Quantifying fugitive emission of VOCs using the Solar Occultation Flux technique (SOF)

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Summary
A new remote sensing method named SOF (Solar Occultation Flux) has been developed during the last years and applied to locate and quantify fugitive hydrocarbon emissions from industry (Fransson and Mellqvist, 2002). The method is based on measuring infrared intensity spectra of the sun from a moving vehicle in combination with mobile point measurements with a parallel infrared system coupled to a White-cell (the latter is used to estimate the plume height). In order to obtain the flux from a particular 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.
Measurements have been demonstrated for quite a few hydrocarbous species from many different industrial source areas, such as process areas, storage tanks, water treatment areas and flare efficiency measurements. In addition to measurements at most swedish refineries and the largest petrochemical industries, the technique has also been applied in Italy and Mexico. In addition to industrial application emission measurements have also been conducted from farming, volcanoes and megacities.
Detection limits down to 0.5 mg·m² can be achieved which corresponds to measuring a point source of 0.5 kg·h⁻¹ at a distance of 50 m with a precision better than 3%.
Trace gas experiments show that an accuracy of 3-5% may be obtained under favorable conditions with emissions from a single point at an open field. This applies under the condition that 10-20 measurements are averaged. Individual measurements are usually within 20% but may deviate as much as 50% from the correct value.
Under more complicated conditions, with emissions occurring from a complex structure with an unknown plume lift larger systematic errors will occur, primarily due to uncertainties in assessing the plume lift and the associated wind field. In cases where most of the emission plume is above the first 20-30 m, which we believe apply for most process area measurements and measurements conducted at distances > 500 m downwind, the uncertainty in the estimated wind is estimated to be 15-30%. Consequently the same accuracy will be obtained in the emission estimates. The accuracy is similar to what is reported for the DIAL technique, where accuracies around 20% are reported. The SOF measurements have not been compared directly with the DIAL technique, but measurements conducted at several swedish industrial facilities (Preem, Scanraff and oilharbor) show emission values which correspond quite well (within 20-30%) with previous DIAL measurements.
The SOF technique is today used at most of the swedish refineries to estimate their annual emissions, instead of using DIAL which has been in the past for almost 10 years.
In comparison to the DIAL technique the SOF method is more cost effective since both considerably cheaper hardware and less manpower is required. This is particularly true for locations with good sun and wind statistics, in contrast to south Sweden, on which measurements on a plant can be conducted within a few days, thanks to the mobility of the method and on-line evaluation capability.
1. Method

The SOF method is a newly patented technique to derive fluxes from various sources. The method is based on recording broadband infrared or UV/visible spectra of the sun with a low-resolution spectrometer which 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. Our new measurement bus, with the solar tracker looking out through the roof is shown in Fig. 1-2. For measuring the infrared spectra a commercial FTIR 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 averaged concentration (molec·cm$^{-2}$) of a large number of species absorbing the radiation along the light path of the sun, for instance aldehydes ammonia, ethylene, CO, ethylene-oxide, HF, HCl, methane, NO2, SO2, propane, propylene, terpenes, and vinyl-chloride. The retrieval is based on using lineparameters from the HITRAN database (Mellqvist 2002) and other databases (NIST, PNL).

![Figure 1. The SOF measurement vehicle. The solar tracker is shown on the right, which independently of the positioning of the car transmits the solar light into the infrared spectrometer. From the spectra the column concentration of the hydrocarbons and ammonia can be retrieved by fitting of the spectral features of these species.](image)
In order to obtain the flux from a particular source, the instrument is positioned on a car which 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. In Fig. 3 a 3D plot of a measurement conducted in the oil harbor of Göteborg, Sweden, is shown. The wind is more or less blowing from the direction of the observation and is illustrated by the green vectors. The solar rays detected by the SOF instrument are shown as red vectors the area in between these vectors correspond to the path averaged concentration (column) observed, which if multiplied by the local windspeed, correspond to the massflux through the area. red here corresponds to the highest alkane column.

