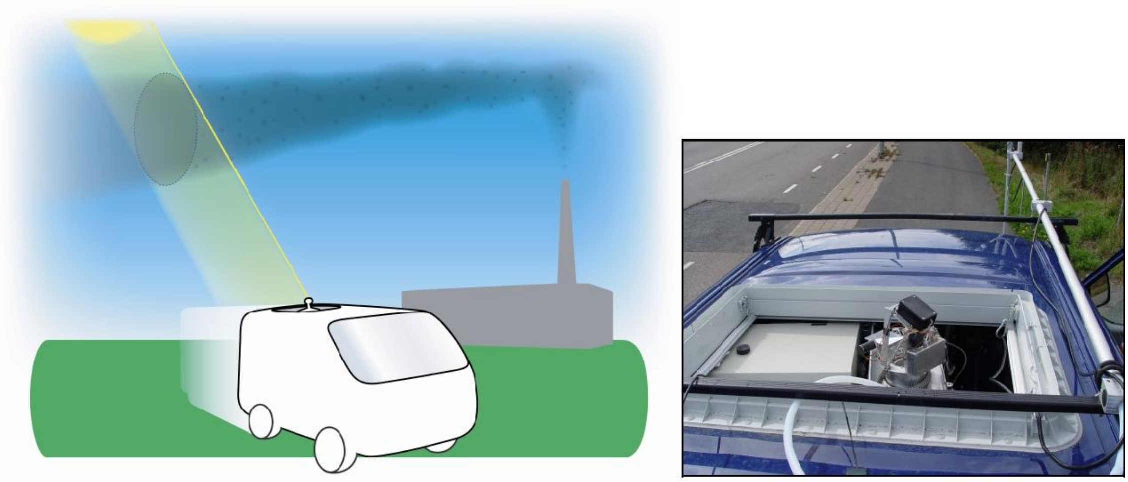


Figure A1.1 In the Solar Occultation Flux method (SOF) gases are measured by observing solar light in the infrared portion of the solar spectrum. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of gas is obtained by multiplication with the wind speed. (Illustration Karin Sjöberg).

The SOF method has been applied in several larger campaigns in both Europe and in the US (Mexico City 2006, Texas 2006/2009/2011/2012/2013; Le Havre 2008, Rotterdam 2008/2010 and Antwerp 2010) and in more than 60 individual plant surveys over the last 7 years. About 10 international reports and several peer reviewed scientific papers (Mellqvist 2010, Foy 2007, De Gouw 2009, Kim 2011, Parrish 2012, Johansson 2013a, Johansson 2013b) have been written so far, applying the SOF method for various industrial measurements. The technique has been validated by comparison to other methods and tracer gas releases and it typically has an uncertainty of 30%, Table 1, mostly due to uncertainties in the wind field.

In the various campaign studies it has been found that the measured emissions obtained with SOF are 3–10 times higher than the reported emission obtained by calculations. For instance in a study in Houston, TexAQS 2006, it was shown that the industrial releases of alkenes for the Houston Galveston area, on average, were 10 times higher than what was reported [Mellqvist 2010]. These results were supported by airborne measurements [De Gouw 2009].

For alkanes the discrepancy factor was about 8 [Mellqvist 2007]. Similar SOF studies in Rotterdam 2008 and 2010 [Mellqvist 2009a], Le Havre 2008 and Antwerp 2011 show overall discrepancies of 4.2, 4.4 and 7.7, respectively. For Swedish refineries the VOC emissions typically correspond to 0.03–0.09 % of the throughput of oil, compared to a typical value of 0.01% obtained with API estimations. Modelers in the USA have responded to the observed discrepancies by increasing the modeled VOC emissions; for instance TCEQ (Texas Commission on Environmental Quality) increases industrial VOCs by ~6 times in ozone modeling (SIP model) and scientists at the US weather service (NOAA-National Oceanographic Atmospheric Administration) (Kim, 2011) have upscaled VOC emissions based on SOF 2006 data in Texas. This improves the agreement with airborne measurements for both VOCs and ozone.

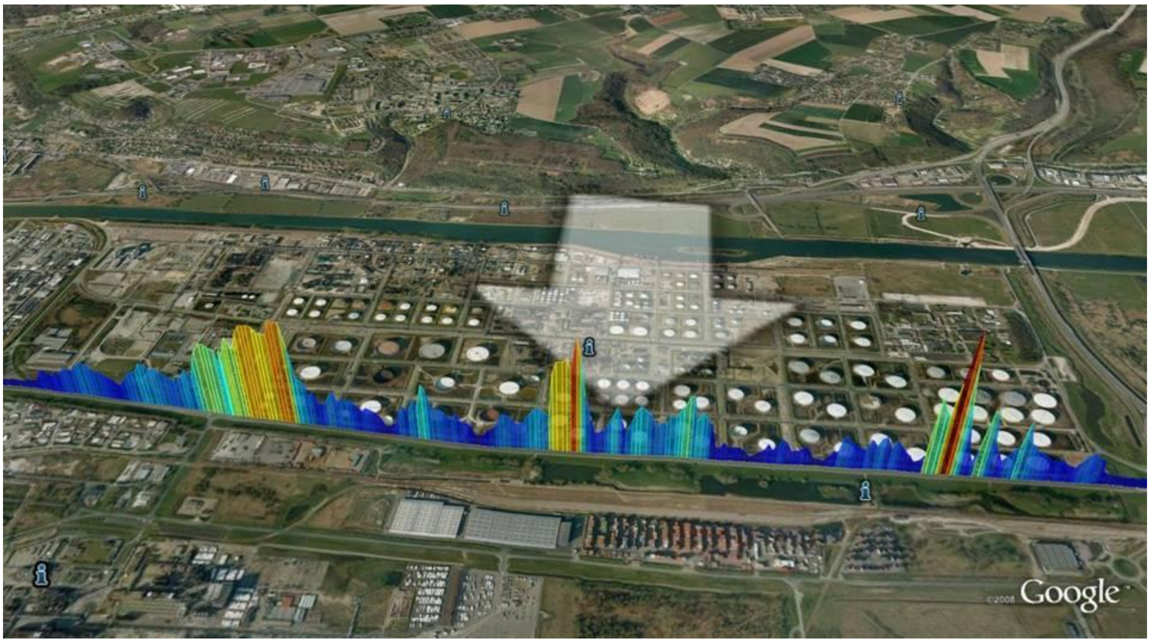


Figure A1.2 A SOF transect past a refinery. The staples and colors shows the integrated amount of butane, as retrieved from the solar spectra. After multiplication with the wind velocity the mass flux is obtained.

In Europe the SOF technique is considered as Best Available Technology for measurements of fugitive emission of VOCs (also DIAL) and it is used together with tracer correlation (Galle 2001) and optical gas imaging to screen the refineries annually, over a time period of about 10 days. The SOF technique is also described in the EPA handbook on remote sensing (2011). The data are used for the annual reporting and to follow up on abatement strategies, such as new tank sealings, flare efficiency etc. At the moment a European standard (CEN TC 264/WG 38) is being worked on for SOF and some other methods.

The SOF technique has the smallest uncertainty when carrying out measurements outside the fenceline of the refineries, since the wind field is then less disturbed and most of the emissions plume has had time to distribute itself over considerable height (100-200 m). Box measurements on the fenceline of the refineries are therefore carried out for estimation of the total refinery emission. Then individual measurements are carried out inside the refinery on available roads, for estimation of emissions of subareas such as process area, product tanks, crude oil tanks, water treatment facility, loading/unloading and flaring. The emission values obtained inside the refinery are always rescaled so that their sum matches the emission value measured at the fenceline. In this manner the uncertainty of the wind field close to tanks etc. is minimized. Emission hotspots located with SOF are often studied in more detail using tracer correlation (meFTIR) and OGI.

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 A.1.3 annual emissions measurements on the fenceline of a Swedish refinery are shown as a histogram, showing all emission measurements binned into different emission intervals. The wind variations normally causes an emission curve that follows a normal distribution while a skew shape of these curves is due to intermittent emissions due to tank cleaning etc. The refinery in Figure A1.3 has been measured 12 times since 1989 (DIAL 4 times and SOF 9 times) and with exception for the first occasion the emission has varied within 30%. This is a strong argument that these measurements give a representative value. 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 (Johansson 2013b) based on the TANKS model, developed by the US API and EPA, an upper estimate of the effects is 30-40% maximum overestimation in the emissions for an EFRT crude oil tank (Mellqvist 2009a), compared to the annual average.

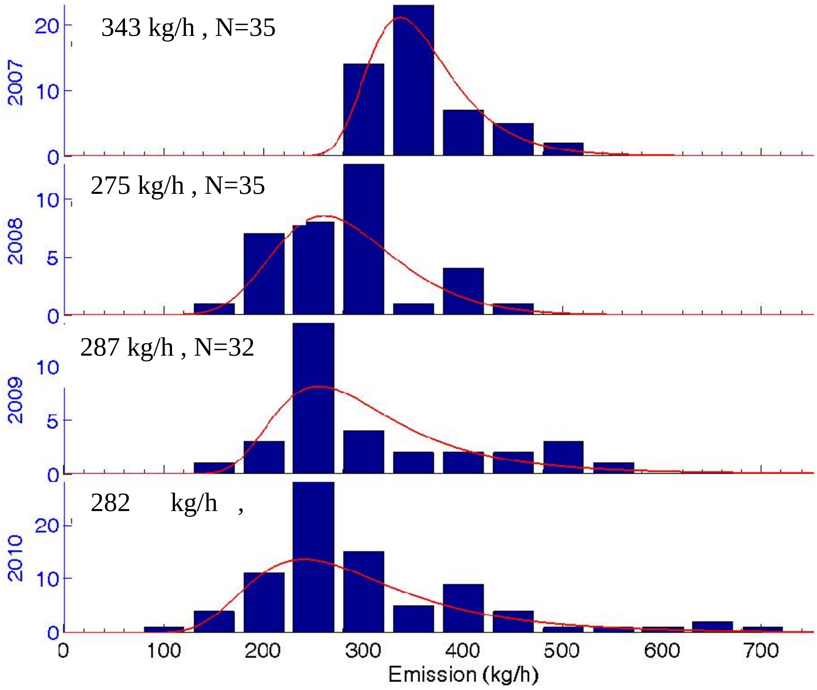


Figure A1.3 Total VOC emission from a refinery over several years. The average emission is given, calculated as weighted average. (Days with large variability are less weighted to minimize the influence of intermittent emissions, weight factor 1/standard deviation of daily emission values). The red curve is a skewed probability function that is fit to the data. The maximum is the most probable emission value.

A1.2 Details of the SOF method

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. In Figure A1.1 a measurement system is shown built into a van. The system consists of a custom built solar tracker, transfer optics and a Bruker EM27 FTIR spectrometer with a spectral resolution of 0.5 cm^{-1}, equipped with a combined MCT (mercury cadmium telluride) detector or an InSb (indium antimonide) detector. Optical filters were used to reduce the bandwidth when conducting alkene and alkane measurements.

