

# Monitoring of VOC emissions from Refineries and Storage Depots using the Solar Occultation Flux method

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## **Abstract**

A new remote sensing method named SOF (Solar Occultation Flux) has been developed since 1997 and applied to locate and quantify fugitive hydrocarbon emissions from industry. The method is based on measuring infrared intensity spectra of the sun from a moving platform, a vehicle or ship. In order to obtain the flux from a particular emission source, the vehicle is driven in such a way that the detected solar light traverses across the actual emission plume. The flux is then obtained as the integrated sum of the retrieved path averaged concentrations, multiplied by the wind speed. With this method, it is possible to quickly scan through an industry and in real time detect leaks, in addition to estimating the total emissions.

The retrieval code has been tested and compared to other published codes for alkanes, HCl and SO<sub>2</sub>, with generally good agreement. Results from a validation experiment utilizing SF<sub>6</sub> trace gas shows that if averaging enough data, 10 traverses, accuracies of 10-20% are obtained from simple emissions sources. Another tracer experiment, simulating emission from a crude oil tank showed an error of 50% when measuring in the *near field* where meteorological disturbances are caused by the tanks. An error analysis using a meteorological model shows that the uncertainties are around 25%, at good conditions. This is caused mainly by uncertainties of the wind field. Strengths of the SOF method includes: mobility, cost effectiveness, specificity of average mass and high signal-to-noise, making far away measurements possible. Weaknesses is that the plume height can not be measured causing uncertainties in the estimated wind and consequently in the derived flux value. Another disadvantage is that it is difficult to conduct measurements during the winter due to the lack of solar light, making the annual estimation uncertain for sources that are dependent on the ambient temperature.

This report describes the results of a measurement project KORUS (Kolvätemätning vid raffinaderier utnyttjande SOF) conducted between 2002 and 2005 with the aim of quantifying the emission of volatile organic compounds (VOC) from four industries, i.e. Preemraff-Göteborg, Preemraff-Lysekil, Shellraff-Göteborg and Oljehamnen-Göteborg. Here the SOF method, has been further developed and successfully tested for its capability of conducting large scale monitoring of fugitive gas emissions from the industry. Each industry was divided into smaller sectors and the emission from each sector was determined as well as the total emission. The total emissions were measured *far away* at distance of 0.5-2 km from the industry, to make most of the plume raise above the first 30-50 m, in which the wind is usually disturbed due to buildings and other structures. In addition, *near field* measurements were conducted inside the industrial sites to assess the leakages but since the wind was very disturbed here all values were rescaled, to add up to the total emission value. In this manner it was possible to obtain VOC leakage rates from process areas, product storage tank areas, crude oil tank areas, water treatment, loading of ships and trucks, cleaning and repair of tanks and leaks and flares.

The SOF instrument was tuned to detect alkanes, which contributes to the dominant fraction of the VOCs emitted from a refinery as measured by independent extractive measurements. Complimentary measurements were conducted to assess the emissions also of the aromatic species, typically 5-10% by mass of the alkanes.

The total emissions from the sites showed different behavior over several years. The Preem refinery at Lysekil and Göteborg showed variabilities within 20-30% while the Shell refinery showed a factor of 4 decrease in the emissions. The oil harbor often showed large temporal variability due to ship and truck loading and various cleaning activities. It was therefore difficult to get a good feeling for the continuous emissions. 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, Solar Occultation, FTIR



<b>1 Introduction</b> .....	<b>7</b>
<b>2 Method</b> .....	<b>7</b>
<b>2.1 Line integrated concentration</b> .....	<b>8</b>
<b>2.2 Flux calculation</b> .....	<b>8</b>
<b>3 Spectroscopy</b> .....	<b>13</b>
<b>3.1 Determination of the VOC compounds in the gas mixture</b> .....	<b>14</b>
<b>3.2 Spectroscopy with the QESOF software</b> .....	<b>16</b>
<b>3.3 Discussion about average carbon number</b> .....	<b>17</b>
<b>4 Validation using tracer releases</b> .....	<b>19</b>
<b>5 Sub-sector and total industry measurements</b> .....	<b>23</b>
<b>6 Error estimation</b> .....	<b>25</b>
<b>6.1 Errors due to limitation in measurement time</b> .....	<b>25</b>
<b>6.2 Spectral evaluation errors</b> .....	<b>27</b>
<b>6.3 Errors in the retrieved flux due to wind properties</b> .....	<b>28</b>
<b>6.4 Conclusion about total errors</b> .....	<b>31</b>
<b>7 Results</b> .....	<b>33</b>
<b>7.1 Measurements on Preemraff-Göteborg</b> .....	<b>33</b>
7.1.1 Applied wind information.....	33
7.1.2 Crude-oil tank-park.....	36
7.1.3 East area .....	38
7.1.4 Process .....	39
7.1.5 Water treatment.....	41
7.1.6 Product tank-park.....	43
7.1.7 Measurements of aromatic hydrocarbons on Preemraff-Göteborg.....	45
<b>7.2 Measurements on Preemraff-Lysekil</b> .....	<b>47</b>
7.2.1 Applied wind information.....	47
7.2.2 Crude-oil tank-park.....	49
7.2.3 Process .....	53
7.2.4 Water treatment facility .....	56
7.2.5 Preskimmer .....	56
7.2.6 Rock cavern exhaust .....	58
7.2.7 Product harbor.....	59
7.2.8 Measurements of aromatic hydrocarbons on Preemraff-Lysekil.....	60
<b>7.3 Measurements on Shellraff</b> .....	<b>62</b>
7.3.1 Applied wind information.....	63
7.3.2 West tank-park .....	64
7.3.3 East tank-park .....	66
7.3.4 Process and hysomer.....	68
7.3.5 LPG and tank-loading area .....	69
7.3.7 Exceptional case with tank 105.....	72
7.3.8 Measurements on the flare on Shellraff.....	72
7.3.9 Measurements of aromatic hydrocarbons on Shellraff .....	73
<b>7.4 Measurements an the Oil harbor</b> .....	<b>74</b>

7.4.1 Total emission.....	75
7.4.2 Emissions divided into areas.....	77
7.4.3 Area 1.....	79
7.4.4 Area 2.....	79
7.4.5 Area 3.....	80
7.4.6 Area 4a.....	81
7.4.7 Area 4b.....	83
7.4.8 Area 5a.....	84
7.4.9 Area 5b.....	84
7.4.10 Area 6.....	86
7.4.11 Area 7.....	86
7.4.12 Loading of ships.....	87
7.4.13 Loading of trucks.....	88
7.4.14 Loading to rock cavern.....	88
7.4.15 Cleaning.....	89
7.4.16 Relevance of point emissions.....	89
7.4.17 Conclusions about the Oil harbor.....	89
7.4.18 Measurements of aromatic hydrocarbons in the Oil harbor.....	90
<b>7.5 Measurements of aromatic hydrocarbons.....</b>	<b>91</b>
<b>8 Discussion and Conclusion.....</b>	<b>97</b>
<b>Acknowledgment.....</b>	<b>98</b>
<b>References.....</b>	<b>99</b>
<b>Abbreviations and commonly used concepts.....</b>	<b>101</b>

# **1 Introduction**

In the years 2002 to 2005, a project (KORUS) was run in cooperation with four industries to explore the possibilities to measure gas emissions of volatile organic compounds (VOC) with a new method based on a mobile instrument that is measuring the solar spectrum while moving. The four industries were three refineries, Preemraff-Göteborg, Preemraff-Lysekil and Shellraff-Göteborg, and the Oil harbor of Göteborg. All industries are located on the west coast of Sweden. This report first gives an overview of the measurement method and then presents the results of the measurements on all four industries. More detailed information about the measurement method can be found in the Licentiate thesis written by Kihlman [1].

The project aimed at further developing the SOF method, in terms of reliability and automation. Simultaneously with the development work, an extensive measurement-program was run to demonstrate and test the capacity of the method for large scale routine monitoring of fugitive gas emissions from the industry.

In the project, 33 days of measurements have been done on Preemraff in Göteborg, 29 days on Preemraff in Lysekil, 23 days on Shellraff in Göteborg and 38 days on the Oil harbor in Göteborg. It has been of special interest to look at trends over the years and it has therefore been important to try to keep the same set-up, for example the positions where measurements are done, what wind information is used, and what software algorithms that are used. All measurements have been evaluated with the same software algorithms. For the measurements of total emissions, the wind-data has been chosen to give as similar wind as possible between the years. However, different strategies on how to obtain the wind have been tested over the years and data from the same position is therefore not always available.

The aerial photographs that have been used in this presentation have been purchased from Lantmäteriet [2].

## **2 Method**

The new method that has been used for the measurements will be named the SOF-method hereafter (Solar Occultation Flux method), see reference [3]. It is a newly patented technique to derive gas emission from various sources. The method is based on recording broadband infrared or UV/visible spectra of the sun with a low-resolution spectrometer that is connected to a solar-tracker. The latter is a mirror device that tracks the sun and reflects the light into the spectrometer independent of its position. For measuring the infrared spectra, a commercial FTIR-spectrometer is used (Bruker OPAG) which today is a standard instrument for gas absorption measurements. From the solar spectra it is possible to retrieve the path-integrated concentration (molecules/cm<sup>2</sup>) of a large number of species absorbing the radiation along the light path of the sun. To obtain the gas emission from a particular source, the measurement car with the SOF-instrument is driven in such a way that the detected solar light traverses across the actual emission plume.

## 2.1 Line integrated concentration

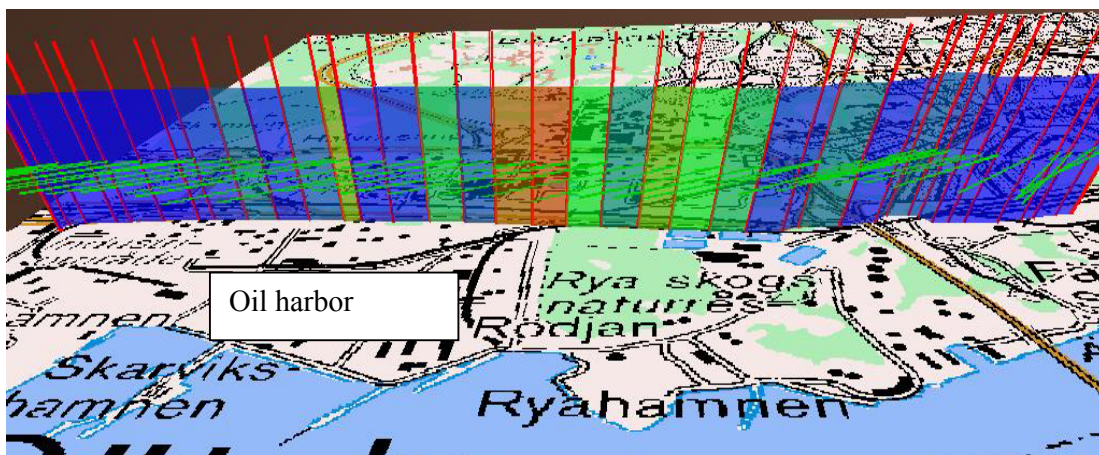
When the spectra measured in the plume are evaluated to retrieve the gas contents, a reference solar-spectrum is included in the spectral fitting. The reference is recorded outside the plume, so that the atmosphere, the inherent structure of the sun and the instrument function are eliminated. Every spectrum provides information of the change of the concentration of molecules that are present between the instrument and the sun. This is called the total column, and is expressed in  $\text{mg}/\text{m}^2$ . The total column can also be expressed in  $\text{ppm}\cdot\text{m}$ , which is defined as the mixing ratio in ppm at 1000 mbar and 293 K over an optical path length of 1 m. The spectral lines of the gas will cause a fingerprint on the measured spectra according to Beer-Lambert's law:

$$I(\lambda) = I_0(\lambda) \cdot \exp\left(-\sigma(\lambda) \cdot \int \text{conc}(x) \cdot dx\right) \quad (2.1)$$

$I$  is the light intensity at wavelength  $\lambda$ ,  $I_0$  is the light intensity before the light enters the gas.  $\sigma$  is the absorption spectra of the gas i.e. the fingerprint. By fitting known fingerprints for the gases to the measured spectrum  $I(\lambda)$ , the line-integrated concentration of the gas  $\left(\int \text{conc}(x) \cdot dx\right)$  is retrieved.

## 2.2 Flux calculation

When the system moves, the solar-ray going between the sun and the mobile instrument is cutting out an area in the sky. The surface integrated concentration of alkanes on this surface will then be determined. This is done by cutting the surface into many pieces by continuously measuring spectrum after spectrum while driving. Each spectrum is evaluated separately to derive the line integrated concentration represented by each spectrum. The position of the car during the traverse is measured with a GPS-device at the beginning and at the end of the measurement of each spectrum. The distance between these two points defines the base of the parallelogram that represents a small piece of the big surface. The surface integration is done by multiplying each line-integrated concentration with this base and then summing up all small parallelograms. The flow of gas through the surface is then determined by a scalar-multiplication in vector representation between the wind-vector and the normal to each small parallelogram. Thus, the calculation of the flux also requires information about the wind on the surface where the measurement is taking place. If the ambient concentrations of the studied gases are zero, the flux through the surface is equal to the emission of gas on the leeward side of the surface. A look at Figure 1 gives an intuitive feeling for the surface where the measurement is done. The wind is more or less blowing from the direction of the observation and is illustrated by the green lines. The solar rays detected by the SOF instrument are shown as red vertical lines. The area between these lines corresponds to the surface integrated concentration observed, which if multiplied by the local wind-speed, corresponds to the mass-flux through the area. The red parallelogram here corresponds to the highest alkane column. The number of spectra taken in the traverse shown in Figure 1 is actually 10 times more than the number of plotted red lines.



**Figure 1.** A 3D plot of a SOF measurement conducted at the oil harbor in Göteborg is shown. The red vertical lines correspond to solar lines. The colors in between the solar lines (blue to red) correspond to the integrated concentration of alkanes (blue is low concentration while green and red are higher). The wind vectors are shown as green horizontal lines pointing into the measurement-surface.

The new measurement car, with the solar-tracker looking out through the roof is shown in Figure 2.



**Figure 2.** The solar-tracker shown on the right transmits the solar light into the infrared spectrometer independently of the positioning of the car.

Figure 3 shows a schematic picture of the components in the measurement system. Figure 4 shows a schematic picture of the solar-tracker and the optics between the solar-tracker and spectrometer. The solar-tracker has been developed and built by the Optical Remote Sensing group at Chalmers.

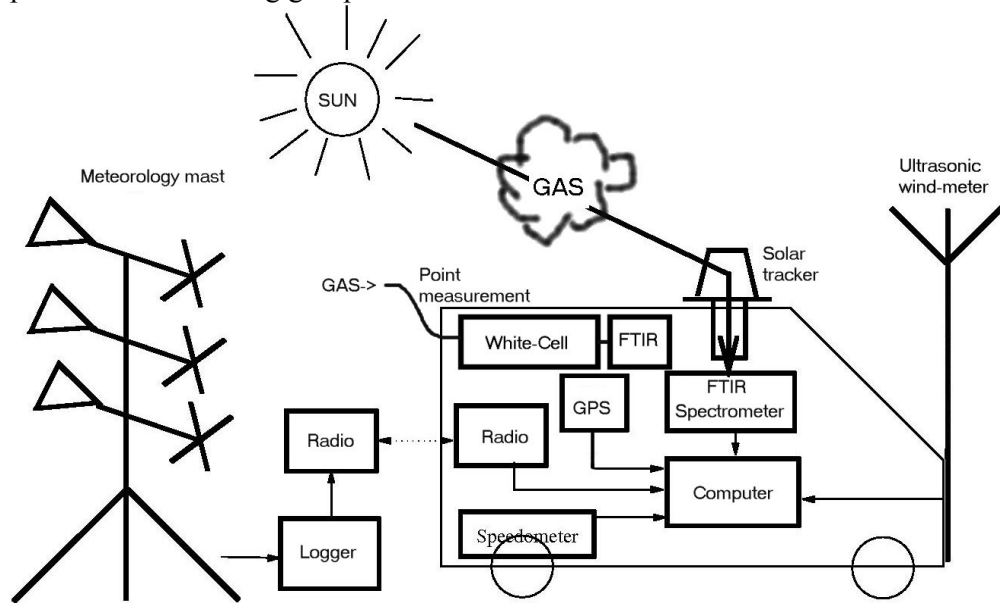


Figure 3. Schematic picture of the mobile measurement-system.

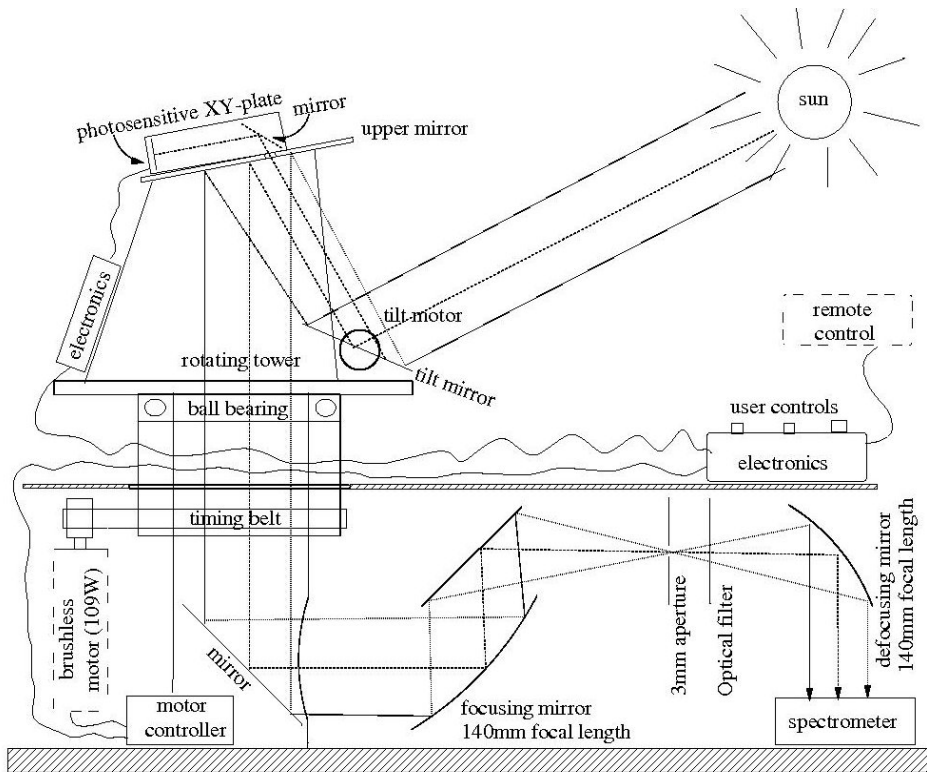
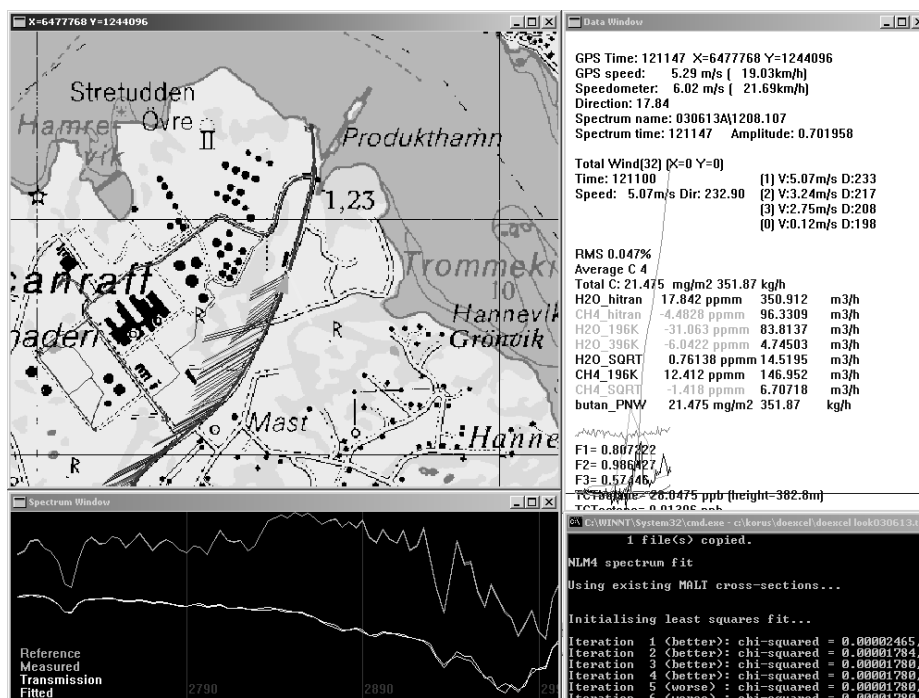


Figure 4. Schematic picture of the solar-tracker and the optics between the solar-tracker and spectrometer.

For conducting the SOF measurements, an on line software named QESOF has been developed by the Optical Remote Sensing group at Chalmers, making it possible to obtain the measurement results on-line. For further information see reference [1]. In Figure 5 the screen of the measurement-computer is shown. The upper left window shows a map of the measurement, with lines pointing toward the wind along the driving route. The measured and fitted absorption spectra are shown in the lower left window, and the retrieved data on the right side.



**Figure 5.** The figure shows the screen of the measurement computer with the presentation by the automatic retrieval software that has been developed, allowing online evaluation of the measured spectra. In the upper left is shown a map of the measurement with lines pointing toward the wind, the measured and fitted absorption spectra in the lower left, and the retrieved data on the right side.

In addition to the SOF-instrument, an extractive measurement system that measure gas concentration in one point is also included in the measurement car. This point measuring instrument consists of a separate FTIR-spectrometer connected to a White cell [4] and is used to estimate whether the plume measured by the SOF instrument resides mostly near the ground or has been lifted significantly upwards. This is information of importance to get valid wind estimation for the SOF measurement. The combination of the point measuring instrument and the SOF instrument yields a first order height profile, in this way. In this report, the point system has not been used to directly quantify the emissions but has only been used in a qualitative way to determine if the plume resides at ground level. It has also been used to determine the aromatics/alkane ratios presented in chapter 7.5. The point measuring device can also be used independently for emission assessment when combined with controlled releases of trace gases, or be used to localize leaks when connected with a long teflon tube. The point measuring instrument has low detection limits, down to ppb levels ( $10^{-9}$ ), a large dynamic range and a high time resolution ( $\approx 10$  seconds).



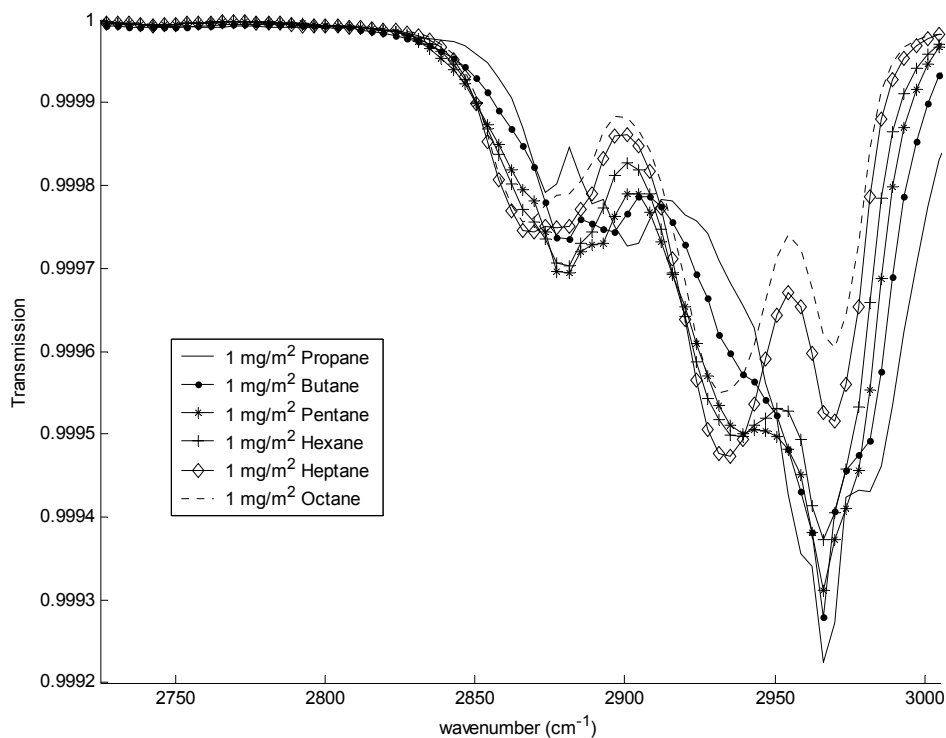


### 3 Spectroscopy

The SOF instrument is sensitive to the alkanes shown in Figure 6. The figure shows the transmission structures for these alkanes. A transmission below one indicates that absorption has occurred. The absorption structure in the chosen wavelength interval is characteristic for absorption related to the vibration/rotation occurring in a bond between a hydrogen atom and a carbon atom. When measuring at a spectral resolution of  $8\text{ cm}^{-1}$  it is difficult to resolve the individual types of alkanes from each other since their spectral shapes are overlapping and similar in shape to each other. However, the absorption strength is approximately proportional to the number of C-H bonds in the molecule. In addition, the molecular mass of an alkane is approximately proportional to the number of C-H bonds in the molecule. Absorption strength will therefore be approximately proportional to the mass of alkanes.

The time it takes to retrieve a spectrum with the FTIR-spectrometer grows with the square of the resolution. Measurements can therefore be performed much faster if performed at low spectral resolution. Alkanes have wide absorption structures and this makes it possible to use low spectral resolution for the quantification. For the measurements on the refineries, it is important that measurements are taken with a high repetitive speed because it is advisable that a traverse is done within a short time so that the local wind direction is kept the same during the whole traverse. Therefore a relatively low resolution of  $8\text{ cm}^{-1}$  has been chosen since it has shown to give the highest repetitive speed in the measurements without losing the capability to identify the average number of carbon atoms in the measured alkane. Spectra are measured with a repetition of 3.2 seconds. When doing leakage search inside the industry area, the distance between measurements need to be short in order to be able to identify the source of a registered emission. Therefore the car is then driven at approximately 10 km/h. When measuring total emissions from a whole industry at a far away distance of approximately 1 km, the car is driven at approximately 40 km/h. The car should not be driven slower than this in order to avoid that the local wind direction changes during the traverse.

It has been realized that the kind of alkane observed in the measurement is an indication of the origin of the gas. Crude oil tanks, gasoline tanks and hot areas in the process area typically emit mainly propane and butane. The water treatment facility emits mainly octane and almost no propane and butane. This fingerprint is especially easy to recognize for the emission from the water treatment. Tanks containing kerosene and heavy gas oil show a mixed emission of propane, butane and octane. To spectrally evaluate propane, butane and octane simultaneously has thus shown to give valuable information about the emission source but this is done at the expense of more noise in the baseline i.e. registered concentration of hydrocarbons even though no hydrocarbons can be expected in the measurement. A more intelligent method has therefore been used that first evaluate the spectrum as butane only. If the evaluated butane concentration is higher than  $12\text{ mg/m}^2$ , 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 species.



**Figure 6.** The picture shows the transmission for 1 mg/m<sup>2</sup> of the alkanes. The shown spectral region is the same as the region where the spectral fitting is performed. The spectral resolution shown has been degraded to the same resolution as for the measurements.

### 3.1 Determination of the VOC compounds in the gas mixture

A field measurement was done where approximately 2 liters of gas were collected into two aluminum-coated bags from the west side of the crude-oil tank-park at Preemraff-Göteborg. This was done on the 21<sup>st</sup> December 2004. The ambient temperature was around 0°C. The gas in the two bags was analyzed with a GC system by IVL (Swedish Environmental Research Institute) within two hours to determine the mix of different hydrocarbons in the sampled gas mixture. Table 2 shows the average retrieved fraction by molecules and the fraction by mass. The species have then been divided into three groups: alkanes, alkenes/alkynes and aromatics and Table 1 summarizes the mixing ratio between the groups. Table 2 also shows the cross sensitivity of each specie in a spectral evaluation of butane. For example 1 mg/m<sup>2</sup> of pure ethylbenzene will be interpreted as 0.27 mg/m<sup>2</sup> of butane by the SOF evaluation. The emissions presented in the KORUS-project are the estimation of emitted alkanes. However, it is possible that other species than the alkanes are interpreted as alkanes and therefore causes an error. To determine this, the cross sensitivity was multiplied with the mass ratios given in Table 2. It was found out that the cross sensitivity of the most abundant alkenes/alkynes and aromatics are low and therefore result in very low errors. In the sample gas-mixture, the alkenes/alkynes only causes an error of 0.07% and the aromatics an error of 0.06% in the spectral evaluation of alkanes. These errors are therefore neglected in the following discussions.

**Table 1.** Gas mixture of different families of hydrocarbons in the samples taken in the plume from a crude-oil tank-park.

	Mixing ratio (%)	Mass ratio (%)
<b>Alkanes</b>	98.9	98.5
<b>Alkenes/Alkynes</b>	0.6	0.5
<b>Aromatics</b>	0.6	1.1
<b>Total:</b>	100	100

**Table 2.** Gas mixture of the emissions from a crude-oil tank-park obtained by collecting air in bags followed by GC-analysis. Aromatic hydrocarbons are printed in italic letters. Alkenes and alkynes are printed in bold letters.

