

July 24, 2020

FluxSense, Inc. Solar Occultation Flux (SOF) by Open-Path Fourier Transform Infra-Red Spectrometry (OP-FTIR) and Ultraviolet Differential Optical Absorption Spectroscopy (UV-DOAS) Measurements

PREPARED BY

Peter G. Zemek, Ph.D.,
Montrose Environmental Group

Robert T. Menzies, Ph.D.,
Jet Propulsion Laboratory, California
Institute of Technology (retired)

Mark Yocke, Ph.D.,
Exponent

John Watson, Ph.D.,
Desert Research Institute

Curtis T. Laush, Ph.D.,
Geosyntec Consultants



This research has been supported by funding from the Western States Petroleum Association (WSPA) and the American Petroleum Institute (API). The contents and conclusions of this report are the responsibility of the listed authors. The consulting group Ramboll served as technical editor for the report.

Contents

SECTION	PAGE
Acronyms and Abbreviations	4
EXECUTIVE SUMMARY	7
Findings	8
Recommendations	9
I. INTRODUCTION	10
II. BASIC TECHNIQUES AND METHODOLOGY	11
A. Solar Occultation Flux (SOF) Technique	12
B. Mobile Differential Optical Absorption Spectroscopy (SkyDOAS)	15
C. Mobile Extractive FTIR (MeFTIR)	16
D. Mobile White Cell DOAS (MWDOAS)	16
E. Meteorological Measurements	17
III. BASIC ASSUMPTIONS APPLIED TO METHODOLOGY	19
A. FluxSense Calculation of Emission Mass Fluxes from Targeted Refineries	19
1. Direct Flux Equation	19
2. Inferred Flux Equation	19
B. Spectroscopy	20
1. Open-Path-Integrated Averages	20
2. Stray Light Interferences	21
3. Atmospheric Emission vs. Absorbance	21
4. Zenith Angle Impact on Reported Concentrations	21
5. Use of Ground-level Measurements to Infer Aloft Concentrations	22
a) Assumed NO ₂ /NO _x Ratios	22
b) Measured NO ₂ /NO _x Ratios	22
C. Error Budget Associated with Techniques	22
1. SOF MeFTIR MWDOAS	22
2. Zenith Sky-UV-DOAS	25
IV. INSTRUMENT PERFORMANCE	26
A. Limits of Detection	26
1. Calculated	26
2. Confidence Interval	26
3. Residual Error Treatments	26
V. BACKGROUND COLLECTION/MEASUREMENT	27
A. Synthetic or Active Backgrounds	27
1. Empirical	27
a) Upstream	27
b) External Cell	27
VI. COMPARISON WITH ANNUALIZED EMISSION INVENTORIES	28

Contents

SECTION	PAGE
VII. CONCLUSIONS	31
A. Limitations of the FluxSense Approach	31
1. Wind Field Variability	32
2. Ambient Concentrations in the SoCAB	32
B. Scientific Evaluation of FluxSense Emission Mass Flux Estimates	32
C. FluxSense Assumption of Well-Mixed Plumes	33
D. Potential for Regulatory Certification of the FluxSense Method	33
E. Potential Uses and Benefits of the FluxSense Approach	34
BIBLIOGRAPHY/REFERENCES	36
APPENDIX A: Wind Roses from Surface Meteorological Stations near Refineries in Southern CA	42
APPENDIX B: Other Sources Accessed By Authors	49
LIST OF TABLES	
Table 1 VOC refinery emission source profiles (percent of Total Organic Gas [TOG]) used by the California Air Resources Board for statewide emission inventories (CARB, 2021)	28
Table 2 Emissions (tons/year) by refinery (FluxSense, 2017)	29
Table 3 2015 ROG emissions (tons/year) from large emitters in the study region (CARB, 2017)	29
LIST OF FIGURES	
Figure 1 Schematic overview of the FluxSense mobile laboratory system with SOF, MeFTIR, MWDOAS and SkyDOAS instruments (Mellqvist et al., 2017)	11
Figure 2 View of MWDOAS instrument mounted atop the FluxSense mobile laboratory (Mellqvist et al., 2017)	12
Figure 3 Illustration and photograph of the SOF Measurement System (Mellqvist et al., 2017)	12
Figure 4 Comparison of IR absorption spectra for 1 mg/m ² of selected n-alkanes detected by FTIR at 8 cm ⁻¹ spectral resolution (Johansson et al., 2014)	14
Figure 5 The FluxSense Sky-DOAS system consisting of a telescope, optical fiber, spectrometer, and control computer (Mellqvist et al., 2017)	15
Figure 6 The MeFTIR instrumentation consisting of a Bruker FTIR spectrometer connected to an optical multi-pass cell (Mellqvist et al., 2017)	16
Figure 7 Wind roses from the Port of Los Angeles monitoring network demonstrating large spatial variability in speed and direction (POLA, 2017)	17
Figure 8 Transmission spectra for water vapor, carbon dioxide, and ozone (Huang et al., 2017)	23
Figure 9 Simulated absorption spectrum for a gas mixture representing the Earth's atmosphere composed of the following percentages derived from the HITRAN data base: H ₂ O: 0.400000 CO ₂ : 0.039445, O ₃ : 0.000003, N ₂ O: 0.000032, CO: 0.000010, CH ₄ : 0.000179, O ₂ : 20.946000, NO ₂ : 0.000002 N ₂ : 78.084000 at 239.798 K, 0.380327 atm (HITRAN, 2012)	23
Figure 10 Comparison of ethene concentrations from the FluxSense SOF and NOAA aircraft over similar time periods near the Houston Ship Channel on September 19, 2006. White triangles are ethene point sources (of sizes proportional to source strengths) from the Texas 2004 emission inventory (De Gouw et al., 2009)	24
Figure 11 Time-averaged concentrations of benzene, 1,3-butadiene, toluene, and m,p-xylene at three different sites during summer and winter (SCAQMD, 2012).	30

ACRONYMS AND ABBREVIATIONS

#	3D	three-dimensional
A	atm	atmosphere
B	BTEX	benzene, toluene, ethylbenzene, and xylenes
C	C₂H₆	ethylene
	CCD	charge-coupled device
	CH₄	methane
	cm	centimeter
	CO	carbon monoxide
	CO₂	carbon dioxide
D	DIAL	differential absorption LIDAR
	DOAS	differential optical absorption spectroscopy
E	EFs	emission factors
F	FEM	federal equivalent method
	FLIR	forward-looking infrared
	FRM	federal reference method
	FROG	fraction of reactive organic gases
	FTIR	Fourier transform infrared spectroscopy
G	GC-MS	gas chromatography/mass spectrometry
H	HCHO	formaldehyde
	HCl	hydrogen chloride
	HF	hydrogen fluoride
	HITRAN	high-resolution transmission molecular absorption database
I	InSb	indium antimonide
	IR	infrared
K	K	kelvin
	kg/m²	kilograms per square meter
	kg/s	kilograms per second
	km	kilometer
L	LIDAR	light detection and ranging

	LOS	line-of-sight
M	m	meter
	m/s	meters per second
	MCT	mercury cadmium telluride
	MeFTIR	mobile extractive Fourier transform infrared spectroscopy
	MET	meteorological station
	mg/m²	milligrams per square meter
	mg/s	milligrams per second
	mph	miles per hour
	MWDOAS	mobile white cell differential optical absorption spectroscopy
N	NDA	non-disclosure agreements
	nm	nanometer
	NO	nitric oxide
	NO₂	nitrogen dioxide
	NO_x	nitrogen oxides
O	O₃	ozone
	OP-FTIR	open-path Fourier transform infrared spectroscopy
	ORS	optical remote sensing
P	PBMS	performance-based measurement system
	PNNL	Pacific Northwest National Laboratory
	ppb	parts per billion
	PPI	plan position indicator
	ppm-m	parts per million-meter
Q	QA/QC	quality assurance/quality control
R	RHI	range height indicator
	ROG	reactive organic gases
S	S/N	signal to noise ratio
	SCAQMD	South Coast Air Quality Management District
	SCD	slant column densities
	SF₆	sulfur hexafluoride
	SO₂	sulfur dioxide

	SoCAB	Southern California Air Basin
	SOF	solar occultation flux
T	TOG	total organic gases
U	UV	ultraviolet
	UV-DOAS	ultraviolet differential optical absorption spectroscopy
V	VOCs	volatile organic compounds

**FLUXSENSE, INC. SOLAR OCCULTATION FLUX (SOF)
BY OPEN-PATH FOURIER TRANSFORM INFRA-RED
SPECTROMETRY (OP-FTIR) AND ULTRAVIOLET
DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY
(UV-DOAS) MEASUREMENTS**

Executive Summary

In January 2018, a panel with expertise in optical remote sensing and real-world source measurements (“Panel”) was assembled with the purpose of providing an independent critical review of the FluxSense method and its ability to quantify facility-wide emissions (i.e., fluxes) of methane (CH₄), non-methane volatile organic compounds (VOCs), benzene, BTEX (i.e., benzene, toluene, ethylbenzene and xylenes), nitrogen oxides (NO_x), and sulfur dioxide (SO₂). This report is a product of that review.