Figure 3. A 3D plot of a SOF measurements conducted at the oil harbor in Göteborg is shown. The red lines correspond to solar lines. The colors in between the solar lines (blue to red) correspond to the integrated concentration (column) of ethylene seen (blue is low concentration while green and red are higher). The wind vectors are shown in green.
In addition to the solar occultation instrument, a mobile FTIR connected to a White cell is also included in the measurement vehicle. This instrument 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 outermost importance to get a sensible wind estimation for the SOF measurement. In a sense the combination of the point measuring device and the SOF instrument yields a **first order height profile**. 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 15-30 s.

For conducting the SOF measurements an online software has been developed, making it possible to obtain the measurement results on-line. In Fig. 4 the screen of the measurements computer is shown, showing a map of the measurement with vectors pointing toward the wind in the upper left, the measured and fitted absorption spectra in the lower left, and the retrieved data on the right side.

**Figure 4.** An automatic retrieval software has been developed. allowing online evaluation of the measured spectra. Here the screen of the measurement computer is shown. In the upper left is shown a map of the measurement with vectors pointing toward the wind in the upper left, the measured and fitted absorption spectra in the lower left, and the retrieved data on the right side.
2. Some applications

In Fig. 5 a SOF measurement is shown conducted on board a ship, cruising south of Göteborg oil harbor and a refinery when the wind was blowing from the north. The path averaged concentration of alkanes (column) is shown as blue to red dots in the upper right, and the same data is shown as a blue line in the lower plot. Here the accumulated flux over the path is shown as the orange line summing up to about 900 kg/h. A measured absorbance spectrum is shown in the upper right together with a fitted calibration spectra from the NIST and HITRAN data base.

Figure 5. SOF measurements conducted on a ship traversing the emission plumes from Göteborg oil harbor and an oil refinery.

In Fig. 6 a SOF measurement conducted south, and downwind of a refinery is shown. The colors correspond to the magnitude of the alkane column (path averaged concentration) with increasing values going from blue to red. The vectors are pointing towards the wind. A strong peak left of the process area can be seen, identifying a strong local source. In Fig. 7. an example of a leakage search application is shown. SOF measurements have been conducted by measuring solar spectra and driving in a circle around a potential source, a malfunctioning vapor recovery unit. It is obvious from the figure that the emissions occur within the area enclosed by the measurements. Again the vectors (lines) point toward the wind direction and the color corresponds to the alkane abundance.
Figure 6. SOF measurement conducted south, and downwind of a refinery is shown. The colors correspond to the magnitude of the alkane column (path averaged concentration) with increasing values going from blue to red. The vectors are pointing towards the wind.

Figure 7. A study of the emissions from a malfunctioning vapor recovery unit. By circling around the area of interest the emissions inside the circled area can be derived.

In Figs 8-10 an example of SOF measurements from polyethylene plant are shown. Fig 8. shows a 3D plot, looking from the north-west. The same measurement is shown in Fig. 9
with the accumulated flux shown as the blue line and corresponding to about 70 kg/h. The point measurement showed very low values indicating a rather high plume lift. We therefore used a high wind, for the flux estimate.

Figure 8. A 3D plot seen above from NW of the Polyethylene plant when conducting SOF measurements on October 22 2003 at 10:55. The red lines correspond to solar lines. The colors in between the solar lines (blue to red) correspond to the integrated concentration (column) of ethylene seen (blue is low concentration while green and red are are higher). The green arrows correspond to windvectors.
Figure 9. SOF measurement past a Polyethylene plant conducted on October 22 2003 at 11:27. The red lines correspond to solar lines. The upper part of the plot correspond to the integrated concentration of ethylene seen in the solar light (column). If the columns are integrated over the plume and multiplied by the windspeed the accumulated flux, is obtained which correspond to the emission at the plant. Here the emission correspond to 67 kg/h. In the SOF scan conducted at 10:55 it was 79 kg/h. These numbers are probably somewhat low.

Figure 10. A measured intensity spectrum of the sun, in a frequency window in which ethylene absorbs. A fitted spectrum consisting of modelled spectra of ethylene and water using line parameters from the HITRAN database, is also shown. The column of ethylene here corresponds to about 40 mg/m².
In Fig. 11 a study on a flare in the Polyethylene plant in Fig. 8 is shown. The flare efficiency was studied by measuring the momentaneous ethylene emission from the flare using SOF, in combination with a point measuring FTIR used to estimate the massflow of ethylene to be burned (Mellqvist 2001). The low efficiency below a flared ethylene amount of 400 kg/h corresponds to points when the steam to fuel-ratio was very high.