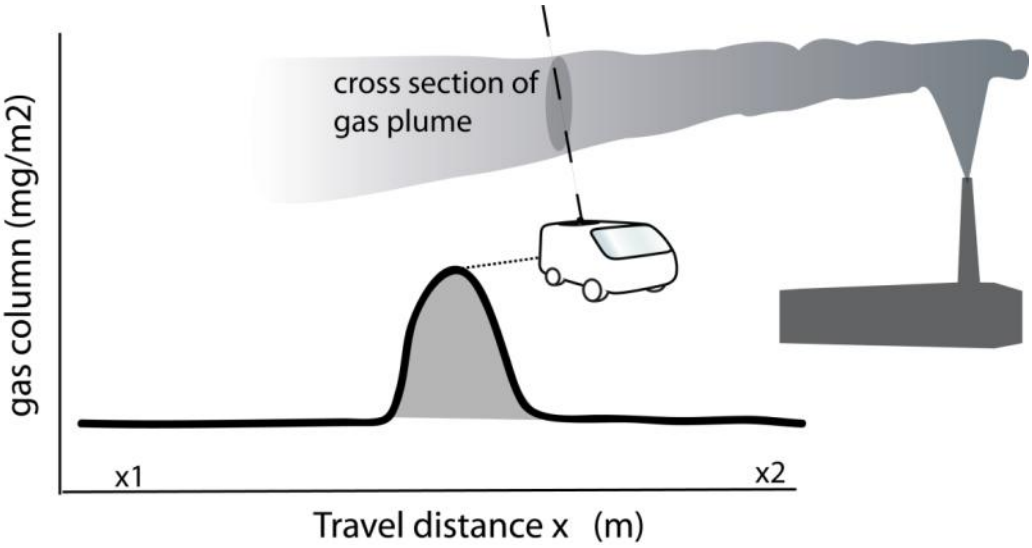


Figure A1.4 Illustration of the SOF measurements.

To obtain the gas emission from a source, the car is driven in such way that the detected solar light cuts through the emission plume, as illustrated in Figure A1.4. To calculate the gas emission the wind direction and speed is also required and these parameters are usually measured from high masts and towers.

The spectral retrieval is performed by a custom software, QESOF (Kihlman 2005b), in which calibration spectra are fitted to the measured spectra using a nonlinear multivariate fitting routine. 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, n-octane and other VOCs (e.g. isobutene, 1,3-butadiene) were obtained from 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 about 3.5 % for the five species.

The SOF system can be operated in two parallel optical modes, one for alkenes and one for alkanes. In this study no measurements of alkenes were carried out since these species usually are emitted from the petrochemical industry rather than refineries.

The alkane optical mode corresponds to measurements in the infrared region between 3.3–3.7 μm (2700–3005 cm^{-1}), using the vibration transition in the carbon and hydrogen bond (CH-stretch). 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 analysis we therefore use calibration spectra of propane, n-butane, and n-octane and fit these to the recorded spectra, using a resolution of 8 cm^{-1}. Aromatics and alkenes also have absorption features in the CH-stretch region, but mainly below 3.33 μm for the most abundant species. A sensitivity study of the SOF alkane retrieval was made for the TexAQS 2006 (Mellqvist 2007), taking into account the typical matrix of VOCs, and this study showed that total alkane mass obtained by the SOF was overestimated by 6.6 %. Here we assume the same uncertainty.

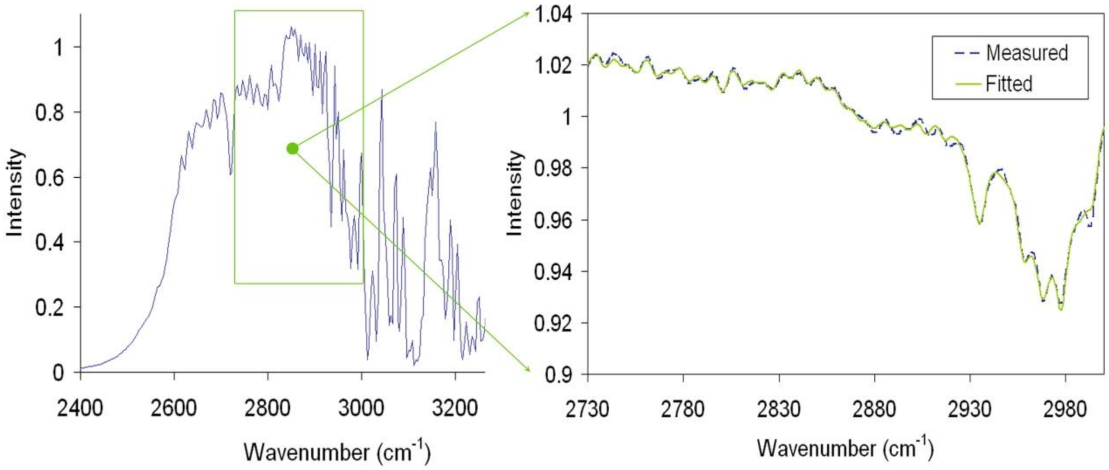


Figure A1.5 Solar spectra in the alkane CH-stretch region, (left) measured downwind a refinery. To the right the measured and the fitted mix of calibration spectra are shown (relative to a clean air background reference), obtained using the QESOF spectral retrieval algorithm.

A1.3 Flux calculation

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 as illustrated in Figure A1.4. 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. 1. Here, **x** corresponds to the travel direction, **z** to the height direction, **u’** to the wind speed orthogonal to the travel direction (x), $\mathbf{u'_{mw}}$ to the mass weighted average wind speed and $\mathbf{H_{mix}}$ 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.

$$flux = \int_{x1}^{x2} \int_{0}^{Hmix} conc(z) \cdot u'(z) \cdot dz\, dx = u'_{mw} \int_{x1}^{x2} column(x) \qquad \text{(Eq. 1)}$$

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

The wind is not straightforward to obtain since it is usually complex close to the ground and increases with the height. The situation is helped by the fact that SOF measurements can only be done in sunny conditions. This is advantageous since it corresponds to *unstable meteorological conditions* for which wind gradients are smoothed out by convection. Over relatively flat terrain with turbulence inducing structures the mean wind varies less than 20 % between 20 and 100 m height using standard calculations of logarithmic wind. This is illustrated for the harbor of Göteborg in Figure A1.6. Here the average daytime wind velocity and wind direction profile for all sunny days during August of 2004 have been simulated [Kihlman 2005a] using a meteorological flow model denoted TAPM (Hurley 2005).

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 kilometers downwind. 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 rapid well-mixed assumption agrees with results from airborne measurements made by NOAA (National Oceanic and Atmospheric Administration) (De Gouw 2009) and Baylor University (Buhr 2006) during the TexAQS 2006 in which also SOF measurements were conducted [Mellqvist 2010]. The NOAA measurements indicate that the gas plumes from the measured industries mix evenly from the ground to 1000 m altitude, i.e. throughout the entire mixing layer, within 1000–2000 s (~25 min) transport time downwind the industrial plants. This indicates a vertical mixing speed of the plume between 0.5 to 1 m/s. This is further supported by Doppler LIDAR (Light Detection And Ranging) measurements by NOAA showing typical daytime vertical mixing speeds of ±(0.5–1.5) m/s [Tucker 2007].

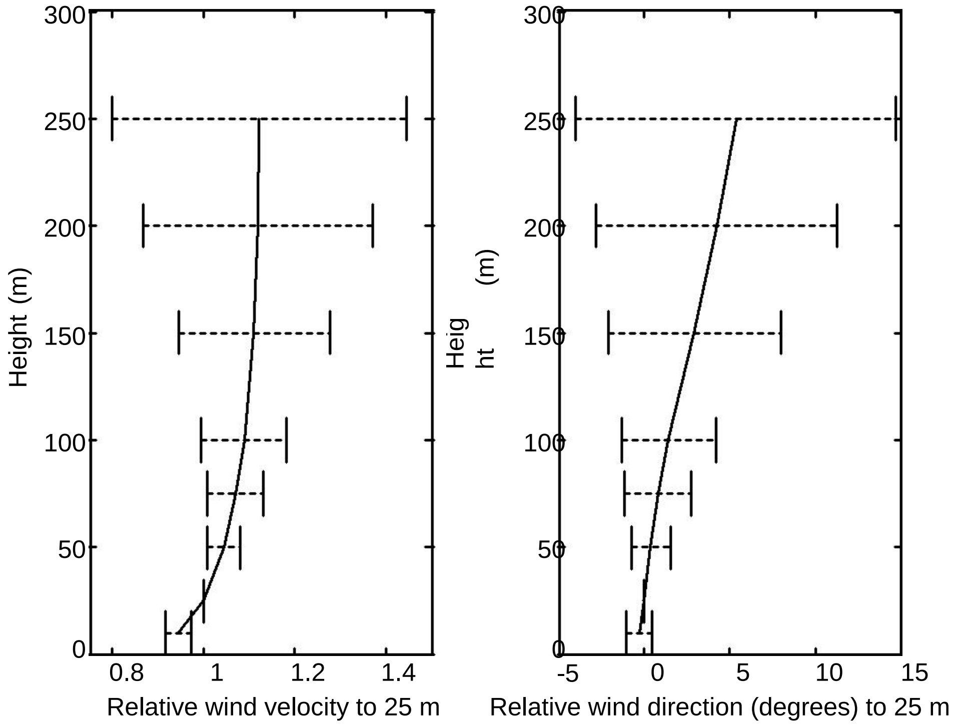


Figure A1.6 Average daytime wind velocity and wind direction profile retrieved by simulation above Göteborg harbor area averaged over all sunny days during a month with a wind-speed of 3–6 m/s at ground. The error bars indicate standard deviation between daily averages [Kihlman 2005a].

In this study, the measurements were conducted downwind of the industries at a typical plume transport time of 100–1000 s. According to the discussion above this means that the emission plumes have had time to mix up to heights of several hundred meters above the ground, above the first 50–100 m where the wind is usually disturbed due to various structures. For this reason we have used the average wind from 0 to 500 m height in the flux calculations.

Figure A1.7 shows a real measurement example illustrating the principle for the SOF and Mobile DOAS measurements. Here a measurement of alkanes, a transect across the plume downwind of a refinery, is shown. The measured gas column of alkanes in the unit mass/area (mg/m^2), as measured by the SOF in the solar light, is plotted versus distance across the plume. The wind was measured simultaneously by a GPS balloon, in the vicinity of the measurement as shown in Figure A1.8 and the 0–200 m value corresponds to 7.9 m/s, while the 0–500 value corresponds to 8.4 m/s. In the flux calculation the columns are integrated across the transect, whereby the integrated mass in unit mass per length unit in the plume (mg/m) is obtained. This value corresponds to an average column value of 48 mg/m2 across the whole transect, over 1300 m. This mass value is then multiplied by the wind speed, to obtain mg/s.

