

THE SOLAR OCCULTATION FLUX METHOD, A NEW TECHNIQUE TO QUANTIFY FUGITIVE VOC EMISSIONS

Johan MELLQVIST

CHALMERS UNIVERSITY OF TECHNOLOGY,

Hörsalsvägen 11, SE-41296 Göteborg

Tel: +46317724850 Fax: +467721884 E-mail: jome@rss.chalmers.se

Jerker SAMUELSSON

CHALMERS UNIVERSITY OF TECHNOLOGY

Bo GALLE

CHALMERS UNIVERSITY OF TECHNOLOGY

Manne KIHLMAN

CHALMERS UNIVERSITY OF TECHNOLOGY

Abstract

A new remote sensing method named SOF (Solar Occultation Flux) has been developed and applied to locate and quantify fugitive hydrocarbon emissions from the industry. The method is based on measuring infrared intensity spectra of the sun from a moving vehicle. In order to obtain the flux from a particular emission source, the vehicle is driven in such a way that the detected solar light moves across the actual emission plume. The flux is obtained as the integrated sum of the retrieved path averaged concentrations, multiplied by the wind speed. Measurements have been demonstrated at many industrial areas for alkanes and olefines but also for other species such as ammonia, carbon monoxide, formaldehyde, hydrogen chloride, hydrogen fluoride and sulfur dioxide. During 2002-2004 an extensive project was carried out in which three refineries and an oil harbor in Sweden were monitored. The results showed that for a typical refinery 0.06% of the throughput was lost due to vaporization. Of the emitted gas 26% originated from the process, 31% from crude-oil tanks, 32% from product tanks, 8% from the water treatment facility and 2% from transport related activities. The measurement errors are estimated to be around 25%. Other applications include farming, volcanoes (Mt Etna and Popocatepetl) and Megacities (Milano, Mexico City).

1. Introduction

Volatile organic compounds (VOCs) produce tropospheric ozone that damage crops and cause severe health problems to humans. VOCs consist foremost of alkanes, alkenes and some aromatics. Refineries are the single largest point sources of VOCs and authorities therefore have requirements to control these emissions. The most common technique for measuring VOCs emitted from refineries and oil industries today is DIAL¹ (Differential Absorption LIDAR). By directing short laser pulses with different wavelengths through the plume, the gas concentrations can be measured. The mass flux is obtained by multiplying the concentration integrated over the cross section of the plume by the wind speed. The DIAL technique is however rather complex and expensive, which has led to little usage of this technique during the more than 15 years it has been available for VOC flux measurements. From a number of different research projects^{2,3,4} a new method called SOF (Solar Occultation Flux), which can be utilized to quantify fugitive emissions, has been developed. Instead of laser pulses, the sun is used as the light source. The SOF method is more cost effective and faster than the DIAL technique and it is easier to automate. In this paper we will describe the SOF method and show results obtained from an extensive monitoring project that was carried out during 2002-2004 at three refineries and an oil harbor in Sweden⁶.

2. Method

The SOF method has been developed since 1998 and it is thoroughly described in a separate paper⁵. It is based on recording broadband infrared spectra of the sun with an infrared spectrometer (FTIR) 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. From the solar spectra it is possible to retrieve the path-integrated concentration (molecules/cm²) between the sun and the spectrometer. In Figure 1 a measurement system is shown built into a van. To obtain the gas emission from a source, the car is driven in such way that the detected solar light cuts through the emission plume. This is illustrated in Figure 2. To calculate the gas emission, the wind direction and speed is also required and these parameters are usually measured from high masts and towers.



Figure 1. On the left the SOF car is shown while measuring emissions from crude oil tanks. The solar-tracker shown on the right transmits the solar light into the infrared spectrometer independently of the positioning of the car.

