

Paper A

Monitoring of VOC emissions from refineries in Sweden using the SOF method

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Manuscript

Monitoring of VOC emissions from refineries in Sweden using the Solar Occultation Flux method

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Short title: Mon. of VOCs from refineries using SOF

Abstract

A new spectroscopic technique for mobile gas flux measurements of VOCs, the Solar Occultation Flux method, has been further developed and successfully tested for its capability of conducting large scale monitoring of fugitive gas emissions from industries. During 2002-2004 three refineries and an oil harbour in Sweden were monitored. The measurement errors were, at good conditions, estimated to be around 25%, caused mainly by uncertainties of the wind field. The SOF instrument was tuned to detect alkanes, which contributes to the dominant fraction of the VOCs emitted from a refinery. Complimentary measurements were conducted to assess the emissions also of the aromatic species, typically 5-10% by mass of the alkanes. Each industry was divided into smaller sectors and the emission from each sector was determined as well as the total emission. With this method, it is possible to quickly scan through an industry and in real time detect leaks. For a typical refinery 0.06% of the mass of the crude oil is lost due to vaporization. Of the emitted gas 26% originates from the process, 31% from crude-oil tanks, 32% from product tanks, 8% from the water treatment facility and 2% from transport related activities.

Keywords: VOC, refinery, emission, SOF, solar occultation, FTIR

Introduction

Emission of volatile organic compounds (VOC) to air is a potential hazard for human health and the environment. The formation of ozone in the lower troposphere takes place through a photochemical reaction driven by VOCs and nitrogen oxides. The formed ozone is a powerful oxidant that causes inflammation of the respiratory tract and exacerbates existing lung disease [1], a serious health problem in many large cities of the world. Ozone in the lower troposphere also has negative impact on the vegetation [2] and contributes to global warming. In Europe, and other parts of the world, the levels of ozone exceed critical levels. Therefore a European protocol exists for abatement of ground level ozone by reducing VOCs and other compounds. (Convention on Long range transboundary pollution, UNECE).

The refineries are the single largest point sources of VOCs, and may contribute significantly to ozone formation on a regional scale. For instance, recent studies [3] have shown that the refineries in Houston may have a major impact on the ozone formation in Texas, although car traffic is the largest emission source of VOCs. In the Corinair 94 inventory [4], the emission of NMVOC from Swedish refineries and petrochemical industries was reported to 12 Kton/year, representing 3% of the anthropogenic emissions in Sweden. In Europe the emission from refineries and petrochemical industries are regulated by the authorities and control programs are required for reporting the VOC leakages.

A commonly used method to estimate the annual emissions from a refinery-process is the EPA method 21 [5]. The concentration of VOC is measured in a point close to valves, pumps and flanges etc. and the measured concentrations are used as screening values. These values are then incorporated into calculations that are based on the typical emission picture for that specific kind of equipment. The calculated emissions from all valves, pumps and flanges etc. on the whole refinery are then summed to estimate the total emission. The most widely used methods for estimations of the emissions of storage tanks and loading and unloading is the EPA AP42 model [6]. This method is completely based on calculations with equations derived from previous measurements on typical tanks where parameters related to the design of the tank, the product in the tank and the meteorological conditions at the site are considered. There are also examples [7,8] where concentration measurements have been done with GC combined with FID or MS. The prime interests in these studies were to identify what concentrations of VOC is expected in the neighborhood of a refinery and to identify the gas mixture of VOC that is emitted. Measurements on refineries have also been done with long-path systems, with FTIR [9,10] and UV-DOAS [8,11]. However, if the emitted amount of gas should be estimated with these methods, they must be complemented with a plume model.

Measurements with the DIAL method [12-14] provide a direct measure of the gas emission when combined with wind measurements. DIAL measurements have been performed both for the estimation of total emissions and to identify the emission from each sector inside a refinery. The measurements conducted in the past has shown that the emissions estimated by calculations were commonly underestimated with a factor 3 to 18 [15], hence indicating the need for more measurements. The DIAL method is however rather complex and expensive which has lead to little usage of this method during the more than 15 years it has been available for VOC flux measurements. In 1997 the development of a new method called SOF (Solar Occultation Flux) was started at

Chalmers University, as described in a parallel paper [16]. The SOF equipment can be placed inside a small car, making it possible to quickly scan through an industry and in real time detect leaks. Compared to DIAL the SOF method has better mobility and cost effectiveness, lower technical complexity, higher specificity and higher signal-to-noise making remote (far away) measurements possible. The weakness of the SOF-method is that the plume height is not determined and there is less possibility to separate emissions sources that are close to each other.

In this study the aim was to investigate whether the SOF method could be employed for large scale monitoring, and to understand the uncertainties involved in the measurements. This has included dedicated technical work building a new solar tracker and automation software for real time analysis that has proven vital for the ability to conduct measurements on larger scale. Results from an extensive monitoring project, denoted KORUS, are presented where the SOF method was applied during 3 years at three refineries and an oil harbour in Sweden. The results have contributed with information that is guiding when determining what actions should be taken to further reduce the emissions on the industries. A report with more details of the conducted measurements in the monitoring program has been published [17].

Methodology

The SOF method is thoroughly described in a separate paper [16]. It is based on recording broadband infrared spectra of the sun with a FTIR spectrometer that is connected to a solar-tracker, Figure 1. 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 (molecules/cm²) between the sun and the spectrometer. To obtain the gas emission from a source, the instrument is placed in a car and is driven in such way that the detected solar light cuts through the emission plume. To calculate the gas emission, the wind direction and speed is also required. The wind was measured from high masts and towers but also using an ultrasonic wind meter positioned on the car.

An additional point measuring FTIR has been utilized in order to obtain information about the plume height and to extend the number of compounds measured. This system has also been used for flux measurements using tracer gas [18].