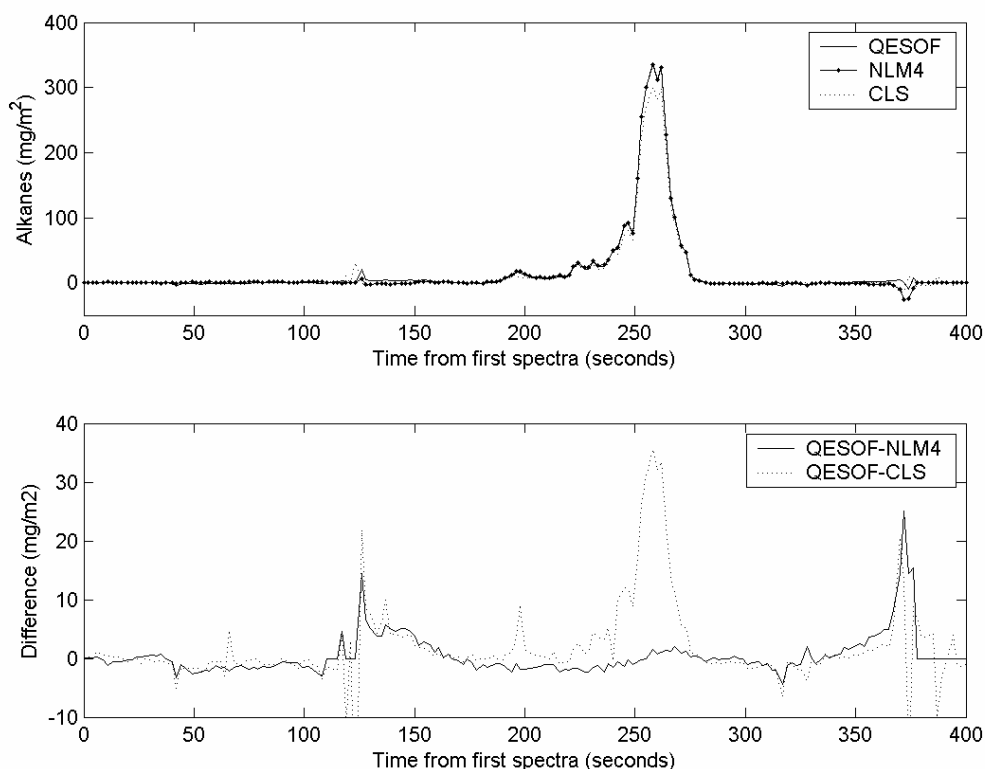
Compound	Mixing ratio by molecules (%)	Mass ratio (%)	Cross sensitivity as mass of Butane
Propane	38.78	32.50	0.98
n-Butane	20.28	22.41	1.00
Ethane	14.48	8.28	0.26
Iso-Butane	8.69	9.59	1.60
n-Pentane	6.20	8.49	1.01
Iso-Pentane	5.66	7.76	1.29
Decane	1.44	3.88	0.74
Hexane	1.12	1.82	0.94
2-Methylpentane	0.98	1.60	1.05
3-Methylpentane	0.47	0.76	1.02
Cyclohexane	0.45	0.72	0.21
n-Heptane	0.27	0.51	0.76
Octane	0.05	0.11	0.55
Nonane	0.01	0.03	0.42
<i>Toluene</i>	<i>0.21</i>	<i>0.37</i>	<i>0.04</i>
<i>Benzene</i>	<i>0.09</i>	<i>0.13</i>	<i>0.00</i>
<i>Ethylbenzene</i>	<i>0.06</i>	<i>0.12</i>	<i>0.27</i>
<i>1,2,4-TMB</i>	<i>0.11</i>	<i>0.24</i>	<i>0.00</i>
<i>1,3,5-TMB</i>	<i>0.01</i>	<i>0.02</i>	<i>0.00</i>
<i>m+p-xylene</i>	<i>0.07</i>	<i>0.14</i>	<i>0.03</i>
<i>o-xylene</i>	<i>0.03</i>	<i>0.05</i>	<i>0.10</i>
<b>Etene</b>	<b>0.10</b>	<b>0.05</b>	<b>0.02</b>
<b>Etyne</b>	<b>0.05</b>	<b>0.02</b>	<b>0.24</b>
<b>Propene</b>	<b>0.23</b>	<b>0.18</b>	<b>0.11</b>
<b>Iso-Butene</b>	<b>0.11</b>	<b>0.12</b>	<b>0.19</b>
<b>C-2-Butene</b>	<b>0.01</b>	<b>0.01</b>	<b>0.34</b>
<b>1,3-Butadiene</b>	<b>0.01</b>	<b>0.01</b>	<b>0.09</b>
<b>T-2-Pentene</b>	<b>0.01</b>	<b>0.02</b>	<b>0.00</b>
<b>C-2-Pentene</b>	<b>0.01</b>	<b>0.02</b>	<b>0.42</b>
<b>1-Butene</b>	<b>0.01</b>	<b>0.01</b>	<b>0.28</b>
<b>T-2-Butene</b>	<b>0.01</b>	<b>0.01</b>	<b>0.75</b>
<b>Propyne</b>	<b>0.01</b>	<b>0.01</b>	<b>0.27</b>
<b>Total:</b>	100	100	

(TMB=Trimethylbenzene)

### 3.2 Spectroscopy with the QESOF software

The results of the spectral fitting algorithm in the specially developed software (QESOF) has been compared and verified with the results retrieved from three other softwares, a Classical Least Square (CLS) method in the Grams software [5], the non-linear NLM4 software developed by Griffith [6]. Verification of the software has also been done on spectral evaluation on measurements of volcanic gases. Spectral evaluations provided by Mike Burton at INGV with a software that has been used for FTIR measurements of volcanic gases [7], were compared with the spectral evaluation of QESOF for the same spectra and showed a very good agreement.

Figure 7 shows a comparison between the QESOF, NLM4 and CLS. The comparison was done on the total alkane concentration in a traverse done with a mobile solar occultation system outside a refinery. At the point of maximum concentration, the figure indicates that the values from QESOF are very similar to the NLM4 code and 10% higher than for the CLS code. The discrepancy towards the CLS algorithm is understandable since the CLS is a linear algorithm and therefore underestimates the concentrations at high values. The parameters used in the evaluation are the same as the standard parameters in the refinery application.



**Figure 7.** Comparison between three spectral algorithms when evaluating total alkane concentration in a traverse done with a mobile solar-occultation system outside a refinery.

The errors in the spectral evaluation with QESOF of a typical VOC gas-mixture were determined by a simulation. This was done by creating a spectrum corresponding to the absorption features of the species in Table 5. These have been set to the same concentrations that were presented in Table 2, i.e. the concentrations measured with the bag-samples. Reference spectrum for Propane and n-Butane were taken from the Pacific Northwest database [8] and the other spectra were taken from the QAssoft database [9]. The absorption was then applied to a measured solar spectrum and the resolution degraded to the same resolution as the measured spectrum (8 cm<sup>-1</sup>). The parameters for the spectral fitting were the same as was used in the KORUS project.

The spectral fitting of n-Butane represents the species with similar absorption structures as n-Butane (i.e. iso-Butane, n-Pentane, iso-Pentane, 2,3-Methylpentane and to some degree n-Hexane). The spectral fitting of n-Octane represents species with high carbon numbers that have similar broad absorption structures as n-Octane (i.e. n-Heptane, Cyclohexane and to some degree n-Hexane)

As can be seen in Table 3, the spectral evaluation overestimates the total simulated alkane-concentration with a factor 1.10 (231.1/210.4). Thus, the conclusion from this study is that for a typical gas-mixture of hydrocarbons emitted from a crude-oil tank-park, the total mass of alkane in the gas-mixture will be determined with an error of **10%**.

**Table 3.** Concentration of alkanes in the error simulation of QESOF.

Alkane specie	Simulted Concentration (mg/m <sup>2</sup> )	Evaluated Concentration (mg/m <sup>2</sup> )
Ethane	18.4	
Propane	72.3	97.1
n-Butane	49.9	114.6
Iso-Butane	21.3	
n-Pentane	18.9	
Iso-Pentane	17.3	
n-Hexane	4.0	
2-Methylpentane	3.6	
3-Methylpentane	1.7	
Cyclohexane	1.6	
n-Heptane	1.13	
n-Octane	0.24	19.4
<b>Total:</b>	<b>210.4</b>	<b>231.1</b>

### 3.3 Discussion about average carbon number

The simultaneous spectral fitting of propane, butane and octane (with respectively 3, 4 and 8 carbon atoms in the molecule) makes it possible to determine the average number of carbon atoms in the mix of alkanes present in the measurement. The average number of carbon atoms is calculated in the measured gas-mixture by the following equation:

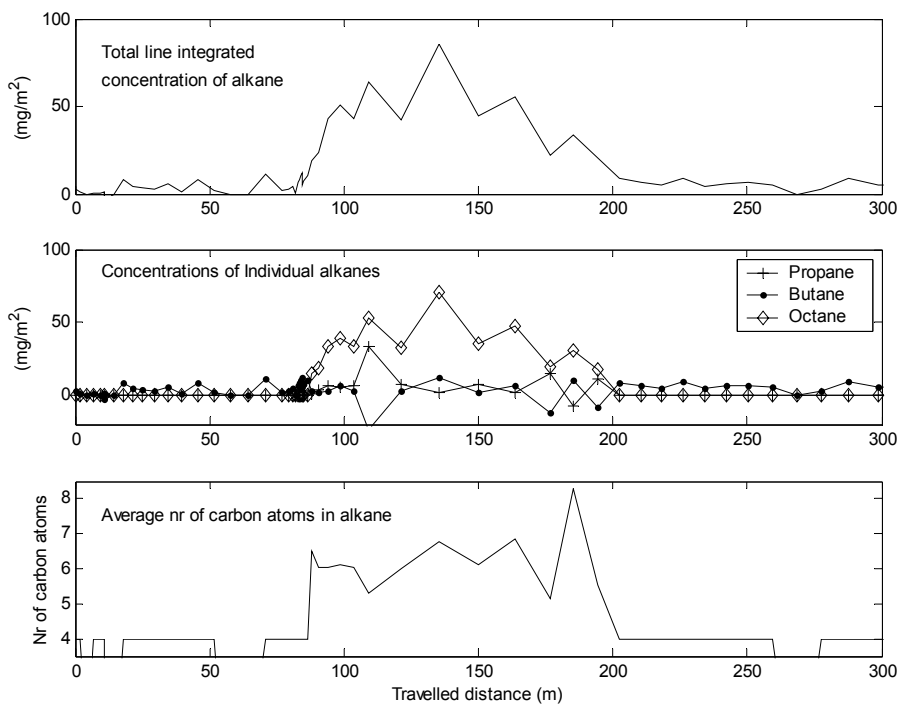
$$C_{avg} = \frac{3 \cdot m_{propane} + 4 \cdot m_{butane} + 8 \cdot m_{octane}}{m_{propane} + m_{butane} + m_{octane}} \quad (3.1)$$

where m stands for the line integrated mass concentration of each specie. It has been realized that the average carbon count is an indication of which source is causing an

emission. Table 4 summarizes the typical average carbon counts that have been observed from the different emission sources. An example of how this was determined is shown in Figure 8 where the measured alkane plume and the calculated average carbon count for a water treatment facility is shown.

**Table 4.** Typical observed carbon count numbers for different kind of equipment.

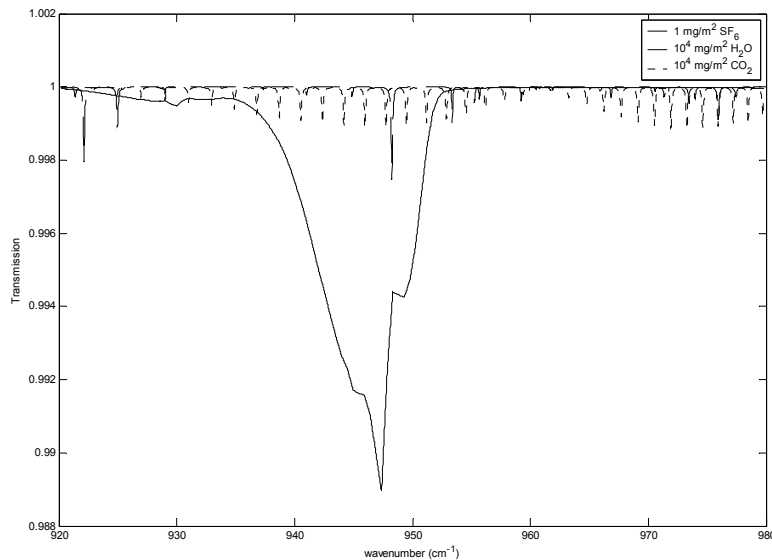
	Typical average carbon-count in the measured gas-mixture.
<b>Process</b>	5
<b>Crude-oil-tank</b>	3.7
<b>Water treatment</b>	6.5
<b>Gasoline-tank</b>	4
<b>Kerosene-tank</b>	6



**Figure 8.** The figure shows the measured concentration of alkanes in a traverse of the plume from a water treatment facility (Preemraff-Göteborg, day 040910, time 15:13). When located in the plume, the average number of carbon atoms can be calculated and used for determining the source of the gas emission. Observe that only butane is evaluated when the alkane concentration is below 12 mg/m<sup>2</sup> and the average carbon count is then 4.

## 4 Validation using tracer releases

The method to retrieve fluxes from traverses with a mobile solar-occultation system was validated on two experiments. In the first experiment, a trace gas (Sulfur-Hexafluoride, SF<sub>6</sub>) was emitted from the top of a 17 m tall mast in the middle of an open field at Åby in Göteborg. Traverses were then done downwind with the measurement system at varying distances from the emission source. The wind was measured with a wind-meter located in the top of the same mast. The true amount of emitted trace gas was estimated by weighting the gas tube before and after the experiment and also measuring the time when the gas was emitted. The emitted gas was always approximately 2 kg/h. The measured peak concentrations were about 10 mg/m<sup>2</sup> for most scans. The spectral evaluation was done in the region 925-975 cm<sup>-1</sup> and included H<sub>2</sub>O, CO<sub>2</sub>, SF<sub>6</sub> and a fitted sky-reference spectra. Spectra for H<sub>2</sub>O and CO<sub>2</sub> were created from the Hitran database [10] at a temperature of 288K and a pressure of 1 atm. SF<sub>6</sub> spectra was taken from the NIST database [11]. Figure 9 shows the transmission spectra for 1 mg/m<sup>2</sup> of SF<sub>6</sub>. As can be seen, SF<sub>6</sub> is absorbing about 1% of the light in its peak at this concentration and this should be easily detected in the measured spectra. There is however a strong absorption-line of H<sub>2</sub>O at wave number 948 cm<sup>-1</sup> that is causing some trouble in the SF<sub>6</sub> retrieval. For the results presented here, non-linear spectral evaluation was used, Norton-Beer strong apodization [12] was used and a polynomial of 4<sup>th</sup> order was also fitted.

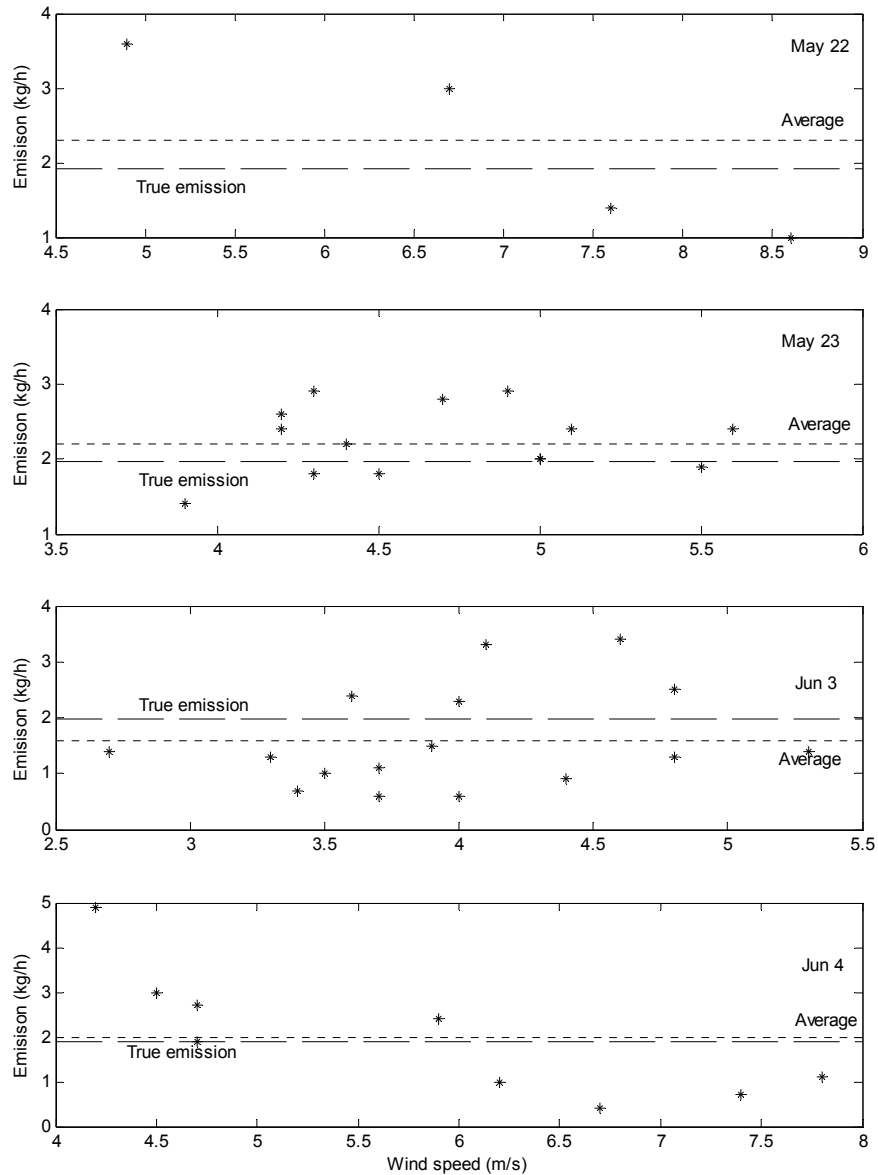


**Figure 9.** The transmission spectra of H<sub>2</sub>O, CO<sub>2</sub> and the reference spectrum for SF<sub>6</sub>.

Table 5 shows the results from the four days when the field experiment was done. The standard deviations for the calculated averages indicates that the result of just one traverse is uncertain and that averaging of many traverses are required to get reasonable results. As can be seen, each traverse has a low reliability but the average over many traverses comes close to the true value. Figure 10 shows a plot of the emissions derived from all the traverses for each day plotted towards the average wind speed during the traverse.

**Table 5.** Summary for each day in year 2002, when measurements on the Åby field were done.

Day	Emitted SF <sub>6</sub> (kg/h)	Calculated average (kg/h)	Number of accepted traverses	Average wind speed (m/s)	Average wind direction	Error
May-22	1.92	2.3±1.3	4	4.9-8.6	152°-169°	20%
May-23	1.97	2.2±0.6	15	3.9-5.6	120°-142°	10%
June-03	1.97	1.6±0.9	16	2.7-5.3	235°-273°	-20%
Jun-04	1.89	2.0±1.4	9	5.9-7.8	152°-191°	5%



**Figure 10.** The figure shows the calculated SF<sub>6</sub> emission versus wind speed on all traverses.



Another experiment was done where SF<sub>6</sub> was emitted from the roof of a crude oil tank. The tank (Tank 105 at Preemraff-Göteborg) is located in a tank-park where nine tanks are standing close together, see Figure 11. It can be expected that the wind field is irregular close to the ground inside the tank-park. Traverses were done on a road along the side of the tank park, approximately 150 m away from the emission point. Figure 11 shows the location of a typical traverse on a map. During day 24-June 2002, eight traverses were successfully retrieved. Table 6 shows all the traverses done during that day. The true released amount of SF<sub>6</sub> was estimated to 2.0 kg/h by weighting the gas-tube before and after the experiment and the retrieved average emission was 3.0±1.1 kg/h which corresponds to an error of 50%.

**Table 6.** The traverses done on day 24-June 2002. True emitted amount of SF<sub>6</sub> has been determined to 2.0 kg/h.

Time (24 h)	Emission SF <sub>6</sub> (kg/h)	Average wind speed (m/s)	Average wind direction
12:45	3.1	6.5	252°
12:54	1.8	7.2	252°
13:05	1.3	6.0	259°
13:17	2.7	7.5	253°
13:29	3.1	5.4	255°
13:56	5.2	7.4	264°
14:05	3.7	7.2	251°
14:24	2.6	7.3	262°
14:31	3.4	6.5	260°
Average	<b>3.0±1.1</b>		



**Figure 11.** A typical traverse done when the SF<sub>6</sub> gas was emitted on top of tank 105. The broad lines along the traverse points towards the wind direction. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBildern)



## ***5 Sub-sector and total industry measurements***

The wind field inside a refinery 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 in the industry and the ground has decreased. When measuring the emission far away, errors induced by the gradient in altitude of the speed and direction of the wind will however be present, see chapter 6.3. Total industry measurements are typically done over 2.5 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.

It is also of interest to know the emission of each sub-sector inside the industry area and measurements inside the industry area are done to get the proportions of the size of emissions from each area. It is preferred that many sections are measured within a limited time-period so that the meteorological conditions can remain the same for the measurements on all sectors. It can then be expected that the proportions between the measured emissions is relevant. 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 by repeated close measurements on each sub sector. 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 values on each sub-sector are then compensated for by dividing the value with the normalization factor. With this approach, much less labor is required since the wind-meters do not need to be moved between each sub-sector each time a new sub-sector is measured. A wind-meter representing the average wind field can then be used, which is typically permanently mounted in an existing tower in the industry area.

Daily averages of emission are calculated for all total measurements and sub-sector measurements done on the same day. During one year, total measurements on an industry were typically collected on four days and close measurements on each sub-sector were done at least on two days. Low variation in the measured emissions over a day is an indication of high quality in the measurements that day and that no exceptional activity was taking place at the industry on that day. A day with low variation of the total emission over the traverses during the day should therefore be more important when determining the total emission during that year. The main purpose of the measurements in the KORUS project was to determine emissions when the refinery was running under normal conditions. Therefore, the daily averages of the emissions for all days during a year are averaged in such a way that the weight of the average of a day is inversely proportional to the standard deviation among the traverses during that day. This will lead to that a day with low variation of the emission over the traverses will be more important when determining the total emission during that year.



## **6 Error estimation**

The errors can be divided into the three following parts:

- (1) Errors due to limitation in measurement time.
- (2) Spectral evaluation errors.
- (3) Errors in the wind measurements.

All parts will be described in the following chapters.

### **6.1 Errors due to limitation in measurement time**

The 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 two to six days within a time-span of a month, it must be assumed that the emissions on those days can represent the average emission the whole year.

Since year 1972, the U.S. Environmental Protection Agency (EPA) has contracted an extensive study to determine the parameters that decides the emissions from organic liquid storage tanks [13]. The results show that emissions from tanks with external floating roofs are increasing with the wind speed [13]. It also shows that emissions from fixed roof tanks are dependent on the level of the liquid surface in the tank. For floating roof tanks, it has also been observed that emissions increase when a tank is emptying i.e. when the roof is on the way down. Emission from all tanks is also dependent on vapor pressure of the stored liquid and is therefore also dependent on the liquid temperature. Emission is also dependent on outer temperature and therefore varies slightly with the seasonal variation. Equations to calculate the dependence from all these factors are presented in [13] but reliable results are dependent on that correct parameters for each tank is determined. Unexplained deviations from the results achieved from the EPA equations for double sealed tanks have also been reported [14].

Thus, this dependence is complicated and the parameters for the EPA equations must more or less be determined for each tank individually. It has been outside the scope of this project to try to compensate the measured emissions to the winds, tank-roof heights and liquid temperature that was present during the days when the measurements were performed. All calculated emissions are therefore presented without compensations to these variations over the year.

If using the strategy of measuring each tank individually during a short time, and then summing the measured emissions from all tanks to determine the total emission from a tank-park, each tank must be compensated for the factors mentioned above individually, to give a reliable total emission estimate. This approach has previously been used with the DIAL method. However in the KORUS project, the whole tank-park is measured at once and the measurements are repeated on different days. It can then be expected that there is a variation in the activity between the tanks in the tank-park and also variations between days that will cancel out each other. This situation causes an average that is relevant for the emission of the whole tank park. The activity on each individual tank can then be neglected.

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 was observed, it could be explained by short-term activities taking place inside the industries. If higher emissions than normal were found during a day and could be explained by short-term activity, then the measurements from that day were discarded. It is therefore believed that the average emission from all days will represent the continuous emission of the industry. For the cases where 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 within this project. An example of one such study was done when an increased emission of 70 kg/h was measured a few hours after opening a tank for maintenance at Shellraff. Shellraff has reported that opening of a tank for maintenance work was done in the eastern tank park at 11 times during the period from summer 2003 to summer 2004. If assuming that the increased emission is maintained during 12 hours after opening the tank, then this will cause an increased emission of 9 ton/year. This should be compared to the average measured emission from the east-tank park of 146 ton/year for 2004. If the assumptions are correct then this indicates that the emission increase related to maintenance of tanks cause a 6% increase in the yearly emissions.

The impression gained during the project indicates that intermittent emissions correspond to 1-10% of the continuous emissions. To simplify the picture, the values presented later in this report correspond to the continuous emissions and do not include intermittent emissions on the industries. There is however a potential error source in that one may fail to detect a situation as intermittent, and the emission estimations will then be too high. Representatives from the industries with knowledge of the activities have been participating in the interpretation of the measurements in order to avoid this.

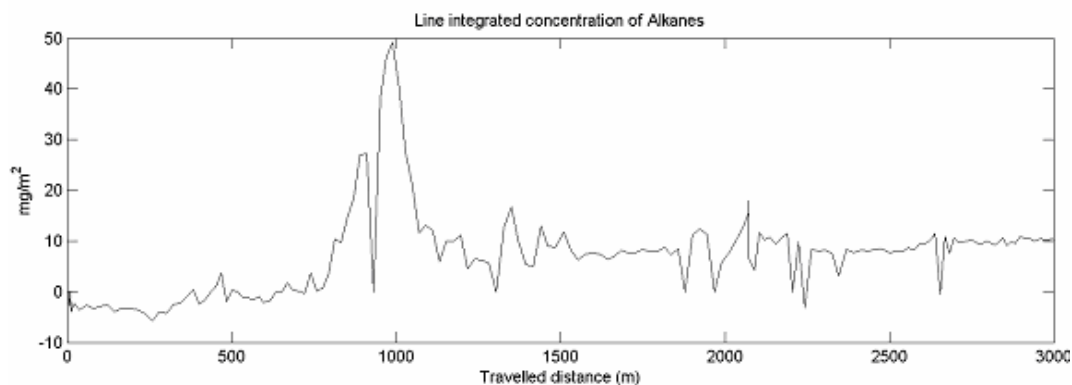
Since there are just a few measurement days each year, the situation is heavily under-sampled and there will be an error in the estimated annual emission due to this. The best dataset produced from the KORUS-project to estimate the variation of the continuous emission is probably five days of total measurements from Preemraff-Lysekil during July-September 2004. This dataset gives an average emission of 509.6 kg/h with a variance of 85.3 kg/h between the average emissions of 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.

## 6.2 Spectral evaluation errors

It was concluded in chapter 3.2 that the alkane mass in a typical gas-mixture from a crude-oil-tank-park was determined correctly with an error of less than 10%.

When conducting SOF measurements, the flux is obtained by adding all columns above the baseline of the traverses. 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 path of the incoming light into the spectrometer is changed during a traverse. Changes in the tilt during a traverse is caused by imperfect aligning of the solar-tracker which causes the output angle to wobble around as the solar-tracker looks in different direction i.e. when the car is changing its direction or the sun moves over the sky. During the KORUS project, the solar-tracker has been under constant development. Therefore, this problem was big in the beginning but is almost not present at all with the latest version of the solar-tracker. Optical filter were also used in earlier measurements but it was found that it also caused baseline drifts. The drift due to the filter could partially be compensated for in the software but it was later decided that optical filters should not be used so that baseline drifts were as much as possible avoided.

Figure 12 represents a traverse with a high baseline error. In the KORUS project, traverses with a baseline error of more than 3 mg/m<sup>2</sup> have been manually rejected and this gives an upper limit for the error of 30%. The evaluation method relies on that the user selects a zero point on the traverse and the baseline error is thus dependent on the choice of the user. Especially for traverses with high noise, it is difficult to locate the zero-point with high certainty. It is however believed that the error will be 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 and become 9.5% <sup>(1)</sup>.



**Figure 12.** The figure shows the line-integrated concentration along a traverse. This shows a big baseline error since the concentration at the endpoint is evaluated to 10 mg/m<sup>2</sup> in a location where no alkane concentration is expected.

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$$^1 \left( 9.5\% = \frac{30\%}{\sqrt{10}} \right)$$

### **6.3 Errors in the retrieved flux due to wind properties**

In the most ideal situation, one should know how the wind vector varies over the whole surface where the gas concentration is measured. The wind should also remain constant in that way while the whole surface is measured. Errors in the retrieved flux will be induced if this is not the case.

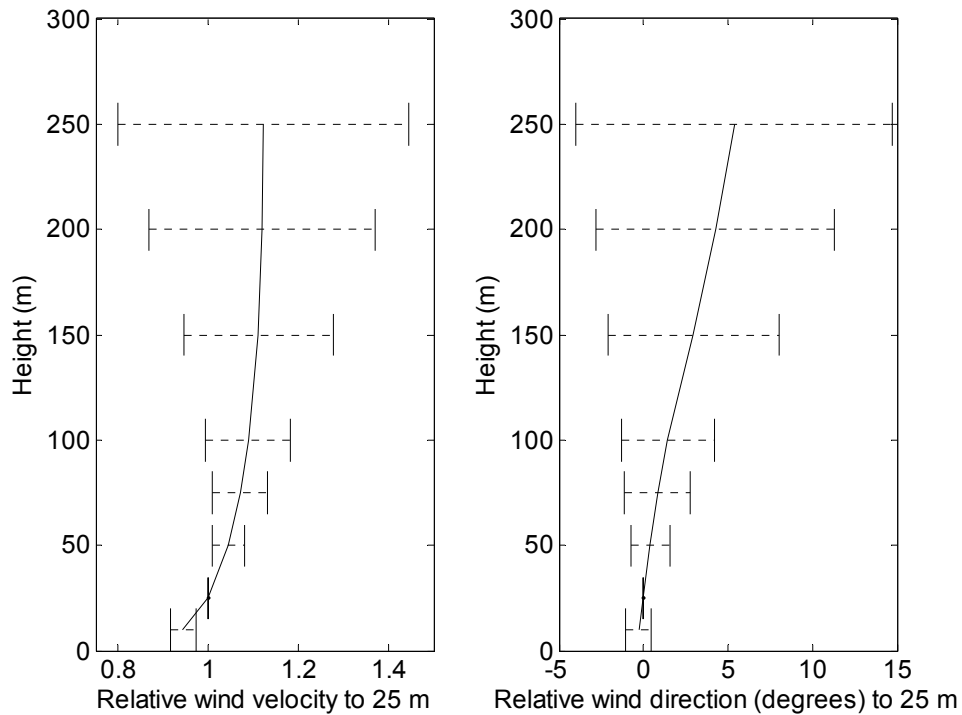
When variations of wind speed and wind direction in time has been observed during a traverse, the calculated flux has been manually discarded if it can be expected that the variations in wind was strong enough to induce large errors. The influence of short timescale variations of the wind has in that way been anticipated.

When using the SOF-technique, the errors in calculated emission caused by the wind, can be considered as coming from two sources. The first is that the actual height of the plume is unknown. The second error is that there is an uncertainty in how much the flux will be underestimated if it were located on a certain height. These error sources are difficult to separate and are therefore here below elaborated as a combined error.

A detailed study of the induced errors due to the wind was made by looking at the variation from a data set retrieved by a simulation of the micrometeorology model TAPM (see reference [15]). The TAPM model simulations were done by the meteorology group at Göteborg University. Simulations were done with the TAPM model for a time-span of two months for three selected positions, Preemraff in Lysekil, Oljehammen in Göteborg and Risholmen in Göteborg. These positions were selected because they are of relevance for the KORUS project. The days simulated were from 1<sup>st</sup> August 2001 to 30<sup>th</sup> September 2001. The available dataset from the simulation are wind speed and wind direction for every hour at 16 different altitudes between 10 and 1000 m. The dataset was used to estimate the errors induced from the limited amount of wind information that was collected during the KORUS campaign. In the KORUS campaign, the used wind information was typically taken from a wind meter located 25 m above ground taking averages of wind speed and direction every 30 seconds.