With the SOF method a large number of species can be measured such as aldehydes ammonia, ethylene, CO, ethylene-oxide, HF, HCl, methane, NO₂, SO₂, propane, propylene, terpenes, and vinyl-chloride. The retrieval is based on using multivariate analysis, fitting calibration spectra which have been recorded in the laboratory to the measured spectra. The calibration spectra are obtained from published reference libraries such as the HITRAN database (www.hitran.com) and databases from NIST (www.NIST.gov) and Pacific Northwest National Laboratories (<http://nwir.pnl.gov>). The retrieval is conducted in real time in an automatic program, denoted QESOF⁸. The computer screen shown while conducting measurements can be seen in Figure 3. The results of the spectral fitting algorithm for alkanes in the software QESOF has been compared and verified with the results retrieved from other software such as the Classical Least Square (CLS) method in the Grams software (Galactic industries) and the non-linear NLM4 software developed by Griffith⁹. The agreement between NLM4 and QESOF is very good, within a few percent while the CLS code agrees less well with discrepancies of 30% in the plume, but this can be explained by several reasons. Verification of the software has also been conducted for the volcanic species HCl and SO₂ by comparison with a code developed by Mike Burton at INGV¹⁰ showing very good agreement, with differences of a few percent.

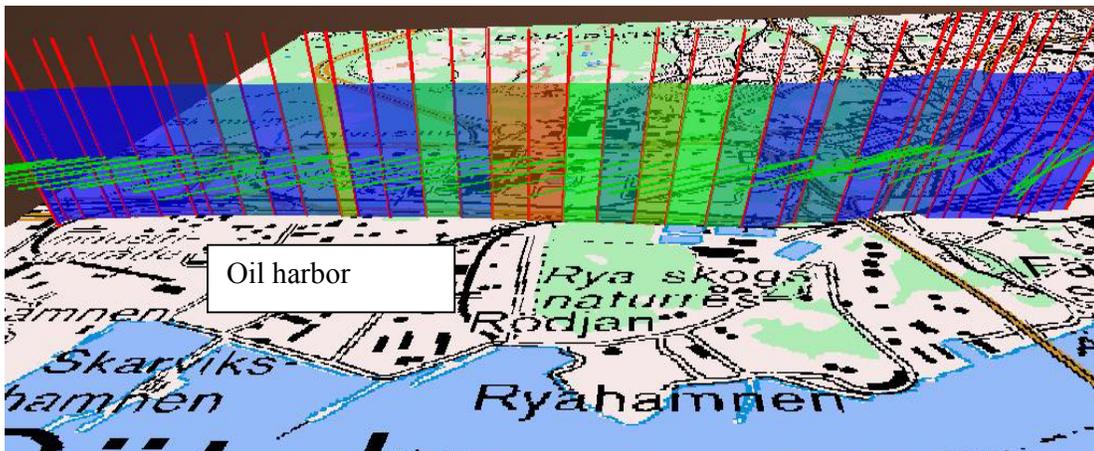


Figure 2. A 3D plot of a SOF measurement conducted at a oil harbor is shown. The red vertical lines correspond to solar lines. The colors in between the solar lines (blue to red) correspond to the integrated concentration of alkanes (blue is low concentration while green and red are higher). The wind vectors are shown as green horizontal lines pointing into the measurement-surface.