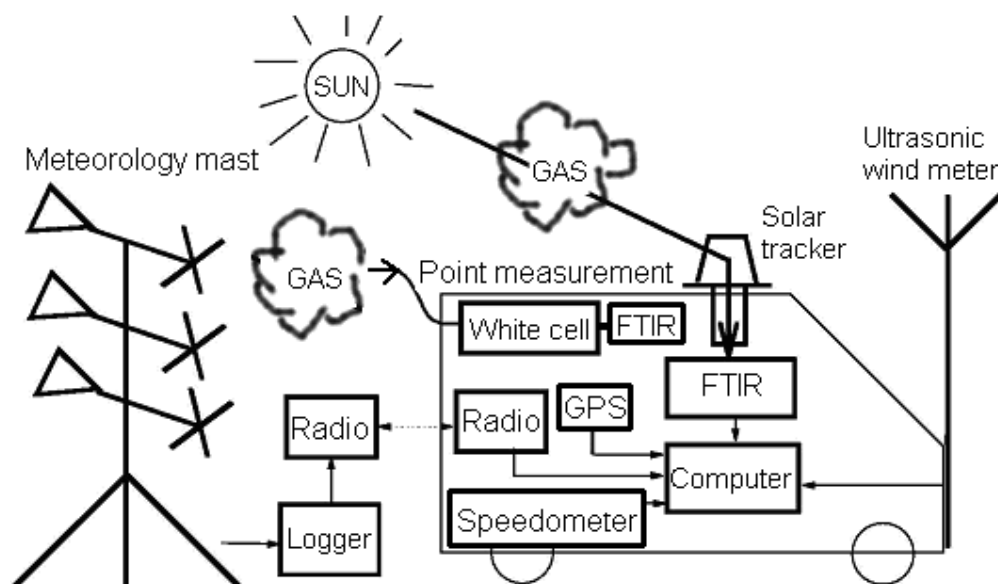


Figure 1. Schematic picture of the mobile measurement-system.

Spectroscopy

The VOCs leaking from refineries correspond mostly to alkanes. These compounds can be measured in the infrared region around 2950 cm^{-1} , using the vibration transition in the carbon and hydrogen bond (CH stretch). The absorption features of the alkanes are similar and interfere with each other. A study of the cross sensitivity of various compounds to butane was conducted by fitting absorbance spectra of butane to other compounds [17]. The results showed that alkanes (C3-C9), had cross sensitivities around one (0.7-1.6), while other compounds had considerably smaller cross sensitivities, around 0.03-0.27 for aromatics and 0.02-0.11 for olefines, respectively. The concentrations of these interfering compounds were then determined by sampling the hydrocarbon mixture in the plume from a crude oil tank. This was conducted by bag sampling followed by quantitative analysis by gas chromatography within 2 hours by an accredited laboratory. The mass fractions in the samples were 98.5% alkanes, 1.1% aromatic hydrocarbons and 0.5 % alkenes/alkynes. Taking the cross sensitivities and gas composition into account shows that interference from non-alkanes is of little importance when measuring on a refinery. It is also clear that the measurements in the CH stretch region within certain error bars, corresponds to the sum of the number of C-H bonds, independently of the assumption of alkanes in the mixture. Both these issues are further discussed in the error analysis section.

Even though the alkane spectra are similar, they are still significantly different so that molecular specificity can be partly obtained. If propane, butane and octane are simultaneously included in the spectral fitting, the average number of carbon atoms in the measured alkane can be calculated. In this study typical observed number of carbon atoms was 3.7 for crude-oil tanks, 4 for gasoline tanks, 6 for kerosene tanks, 5 for process and 6.5 for the water treatment facility. The simultaneous fitting of multiple reference spectra yields valuable information but it is done at the expense of more noise in the baseline. A two-step method has therefore been used that first evaluates the spectrum as butane only. If the evaluated butane concentration is higher than 12 mg/m^2 , a new

spectral evaluation is done with propane, butane and octane. The sum of the three is taken as the total concentration of alkanes and is sensitive to the presence of all alkanes since other alkanes have spectral absorption structures similar to these three. In addition to the alkanes, for which reference spectra from PNW database were used [19], synthesized spectra of H₂O, HDO and CH₄ were also included in the spectral fitting obtained by using line parameters in the HITRAN database [20]. The spectral retrieval was conducted in the interval 2725-3005 cm⁻¹ at 8 cm⁻¹ resolution.

To render the SOF method more effective, an on line software was developed to allow real time evaluation of alkanes when measuring gas emissions from the refineries. The program retrieves the line-integrated concentrations of the gases of interest from the spectra with a nonlinear algorithm [21]. It combines this with the position of the vehicle retrieved by GPS, and wind information from wind-meters and calculates the flux of gas through the surface that is sliced out along the path the vehicle is driving. It gives a graphical representation of the measured flux on a map while the measurement is running. The software was tailored to work with the Bruker OPAG and the Bruker IrCube spectrometers, and to do spectral evaluation with a resolution between 0.5 and 12 cm⁻¹. Two separate measurement systems were built with these two spectrometers.

Aromatic emissions

It is difficult to measure aromatic compounds using the SOF method. In order to be able to estimate emissions of the latter compounds an approach was adapted in which the ratios of aromatic hydrocarbons to alkanes was measured in different parts of the refinery such as in the plumes from the waste water treatment area, process area, and crude oil tanks. The aromatic compounds were sampled with TENAX® absorption tubes that were later analyzed with GC. The alkanes were measured by the point FTIR shown in Figure 1. The results showed that the average mass fraction of aromatic hydrocarbons were 3% in a crude-oil tank-park, 11% from a process, 14% from a product tank-park and 15% from a water treatment facility. Thus, most of the VOC emission on a refinery is in the form of alkanes. Aromatic emissions were later obtained by multiplying the aromatic/alkane ratios with the emission values of alkanes obtained from the SOF method.