The FluxSense method employs optical remote sensing (ORS) approaches for ambient and fenceline detection and measurement of emissions flux from various stationary sources of atmospheric pollutants. Four techniques are used to measure fluxes of various chemical constituents, with all of the instrumentation utilized to employ these techniques housed in one mobile platform, i.e. a van. This enables the measurement team to drive around and collect measurements at sites with several spread-out sources of emissions. The four techniques are:

1. Solar occultation flux (SOF), which applies Fourier transform infrared spectroscopy (FTIR) to measure attenuation of direct solar infrared (IR) radiation (in the 2-16 μm region) as it passes through the atmosphere according to its telescope field of view. SOF relates the measured absorption spectra to those of selected VOCs, particularly alkanes and alkenes. The SOF instrument is always pointed directly at the sun;
2. Mobile differential optical absorption spectroscopy (DOAS), which FluxSense refers to as “SkyDOAS”. This technique relies on scattered ultraviolet (UV) and visible sunlight as its radiation source. It is always pointed towards the zenith viewing nitrogen dioxide (NO₂), SO₂, and formaldehyde (HCHO) absorption spectra in the scattered solar radiation that reaches the ground;
3. Mobile-extractive FTIR, which is a fixed pathlength sensing tool that provides further spectral analyses of chemical constituents in the near ground-level emission plume; and
4. Mobile white-cell DOAS, which is also a fixed pathlength sensing tool that analyzes emission plumes near ground level.

FluxSense Inc. has been deploying this combination of sensing techniques in the field for several years, mainly in Europe and the United States. This report provides an assessment of the inherent uncertainties of the FluxSense approach in estimating emission mass fluxes. It also discusses the ancillary data required for estimation and evaluation of FluxSense’s emission flux calculation results. A summary of the Panel’s findings and recommendations for the most appropriate uses of the FluxSense method follows.

FINDINGS

1. Many of the underlying assumptions of the FluxSense method do not apply to refineries in urban areas with complex terrains and the presence of multiple sources. Some key parameters of emissions characterization methodologies include: plume height, thickness, and width; percentage of plume capture; actual cross-sectional wind across measured plume parcels; influence of transient external sources; and congruency of upwind and downwind plume parcels. Uncertainties with respect to these parameters are not quantified, despite being important contributors to the overall uncertainty. FluxSense estimates that its errors are in the range of 30 to 50%, based mainly on software processing errors, hardware calibration, and data from a limited number of tracer field experiments. Uncertainties related to the use of the High-resolution Transmission Molecular Absorption Database (HITRAN) spectral library and sources of “reference spectra” were not apparent in the documents available to the Panel. It is probable that combined errors exceed the 30-50% range cited, particularly when applied to dispersed and intermittent refinery emissions.
2. The FluxSense system requires ideal weather conditions during midday hours, which limits its ability to distinguish pollutant patterns that may vary diurnally. This constrains its practical value for extrapolation to a 24-hour emission cycle and annual emission inventory entries for determination of compliance with annual emissions limits.
3. The first step in the FluxSense determination of emissions fluxes (VOCs, NO_x , BTEX, etc.) is the estimate of the integrated column mass (measured in milligrams per square meter (mg/m^2)) using spectroscopic techniques as the vehicle moves across the horizontal extent of the plume. During this step, small instrumental irregularities that are not modeled can lead to large uncertainties in estimation of the column mass. For example, water vapor in the atmosphere and in the plume strongly absorbs infrared radiation (IR) in the same spectral region as the column-integrated alkanes and alkenes, potentially interfering with the estimation of VOC mass in the column. The upwind and downwind instrument passes do not sample the same air parcels, so differences between the upwind and downwind measured absorbance spectra may not be specific to the target facilities’ emissions in environments with multiple sources. As a result, estimates of the VOC column mass in the refinery plume may differ from reality by a factor of two or more. A similar issue can occur when mass estimates in plumes measured by the zenith SkyDOAS are subject to uncertainties in modeling atmospheric scattering or scattering due to particulate matter in the plume. This issue applies to all compounds that absorb in the ultraviolet region and the magnitude of the uncertainty depends heavily on the accuracy of the scattering model that is used.
4. The second step in deriving the emission flux estimate involves measuring spatially dependent wind speeds and directions. Insufficient measurements of three-dimensional wind field complexities add further uncertainty to the quantitative accuracy of the emission flux estimates. Accurate wind field measurements must be collected at various vertical levels and possibly multiple locations in the immediate vicinity of each FluxSense sampling pass.
5. Although there are inherent uncertainties associated with the FluxSense method that limit its utility for quantitative annual emission estimates, it can be useful for revealing previously unidentified emissions hot-spots, process leaks, and other atypical fugitive VOC sources within refineries. It may help locate process upsets, pollutant migration onto a site, or leaks from nearby storage tanks, piping, or other facility equipment, as well as detect previously unidentified polluters in areas where it is operated.
6. Lack of access to FluxSense proprietary algorithms and standard operating procedures prevents this Panel from evaluating errors or sources of erroneous procedures that may affect the final quantitative numbers reported for individual pollutants. This is especially important when discussing how background concentrations are calculated and how inverse spectral peaks associated with certain target compounds present in the upper stratosphere are treated.

RECOMMENDATIONS

1. The FluxSense calculation methods and algorithms should be provided to interested parties and concerned stakeholders so that defensible uncertainties may be estimated. If procedures are proprietary, then proper intellectual property protection provisions might be established within accompanying non-disclosure agreements (NDA). Full transparency of algorithms and procedures to document error budgets from all aspects of the tool and clarify the assumptions that are made may enable users to evaluate emission flux uncertainties and reduce them where possible.
2. Use of the FluxSense system should be considered as a complement to other remote sensing or conventional monitoring technologies to contribute to developing consensus flux estimates. Operators of the FluxSense system have demonstrated that it is capable of detecting the presence of individual pollutants around refineries and as such, can be a useful qualitative tool for identifying hot-spots and problem areas or comparing relative emissions from facilities.
3. Additional verification studies of the methodology should be considered. For example, carefully designed tracer-based field verification studies that are representative of the types of sources to be studied and cited in the literature could be conducted in the specific areas of intended or past FluxSense system deployments. Such studies could release controlled emissions fluxes to scientifically challenge and quantify the uncertainties of the FluxSense flux calculations. Tracers that do not mimic the absorption spectra of the actual pollutants address only a subset of the inherent uncertainties, so tracers that do mimic the absorption spectra of the actual pollutants should be used.

I. Introduction

In January 2018, a panel with expertise in optical remote sensing, real-world source measurements, and emission inventories was assembled with the purpose of providing an independent critical review of the FluxSense methodology to judge its ability to quantify facility-wide mass emissions (i.e., fluxes) of methane (CH₄), non-methane volatile organic compounds (VOCs), benzene, BTEX (i.e., benzene, toluene, ethylbenzene and xylenes), nitrogen oxides (NO_x), and sulfur dioxide (SO₂). This report is a product of that review. In the process of producing this report, the Panel investigated previously published reports, presentations, and publications on the FluxSense techniques and methodology, other independently published relevant reviews, and South Coast Air Quality Management District (SCAQMD) reports and presentations regarding fenceline monitoring using optical remote sensing techniques (“SCAQMD studies”). The Panel considered various factors, including the underlying key assumptions in the methodology, the accuracy and representativeness of the approach to the measurement of fluxes, the degree to which the FluxSense results are dependent upon proprietary calculations, assumptions, and software (i.e., “black-boxes”), and the likelihood of a path to regulatory acceptance of this method.

Section II provides a description and Section III provides a critical review of the FluxSense methodology, including the Solar Occultation Flux (SOF), zenith-viewing Ultraviolet Differential Optical Absorption Spectroscopy (UV-DOAS), extractive FTIR, and white cell UV-DOAS techniques. This section also includes a discussion of the various components of the error budget associated with the methodology. Section IV addresses the overall instrument performance, including detection sensitivities, calibration and validation, reliance on external source materials, precision and accuracy, and long-term stability. Section V addresses the adequacy of the understanding of the “background,” not attributed to the emission source in question. Understanding background levels of pollutants is essential for determination of the emissions and fluxes attributed to the point source and its extended facility (i.e., facility the point source is associated with). Section VI is a summary of comparisons with annualized emission inventories. Finally, concluding statements are found in Section VII.