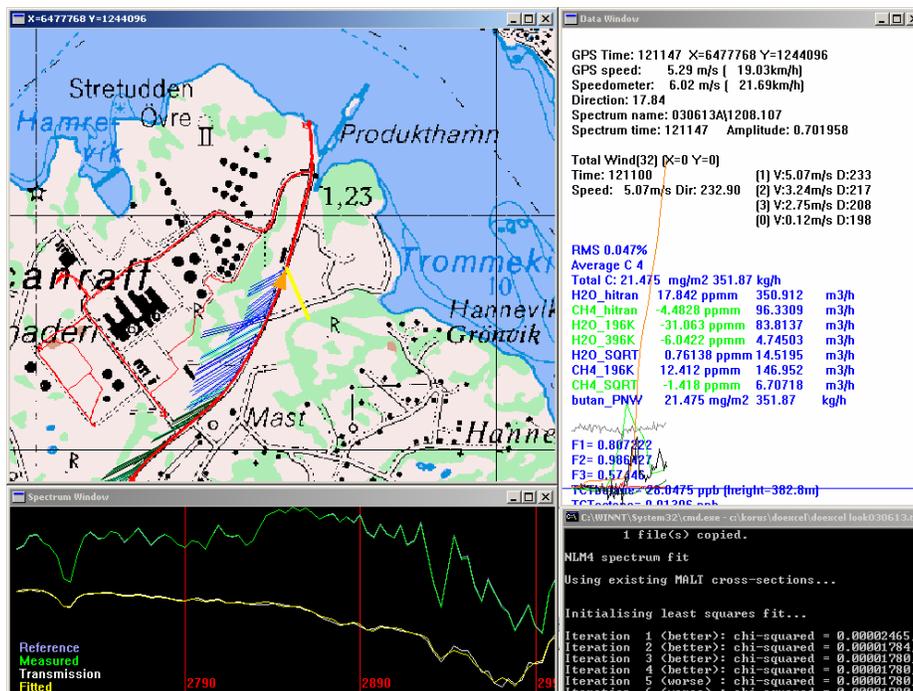


Figure 3. The screen of the measurement computer for the automatic retrieval software QESOF, developed for real-time evaluation of the measured spectra. In the upper left is shown a map of the measurement with lines pointing toward the wind, the measured and fitted absorption spectra in the lower left, and the retrieved data on the right side.

3. Validation and error analysis

The measurement error for the SOF measurements is mainly due to uncertainties of the wind used in the calculation. Since the wind is rather disturbed close to the ground, near buildings and forest, an approach has been taken in which the measurements are conducted at a certain distance from the sources, 0.5-1 km, to make most of the plume enter above the first disturbed layer of 30-40 m height. In this case, it has been shown⁶⁻⁸ that the uncertainty of the SOF method is around 20-30%, when averaging over several measurements.

Several validation experiments of the SOF technique have been conducted by releasing tracer gas (SF_6) at a known rate and then measuring the release using the SOF method. In one experiment SF_6 was emitted from the top of a 17 m tall mast in the middle of an open field⁵. Traverses were then done downwind with the SOF measurement system at varying distances from the emission source, Figure 4. The retrieved average emission value differs by 11% but discrepancies of up to 50% can be obtained for single measurements⁵. Releases of SF_6 from oil tanks have also been conducted at several refineries showing discrepancies of 50% for close by measurements and smaller, 30%, when measuring further away from the tanks. This is consistent with the error analysis described above.

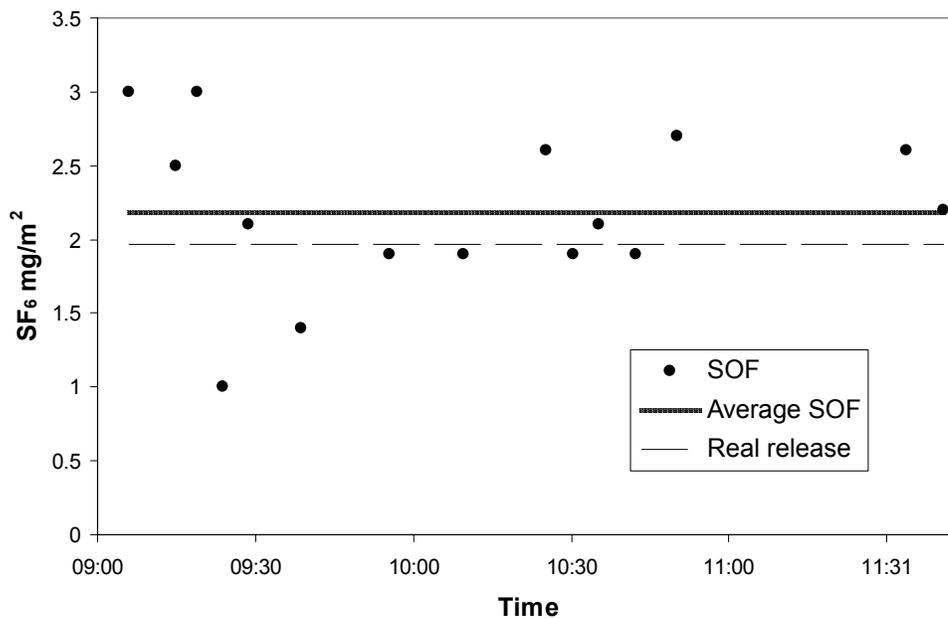


Figure 4. Results from a validation experiment in which SF_6 was emitted from a 17 m mast at an open field and measurement with the SOF method were conducted. The average of the measured emissions was 11% higher than the real release rate.