For simulating the error of a typical total measurement on a refinery, 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 can be distributed anywhere between 0 and 100 m above ground with equal probability. It is further assumed that the plume from the process can be distributed anywhere between 100 and 300 m above ground. The wind data from all hours between 9:00 and 17:00 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 13 shows the average wind profile retrieved by the selected data. The error bars show the standard deviation between daily averages.



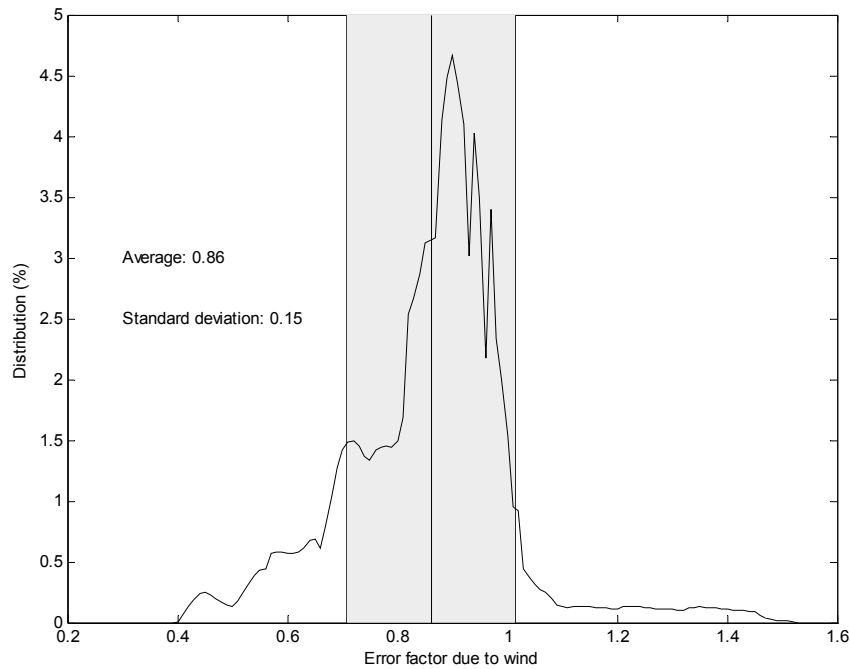


**Figure 13.** The figure shows the wind velocity and wind direction profile retrieved by simulation and averaged over daytime all sunny days with a wind-speed of 3-6 m/s at ground. The error bars indicate standard deviation between daily averages.

The selected data is then combined with the probability distributions of the process plume and the tank-park plume and a combined probability distribution curve is finally calculated. The average of the distributions and the variance is shown in Table 7 and corresponds to the overestimation done when calculating the emission. An overestimation below one tells that the calculated emission is lower than the true emission and is thus actually an underestimation. The error due to wind velocity and direction is individually presented as well as the combined error due to both. The probability function for the bolded case in Table 7 is shown in Figure 14. A slot-size of width 0.01 has been used for the distribution. Some examples might explain this figure. The figure shows that there is 5% chance to have a overestimation factor in the range  $0.9 \pm 0.005$  and 0,12% chance of having an overestimation in the range  $1.2 \pm 0.005$ . For the error in wind direction, it is assumed that the car is driven at an angle of  $45^\circ$  to the wind direction and always in the direction that causes an underestimation and represents an upper limit on the expected error. The error factor for the tank-park and the process are given individually as well as the case where the two emission sources are both considered.

**Table 7.** 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	<b>0.86±0.15</b>



**Figure 14.** The distribution of the error factor for the simulated case when including all data-points between time 9:00 and 17:00 on days with high sun-radiation. The shaded area represents the standard deviation around the average value 0.86. Both the effect of wind-speed and wind-direction has been included.

For determining the total error in the yearly estimate from a refinery the case that is bolded in Table 7 is used. Thus the systematic error is expected to be  $\sigma_{wind,sys} = -14\%$  and the standard deviation between days to  $\sigma_{wind,day} = 15\%$ .

Errors in calculated flux due to variations of the wind with location is another consideration but this issue was not possible to study with the available dataset. There are also variations in the wind with a much shorter timescale than 1 hour. The induced errors in calculated flux from the short timescale variations in wind can however be expected to reduce by taking the average of many traverses in one day. About 10 traverses of the same kind are done on a good measurement-day and are averaged to represent the emission on that day. The errors due to short timescale variations are therefore expected to be much lower than the errors due to the altitude and wind profile variations and will therefore be ignored hereafter.

## 6.4 Conclusion about total errors

The combined errors from all expected error sources for the total emission measurements can be calculated by:

$$\sigma_{total} = \sigma_{wind,sys} + \sqrt{\sigma_{alkane}^2 + \sigma_{cross}^2 + \frac{\sigma_{wind,day}^2 + \sigma_{BL}^2 + \sigma_{true}^2}{N}} \quad (6.1)$$

As concluded in previous chapters, the error in the spectral evaluation is  $\sigma_{alkane} = 10\%$  (chapter 3.2). There is also an uncertainty in the spectral cross section used that contributes with an error  $\sigma_{cross} = 10\%$  and the systematic error due to wind is  $\sigma_{wind,sys} = -14\%$ . These three errors are systematic and do not reduce by averaging the measurements over many days. The statistical error in the daily averages due to the wind is  $\sigma_{wind,day} = 15\%$  (chapter 6.3), the variation between days induced by the baseline error is  $\sigma_{BL} = 9.5\%$  (chapter 6.2) and the true variation between days  $\sigma_{true} < 17\%$  (chapter 6.1). The true variation is possibly less than 17% but setting it to 17% will give an upper limit of the expected error. These three errors are not systematic and will reduce when averaging over the number of measurement days, here denoted by letter N. Measurements are typically done on four days (N=4) and the total error in the estimate of yearly emission will then be calculated by equation 6.1 to  $\sigma_{total} = 19\%$ . Measurements will however on average be underestimated with a factor 14% due to the systematic error in the wind.

The errors associated with leakage-search measurements will here be handled with the same equation for a comparison. The measurements on subsections of the industry, for example on a crude oil tank are typically done on four 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 ground, the errors in the measurements of both wind-direction and wind-speed are expected to be high. This was observed in the trace gas experiment in chapter 4 where the flux was determined with an error of 50%. Assuming no systematic error 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 is:

$$\sigma_{tank} = \sqrt{0.10^2 + 0.10^2 + \frac{0.5^2 + 0.4^2 + 0.095^2}{4}} = 35\% \quad (6.2)$$

Thus there will be more errors in the estimation from individual tanks than for the total emission-measurements.

For the measurement on the water treatment it is also expected that the error caused by the spectral evaluation is larger since the gas-mixture of alkanes have been observed to be quite different there than on the rest of the refinery. Since no bag-measurements have been done to determine this gas-mixture, it is unknown but a qualified guess is that the spectral error is not above 30%.



## **7 Results**

The following chapter gives details about the measurements performed in the project.

### **7.1 Measurements on Preemraff-Göteborg**

During the years 2002-2004, measurements were done on Preemraff during 11 days each year, distributed over July/September-2002, August/September/October-2003 and August/September-2004.

The total emissions of alkanes from the whole refinery for the years 2002, 2003 and 2004 were calculated to 395, 230 and 306 kg/hour (3463, 2016 and 2682 ton/y). The calculations are based on far-away measurements with the SOF method, with a distance of about 200 m to 1 km away from the industry. For all three years, calculation of the total emissions were done by adding the yearly average for the crude oil tank park and the yearly average for the east area where the yearly averages are based on daily averages of measurements with the SOF methods. The daily averages of the measurements on each area and each year is given in Table 8.

The refinery has been parted in four larger regions, crude oil tank-park, product tanks, process and water treatment facility and the emissions from each region has been retrieved by making measurements closer to each region, see Figure 15 and Table 9. Each region will be discussed in detail in the following sections.

#### **7.1.1 Applied wind information**

During year 2002, wind-meters were permanently mounted on the hill located north east of the crude oil tank-park. This wind information was used for the measurements on the crude-oil tanks that year. A wind-meter was mounted on top of the workshop building and this wind information was used for the total measurements on the east area that year.

The strategy changed between year 2002 to 2003 to rely more on wind-meters permanently placed on high locations when doing total measurements. A wind-meter was mounted on the top of the tower on Preemraff-Göteborg, about 35 m above the surface. The data from this wind-meter was used for the total measurements in 2003 and 2004.

For close measurements inside the industry-area, wind-meters mounted on mobile masts with heights of 10 m, 17 m and 24 m were also used on various locations. In addition, a mobile wind meter mounted on the measurement car was sometimes used.

**Table 8.** Measurement days relevant for calculation of total emission on Preemraff-Göteborg.

Day	Total (kg/h)	Crude oil tank-park (kg/h)	East Area (kg/h)	Wind speed (m/s)	Wind direction
12-Sep-2002		82.0 v		3.9-4.6	286°-290°
13-Sep-2002			376.6 e	2.7-3.6	320°-326°
18-Sep-2002			152.7 e	2.4-4.6	266°-349°
20-Sep-2002		183.4 v		4.0-5.7	280°-312°
23-Sep-2002			130.3 e	3.1-4.0	278°-351°
24-Sep-2002		172.0 v		3.1-3.9	238°-284°
<b>2002 Average</b>	<b>395.2</b>	147.9	247.3		
18-Aug-2003		50.1 t	148.9 e	2.4-3.6	180°-199°
22-Aug-2003		192.3 v		8.0-9.9	256°-273°
25-Aug-2003			235.6 e	4.1-5.3	299°-319°
28-Aug-2003		54.7 t	169.9 e t	4.1-5.6	200°-225°
2-Sep-2003		71.5 t	119.0 t	4.5-5.8	169°-208°
16-Sep-2003			144.7 e	3.3-5.5	281°-300°
<b>2003 Average</b>	<b>229.8</b>	78.8	151.0		
5-Aug-2004		95.6 t	195.3 t	3.0-4.2	217°-246°
10-Aug-2004		160.0 v		1.9-5.4	257°-320°
11-Aug-2004			388.8 e	4.4-4.5	325°-331°
12-Aug-2004			224.0 e	4.1-5.0	315°-330°
18-Aug-2004		164.0 t	148.1 t	3.6-5.9	186°-227°
3-Sep-2004			113.3 t	3.6-4.7	186°-244°
9-Sep-2004		103.9 t	169.0 t	5.4-6.9	219°-242°
10-Sep-2004		128.7 t	198.7 t	4.0-7.6	206°-232°
16-Sep-2004		50.0 v	141.1 e	2.6-5.5	248°-337°
<b>2004 Average</b>	<b>306.1</b>	116.5	189.6		

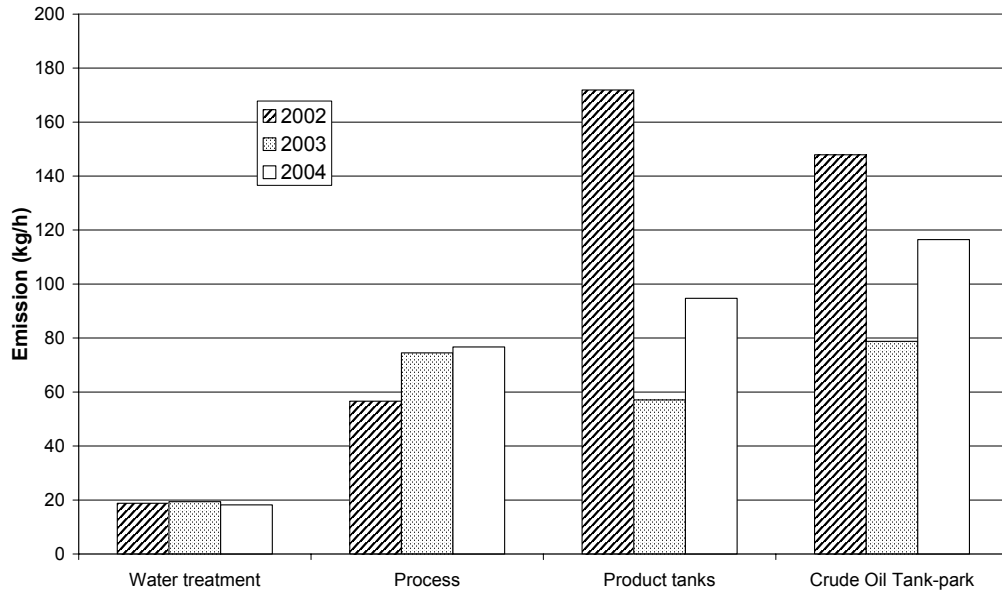
v=Measured on Volvovägen

t=Measured on Torslandavägen, Road 155

e=Measured on road east of entrance

**Table 9.** Emissions of alkanes from the different regions on Preemraff-Göteborg.

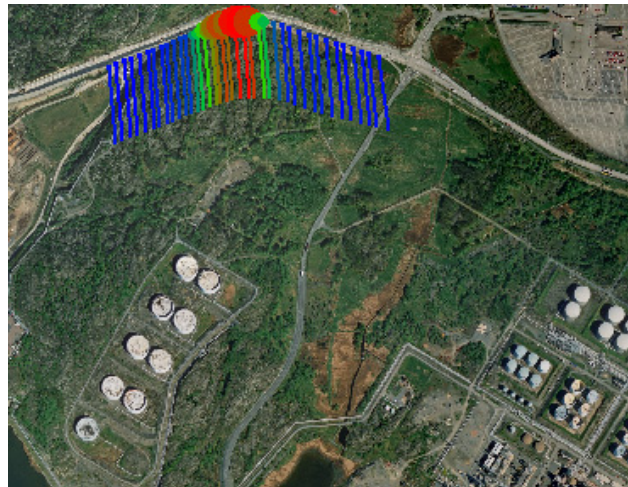
Source	Emission 2002 (kg/h)	Emission 2003 (kg/h)	Emission 2004 (kg/h)
Crude-oil tank-park	147.9	78.8	116.5
Process	56.6	74.5	76.7
Product Tank-park	171.9	57.1	94.7
Water treatment facility	18.8	19.4	18.2
<b>Total:</b>	<b>395.2</b>	<b>229.8</b>	<b>306.1</b>



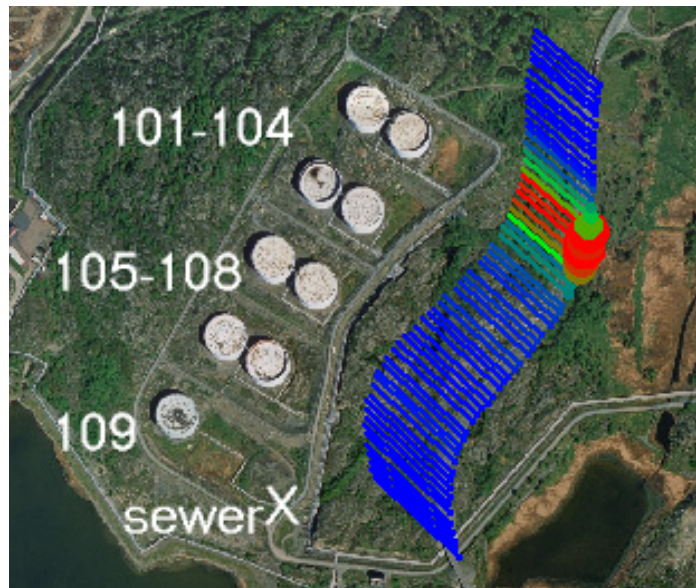
**Figure 15.** Measured emissions of alkanes from Preemraff-Göteborg during 3 years.

### 7.1.2 Crude-oil tank-park

Total measurements on the crude oil tank-park were done either along road 155, see Figure 16, or along the road located 200 m east of the tank park, see Figure 17. Figure 18 and Table 10 summarizes the results from the measurements on the crude-oil tank park. During year 2003 a point emission source was detected in the south-east corner and was identified to be a sewer. The location of the sewer is marked with a cross in Figure 17. During the measurements in year 2004, the emissions from the sewer were almost zero. No measurements on the sewer could be retrieved from the measurements done in year 2002.



**Figure 16.** Measurement on crude oil tank park, day 2 September 2003 (11:32) along road 155. The lines indicate the wind direction (they point towards a possible emission source). Red lines indicates points where high line integrated concentrations have been measured. Blue lines indicate points with low concentrations. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 17.** Measurement on crude oil tank-park day 20 September 2002 (11:35) along the road located 200m east of the tank-park. Red points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

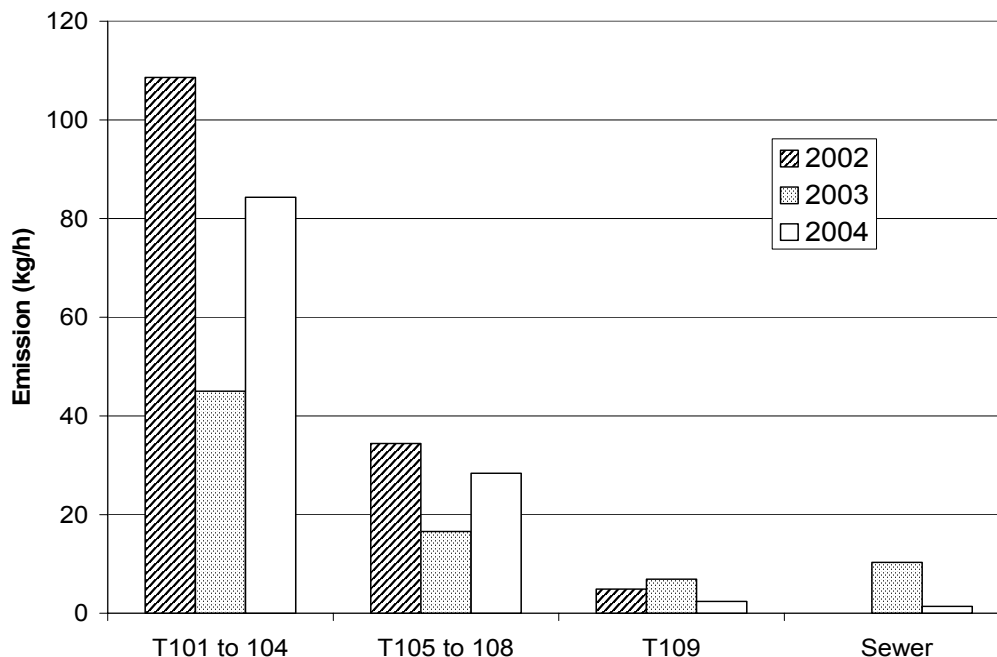


**Table 10.** Details of the measurements done on the crude-oil tank-park

Day	Crude-oil tank-park (kg/h)	T101 to 104 (kg/h)	T105 to 108 (kg/h)	T109 (kg/h)	Sewer (kg/h)	Wind speed (m/s)	Wind direction
12-Sep-2002	82.0	63.3	21.8	1.2		3.9-4.6	286°-290°
20-Sep-2002	183.8	72.3	21.5	3.6		4.0-5.7	280°-312°
24-Sep-2002	171.7					3.1-3.9	238°-284°
2002 <b>Average*</b>	<b>147.9</b>	(68.3) <b>108.6</b>	(21.6) <b>34.4</b>	(3.1) <b>4.9</b>			
18-Aug-2003	50.1	90.5				2.4-3.6	180°-199°
22-Aug-2003	192.3					8.0-9.9	256°-273°
28-Aug-2003	54.7					4.1-5.6	200°-225°
1-Sep-2003		49.3	33.5	1.0		0.8-6.0	35°-337°
2-Sep-2003	71.5					4.5-5.8	169°-208°
13-Oct-2003				4.3	12.4	3.1-3.6	49°-52°
14-Oct-2003		21.6	18.3	11.5	12.6	3.9-5.4	6°-9°
2003 <b>Average*</b>	<b>78.8</b>	(54.7) <b>45.0</b>	(20.1) <b>16.6</b>	(8.4) <b>6.9</b>	(12.5) <b>10.3</b>		
5-Aug-2004	95.6					3.0-4.2	217°-246°
10-Aug-2004	160.0					1.9-5.4	257°-320°
18-Aug-2004	164.0					3.6-5.9	186°-227°
9-Sep-2004	103.9					5.4-6.9	219°-242°
10-Sep-2004	128.7	166.0	50.8			4.0-7.6	206°-232°
16-Sep-2004	50.0	70.2	13.4	2.5	1.4	2.6-5.5	248°-337°
2004 <b>Average*</b>	<b>116.5</b>	(87.4) <b>84.3</b>	(29.5) <b>28.4</b>	(2.5) <b>2.4</b>	(1.4) <b>1.4</b>		

(\*) Weighted average using the inverse of standard deviation on each day as the weight.

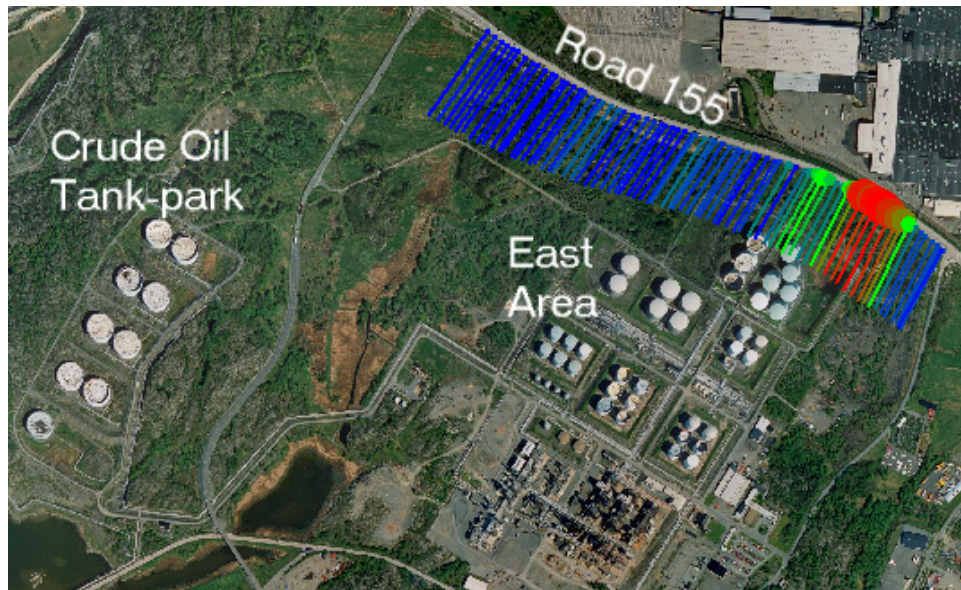
Note: The measurements done close to the tanks has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.



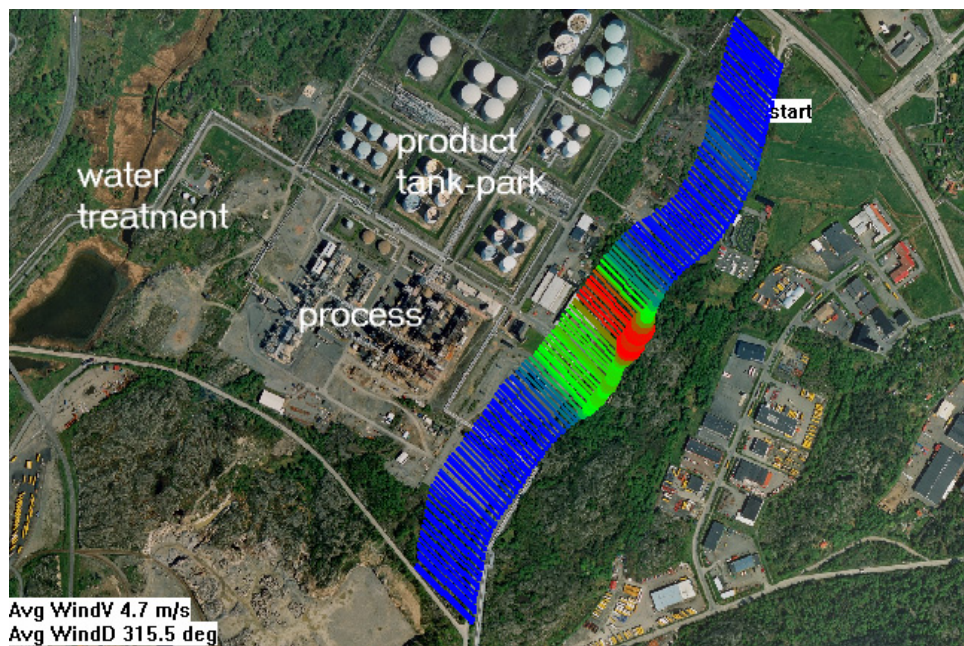
**Figure 18.** Emissions of alkanes from the crude-oil tank-park on Preemraff-Göteborg.

### 7.1.3 East area

The east area consists of the process, water treatment and product tank-park. Total measurements on the east area were done either on road 155, see Figure 19, or on the road running along the east side of the industry area, see Figure 20. The yearly averages of the measurements on the east area have been added to the yearly average for the crude-oil tank-park to calculate the total emission from Preemraff-Göteborg.



**Figure 19.** Total measurements on east area 2-September-2003 (13:25) along road 155. Red points correspond to the highest values (*Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden*)



**Figure 20.** Total measurements on east area 25-August-2002 (13:45) along the road running along the east side of the industry area. White points correspond to the highest values (*Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden*)

### 7.1.4 Process

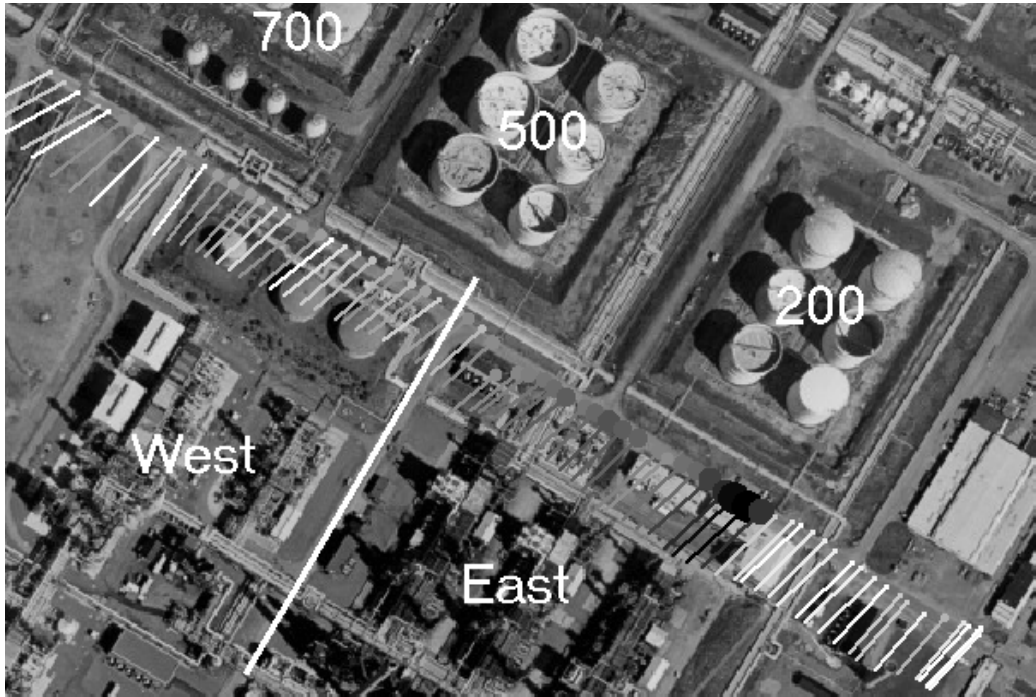
Table 11 lists the daily averages over all three years. Measurements have been done along the road that runs between the main entrance and the water treatment facility, see Figure 21 and on the road running along the east side of the industry area, see Figure 22.

The process has been divided into the west and east side and the proportion of emission between them have been calculated to 32% for west process and 68% for east process. The line that divides west from east is indicated in Figure 21. The east process is handling more volatile compounds and it is therefore reasonable that most of the emissions should come from the east process.

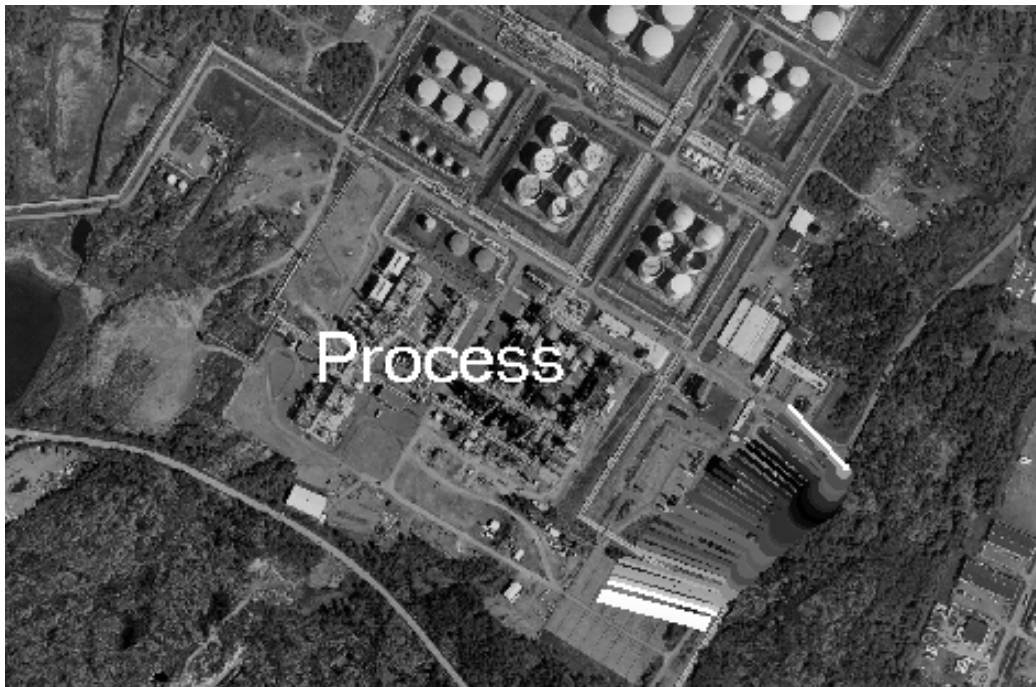
**Table 11.** Details of the measurements done on the process.

Day	Nr of traverses	Process (kg/h)	West Process (kg/h)	East Process (kg/h)	Wind speed (m/s)	Wind direction
9-Jul-2002	4	63.1	8.1	52.7	3.2-4.2	177°-185°
12-Jul-2002	3	66.3	18.9	40.0	2.3-4.2	165°-217°
18-Sep-2002	2	58.5			3.2-4.4	298°-332°
23-Sep-2002	2	51.7			2.7-3.5	281°-292°
<b>2002 Average*</b>	(11)	<b>56.6</b>	15.2 (24%)	47.8 (76%)		
25-Aug-2003	3	109.6			3.5-5.2	295°-319°
28-Aug-2003	4	108.3	42.7	90.4	4.5-5.6	207°-314°
16-Sep-2003	3	48.6			4.0-5.7	281°-310°
<b>2003 Average*</b>	(10)	<b>74.5</b>	42.7 (32%)	90.4 (68%)		
18-Aug-2004	7	72.0	33.1	38.8	3.4-4.8	173°-198°
3-Sep-2004	17	60.0	22.4	37.3	3.4-4.8	175°-233°
9-Sep-2004	10	89.0	37.4	51.4	4.6-6.6	211°-230°
10-Sep-2004	10	96.3	30.1	66.0	5.3-7.3	190°-241°
<b>2004 Average*</b>	(44)	<b>76.7</b>	31.1 (38%)	50.0 (62%)		
<b>Average All years</b>	(65)	<b>69.3</b>	<b>32%</b>	<b>68%</b>		

(\*) Weighted average using the inverse of standard deviation on each day as the weight.