II. Basic Techniques and Methodology

The SOF technique estimates ground-level concentrations from 1) integrated column concentrations between the surface and the sun that surround the facility under study, 2) vertical profiles of wind speeds and directions, and 3) assumptions about plume geometries and stability of emissions and other meteorology during an experiment. SOF uses a passive FTIR with a telescope and heliostat to track the sun's ever-changing position in order to use it as a source of IR energy. SOF also uses a columnar UV detector and peripherals to collect stray UV rays in order to determine a target compound's signature and absorbance as a function of frequency. These columnar techniques provide long optical path lengths that require simplifying assumptions for vertical mixing and plume shapes in the field of view, to determine optical density (measured in parts per million-meter (ppm-m)). Meteorological stations (MET) data and/or a light detection and ranging (LIDAR) system are sometimes used to calculate vertical mixing and directly measure the plume shapes. Determining

these parameters is necessary for an accurate flux measurement. It should be noted that the current FluxSense method does not provide for a scanning or horizontal LIDAR measurement and that LIDAR data in southern California studies was provided by the SCAQMD. The additional equipment consists of an extractive FTIR and UV system in a horizontal configuration for ground-level measurements while the vehicle is not moving, or moving slowly. A schematic of the FluxSense platform is depicted in Figure 1. The following five sections (A through E) describe each of the four main gas detection components that make up FluxSense's platform (i.e. SOF, SkyDOAS, MeFTIR, and MWDOAS) and the wind measurements technology.

The SOF technique used to determine most of the target compounds is complementary to the UV-DOAS method because there is some overlap of target compounds detected by each technology which may be compared. FluxSense optimized the UV-DOAS system for benzene and associated aromatics, but it can still detect some sulfur compounds and

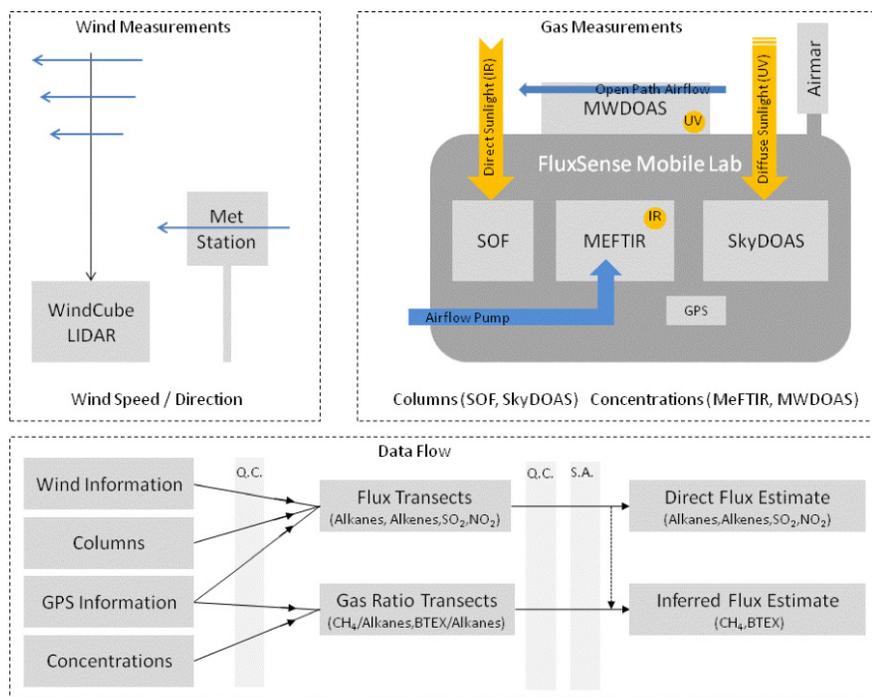


Figure 1. Schematic overview of the FluxSense mobile laboratory system with SOF, MeFTIR, MWDOAS and SkyDOAS instruments (Mellqvist et al., 2017).

ozone. However, there are trade-offs with optimizing a UV-DOAS system for benzene. UV-DOAS is the technology of choice for open-path systems measuring benzene and other aromatics and carbonyls such as acrolein and formaldehyde. FluxSense does not address a common source of uncertainty from some UV-DOAS systems that generate large amounts of ozone, which can interfere with the benzene quantification spectra in a UV-DOAS system. If ozone levels are allowed to increase they may overwhelm the software's capability to separate the benzene spectrum from the ozone spectrum. Additionally, benzene is only detectable by SOF when the signal to noise ratio (S/N) of the instrument is sufficiently high to separate benzene from the FTIR spectra of other compounds. It is therefore important to address the uncertainty as it applies to both SOF and UV-DOAS systems.

A. SOLAR OCCULTATION FLUX (SOF) TECHNIQUE

As noted, the SOF method measures attenuation of IR from the sun by FTIR and relates the absorption spectra to alkane and alkene abundances in the path between the sun and the detector. The mobile platform (Figures 2 and 3) moves around the selected facility with the intent to determine upwind and downwind column abundances (i.e., quantities) of the target compound. Passive Differential Optical Absorption Spectroscopy (SkyDOAS) is also located on a separate mobile platform to detect near-ultraviolet (310-350 nanometers (nm)) radiation absorbed from scattered sunlight. These spectra are used to estimate SO_2 , NO_2 , and HCHO column concentrations. In-plume point measurements downwind of a facility are taken using collocated mobile extractive Fourier Transform infrared spectroscopy (MeFTIR) and Mobile White Cell differential optical absorption spectroscopy (MWDOAS) sensors for CH_4 , alkanes, and BTEX concentrations. Wind speeds and directions are measured on towers or with vertical profilers and the upwind concentrations are subtracted from the downwind concentrations to estimate emission fluxes. Using FTIR detection (Griffiths, 2017) with the sun as a light source (Angström, 1964) has been widely applied to quantify concentrations of organic and inorganic gases. The unique aspect of the FluxSense approach is the coupling of FTIR with a sun tracker, which allows the column sensor to be moved



Figure 2. View of MWDOAS instrument mounted atop the FluxSense mobile laboratory (Mellqvist et al., 2017).

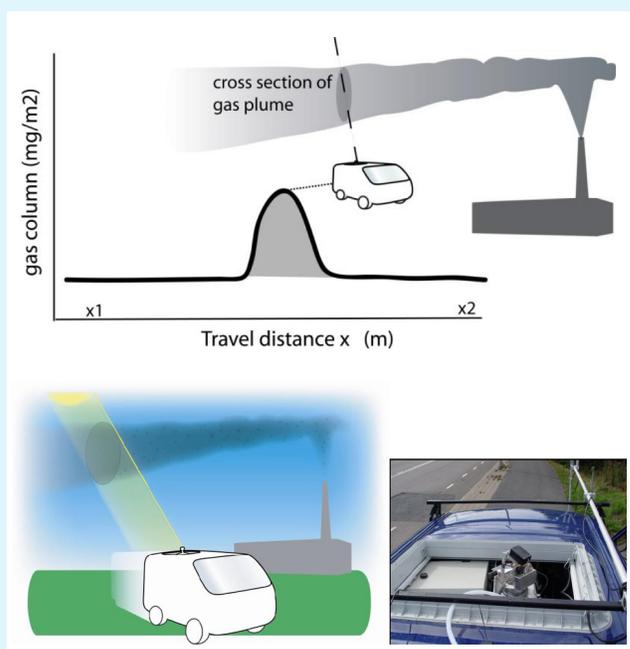


Figure 3. Illustration and photograph of the SOF Measurement System (Mellqvist et al., 2017).

without having to manually re-orient the focusing telescope. Objectives of SOF monitoring include estimating emission factors (EFs) for selected VOCs, identifying fugitive VOC emission hotspots, creating EFs that can be related to meteorological and process variables, and evaluating uncertainty and variability of existing EFs.

The SOF is a proprietary method of FluxSense Inc., first introduced in 1999 (Mellqvist, 1999). At SOF's foundation, like all FTIR approaches, is the absorption of IR energy at wavelengths within the solar light spectrum by certain VOC and other gases. The SOF FTIR spectrometer is equipped with both indium antimonide (InSb) and mercury cadmium telluride (MCT)-type IR detectors. A small optical lens system is mounted on the solar tracking device so as to be continuously pointed at the sun as the mobile instrument platform is driven along roadways. Time-averaged solar spectral measurements are recorded by the SOF FTIR system approximately every 1-5 seconds as the instrumented vehicle moves at speeds in the range of 10-50 miles per hour (mph). From the solar spectra, path-integrated concentrations (measured in mg/m^2) are obtained for IR absorbing gases present in the air column between the sun and the FTIR instrument.

There are a large number of chemical species that absorb light at wavelengths in the IR spectrum. They include VOCs (such as alkanes and olefins), ammonia, CO , SO_2 , NO_2 , hydrogen fluoride (HF), hydrogen chloride (HCl), and vinyl chloride. Notably, CH_4 , water vapor, and carbon dioxide (CO_2) are strong IR absorbers and are present in the atmosphere at relatively high concentrations, so they can interfere with an FTIR's ability to detect and quantify trace VOC concentrations. Aerosols (airborne particles) also interfere with FTIR VOC discrimination. In the SCAQMD studies, FluxSense used SOF to focus on three non-methane alkanes: propane, n-butane, and octane. It appears that some alkene (including ethylene and propylene) concentrations may have been measured but not reported.