Flux measurements of sub-sectors and total industry

The wind field inside an industry area is expected to be very complex since there are many large buildings that cause disturbances in the wind-field. It is therefore difficult to determine the wind field inside the industry area. When determining the total emission from a refinery it has therefore been done with measurements approximately 1 km away from the industry, where it is expected that the plume has risen to altitudes where the turbulence imposed by the structures and the ground has decreased. When measuring the emission far away, the errors induced by the variation in height of the wind-speed and direction will however be present. Total industry measurements are typically done over 3 hours and about 10 traverses can then be collected during good conditions. All traverses done in one day are averaged and are taken to represent the average emission that day. Figure 2 shows an example of how the measurement car was driven to measure the total emission from Refinery A. When conducting far away measurements the speed of the car

was 40 km/h, to minimize wind changes, and 10 km/h for close by measurements. Typically 16 spectra were coadded, yielding a sampling time of 3 s.

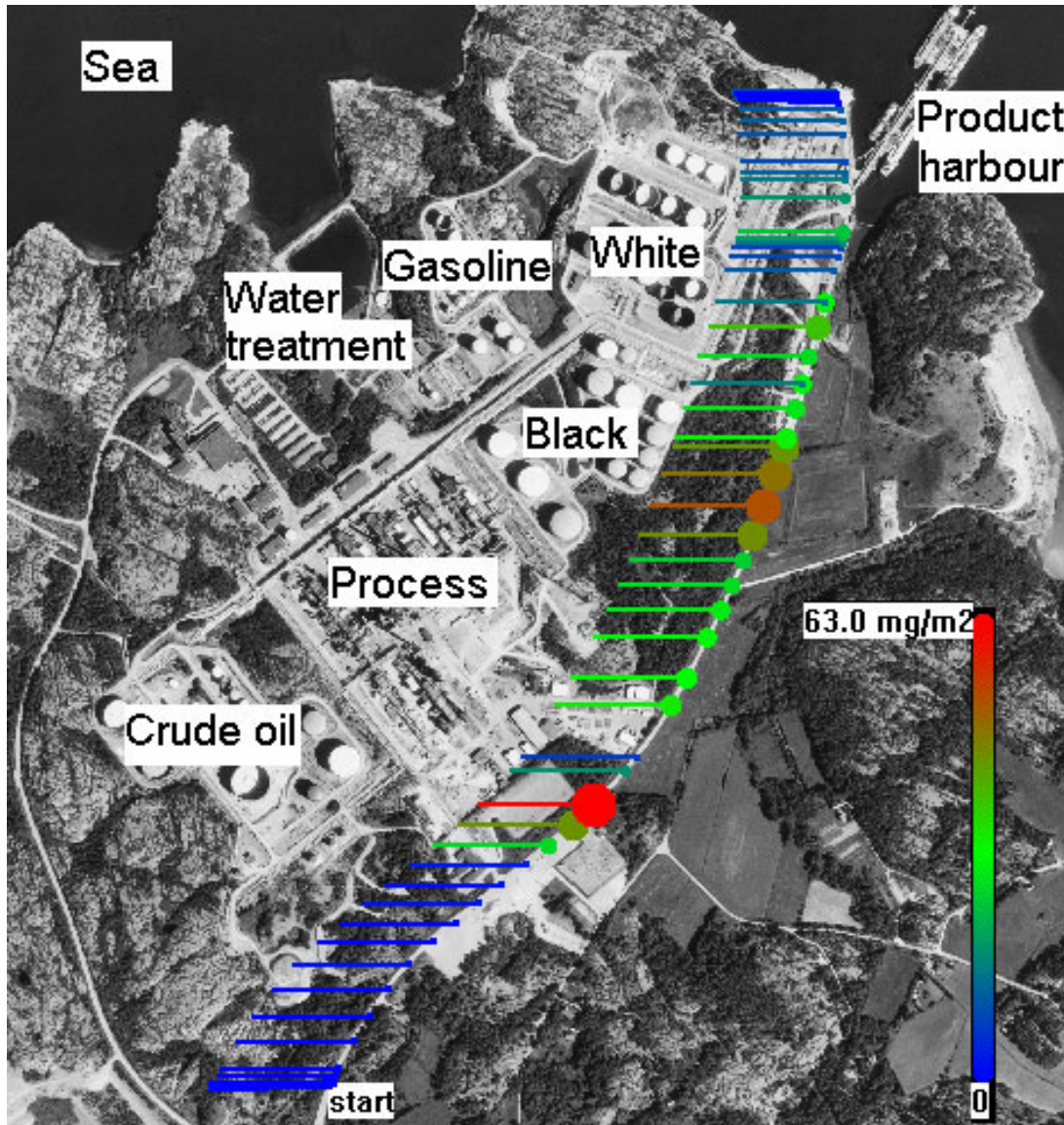


Figure 2. The figure shows how the measurement car was driven to do a total measurement on Refinery A. The car was driven along the road to the product harbour. The position of the car when the measurement of a new spectrum was started is indicated with dots with attached lines. The lines indicate the wind direction (they point towards a possible emission source). Dark dots indicates points where high line integrated concentrations have been measured. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

It is also of interest to know the emission of each sub-sector inside the industry and measurements inside the industry area are done to get the proportions of the emissions from each area. It is preferred that many sectors are measured within a limited time-period so that the meteorological conditions remain the same for the measurements on all sectors. The calculated emissions for the sub-sectors will typically be too high since the

wind-speed just behind a tank is lower than the average wind-field. However, the size proportions between the sub-sectors can be decided. The estimated emission for all sub-sectors are summed and a normalization factor is determined by dividing this sum with the total emission measured approximately 1 km away. The errors in the absolute emission on each sub-sector are then compensated by dividing the value with the normalization factor. With this approach, much less labor is required for the meteorological measurements since a few single wind-meters representing the average wind field can be used. These are typically permanently mounted in existing towers in the industry area or mobile masts.

The subsectors correspond to areas with similar products or processes and these were usually chosen by the industries themselves. However, there are limitations in how the sub-sectors can be chosen since it must be possible to drive between each sub sector in order to separate them and there must not be strong emission sources behind a weak source.