**Figure 21.** Example of measurement on the process along the road running from the main entrance to the water treatment facility. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 22.** Example of measurement on the process 18-September-2002 along the road running along the east side of the industry area. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden).

### 7.1.5 Water treatment

The calculated average emissions from the water treatment were 18.8, 19.4 and 18.2 kg/hour for year 2002, 2003 and 2004. The yearly average has been almost constant. However, big daily variations have been observed. Highest daily average was 33.2 kg/hour and occurred 23 September-2003. Measurements on that day indicate that a big part of the measured emissions originates from an open well located 50 m southwest of the water treatment facility, see Figure 23.

Other days have also indicated high emissions from this well. Correlation measurements with trace-gas were performed on the well day 24 November-2004 and indicated a point source of 10 kg/h that day. However, it is not possible to say from this measurement how big part of the yearly emission that is emitted from the well.

The water treatment facility is located apart from other emission sources and this has made it possible to perform many measurements during the three years. Table 12 lists the daily average over all three years. For year 2002, wind-information was collected with a wind-meter mounted on a mobile mast with a height of 10 m located northeast of the facility. For year 2003 and 2004, wind-information from the wind-meter in the tower was used, but the wind speed was scaled with 50% to correspond to the wind-speed that was measured with the wind-meter that is mounted in the front of the measurement-car.

**Table 12.** Details of the measurements done on the water treatment facility.

Day	Nr of traverses	Average (kg/h)	Wind speed (m/s)	Wind direction
9-Jul-2002	4	13.1	3.0-4.8	173°-189°
18-Sep-2002	2	26.0	5.4-5.7	301°-308°
24-Sep-2002	8	12.0	2.0-3.9	165°-188°
<b>2002</b>		<b>18.8</b>		
<b>Average*</b>				
28-Aug-2003	3	14.0	1.9-2.8	210°-214°
2-Sep-2003	3	17.8	4.2-4.6	169°-170°
23-Sep-2003	8	33.3	3.5-5.6	241°-265°
<b>2003</b>		<b>19.4</b>		
<b>Average*</b>				
18-Aug-2004	10	20.6	1.7-2.2	172°-205°
3-Sep-2004	27	13.9	1.6-2.6	181°-240°
9-Sep-2004	35	17.5	2.3-4.2	217°-233°
10-Sep-2004	5	22.2	1.7-3.8	205°-245°
<b>2004</b>		<b>18.2</b>		
<b>Average*</b>				

(\*) Weighted average using the inverse of standard deviation on each day as the weight.





**Figure 23.** Example of measurement on the water treatment facility day 23-September 2003. Dark points correspond to the highest values. (*Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden*).

### **7.1.6 Product tank-park**

It has been difficult to retrieve the total emission from the product tank-park from direct measurements. Measurements were done along the road running from the main entrance to the water treatment facility when the wind was coming from north but it was later found out that the emissions from the process were interfering in those measurements. The path of the sun-ray between the sun and the measurement car is passing over the process in most measurements and was therefore cutting through the plume from the process even if the process is located leeward of the position of the measurements. This problem was first not anticipated but it was later found out when it was realized that the plume lift from the process was stronger than expected. It was therefore decided at a later stage that the emission from the product tanks should be calculated by taking the yearly average of the whole eastern part and subtract the yearly average for the process and water treatment facility, to get the yearly average for the product tank-park.

Close measurement by driving inside the product tank-park has been done to identify which tank-groups that have high emissions. The same problem occurred, i.e. that the sun-ray was traversing the process-plume, when measuring close to the 200, 500 and 700 tank-groups that are located close to the process. However, a few close measurements were possible on these tanks early in the day when the sun-ray was passing almost parallel to the road that runs between the main entrance and the water treatment facility. Therefore, few close measurements have been possible to conduct on these tank-groups. Tank groups 300, 400 and 600 are located further away from the process and the problem has therefore not occurred when measuring on them. The close measurements on the tank-groups have a low absolute accuracy and the measured emissions have therefore been normalized so that the sum of all tank groups is equal to the calculated total emission from the product tank-park. Table 13 shows details of the measurements done on the product tank-park. Since the measurements on individual tank-groups have low accuracy, only the average emission for all years should be used to make comparisons between individual tank-groups, see Figure 24.

**Table 13.** Detailed information of the measurements on tank-groups in the product tank-park.

Day	Product Tank park Total (kg/h)	200	300	400	500	600	700
<b>Contents of tanks</b>		Slops Naphtha Isomerate Gasoline	Slops Gas oil MK1- diesel	LGO <sup>1</sup> kerosene	Isomerate Reformate CCS <sup>4</sup>	HGO <sup>2</sup> Slops	Reformate MTBE <sup>3</sup> Naphtha
9-Jul-2002		25.2	27.5	11.8	19.9		30.0
12-Jul-2002					19.9		
11-Sep-2002		13.7	14.6		24.7	13.0	19.8
12-Sep-2002		39.1	8.9	4.6	24.1	8.5	
13-Sep-2002		37.9	35.6	20.8		2.7	
19-Sep-2002							22.0
<b>2002</b>		(34.8)	(23.0)	(11.5)	(22.9)	(7.8)	(27.0)
<b>Average*</b>	<b>171.9</b>	<b>47.1</b>	<b>31.0</b>	<b>15.6</b>	<b>30.9</b>	<b>10.5</b>	<b>36.6</b>
25-Aug-2003			17.5	8.9	23.5		
28-Aug-2003							
1-Sep-2003			22.1	4.5			13.1
16-Sep-2003				5.1			
13-Oct-2003		37.1		1.7	31.7		23.5
14-Oct-2003		27.8	10.2	8.7	19.5	18.8	55.4
<b>2003</b>		(33.0)	(17.1)	(5.5)	(24.9)	(18.8)	(37.8)
<b>Average*</b>	<b>57.1</b>	<b>13.7</b>	<b>7.1</b>	<b>2.3</b>	<b>10.4</b>	<b>7.8</b>	<b>15.7</b>
16-Sep-2004		30.2	13.2	12.4	24.6	10.1	10.8
27-Sep-2004				10.8	42.0	8.6	
<b>2004</b>		(30.7)	(13.4)	(11.3)	(37.2)	(9.5)	(10.8)
<b>Average*</b>	<b>94.7</b>	<b>25.7</b>	<b>11.2</b>	<b>9.5</b>	<b>31.2</b>	<b>8.0</b>	<b>9.1</b>
<b>Average</b>							
<b>All years</b>	<b>114.2</b>	<b>28.8</b>	<b>16.4</b>	<b>9.1</b>	<b>24.2</b>	<b>8.8</b>	<b>20.5</b>

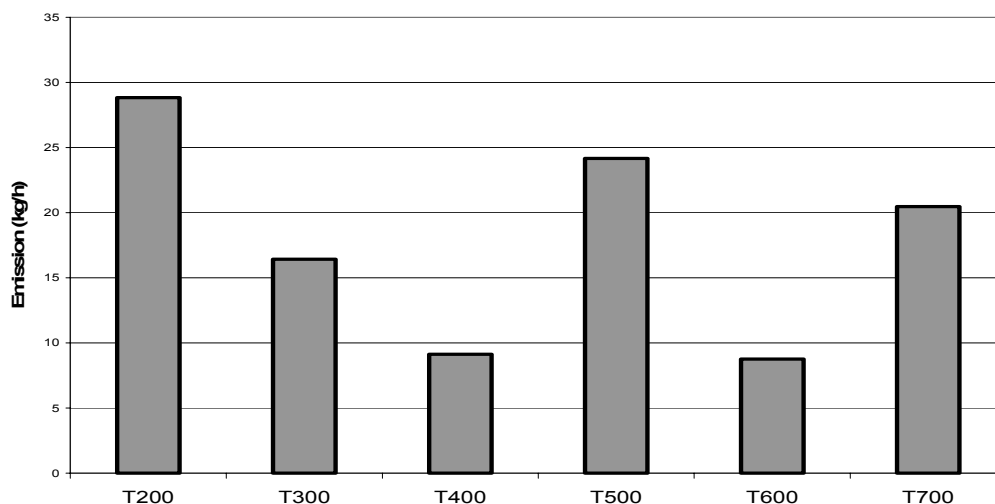
(1) LGO=Light Gas Oil

(2) HGO=Heavy Gas Oil

(3) MTBE=Methyl-Tertiary-Butyl-Ether

(4) CCS=Catalytic Cracked Spirit

(\*) Weighted average using the inverse of standard deviation on each day as the weight.



**Figure 24.** Average emission over all years for individual tank-groups in the product tank-park.

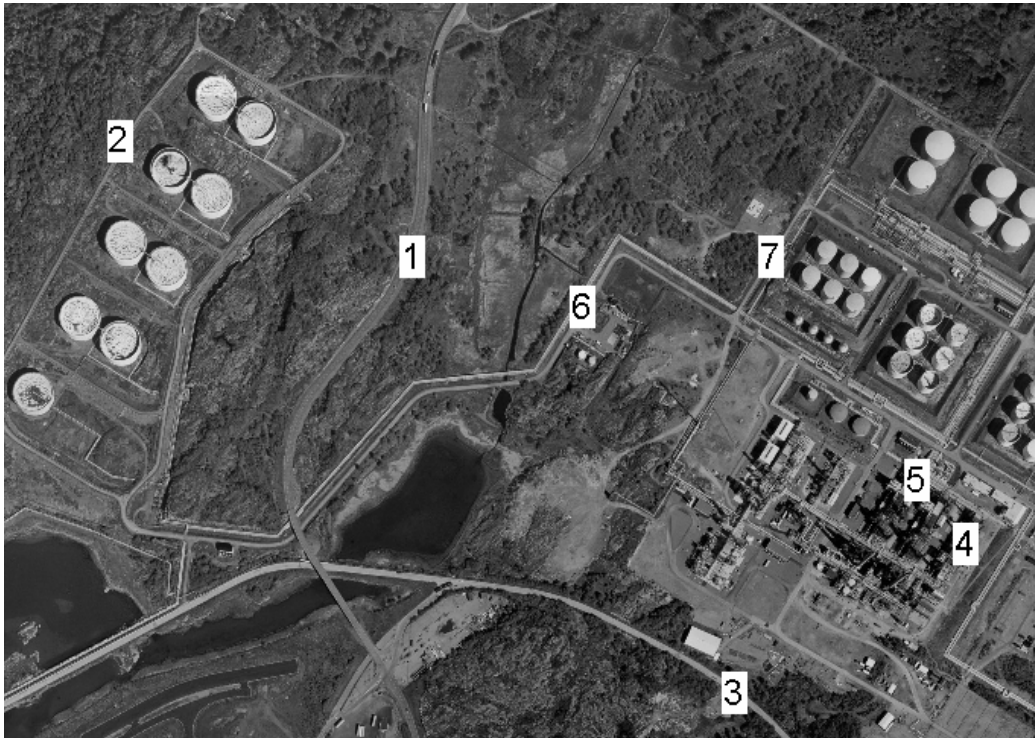


### 7.1.7 Measurements of aromatic hydrocarbons on Preemraff-Göteborg

Measurements of aromatic hydrocarbons have been done with the method described in chapter 7.5. Five samples were collected in the crude oil tank-park, four samples in the east process, two samples from the water treatment facility and one sample from tank group 700 in the product tank-park. The measurements are summarized in Table 14. These measurements have been added to the larger database of measurements that have been collected during the KORUS-project. The complete results derived from the whole database have been used when calculating the average emissions of aromatic hydrocarbons from Preemraff-Göteborg. This is further described in chapter 7.5. The FTIR-point measurement system is mounted inside the measurement car. Therefore, measurements were always done on roads, with the exception of the measurements in the process, where long tubes were connected to the system in the car and air was sucked in from higher positions above the process complex. Figure 25 shows the positions where the samples were collected.

**Table 14.** Mass proportion between aromatics/alkane from point measurements done with TENAX-tubes and GC-analysis and simultaneous point-measurements of Butane with FTIR. The numbers in the column marked Pos refers to the positions in Figure 25.

Measurement site	Pos	Date	Benzene	Toluene	Ethyl-benzene	m+p-xylene	o-xylene	GC Aromatics Weight (ng)	FTIR Butane Weight (ng)	Aromatics/Butane Ratio %
Preem SE crude oil	1	040802	0,239	0,221	0,067	0,258	0,215	62,5	888	7,0
Preem crude oil tank park	2	040816	0,372	0,336	0,044	0,197	0,050	107,6	5767	1,9
Preem crude oil tank park	2	040816	0,372	0,334	0,045	0,199	0,050	79,2	3645	2,2
Preem cleaning	6	040816	0,215	0,474	0,053	0,201	0,057	745,7	3657	20,4
Preem cleaning	6	040816	0,211	0,477	0,053	0,202	0,056	821,2	4103	20,0
Preem process	3	040816	0,162	0,414	0,069	0,275	0,080	239,9	1107	21,7
Preem East proc	4	040817	0,178	0,622	0,037	0,132	0,032	202,6	4678	4,3
Preem East proc	4	040817	0,188	0,366	0,067	0,301	0,079	89,7	3748	23,9
Preem process Butane tower	5	040817	0,184	0,375	0,069	0,295	0,076	250,1	2702	9,3
Preem 700 tanks	7	040818	0,069	0,507	0,241	0,120	0,063	767,0	-	-
Preem crude oil tank park.	2	041221	0,249	0,398	0,050	0,250	0,055	41,8	5225	0,8
Preem crude oil tank park.	2	041221	0,236	0,339	0,118	0,049	0,207	70,5	5875	1,2



**Figure 25.** Numbers indicates the positions where samples were taken to retrieve the ratio between aromatic hydrocarbons and alkanes. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden).

## 7.2 Measurements on Preemraff-Lysekil

Measurements were done over 14 days in May/June/October-2003 and 15 days in July/September-2004. The total emissions of alkanes from the whole refinery for years 2003 and 2004 were calculated to 550 kg/h and 537 kg/h (4818 and 4704 ton/y), see Table 15. The calculations are based on far-away measurements with the SOF method along the road to the product harbor on the east side of the industry area, when the wind was coming from west, see Figure 26.

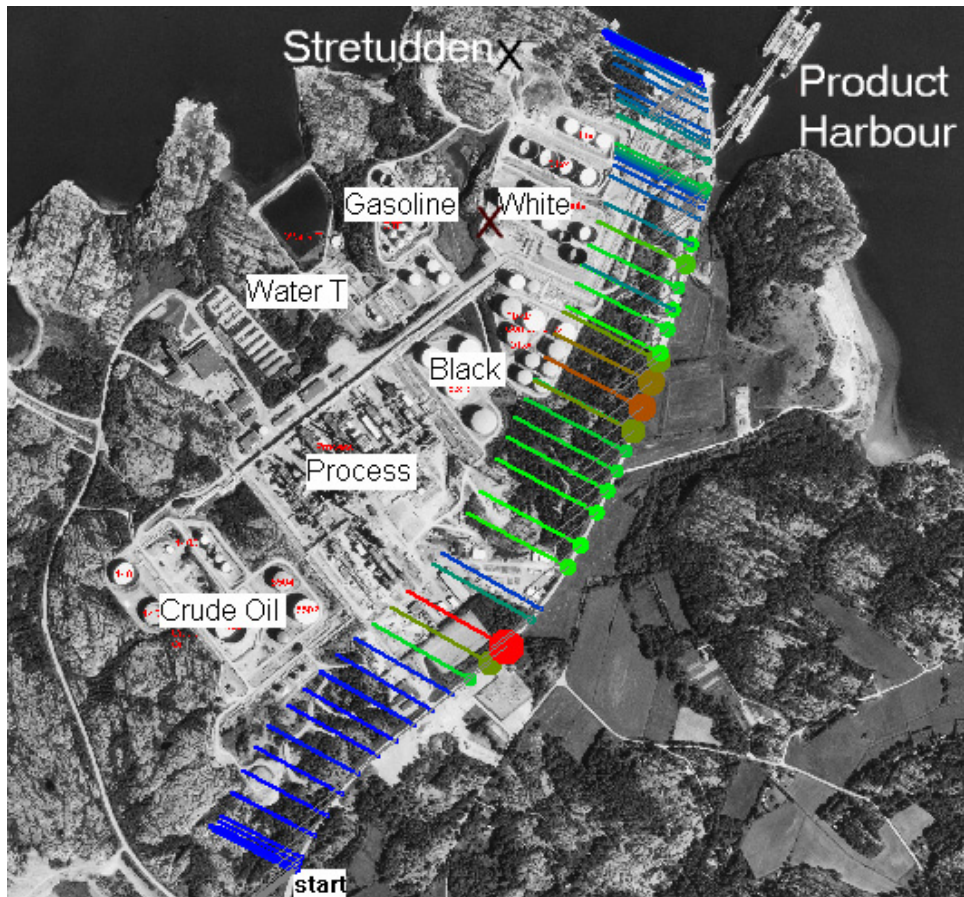
The refinery has been divided in nine regions and the emissions from each region has been retrieved by making measurements closer to each region, see Figure 27. Each region will be discussed in detail in the following sections.

**Table 15.** Emissions of alkanes from the different regions on Preemraff-Lysekil.

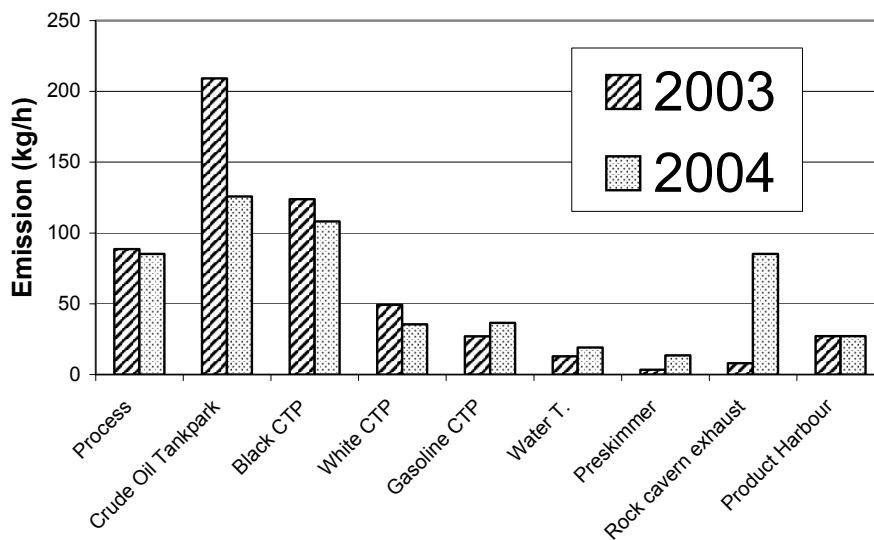
Source	Emission 2003 (kg/h)	Emission 2004 (kg/h)
Process	88.7	85.2
Crude-Oil-Tank-Park	209.4	125.9
Black Components Tank-park	124.1	108.1
White Components Tank-park	49.4	35.6
Gasoline Components Tank-park	27.0	36.5
Water Treatment Facility	12.2	19.2
Preskimmer	3.5	13.5
Rock Cavern Exhaust	8.0	85.3
Product Harbor	27.3	(27.3)
Total:	<b>549.6</b>	<b>536.6</b>

### 7.2.1 Applied wind information

During year 2003 and 2004, a wind-meter was mounted on the top of the lighthouse called Stretudden, 35 m above ground. The wind direction from this meter was corrupt for a number of days. Therefore, information about wind-direction has been collected from the wind-meter belonging to Preemraff-Lysekil that is permanently mounted in the White Components Tank-park. The wind speed has anyhow been retrieved from the meter in the lighthouse. All total measurements have used this combination of wind-information because it makes it easier to compare total measurements between different days.



**Figure 26.** Total measurement day 12 July 2004 (15:40) along the road to the product harbor. The positions of the two wind-meters are marked with X. The lines indicate the wind direction (they point towards a possible emission source). Red lines indicates points where high line integrated concentrations have been measured. Blue lines indicate points with low concentrations. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 27.** Measured emissions of alkanes from Preemraff-Lysekil.

## 7.2.2 Crude-oil tank-park

Table 16 shows the results for the crude oil tank-park. Total measurements on the crude oil tank-park has been done on the road that divides the process from the crude oil tank-park, see Figure 28. Close measurements have been done inside the tank-park to measure the emission from each tank. The daily averages from these measurements are given in Table 16. Figure 29 shows the emission for each tank for the two years. Tanks 1403-1405 and 4404 are located close together and it has not been possible to split them up further. These tanks are called tank group 1403-1405 hereafter. They contain heavy and light residues, acidified water and heavy crack naphtha.

It has not been possible to make close measurements on the tanks 5502 and 5504 (containing naphtha) to identify the emission from these tanks. The best situation for this would be if the wind is coming from east and this never happened during the measurement days. However, point measurements close to the tanks have indicated that the emissions from these tanks are low in comparison with the other tanks.

There are few measurements on the tank-group 1403-1405 from year 2003 but they indicate an increase of the emissions from these tanks from 2003 to 2004. This conclusion is also supported by the fact that the strongest emissions when doing measurements on total emission from the crude-oil tank-park often points towards these tanks. An example of this is shown in Figure 28.

**Table 16.** Details of the measurements of alkane emission from the crude oil tank-park.

Day	Crude-oil Tank park (kg/h)	Wind speed (m/s)	Wind direction	T1401 (kg/h)	T1402 (kg/h)	T1406 (kg/h)	Tank group 1403-1405 (kg/h)
030601	199.0	2.1-4.1	233°-239°	11.7	26.7	148.5	17.7
030602	177.1	1.8-4.3	242°-248°	19.6	15.2	103.7	20.8
030613				19.7	6.1		
<b>2003 Average*</b>	(187.1) <b>209.4</b> (100%)			(15.7) <b>18.4</b> (9%)	(16.4) <b>19.2</b> (9%)	(127.9) <b>149.6</b> (71%)	(19.0) <b>22.2</b> (11%)
040707	133.9	2.7-6.5	195°-258°			42.7	
040708				3.8	5.5	46.1	
040717	150.6	3.0-4.3	191°-231°	2.8	21.5	34.1	
040720	92.2	2.7-6.7	252°-267°	13.5	10.8	51.6	63.3
040728	52.3	2.6-4.4	194°-236°	2.4	1.9	29.4	19.6
040906	98.6	6.6-7.7	293°-298°				
040907	81.4	4.8-9.2	291°-325°				
<b>2004 Average*</b>	(103.2) <b>125.9</b> (100%)			(9.3) <b>12.8</b> (10%)	(13.6) <b>18.7</b> (15%)	(38.5) <b>52.8</b> (42%)	(30.4) <b>41.7</b> (33%)
<b>Average All years</b>	<b>167.2</b>			<b>15.5</b> (9%)	<b>18.9</b> (11%)	<b>101.1</b> (60%)	<b>31.9</b> (19%)

(\*) Weighted average using the inverse of standard deviation on each day as the weight.

Note: The measurements done close to the tanks has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.

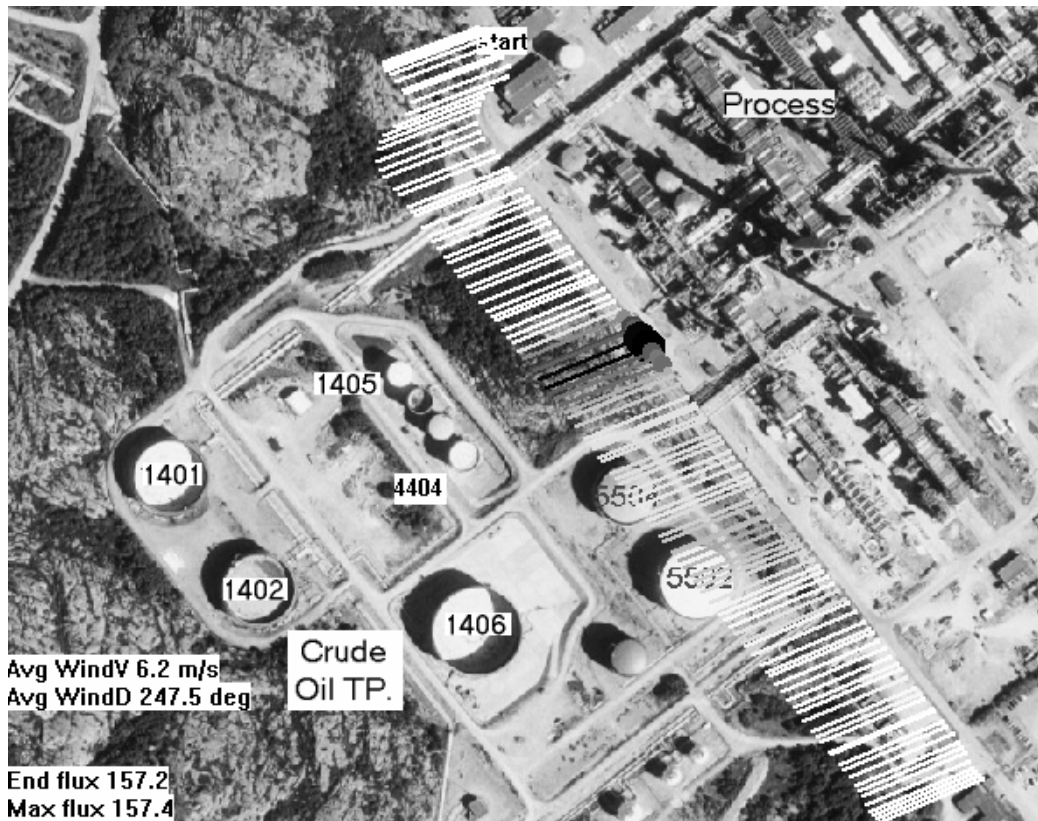


Figure 28. Measurement on crude oil tank-park day 7 July 2004. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

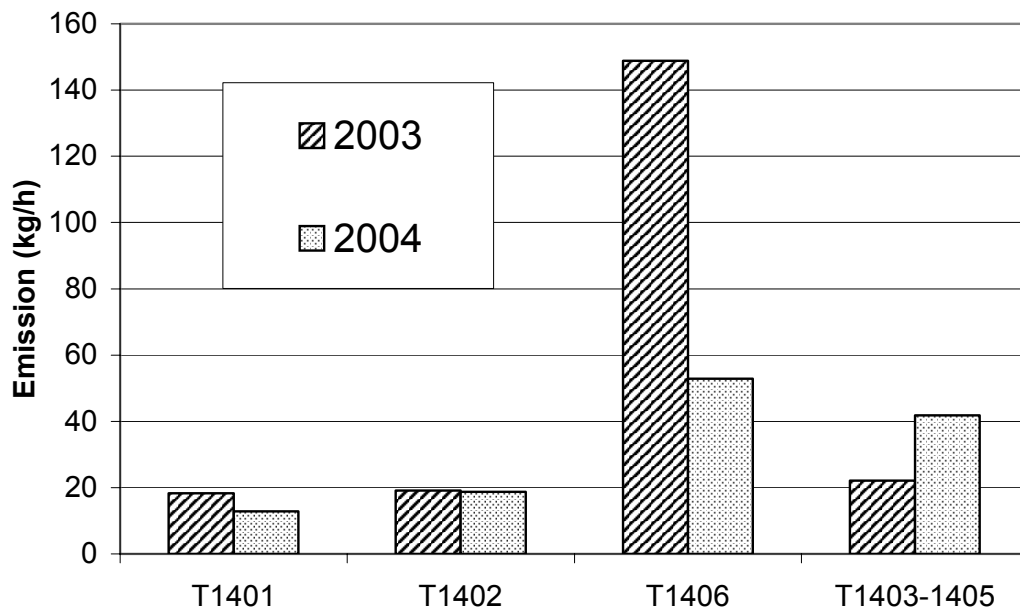


Figure 29. Yearly averages from the tanks in the crude oil tank-park on Preemraff-Lysekil.

An example of how close measurements were done on tank 1406 is shown in Figure 30. The measurements indicate that emissions from tank 1406 were high year 2003 and much lower year 2004. Earlier measurements with the DIAL method have also shown high emissions from this tank and it has been known that the floating roof on the tank is not circular and therefore not tight. Before year 2003, a second seal was built around the tank-roof in hope that it would decrease the emissions, but the measurements from 2003 shows that the emissions were still high after the tank has been rebuilt. No changes or maintenance work have been made to the construction between year 2003 and 2004. Table 17 shows more details about this tank during the days when measurements were done. The information indicates that the reduction of emission is possibly a result of change of crude oil type. This is unexpected since the crude oil types Gullfaks C and DUC should have similar properties. In particular, the LPG-contents of the crude oil, that can have importance for the emissions, have only changed from 1.85% to 1.59%. More measurements are required to actually tell if the reduction of emissions is a result of the change of crude-oil type.

A new study using trace gas releases and the FTIR point measuring system has been done during July/August-2005 and a report on the results will be published by Samuelsson and Mellqvist in 2006.