Published spectral libraries from the HITRAN (Rothman et al., 2003) and Pacific Northwest National Laboratory (PNNL) (Sharpe et al., 2004) infrared databases are used in conjunction with a proprietary software package called QESOF (Kihlman et al., 2005) to model line strengths from column-integrated concentrations (reported in mg/m^2) of

individual chemical species or classes of species. The processing of spectral data is a source of uncertainty in determining the path-integrated concentration results from any system employing the FTIR measurement method.

Emissions fluxes (in kilograms per second (kg/s)) are estimated by multiplying the averaged SOF plume column concentrations (in kg/m^2) by the wind velocity in meters per second (m/s), and the horizontal extent of the plume in meters. These are combined to obtain the flux in kg/s . The measured column concentration is independent of the vertical extent of the plume, since in the SOF method, the entire vertical extent of the plume is always captured.

FluxSense refers to the wind velocity as the "mass average wind speed of the plume." This parameter is estimated based on wind measurements and a number of assumptions. Corrections to wind velocity are also made to account for the slant angle of the sun. FluxSense acknowledges that their process of estimating this wind speed is "not straightforward."

The FluxSense SOF vehicle is deployed along surface roadways that surround a targeted chemical or petrochemical facility. The basic SOF measurement strategy is to sample both upwind and downwind of the facility so that the upwind concentrations can be subtracted from the downwind ones. Ideally, the roadways are aligned perpendicular to the "local" wind directions expected during sampling periods. The downwind legs are designated as those expected to lie within or beneath targeted facility plumes. Column concentrations are averaged along the sample legs, after determining which sample columns passed through the facility plumes and which did not. Ambient (i.e., background) concentrations are those determined to be "upwind" of the facility. The FluxSense measurement vehicle can only be at one location at a time. Therefore, the air parcels sampled along one leg are not the same air parcels sampled along earlier or later legs.

FluxSense reports that since 2006, the SOF method has been used during several large air measurement campaigns and for more than 60 individual plant surveys in Europe, the United States, and Mexico (FluxSense, 2014). It has also undergone performance evaluation against other measurement methods and for facilities using known tracer gas releases. In Sweden, SOF has been used in combination with tracer gas releases/

measurements and forward-looking infrared (FLIR) gas imaging cameras for annual plant surveys. FluxSense cites performance tests suggesting that SOF has an uncertainty of around 30% (standard deviation) (FluxSense, 2014). Based on this information, FluxSense states that SOF is a “proven” method. However, FluxSense reports that the largest source of SOF uncertainties results from uncertainties in wind field determinations. These uncertainties can be much larger than the quoted 30% value in areas with complex, three-dimensional, time-varying wind fields that are not well-characterized on the scales of SOF measurements. It may be more appropriate to characterize the SOF method as frequently used, but not yet evaluated comprehensively, for many complex situations.

Figure 4 compares IR absorption spectra for different alkanes measured by the FTIR (Johansson et al., 2014). The alkane peaks are in the C-H stretch band with a wavenumber range of ~2700 to 3000 cm^{-1} . The spectra are relatively clean of IR absorption from non-alkane compounds. Most of the variability is among the shorter alkanes, with more uniformity for the longer alkanes. The alkanes illustrated are commonly found in ambient air, but there are typically others present in emissions from

refineries and other sources. The integrated area across the wavenumbers should theoretically be nearly equivalent for all alkanes. This idea forms the basis for extrapolating the fittings for a few representative spectra to the integrated IR absorption in this region. The presence of branched alkanes and cyclo-alkanes may cause interferences if they are present in abundance (see iso-pentane in Figure 4).

Since there is much collinearity among alkane spectra, the ambient spectra are reproduced by a linear combination of spectra for ethane, propane, n-butane, iso-pentane, and n-octane along with methane and water absorption in the region commonly performed by classical least squares (CLS) software. Only the contributions from the sum of these alkanes are used to estimate the concentration in the vertical column.

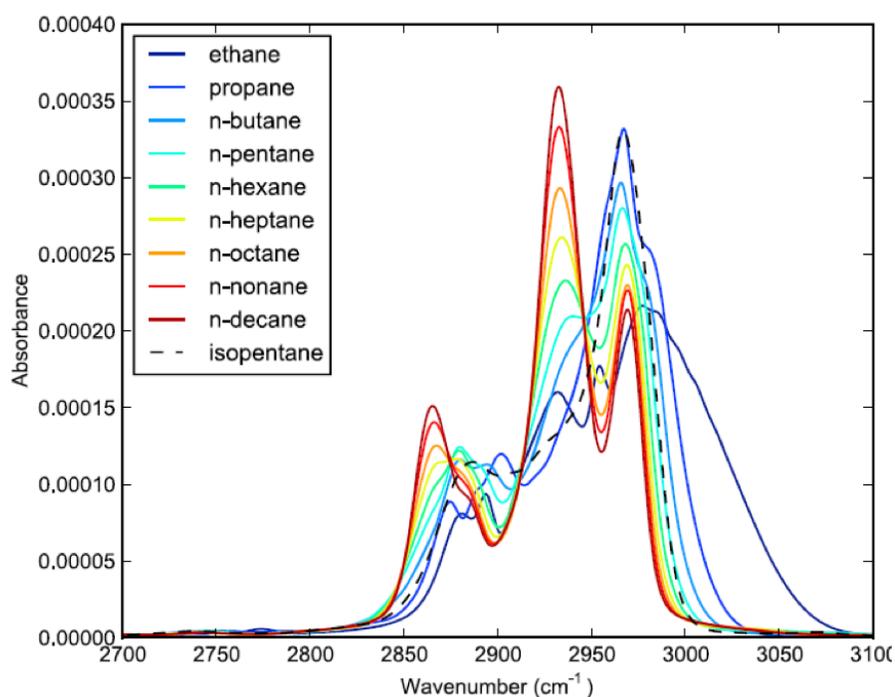


Figure 4. Figure 4. Comparison of IR absorption spectra for 1 mg/m^2 of selected n-alkanes detected by FTIR at 8 cm^{-1} spectral resolution (Johansson et al., 2014)."



Figure 5. The FluxSense SkyDOAS system consisting of a telescope, optical fiber, spectrometer, and control computer (Mellqvist et al., 2017).

B. MOBILE DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY (SKYDOAS)

The SkyDOAS measurement method is similar to the SOF system, but rather than relying on direct IR light from the sun as a radiation source, it utilizes scattered UV and visible sunlight. Instead of an FTIR spectrometer and InSb/MCT detector, the FluxSense SkyDOAS uses a Czerny-Turner spectrometer and a liquid-cooled charge-coupled device (CCD) camera (see Figure 5). Additionally, the SkyDOAS method employs a telescope that is always pointed toward the zenith rather than the sun itself as with the SOF method. Averaging times for the SkyDOAS system are typically 1 to 5 seconds.

A UV-DOAS is capable of measuring concentrations of SO_2 , NO_2 , ozone (O_3), and HCHO, and possibly the transient associated oxygen pair, O_4 , whose concentration may be used to determine future ozone formation or time constants for oxygenated VOCs which is a common sink for removal from the atmosphere. However, there was no data for O_3

reported in the FluxSense studies or in the SCAQMD studies; FluxSense only reported the SO_2 , NO_2 , and HCHO concentrations measured by its SkyDOAS system. Absorption line parameters for these species were obtained from published sources. Several applications of passive DOAS to industrial source measurements have been reported in the literature (Lin et al., 2004; Chiu et al., 2005; Stutz et al., 2016; Thoma et al., 2016; Olaguer et al., 2017). FluxSense operated the SkyDOAS and the SOF simultaneously. Thus, the species measured by the SkyDOAS complement the non-methane alkane concentrations reported from the FluxSense SOF. FluxSense estimation of emissions fluxes from SkyDOAS concentrations follows the same approach used with SOF (i.e., by multiplying the averaged plume column concentration data by the “mass average wind speed of the plume”). Therefore, the limitations of flux calculations using SkyDOAS data are very similar to those which use SOF data.

C. MOBILE EXTRACTIVE FTIR (MEFTIR)

The MeFTIR system may be used for spatial concentration measurements at a point in time and space, or to support the SOF measurements. MeFTIR employs a mid-infrared FTIR spectrometer in combination with a closed multi-pass optical cell. Light from an internal IR source is first transmitted through the multi-pass optical cell and then enters the FTIR's optical aperture. Selectable optical path lengths from about 10 to 107 meters are possible, which afford detection sensitivities in the low parts per billion (ppb) range and averaging times of 5 to 15 seconds. The near-ground ambient air is pumped through the optical cell as the instrumented vehicle is driven along its sampling route. The FluxSense MeFTIR is operated simultaneously with SOF.