Results from intercomparison exercises with other flux measuring techniques are not available. An indication, however, of the validity of the SOF technique is the following: During 1995 and 1999 the DIAL technique, operated by a commercial company, was applied to estimate emission from a certain refinery in Sweden. According to official reports to the provincial government they estimated fugitive emission from the whole process area corresponding to 64 and 87 kg/h of alkanes during 1995 and 1999, respectively, with reported error bars of 15-20%. The SOF method was applied two years later, in 2001, to our knowledge measuring in a similar geometry along the main refinery road. Measurements of the process area during two days yielded a total flux of

74±20 kg/h. This falls surprisingly close to the values spanned by the DIAL measurements. The measurements were not conducted at the same occasion, but the process area seems quite constant since the values for 2002, 2003 and 2004 are similar.

4. Measurements of total VOC emissions

In Figure 5 a SOF traverse conducted downwind a refinery is shown, as part of a measurement project conducted between 2002 and 2004 at 3 refineries and an oil harbor in Sweden⁶. The amount of alkane species retrieved in the solar light is indicated by the color scale where red corresponds to maximum values (here 60 mg/m²). The lines point towards the wind, i.e. towards a potential source. It can be seen that there are several plumes, interpreted as emissions originating from the crude oil tank park (*left*) and combined process and component tank park area (*right*). Also the plume from the water treatment can be seen between the two large plumes. Usually 5-10 individual traverses are averaged over a day in order to obtain an emission value with sufficient accuracy (20-30%)⁶⁻⁸. In Figure 6 emission values of alkanes from the refinery in Figure 5 are shown obtained over several years. The variability of the total emissions is believed to be caused by process changes inside the refinery and partly by variations in the measurement parameters (position of SOF and wind measurement). Measurements at other refineries show in some cases less variability and in some cases much larger, in the latter case this is caused by process changes. The results in the measurement project shows that on average 0.06% of the crude oil throughput leaks out to the atmosphere⁶⁻⁷ and most of these emissions is in the form of alkanes (98.5%).