For Refinery A, the emissions were divided into nine sectors and the emission from each sector is shown in Table 1. Figure 3 shows how a measurement was done on a sub-sector, in this case the crude oil tank-park on Refinery A. The emissions have been further divided into individual tanks, when this was possible and of interest to the industries.

Table 1. Emissions of alkanes (kg/h) from the different sectors on Refinery A. First number in parenthesis indicates number of measurement days. Second number indicates total number of traverses the whole year.

Source	Year 2003		Year 2004	
Process	88	(1, 6)	85	(5, 17)
Crude-oil tank-park	209	(2, 25)	126	(6, 68)
Black components tank-park	124	(2, 8)	108	(2, 14)
White components tank-park	49	(3, 21)	36	(2, 19)
Gasoline components tank-park	27	(2, 24)	37	(5, 29)
Water treatment facility	12	(4, 22)	19	(2, 10)
Preskimmer	3.5	(2, 17)	14	(5, 32)
Rock cavern exhaust	8.0	(1, 4)	85	(3, 12)
Product harbour	27	(2, 17)	27*	
Total	550	(2, 22)	537	(5, 42)

* The product harbour was not measured 2004 and the same emission as 2003 was assumed.

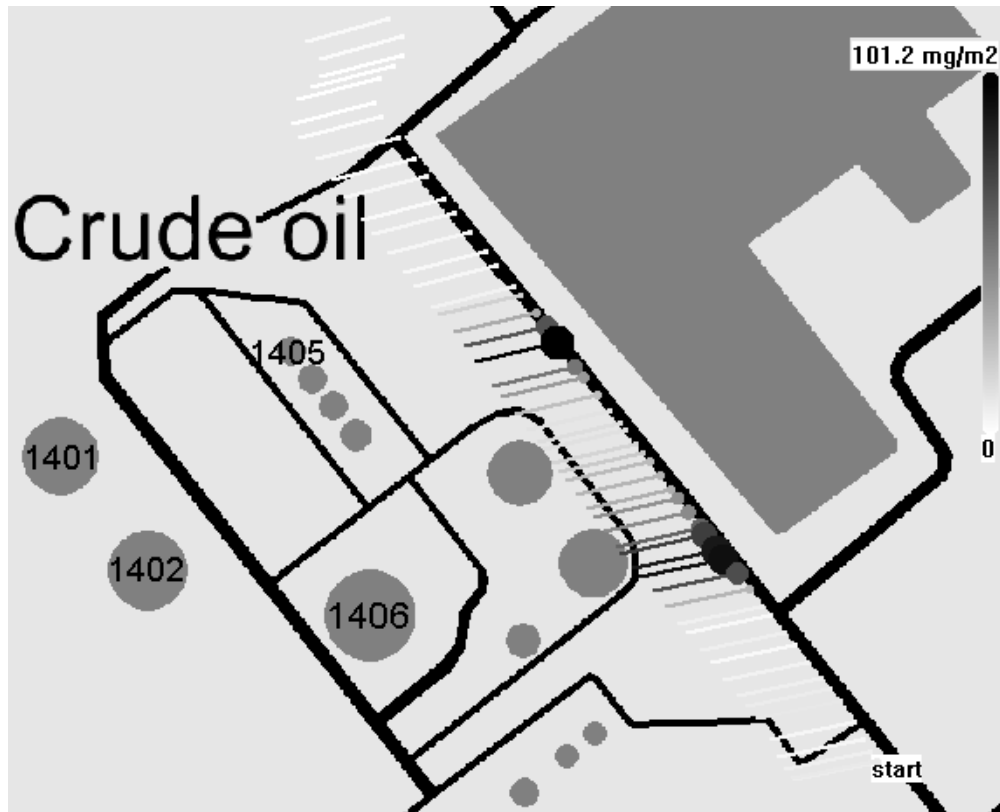


Figure 3. The figure shows how the measurement car was driven to measure the emission from the crude-oil tank-park on Refinery A.

Results

Continuous emissions

One aim of the measurements is to make an estimation of the total emission from a refinery during a whole year. Since total measurements have only been done on a few days within a time-span of a month, it must be assumed that the emissions on those days can represent the average emission for the whole year.

VOC emission from a refinery can be divided into continuous emissions and intermittent emissions caused by short-term activities. On many occasions when higher emissions than normal were observed it could be explained by short-term activities taking place and the measurements from that day were then discarded.

The best data produced from the industry monitoring project to estimate the variation of the continuous emission is five days of total measurements from Refinery A during July-September 2004. This data gives an average emission of 509.6 kg/h with a variance of 85.3 kg/h between the five days thus giving a standard deviation of 17% between days. It is possible that some of this variation is due to errors in the measurements but it is still safe to assume that the true variation in the total emission has a standard deviation of less than 17% between days for this case. With this approach, variations in the wind were partly captured which may have an impact on the emissions. However, the effect of the annual variation in the temperature was not captured.

Intermittent emissions

Intermittent emissions were more frequently observed at the oil harbour than at the refineries. The reason is that more than ten different companies are working independently with activities in the area that temporarily causes emissions, such as loading of trucks and ships, filling of caverns, and cleaning of tanks and pipes. An example of measurements during an intermittent emission in the oil harbour is shown in Figure 4, illustrating both a strong short-term emission and how the emission returns to the average emission. On several occasions high emissions were found which originated from loading of ships. When ships are loading low volatile products (class II and III) in the harbour this is generally done without vapor recovery unit. High emissions from such loading were found on cases where the ships had previous loads with high volatile products (class I). The reason is probably that the old volatile load was pushed out when the ship was refilled with a low volatile product. Emissions were varying between 10-300 kg/h. Measurements over a full loading cycle are needed to more accurately determine the average emission. There is a potential error source in that one may fail to detect a situation as intermittent, and the estimation of continuous emission will then be too high.