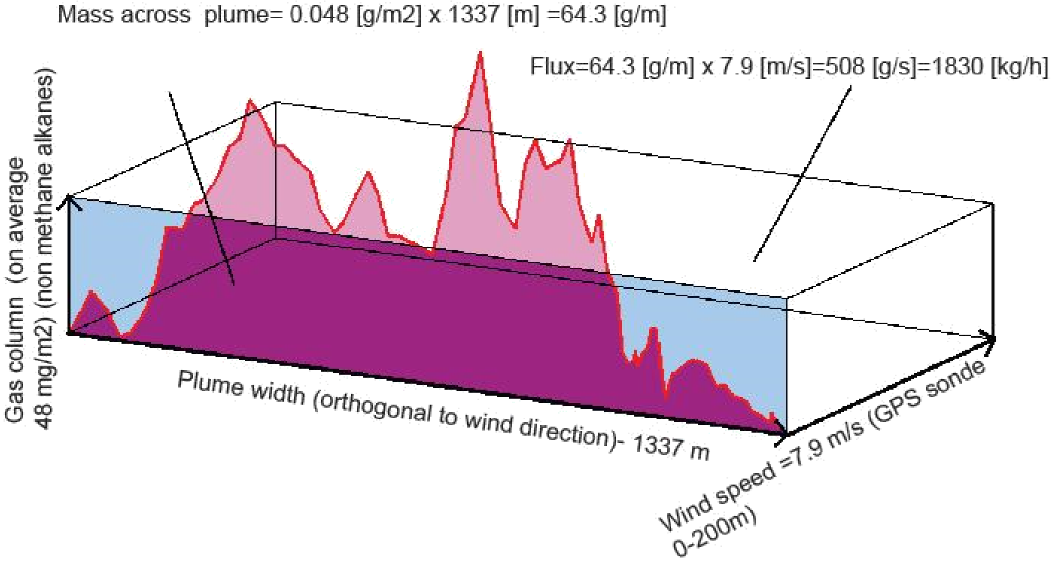


Figure A1.7 Illustration of the flux calculation in the SOF method for a measurement of alkanes conducted downwind of a refinery. The gas column of alkanes, retrieved from the spectra, is plotted versus distance. In the flux calculation the gas columns are integrated along the measurement transect, corresponding to the lilac area. This area, which is the integrated mass of the plume, corresponds to the same mass as an average column of 48 mg/m^2 integrated along the transect of 1337 m. The integrated mass is then multiplied with the wind speed yielding the flux in mass per seconds. Here an average wind speed from ground to 200 m was used corresponding to 7.9 m/s obtained from the GPS sonde.

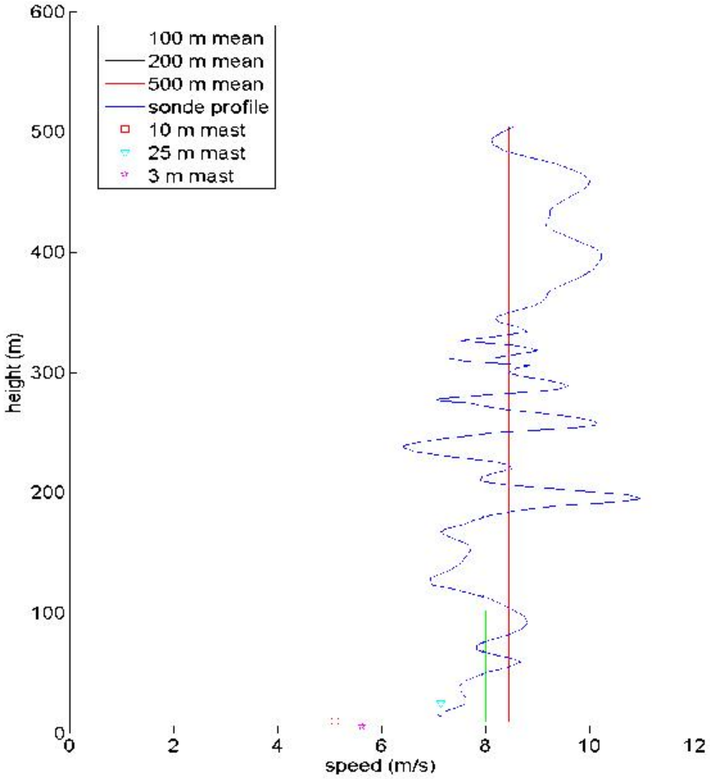


Figure A1.8 Wind profile measured with a GPS sonde less than ten minutes after the alkane transect shown in Figure A1.7above. The wind speed versus height is shown for the balloon measurements in addition to the 0–500 and the 0–200 m average values, and values for several masts at the refinery.

To verify that a measured flux is originating from a specific area upwind of where the emission was detected, another measurement transect needs to be performed upwind of that area to make sure that the emission is not coming from another source further away. If no significant flux is detected on the upwind side, this measurement does not need to be repeated for every downwind transect. If a smaller flux is measured on the upwind side than on the downwind side, the emission from the area in between is the difference between these fluxes. In this case the upwind transect needs to be repeated with every downwind transect. This type of emission measurements is preferably avoided since it might increase the uncertainty. Upwind measurements were performed for all areas during the study, but they are not presented in the result chapter.

A2. Mobile DOAS

A2.1 General

Mobile DOAS (Differential Optical Absorption Spectroscopy) measurements of scattered solar light in zenith direction were carried out in parallel with the SOF measurements, from the same vehicle, in order to measure formaldehyde, NO_2 and SO_2. DOAS works in the ultraviolet (UV) and visible wavelength region while SOF works in the infrared region and hence there are large differences in spectroscopy and in the used spectrum evaluation methods. However, both methods measure vertical columns which are integrated along measurement transects and multiplied by the wind to obtain the flux. The principle of flux-measurements using Mobile DOAS is hence the same as for SOF, although it is not necessary to compensate for any slant angle observations since the telescope is always pointing towards zenith. The DOAS system also works under cloudy conditions in contrast to SOF, although the most precise measurements are conducted in clear sky. The system is explained in Johansson (2013b).

The DOAS method was introduced in the 1970's (Platt 1979) and has since then become an increasingly important tool in atmospheric research and monitoring both with artificial light sources and in passive mode utilizing the scattered solar light. In recent time the multi axis DOAS method (scanning passive DOAS) has been applied in tropospheric research for instance measuring formaldehyde (Heckel 2005). Passive DOAS spectroscopy from mobile platforms has also been quite extensively applied in volcanic gas monitoring (Galle et al., 2002) for SO_2 flux measurements and for mapping of formaldehyde flux measurements in megacities (Johansson 2009). Mobile DOAS has only been used to a limited extent for measurements of industries; Rivera et al. (2009c) did SO_2 measurements on a power plant in Spain for validation purposes. They also made measurements at an industrial conglomerate in Tula in Mexico (Rivera 2009d) and measurements of SO_2, NO_2 and HCHO during the TexAQS 2006 campaign (Rivera 2009a, 2009b). There are also groups in both China and Spain working with mobile mini DOAS.

A2.2 Details of the method

The Mobile DOAS system used in this project, shown in Figure A1.9 and Figure A1.10, has been developed for airborne surveillance of SO_2 in ship plumes [Mellqvist 2008a, Johansson 2013a] but has for this project been modified to also measure HCHO and NO_2. It consists of a UV spectrometer (ANDOR Shamrock 303i spectrometer, 303 mm focal length, 300 µm slit) equipped with a CCD (charge-coupled device) detector (Newton DU920N-BU2, 1024 by 255 pixels, thermoelectrically cooled -70^{O} C). The spectrometer has wavelength coverage of 309 to 351 nm and a spectral resolution of 0.63 nm (1800 grooves/mm holographic grating). The spectrometer is connected to a quartz telescope (20 mrad field of view, diameter 7.5 cm) via an optical fiber (liquid guide, diameter 3 mm). An optical band pass filter (Hoya) is used to prevent stray light in the spectrometer by blocking wavelengths longer than 380 nm.

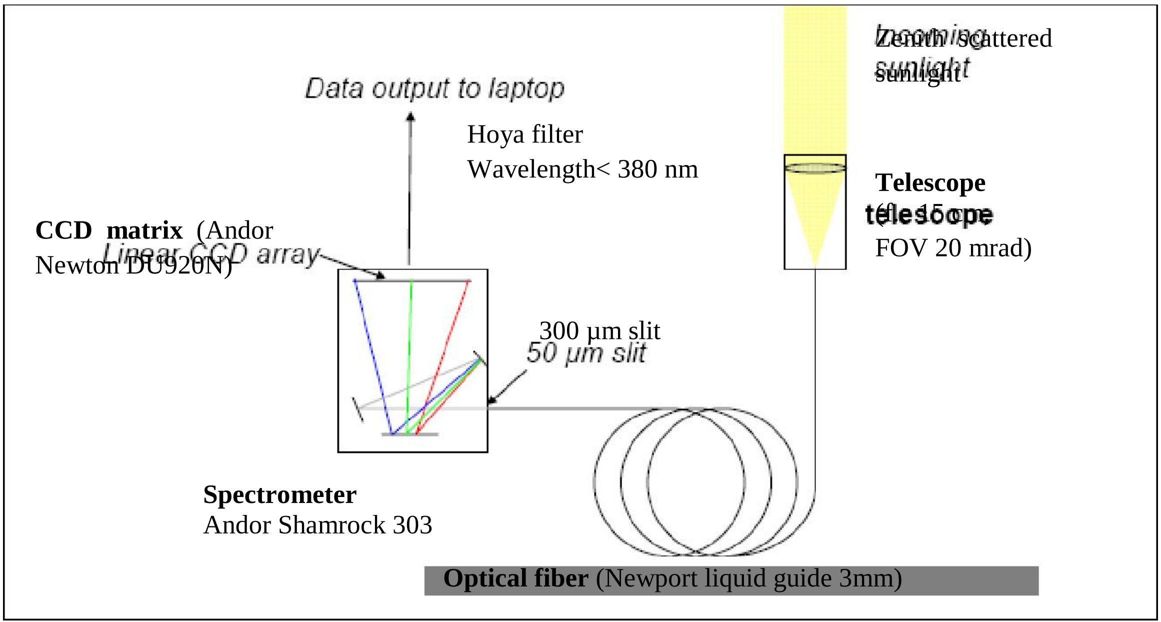


Figure A1.9 Overview of the Mobile DOAS system used. Scattered solar light is transmitted through a telescope, and an optical fiber to a UV/visible spectrometer. From the measured spectra the amount of HCHO, NO_2 and SO_2 in the solar light can be retrieved.

The DOAS system measures ultraviolet spectra in the 308–352 nm spectral region from which total columns of HCHO, NO_2 and SO_2 can be retrieved, Figure A1.11. HCHO and NO_2 are retrieved between 324 to 350 nm, together with the interfering species O_3, O_4 and SO_2. SO_2 and O_3 is then retrieved between 310 to 324 nm together with the NO_2 and HCHO columns obtained from the previous retrieval at 324–350 nm.

In the spectral evaluation the recorded spectra along the measurement transect are first normalized against a reference spectrum recorded upwind 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, and 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 according the algorithms proposed by Platt and Perner (1979), and then calibration spectra are scaled to the measured ones by multivariate fitting. Here we have used a software package denoted QDOAS (Van Roozendael 2001) developed at the Belgian Institute for Space Aeronomy (BIRA/IASB) in Brussels.