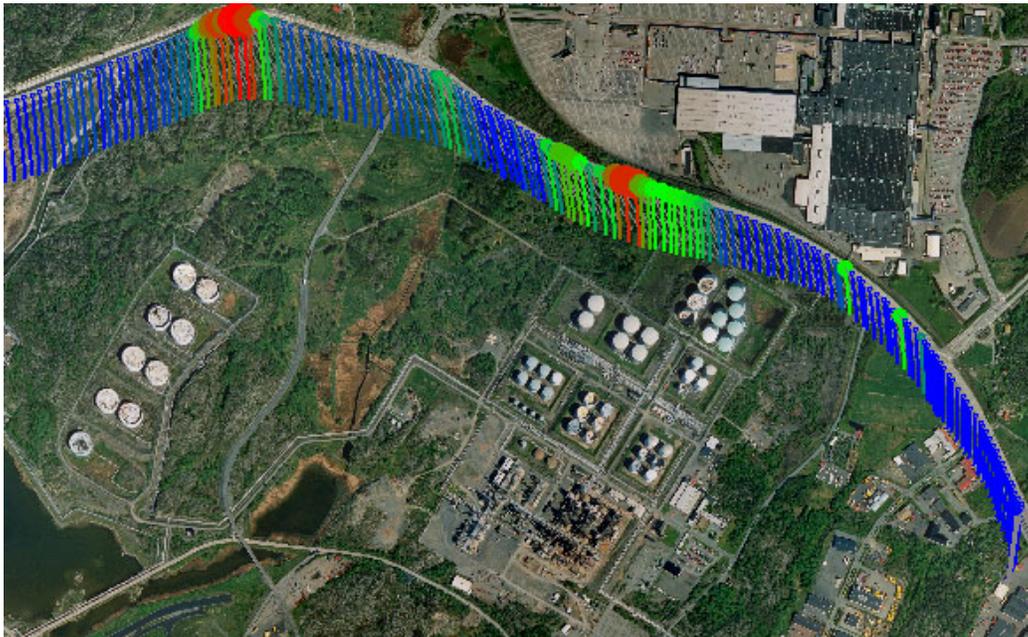


Figure 5. VOC measurements downwind a refinery. Red lines indicates points where high line integrated concentrations have been measured (maximum value 60 mg/m² here). Blue lines indicate points with low concentrations. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden)

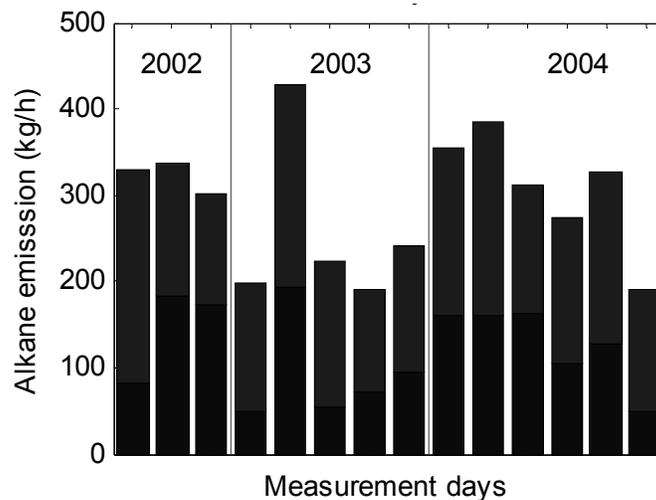


Figure 6. The total emissions of VOCs (daily averages) from the refinery shown in Figure 5 over several years.

5. Leakage search

The SOF method can also be used to measure close to the sources, in order to estimate the emissions from specific sources such as flares, process areas, crude oil tank areas, water treatment areas, ship loading etc. Measurements conducted close to the sources, are usually associated with larger uncertainties than given above, i.e. larger than 30%, due to the fact that the wind field is more disturbed. In general the emission will be overestimated, but this depends on the measurement situation and applies for instance for storage tanks. At first order, it might be assumed that the overestimation, i.e. error, is about the same at all source areas when conducting close by measurements and this makes it possible to obtain relative emission values. For instance the results in the measurement project showed that 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.

In Figure 7 an example of a leakage measurement in an oil harbor is shown, in which a tank area has been encircled. It is obvious from the figure that there is a strong leakage of VOC in the upper right corner. The emissions originate from a malfunctioning vapor recovery unit (VRU). In Figure 8 an example of VOC leakages when loading two ship with low volatile product, class II, is shown corresponding to 125 kg/h over several hours. Loading of this product should not create large emissions, but in this case the ships had previous loads of high volatile product which caused the high emissions.



Figure 7. SOF measurements in an oilharbor is shown. Most of the leakages originate from a malfunctioning vapor recovery unit. Red lines indicates points where high values have been measured (maximum value 160 mg/m^2 here) while blue indicates low values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden).