![Graph showing efficiency of flare burning ethylene](image)

**Figure 11.** The efficiency of flare burning ethylene was studied by measuring the momentaneous ethylene emission from the flare using SOF, in combination with a point measuring FTIR used to estimate the mass flow of ethylene to be burned (Mellqvist 2001). The low efficiency below a flared ethylene amount of 400 kg/h corresponds to points when the steam to fuel-ratio was very high.

### 3. The quality of the measurements

The overall errors for the SOF measurements correspond to the systematic errors, together with the statistical errors. The statistical errors, as defined in this study, can be described with a normal distribution. The individual errors will then be superimposed as the square root of the errors added in quadrature:

\[
\text{Statistical error} = \sqrt{\sigma_c^2 + \sigma_{S/N}^2 + \sigma_u^2 + \sigma_{uH}^2}
\]  

| \(\sigma_c\) | Relative error in the absorption cross section (5-10%). |
| \(\sigma_{S/N}\) | Relative S/N error and spectral interference effects. Here estimated from the standard deviation in the baseline of the column measurements, typically 0.3-0.6 mg/m². This corresponds to a uncertainty of 0.3-6% for a total column measurement of 100-10 mg/m² |
| \(\sigma_u\) | Relative uncertainty in the wind speed estimation. Typically 15-20% for a single plume scan and 5-8% for 8 scans. |
Compliment to Fransson and Mellqvist 2002, July 2 2004

Relative uncertainty in the wind speed due to uncertainties in the estimation of the plume height. The SOF measurements do not contain any information about the height of the plume. Since there are considerable height gradients in the wind speed this will cause errors if the wrong plume height is assumed. Measurements carried out during this project at Port of Göteborg using a 17-meter meteorological mast showed a wind gradient of about 16% between 17 and 10 meters and 25% between 17 and 4 meters, Figure 5. A realistic error of the height estimation of the plume is probably ±5 meters, which according to the measurements in Figure 5 corresponds to a 12% error in the wind speed estimation. Here we assume this error can be described by a normal distribution.

Relative uncertainty in the total column due to the variability in the wind direction over a plume scan (approximately 22°). A plume that is traversed at an angle of 90° causes an 8% effect on the column. The subsequent error in the plume measurement is quite sensitive to how close to 90° the angle between the wind and the direction of movement is. At angles of 80° and 70° errors of 16% and 25% respectively are obtained. For eight scans the errors are 1-7%.

In order to estimate the magnitude of the statistical errors, a few cases have been calculated according to Eq. 1, which are shown in Table 1. For the best case scenario a column of 100 mg/m² was assumed, which is typical for a plume measurement on a strong emission source. In addition, the error estimates for the other uncertainty sources are listed in Table 1. It can be seen that the statistical errors vary between 14 and 19%. In addition the systematic error will be superimposed.

<table>
<thead>
<tr>
<th>Estimation</th>
<th>Comment</th>
<th>$\sigma_c$</th>
<th>$\sigma_{S/N}$</th>
<th>$\sigma_u$</th>
<th>$\sigma_{alt}$</th>
<th>$\sigma_o$</th>
<th>Statistical 1σ error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Best case</strong></td>
<td>Strong plume 100 mg/m², 90° traversing angle*</td>
<td>5%</td>
<td>0.3%</td>
<td>5%</td>
<td>12%</td>
<td>1%</td>
<td>14%</td>
</tr>
<tr>
<td><strong>Worst case</strong></td>
<td>Weak plume 10 mg/m², 80° traversing angle*</td>
<td>10%</td>
<td>6%</td>
<td>7%</td>
<td>12%</td>
<td>5%</td>
<td>19%</td>
</tr>
<tr>
<td><strong>Typical case</strong></td>
<td>Intermediate plume, 80° traversing angle*</td>
<td>5%</td>
<td>3%</td>
<td>5%</td>
<td>12%</td>
<td>7%</td>
<td>16%</td>
</tr>
</tbody>
</table>

* Angle between the wind and the direction of movement when traversing the plume.