The MeFTIR instrument (see Figure 6) provides more detailed VOC speciation than the SOF FTIR. FluxSense reported MeFTIR concentrations of several alkane and alkene species, including methane (FluxSense, 2017). FluxSense used ground-level MeFTIR data to supplement the SOF non-methane alkane data. Additionally, FluxSense used ground-level MeFTIR to estimate plume heights after the mixing zone was measured by the SCAQMD LIDAR. These calculations assumed uniform vertical plume mixing from the ground up to the maximum plume height and divided the averaged SOF column concentrations by the corresponding MeFTIR average concentrations.

D. MOBILE WHITE CELL DOAS (MWDOAS)

FluxSense measured near-ground-level concentrations of BTEX using mobile MWDOAS. Their MWDOAS system consists of an open, multi-pass optical cell ("white" cell) with a 2.5 m path-length that is mounted on the roof of the instrument vehicle so as to be exposed to ambient air. Multiple reflections within the white cell mirror system yield an overall path length of 210 m, resulting in low detection limits (ppb) and averaging times of about 8 seconds. Light from an internal UV lamp is transmitted through the open-path white cell and then analyzed in a DOAS UV spectrometer.

FluxSense operated their MWDOAS and MeFTIR systems simultaneously near targeted zones within refineries. This means that MeFTIR and MWDOAS were only used to make measurements at certain places and times. These data were extrapolated to atmospheric concentrations at other times and places. FluxSense's Benzene and BTEX flux rates are based on this intermittent or one-time measurement. A number of plumes transects were made at close range to zones expected to have non-buoyant, low-level plumes in order to collect in-situ plume measurements. The MWDOAS and MeFTIR data collected were analyzed and merged in order to estimate BTEX/alkane concentration ratios. These data were averaged to produce an average BTEX/alkane ratio for each zone, which was then used to extrapolate to atmospheric conditions.

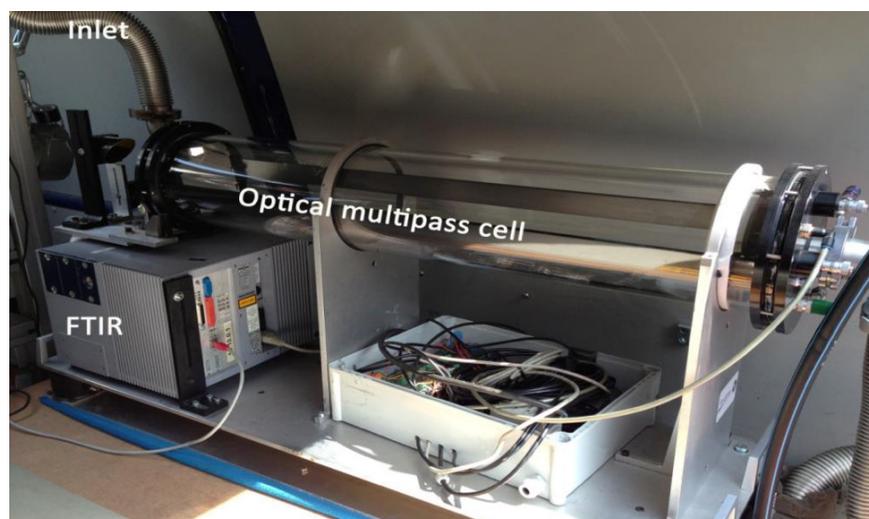


Figure 6. The MeFTIR instrumentation consisting of a Bruker FTIR spectrometer connected to an optical multi-pass cell (Mellqvist et al., 2017).

E. METEOROLOGICAL MEASUREMENTS

Information regarding wind speed and direction is critical to the FluxSense emission estimation approach. It is used for planning measurement campaigns and navigation of the mobile laboratory along sampling routes both upwind and downwind of the targeted refineries or chemical plants. Wind information is needed both at the surface and aloft (throughout the plume). Since wind patterns are known to vary significantly in both time and space (as Figure 7 demonstrates), it is incumbent upon the FluxSense system to measure them with sufficient temporal and spatial resolution in close proximity to the plumes being sampled.

The FluxSense method assumes that “wind speed information below an altitude of 40 m does not influence the flux calculations”, but this is highly dependent on the flow characteristics of the region (Johansson et al., 2014). The surface wind directions and speeds in the Southern California Air Basin

(SoCAB) sub-region where most refineries are located are highly variable over short distances, owing to SoCAB’s complex terrain and proximity to the coast (Johansson et al., 2014, Figure 3). The situation is similar for Bay Area refineries, especially for near-surface releases which are more difficult to characterize than ducted emissions from elevated stacks. Plumes from these releases are not homogeneously mixed to “several hundred meters” as close to the sources, as indicated by Mellqvist et al. (2017), and thus the SOF assumption does not necessarily hold true. In the case of the SCAQMD studies, FluxSense deployed the following three meteorological sensor systems:

1. One 3D infrared wind LIDAR (WINDCUBE Model 100S). This instrument provided vertical wind profiles from 50 m to about 1,000 m above the sampling site, with a 25-m vertical resolution and 10-minute averaging. It was located at one of four potential locations nearby four of the six targeted refineries. It is important to note that the LIDAR measurements depend on backscattering



Figure 7. Wind roses from the Port of Los Angeles monitoring network demonstrating large spatial variability in speed and direction (POLA, 2017).

from particulates within the volume of air that is being probed. Particulate concentrations and size distributions within the plume can be distinguished from those in the surrounding air masses and may therefore have the potential to provide plume geometry estimates.

2. One portable anemometer (RM Young Model 05108) with a 10-m mast. This was installed at open locations for the period of interest nearby the targeted refinery.
3. One portable sensor (AIRMAR Weather Station model 200 WXZ) mounted on the roof of the FluxSense instrumented vehicle. The portable sensor provided information about temperature, pressure, relative humidity, wind speed, and wind direction, corrected for vehicle orientation.

The SCAQMD-provided wind LIDAR information about the vertical distribution of the wind field was used in calculations of aloft plume mass fluxes. The surface meteorological sensor data were used for estimating horizontal wind variations in areas far from the LIDAR locations. The portable sensor was used as a real-time aid in positioning the vehicle relative to the expected upwind airmass and downwind plume locations.

III. Basic Assumptions Applied to Methodology

A. FLUXSENSE CALCULATION OF EMISSION MASS FLUXES FROM TARGETED REFINERIES

FluxSense applies two methods for calculating emission mass fluxes which they term “Direct Flux Measurement” and “Inferred Flux Measurement”. It could be argued that both of these terms are imprecise because emissions fluxes are not directly “measured” by FluxSense. In principle, mobile, open-path concentration measurements, such as those made by FluxSense, may offer advantages over other air measurements technologies. Open-path measurements may be representative of pollutant mass within larger sample volumes (columns) and/or within plumes that may be inaccessible to ground-based, fixed-location monitors. Neither the SOF FTIR nor the SkyDOAS instruments directly measure emission mass fluxes (in mg/s) past a facility boundary. FluxSense estimates emissions masses using a simple conceptual model of the atmosphere as described in the equations below, in combination with their measured column concentrations and measured wind data. More realistic models that consider plume shape and vertical wind structures have been applied by others to estimate emission fluxes starting with conventional types of plume concentration measurements (Piccot et al., 1994, Wei et al., 2016).

1. Direct Flux Equation

The equation used by FluxSense to calculate direct emission mass flux is presented below (Mellqvist et al., 2015, p.32). The emission mass flux Q , in kilograms per second (kg/s) of species j , for a single transect T , across the plume P , along driving path l , is expressed by the following integral:

$$Q_T^j = \bar{v}_T \cdot \int_P C_l^j \cdot \cos(\theta_l) \cdot \sin(\alpha_l) dl$$

where:

\bar{v}_T = average wind speed at plume height for the transect (m/s),

C_l^j = measured slant column densities for the species j as measured by SOF or SkyDOAS (kg/m²),

θ_l = angles of the light path from zenith,

α_l = angles between the wind directions and driving directions,

dl = driving distance across the plume in meters (m).

In essence, FluxSense estimates emission mass fluxes for each chemical compound by integrating (along the van’s driving path) the products of the contemporaneous average orthogonal wind speed component and the column concentration kilograms per square meter (kg/m²). Corrections are also made for the light path (slant) angle. This simple model has an obvious limitation in that estimated emissions are directly proportional to wind speed, regardless of activities within the facility. This simplification breaks down under calm, stagnant conditions and also under high wind conditions.

2. Inferred Flux Equation

For chemical species that are not detected by the SOF, FluxSense can infer mass fluxes by multiplying averaged ratios of BTEX/alkane and CH₄/alkane concentrations measured by the MWDOAS and MeFTIR systems by averaged alkane ‘direct’ flux values obtained using the SOF data (Mellqvist et al., 2015). The equation used for the inferred flux calculations is also provided in the report by Mellqvist et al., but is not reproduced here.

FluxSense notes that averaged values were used in its inferred flux calculations because SOF, MWDOAS, and MeFTIR measurements were not necessarily contemporaneous. They point out that the uncertainties in their inferred estimates of average total refinery BTEX and CH₄ emissions are larger than those for their direct flux estimates for alkanes.