The calibration spectra used here for the various gases are obtained from the following: HCHO (Cantrell 1990), NO_2 (Vandaele 1998), SO_2 (Bogumil 2003), O_3 (Burrows 1999) and O_4 (Hermans 1999). In addition to these calibration spectra it is also necessary to fit a so called Ring spectrum, correcting for spectral structures arising from inelastic atmospheric scattering (Fish 1995). The Ring spectra used have been synthesized with a component of the QDOAS software, which uses a high resolution solar spectrum to calculate the spectrum of Raman scattered light from atmospheric nitrogen and oxygen, convolves this spectrum and the high resolution solar spectrum with the instrument lineshape and calculate the ratio between them. One problem with the acquired spectra is the fact that the wavelength scale of the spectrometer was variable with shifts in the wavelength scale for the individual spectra. Even though these shifts were minute, within 0.02 nm, they still cause large residuals when normalizing the spectra to the reference spectrum. To overcome this we have used the QDOAS program, to characterize the wavelength calibration of the spectra by comparing the positions of the solar absorption lines with a high-resolved solar spectrum. This improved the results quite considerably. An example of a fit can be seen in Figure A1.11 in which a calibration spectrum of formaldehyde has been fitted to the measured differential absorbance. This differential spectrum corresponds to a high pass filtered atmospheric spectrum with the features of ozone, NO_2 and spectrum of inelastic atmospheric scattering removed.

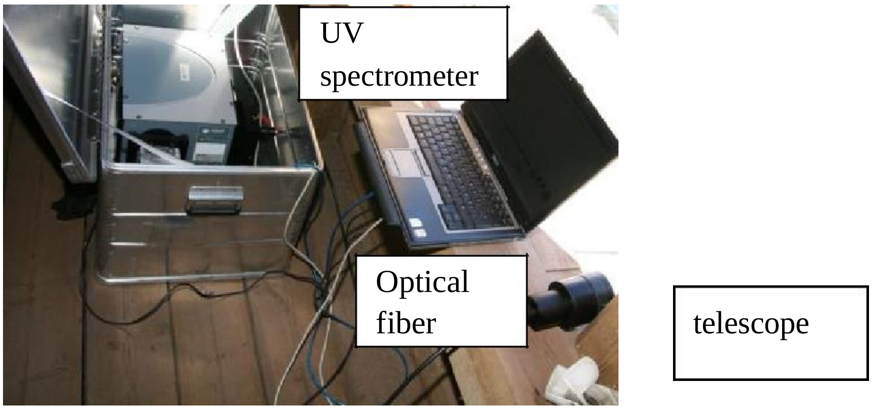


Figure A1.10 The Mobile DOAS system consisting of a UV spectrometer, optical fiber and UV telescope.

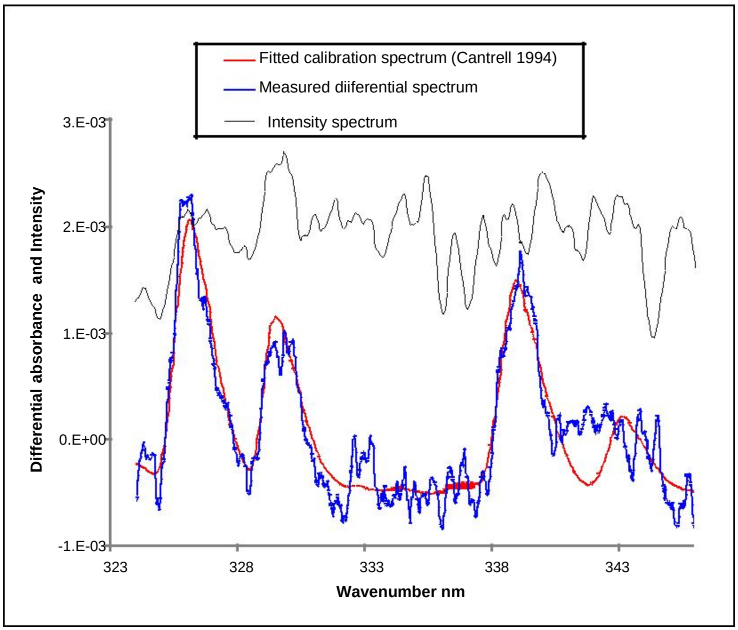


Figure A1.11 Ultraviolet spectrum (Intensity counts versus wavelength) measured south west of HSC by the Mobile DOAS system on May 20 2009, 10:40, adapted from Mellqvist 2010. From this spectrum a formaldehyde column of 3.8×10^{16} molecules/cm^2 was derived by fitting a calibration spectrum to the measured high pass filtered absorbance (after subtraction of ozone, NO_2 and inelastic atmospheric scattering).

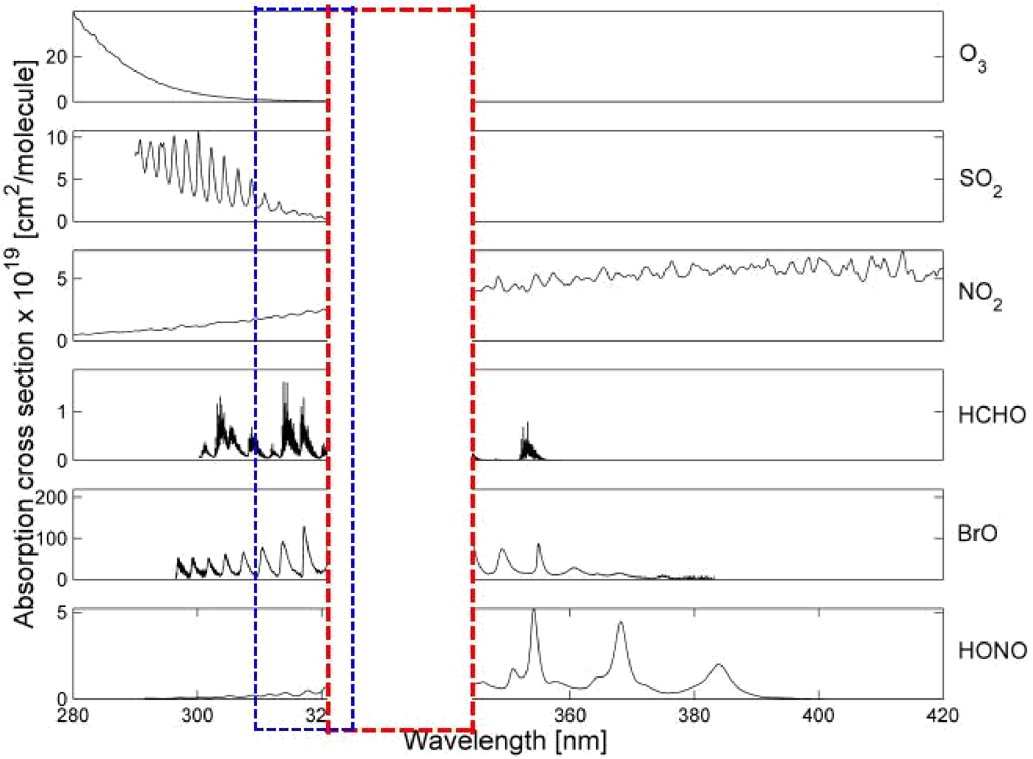


Figure A1.12 Absorption cress section for various species

A3 Mobile extractive FTIR and tracer correlation

Column measurements using SOF are often complemented by mobile extractive measurements using multi reflection absorption in the infrared region (MeFTIR) or UV (White cell DOAS). Such extractive measurements have better speciation than the SOF measurements and by measuring the composition of various VOCs downwind the studied industries it is possible to infer emissions of more species than obtained by the SOF instrument alone. The extractive measurements can be complemented by tracer gas releases at the sources to estimate emissions independently from the SOF.

A3.1 Details of MeFTIR system

The extractive FTIR system contains a spectrometer of the same type used for the SOF system, Bruker IRCube, but utilizes an internal glow bar as an infrared radiation source instead of the sun, and transmits this light through a measurement cell.

The spectrometer is connected to an optical multi-pass cell (Infrared Analysis Inc.) operated at 40 m path- length, Figure A1.13. The transmitted light is detected simultaneously with an InSb-detector (indium antimonide) in the 2.5–5.5 µm (1800–4000 cm^{-1}) region and a MCT (mercury cadmium telluride) detector in the 8.3–14.3 µm (700–1200 cm^{-1}) region. Temperature and pressure averages in the cell were integrated over the cycle of each spectrum. Atmospheric air is continuously pumped with high flow through the optical cell from the outside, taking the air in from the roof of the van through a Teflon tube. A high flow pump is used to ensure that the gas volume in the cell was fully replaced within a few seconds. Spectra were subsequently recorded with an integration time of typically 10 seconds. A GPS-receiver is used to register the position of the van every second.

The concentration in the spectra is analyzed online, fitting a set of calibration spectra based on the Hitran2000 infrared database (updated to the 2007 edition) (Rothman et al. 2003) and the PNL database (Sharpe 2004) in a least-squares fitting routine [Griffith 1996].

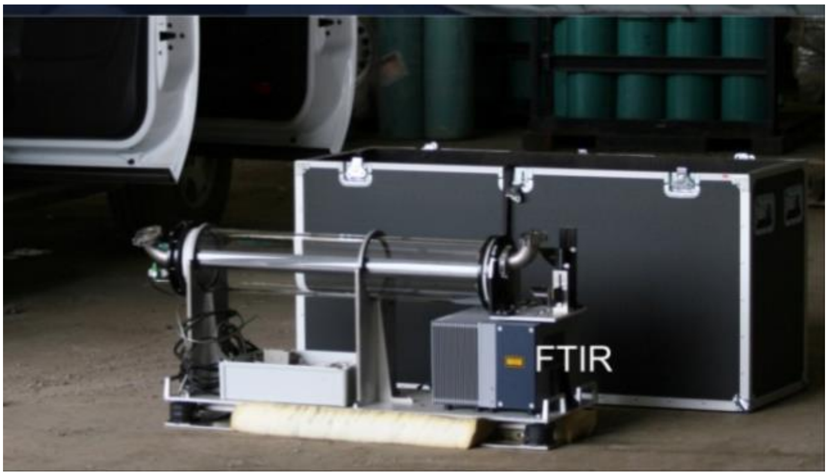


Figure A1.13 The MeFTIR instrument used in parallel with the SOF system during the campaign. The gas is extracted into the White-cell where it is analysed by infrared absorption measurements. The residence time in the gas cell, and hence the measurements time resolution, is a few seconds.

A3.2 Tracer correlation measurements

Tracer correlation involves a common practice of measuring pollutant emission rates while releasing a known concentration of a tracer gas, Figure A1.14. The subsequent simultaneous measurement of this tracer gas and the pollutant of interest downwind from the release provide sufficient information to determine or validate the emissions flux measurements. The release of a known concentration of a tracer gas assists in tracking the plume and sources or sinks of the pollutant of interest into the plume. The majority of tracer gas studies use cell-based technologies, like CRDS (Cavity Ring Down Spectrometers) and FTIR to measure the tracer gas and the compound of interest. However, some studies are expanding the use of tracer gas release to open-path techniques to evaluate the distribution over a large area.

Tracer correlation has been applied at Swedish refineries since 8 years for measurements of isolated features such as water treatment areas, ship or truck loading and individual tank emissions as well as landfills (Galle, 2001, Börjesson 2009, Eastern research group). A mobile extractive FTIR system is then used based on a multi reflection cell coupled to an FTIR in a measurements vehicle. The meFTIR system measures the concentration of gases close to the ground. A 50 m tube can be coupled to the gas analysis cell so one can measure at some distance from the car, for instance high up or in process areas.