In order to study the measurement errors further, a tracer gas experiment was conducted on an open field. SF₆ was emitted from a 21 m mast, with a rate of 1.97 kg·h⁻¹. SOF measurements where conducted at various distances downwind (50-175m). 20 measurements are shown in Fig. 12. It can be seen that most data points (72%) agree quite well (within 20%) with the actual emission while some differs as much as 50%. Averaging all 20 measurements yields a value within 3% of the real one.
Figure 12. A tracer gas experiment was conducted on an open field. The tracer, SF₆, was emitted from a 21 m mast, with a rate of 1.97 kg·h⁻¹. SOF measurements were conducted at various distances downwind (50-175m). It can be seen that most measured data points, red dots, agree quite well with the actual emission (grey line) while some differ as much as 50%. Averaging all 20 measurements yields a value within 3% of the real one.

The example in Fig. 12 corresponds to a fairly straightforward measurement situation. Under more complicated conditions, with emissions occurring from a complex structure with an unknown plume lift larger systematic errors will occur, primarily due to uncertainties in assessing the plume lift and the associated wind field. In cases where most of the emission plume is above the first 20-30 m, which we believe apply for most process area measurements and measurements conducted at distances > 500 m downwind, the wind will be fairly undisturbed and increase slowly with height, following a logarithmic expression according to Eq 2, where z corresponds to the height and U* and zo are constant depending on the local conditions. Over open sea this formula yields that the difference in the windspeed is 25-35% between 15 to 50 m.

\[ U = U*/k \ln[z/z_0] \]  

(Eq 2)

In Fig. 13, a wind profile measure downwind a refinery is shown. The winds below 25 m were measured using a 21 m mast and a 5 mast positioned 50 m downwind the refinery. The measurements at 110 m were conducted at a nearby Bridge. A model wind profile, following Eq. 2 has been fitted to the data. If the plume is distributed between 20 to 75 m, which is quite probable at a few hundred meters downwind a process plant the uncertainty in the wind assessment is within 15%. Based on this we assume the accuracy in the emission assessment caused by uncertainties in the wind assessment to be 20-30%, and if sufficient number of measurements scans are conducted, this value will dominate over the statistical error.
Figure 13. Wind measurements downwind a refinery are shown as red points. In the blue a model wind is shown, when fitting a logarithmic expression according to Eq. 2.

In Table 2 a comparison between DIAL measurements conducted at a particular refinery in 1999 and 1995 are compared to SOF measurements conducted in 2001. It can be seen that the numbers are rather consistent, and definitely within the accuracy level 20-30%, claimed above. This comparison is of course not ideal since the measurements were conducted on different years. We however obtain similar results for other plants.

Table 2. VOC emissions on Preem refinery in kg/h obtained by the SOF technique 2001, compared with emissions measured with DIAL in 1999 and 1995. The number of measurements with the SOF method on each area is also presented.

<table>
<thead>
<tr>
<th>Area</th>
<th>SOF (no of scans) 2001</th>
<th>DIAL 1999</th>
<th>DIAL 1995</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil tanks</td>
<td>56 ±16 (8)</td>
<td>56 (wind normalised 4 m/s)</td>
<td>62 (wind normalised 4 m/s)</td>
</tr>
<tr>
<td>Process plant E</td>
<td>54 ±19 (7)</td>
<td>52</td>
<td>56</td>
</tr>
<tr>
<td>Process plant W</td>
<td>20 ±5 (5)</td>
<td>35</td>
<td>7.5</td>
</tr>
<tr>
<td>Water treatment</td>
<td>19 ±3 (3)</td>
<td>25</td>
<td>11</td>
</tr>
</tbody>
</table>
4. Availability of the technique

The technique has been developed at the Optical remote sensing at Chalmers university of technology. At present a project is conducted where the technique is used on 75% of the Swedish refineries. Considerable emphasis is put on studying uncertainties.

The technique is partly commercialized by an associated company, FluxSense AB, (www.fluxsense.se), who offers and conduct consultant measurements. In the future the plan is also to provide instruments.

5. References

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