In its application of the two methods above to the SOF and SkyDOAS data, FluxSense makes several explicit and implicit assumptions. Key assumptions include the following:

1. Measured upwind column concentrations are representative of the ambient air into which emissions from the targeted facility are emitted, i.e., targeted emissions are emitted into the same air parcels as those sampled along the upwind legs.
2. The combined concentration signatures of emissions from all sources other than the targeted facility are captured in measurements of “upwind” ambient air.
3. Wind speeds and wind directions measured by LIDAR and/or surface meteorology systems are representative of the winds above downwind sampling legs.
4. Horizontal and temporal variations in winds between the upwind and downwind legs are negligible both near the surface and at heights above the targeted plume heights.
5. Targeted plumes are usually well-mixed vertically and touch the ground.
6. The depths of targeted plumes can be appropriately calculated by dividing column concentrations by the corresponding surface concentrations (as measured by the MeFTIR and MWDOAS systems).
7. A single average wind speed is applicable across the entire depth and width of a targeted plume.

B. SPECTROSCOPY

It is stated that the absorption cross sections of the various alkanes measured in the SOF method are known to about $\pm 3.5\%$ in accuracy (Sharpe et al., 2004). Consequently, the uncertainty due to imperfect spectroscopic knowledge is at this level. The $\pm 3.5\%$ uncertainty is a reasonable assumption for each individual species that is a significant contributor in the spectral region of the C-H stretch fundamental, at a specific laboratory temperature. In the real atmosphere, particularly in a plume for which temperature has not fully equilibrated with the ambient, this is an optimistic assumption. In a fence line measurement scenario encircling a large refinery that contains numerous large tanks, the “plume” can be a complex mixture.

The distance to the various potential sources can vary over a wide range. Numerous absorption lines in these bands have line strengths that are temperature-dependent. The temperature dependence of the various line broadening coefficients is not known to within $\pm 3.5\%$ accuracy. Additionally, the presence of large water vapor mixing ratios in the plume adds to the uncertainty, especially in coastal areas. Water vapor lines make a major contribution to the overall IR absorption in this region of the spectrum, and those line strengths are highly temperature sensitive. There may also be an influence due to the collision broadening of the alkane absorption lines by water vapor molecules and those line broadening coefficients can affect the overall absorption band shapes.

In summary, attaching a $\pm 3.5\%$ uncertainty to the spectroscopic knowledge in the overall error budget (Johansson et al., 2014) is optimistic for the IR spectra as the real uncertainty can be much higher for the SOF technique. The UV/visual spectra utilized by the DOAS measurements are not as complex. However, the retrievals (i.e., quantitative estimates derived from the spectra) of the NO_2 , SO_2 , and formaldehyde column abundances in the plume are complicated by the atmospheric and in-plume scattering processes, which influence the absorption path lengths.

1. Open-Path-Integrated Averages

Any constituent in the path through the atmosphere that has an overlapping spectral absorption feature can affect the SOF and mobile SkyDOAS measurements. As previously stated, the presence of water vapor in the atmosphere affects the retrievals of VOCs in the 700 to 3000 cm^{-1} spectral region. The zenith SkyDOAS measurement of NO_2 in the plume is influenced by the stratospheric and ambient tropospheric NO_2 slant column densities (Noxon, 1975; Wenig et al., 2004; Chen et al., 2009). This is also true for the SO_2 column (Hopfner et al., 2015; Theys et al., 2015). FluxSense operates under the basic assumption that contributions from interfering species either have negligible interferences with emissions from the source under test, or that such interferences can be estimated with sufficient accuracy to be eliminated, relying heavily on the differential between “downwind” and “upwind” baseline measurements to eliminate the effects of background species.

The accuracy and adequacy of the SOF and

mobile SkyDOAS techniques are sensitive to meteorological conditions. If the wind speed is low or gusty with frequent changes in direction, the plume cross section capture is uncertain, making SOF and mobile SkyDOAS measurements not worthwhile in such circumstances as variable wind speed and direction during the measurement period significantly degrade the accuracy of the emission flux determination. Additionally, wind direction must be known and stable over the duration of the measurement in order to effectively sample both the upwind and downwind planes. The duration of the measurement, including both upwind and downwind transects, must be short compared to the time scales of variability of the surrounding potential interferences. For a small, isolated source under test, these are reasonable assumptions. In the case of a larger facility in an area that includes other stationary sources and a large number of mobile sources, interferences are more difficult to eliminate when the upwind-downwind measurement duration is several tens of minutes. Assessing this possibility requires adequate wind sensing on short time scales.

Another FluxSense assumption is that the entire plume cross section is “captured” by the SOF or mobile SkyDOAS techniques. Viewing the sun in the infrared, from a platform about one meter above ground level relatively effectively captures the emission plume for a wide range of solar zenith angles, but SOF may still have issues even near midday at high latitudes in the winter months. The mobile SkyDOAS method views the zenith, which mitigates stray light scattering issues.

2. Stray Light Interferences

Stray light can affect both the atmospheric column and the spectrometer. Stray light effects are not discussed at any length in the FluxSense documents that have been made available to the Panel. Thus, the Panel inferred that the assumption made by FluxSense is that stray light interferences are negligible. This would be the case if the spectrometer designers included some spatial filtering in their spectrometer optics to partially mitigate stray light interferences. Stray light effects can be particularly troublesome in an environment with high particulate concentrations.

Stray light also has an inherent effect on the mobile SkyDOAS measurements. Scattering is intense in the ultraviolet region and this method depends

fundamentally on atmospheric scattering. The variability of UV scattering in the lower atmosphere over short spatial and time scales is a factor in the overall SkyDOAS uncertainty budget.

3. Atmospheric Emission vs. Absorbance

A drawback of absorbance measurements is that with stronger spectral absorption features, saturation occurs, causing the relationship between molecular column abundance and absorbance to become nonlinear. In effect, sensitivity to changes in the column abundance decreases and the error bars associated with fitting to reference spectra begin to grow. This affects the dynamic range capability of absorbance spectroscopy. In contrast, emission spectroscopy does not have this fundamental limitation. In absorbance spectroscopy retrievals, the saturation effect results in negative (inverse) peaks at the same location (frequency) of the positive absorbance peaks, creating uncertainty in the cumulative absorbance peak area and intensity. There are other factors, not discussed in the scope of this report, that will also limit the dynamic range. The FluxSense documents that have been made available do not contain a discussion of the impacts of spectral feature saturation.

Each of the measurement techniques used by FluxSense employs absorbance spectroscopy. With the MeFTIR (using a globar source) and the MWDOAS (using a xenon arc lamp), absorbance can, in theory, be controlled to within the linear region by varying the absorption path length.

4. Zenith Angle Impact on Reported Concentrations

At any given time and location, the solar zenith angle can be obtained from various sources. This is an especially important principle for the SOF measurements. For a given plume cross section as it advects over the measurement plane, the plume thickness along the line of sight to the sun increases with increasing zenith angle. This must be accounted for in the data analysis and retrievals. The plume thickness is proportional to the secant of the zenith angle measurement, an approximation that applies to a wide range of zenith angles. The FluxSense SOF data examples shown in the documents reviewed by the Panel indicate that operation can be constrained to a period of less than 4 hours about midday.

5. Use of Ground-level Measurements to Infer Aloft Concentrations

The assumptions made by FluxSense when determining aloft concentrations through ground-level measurements are that plume dispersion at the measurement plane is such that the lower boundary is within a few meters of the ground and that it is uniformly mixed within the vertical boundaries of the plume. However, plume dynamics are more complicated than this. The traditional assumption is that motions that spread the vertical dimension of the plume are in the range 0.5 to 1 m/s and that vertical lift during early stages is governed by the plume buoyancy. Altogether, the ability of the MWDOAS sensor on the roof of the vehicle to sense a representative sample of the plume depends heavily on the local meteorology and the distance from the source(s).