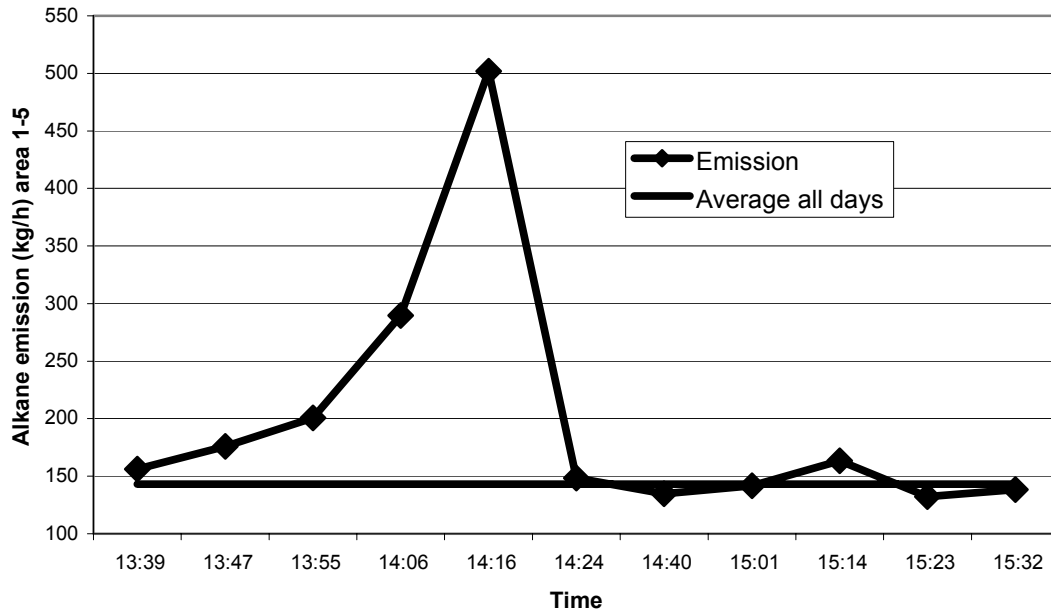


Figure 4. Measured emission of alkanes from an oil harbour. The emission values gradually increased with a peak around 14:10 and then stabilized close to the continuous emission average of 143 kg/h. The reason for the peak in the emission is either loading of a ship with gas-oil or filling of a tank, both finishing at around 14:00.

When short-term emissions were discovered, some sporadic tests were done afterwards to try to identify how big the emissions are in comparison to the continuous emissions. It has however become clear that a thorough study of this issue requires much more time and effort than what was available. Some calculations of the contribution of short-term activity are shown in Table 2. All examples are based on measured emissions, the frequency of each short-term activity has been based on statistics but the duration of the short-term emissions have been guessed.

Table 2. Calculated examples of the relevance of intermittent emissions compared to the continuous emission, based on the measurements and the here given assumptions.

Assumptions	Intermittent emission compared to continuous emission
Cleaning activities causing emissions of 100 kg/h during 2 h every day at the oil harbour.	(73 ton of total 1600) 5%
Loading of ships in the oil harbour causing emissions of 100 kg/h for 12 h every third day.	(146 ton of total 1600) 10%
Rock cavity in the oil harbour is filled causing emission of 149 kg/h and is done 3 times a year during 48 hours.	(21 ton of total 1600) 1%
Cleaning a tank at Refinery B causing emission of 70 kg/h for 12 h and is done 11 times during a year.	(9 ton of total 146) 6%

General results from 3 years of monitoring

From the collected data some general statements of the VOC emissions from the four studied industries can be done. The alkane emission was divided into five groups and compared between the industries. Table 3 shows the emission from these five groups and also the total emissions of alkanes measured on the four industries. The annual throughput of refined crude oil is 10 Mton/y for Refinery A, 5 Mton/y for Refinery B and 3 Mton/y for Refinery C. Reflecting this, the emissions have been normalized to annual throughput in Table 4 to give the emission in each sector as ton alkanes per Mton refined crude oil.

Table 3. Summary of the measured emissions of alkanes from the four industries. First number in parenthesis indicates number of measurement days. Second number indicates total number of traverses.

Emission each year (ton/y)	Refinery A	Refinery B	Refinery C	Oil Harbour
Total 2002	-	-	3464 (3, 13)	-
Total 2003	4818 (2, 22)	3051 (4, 19)	2014 (5, 27)	1771 (2, 11)
Total 2004	4704 (5, 42)	1070 (3, 18)	2683 (6, 38)	1788 (4, 15)

Averages all years (ton/y)				
Total	4760 (7, 64)	2060 (7, 37)	2720 (14, 78)	1780 (6, 26)
Process	760 (6, 23)	930 (12, 140)	610 (7, 54)	0
Crude-oil tanks	1470 (8, 93)	410 (9, 61)	1000 (10, 66)	0
Product-tanks	2080 (16, 115)	260 (7, 39)	940 (14, 78)	1115 (6, 26)
Water treatment Facility	140 (6, 32)	390 (7, 37)	160 (7, 91)	0
Transport related activity	240 (2, 17)	80 (3, 11)	0 ⁽¹⁾	665 (12, 60)

(1) Transport to/from Refinery C is only done through pipelines to the oil harbour

Table 4. Normalized alkane emission in ton per megaton refined crude oil.

	Refinery A	Refinery B	Refinery C	Average
Process	76	186	203	155 (26%)
Crude-oil tanks	147	82	333	187 (31%)
Product tanks	208	52	310	190 (32%)
Water treatment facility	14	78	53	48 (8%)
Transport related activity	24	16	0	13 (2%)

Total (ton/Mton)	476	412	907	598
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Thus for a typical refinery, about 0.06% (598 ton/Mton) of the mass of the crude oil is lost due to vaporization to the atmosphere. Of the emitted gas, 26% originates from the process, 31% from crude-oil tanks, 32% from product tanks, 8% from the water treatment facility and 2% from transport related activities. As transport related activity was counted loading/unloading to/from ships and trucks inside the industry areas. Transport related activities are typically intermittent and are therefore difficult to quantify. Therefore, this value has a high uncertainty.