To study emissions from a certain tank or other sources, tracer gas is released from the tank and then the tracer and gas is measured downwind of the tank, Figure A13. From this ratio together with the amount of tracer released it is possible to obtain the emission rate from the tank without any measurement of the wind. In this manner it is possible to obtain the emission from the tank, over a full cycle for instance also at night. The uncertainty for meFTIR is estimated to be around 20% for isolated sources.

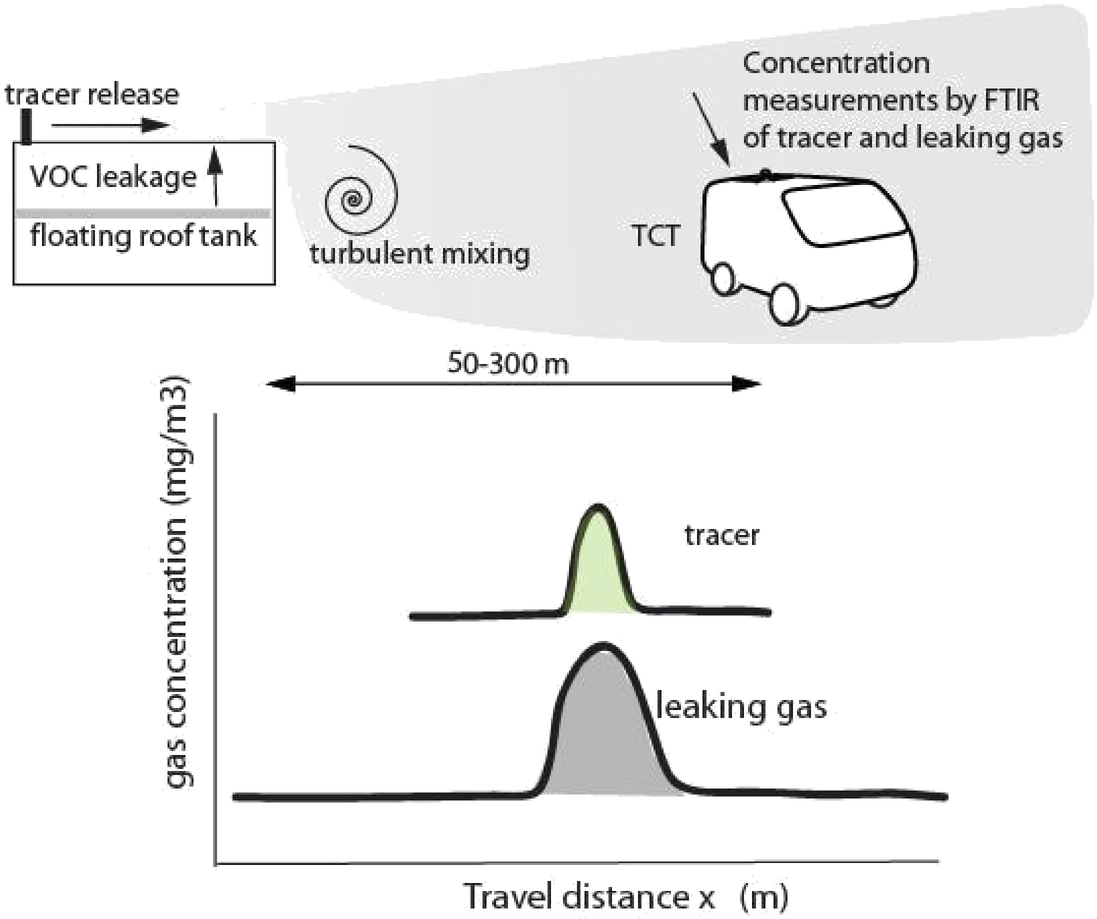


Figure A1.14. Here the meFTIR method, used together with SOF in the measurements van is illustrated when conducting emission measurements from a leaking crude oil tank. Trace gas, usually N_2O or SF_6, is positioned on the upwind side of the tank, and then it mixes with the leaking VOCs from the tanks. The measurements are conducted downwind by driving through the plumes of the tracer gas and the leaking gas. The dilution factor for the trace gas is obtained as the ratio between the tracer release rate and the measured tracer concentration, averaged over the plume. To obtain the emission rate of VOCs the dilution factor is multiplied by the average concentration of VOC over the plume. The assumption here is hence that the leaking gas, leaking through the tank sealing dilutes in the same manner as the tracer, release in one or a few points.

A4 Mobile White Cell DOAS

In addition the concentration measurements of alkanes with the Mobile extractive FTIR above a similar UV system is often used to measure also aromatic VOCs (Benzene, Toluene, and xylenes. In a validation test on Houston in October 2013 this system was tested against PTR-MS, showing good agreement and sub-ppb sensitivity for benzene and other species (Johansson 2013c).

The Mobile White Cell DOAS (MW-DOAS) which is developed by Chalmers University of Technology (Pontus Andersson) and FluxSense AB is based upon the White Cell configuration described by Doussin (1999), Figure A1.15). The cell has a base path of 2.5 m and with 86 reflections the total distance that the light travels is thus 210 m. All mirrors used in the cell have special UV high reflectivity coatings that have a reflectivity of 99.7 % in the wavelength region 250 -280 nm. The light source used is a 75 W Xenon arc lamp coupled into a UV fiber that further transmits the light into the multi reflection cell. After passing through the cell the light is coupled into a fiber bundle transmitting the light into a UV spectrometer (303 mm focal length) equipped with a CCD detector. The spectrometer has wavelength coverage between 243 nm and 286 nm. The wavelength calibration is carried out using a hollow cathode Pb lamp. Several aromatic compounds exhibit strong absorption lines in this region. Measured cross-sections are obtained from the scientific literature (Etzkorn, 1999, Fally 2009). The DOAS analysis was done online using the custom software DOASIS and QDOAS (Fayt, 2001; (Van Roozendael 2001).

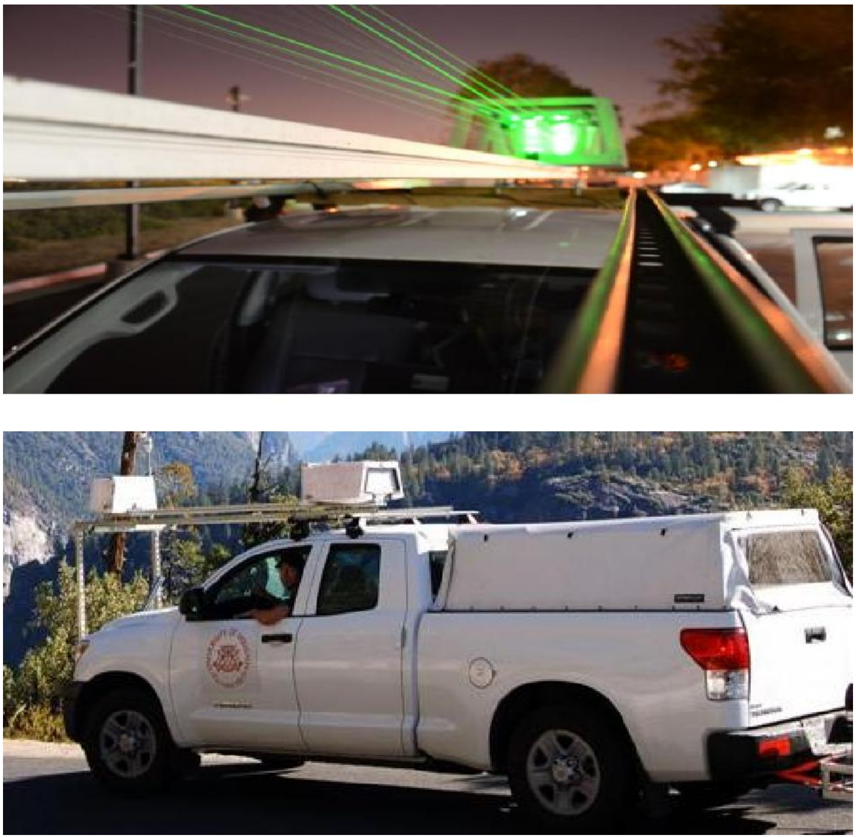


Figure A1.15 The MW-DOAS system mounted on the roof of a van, yielding sub ppb sensitivity for benzene and other aromatics.

A5 Measurement uncertainty and quality assurance

A5.1 Measurement uncertainty SOF and Mobile DOAS

The main uncertainty for the flux measurements in the SOF and Mobile DOAS measurements comes from the uncertainty in the wind field. Table A1.1 shows the estimated uncertainties for the flux measurements during a SOF campaign in Houston 2011; these uncertainties are rather typical for SOF and mobile DOAS measurements.

Table A1.1 Uncertainty estimation of the flux measurements (the variability of the sources not taken into account).

	Wind Speed a)	**Wind Direct** b)	**Spectroscopy (cross sections)** c)	**Retrieval error** d)	**Composite flux measurement uncertainty** e)
Alkanes	16–30 %	6–9 %	3.5 %	12 %	21–34 %
Ethene	16–30 %	6–9 %	3.5 %	10 %	20–33 %
Propene	16–30 %	6–9 %	3.5 %	20 %	27–37 %
HCHO	16–30 %	6–9 %	3 %	10 %	20–33 %
SO_2	16–30 %	6–9 %	2.8 %	10 %	20–33 %
NO_2	16–30 %	6–9 %	4 %	10 %	20–33 %

a) Comparing mast wind averages with the 0–500 m GPS sonde averages, the max data spreads 16–30 % (1σ, 30 %)
b) The 1σ deviation among the wind data compared to the 0–500 m sonde is 18º. For a plume transect orthogonal to the wind direction, which is always the aim, this would give a 6 % error. For a measurement in 75º angle the error is 9 %.
c) Includes systematic and random errors in the cross section database.
d) The combined effects of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect and error of the SOF alkane mass retrieval. Estimated for SOF.
e) The composite square root sum of squares uncertainty

A5.2 Validation and comparisons

The performance of the SOF method has been tested by comparing it to other methods and tracer gas release experiments, according to Table A1.2. In one experiment, tracer gas (SF_6) was released from a 17 m high mast on a wide parking lot. The emission rate was then quantified by SOF measurements 50–100 m downwind the source, yielding a 10 % accuracy for these measurements when averaging 5–10 transects [Kihlman 2005b].

More difficult measurement geometries have also been tested by conducting tracer gas releases of SF_6 from the top of crude oil tanks. For instance, in an experiment at Nynas refinery in Sweden tracer gas was released from a crude oil tank. In this case, for close by measurements in the disturbed wind field at a downwind distance of about 5 tank heights, the overestimation was 30 %, applying wind data from a high mast (Kihlman 2005a; Samuelsson 2005b). A similar experiment was carried out by releasing SF_6 in the process area of a petrochemical plant, using 5 different release points. The SF_6 release was measured 300 m downwind using SOF with meteorological data from a nearby mast. The SOF data were 15% higher than the actual released data, i.e. 2.18±0.3 kg/h compared to 1.89 kg/h.