FluxSense also relies on the assumption that the aromatic/alkane ratios measured by either the MeFTIR/MWDOAS at the vehicle location or from analyses of canister samples are representative of the overall plume ratio. The measured SOF alkane emission flux, along with the ratio obtained at the vehicle location or canister location, provides an estimate of the overall BTEX flux.

a) Assumed NO_2/NO_x Ratios

Nitrogen monoxide (NO) that is emitted at the source reacts with VOCs and O_3 in air to form NO_2 . The atmospheric chemistry of NO to NO_2 conversion is complex, involving multiple chemical and photochemical reactions with various reaction rates (Friedlander and Seinfeld, 1969; Seinfeld and Pandis, 2012). In the presence of reactive hydrocarbons, hydrocarbon oxidation can play a key role. This also applies to the reactions in the plumes. FluxSense measures NO_2 with the mobile SkyDOAS system and relies on a chemical transport/dispersion model that predicts the NO_2/NO_x ratio vs. downwind distance from source for low to moderate wind speeds (Mellqvist et al., 2016). The assumptions made in this model were not provided in the documents reviewed by the Panel. It is assumed that FluxSense adjusts both the ratio (according to distance from the source) and the wind speed in order to derive NO_x concentrations for a variety of conditions. At source distances closer than ~600 m, the uncertainty of this ratio increases.

b) Measured NO_2/NO_x Ratios

FluxSense measures NO_2 column concentrations using SkyDOAS. NO_x emissions from industrial facilities are typically a combination of NO and NO_2 . The emitted NO/ NO_2 ratio for combustion sources is typically in the range of 0.70 to 0.95, so the majority of the NO_x is emitted as NO. After its release into the atmosphere, freshly emitted NO quickly reacts with ambient O_3 to form NO_2 . Close to the source, the amount of NO_2 that is produced will be limited by the availability of ambient O_3 (termed “ozone-limited” conversion). Due to ozone-limited chemical conversion, some fraction of emitted NO is not converted to NO_2 until NO concentrations in the plume decline to the level of ambient ozone concentrations. A fraction of the NO_2 that FluxSense measured would have formed from NO_x emitted as NO. This indicates that the FluxSense approach can systematically overestimate NO_2 emissions while often underestimating total NO_x emissions.

C. ERROR BUDGET ASSOCIATED WITH TECHNIQUES

1. SOF MeFTIR MWDOAS

The SOF uncertainty associated with the spectroscopic knowledge is much larger than the 3% that is often quoted. The absorption cross sections of several of the individual VOCs (alkanes and alkenes) have been measured at a reference temperature with stated accuracies in the 2-3% range. Realistically, the spectra associated with a mixture of several molecules, with overlapping absorption lines and branches, at temperatures that can depart significantly from the reference temperature produces additional uncertainty. Plumes from an extended source region (e.g., a refinery) are not homogeneously mixed as they originate from a variety of sources, some intermittent, at different distances and plume temperatures. These separate plumes would coalesce only at distances of several kilometers (km) downwind. At these distances, other concerns materialize such as capture of the entire plume and the potential influence of other sources in the neighborhood. In addition, if certain absorption features in the spectrum are saturated, the spectral fitting uncertainty increases. The Panel estimates that overall uncertainty associated with the spectral fitting is likely to be 10% or more.

As discussed in Section III.B.4, the assumed atmospheric path length in the SOF technique depends on knowledge of the solar zenith angle at each location and time of day, as well as the stability of the pointing. The impact of a zenith angle error of 0.5 degrees would correlate to an error in retrieved column abundance of less than 1% for mid-latitude locations near midday during summer months. During winter months, the error can grow to 2%, for example, at a latitude of 40 degrees north.

The SOF retrieval of a VOC column can be complicated by the presence of spectral interference due to water vapor. When the land surface features are inhomogeneous and near water bodies, as in California urban areas with refineries, the water vapor column within the convective boundary layer can fluctuate over relatively small spatial scales, e.g. from 0.1 to 1 km. The boundary layer typically contains about 80% of the total atmospheric column abundance. In addition, the water vapor column in the plume downwind can be significantly larger than the upwind column abundance, depending on the types of sources. For example, results from one study indicate that a transmittance of about 0.5 in the 2950 cm^{-1} region where the VOC absorption peaks corresponds to an absorbance of 0.3 (Johansson et al., 2014, Figure 3). The value of the continuum is somewhat ambiguous in this spectral region, which is another source of uncertainty. This is largely due to water vapor absorption as indicated in Figure 8. This can be compared to the results from the study by Johansson et al., which indicate that the absorbance sensitivity that is required for accurate measurement of the VOC column with a 10 mg/m^2 precision is of the order 10^{-3} (Johansson et al., 2014, Figures 1 and 3). The retrieval must estimate the water vapor column absorbance with an accuracy of less

than 1% in order to achieve 10 mg/m^2 VOC column accuracies. The spectral shape and amount of water vapor absorbance depends on the vertical profiles of the temperature and the water vapor itself (both in-plume and in the background atmosphere), which are not measured. A water vapor column estimate with 10% accuracy would be very good under those circumstances. This implies a 100 mg/m^2 uncertainty. Although a spectral “fit” may look quite good, as in Figure 3 of Johansson et al. (2014), the retrieval method is not known in detail and it is likely that some residual water vapor is included in the fit. If this is the case, a large bias would result.

Figure 9 also demonstrates the potential for substantial interference from common atmospheric gases in the 3333 to 3700 nm (2700 to 3000 cm^{-1}) portion of the IR spectrum used for alkane quantification.

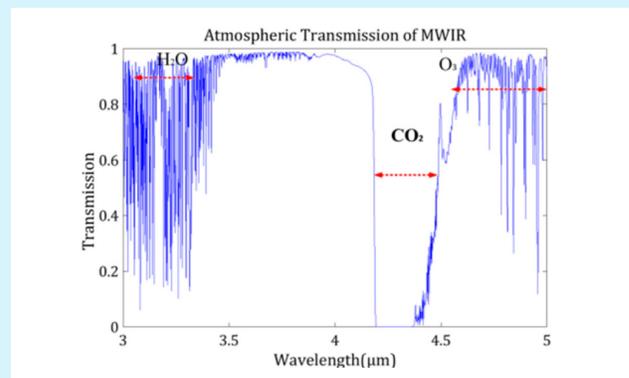


Figure 8. Transmission spectra for water vapor, carbon dioxide, and ozone (Huang et al., 2017).

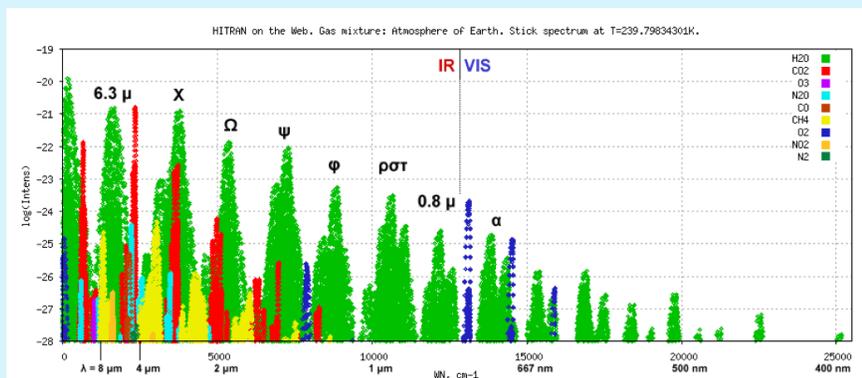


Figure 9. Simulated absorption spectrum for a gas mixture representing the Earth's atmosphere composed of the following percentages derived from the HITRAN data base:

H_2O : 0.400000 CO_2 : 0.039445,
 O_3 : 0.000003, N_2O : 0.000032,
 CO : 0.000010, CH_4 : 0.000179, O_2 :
 20.946000, NO_2 : 0.000002 N_2 :
 78.084000 at 239.798 K, 0.380327
 atm (HITRAN, 2012).

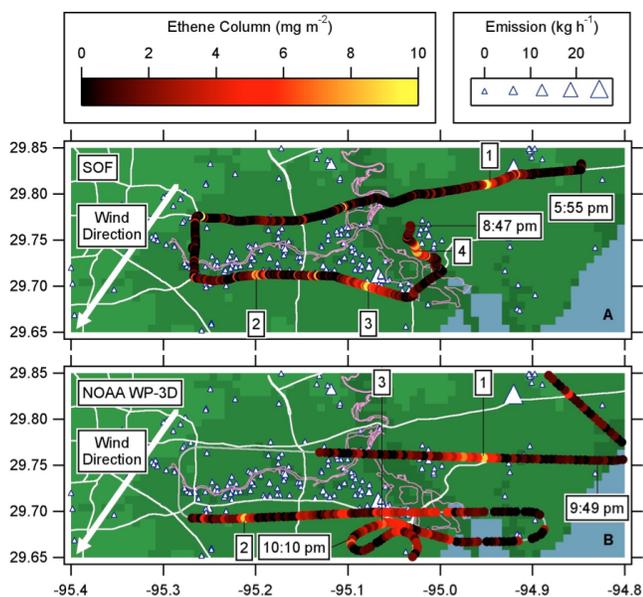


Figure 10. Comparison of ethene concentrations from the FluxSense SOF and NOAA aircraft over similar time periods near the Houston Ship Channel on September 19, 2006. White triangles are ethene point sources (of sizes proportional to source strengths) from the Texas 2004 emission inventory (De Gouw et al., 2009).

Uncertainties associated with estimating the wind field cover a wide range, depending on the atmospheric conditions and the available wind measurement capability. The wind field near midday (when the SOF measurement is made) is a result of several influences (Pasquill, 1971; Seinfeld and Pandis, 2012). The horizontal wind speed increases with height above the surface. However, the rate of increase and the height of the turbulent layer depend on multiple parameters, especially when traversing complex structures such as those in a refinery. Eddies of various dimensions cause fluctuations that can occur on short time scales. Thus, when the SOF method is applied over the perimeter of a refinery, the time scales of upwind and downwind data acquisition need to be specified.