Figure 5 shows the measured daily averaged total emission from each industry. The emissions from Refinery B were substantial during the early part of 2003, probably caused by leaks that emerged in an isomerisation process area during a complete maintenance stop conducted 2 weeks prior to the first SOF measurements. The emissions were reduced after having conducted several documented repairs of the process equipment. In 2004 the emission decreased even more, probably caused by a tenfold of documented repairs in the main process area. The measurements showed that the emission picture returned to normal within less than a year and that measuring every year yields valuable information. The relatively low cost of the method motivates annual routine measurements in order for rapid assessment of new leaks and better control of the plant. The apparent low variability in the Oil harbour is a result of that days with unusually high emissions has been discarded and treated as intermittent activity.

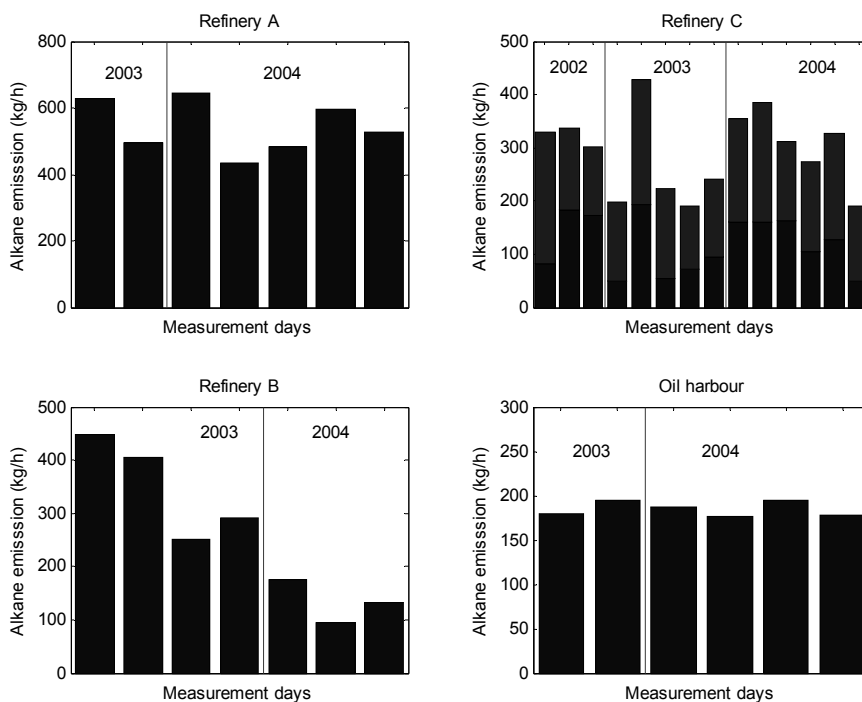


Figure 5. The figure shows the measured daily averaged total emission on each industry.

Discussion

The SOF method is based on two parts, mobile spectroscopic measurements and measurements of the wind at the plume height. Both parts cause uncertainties in the flux values and this will be further discussed here.

Plume height determination

The plume height cannot be determined by the SOF method. Since the wind should be measured at the plume height to determine the gas emission rate, this must therefore be assumed and can thus cause errors if done incorrectly. In order to get more height information the point measuring system shown in Figure 1 was applied. With this system it was possible to obtain the ratio between the alkane concentration on the ground and the alkane column measured in the solar beam with the SOF. In general the plume from the process areas seems to raise very quickly, since little gas was found at ground level, while the plumes from a tank park seems to be well mixed from tank height (25 m) to the ground. In order to quantify this better an experiment was done to determine the plume height from a refinery process and a product tank park. Air was sucked in through a long teflon tube connected to a point measurement system located in the car and the tube end was lifted between the ground and 50 m height. The expected center of emission was located 250 m from the measurement point both for the process and product tank park. The local wind direction determined if a measurement was done on the process or the tank park. Figure 6 shows the distribution of all measurements and the average profile. This indicates that the tank park plume is located close to ground and the concentration decreases at 50 m. The center of the plume is located at approximately 25 m. From the process there is zero concentration on ground and the plume starts at 25 m. The center of the plume is probably located well above 50 m but measurements higher up is required to actually tell.

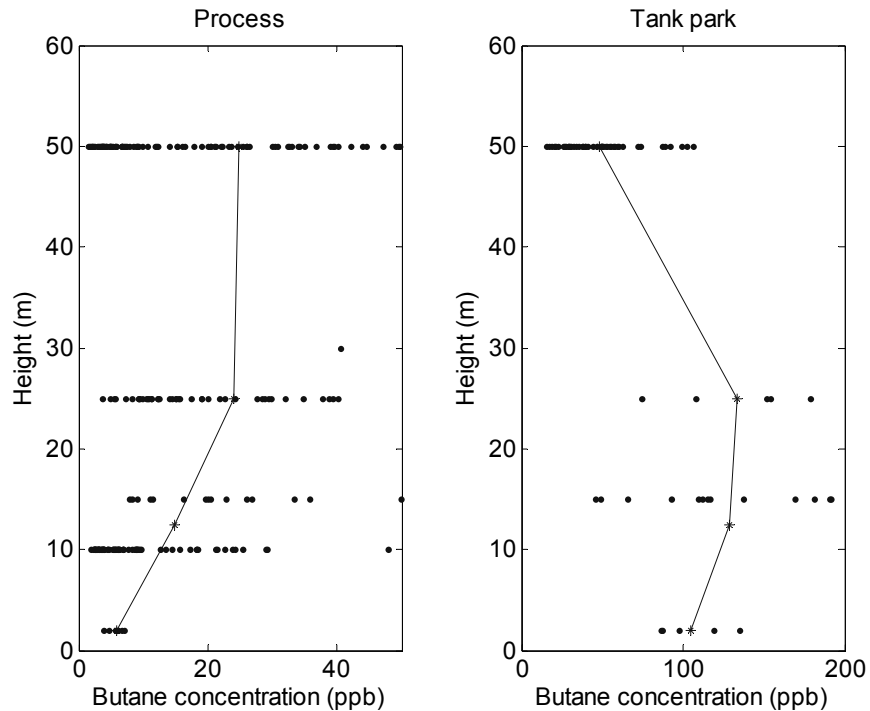


Figure 6. The dots indicate the concentration measurements. The lines indicate the average concentration profile.