The SOF method has also been compared against other methods. In another experiment at the Nynas refinery a fan was mounted outside the ventilation pipe, sucking out a controlled VOC flow from the tank. The pipe flow was measured using a so called pitot pipe and the concentration was analyzed by FID (Flame ionization detector) which made it possible to calculate the VOC emission rate, which was 12 kg/h. In parallel, SOF measurements were carried out at a distance corresponding to a few tank heights, yielding an emission rate of 9 kg/h, a 26 % underestimation in this case. Similar measurements from a joint ventilation pipe from several Bitumen cisterns yielded a FID value of 7 kg/h and only 1 % higher emission from the SOF measurements (Samuelsson 2005b).

During the TexAQS 2006 the SOF method was used in parallel to airborne measurements of ethene fluxes from a petrochemical industrial area in Mont Belvieu (De Gouw 2009). The agreement was here within 50 % and in this case most of the uncertainties were in the airborne measurements. The SOF method has not been directly compared to the laser based DIAL method (Differential Absorption LIDAR) (Walmsley 1998) which is commonly used for VOC measurements. Nevertheless, measurements at the same plant in Sweden (Preem refinery) yield very similar results when measuring at different years. Differences have been seen for bitumen refineries however (Samuelsson 2005b). Rivera et al. (2009) did Mobile DOAS measurements of SO_2 on a power plant in Spain and the average determined flux with the DOAS came within 7 % of the values monitored at the plant measurements. All in all the experiment described above is consistent with an uncertainty budget of 20–30 %.

Table A1.2 Validation experiments and instrument comparisons for the SOF technique

Experiment	Comment	SOF kg/h	**Reference kg/h**	**Difference**
Single SF_6 tracer releases from 17 m mast, *(Fransson, 2002)*	SOF measurements on a parking lot 100 m away	2.2	1.97 Tracer release rate from weighing	10%
SF_6 tracer release from the top of crude oil tank (*Samuelsson, 2005*)	SOF measurements 3 tank heights away	13 +5.4	9.5	36%
SF_6 tracer release at VOC leakage points in the process area of an petrochemical plant (Naphta cracker). (*Confidential data*)	SOF measurements 500 m away	2.18±0.3	1.89	15%
Controlled VOC emission from bitumen pipe (Samuelsson 2005)	SOF measurements downwind bitumen tank park	7	7.1	+1%
Controlled VOC emission from crude tank (*Samuelsson, 2005)*	SOF measurements 3 tank heights away. Heated tank with single vent. A fan was mounted and then the flow and concentration was measured in the vent.	9	12 FID+ pitot pipe flow rate	-26%
Large scale ethene emission from Mont Belvieu, E Texas *(Mellqvist, JGR 2009;* *De Gouw, 2009)*	SOF measurements 500m- 3 km downwind and airborne measurements by NOAA	390	480 NOAA WP 3 Orion aircraft	-20% difference
VOC emissions from process area in Preem refinery Gothenburg (*Kihlman 2005*)	Measurements by DIAL in 1999 comparison to SOF in 2005	56±16	56 DIAL 1999	0%

A5.3 Quality assurance

A formalized QA/QC protocol has not yet been adopted for the SOF method or for Mobile DOAS. However, the spectroscopic column concentration measurements is basically the same as a long path FTIR measurement through the atmosphere corresponding to an effective path length of about 5 km for atmospheric background constituents. For such measurements, there is an EPA guidance document (FTIR Open-Path Monitoring Guidance Document," EPA-600/R-96/040, April 1996).

In addition the US-EPA has developed a test method (OTM 10, Optical Remote Sensing for Emission Characterization from Non- Point Sources), (Thoma 2009) for fugitive emission of methane from landfills. This method is based on measuring the gas flux by integrating the mass across the plume and then multiplying with the wind speed. The mass is here measured by long path FTIR or tuneable diode lasers. The OTM 10 is hence quite similar to the SOF method, since it uses long path FTIR but more importantly since it determines the flux in the same principal manner. The spectral retrieval code used in the SOF method (QESOF) (Kihlman 2005a) relies on principles adopted by the NDACC community (Network for the detection of atmospheric composition change. www.ndsc.ncep.noaa.gov), 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 QESOF code has been evaluated against several published codes developed within NDACC with good agreement, better than 3 %.

Even though a formalized QA/QC protocol is missing there are several QA procedures carried out prior to conducting the SOF measurements. This includes checking the instrumental spectral response (usually done by measuring solar spectra and investigating the width and line position of these) and investigating that the instruments measures in the same manner, independent of the direction of the instrument relative to the sun. Usually the instrument is aligned to have the same light response in all directions.

The FTIR instrument, used in SOF, is not calibrated prior to measurements but one instead relies on calibration data from the scientific literature. This is appropriate as long as the instrument is well aligned, and whether the alignment has been sufficient can actually be checked afterwards by investigating the widths and shape of the absorption lines in the measured solar spectra.

Noteworthy is the fact that the spectra are stored in a computer and that the spectral analysis is conducted afterwards which makes it possible to conduct quality control on the data. From this analysis the individual statistical error is obtained for each measurement. Quality control is also conducted by removing "bad" spectra".

For open path DOAS standardization work is carried out which is very similar to this application from a spectroscopic point of view. For instance the US EPA has tested several long path instruments within their environmental technology verification program with good results.

The spectral evaluation used in this study is similar to many other studies since we rely on a software package widely used by the DOAS community (QDOAS) and we use published calibration reference data. The most important issue when it comes to quality assurance is to investigate the lineshape of the spectrometer and the wavelength calibration. During the campaign this was done by regular measurement with a low pressure Hg calibration lamp. The wavelength calibration was also corrected afterwards by comparing the measured spectra to a solar spectrum, and then shifting them accordingly to the difference. The quality of the data can be checked by investigating the spectral fitting parameters and in this way remove bad data.

A6 References

Bogumil, K. et al., 2003, Measurements of Molecular Absorption Spectra with the SCIAMACHY PreFlight Model: Instrument Caracterization and Reference Data for Atmospheric Remote-Sensing in the 230–2380 nm Region, J. Photoch. Photobio. A, 157, 167–184

Burrows, J.P et al., 1999, Atmospheric Remote-Sensing Reference Data from GOME: 2. Temperature-Dependent Absorption Cross Sections of O3 in the 231–794 nm Range, Journal of Quantitative Spectroscopy and Radiative Transfer 61, 509–517

Börjesson, G., J. Samuelsson, J. Chanton, R. Adolfsson, B. Galle, and B.H. Svensson. 2009. A national landfill methane budget for Sweden based on field measurements, and an evaluation of IPCC models. Tellus, 61B: 424–435.

Cantrell CA, Davidson JA, McDaniel AH, Shetter RE, Calvert JG. 1990, Temperature dependent formaldehyde cross sections in the near-ultraviolet spectral region. J Phys Chem, 94:3902–8.

De Gouw, J.A., et. al. (2009), Airborne Measurements of Ethene from Industrial Sources Using Laser Photo-Acoustic Spectroscopy, Environmental Science and Technology, 43, 2437–2442.

Doussin J. F.;Dominique R.; Patrick C., Applied Optics, 38 4145 (1999)

Eastern Research Group, Inc. 2010. Evaluation of Large Area Methane Emission Source Methods: Mobile and Stationary Plume Measurements Using the Tracer Correlation Approach. Final Report for U.S. EPA. May 30

EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux, December 2011, Office of Air Quality Planning and Standards , Air Quality Analysis Division Measurement Technology Group , Research Triangle, North Carolina, 27711, editor Dennis K. Mikael, http://www.epa.gov/ttn/emc/guidlnd/gd-052.pdf

Etzkorn, T., B. Klotz, S. Sørensen, I.V. Patroescu, I. Barnes, K.H. Becker, and U. Platt, "Gas-phase absorption cross sections of 24 monocyclic aromatic hydrocarbons in the UV and IR spectral ranges," Atmos. Environ. 33, 525-540 (1999).

Fally, S., M. Carleer, and A. C. Vandaele, "UV Fourier transform absorption cross sections of benzene, toluene, meta-, ortho-, and para-xylene", J. Quant. Spectrosc. Radiat. Transfer 110, 766-782 (2009).

Fayt, C. and Van Roozendael, M., 2001. QDOAS 1.00 Software User Manual, BIRA-IASB.

Fish, D.J. and Jones, R.L., 1995. Rotational Raman scattering and the ring effect in Zenith-sky spectra. Geophysical Research Letters, 22(7): 811–814.

Foy, B., ... Mellqvist, J., et al., Modeling constraints on the emission inventory and on vertical dispersion for CO and SO2 in the Mexico City Metropolitan Are using Solar FTIR and zenith sky UV spectroscopy, Atmos. Chem. Phys., 7, 781–801, 2007

Fransson, K., and J. Mellqvist, (2002), Measurements of VOCs at Refineries Using the Solar Occultation Flux Technique, Chalmers University of Technology, Göteborg, Sweden.

Galle, B.; Mellqvist, J., et al., Ground Based FTIR Measurements of Stratospheric Trace Species from Harestua, Norway during Sesame and Comparison with a 3-D Model, JAC, 1999, 32, no. 1, 147–164.

Galle, B., J. Samuelsson, B.H. Svensson, G. Börjesson, "Measurements of methane emissions from landfills using a time correlation tracer method based on FTIR absorption spectroscopy." Environ. Sci. Technol. 35: 21–25. 2001.

Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A.J.S., Edmonds, M. and Horrocks, L., (2002), A miniaturised ultraviolet spectrometer for remote sensing of SO_2 fluxes: A new tool for volcano surveillance, Journal of Volcanology and Geothermal Research, 119 241–254

Gratien, A. et al (2007), UV and IR Absorption Cross-sections of HCHO, HCDO, and DCDO, J. Phys. Chem. A, 111, 11506–1151

Griffith D.W.T., Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra. Applied Spectroscopy, 1996. 50(1): p. 59–70.

Heckel, A., A. Richter, T. Tarsu, F. Wittrock, C. Hak, I. Pundt, W. Junkermann, and J.P. Burrows, MAX-DOAS measurements of formaldehyde in the Po-Valley, Atmospheric Chemistry and Physics, 5, 909–918, 2005.

Hermans, C.et al., Absorption cross-sections of atmospheric constituents: NO_2, O_2, and H_2O, Environ. Sci. Pollut. R. , 6, 151–158, 1999.

Hurley, P.J., Physick W.L., and Luhar A.K., TAPM: A practical approach to prognostic meteorological and air pollution modelling. Environmental Modelling and Software, 2005. 20(6): p. 737.

Johansson, M., C. et al, 2009, Mobile mini-DOAS measurement of the outflow of NO_2 and HCHO from Mexico City, Atmos. Chem. Phys., 9, 5647–5653

Johansson, J., et al., 2013a, Quantitative Measurements and Modeling of Industrial Formaldehyde Emissions in the Greater Houston Area during Campaigns in 2009 and 2011, accepted by Journal of Geophysical

Research – Atmospheres, 2013JD020159R.