**Table 17.** Details for tank 1406 during the days when measurements were done.

Day	Measured emission (kg/h)	Wind speed (m/s)	Media-temp. (°C)	Outer temp. (°C)	Tank roof level	Crude oil type
1-June-2003	149	1.8-3.4	24	19	Top	Gullfaks C 49% DUC 43% Gullfaks A 8%
2-June-2003	104	2.2-3.5	25	20	Top	Gullfaks C 49% DUC 43% Gullfaks A 8%
16-Oct-2003	54	3.4-3.9	22	8	Top	Gullfaks C 36% DUC 64%
7-Jul-2004	43	2.9-3.8	22	16	Top	DUC 100%
8-Jul-2004	46	3.0-4.3	22	20	70% of top	DUC 100%
17-Jul-2004	34	4.7-5.4	22	19	Top	DUC 100%
20-Jul-2004	52	3.0-4.2	22	18	Low	DUC 100%
28-Jul-2004	29	3.6-4.2	22	19	Top	DUC 100%

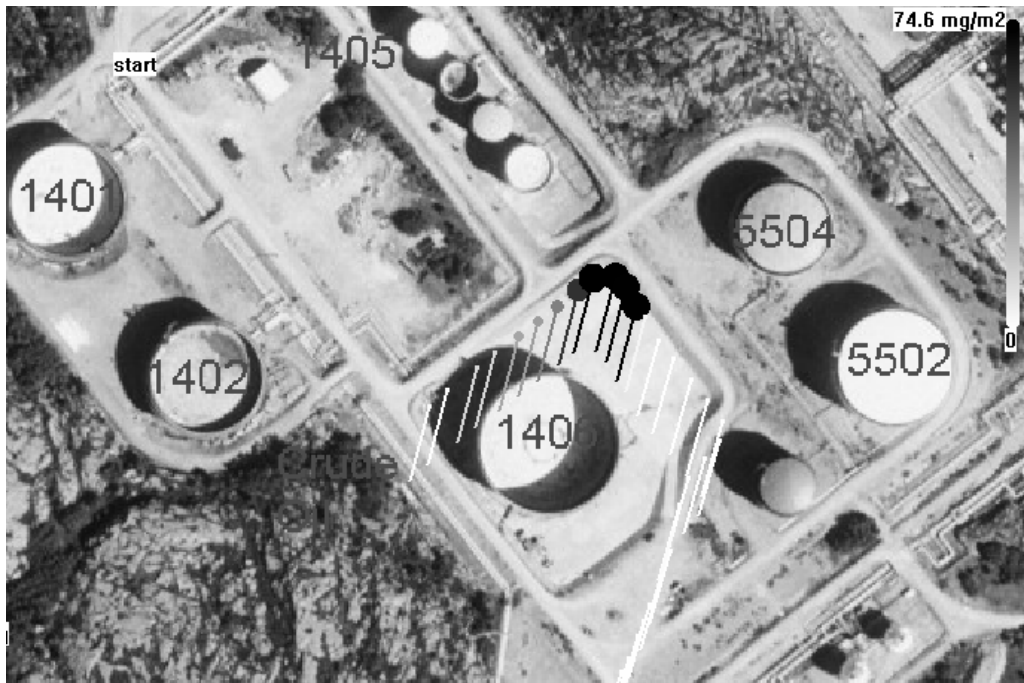
Vapor pressures:

Gullfaks C 0,61 kp/cm<sup>2</sup>  
DUC 0,62 kp/cm<sup>2</sup>

LPG-content according to lab-tests done on the arrival of the Crude-oil load:

Gullfaks C year 2003 1.85%  
DUC year 2003: 1.79%  
DUC year 2004: 1.59%





**Figure 30.** Close measurement on tank 1406, day 17 July 2004. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden).



### 7.2.3 Process

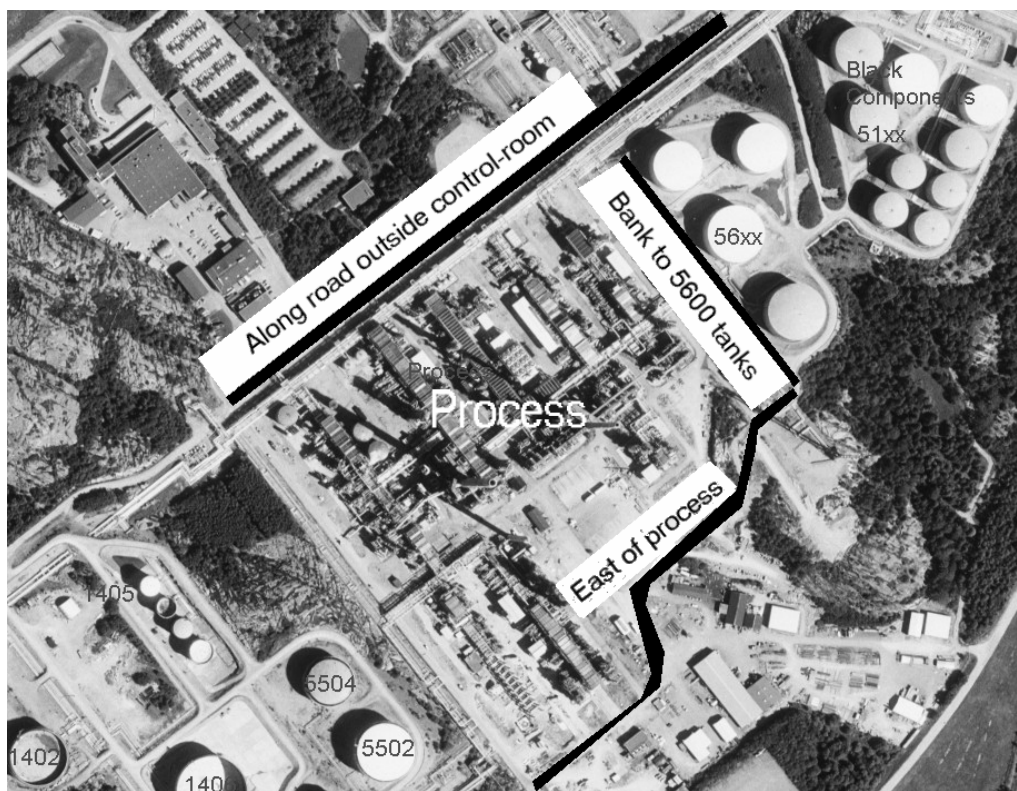
During year 2003, process measurements were only done 21 June. Six traverses were then done on the east side of the process when the wind was coming from west. During year 2004, measurements were done on the process on five days. Details about the measurements are given in Table 18. Three different positions have been used, depending on the wind direction, see Figure 31.

**Table 18.** Details of the measurements of alkane emissions from the process.

Day	Process (kg/h)	Wind speed (m/s)	Wind direction	Position
030621	79.3	5.6-7.1	290°-303°	East of process
<b>Average* 2003</b>	(79.3) <b>88.7</b>			
040716	102.5	4.6-5.8	277°-295°	East of process
040717	96.2	3.2-4.5	168°-184°	Along the road outside the control room
040728	81.1	3.6-4.0	201°-214°	Along the road outside the control room
040729	94.3	3.0-4.1	238°-250°	On the bank to the 5600 tanks.
040730	59.8	1.1-2.7	76°-133°	Along the road outside the control room
<b>Average* 2004</b>	(69.8) <b>85.2</b>			

(\*) Weighted average using the inverse of the standard deviation each day as the weight.

Note: The measurements done close to the process has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.



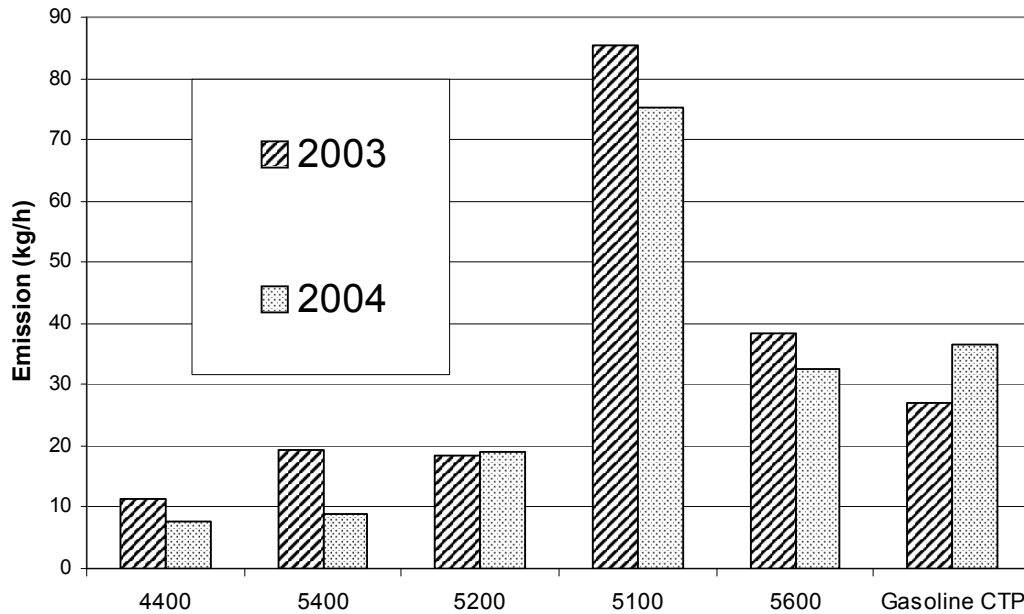
**Figure 31.** The different measurement paths when measuring emission from the process. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden).

### 7.2.4 Product tank-park

The product tank-park has been divided into three larger groups: White components tank-park that contains lighter components, Black components tank-park that contains heavier components, and Gasoline components tank-park.

White Components Tank-park consists of the tank groups 4400, 5400 and 5200 where all tanks contain lighter components. Black Components Tank-park consists of the tank groups 5100 and 5600 where all tanks contain heavier components. The group called Gasoline components tank-park is situated apart from the other product tanks and has not been divided into smaller groups. One of the tanks in the 5400-group was inactive due to maintenance work during the measurements in 2004.

It has been difficult to separate the individual tank groups and the calculated emission for each tank group therefore has low reliability. The calculated emissions from the three larger groups have higher reliability. Figure 32 shows the emissions from all tank-groups in the product tank-park for both years. Table 19 to Table 21 give the details of the measurements on each tank-group.



**Figure 32.** Yearly averages from the tanks in the product tank-park at Preemraff-Lysekil.

**Table 19.** Details of the measurements of alkane emissions from the White components tank-park.

Day	White CTP. Total (kg/h)	Wind speed (m/s)	Wind direction	Tank group 4400 (kg/h)	Tank group 5400 (kg/h)	Tank group 5200 (kg/h)
<b>Tank contents</b>				Diesel MTBE	Gasoline	Kerosene Gas oil
31-May-2003	42.3	5.1-6.6	303°-321°	14.6 7.0 12.4	21.3	20.8
21-June-2003	50.8	5.2-6.7	283°-305°			
26-June-2003						
27-June-2003	41.1	2.5-6.3	51°-309°			
<b>Average* 2003</b>	(44.1) <b>49.4 kg/h</b>			(11.0) <b>11.4</b>	(18.9) <b>19.6</b>	(17.6) <b>18.3</b>
16-July-2004	23.3			3.1	7.5	12.3
27-July-2004	36.0			5.0	8.8	19.9
30-July-2004				8.0		
<b>Average* 2004</b>	(28.8) <b>35.6 kg/h</b>			(6.7) <b>7.7</b>	(7.8) <b>9.0</b>	(16.4) <b>18.9</b>

**Table 20.** Details of the measurements of alkane emissions from the Black components tank-park.

Day	Black CTP. Total (kg/h)	Wind speed (m/s)	Wind direction	Tank group 5100 (kg/h)	Tank group 5600 (kg/h)
<b>Tank contents</b>				Heavy Gas Oil	Gas Oil Vacuum Gas Oil
21-June-2003	60.7	5.6-6.7	284°-302°	51.4	9.5
27-June-2003	116.8	6.5-6.5	307°-307°	68.5	42.3
<b>Average* 2003</b>	(110.9) <b>124.1</b>			(58.2) <b>85.5</b>	(26.1) <b>38.4</b>
16-July-2004	117.7	3.8-6.1	252°-291°	93.5	23.7
27-July-2004				63.3	51.6
28-July-2004	53.4	2.7-3.5	191°-223°	38.9	13.3
<b>Average* 2004</b>	(88.6) <b>108.1</b>			(68.7) <b>75.4</b>	(29.9) <b>32.7</b>

**Table 21.** Details of the measurements of alkane emissions from the Gasoline components tank-park.

Day	Gasoline CTP. (kg/h)	Wind speed (m/s)	Wind direction
31-May-2003	18.1	5.0-5.8	311°-313°
21-June-2003	34.3	2.8-5.5	220°-276°
<b>Average* 2003</b>	(24.1) <b>27.0</b>		
16-July-2004	18.2	7.3-8.0	247°-253°
17-July-2004	48.7	2.9-4.1	199°-222°
24-July-2004	17.9	5.9-8.3	232°-240°
27-July-2004	48.4	4.3-5.3	235°-243°
30-July-2004	27.1	1.7-5.0	240°-328°
<b>Average* 2004</b>	(29.9) <b>36.5</b>		

(\*) Weighted average using the inverse of standard deviation on each day as the weight.

Note: The measurements done close to the tanks has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.

### 7.2.4 Water treatment facility

Measurements on the water treatment facility have either been made along the road outside the control-room or down by the water treatment facility along the north side, see Figure 33. The measurements done on the north side are very close to the source. Also, the water treatment facility is located in a valley. Therefore different wind information has to be used depending on where the traverses with the car were done. For the traverses along the north side, the wind was taken from averages over one minute from the wind-meter in the front of the measurement car. This wind-meter is described in detail in reference [1]. Table 22 shows the daily averages, the measurement positions and what wind information that has been used for each day.

**Table 22.** Details of the measurements of alkane emissions from the water treatment facility.

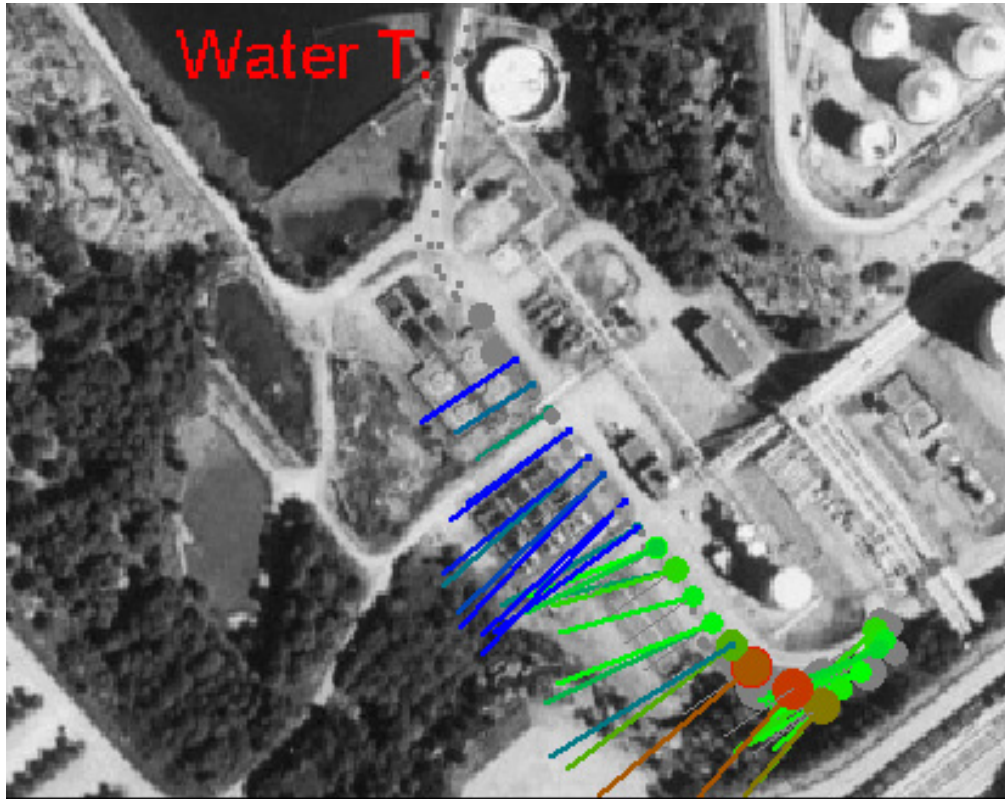
Day	Emission (kg/h)	Measurement position	Wind information	Wind speed (m/s)	Wind direction
31-May	8.2	Along the road outside the control room	Preemraff-Lysekil's own wind meter in White CTP.	3.3-4.4	273°-318°
5-June	11.3	Along north side.	Wind-meter on car.	2.3-3.2	172°-223°
16-June	8.1	Along the road outside the control room	Wind meter on road.	2.4-3.4	215°-263°
25-June	12.3	Along the road outside the control room	Preemraff-Lysekil's own wind meter in White CTP.	4.5-5.6	314°-324°
<b>Average* 2003</b>	(10.9) <b>12.2</b>				
17-July	18.2	Along north side.	Wind-meter on car.	2.7-3.1	175°-212°
30-July	13.1	Along the road outside the control room	Preemraff-Lysekil's own wind meter in White CTP.	4.1-4.9	318°-327°
<b>Average* 2004</b>	(15.8) <b>19.2</b>				

(\*) Weighted average using the inverse of standard deviation on each day as the weight.

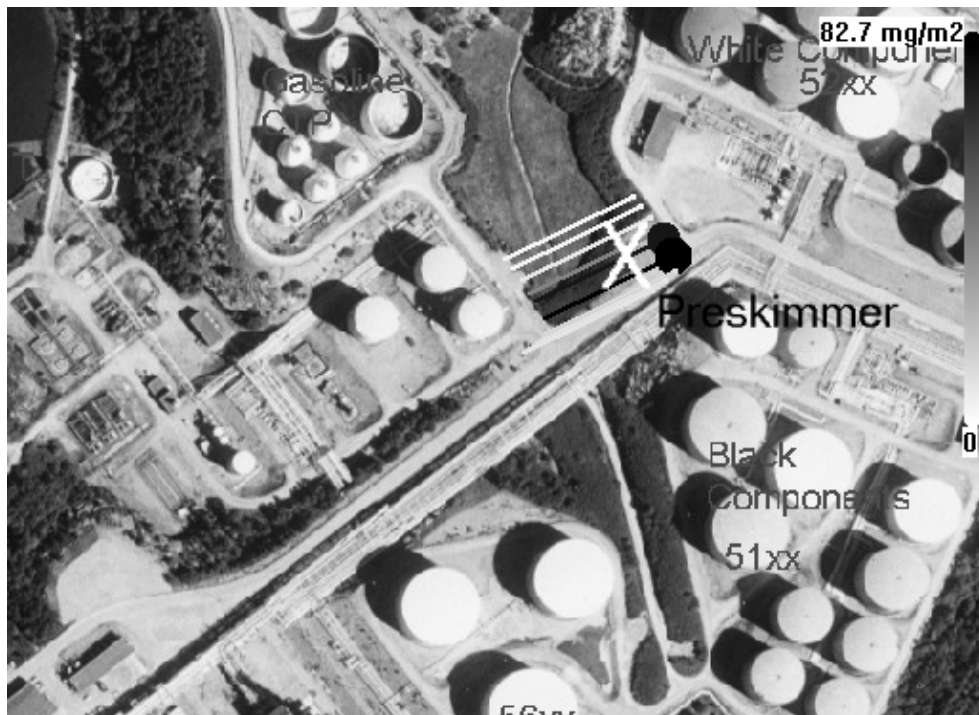
Note: The measurements done close to the tanks has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.

### 7.2.5 Preskimmer

While measuring in summer 2004, it was discovered that the preskimmer was a significant point source and this motivated a special study of the preskimmer. The preskimmer is located between the Gasoline Components tank-park and the White Components tank-park. Some of the waste water first pass the preskimmer where the preskimmer takes care of large debris before it gets to the waste water facility. From old measurements from year 2003, a few measurements could be retrieved but these measurements do not have as high quality as from year 2004. However they indicate clearly that the preskimmer had lower emissions year 2003. Average was **3.5 kg/h** for year **2003** and **13.4 kg/h** for year **2004**. Figure 34 shows a measurement on the preskimmer.



**Figure 33.** Example of traverse done along north side on the water treatment. Red points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 34.** Example of measurement done on the preskimmer day 16 July 2004. The position of the preskimmer is marked with X. Dark points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.2.6 Rock cavern exhaust

While measuring in summer 2004, a strong point source was discovered when the total measurements were done all the way to the northeast point along the coastline. The source was identified to the rock cavern exhaust that is located on the hill and is marked with X on the map in Figure 35. Since this source was not known before, it has probably been missed in the total measurements year 2003. From old measurements from year 2003, a few measurements could be found that indicated a source at this point. However, it shows a much lower emission. The average emissions were **6.9 kg/h** for **2003** and **84.0 kg/h** for year **2004**.

The emissions from the exhaust depend on the activity with the rock cavern, for example if products are pumped to boats or if the cavern is filled. The source can therefore not be assumed to be constant and it is therefore difficult to say if a real increase in the emissions has occurred between year 2003 and 2004.



**Figure 35.** Example of traverse done on the rock cavern exhaust, day 29 July 2004. The position of the rock cavern exhaust is marked with X. Dark points correspond to the highest values (*Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden*)



### 7.2.7 Product harbor

Two measurement days on the product harbor were done year **2003** and the average emission was calculated to **27.3 kg/h**. Because emissions from the product harbor is not detected in the measurements of total measurements that was described in section 7.2, this 27.3 kg/h has been added to the measured total emissions to estimate the total emission from Preemraff-Lysekil. No measurements were done on product harbor during 2004. To be able to compare the total-emission between the two years, it has been assumed that the emission year 2004 was also 27.3 kg/h. However, the product harbor has been equipped with a new VRU between year 2003 and 2004 to reduce the emissions. This has not been considered in this study. Figure 36 shows an example of traverse done on day 27 June 2003.



**Figure 36.** Example of traverse done on the product harbor, day 27 June 2003. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.2.8 Measurements of aromatic hydrocarbons on Preemraff-Lysekil

Measurements of aromatic hydrocarbons have been done with the method described in chapter 7.5. One sample was collected in the crude oil tank park, two samples from the process, two samples from the water treatment facility and three samples from the product tank-park. The measurements are summarized in Table 23. These measurements have been added to the larger database of measurements that have been collected during the KORUS-project. The complete results derived from the whole database have been used when calculating the average emissions of aromatic hydrocarbons from Preemraff-Lysekil. This is further described in chapter 7.5. The FTIR-point measurement system is mounted inside the measurement-car. Therefore, measurements were always done on roads. Figure 37 shows the positions where the samples were collected.

**Table 23.** Mass proportion between aromatics/alkane from point measurements done with TENAX-tubes and GC-analysis and simultaneous point-measurements of Butane with FTIR. The numbers in the column marked Pos refers to the positions in Figure 37.

Measurement site	Pos	Date	Benzene	Toluene	Ethyl-benzene	m+p-xylene	o-xylene	GC Aromatics Weight (ng)	FTIR Butane Weight (ng)	Aromatics/Butane Ratio %
Preemraff-Lysekil tank 1406	1	040707	0,169	0,253	0,092	0,301	0,184	52,6	3806	1,4
Preemraff-Lysekil process	2	040707	0,084	0,237	0,109	0,392	0,178	45,1	507	8,9
Preemraff-Lysekil process	2	040713	0,082	0,158	0,113	0,470	0,177	218,9	3748	5,8
Preemraff-Lysekil black comp tanks	3	040712	0,047	0,215	0,073	0,299	0,366	593,8	3811	15,6
Preemraff-Lysekil white comp tanks	4	040714	0,057	0,349	0,109	0,379	0,105	648,3	1664	39,0
Preemraff-Lysekil gasoline comp tanks	5	040713	0,059	0,414	0,093	0,333	0,101	511,1	3789	13,5
Preemraff-Lysekil water treatment	6	040713	0,164	0,450	0,075	0,245	0,066	582,5	3959	14,7
Preemraff-Lysekil preskimmer	7	040713	0,070	0,318	0,106	0,383	0,123	501,0	3902	12,8



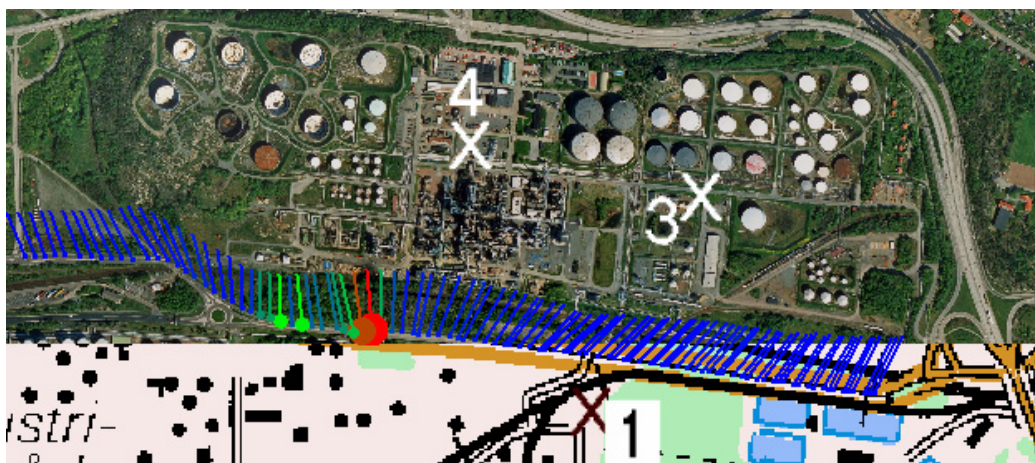


**Figure 37.** Numbers indicates the positions where samples were taken to retrieve the ratio between aromatic hydrocarbons and alkanes. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.3 Measurements on Shellraff

Measurements were done over 14 days in July/August/October-2003 and 9 days in May/June/October-2004. Shellraff had a total production stop in May-June 2003 and production was started about two weeks before the measurements were started. There was also intensive maintenance work being done on the tanks in the east tank-park. Therefore, many non-routine situations did occur within the industry when the measurements were done in 2003. The measurements done year 2004 are probably more representative for the industry when it is running under normal conditions.

The total emissions of alkanes from the whole refinery for years 2003 and 2004 were calculated to 348 kg/h and 122 kg/h (3051 and 1070 ton/y). The calculations are based on far-away measurements with the SOF method along Oljevägen, when the wind was coming from north, see Figure 38. The reasons for the reductions can primarily be found in reductions in the emissions from the process, hysomer and water treatment facility.

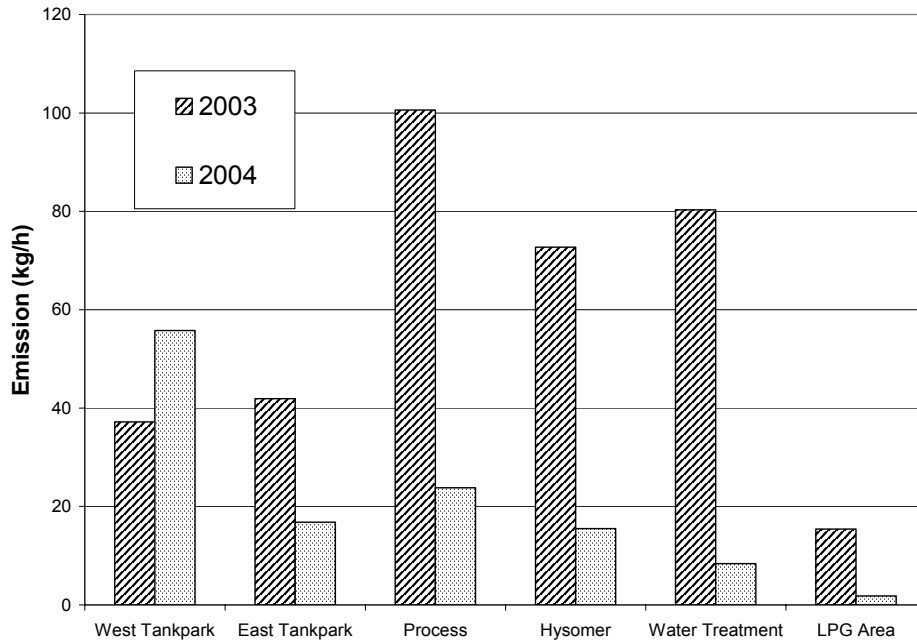


**Figure 38.** Total measurement day 10 July 2003 (14:49) along Oljevägen. The positions of the four wind-meters are marked with X. The lines indicate the wind direction (they point towards a possible emission source). Red lines indicates points where high line integrated concentrations have been measured. Blue lines indicate points with low concentrations. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

The refinery has been parted in six regions and the emissions from each region has been retrieved by making measurements closer to each region, see Table 24 and Figure 39. Each region will be discussed in detail in the following sections.

**Table 24.** Emissions of alkanes from the different regions on Shellraff in Göteborg.

Source	Emission 2003 (kg/h)	Emission 2004 (kg/h)
West Tank park	37.2	55.8
East Tank park	41.9	16.8
Process	100.6	23.8
Hysomer	72.7	15.5
Water Treatment Facility	80.3	8.4
LPG area	15.4	1.8
<b>Total:</b>	<b>348.1</b>	<b>122.1</b>



**Figure 39.** Measured emissions of alkanes from Shellraff in Göteborg.

### 7.3.1 Applied wind information

For the total measurements done year 2003, wind information was taken from a wind meter mounted 17 m above ground except day 15-Aug-2003 when it was mounted 24 m above ground. The wind meter was placed at the main entrance to the Oil harbor, see position marked with X number 1 in Figure 38. For the total measurements day 8-Sept-2004 wind information was taken from wind meter placed 24 m above ground on the same place as for the measurements year 2003. For the total measurements day 20-May-2004 and 24-May-2004 wind information was taken from a wind meter placed 17 m above ground close to the docks in the Oil harbor, position is marked in Figure 38 with X number 2.

For close measurements inside the industry-area, a wind meter mounted on a mobile mast with a height of 24 m was also used on the position marked X number 3. Wind information was also sometimes taken from a wind meter that was permanently mounted on the lamp-tower that is located north of the process, position is marked X number 4.

### 7.3.2 West tank-park

Table 25 shows the results for the west tank-park. Total measurements on the west tank-park has been done on the road that runs north from the hysomer when the wind is coming from west, see Figure 40. Total measurements on the west tank-park have also been retrieved from the measurements along Oljevågen when the wind is coming from north.

Close measurements have been done inside the tank-park to measure the emission from each tank. Figure 41 shows an example of close measurement on tank 107 and 109. The daily averages from these measurements are given in Table 25. It has only been possible to identify tanks 105, 107, 108 and 109 in the close measurements. The emissions from the other tanks were lower than the detection limit of the instrument and the emissions of the other tanks have therefore been assumed to be zero. Since the measurements from each tank have low reliability, only the averages over both years should be used to make conclusions. This gives an average emission of 46.6 kg/h.

