

Using Solar Occultation Flux and Other Optical Remote Sensing Techniques to Fully Characterize and Quantify Fugitive Emissions

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INTRODUCTION

Industrial VOC emissions may contribute significantly to ozone formation¹. In order to improve the understanding of their influence FluxSense Inc. has undertaken a comprehensive emission study in the LA basin on behalf of the South Coast Air Quality Management district. Gas emissions at different refineries and small sources such as oil wells, petrol stations and oil depots and oil platforms were measured using several unique optical methods. The methods include the Solar Occultation Flux Method (SOF)^{2,3} which is an optical remote sensing technique for quantifying fugitive VOC emissions from industrial sources. Measurements were carried out in September/October 2015 in the Wilmington and Carson area (Los Angeles, California) to study fugitive emissions from both industrial facilities (e.g. refineries and storage tanks) and small point sources (e.g. gas stations, oil wells, and others). The measurements in this study were quality assured by carrying out a controlled tracer release study and side by side measurements with several other techniques. During this presentation the capabilities of all these ORS techniques will be discussed in detail along with some of the main results from the field campaign in Los Angeles.

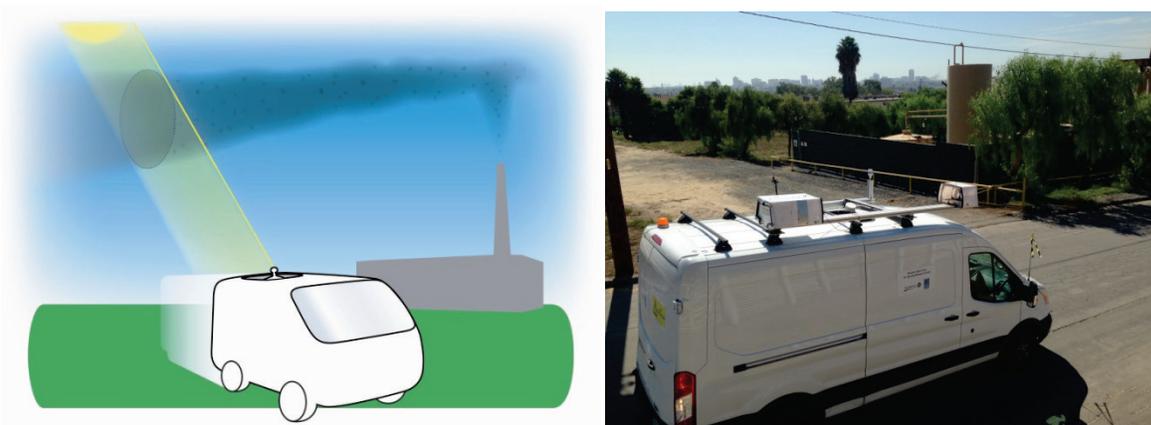
METHOD

The methodologies and techniques used are shown in Table 1 with corresponding detection levels. In addition a short description of each technique is given and further information can be found in the report of a previous pilot study^{4,5} or elsewhere⁶.

The SOF (Solar Occultation Flux) method^{2,3} is based on the recording of broadband infrared spectra of the sun with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of its position. Using multivariate optimization it is possible from

these solar spectra to retrieve the path-integrated concentrations (referred to as column concentrations), in the unit mg/m^2 , of various species between the sun and the spectrometer. The measurements are carried out from a mobile platform making it possible to circumvent leaking areas discriminating between upwind and downwind mass fluxes. The column measurements are combined with wind measurements to estimate the gas flux. In this study a wind LIDAR operated by SCAQMD was utilized.

Figure 1. In the Solar Occultation Flux method (SOF) gases are measured by observing solar light in the infrared portion of the solar spectrum. The instrument is placed in a vehicle which is moved across the plume. From the accumulated mass measured across the plume the flux of gas is obtained by multiplication with the wind speed.



Mobile DOAS (Differential Optical Absorption Spectroscopy) measurements⁷ of scattered solar light in zenith direction was carried out in parallel with the SOF measurements, from the same vehicle, to measure formaldehyde, NO_2 and SO_2 . DOAS works in the ultraviolet (UV) and visible wavelength region while SOF works in the infrared region and hence there are large differences in spectroscopy and in the used spectrum evaluation methods. However, both methods measure vertical columns which are integrated along measurement transects and multiplied by the wind to obtain the flux. The principle of flux-measurements using Mobile DOAS is hence the same as for SOF, although it is not necessary to compensate for any slant angle observations since the telescope is always pointing towards zenith. The DOAS system also works under cloudy conditions in contrast to SOF, although the most precise measurements are conducted in clear sky.

Table 1 Techniques used with detection limits and parameters measured .

Parameter	SOF	Mobile sky DOAS	Mobile Extractive FTIR (MeFTIR)	Mobile White cell DOAS (MW-DOAS)
Compounds	Alkane, C ₂ H ₄ , C ₃ H ₆ , C ₄ H ₈ , NH ₃	NO ₂ , SO ₂ HCHO	Alkane, CH ₄ , C ₂ H ₄ , C ₃ H ₆ , C ₄ H ₈	BTEX
Detection limit	0.1-5 mg/m ²	0.1-5 mg/m ²	1-10 ppb	0.2-3 ppb
Flux limit	0.2-1 kg/hr	1 kg/hr	0.2-2 kg/hr	1 -2 kg/hr
Meas. mode	Vert. Column	Vert. Column	Point Sample	Point Sample
Wind Speed	2-12m/s	2-12m/s	2-12m/s	2-12m/s
Time response	1-5 sec	1-5 sec	5-15 sec	1-30 sec
Typical accuracy in column and concentration measurement	3-5%	3-5%	3-5%	3-7%
Typical accuracy in flux estimate using wind LIDAR data	<25%	<25%	<25% (with tracer)- <35%*(with SOF)	<25% (with tracer)- <35%*(with SOF)
Complementary activity to obtain flux	Wind measurement from mast, and balloon, or LIDAR	Wind measurement from mast and balloon or LIDAR	For point sources tracer gas releases (N ₂ O, acetylene) For large sources, ratio measurements on the ground of pollutant X versus alkane. This value is multiplied by SOF alkane value to obtain a flux.	<i>Operated in parallel with MeFTIR.</i> <i>For large sources, ratio measurements on the ground of pollutant X versus alkane. This value is multiplied by SOF alkane value to obtain a flux.</i>

*Uncertainty depends if tracer gas is used

The column measurements using SOF were complemented by mobile extractive measurements using multi-reflection absorption cells in the infrared region (MeFTIR) or UV (Mobile White cell DOAS). Such extractive measurements have better speciation than the SOF measurements and by measuring the composition of various VOCs downwind the studied industries it is possible to infer emissions of more species than obtained by the SOF instrument alone, i.e.

aromatic VOCs (BTEX) and methane. Here it is assumed that the ratio of BTEX versus alkanes that is measured on the ground represents the overall ratio in the emission plume. This may not be true, especially for the process area, and therefore the derived emission value is more uncertain. The extractive measurements were also complemented by tracer gas releases at the sources to estimate emissions independently from the SOF, using the tracer correlation approach⁸.

SUMMARY

Emission measurements of VOCs have been carried out with several unique optical remote sensing techniques during a 2 month campaign in the LA basin. During this period the VOC emissions from six refineries in the LA and Long beach basin were quantified on 5-10 days per site. In addition emissions from several oil storage depots, petrol stations, and many oil wells with cisterns were quantified.

The methods were compared in several side-by-side measurements with other techniques and in an experiment with a controlled tracer source release. The measurement and validation results will be presented during the workshop.

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