Johansson, J., et al., 2013b, Emission Measurements of Alkenes, Alkanes, SO_2 and NO_2 from Stationary Sources in Southeast Texas over a 5-year-period Using SOF and Mobile DOAS, which has been submitted for possible publication in Journal of Geophysical Research - Atmospheres. accepted by Journal of Geophysical Research – Atmospheres,, 2013JD020485.

Johansson, J., Mellqvist, J., et al., Quantification of industrial emissions of VOCs, NO2 and SO2 by SOF and Mobile DOAS during DISCOVER-AQ, AQRP project 13-0051, AQRP report, Dec 7 2013c

Kihlman, M. (2005a), Application of solar FTIR spectroscopy for quantifying gas emissions, Technical report No. 4L, ISSN 1652-9103, Department of Radio and Space Science, Chalmers University of Technology, Gothenburg, Sweden.

Kihlman, M., J. Mellqvist, and J. Samuelsson (2005b), Monitoring of VOC emissions from three refineries in Sweden and the Oil harbor of Göteborg using the Solar Occultation Flux method, Technical report, ISSN 1653 333X, Department of Radio and Space, Chalmers University of Technology, Gothenburg, Sweden.

S.-W. Kim,..Mellqvist, J., et al., Evaluations of NOx and highly reactive VOC emission inventories in Texas and their implications for ozone plume simulations during the Texas Air Quality Study 2006S, Atmos. Chem.Phys., 11, 11361–11386, 2011, www.atmos-chem-phys.net/11/11361/ 2011/doi:10.5194/acp-11-11361-2011

Mellqvist, J., Application of infrared and UV-visible remote sensing techniques for studying the stratosphere and for estimating anthropogenic emissions, doktorsavhandling, Chalmers tekniska högskola, Göteborg, Sweden, 1999a

Mellqvist, J och Galle, B., Utveckling av ett IR absorptionssystem användande solljus för mätning av diffusa kolväteemissioner, Rapport till Preems miljöstiftelse juli 1999b.

Mellqvist, J., Arlander, D. W., Galle, B. and Bergqvist, B., Measurements of Industrial Fugitive Emissions by the FTIR-Tracer Method (FTM), IVL report, 1995, B 1214.

Mellqvist, J., Flare testing using the SOF method at Borealis Polyethylene in the summer of 2000. 2001, Chalmers University of Technology. (Available at www.fluxsense.se)

Mellqvist, J., J. Samuelsson, C. Rivera, B. Lefer, and M. Patel (2007), Measurements of industrial emissions of VOCs, NH_3, NO_2 and SO_2 in Texas using the Solar Occultation Flux method and mobile DOAS, Project H053.2005, Texas Environmental Research Consortium., Texas. (http://www.harc.edu/projects/airquality/Projects/Projects/H053.2005)

Mellqvist, J.,Berg N. and Dan Ohlsson, 2008a, Remote surveillance of the sulfur content and NOx emissions of ships, Second international conference on Harbours, Air Quality and Climate Change (HAQCC), Rotterdam.

Mellqvist, J., Johansson, J.,Samuelsson, J., Rivera, C., Lefer, B. and S. Alvarez (2008b), Comparison of Solar Occultation Flux Measurements to the 2006 TCEQ Emission Inventory and Airborne Measurements for the TexAQS II, Project No. 582-5-64594-FY08-06 , TCEQ report., Texas. (available at http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/20081108-comparison_solar_occultation_flux_measurements.pdf)

Mellqvist, J., et al. (2009a), Emission Measurements of Volatile Organic Compounds with the SOF method in the Rotterdam Harbor 2008, available at www.fluxsense.se

Mellqvist, J., J. Samuelsson, J. Johansson, C. Rivera, B. Lefer, S. Alvarez, and J. Jolly (2010), Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method, J. Geophys. Res.,115, D00F17, doi:10.1029/2008JD011682.

Parrish, D.D., Ryerson, T.B., Mellqvist, J. et al., Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region, Atmos. Chem. Phys., 12, 3273-3288, 2012:

Platt, U., D. Perner, and H.W. Pätz, Simultaneous Measurement of Atmospheric CH_2O, O_3 and NO_2 by Differential Optical Absorption, Journal of Geophysical Research, 84 (C10), 6329–6335, 1979.

Rivera, C. et al., (2010), Quantification of NO_2 and SO_2 emissions from the Houston Ship Channel and Texas City during the 2006 Texas Air Quality Study, J. Geophys. Res., 115, D08301, doi:10.1029/2009JD012675

Rivera , C., Application of Passive DOAS using Scattered Sunlight for quantification of gas emission from anthropogenic and volcanic sources (2009a), Dissertation, ISBN 978-91-7385-317-0, ISSN 0346

Rivera, C., J.A. Garcia, B. Galle, L. Alonso, Y. Zhang, M. Johansson, M. Matabuena, and G. Gangoiti (2009b), Validation of optical remote sensing measurement strategies applied to industrial gas emissions, Int. J. Remote Sens., vol 30, no 12, p3191–3204.

Rivera, C., et al. (2009c),Tula industrial complex (Mexico) emissions of SO_2 and NO_2 during the MCMA 2006 field campaign using a mobile mini_DOAS system, Atmos. Chem. Phys., 9, 6351–6361, 2009.

Rothman et al. (2003), HITRAN 2000, Journal of Quantitative Spectroscopy and Radiative Transfer, vol. 82, pp. 5–44.

Samuelsson, J., Börjesson, G., Svensson, B., Galle, B., Metan från avfallsupplag i Sverige (Methane from landfills in Sweden), final report to the Swedish Energy Agency, projekt nr P10856-4, December 2005a. In Swedish (www.stem.se), can be ordered from Studsviksbiblioteket, 611 82 Nyköping, Sweden, www.lib.kth.se/SB/service/stemavf.html.

Samuelsson, J., et. al., VOC measurements of VOCs at Nynas Refinery in Nynäshamn 2005b *(Utsläppsmätningar av flyktiga organiska kolväten vid Nynas Raffinaderi i Nynäshamn 2005, in Swedish*), Bitumen refinery official report to provincial government 2005, Available at: http://www.fluxsense.se

Sharpe, S., et al. (2004), Gas-Phase Databases for Quantitative Infrared Spectroscopy, *Applied Optics*, *58*(12).

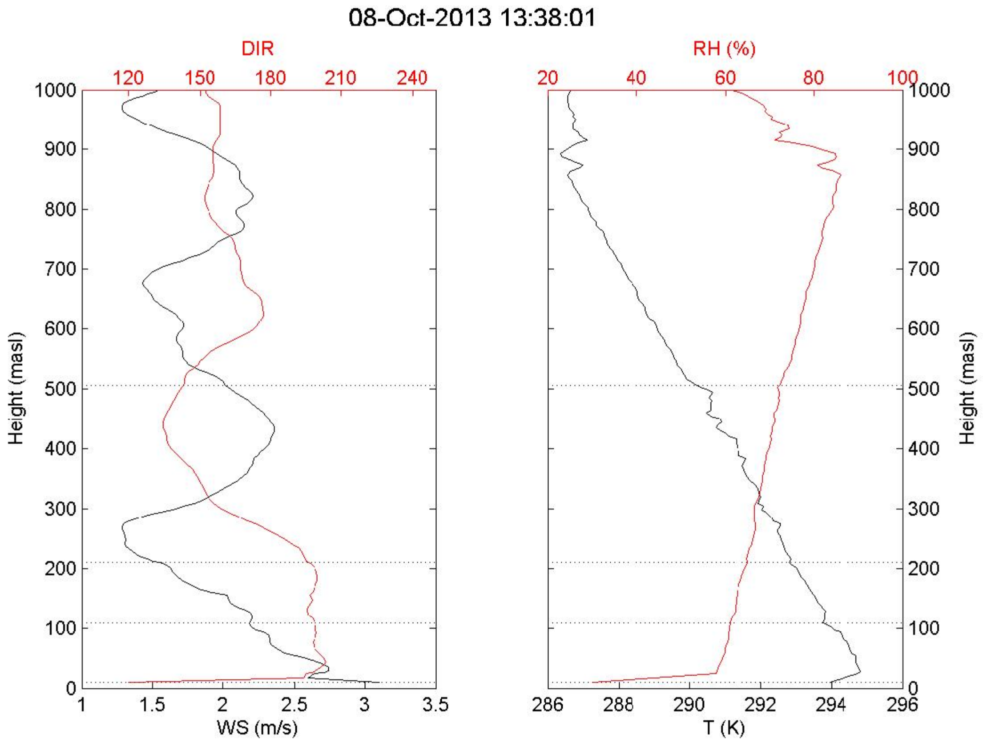
Thoma, E. et al. (2009), Development of EPA OTM 10 for Landfill Applications, in print, Journal of Environmental Engineering

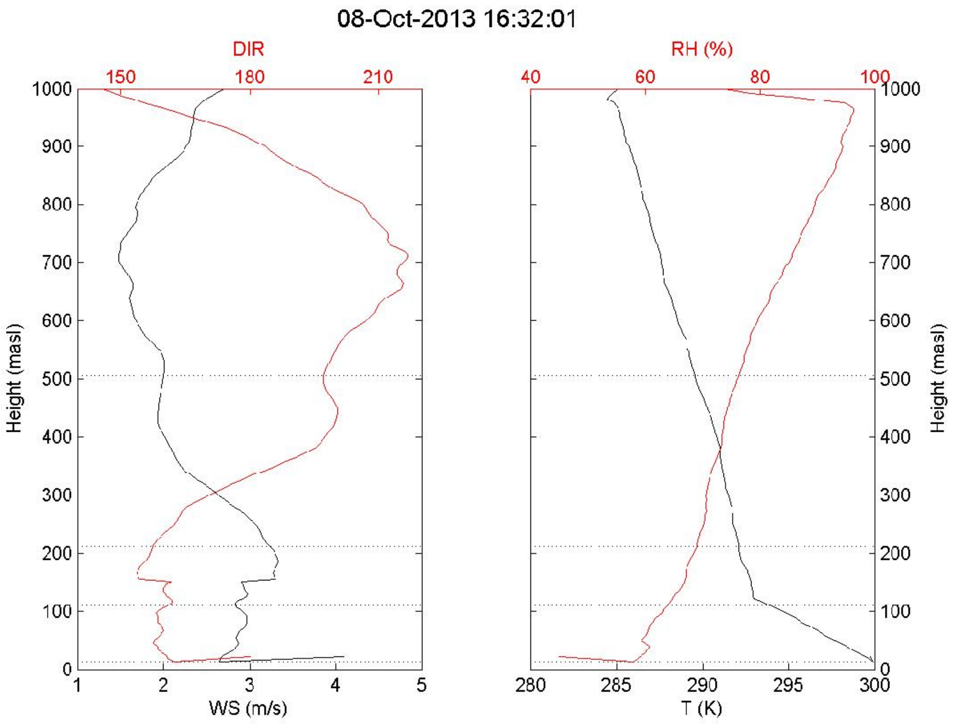
Vandaele A.C., C. Hermans, P.C. Simon, M. Carleer, R. Colin, S. Fally, M.F. Mérienne, A. Jenouvrier, and B. Coquart, Measurements of the NO_2 absorption cross-section from 42000 cm-1 to 10000 cm-1 (238–1000 nm) at 220 K and 294 K, J.Q.S.R.T., 59, 171–184 (1998)