In Figure 7 results from a plume height experiment is shown in which simultaneous measurements with the SOF and the point measuring system were conducted downwind a crude oil tank. The points with maximum concentrations were measured to 370 mg/m^2 and 3 mg/m^3 in the SOF and point measurement respectively. Assuming a constant concentration from ground and up, this gives a path-length of around 120 m. By taking into account the slant column to the sun, the height of the column is halved to 60 m. Note that the positions do not coincide due to the slant angle of the SOF measurements and a time delay in the point measuring system.

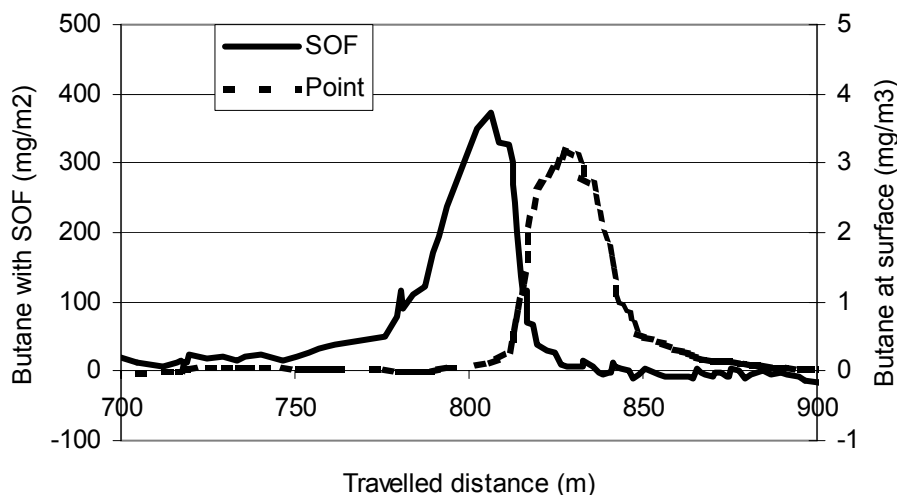


Figure 7. Simultaneous measurement with the SOF (left peak) and the point measurement at the surface (right peak) close to a crude oil tank.

Spectral evaluation errors

The error in the spectral evaluation of a typical VOC gas-mixture was determined by a simulation, by creating a synthetic spectrum at 8 cm^{-1} resolution that included absorption of the alkanes given in Table 6, superimposed on a real measured solar spectrum. The concentrations of the alkanes correspond to the ones measured by bag-samples in the crude-oil tank-park on Refinery C. Reference spectrum for Propane and n-Butane were taken from the QASoft database [22] and the other spectra were taken from the PNW database [19]. The total amount of alkanes in the synthetic spectrum was then obtained by simultaneous fitting of 3 compounds: propane, n-butane and octane.

The spectral fitting of n-Butane represents compounds with similar absorption structures as n-Butane (iso-Butane, n-Pentane, iso-Pentane and to some degree n-Hexane). The spectral fitting of n-Octane represents compounds having similar broad absorption structures as n-Octane (n-Heptane, Cyclohexane, 2-Methylpentane, 3-Methylpentane and to some degree n-Hexane).

As can be seen in Table 5, the spectral evaluation overestimates the total simulated alkane-concentration with 10%, for this typical crude oil gas-mixture. We assume that the overall uncertainty in the total alkane estimation at a refinery is of the same size. There is also an uncertainty in the spectral cross sections used that contributes with an error of 10%.

Table 5. Concentration of alkanes in the error simulation. Here 3 compounds, propane, n-butane and octane were fitted simultaneously to a synthetic spectrum corresponding to the concentration in the left column.

Alkane compound	Simulated concentration (mg/m ²)	Evaluated concentration (mg/m ²)	
Ethane	18		
Propane	72	97	
n-Butane	50	115	
Iso-Butane	21		
n-Pentane	19		
Iso-Pentane	17		
n-Hexane	4.0		
2-Methylpentane	3.6	19	
3-Methylpentane	1.7		
Cyclohexane	1.6		
n-Heptane	1.1		
n-Octane	0.24		
Total:	210		231

When conducting SOF measurements, the flux is obtained by adding all columns above the baseline of the traverses. The baseline is the registered concentration at a position with zero alkane concentration. If the baseline drifts around, which was the case in many earlier measurements, it will cause an error. The drift in the baseline occurs if the tilt of the incoming light into the spectrometer is changed during a traverse. This will occur if the solar-tracker is misaligned causing the output angle to wobble around at different viewing directions. Baseline drift is also caused by temperature variations in the transmittance properties of the optical filters if this is used. The size of this effect is dependent on the spectral characteristics of the filter and can be partly compensated for in the software.

In the monitoring project, traverses with a baseline error of more than 3 mg/m² were manually rejected and this gives an upper limit for the error of 30%. It is here assumed that the error is Gaussian distributed and will thus decrease when taking average of many traverses in the same day. Typically, 10 traverses are averaged and the error for the average due to baseline errors will then reduce to $9.5\% = 30\% / \sqrt{10}$. The uncertainties caused by baseline drift are applicable for the results here, but today this problem has been minimized.

Errors in the retrieved flux due to wind properties

Calculation of emission relies on information of how the wind varies over the whole surface where the gas is measured. Since this information is not possible to completely retrieve, errors in the calculated emission will be induced. In the monitoring project, wind information was typically taken from a wind meter located 25 m above ground recording averages of wind speed and direction every 30 seconds. Since there are variations both in wind speed and direction with height, there is a discrepancy between the wind at the position of the plume and the wind measured at 25 m. This error is difficult to determine since the height of the plume cannot be determined by the gas measurements.