**Table 25.** Details of the measurements of alkane emission from the west tank-park

Day	West tank-park (kg/h)	Wind speed (m/s)	Wind direction	T105 (kg/h)	T107 (kg/h)	T108 (kg/h)	T109 (kg/h)
<b>Tank content</b>				Water & oil residues	Crude oil	Crude oil	Visbreaker gas-oil
030709	39.8	2.6-6.2	260°-294°	12.5			
030729	34.4	2.6-3.1	294°-309°				
030730	48.9	2.8-3.2	295°-305°	14.4	10.0	20.6	11.1
030731	47.7	2.1-3.9	160°-205°	15.6	21.0	21.6	6.0
030801		2.3-3.1	155°-180°	1.1			
031015	30.9	1.8-4.3	20°-53°				
<b>2003 Average*</b>	(39.0) <b>37.2</b> (100%)			(15.1) <b>9.8</b> (26%)	(16.5) <b>10.7</b> (28.8%)	(19.6) <b>12.7</b> (34%)	(6.2) <b>4.0</b> (11%)
040520	108.9	5.5-6.8	282°-299°	69.8 45.0 3.5			
040610		6.2-9.0	257°-271°				
040615	89.9	5.6-7.7	285°-295°				
040616	66.1	5.1-7.5	312°-333°	18.5 x	15.0	21.0	
040908	30.3	3.4-6.0	24°-330°				
<b>2004 Average*</b>	(89.2) <b>55.8</b> (100%)			(18.5) <b>12.5</b> (22%)	(28.0) <b>18.8</b> (34%)	(33.0) <b>22.2</b> (40%)	(3.5) <b>2.4</b> (4%)
<b>Average All years</b>	<b>46.6</b>			<b>11.1</b> (24%)	<b>14.8</b> (32%)	<b>17.5</b> (38%)	<b>3.2</b> (7%)

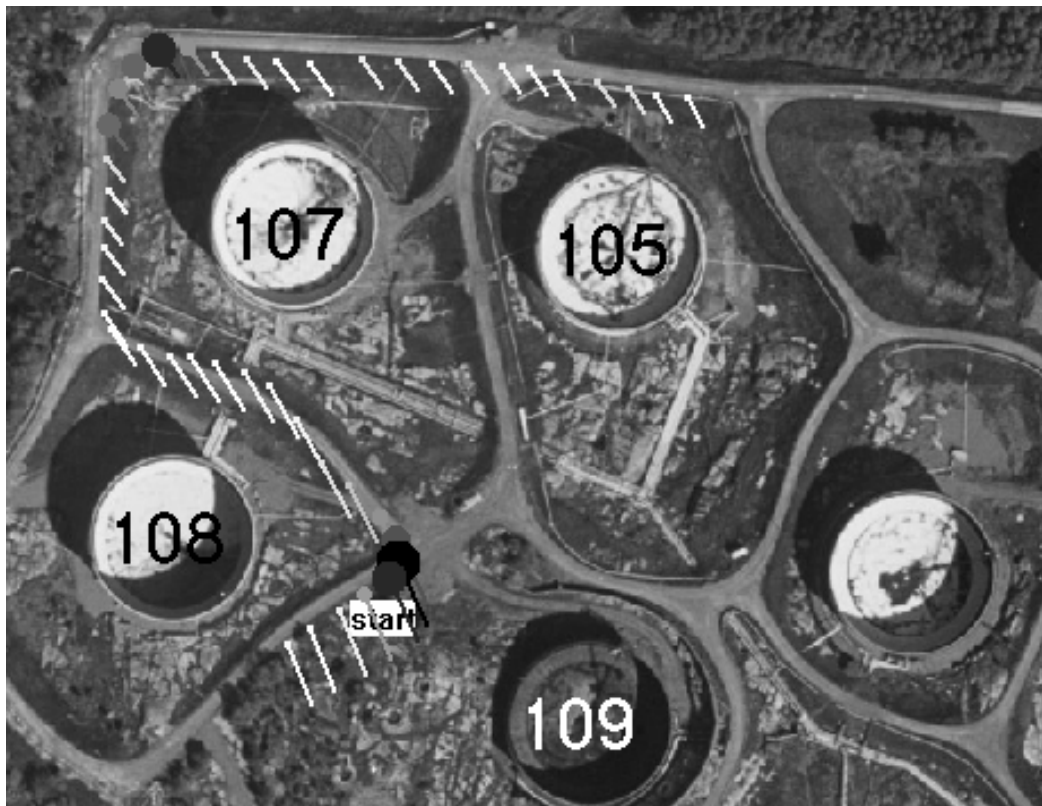
(\*) Weighted average using the inverse of standard deviation on each day as the weight.

(x) Tank 105 on day 040616 was calculated by taking measurements of T105+107 giving 33.5 kg/h and subtracting T107 giving 33.5-15.0=18.5 kg/h. This number has low reliability.

Note: The measurements done close to the tanks has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.



**Figure 40.** Example of total measurement on the west tank-park, day 29 July 2003. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 41.** Example of close measurement on crude oil tank 107 and tank 109, day 31 July 2003. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.3.3 East tank-park

Total measurements on the east tank-park have been done along the road that is going to the east from the process as shown in Figure 43. Total measurements have also been done along Oljevågen. The tanks in east tank-park have been divided into groups according to Figure 42. The groups are hereafter called tank-group 301-318, 310-320, 321-325, 326-329 and tank 330. Close measurements on the tanks were made on the roads between the tanks. Traverses of the kind that is shown in Figure 43 were also sliced into segments corresponding to the different tank-groups.

The emissions from each tank-group are shown in Table 26. It has been difficult to separate the individual tank groups and the calculated emission for each tank group therefore has low reliability. Since the measurements from each tank have low reliability, only the averages over both years should be used to make conclusions. This gives an average emission of 29.4 kg/h.

**Table 26.** Details of the measurements of alkane emission from the east tank-park on Shellraff

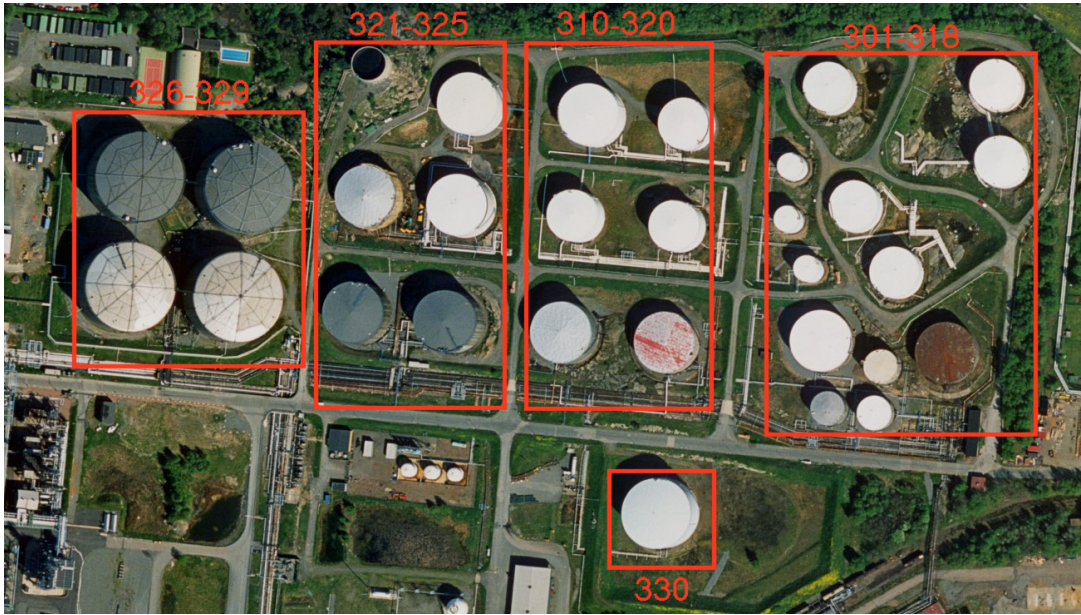
Day	East Tank park (kg/h)	Wind speed (m/s)	Wind direction	Group 301-318 (kg/h)	Group 310-320 (kg/h)	Group 321-325 (kg/h)	Group 326-329 (kg/h)	Tank 330 (kg/h)
<b>Tank content</b>				Class 1,2 & 3	Class 1 & 3	Class 3	Class 3	BTX
5-Jul-2003		3.0-3.8	73°-77°	8.3	4.2	5.5	7.3	
10-Jul-2003	57.1	2.3-4.1	10°-347°					
15-Jul-2003	123.5 x	1.9-6.0	15°-56°	18.3 x	63.2 x	31.8 x	30.0 x	17.2
30-Jul-2003		2.5-6.3	26°-59°		6.6			
1-Aug-2003		3.7-5.5	169°-181°			10.2		5.1
26-Aug-2003	36.1	2.1-4.0	20°-348°					
<b>2003 Average*</b>	(43.9) <b>41.9</b> (100%)			(8.3) <b>8.7</b> (21%)	(5.4) <b>5.6</b> (13%)	(7.9) <b>8.3</b> (20%)	(7.3) <b>7.6</b> (18%)	(11.2) <b>11.7</b> (28%)
20-May-2004	17.0	3.7-6.2	282°-307°					
24-May-2004	32.0	3.7-6.7	287°-308°					
15-Jun-2004	38.8	5.1-7.3	283°-315°					
16-Jun-2004	20.2	5.6-6.9	307°-325°	6.4	3.2	4.6	6.9	
8-Sep-2004	22.5	4.1-6.1	25°-306°					
14-Oct-2004		4.2-6.1	102°-121°					2.5
<b>2004 Average*</b>	(26.9) <b>16.8</b> (100%)			(6.4) <b>4.6</b> (27%)	(3.2) <b>2.3</b> (14%)	(4.6) <b>3.3</b> (19%)	(6.9) <b>4.9</b> (29%)	(2.5) <b>1.8</b> (11%)
<b>Average all years</b>	<b>29.4</b>			<b>6.6</b> (23%)	<b>4.0</b> (13%)	<b>5.8</b> (20%)	<b>6.3</b> (21%)	<b>6.7</b> (23%)

(\*) Weighted average using the inverse of standard deviation on each day as the weight.

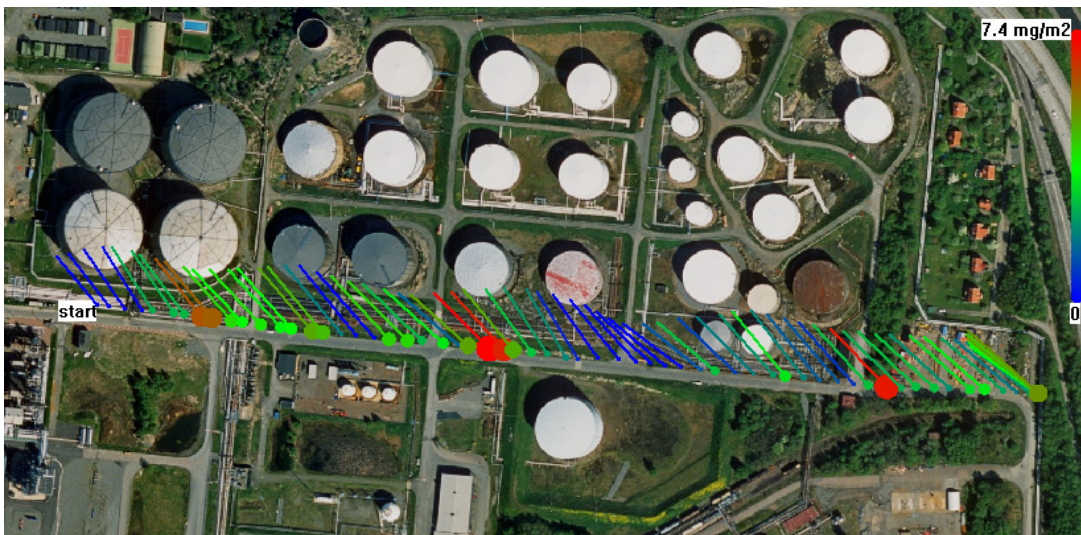
(x) Tank 312 was open for maintenance work from 11-Jul-2003 to 15-Jul-2003. The day 15-Jul-2003 is therefore exceptional and has not been included in the average.

Note: The measurements done close to the tanks has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.





**Figure 42.** Figure shows how the east tank-park has been divided into tank-groups. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 43.** Example of total measurement on east tank-park, day 16 June-2004 (10:10). Measurements on individual tank-groups have also been extracted from these traverses. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.3.4 Process and hysomer

Table 27 shows the daily averages of the measurements on the process and hysomer together with measurement position. The total measured emission is also shown in the table to make comparisons easier. Figure 44 shows the change of emissions during both years. The reason for the reductions in emissions is probably that process-equipment was leaking after the total production stop and the leaking equipments were later found and repaired.

Between 1-Aug-2003 and 15-Aug-2003 there is a drop in total emission from the whole refinery that coincides with a drop in the emission from the hysomer. For July/September-2003 there are three documented repairs that have been done because leaks were detected.

Between 26-Aug-2003 and 20-May-2004 there is another drop in the total emission from the whole refinery that coincides with a drop in the emission from the process. Between these two dates, there are seven documented repairs that has been done because leaks were detected or because of equipment breakdown.

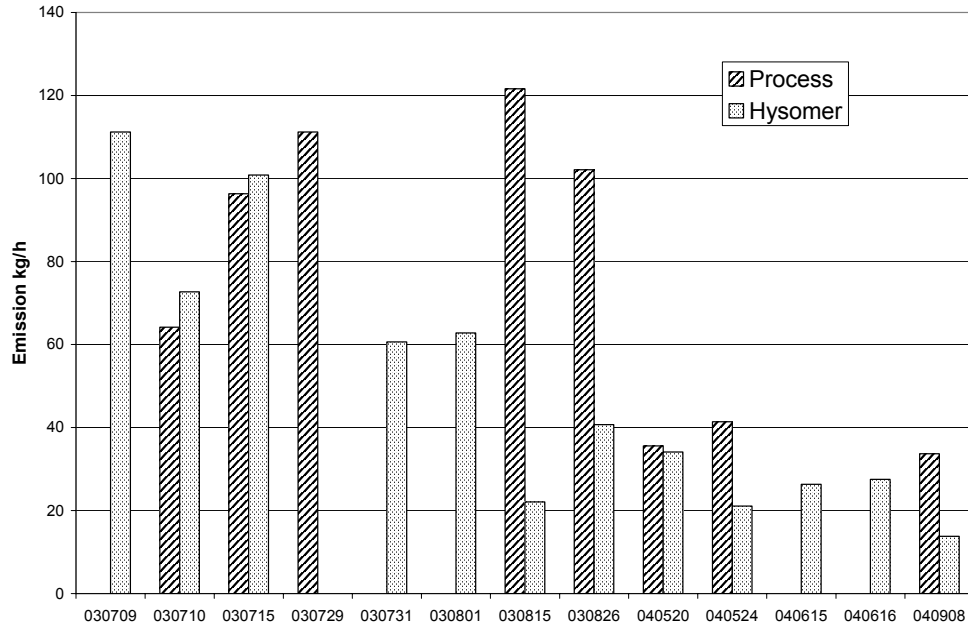
**Table 27.** Details of the measurements done on the hysomer and process.

Day	Hysomer (kg/h)	Process (kg/h)	Measurement position	Total Shellraff (kg/h)	Wind speed (m/s)	Wind direction
9-Jul-2003	111.2		Between hysomer and process.		3.3-6.4	263°-289°
10-Jul-2003	72.7	64.2	Oljevågen	398.5	3.0-5.0	6°-328°
15-Jul-2003	100.8	96.3	Oljevågen	397.4	3.9-4.5	35°-54°
29-Jul-2003		111.2	North east of process.		2.9-4.2	213°-260°
31-Jul-2003	60.6		North of hysomer.		2.2-5.1	162°-218°
1-Aug-2003	62.8		North of hysomer.		1.8-4.0	153°-202°
15-Aug-2003	22.1	121.6	Oljevågen	257.8	4.8-5.3	306°-313°
26-Aug-2003	40.7	102.1	Oljevågen	293.0	2.5-3.9	24°-354°
<b>2003 Average*</b>	(76.1) <b>72.7</b>	(105.3) <b>100.6</b>		<b>348.1</b>		
20-May-2004	34.1	35.6	Oljevågen	174.7	3.1-8.0	309°-333°
24-May-2004	21.1	41.4	Oljevågen	95.7	3.7-7.4	296°-307°
15-Jun-2004	26.3		Between hysomer and process.		4.4-9.4	269°-300°
16-Jun-2004	27.5		Between hysomer and process.		3.8-8.0	281°-312°
8-Sep-2004	13.8	33.7	Oljevågen	113.5	3.0-5.9	25°-359°
<b>2004 Average*</b>	(24.8) <b>15.5</b>	(38.0) <b>23.8</b>		<b>122.1</b>		

(\*) Weighted average using the inverse of standard deviation on each day as the weight.

Note: The measurements done close to the process and hysomer has been normalized so that the sum is equal to the total emission measured far away. Values before normalization are given in parenthesis.

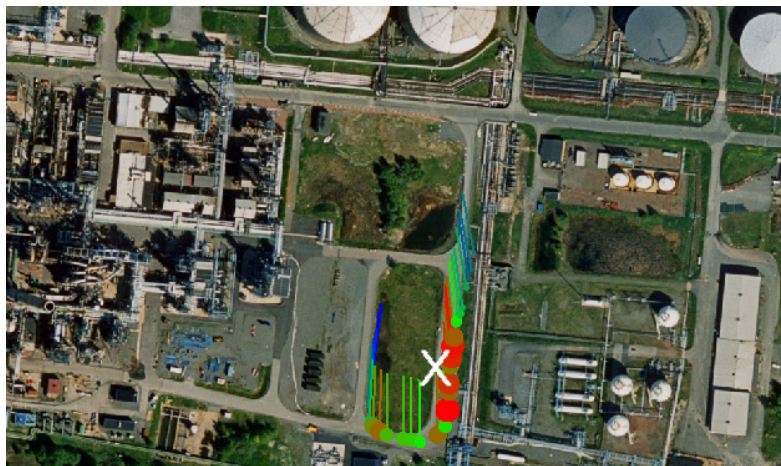




**Figure 44.** Figure shows the change of emissions from process and hysomer. Notice the drop in hysomer emissions after 1-August-2003 and the drop in process emission after 26-August-2003.

### 7.3.5 LPG and tank-loading area

The LPG and tank-loading area has been difficult to measure on since the Oil harbor, the process and eastern tank-park is located on south, west and north side and that they have high emissions in comparison with the low emissions that has been observed from this area. The days 23-July-2003, 1-August-2003 and 14-October-2004, the emissions were measured to 19.3, 14.6 and 1.7 kg/h respectively. On all occasions were tank-trucks present for filling. There is a big possibility that surrounding emission sources have interfered with these measurements. The measurements should therefore only be interpreted as upper limits for the emissions. Figure 45 shows an example of traverse done to the tank-loading area.



**Figure 45.** Close measurement on the tank-loading area day 23 July 2003 (13:12). The position of the tank-truck is marked with X. Red points correspond to the highest values. (Aerial photo: Copyright Lanmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.3.6 Water treatment facility

Table 28 shows the daily averages together with measurement position. The total measured emission is also shown in the table to make comparisons easier. Large variations in the emissions were observed during 2003. On days 31-July-2003 and 1-August-2003, large emissions were also observed from the coarse water filter that is located close to the water treatment. The measurements on the coarse water filter were done close and has therefore been overestimated but probably not with a factor above two.

Measurements on the water treatment facility were either done on the north side when the wind was coming from south, see Figure 46, or along Oljevågen when the wind was coming from north, see Figure 47.

The activity in the water treatment facility was abnormal during the period when measurements were done in 2003. The reason for this was that extensive maintenance work were done on the tanks in eastern tank-park and this caused oil contaminated water from the cleaning and emptying of the tanks, and this water had to be taken care of by the water treatment facility. The emissions measured in 2004 are probably more representative for routine operation.

**Table 28.** Measured emissions from the coarse water filter, the water treatment facility, and total emission from Shellraff.

Day	Total emission Shellraff (kg/h)	Coarse water filter (kg/h)	Water treatment facility (kg/h)	Measurement position for water treatment facility	Wind speed (m/s)	Wind direction
10-Jul-2003	398.5		56.4	Oljevågen	3.0-4.5	10°-321°
15-Jul-2003	397.4		131.3	Oljevågen	3.2-4.5	27°-42°
31-Jul-2003		125.5	50.9	North of the water treatment	2.5-4.0	167°-203°
1-Aug-2003		186.1	46.7	North of the water treatment	2.0-3.6	145°-207°
15-Aug-2003	257.8					
26-Aug-2003	293.0					
<b>2003</b>			(84.1)			
<b>Average*</b>	<b>348.1</b>		<b>80.3</b>			
20-May-2004	175.5		29.6	Oljevågen	5.9-7.6	311°-335°
24-May-2004	95.5		7.6	Oljevågen	3.7-6.1	283°-311°
8-Sep-2004	132.0		8.6	Oljevågen	2.2-4.7	4°-21°
<b>2004</b>			(13.4)			
<b>Average*</b>	<b>122.1</b>		<b>8.4</b>			

(\*) Weighted average using the inverse of standard deviation on each day as the weight.



**Figure 46.** Close measurement on the water treatment facility along the north side. The positions of the water treatment pool and coarse water filter are marked with X. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 47.** Measurement on the water treatment facility along Oljevågen. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.3.7 Exceptional case with tank 105

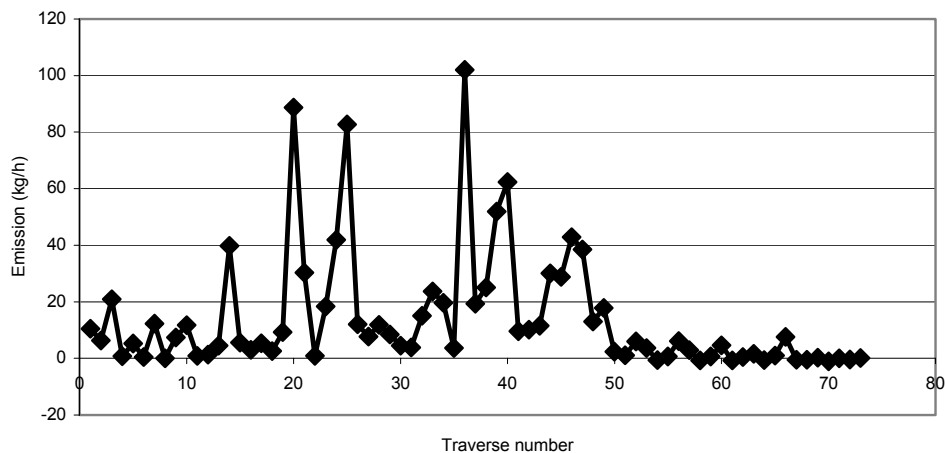
During day 8-June-2004, traverses for measuring total emissions were done along Oljevågen. It was quickly observed that emissions were much higher than normal. The measurements indicated a strong emission source inside the west tank-park. Measurements were then done inside the west tank-park and the point source was identified to be tank 105 containing residues of water mixed with oil. This was immediately reported to the personnel-in-charge. After investigations, it was found out that the tank-roof was tilting. This was fixed just a few hours later. Table 29 shows the total measurements done along Oljevågen before the roof was fixed. Total emissions should be compared to the average emission for 2004 that were 122.1 kg/h.

**Table 29.** Results of individual traverses on day 8-June-2004 when the roof of tank 105 was tilting.

Time	Total emission Shellraff (kg/h)	Tank 105 (kg/h)	Wind speed (m/s)	Wind direction
12:45	1490		5.0	36°
12:55	541		4.6	59°
13:15	691	125.5	4.7	44°
13:25	830	186.1	4.5	39°
13:40	199		3.3	55°
13:50	714		3.9	39°
14:10	633		3.1	42°

### 7.3.8 Measurements on the flare on Shellraff

Measurements on the flare were done on day 14-July-2003 during 1.5 hours by driving back and forth about 50 meters in such way that the sun-ray traversed the flare. This resulted in 73 traverses and the average of all traverses were 15 kg/h. Figure 48 shows the variation over the whole set of traverses. The emission is higher than what has been observed on other measurements. After the total production stop earlier year 2003, there was an error in the control of the flare that caused it to pulsate. This can probably explain the high measured emission. The problem with the flare was fixed later in year 2003.



**Figure 48.** Results of individual traverses to measure the emission from the flare.

### 7.3.9 Measurements of aromatic hydrocarbons on Shellraff

Measurements of aromatic hydrocarbons have been done with the method described in chapter 7.5. One sample was collected close to crude oil tank 108, one sample just outside the process and one sample from tank 330. Tank 330 contains a mixture that is rich of aromatics (BTX). The sample taken outside tank 330 saturated due to too high concentration of aromatic hydrocarbons and from this measurement it was only possible to say that the aromatics/butane ratio was higher than 20%. Since this measurement is uncertain, it has not been used any further. The successful measurements are summarized in Table 30. These measurements have been added to the larger database of measurements that have been collected during the KORUS-project. The complete results derived from the whole database have been used when calculating the average emissions of aromatic hydrocarbons from Shellraff. This is further described in chapter 7.5. The FTIR-point measurement system is mounted inside the measurement-car. Therefore, measurements were always done on roads. Figure 49 shows the positions where the samples were collected.

**Table 30.** Mass proportion between aromatics/alkane from point measurements done with TENAX-tubes and GC-analysis and simultaneous point-measurements of Butane with FTIR. The numbers in the column marked Pos refers to the positions in Figure 49.

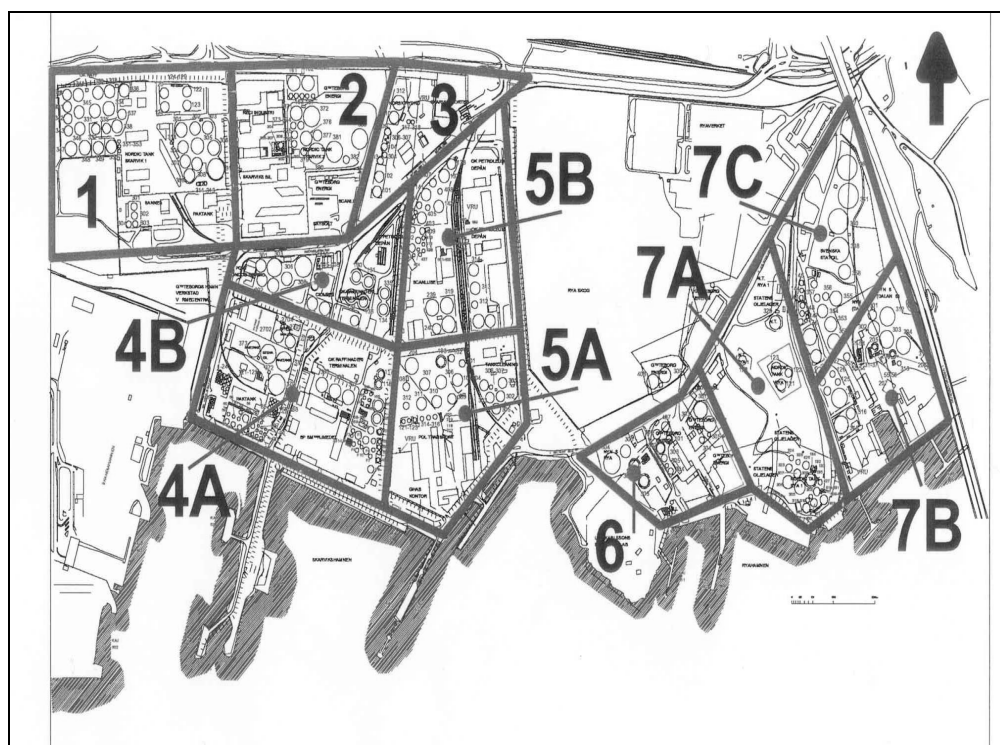
Measurement site	Pos	Date	Benzene	Toluene	Ethyl- benzene	m+p- xylene	o- xylene	GC Aromatics Weight (ng)	FTIR Butane Weight (ng)	Aromatics/ Butane Ratio %
Shell tank 108	1	040705	0,251	0,293	0,063	0,283	0,110	118,16	3403	3,5
Shell process	2	040705	0,160	0,386	0,065	0,308	0,081	590,19	3841	15,4



**Figure 49.** Numbers indicates the positions where samples were taken to retrieve the ratio between aromatic hydrocarbons and alkanes. Dark points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

## 7.4 Measurements an the Oil harbor

More than ten different companies operate at different sites in the Oil-harbor of Göteborg, see Figure 50. In contrast to the refineries included within the KORUS project, the emissions of the oil-harbor show higher variability caused by the fact that there are many parties working independently with activities that temporarily causes emissions of VOC, such as loading of trucks and ships, filling of caverns, and cleaning of tanks and pipes. This fact makes it difficult to derive annual emissions from the measurements, since the point activities often contribute to a significant fraction of the emissions. For the estimation of the continuous emissions, it was decided to use measurement days when the emissions were the lowest. On the other days, part of the emission was assumed to originate from the point activities mentioned above and comparing to logbooks has proved this. Periods when vapor recovery units have been badly performing or malfunctioning and occasions when the loading of ships created high emissions are examples of point releases



**Figure 50.** The figure shows the different areas in the oil-harbor of Göteborg from which the VOC emissions have been estimated (area 1-7). Different operators work in each area.

The measurements were conducted in August/September 2003 (17 days) and May/June 2004 (21 days). In 2003 substantial fluxes of VOC were often encountered leeward of the Preem gasoline-loading site in area 5b and this masked other emissions. This source was significantly reduced in 2004 due to a replacement of a vapor recovery unit. More emphasis has therefore been put on the results from the latter year. The wind was measured from three mobile masts (17 m, 21 m and 3 m) positioned in the northeast part of area 3, east part of area 5a and north part of area 7a, respectively.

A serious problem is the large variability in the harbor. Even though more days were spent at the oil harbor than at any of the refineries within the KORUS project, the continuous emissions are still based on very few measurements, which makes the emission values uncertain. Secondly, to be able to understand the importance of point emissions for the total emissions, it is important to measure these over their full emission cycles and this has not been possible to do within the scope of the project.

#### 7.4.1 Total emission

The total continuous emissions in 2003 are estimated to be around 185 kg/h (around 1600 tons/year) with a 30-40% uncertainty and this is based on two days when the variability was low, i.e. 8-August and 11-August, 2003, see Table 31. If all measurement days in 2003 were included to calculate the total emission, the value almost doubled. The total emission for 2004 is estimated to be 187 kg/h (around 1600 tons/year). This value corresponds to the average emission over 4 days, i.e. 27-May, 2-June, 3-June and 5-August. The emissions in this case were obtained by averaging area 1-5 over the days mentioned above, see Table 32, while area 6-7 was measured separately, also on other days in the beginning of May, corresponding to 44 kg/h. The almost identical emission values in 2003 and 2004 are just coincidental since the estimated precision is around 10-20%. The accuracy is estimated to be within  $\pm 30\%$ . The emission from the eastern part (area 7) was potentially higher than normal since several class I tanks were open due to repair work both in 2003 and 2004. The emissions were however similar to what was obtained by SOF in June 2001, by measuring from a ship, see reference [3].

The total emission values measured here, 1600 tons, can be compared to previous measurements of 2300 tons in 1996 and 1100 tons in 1999, obtained by the DIAL technique by Spectrasyn Ltd [16], and Shell Global solution [17], respectively. In August 2001, SOF measurements were also conducted during one single day corresponding to 1650 tons/year.

**Table 31.** Emission values for 2003 for occasions when the whole oil harbor was traversed. The uncertainty is 30-40%, mainly due to systematic errors in measuring the wind correctly.

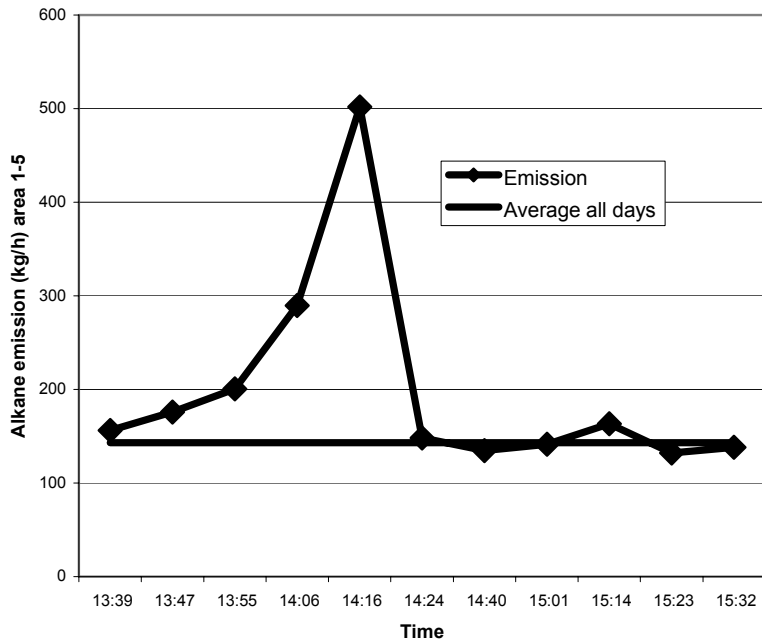
Day	Time span	Nr of traverses	Emission kg/h	Wind
030808	1230 –1546	7	180 $\pm$ 40	3.0-4.2m/s 203°-239°
030811	1631 –1703	4	195 $\pm$ 80	2.7-3.8m/s 209°-224°
<b>Average</b>	-	<b>(total 11)</b>	<b>185<math>\pm</math>11</b>	-

**Table 32.** The emissions for areas 1 to 5 in year 2004. This average value was used together with the average value from areas 6 to 7 to estimate the total emissions (total 143+44=187 kg/h).