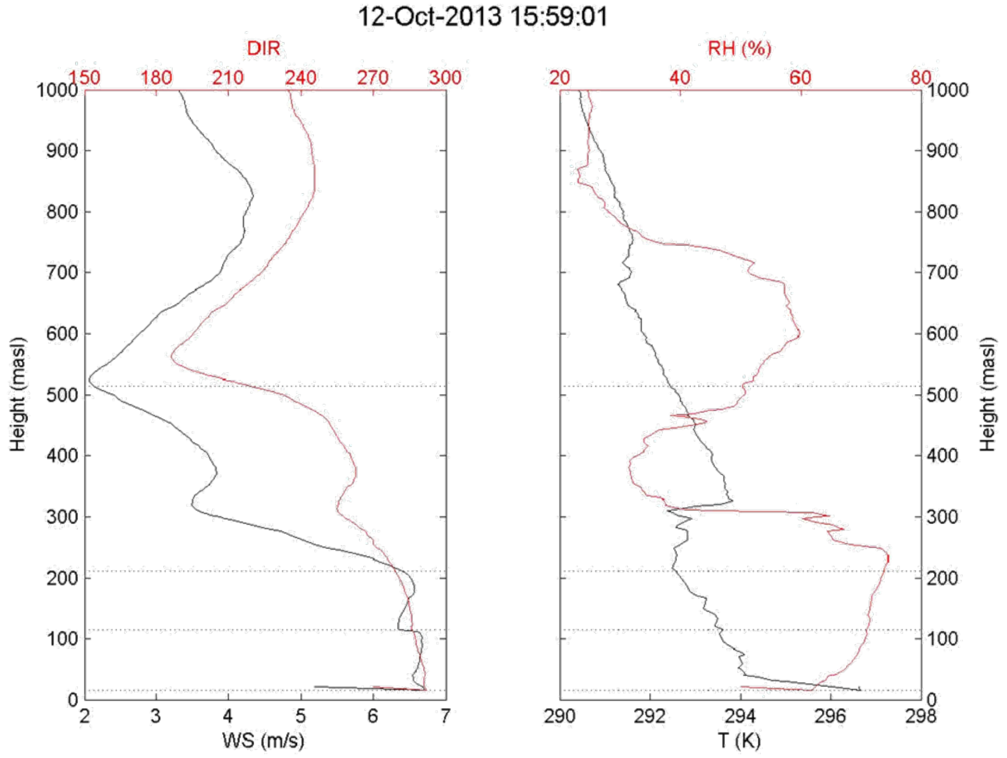
Walmsley, H. L., and S. J. O'Connor (1998), The accuracy and sensitivity of infrared differential absorption lidar measurements of hydrocarbon emissions from process units. *Pure Appl. Opt.*, *7*, 907–925.

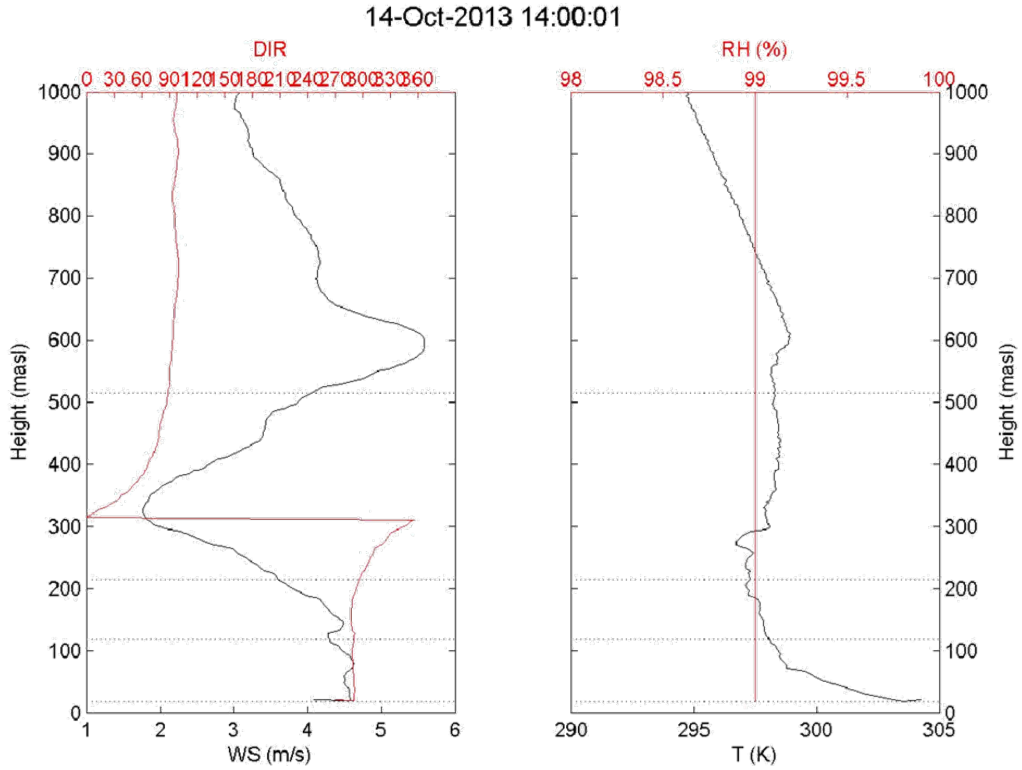
A7 Wind Data and Evaluation

A7.1 GPS wind sondes






12-Oct-2013 15:59:01
DIR
150 180 210 240 270 300
Height (masl)
1000 900 800 700 600 500 400 300 200 100 0
2 3 4 5 6 7
WS (m/s)
RH (%)
20 40 60 80
290 292 294 296 298
T (K)


14-Oct-2013 14:00:01
DIR
0 30 60 90 120 150 180 210 240 270 300 330 360
Height (masl)
1000 900 800 700 600 500 400 300 200 100 0
1 2 3 4 5 6
WS (m/s)
RH (%)
98 98.5 99 99.5 100
290 295 300 305
T (K)

A7.2 Mast Wind Comparison

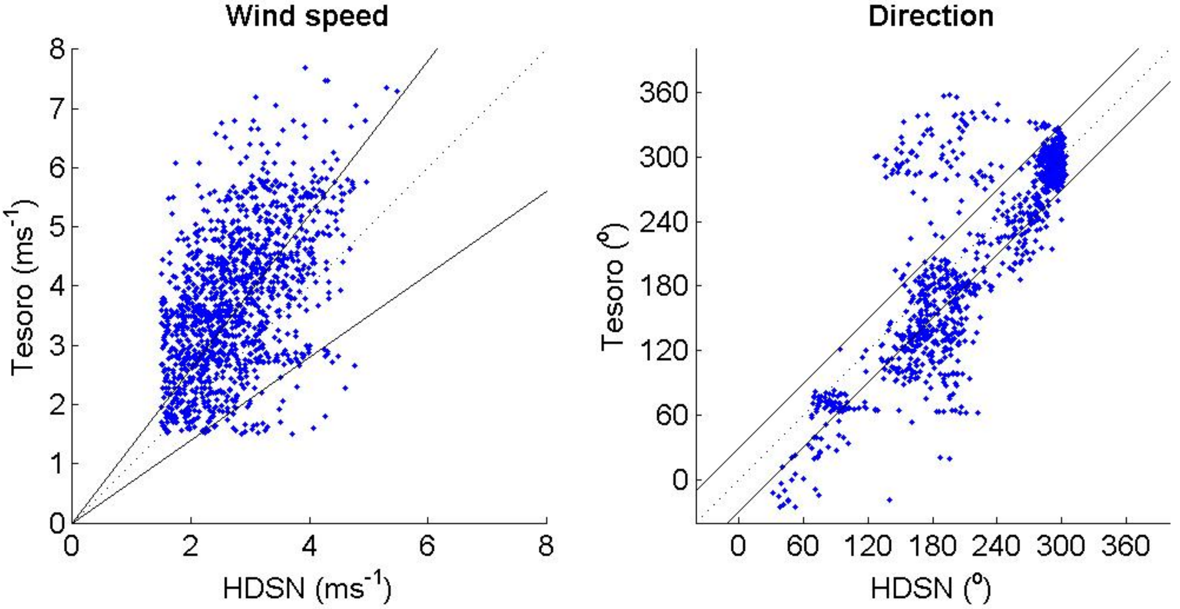


Figure A7.1 . Comparison of 5 minute winds from Tesoro Carson^0 and SCAQMD station HDSN limited to wind speeds greater than 1.5 m/s. Solid lines denote +/- 30 % or +/- 30 from the 1:1 (dashed) line for wind speed and direction, respectively.

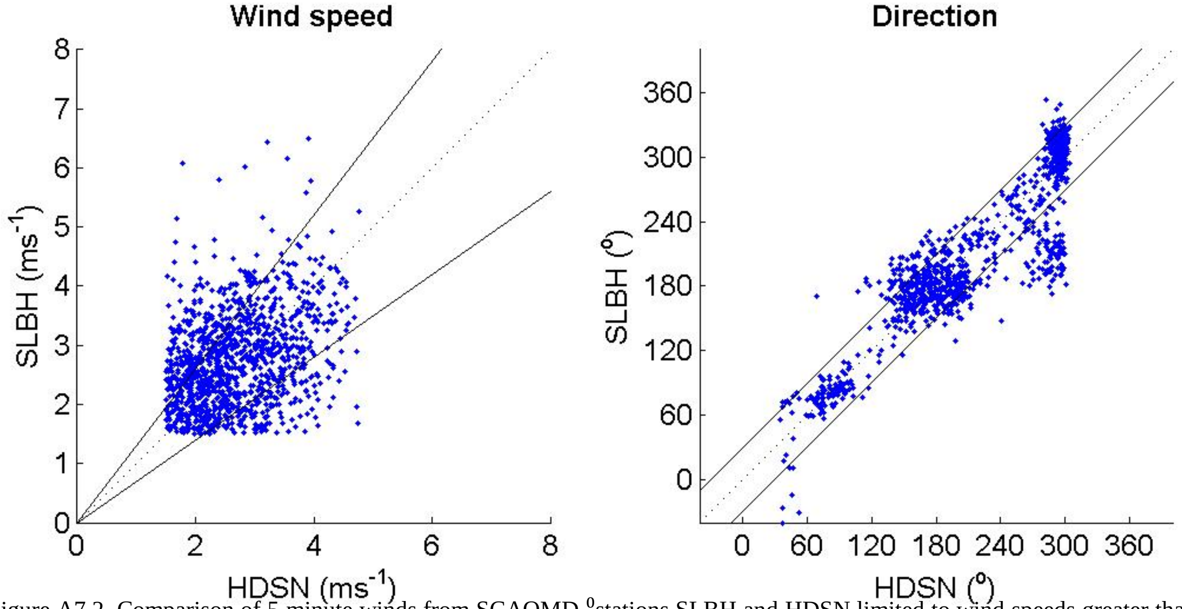


Figure A7.2. Comparison of 5 minute winds from SCAQMD ^{0}stations SLBH and HDSN limited to wind speeds greater than 1.5 m/s. Solid lines denote +/- 30 % or +/- 30 from the 1:1 (dashed) line for wind speed and direction, respectively.