A study of the errors due to the wind was made by looking at the variation in a dataset retrieved by a simulation of the micrometeorology model TAPM [23]. Simulations were done for the time-span from 1st August to 30th September 2001 for three selected positions of relevance for the monitoring project. The used data from the simulation consists of wind speed and wind direction for every hour at 16 different altitudes between 10 and 1000 m and also the solar radiation at the surface.

For simulating the error of a typical total measurement of an industry, a case is simulated where a process and a tank-park is assumed to emit the same amount of VOC. It is assumed that the plume from the tank-park is equally distributed from the ground to 100 m above. It is further assumed that the plume from the process is equally distributed between 100 and 300 m above ground. The wind data from all hours between 9 and 17 on days with high-sun radiation and with a wind speed of 3-6 m/s at an altitude of 25 m are then selected. There are valid wind data on 25 days that fulfilled these criteria. Figure 8 shows the average wind profile retrieved by the filtered data. The error bars show the standard deviation between daily averages.

The selected wind data is then combined with the height distributions of the VOCs in the process plume and the tank-park plume and a combined height distribution curve is finally calculated. The average of the distributions and the variance is shown in Table 6 and corresponds to the overestimation done when calculating the emission. The error due to wind velocity and direction is individually presented as well as the combined error due to both. For the error in wind direction, it is assumed that the car is driven at an angle of 45° to the wind direction and always in the direction that causes an underestimation and this represents an upper limit on the expected error. The overestimation for the tank-park and the process are given individually as well as the case where the two emission sources are both considered.

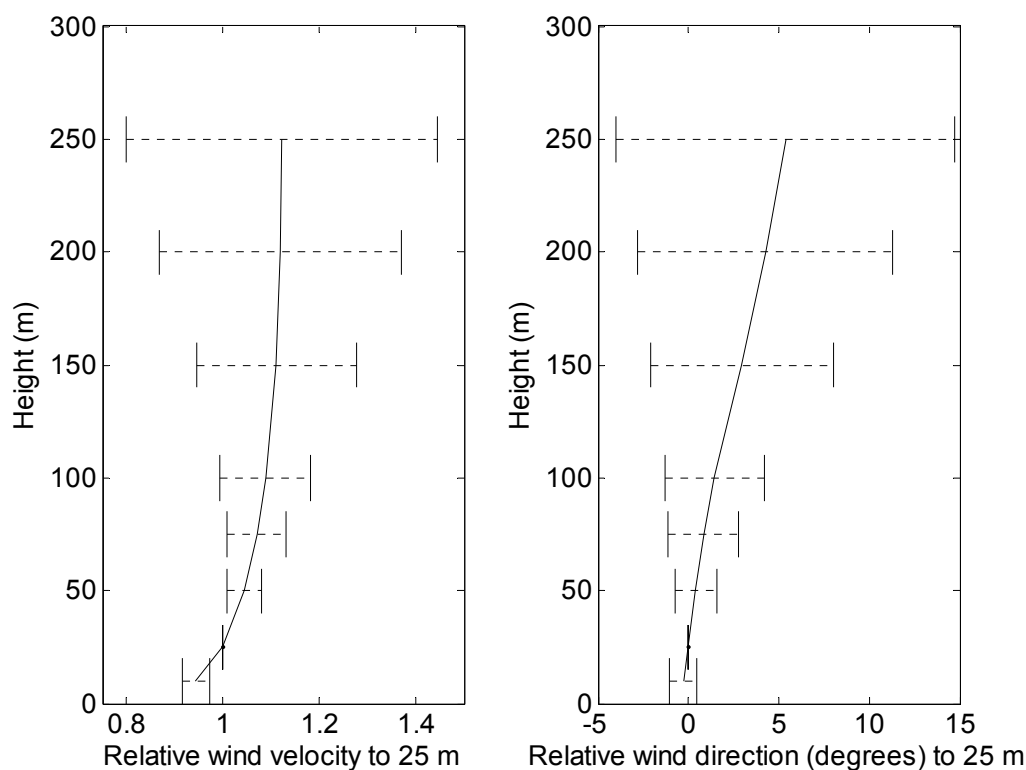


Figure 8. The figure shows the wind velocity and wind direction profile retrieved by simulation and averaged over daytime all sunny days with a wind-speed of 3-6 m/s at ground. The error bars indicate standard deviation between daily averages.

Table 6. Error factors in the retrieved flux due to wind variations with height.

	Factor due to wind velocity	Factor due to wind direction	Combined factor due to wind velocity and direction
Tank-park (0-100 m)	0.97±0.06	0.98±0.02	0.95±0.07
Process (100-300 m)	0.92±0.18	0.85±0.11	0.80±0.23
50% tank-park 50% process	0.95±0.13	0.91±0.07	0.86±0.15

For determining the total error in the yearly estimate from a refinery, the case that is bolded in Table 6 is used. Thus the systematic error is expected to be -14% and the standard deviation between days 15%.

Conclusion on total error

The total error is calculated by taking into account the three systematic errors: the error in the spectral evaluation of alkane, the error in spectral cross section and error due to the wind, and the three temporarily errors that occur due to variation between days: true variation, baseline error and variation due to wind. Measurements are typically done on four days and the total error in the estimate of yearly emission will then be 19%, obtained

as the square root sum of the quadratic errors. Measurements will however on average be underestimated with a factor 14% due to the systematic error in the wind.

The measurements on sub-sectors of the industry, for example on a crude oil tank are typically conducted over four individual days but a higher true variation between days is also expected from a single crude oil tank. Due to the complexity of the wind-situation close to the ground, the errors in the measurements of the wind are expected to be high. Assuming a systematic error of 25% and a standard deviation of 50% due to the wind and a variation in the true emission of 40% between days, the error for a tank measurement will be 35%. For close by measurements of tanks this uncertainty is probably low, as has been shown elsewhere by tracer experiments [16, 21].

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