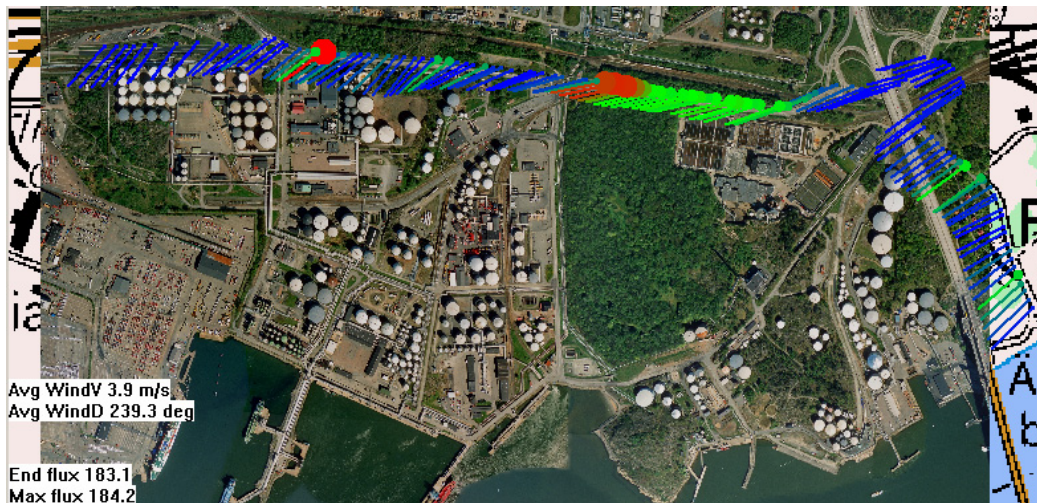
Day	Time span	Nr of traverses	Emission kg/h	Wind
040527	1546 –1656	5	143 $\pm$ 50	3.1-4.1m/s 222°-229°
040602	1109 –1109	1	132	3.5-3.5m/s 217°-217°
040603	1440 –1513	5	150 $\pm$ 18	3.0-3.8m/s 221°-240°
040805	1124 –1153	4	134 $\pm$ 20	2.2-3.6m/s 221°-236°
<b>Average</b>	-	<b>(total 15)</b>	<b>143<math>\pm</math>7</b>	-

An interesting example of VOC measurements with SOF in the oil harbor is shown in Figure 51 for 3-June-2004, illustrating both a strong point emission and how the emission returns to the same value as the average emission.





**Figure 51.** Total emission of VOC from the areas 1 to 5 versus time on 3-June-2004, measured from the north side on Oljevägen. The emission values gradually increased with a peak around 14:10. The emission values stabilized at 154 kg/h and this is very 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 at quay 521 or filling of a tank (T336) at the company CiClean, both finishing at around 14:00.



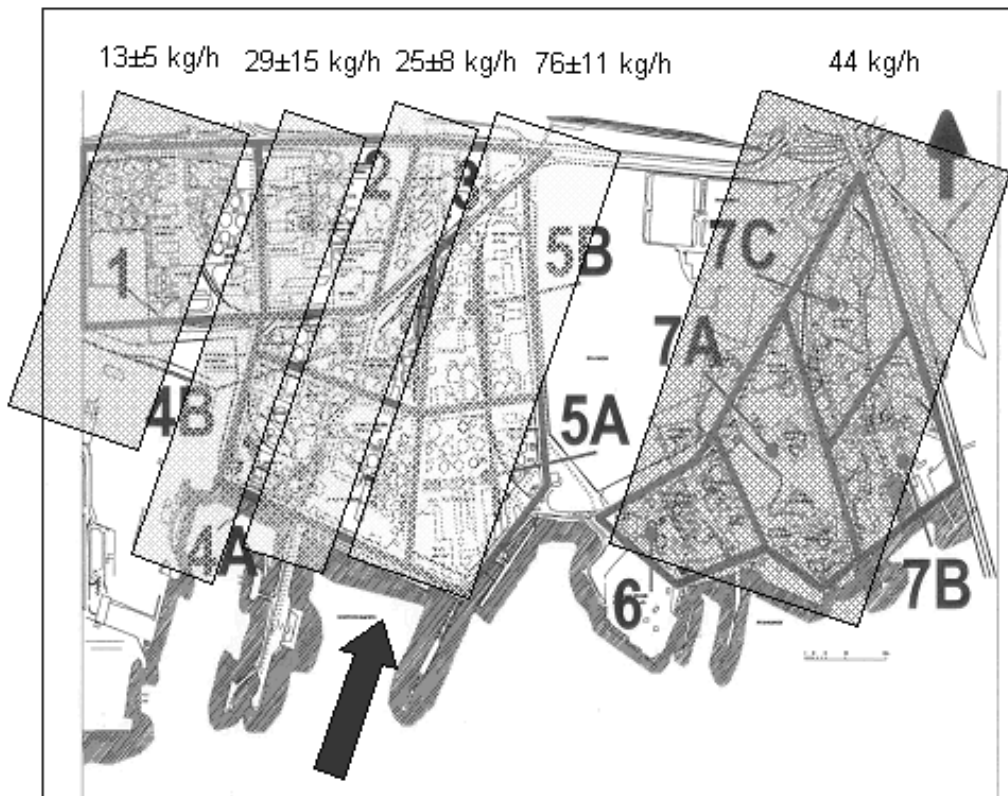
**Figure 52.** A SOF emission measurement of alkanes at the oil harbor on 3-June-2004, for a traverse across the gas plume from the whole area. An emission value of 183 kg/h is obtained for this particular traverse. The lines indicate the wind direction (they point towards a possible emission source). Red lines indicates points where high line integrated concentrations have been measured. The red points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBildern)



#### 7.4.2 Emissions divided into areas.

It is possible to make a first separation of the emission into smaller sectors from the measurements performed along Oljevågen, see Figure 52. However, this road runs close to area 1 and area 2 and this causes an overestimation of the emissions from these areas. In Figure 53 the average emissions from various sectors along the main measurement road is shown and the rectangles correspond to the areas upwind, which will contribute to this value. These values are based on several days in May, June and August 2004. Occasions of high emissions due to point activities have been excluded.

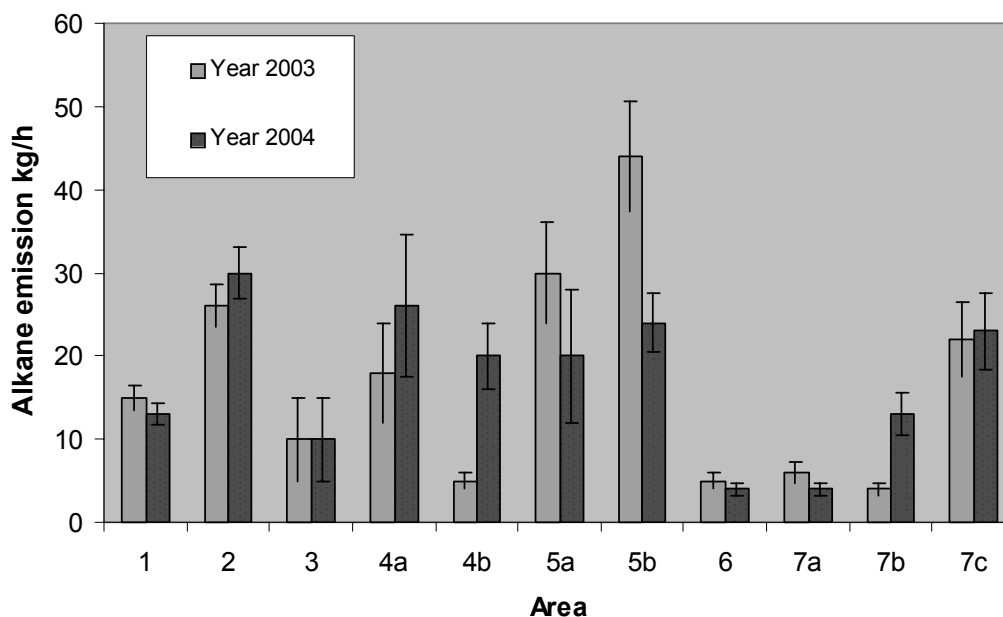
In Table 33 the emissions divided into the 11 areas is shown for 2003 and 2004. Only data corresponding to normal operation have been included and data with high emissions have been removed. Some sectors in the oil harbor, such as area 3, area 5a and area 5b are more or less surrounded by other emission sources, and in order to obtain emission values, the emission value from the upwind side had to be subtracted from the emission value on the downwind side. For large upwind concentrations this increases the uncertainty significantly and that was the case for area 5a and 4a, and partly for 5b and 4b. Figure 54 shows a graph of the emissions per area including rough indicators of the precision.



**Figure 53.** The average emission values in 2004 obtained for several sectors when measuring in southerly wind from Oljevågen. The area of emission corresponding to each sector is indicated with the rectangle. The values correspond to averages over several days between May 2004 and August 2004. Days with high values, due to point emissions have not been included.

**Table 33.** The distribution between areas for continuous emissions. (High point emissions have been removed).

Area	2003 kg/h	2004 kg/h	Change	Comment
1	15	13	-13%	Good reliability.
2	26	30	15%	Good reliability.
3	10	10	0%	Uncertain value.
4a	18 (24-12)	26 (34-17)	44%	The relative distribution between 4a and 5a uncertain but the sum is good.
4b	5	20	300%	Variable in 2004.
5a	30 (24-36)	20 (12-29)	-33%	Uncertain for 2004. See comment on 4a
5b	44	24	-45%	The relative distribution between 4b and 5b uncertain in 2004 but the sum is good. Strong point emissions from the VRU have been discarded.
6	5	4	-20%	Good reliability.
7a	6	4	-33%	Uncertain value.
7b	4	13	225%	Uncertain value.
7c	22	23	5%	Fair. The values may be overestimated since several gasoline tanks were open to the atmosphere
<b>Sum</b>	<b>185</b>	<b>187</b>		The fact that the values are the same is coincidental since the precision is around 10-20%



**Figure 54.** The estimated emission per area in the oil harbor for 2003 and 2004. Rough indicators of the precision are given. Note that some sectors are coupled, for instance 4a and 5a, since the values were subtracted from each other and this makes them individually more uncertain, although the sum is good.

### 7.4.3 Area 1

In this area the company VOPAK is storing volatile (class I) products. The emissions are low, in general, and the plume is indistinct. Many measurements have been conducted on various days and wind directions. Since the measurements are conducted close to the high tanks, the wind field is complicated and the wind speed is generally lower than at the mast where the wind was measured and this will cause an overestimation of the flux values. The measurements show an average emission of  $15 \pm 0.5$  kg/h for 2003 (August 8, 11 and 15) and  $13 \pm 5$  kg/h for 2004 (May 19, 20, 27 and June 4). Figure 55 shows an example of a traverse of area 1.

SOF measurements in 2001, see reference [3], on August 16 showed a much more distinct plume than in 2003 and 2004 with emission values of about 30 kg/h. The reason for the large change is probably that the tanks were rebuilt after the 2001 measurements.



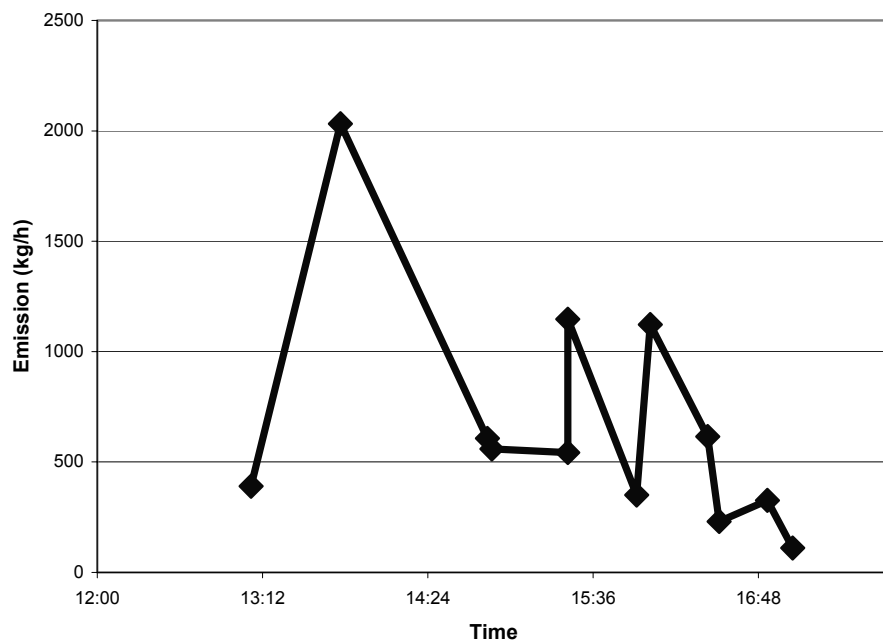
**Figure 55.** SOF emissions measurements at area 1 showing values around 13 kg/h. White points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

### 7.4.4 Area 2

In 2004, two companies operated in this area, VOPAK having storage tanks for volatile products (class I), and RECI taking care of resins in a batch process, potentially causing emissions with a large variability. The latter facility was installed in late 2003. It is not possible to distinguish between VOPAK and RECI in the measurements since they are very close to each other. The average emissions in 2003 and 2004 were similar,  $26 \pm 15$  and  $30 \pm 15$  kg/h. This indicates low continuous alkane emissions from RECI since it was installed after 2003, if the emissions from the VOPAK storage tanks are assumed to be the same. The 2003 results are, however rather uncertain due to few available measurements.

On several occasions in 2004, very high fluxes were measured in the vicinity of this area, but a more thorough analysis later showed that these were caused by point activities somewhere from area 4b. In 2003, very high emissions from area 2 were

measured, which supposedly were caused by cleaning of a pipeline in area 2, pumping 3 m<sup>3</sup> of gasoline into a cleaning vehicle, see Figure 56 and Figure 57. The fluxes are however very high and it is difficult to believe that the cleaning was the only reason. This case was the only time this event was observed on area 2, but it clearly indicated that emissions from point activities may be of importance even averaged over a full year.



**Figure 56.** Point leakages from area 2 on 11 August 2003, probably due to cleaning of a pipeline. Note that the continuous emission value is around 30 kg/h at this area.



**Figure 57.** Point leakages from area 2, due to cleaning of a pipeline, see Figure 56. White points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

#### 7.4.5 Area 3

In this area, operated by Norsk Hydro, fluxes of 20-40 kg/h were often encountered but these are very difficult to separate from the background, since area 2 was often upwind. The loading of trucks and the vapor recovery unit (VRU) does not show obvious emissions and the leaks more likely come from the gasoline tanks 101 and 102, marked by a circle in Figure 58. By combining measurements in two different

directions a qualified guess is that emissions correspond to about 10 kg/h from this area but this value is quite uncertain. See Figure 58 and Figure 59.



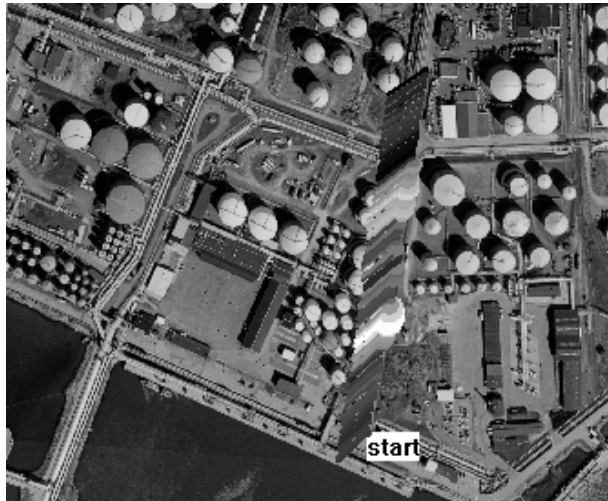
**Figure 58.** SOF measurements on area 3 on May 31 2004 corresponding to  $13 \pm 3$  kg/h. The gasoline tanks 101 and 102 are marked by a circle. Here the wind is coming from area 2 where emissions usually are found. White points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 59.** SOF measurements on area 3 on day 15-August-2003 corresponding to 25 kg/h. White points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

#### 7.4.6 Area 4a

In Area 4a Preem and Nordic storage are operating. Both in 2003 and 2004 distinct emissions were detected in this area when measuring on the east side, as can be seen in Figure 60 and Figure 61. The average emission increased by almost 50% between 2003 and 2004, 18 to 26 kg/h, respectively, and the position of the leakage got more northerly in 2004. The measurements at area 4a are very close to large structures, and the wind is therefore very difficult to assess. To obtain the emission values given above, 30% less wind speed than at the wind mast has been assumed but this is probably still too high, and a large uncertainty interval has therefore been given in Table 33. In 2004 the emission was probably caused by a leakage of gasoline that occurred in the early spring in 2004, close to the place where the highest line integrated concentrations were obtained. During the measurement period, May 18-June 21, gasoline-containing water from a pit, dug close to the leakage point, was frequently pumped out and pumped into deposit tanks in the middle and lower part of area 4b (Ciclean).



**Figure 60.** SOF measurement on area 4a on September 24 2003 corresponding to 46 kg/h in this measurement. White points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 61.** SOF measurement on area 4a and 5a on May 31 2004. Emissions from the whole area correspond to about 26 kg/h. The west part of the area correspond to about 5 kg/h here. The main emission is potentially caused by a previous gasoline leakage along pipelines which occurred in early spring. White points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

#### 7.4.7 Area 4b

In this area Preem has several tanks and Ciclean has tanks for storage of polluted drainage water after leaks, tank cleaning etc. Several days of reliable measurements have been conducted here both in 2003 and 2004 (4-Aug, 7-Aug, 28-Aug in 2003 and 18-May, 19-May, 31-May and 3-June in 2004) and the emissions show a significant increase from  $5\pm 0.5$  to  $20\pm 5$  kg/h, between the two years. The emissions are on a constant low level in 2003 but more variable in 2004. The reason for this is not completely understood, but potentially it could be coupled with the leakage at 4a, since gasoline-containing water was pumped into tanks in area 4b. Figure 62 shows an example of a measurement done on area 4b.

On one occasion on May 17 2004, SOF measurements were conducted northward of area 4a while gasoline-containing water was pumped into a deposit tank. High emissions of 164 kg/h were measured 30 minutes after completion of the pumping, as can be seen in Figure 63.



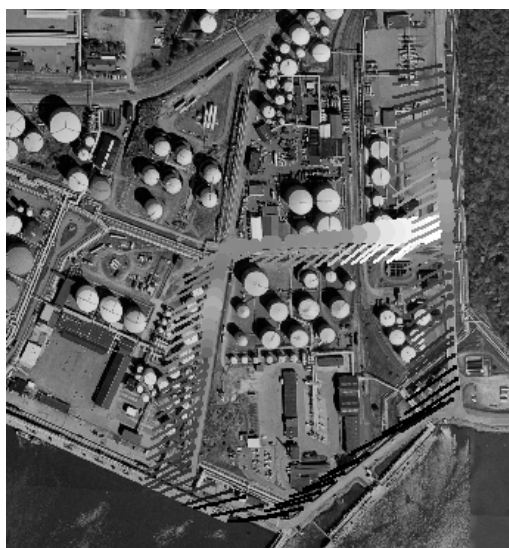
**Figure 62.** SOF measurement on area 4b on 31-May-2004 corresponding to about 10 kg/h in this measurement. White points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 63.** SOF measurement on 17-May-2004, 30 minutes after having completed pumping of gasoline containing drainage water to a tank. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

#### 7.4.8 Area 5a

At area 5a there is a gasoline truck loading, operated by Shell. A VRU is installed in the west part of the area. When the VRU is malfunctioning, which was often the case in 2003, and on several occasions in 2004, the volatile gases are emitted through a vent on a tank placed in the northeast part of the area. Such a case is shown in Figure 64 where high emissions of about 100 kg/h were measured. Most measurements from this area have been conducted from the east side, in westerly wind, and this means that the emissions from area 4a also have been measured at the same time. The average emission from the sum of the areas 4a and 5a were 48 and 46 kg/h in 2003 and 2004, respectively, discarding cases when the fluxes were unusually high due to a malfunctioning VRU. Since the emission from area 4a increased in 2004 the emission from area 5a, seems to have been lowered. The estimated emissions from this area are thus  $30\pm 6$  and  $20\pm 8$  for 2003 and 2004, respectively.



**Figure 64.** High emissions from area 5a are shown here due to a temporarily malfunctioning VRU. The VOC emission corresponds to around 100 kg/h. White points correspond to the highest values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

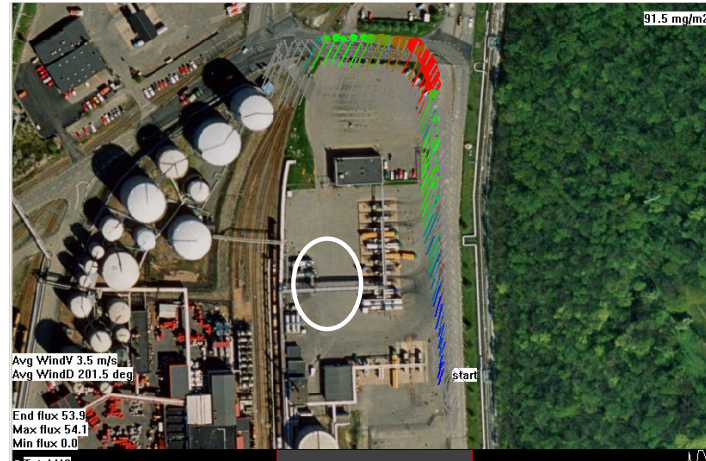
#### 7.4.9 Area 5b

In this area there is a gasoline truck loading facility operated by Preem. In addition, there are storage tanks for the gasoline in the northern part of the area. In 2003 large emissions were very often detected downwind of this area, and this was caused by the use of an under-dimensioned VRU. The volatile gases were pumped through a kerosene tank absorbing the vapors. When the system was saturated, high emissions were obtained from this unit, typically some hour after the max intensity in the loading. In Figure 65 a measurement is shown on August 11 2003 at 10:45 showing an emission of 50 kg/h from the VRU. Typically the emission was in the order of 100 kg/h. In early September 2003 a new VRU was installed. In general this unit seems to work fine and strong emissions are seldom observed here since then. Even with the recovery unit there are occasions when point emissions have been detected and such an example is shown in Figure 66, corresponding to 18-May-2004 at 16:55. Also on 19-May several similar measurements were conducted.

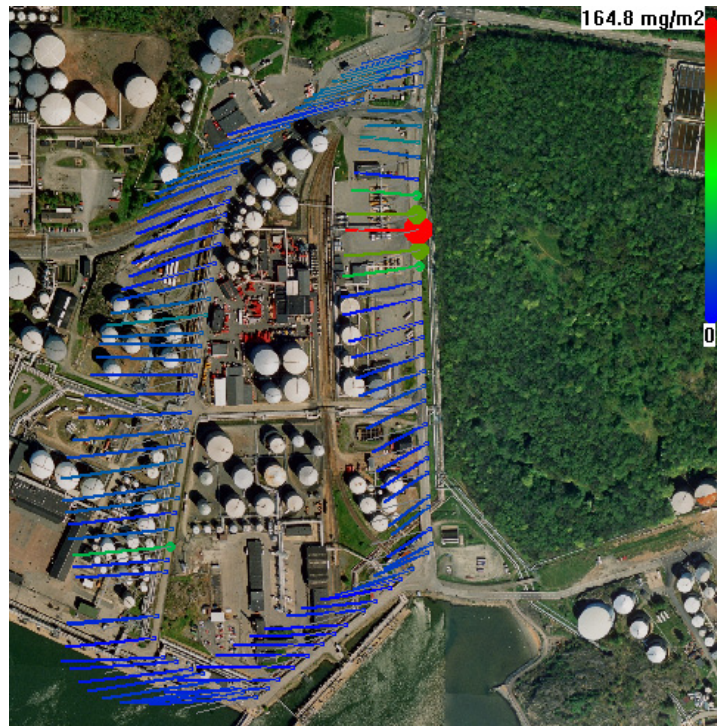
The measurements have been conducted from the east side, in westerly wind, so that emissions from area 4b were measured at the same time. The average emission from



the sum of the areas 4b and 5b were 49 and 44 kg/h in 2003 and 2004, respectively, discarding cases when the fluxes were unusually high due to the malfunctioning VRU. Since the emission from area 4b increased strongly in 2004 the emission from area 5b, thus have been lowered. The estimated emissions from this area are thus 44 and 24 kg/h for 2003 and 2004, respectively.



**Figure 65.** SOF measurement at Preem-truck-loading on area 5b on day 11-August-2003 (10:45). Emission values of about 50 kg/h were measured here. Typically the emission was in the order 100 kg/h. The circle indicates the position of the VRU. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



**Figure 66.** Also in 2004 high emissions were occasionally found at area 5b, here 150 kg/h are emitted 18-May-2004 (16:55). Also on May 19 high emissions were detected. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

#### 7.4.10 Area 6

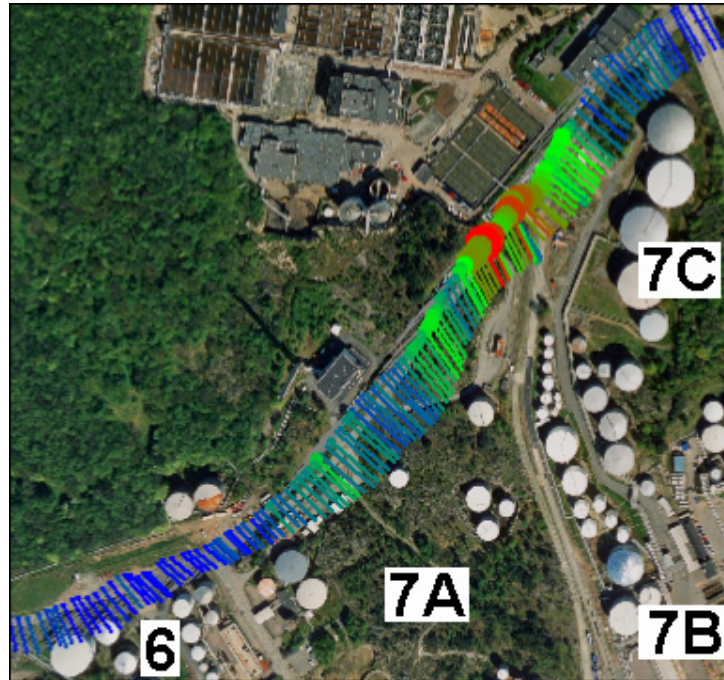
This area showed small emissions of about 4-5kg/h in both 2003 and 2004, see Figure 68.

#### 7.4.11 Area 7

In the eastern part of the oil harbor there are three areas: 7a, 7b and 7c. The topography and prevailing wind direction makes it difficult to conduct measurements here. Figure 67 shows a measurement in 2003 when the emissions were obtained from the opposite side of the bridge Älvsborgsbron and the total corresponded to 35 kg/h. Measurement have also been conducted from the road north of the harbor, i.e. Oljevägen. The average emissions from the total area 7 (7a, 7b and 7c) are 32 and 40 kg/h for 2003 and 2004, respectively. In Figure 68 a SOF measurement in easterly wind is shown and it is obvious that most emissions emanate from area 7b or 7c. Other close by measurements shows that most emissions comes from the class I tanks in area 7c. The emission in both 2003 and 2004 was potentially higher than normal since several gasoline tanks were open due to repair work. The emissions were however similar to what was obtained by SOF in June 2001, by measuring from a ship see reference [3].



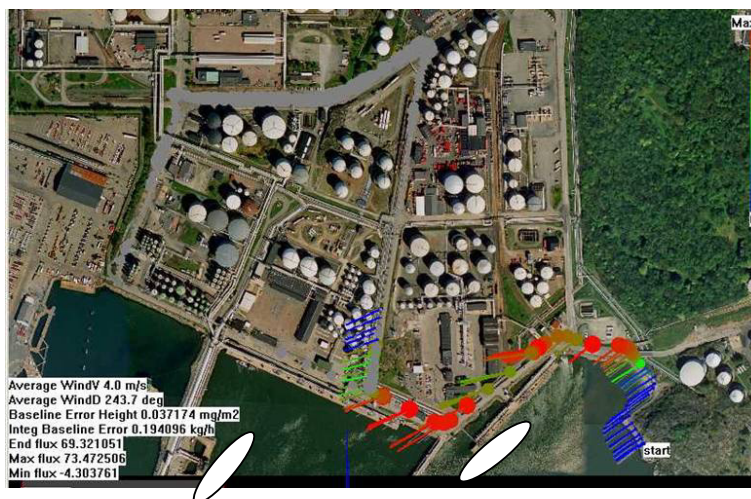
**Figure 67.** Emission from area 7 measured in 2003 and corresponding to 35 kg/h. White points correspond to the highest values. (*Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden*)



**Figure 68.** Eastern part of the oil harbor on 8 September 2003. Here a sum of 27 kg/h was measured with a partitioning according to 5 kg/h from area 6, 7 kg/h from area 7a and 15 kg/h from area 7c. Red points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

#### 7.4.12 Loading of ships

On several occasions high emissions were found in the harbor, which seemed to originate from loading of ships. Figure 69 shows an example when several ships were loading low volatile products (class II and III), and this is generally done without VRUs. These ships had previous loads with high volatility (class I) and this probably caused the observed emissions, probably when the old volatile load was pushed out.



**Figure 69.** SOF measurements in the emission plume of ships loading class III fuel. on 14 May 2004. An emission plume of  $125 \pm 25$  kg/h was measured between 15:00-16:00. The two ships indicated in the figure at quay 519 (left) and quay 509 (right) are loading class III product but was previously loaded with class I cargo. Red points correspond to the highest values (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)



During the time of the measurement in Figure 69, a ship that had a previous load of naphthalene (class I) was loading class III product (EO1 and MK1) at quay 509 (right ship in the figure). In addition, at quay 519, another ship which had a previous load of crude oil (class I) was loading class III (EO4) product (left ship). In Table 34 a few other occasions have been summarized. Quite a few other examples of high emissions were observed from other ships during both 2003 and 2004, varying between 10-300 kg/h, although it has not always been possible to investigate their previous load etc. In order to get a grip about these emissions, more dedicated measurements should be conducted where the emissions from ships are measured for longer time, over a full loading cycle.