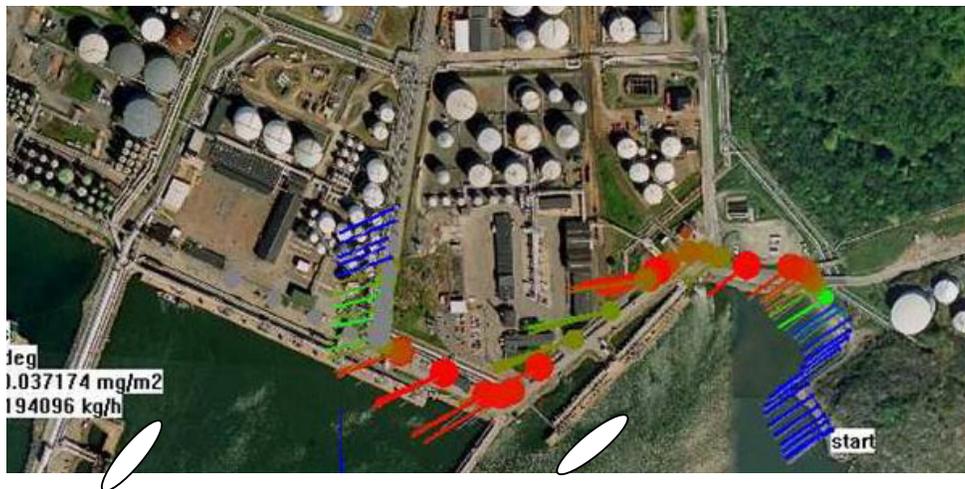


Figure 8. SOF measurements of two ships loading low volatile product class II, but with a previous high volatile cargo (class I). An emission rate of 125 kg/h was obtained. Red lines indicates points where high values have been measured here) while blue indicates low values. (Aerial photo: Copyright Lantmäteriet 2004-11-09. Ur Din Karta och SverigeBilden).

6. Conclusions

In this paper results from a monitoring project are given in which the VOC leakages at four industries have been monitored during three years using the SOF method. 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. It was found that for a typical refinery, about 0.06% (598 ton/Mton) of the mass of the crude oil throughput was lost due to vaporization to the atmosphere. Of the emitted gas, 26% originated from the process, 31% from crude-oil tanks, 32% from product tanks, 8% from the water treatment facility and 2% from transport related activities.

In the past, a method based on the DIAL technique¹ has been used to measure VOC emissions from the refineries in this study. In comparison, the two methods show similar emission values for measurements at the same industrial plant, although a direct comparison has not been made. The SOF method is more mobile, cost effective, shows higher specificity and better signal-to-noise making it possible to conduct far away measurements. The main weakness of the method is in the incapability to measure plume height wherefore an uncertainty in the derived flux will be obtained since the estimated wind will have an uncertainty. This improves when measuring far away.

7. References

1. Milton, M. J. T.; and Woods P. T., Applied Physics, 1992, B 54.
2. Galle, B.; Mellqvist, J., et al., Ground Based FTIR Measurements of Stratospheric Trace Species from Harestua, Norway during Sesame and Comparison with a 3-D Model, JAC, 1999, 32, no. 1, 147-164.
3. Mellqvist, J., Arlander, D. W., Galle, B. and Bergqvist, B., Measurements of Industrial Fugitive Emissions by the FTIR-Tracer Method (FTM), IVL report, 1995, B 1214.
4. Galle, B., Axelsson, H., Mellqvist J. and Rudin, L., "A Method for Measurements of Large Scale Fluxes of Tropospheric Trace Gases", in EUROTRAC Symposium '92, Garmisch-Partenkirchen, 23-27 March 1992.
5. Mellqvist J., et al., The Solar Occultation Flux method, a nouvelle technique for quantifying fugitive gas emissions. Submitted to Environmental Science and Technology, 2005.
6. Manne Kihlman, M., Mellqvist, J. and Samuelsson, J., Monitoring of VOC emissions from three refineries in Sweden and the Oil harbour of Göteborg using the Solar Occultation Flux method, RR. report (Göteborg) No. 1, , ISSN 1653 333X, 2005
7. Kihlman, M., Mellqvist, et al., Monitoring of VOC emissions from refineries in Sweden using the SOF method, submitted to Environmental Science and technology, 2005
8. Kihlman, M., Application of solar FTIR spectroscopy for quantifying gas emissions, Technical report No. 4L, Department of Radio and Space Science, ISSN 1652-9103, 2005
9. Griffith D.W.T., Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra. Applied Spectroscopy, 1996. 50(1): p. 59-70.
10. Burton M.R., et al., Diurnal changes in volcanic plume chemistry observed by lunar and solar occultation spectroscopy. Geophysical Research Letters, 2001. 28: p. 843-846.

Acknowledgements

The authors would like to thank Anders Strandberg, Andreas Nilsson, Elisabeth Undén, Gunner Hanehøj, Karin Fransson, Samuel Brohede and Åke Fält that have participated in the field measurements.