The Solar Occultation Flux (SOF) Method, a new technique for the quantification of fugitive emissions of VOCs

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ABSTRACT
A new remote sensing method named SOF (Solar Occultation Flux) has been developed during the last years and has been 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 vehicle. In order to obtain the flux from a particular emission source, the vehicle is driven in such as 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 hydrocarbon species from many different industrial source areas, such as process areas, storage tanks, water treatment areas and flares. 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 been conducted from farming, volcanoes (MtEtna and Popocatetepi) and mega cities (Milano, Mexico City) for other species than VOC's.

Introduction
Volatile organic compounds (VOCs) produce tropospheric ozone that can damage crops and cause severe health problems to humans. VOCs consist foremost of alkanes, alkenes and some aromatics. Emissions from refineries are regulated by the authorities. To meet the requirements a control program including a suitable method for measuring diffuse leakages is essential. The most commonly used technique for measuring VOCs emitted from refineries and oil industries today is DIAL (Differential Absorption LIDAR)\(^3\). 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 lead 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\(^3,4\) a new method called SOF (Solar Occultation Flux), which can be utilised 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.

Method and Results
The SOF method is a newly patented technique to derive gas 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. For
measuring the infrared spectra a commercial FTIR (Fourier Transform InfraRed) is used, today a standard instrument for gas absorption measurements. By driving the instrument through the plume, combined with the use of solar light, the number of molecules in the plume cross section is integrated. As for the DIAL method, the mass flux is calculated by multiplying the measured number of molecules by the wind speed. From the solar spectra it is possible to retrieve the path averaged concentration \((\text{molec} \cdot \text{cm}^{-2})\) 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 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 and PNL. With the SOF method detection limits down to 0.5 mg·m\(^{-3}\) 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%.

In Figure 1 an absorbance spectrum is shown recorded in the solar light downwind of a plant producing ethylene oxide. The absorbance spectrum was obtained by dividing the spectrum measured in the plume with a "clean air" reference spectrum. In addition, in Fig.1, are shown calibration spectra of ethylene and water which have been been fitted to the measured spectrum by multivariate analysis. The path averaged concentration of ethylene in the spectrum was estimated to be 21 mg/m\(^2\). The difference between the measurement and fit is shown as the residual. In Figure 2. is shown a flare efficiency measurement from a flare on polyethylene plant. The amount of ethylene leaking out from the flare was here analysed using SOF measurements.

Figure 1: An absorbance spectrum of ethylene measured in the solar light downwind of a petrochemical plant. In addition fitted calibration spectra of water and ethylene are shown.
Figure 2: Flare efficiency measurements on a Polyethylene plant. The amount of ethylene released after combustion in the flare was here estimated using SOF and plotted versus the amount of ethylene to be flared. The combustion efficiency is indicated.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{flare-efficiency.png}
\caption{Flare efficiency measurements on a Polyethylene plant.}
\end{figure}

**Conclusions**

The SOF technique provides a powerful tool for measuring VOC emissions from the industry. The method can at present be used to obtain emission values from various industrial areas and various species of interest can be studied, such as alkenes, alkanes, and ammonia. In this paper we have shown an example of combustion efficiency measurements on an ethylene flare but many applications have already been demonstrated such as estimation of fugitive emissions from refineries and tank storage, ammonia measurements from fertilization.

**References**