**Table 34.** A few examples of ships loading class III product with a previous load of class I.

Date	Ship	Quay	Product	Previous load	Emission
14-May-2004	Shravan	519	EO4 (III)	Crude (I)	
	Saxen	509	MK1 EO4 (III)	Naphthalene (I)	125 kg/h
19-May-2004	Shravan	519	EO4 (III)	Crude (I)	75 kg/h
24-May-2004	Baltic Chall	511	EO4 (III)	V60 (I)	
	Helen Knut	509	Jet A1 (II)	Jet A1 (II)	250 kg/h

#### 7.4.13 Loading of trucks

In the oil harbor there are several areas where loading of gasoline trucks is conducted. Most of the loading is carried out early in the morning, around 6-8 am, and some loading is also carried out around midday. It is impossible to conduct SOF-measurements before sunrise, and therefore no measurements were conducted when most loading occurs. However, trace gas experiments were done at the Preem loading facility, 5b, in 2003 during the morning loading to investigate the emissions from the old VRU. This system was under-dimensioned and the emissions occurred when the VRU had been saturated, some time after the morning loading. The location of the VRU is shown in Figure 65. At the Shell truck loading facility on area 4a, the same situation was observed, at conditions when the VRU was malfunctioning. At other truck-loading areas such as area 3 and area 7, this pattern was not observed. In a future study the loading at each site should be studied more carefully using tracer gas experiments, in order to investigate the loading in the early morning.

#### 7.4.14 Loading to rock cavern

On 27-May-2004, large emissions of  $149 \pm 58$  kg/h were observed for several hours, west of area 1. It was found that the emissions were coming from the release vent of a rock cavity, when filling it with crude oil from an oil tanker. The rock cavity is operated by Nynäs refining, and contains crude oil for Bitumen production at the nearby refinery. Even though the emissions were relatively high, there are only a few such occasions every year, according to Nynäs refining. Therefore the emission will have little effect on the yearly emission from the oil harbor.

#### 7.4.15 Cleaning

During the oil harbor measurements in 2003 and 2004, high emissions were often encountered, that could be traced to activities of tank cleaning, pumping polluted drainage water etc. The strongest example so far is probably the one shown in the Figure 56 and Figure 57 with momentarily emissions as high as 2000 kg/h, due to cleaning of a pipeline in area 2. Another example was shown in Figure 63, with emission of 164 kg/h when a truck belonging to the company Tankcleaning pumped polluted drainage water, containing gasoline, to a deposit tank. A third example was on 17-May-2004 when huge fluxes, up to 500 kg/h were encountered between 9:00 and 10:00 on the main road, Oljevågen, at southerly wind. Logbooks indicate pumping activities at the quay 511, but this has to be further looked into, since the emission may come from loading a ship as well.

#### 7.4.16 Relevance of point emissions

A relevant question is how much point activities may contribute to the total emissions. A few rough calculation examples are shown in Table 35, indicating that point activities may contribute to 5-15% of the total emissions, if the assumptions are appropriate.

**Table 35.** Calculation examples of the potential relevance of point emissions to the annual emissions, based on the measurements and the here given assumptions.

Cases	VOC emission and contribution to total
Assume that cleaning activities causes emissions of 100 kg/h during 2 h every day at the oil harbor	73 ton (5%)
Assume that loading of ships causes emissions of 100 kg/h for 12 h every third day.	146 tons, (10%)
Assume that the rock cavity is filled 3 times a year during 48 hours.	21 tons (1%)

#### 7.4.17 Conclusions about the Oil harbor

In the KORUS project the understanding of time and position variability of the VOC emissions in the oil harbor was improved. The main difficulty encountered has been the fact that there are many activities causing temporary releases of volatile hydrocarbons, and that these emissions often are considerably larger than the continuous emissions. However, on a yearly basis the point emissions should only contribute to 5-15% of the total emissions. In a future project there should be more focused studies on the point activities, to better understand their contribution to the total emissions, and also to better be able to derive the continuous emissions.

#### 7.4.18 Measurements of aromatic hydrocarbons in the Oil harbor

Measurements of aromatic hydrocarbons have been done with the method described in chapter 7.5. One sample was collected on the road between area 5a and 5b when the wind was coming from south and thus represents the emissions from area 5a. Another sample was taken close to area 7b when the wind was coming from south-east and thus represents the emissions from 7b. The measurements are summarized in Table 36. These measurements have been added to the larger database of measurements that have been collected during the KORUS-project. The complete results derived from the whole database have been used when calculating the average emissions of aromatic hydrocarbons from the Oil harbor. This is further described in chapter 7.5. The FTIR-point measurement system is mounted inside the measurement-car. Therefore, measurements were always done on roads. Figure 70 shows the positions where the samples were collected.

**Table 36.** Mass proportion between aromatics/alkane from point measurements done with TENAX-tubes and GC-analysis and simultaneous point-measurements of Butane with FTIR. The numbers in the column marked Pos refers to the positions in Figure 70.

Measurement site	Pos	Date	Benzene	Toluene	Ethyl-benzene	m+p-xylene	o-xylene	GC Aromatics Weight (ng)	FTIR Butane Weight (ng)	Aromatics/Butane Ratio %
Oil harbor Statoil airfuel/gasoline	1	040806	0,112	0,525	0,060	0,238	0,065	268,998	3829	7,0
Oil harbor Shell loading product	2	040806	0,169	0,540	0,050	0,187	0,054	308,923	4464	6,9



**Figure 70.** Numbers indicates the positions where samples were taken to retrieve the ratio between aromatic hydrocarbons and alkanes. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBildern.

## **7.5 Measurements of aromatic hydrocarbons**

Point measurements were done on all four industries to determine the emission of aromatic hydrocarbons by determining the ratios between the concentration of aromatics and alkanes.

In order to determine the aromatics/alkane ratios, a combination of two measurement methods were used simultaneously. Measurements with a FTIR instrument were done to determine the butane concentration and air sampling with TENAX adsorption tubes were done to determine the concentration of aromatic hydrocarbons. The adsorption tubes were later analyzed with a gas chromatograph by IVL, the Swedish Environmental Research Institute, to determine the mass of aromatic hydrocarbons in the amount of air that had been sucked through the tube. Five different types of aromatics were possible to determine with the method: benzene, toluene, ethylbenzene, m+p-xylene and o-xylene. The separate system with the FTIR-spectrometer was analyzing the air sucked in to an enclosed White cell. The spectral evaluation for the FTIR was set to analyze the concentration of butane in the White cell. The air pumped through the adsorption tubes and the White cell was not the same but was collected at almost the same point, only differing with a few centimeters. The White cell and FTIR were situated inside the measurement car. Therefore, for practical reasons, measurements were always done where it was possible to drive with the car. When sampling inside the process area of Preemraff-Göteborg, the air-tubes for both systems were sometimes elongated with up to 15 m and its end points lifted to the top of the process so that the air was collected there.

Each measurement took between a few minutes and two hours to perform depending on how high the concentration of butane was. The FTIR was giving butane concentration in real time which made it possible to adjust the duration of the time when air was pumped through the adsorption tube so that the mass of collected aromatics could be expected to be enough to give good accuracy when later analyzing the tube with GC.

The concentration of butane that was measured with the FTIR was multiplied with the volume of air that was pumped through the adsorption tubes to get the expected mass of alkane for the same amount of air (in volume) as was analyzed with the adsorption tubes. The amount of aromatics found in each adsorption tube is presented in Table 37 together with the mass of butane that was retrieved from the FTIR-measurement.

During the KORUS project, twelve point-measurements of aromatic hydrocarbons were done year 2004 on Preemraff-Göteborg, eight on Preemraff-Lysekil, two on Shellraff and two in the Oil harbor of Göteborg. This number of samples is too low to represent the big variation in aromatic hydrocarbon concentration that is expected on these industries. All samples have therefore been grouped into four categories: crude-oil-tanks, process, product-tanks and water-treatment. An average aromatics/butane ratio has then been calculated for each category and is shown in Table 38. It has then been assumed that the characteristic aromatic/butane ratio on average is the same at all industries for equipment of the same category. By multiplying the amount of alkane emissions from the industries with the relevant aromatics/alkane ratios, an estimate of the emission of aromatic hydrocarbons were done.

**Table 37.** Mass proportion between aromatics/alkane from point measurements done with TENAX-tubes and GC-analysis and simultaneous point-measurements of Butane with FTIR.

Measurement site	Category	Date	Benzene	Toluene	Ethyl- benzene	m+p- xylene	o- xylene	GC Aromatics Weight (ng)	FTIR Butane Weight (ng)	Aromatics/ Butane Ratio %
Preem SE crude-oil	C	040802	0,239	0,221	0,067	0,258	0,215	62,5	888	7,0
Preem crude-oil tank park	C	040816	0,372	0,336	0,044	0,197	0,050	107,6	5767	1,9
Preem crude-oil tank park	C	040816	0,372	0,334	0,045	0,199	0,050	79,2	3645	2,2
Preem cleaning	W	040816	0,215	0,474	0,053	0,201	0,057	745,7	3657	20,4
Preem cleaning	W	040816	0,211	0,477	0,053	0,202	0,056	821,2	4103	20,0
Preem process	P	040816	0,162	0,414	0,069	0,275	0,080	239,9	1107	21,7
Preem East proc	P	040817	0,178	0,622	0,037	0,132	0,032	202,6	4678	4,3
Preem East proc	P	040817	0,188	0,366	0,067	0,301	0,079	89,7	3748	23,9
Preem process butane tower	P	040817	0,184	0,375	0,069	0,295	0,076	250,1	2702	9,3
Preem 700 tanks	R	040818	0,069	0,507	0,241	0,120	0,063	767,0	-	-
Preem crude-oil tank-park.	C	041221	0,249	0,398	0,050	0,250	0,055	41,8	5225	0,8
Preem crude-oil tank-park.	C	041221	0,236	0,339	0,118	0,049	0,207	70,5	5875	1,2
Preemraff-Lysekil tank 1406	C	040707	0,169	0,253	0,092	0,301	0,184	52,6	3806	1,4
Preemraff-Lysekil process	P	040707	0,084	0,237	0,109	0,392	0,178	45,1	507	8,9
Preemraff-Lysekil process	P	040713	0,082	0,158	0,113	0,470	0,177	218,9	3748	5,8
Preemraff-Lysekil black comp tanks	R	040712	0,047	0,215	0,073	0,299	0,366	593,8	3811	15,6
Preemraff-Lysekil white comp tanks	R	040714	0,057	0,349	0,109	0,379	0,105	648,3	1664	39,0
Preemraff-Lysekil gasoline comp tanks	R	040713	0,059	0,414	0,093	0,333	0,101	511,1	3789	13,5
Preemraff-Lysekil water treatment	W	040713	0,164	0,450	0,075	0,245	0,066	582,5	3959	14,7
Preemraff-Lysekil preskimmer	W	040713	0,070	0,318	0,106	0,383	0,123	501,0	3902	12,8
Shell tank 108	C	040705	0,251	0,293	0,063	0,283	0,110	118,16	3403	3,5
Shell process	P	040705	0,160	0,386	0,065	0,308	0,081	590,19	3841	15,4
Oil harbor Statoil airfuel/gasoline	R	040806	0,112	0,525	0,060	0,238	0,065	268,998	3829	7,0
Oil harbor Shell- loading product	R	040806	0,169	0,540	0,050	0,187	0,054	308,923	4464	6,9

Category: P=process, W=water treatment, C=crude oil tanks, R=product tanks.

The errors in the estimations of aromatic emission are high which is visible in the high standard deviations. The errors are believed to be especially high for the measurements on the refinery processes, since high variability has been observed depending on what position inside the process the sample was taken at. It is difficult to acquire a measurement on a mixed plume representing the average process emission since the plume rises quickly to a high altitude. The low standard deviation for the measurements on water-treatments indicates that those measurements probably represent the true situation quite well.



**Table 38.** The table shows the measurements grouped according to category and the calculated average aromatic/alkane ratio for each category.

Crude-oil-tanks	Mass ratio % aromatics/alkane
Preem SE crude oil	7,0
Preem crude-oil tank park	1,9
Preem crude-oil tank park	2,2
Preem crude-oil tank-park.	0,8
Preem crude-oil tank-park.	1,2
Preemraff-Lysekil tank 1406	1,4
Shell tank 108	3,5
<b>Average</b>	<b>2,6</b>
<b>Standard deviation</b>	<b>2,1</b>

Process	Mass ratio % aromatics/alkane
Preemraff process	21,7
Preemraff east proc	4,3
Preemraff east proc	23,9
Preem process butane tower	9,3
Preemraff-Lysekil process	8,9
Preemraff-Lysekil process	5,8
Shell process	15,4
<b>Average</b>	<b>12,8</b>
<b>Standard deviation</b>	<b>7,7</b>

Product-tanks	Mass ratio % aromatics/alkane
Preemraff-Lysekil Black comp tanks	15,6
Preemraff-Lysekil white comp tanks	39,0
Preemraff-Lysekil gasoline comp tanks	13,5
Oil harbor Statoil airfuel/gasoline	7,0
Oil harbor Shell loading product	6,9
<b>Average</b>	<b>16,4</b>
<b>Standard deviation</b>	<b>13,2</b>

Water-treatment related	Mass ratio % aromatics/alkane
Preemraff cleaning	20,4
Preemraff cleaning	20,0
Preemraff-Lysekil water treatment	14,7
Preemraff-Lysekil preskimmer	12,8
<b>Average</b>	<b>17,0</b>
<b>Standard deviation</b>	<b>3,8</b>

The five different aromatic compounds that were determined with the GC-analysis had a distribution according to Table 39 for the four different categories.

**Table 39.** Distribution of different aromatics for the four different categories of equipment as acquired by measurements with adsorption tubes and GC (IVL).

Specie	Crude-oil-tanks (%)	Process (%)	Product-tanks (%)	Water-treatment (%)
<b>Toluene</b>	38.5	36.5	38.0	43.0
<b>m+p-xylene</b>	28.6	31.0	30.0	25.8
<b>Benzene</b>	21.2	14.8	8.3	16.5
<b>o-xylene</b>	6.2	10.0	15.7	7.6
<b>Etylbenzene</b>	5.5	7.6	8.1	7.2
<b>Sum:</b>	100%	100%	100%	100%

Table 40 and Table 41 show the estimated emissions of aromatic hydrocarbons from Preemraff-Lysekil. It has been assumed that the emissions from the rock cavern exhaust and the product harbor is best represented by product tanks.

**Table 40.** Estimated emission of total aromatic hydrocarbons from Preemraff-Lysekil.

Source	Category	Emission 2003 (kg/h)	Emission 2004 (kg/h)	Average (kg/h)
Process	P	11±7	11±7	<b>11±7</b>
Crude oil tanks	C	5±4	3±3	<b>4±4</b>
Black CTP	R	20±16	18±14	<b>19±15</b>
White CTP	R	8±7	6±5	<b>7±6</b>
Gasoline CTP	R	4±4	6±5	<b>5±4</b>
Water treatment	W	2±0	3±1	<b>3±1</b>
Preskimmer	W	1±0	2±1	<b>1±0</b>
Rock cavern exhaust	R	1±1	14±11	<b>8±6</b>
Product harbor	R	4±4	4±4	<b>4±4</b>
<b>Total:</b>		<b>58±43</b>	<b>68±49</b>	<b>63±46</b>

Category: P=process, W=water treatment, C=crude oil tanks, R=product tanks.

**Table 41.** Estimated emission in kg/h of different aromatics from different parts of Preemraff-Lysekil.

Source	Toluene	m+p-xylene	Benzene	o-xylene	Etylbenzene	Sum (kg/h)
Process	4.1	3.5	1.6	1.1	0.8	<b>11</b>
Crude oil tanks	1.7	1.2	0.9	0.3	0.2	<b>4</b>
Black CTP	7.2	5.7	1.6	3.0	1.5	<b>19</b>
White CTP	2.6	2.1	0.6	1.1	0.6	<b>7</b>
Gasoline CTP	2.0	1.6	0.4	0.8	0.4	<b>5</b>
Water treatment	1.1	0.7	0.4	0.2	0.2	<b>3</b>
Preskimmer	0.6	0.4	0.2	0.1	0.1	<b>1</b>
Rock cavern exhaust	2.9	2.3	0.6	1.2	0.6	<b>8</b>
Product harbor	1.7	1.3	0.3	0.7	0.4	<b>4</b>
<b>Total:</b>	<b>24</b>	<b>19</b>	<b>7</b>	<b>9</b>	<b>5</b>	<b>63</b>

Table 42 and Table 43 show the estimated emissions of aromatic hydrocarbons from Preemraff-Göteborg.

**Table 42.** Estimated emission of total aromatic hydrocarbons from Preemraff-Göteborg.

Source	Emission 2002 (kg/h)	Emission 2003 (kg/h)	Emission 2004 (kg/h)	Average (kg/h)
Crude oil tanks	4±3	2±2	3±2	3±2
Process	7±4	9±6	10±6	9±5
Product tanks	28±22	9±7	15±13	18±14
Water treatment	3±1	3±1	3±1	3±1
<b>Total:</b>	<b>42±31</b>	<b>24±16</b>	<b>31±22</b>	<b>33±23</b>

**Table 43.** Estimated emission in kg/h of different aromatics from different parts of Preemraff-Göteborg.

Source	Toluene	m+p-xylene	Benzene	o-xylene	Etylbenzene	Sum (kg/h)
Crude oil tanks	1.1	0.9	0.6	0.2	0.2	3
Process	3.2	2.7	1.3	0.9	0.7	9
Product tanks	6.7	5.3	1.5	2.8	1.4	18
Water treatment	1.4	0.8	0.5	0.2	0.2	3
<b>Total:</b>	<b>12.5</b>	<b>9.7</b>	<b>3.9</b>	<b>4.1</b>	<b>2.5</b>	<b>33</b>

Table 44 and Table 45 show the estimated emissions of aromatic hydrocarbons from Shellraff. The emission from the LPG area has been assumed to be zero. The west tank-park has been assumed to be best represented by crude-oil tanks and the east-tank-park has been assumed to be best represented by product tanks.

**Table 44.** Estimated emission of total aromatic hydrocarbons from Shellraff.

Source	Category	Emission 2003 (kg/h)	Emission 2004 (kg/h)	Average (kg/h)
West tank-park	C	1±1	1±1	1±1
East tank-park	R	7±6	3±2	5±4
Process	P	13±8	3±2	8±15
Hysomer	P	9±6	2±1	6±3
Water treatment	W	13±3	1±0	7±2
<b>Total:</b>		<b>44±23</b>	<b>11±7</b>	<b>27±15</b>

Category: P=process, W=water treatment, C=crude oil tanks, R=product tanks.

**Table 45.** Estimated emission in kg/h of different aromatics from different parts of Shellraff

Source	Toluene	m+p-xylene	Benzene	o-xylene	Etylbenzene	Sum (kg/h)
West tank-park	0.5	0.3	0.3	0.1	0.1	1
East tank-park	1.8	1.4	0.4	0.8	0.4	5
Process	2.9	2.4	1.2	0.8	0.6	8
Hysomer	2.1	1.7	0.8	0.6	0.2	6
Water treatment	3.2	1.9	1.2	0.6	0.5	7
<b>Total:</b>	<b>11</b>	<b>8</b>	<b>3</b>	<b>3</b>	<b>2</b>	<b>27</b>

Table 46 and Table 47 show the estimated emissions of aromatic hydrocarbons from the Oil harbor in Göteborg. It has been assumed that all areas are best represented as product-tanks.

**Table 46.** Estimated emission of total aromatic hydrocarbons from the Oil harbor in Göteborg.

Area	Category	Emission 2003 (kg/h)	Emission 2004 (kg/h)	Average (kg/h)
1	R	2±2	2±2	2±2
2	R	4±3	5±4	5±4
3	R	2±1	2±1	2±1
4a	R	3±2	4±3	4±3
4b	R	1±1	3±3	2±2
5a	R	5±4	3±3	4±3
5b	R	7±6	4±3	6±4
6	R	1±1	1±1	1±1
7a	R	1±1	1±1	1±1
7b	R	1±1	2±2	1±1
7c	R	4±3	4±3	4±3
<b>Total:</b>		<b>30±24</b>	<b>31±25</b>	<b>31±25</b>

Category: P=process, W=water treatment, C=crude oil tanks, R=product tanks.

**Table 47.** Estimated emission in kg/h of different aromatics from different parts of the Oil harbor in Göteborg.

Area	Toluene	m+p-xylene	Benzene	o-xylene	Etylbenzene	Sum (kg/h)
1	0.9	0.7	0.2	0.4	0.2	2
2	1.8	1.4	0.4	0.7	0.4	5
3	0.6	0.5	0.1	0.3	0.1	2
4a	1.4	1.1	0.3	0.6	0.3	4
4b	0.8	0.6	0.2	0.3	0.2	2
5a	1.6	1.2	0.3	0.6	0.3	4
5b	2.1	1.7	0.5	0.9	0.5	6
6	0.3	0.2	0.1	0.1	0.1	1
7a	0.3	0.2	0.1	0.1	0.1	1
7b	0.5	0.4	0.1	0.2	0.1	1
7c	1.4	1.1	0.3	0.6	0.3	4
<b>Total:</b>	<b>12</b>	<b>9</b>	<b>3</b>	<b>5</b>	<b>2</b>	<b>31</b>

## 8 Discussion and Conclusion

The VOC leakages at four industries have been monitored during three years. A full screening at an industrial site typically consisted of 10-15 measurement days, conducted over a period of 4-5 weeks. From the measurements the total VOC emission from the whole industrial facility has been quantified with an uncertainty of around 25%, measured over several days at varying meteorological conditions. Furthermore, has it been possible to estimate the emissions also from specific source areas, such as the process areas, the water treatment and the product and crude oil tank areas. Also emissions from intermittent activities such as ship and truck loading, tank cleaning and flaring have been measured.

In the past, a method based on the DIAL technique has been used to measure VOC emissions from the refineries in this study, see references [16-18]. In comparison, the SOF method shows both strengths and weaknesses.

A few strengths of the SOF method are:

- *Mobility*: it is possible to scan quickly through an industry in the search for potential emission sources. At the right meteorological conditions, a few hours of measurements will give a good overview of the main emissions at a specific site. As a result, new emission sources have been discovered that were not anticipated before.
- *Cost effectiveness*: the hardware is cheaper and with less technical complexity than for the DIAL method. This makes it possible to conduct more frequent measurements ( see section 7.3).
- *Specificity*: in contrast to the DIAL method the SOF technique has the capability to identify the average hydrocarbon in the measured gas.
- *Signal-to-noise*: the measurements sensitivity is high since solar light is being used. This makes measurements far away possible.

A few weaknesses of the SOF-method are:

- *Incapability to measure plume height*: An uncertainty in the derived flux will be obtained since there is no possibility to determine the height of the plume wherefore the estimated wind will have an uncertainty. This improves when measuring far away.
- *Separation of sources*: it is sometimes difficult to separate emissions sources that are close to each other.
- *Annual average*: it is difficult to conduct measurements between November to February due to the lack of solar light and low sun elevation. This makes it difficult to measure under cold conditions for which the emissions might be different, especially for non heated tanks, such as crude oil tanks.

Experience has shown that much more work is required the first year SOF measurements are done at an industry. It takes time to learn which surrounding sources that can interfere, both from sources inside the same industry, or from neighboring industries. The latter was the case with Shellraff and the Oil harbor in Göteborg that are located beside each other. It also takes time to understand what variability that can be expected from the different sources. With knowledge about these factors, it is considerably easier to repeat measurements the following years at the same industries.

From the data that were collected in the KORUS project, some general statements of the VOC emissions from the three studied refineries can be done. The alkane emission has been divided into five groups and compared between the refineries in Table 48.

**Table 48.** The measured alkane emission in **ton/year** from the different parts of the refineries.

Refinery	Total	Process	Crude-oil tanks	Product tanks	Water treatment facility	Transport related activity
Preemraff-Lysekil	<b>4760</b>	760 (16%)	1470 (31%)	2080 (43%)	140 (3%)	240 (5%)
Preemraff-Göteborg	<b>2720</b>	610 (22%)	1000 (37%)	940 (35%)	160 (6%)	0 <sup>(1)</sup>
Shellraff	<b>2060</b>	930 (45%)	410 (20%)	260 (13%)	390 (19%)	80 (4%)

(1) Transport to/from Preemraff-Göteborg is done through pipelines to the Oil harbor in Göteborg.

The annual throughput of refined crude oil is twice as large for Preemraff-Lysekil compared to the other two refineries. To reflect this, the emissions have been normalized to annual throughput in Table 49 to give the emission in each section as ton alkanes per Mton refined crude oil.

**Table 49.** Normalized alkane emission in **ton per megaton** refined crude oil.

Refinery	Total (ton/Mton)	Process	Crude-oil tanks	Product tanks	Water treatment facility	Transport related activity
Preemraff-Lysekil (10 Mton/year)	<b>476</b>	76	147	208	14	24
Preemraff-Göteborg (3 Mton/year)	<b>907</b>	203	333	310	53	0
Shellraff (5 Mton/year)	<b>412</b>	186	82	52	78	16
Average:	<b>598</b>	155 (26%)	187 (31%)	190 (32%)	48 (8%)	13 (2%)

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.

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## References

1. Kihlman M., *Application of solar FTIR spectroscopy for quantifying gas emissions*. To be published in Sep-2005, Licentiate thesis at Chalmers: Gothenburg.
2. Lantmäteriet. 2005 [cited; Available from: <http://www.lantmateriet.se>].
3. Fransson K. and Mellqvist J., *Measurements of VOCs at Refineries Using the Solar Occultation Flux Technique*. 2002, Chalmers report.
4. White J.U., *Very long optical paths in air*. Journal of the Optical Society of America, 1976. **66**: p. 411-416.
5. *GRAMS/AI*. 2004, Galactic Industries Corporation.
6. Griffith D.W.T., *Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra*. Applied Spectroscopy, 1996. **50**(1): p. 59-70.
7. Oppenheimer C., et al., *Remote measurement of volcanic gases by Fourier transform infrared spectroscopy*. Applied Physics B: Lasers and Optics, 1998. **67**(4): p. 505.
8. *Pacific Northwest National Laboratory*. 2004 [cited; Available from: <https://secure.pnl.gov/nsd/nsd.nsf/Welcome>].
9. Hanst P.L., *QASoft '96, Database and quantitative analysis program for measurements of gases*. Infrared Analysis Inc., 1996.
10. Benner D.C., et al., *The HITRAN molecular spectroscopic database: Edition of 2000 including updates through 2001*. Journal of Quantitative Spectroscopy and Radiative Transfer, 2003. **82**(1-4): p. 5.
11. P.M. Chu F.R.G., G.C. Rhoderick, and W.J. Lafferty, *The NIST Quantitative Infrared Database*. J. Res. Natl. Inst. Stand. Technol., 1999. **104**(59).
12. Norton R.H. and Beer R., *New Apodizing Functions For Fourier Spectrometry*. Journal Of The Optical Society Of America, 1976. **66**(3): p. 259-264.
13. EPA. *AP42, 5ed. Organic Liquid Storage Tanks*. 1997 [cited; Available from: <http://www.epa.gov/ttn/chief/ap42/>].
14. Mattson K.-G., *Personal communication about tank 1406*. 2005, Preemraff-Lysekil.
15. 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.

16. Milton M.J.T., et al. *Measurements of fugitive hydrocarbon emissions with a tunable infrared dial*. 1992. Cambridge, MA, USA: Publ by NASA, Washington, DC, USA.
17. Walmsley H.L. and O'Connor S.J. *The measurement of atmospheric emissions from process units using differential absorption LIDAR*. 1997. Munich, Germany: The International Society for Optical Engineering.
18. Robinson R.A., Woods P.T., and Milton M.J. *DIAL measurements for air pollution and fugitive-loss monitoring*. 1995. Munich, Ger: Society of Photo-Optical Instrumentation Engineers, Bellingham, WA, USA.



## **Abbreviations and commonly used concepts**

Alkanes	Organic compound that consists of n carbon atoms and 2n+2 hydrogen atoms. Their names and chemical formula are: Methane CH <sub>4</sub> Ethane C <sub>2</sub> H <sub>6</sub> Propane C <sub>3</sub> H <sub>8</sub> Butane C <sub>4</sub> H <sub>10</sub> Pentane C <sub>5</sub> H <sub>12</sub> Hexane C <sub>6</sub> H <sub>14</sub> Heptane C <sub>7</sub> H <sub>16</sub> Octane C <sub>8</sub> H <sub>18</sub> Nonane C <sub>9</sub> H <sub>20</sub> Decane C <sub>10</sub> H <sub>22</sub>
Alkenes	Organic compounds with a double bond between two carbon atoms.
Alkynes	Organic compounds with a triple bond between two carbon atoms.
Aromatic hydrocarbons	Ring shaped molecules that mainly consist of carbon and hydrogen atoms.
Carbon number	The number of carbon atoms in an alkane-molecule. For example butane has a carbon number of 4.
DIAL	Differential Absorption LIDAR
Flux	In this report this is used to represent the gas-flow.
FTIR-spectrometer	Fourier Transform Infra-Red-spectrometer
GC-Analysis	Gas Chromatographic-Analysis A lab-test that is used to determine the composition of a gas.
GPS	Global Positioning System. A method to determine the position of cars and boats by receiving radio signals from satellites.
KORUS	The name of the measurement project. KOlvätemätning på Raffinaderier Utnyttjande SOF. This is a Swedish abbreviation meaning measurement of hydrocarbons on refineries using SOF.
OPUS	The name of a spectral software developed by the spectrometer manufacturer Bruker.
Spectral resolution	Spectral resolution is in this report defined in the same way as

in the OPUS software i.e. as the full width at half maximum of a peak when triangular apodization is used.

SOF	Solar Occultation Flux
VOC	Volatile Organic Compounds. Compounds that are in gas form at room temperature and where the molecules consists of atoms of carbon and hydrogen to a high degree. This includes the alkanes, alkenes, alkynes and aromatic hydrocarbons.
VRU	Vapour Recovery Unit
TENAX-tube	A metal tube where the inside is coated with coal. When air is pumped through the tube, the VOC content in the air is absorbed into the coal. The absorbed VOC can later be released by heating the tube and then analyzed with a GC.
Total column	The concentration of a chemical compound in air integrated along a line. The unit of this can be $\text{mg}/\text{m}^2$ , $\text{molecules}/\text{m}^2$ or $\text{ppm}\cdot\text{m}$
QESOF	Quantitative Evaluation of Solar Occultation Flux. The name of the software that was developed to evaluate SOF-measurements.
White cell	A White cell is an optical set-up that gives a folded light path with the help of mirrors inside an enclosed tube. The air that is to be analyzed is pumped into the tube. The White cell used in the KORUS-project has a 0.8 m long tube and has a folded light path of 96 m. New air is constantly pumped into the tube so that the air is exchanged every 30 seconds approximately.