The flux measurement requires knowledge of the wind speed and direction vs. height above ground level over the cross section of the plume(s). The vertical dimension of the plume at the plane of the SOF measurement is modeled, not measured, and the associated uncertainty can lead to estimated error in the 30-50% range.

During the Texas AQS 2006 campaign (DeGouw et al., 2009), results of the inter-comparisons between the FluxSense SOF and airborne measurements of highly

reactive VOCs showed discrepancies as large as a factor of 2 on some days, although much less on other days (Mellqvist et al., 2010). An overall discrepancy of 50% was quoted.

Figure 10 illustrates several of the limitations of the upwind/downwind method by both SOF and airborne measurements of ethene. Assuming that the methods are completely comparable, there are large differences in the locations and magnitudes of the measured concentrations, typically owing to hot-spots that might have intermittent emissions. Upwind concentrations can be large and variable with time and location. Average emissions for the complex appear to be dominated by a few large sources.

The use of a Doppler wind LIDAR that acquires data in the same time frame as the SOF measurement is a significant added capability. The data acquisition time is important. The LIDAR measures the line-of-sight (LOS) wind component and the commercial Leosphere Wind Cube LIDAR comes with two scan options: plan position indicator (PPI) and range height indicator (RHI), with a dead zone of 50 meters. The assumptions in deriving the horizontal wind component from these scans is that horizontal divergence over the spatial scale of interest at each height level is negligible and the vertical component can be removed due to averaging over space and time (Menzies and Hardesty, 1989). Two example studies indicate emissions are highly variable in time (Tisopoulos et al., 2016; Polidori et al., 2016). Significant variability occurs over 5 to 10-minute time frames in these examples. It is unknown whether or not LIDAR can produce high quality wind field displays in time periods shorter than these time scales.

The FluxSense method for obtaining estimates of BTEX fluxes depends on ground-level MeFTIR measurements of concentrations of both alkanes/alkenes and aromatics. The resultant ratio is then applied to the plume as a whole to derive the BTEX fluxes. Representativeness is an issue with this method, as it is uncertain whether the measurement at the ground level is representative of the amalgamated plume when there are multiple potential sources within the area being monitored. If the objective is to measure BTEX fluxes from a refinery that is within or near a metropolitan area, other methods would be preferable. For example, flask samples mounted to tethered balloons or drones can be used to collect samples at suitable locations in the plume to be analyzed later

using gas chromatography/mass spectrometry (GC-MS) or FTIR.

2. Zenith Sky-UV-DOAS

As previously discussed, the zenith SkyDOAS method is used by FluxSense to measure NO_2 , SO_2 , and formaldehyde concentrations. The same sources of error that affect the SOF retrievals also affect the DOAS retrievals. In addition, the SkyDOAS retrieval depends on modeling scattering in the atmosphere and in the plume, introducing additional error. Atmospheric scattering is much greater in the UV range than in the IR range. An adequate understanding of the vertical profile of aerosol scattering is important as aerosols within the plume can affect the UV photon path length due to multiple scattering.

a) Error Associated with NO_2 Measurements

The discussion of NO_2 retrieval error sources in Chen et al. (2009) is applicable to this analysis of FluxSense. One source of error results from uncertainty of the NO_2 absorption cross section and its temperature dependence, estimated to be about 10% relative error. Another error source in determination of the NO_2 mass column in the plume is uncertainty in the estimated stratospheric slant column densities (SCDs), although this should have little impact on the FluxSense upwind-downwind differential. This UV spectral technique was developed in order to determine stratospheric NO_2 column abundances by collecting measurements during the twilight period, when the sensitivity of the zenith sky observation is enhanced by the long light path in the stratosphere (Noxon, 1975; Noxon, 1979).

Certain sources of error are specific to the southern California region. There is significant diurnal and seasonal variability in the stratospheric column and, in the case of the FluxSense measurements in southern California (S. CA), the uncertainty in the ambient NO_2 column abundance in the boundary layer can also contribute significantly to the error associated with determination of the NO_2 column mass in the plume. Concentrations in the LA Basin can often reach 0.1 ppm. A 0.1 ppm concentration integrated over the depth of the midday boundary layer (e.g., ~ 1 km) is typical of a NO_2 column mass density integrated over a plume thickness of a few hundred meters (e.g., 50 mg/m^2). Scattering within the plume also causes uncertainties in the retrievals. For solar zenith angles in the 20 to 50-degree range, the estimated total

uncertainty in the plume column mass measurement is 40 to 50%. The additional contribution of the uncertainty in wind field across the plume is the same as for the SOF measurement discussed previously.

b) Error Associated with SO_2 Measurements

Sources of error for the SO_2 measurement are in the same categories as discussed for NO_2 above. The uncertainty of the SO_2 UV absorption cross section and its temperature dependence are estimated to contribute about 10% relative error. The error source in determination of the SO_2 mass column in the plume that is due to uncertainties in the estimated tropospheric and stratospheric column densities depends heavily on volcanic activity. The volcanic influence in the upper troposphere and lower stratosphere has been low for the past several years, resulting in stratospheric column concentrations of 10^{14} molecules/cm² (Hopfner et al., 2015), about an order of magnitude less than NO_2 columns. In the lower troposphere, particularly the boundary layer, local/regional pollution adds to the SO_2 column. Ambient SO_2 mixing ratios in the SoCAB are now ~ 20 ppb (1-hour peak). These mixing ratios are less than those of NO_2 , by a factor of 4 to 5. Consequently, the uncertainties due to the ambient atmospheric SO_2 column abundance are small. Separation of the SO_2 UV spectrum from the ozone absorption spectrum (Theys et al., 2015), as well as scattering due to aerosol particles, also contribute to uncertainty in the retrieval. Errors in the retrieval result in a total uncertainty in the plume column mass measurement of about 40%.

c) Error Associated with HCHO Measurements

The uncertainties associated with retrievals of HCHO column mass in the plume arise from the same sources as discussed for NO_2 and SO_2 . The chemical reactivity of HCHO in the lower troposphere results in the boundary layer containing the major fraction of the vertical column. Boundary layer HCHO mixing ratios vary over a considerable range, and a significant vertical column retrieval uncertainty is due to the uncertainty in estimating the height of the well-mixed boundary layer (Heckel et al., 2005). The uncertainty associated with retrievals of the plume column mass is estimated to be 50%.

IV. Instrument Performance

A. LIMITS OF DETECTION

1. Calculated

As displayed in Figure 9, the absorbance sensitivity that is required for accurate detection of the VOC amount in a 1 mg/m^2 column using the SOF method is of the order 10^{-4} . Although FluxSense cites detection limits in the range of 0.1 to 5 mg/m^2 , a realistic detection limit for the mobile SOF when driving along a road is estimated to be 10 mg/m^2 corresponding to an absorbance of 10^{-3} . The lower limit of the range reported by FluxSense may be the limit due to the random noise in the detector signal chain or channel spectra of various periodicities. Instrument-related sources of error include instrument channel spectra, instrument line shape function, apodization error, field-of-view uncertainties (caused by small optical misalignments), and detector saturation (dynamic range of linearity) (Rinsland et al., 1998; Smith et al., 2004). The standing waves produced by small amounts of scattering from the optical surfaces in the instrument produce undulations with various periodicities in the continuum, with corresponding undulations in the absorbance baseline. The combination of these effects leads to estimated errors of 5 to 10%. Rinsland et al. (1998) and Smith et al. (2004) retrievals were based on measurements of sharp spectral features (the line spectra of CH_4 , CO_2 , and CO (carbon monoxide) and Q-branch features in ethylene (C_2H_6)). Although the FluxSense spectrometer resolution is quoted as $\sim 0.5 \text{ cm}^{-1}$, the VOC spectral features are broad compared with the line spectra of CH_4 , CO_2 , and CO , and the FluxSense spectral fitting in their retrieval is at an 8 cm^{-1} resolution. This mitigates the significance of some of these instrumental error sources at the expense of reduction in sensitivity and susceptibility to interfering species.

In the SOF method, the “instrument” includes the solar tracker. Fluctuations in solar irradiance due to pointing fluctuations and nonuniformity across the solar disk are likely to be at least a few percent. Averaging over a period of several seconds might reduce this source of fluctuation by an order of magnitude.

The stated detection limit for the mobile zenith SkyDOAS components (NO_2 , SO_2 , HCHO) is also 0.1 to 5 mg/m^2 . The contribution of the solar irradiance fluctuations due to sun tracker movements is not relevant in the error budget, like it is for the SOF method. Other instrumental sources of error appear to amount to an equivalent $\sim 0.5 \text{ mg/m}^2$ uncertainty (Heckel et al., 2005).

2. Confidence Interval

The uncertainties quoted above are meant to be 1-sigma uncertainties (see Appendix A [of FluxSense, 2017] for a more detailed description of 1-sigma uncertainties and other statistics related to the software algorithm). The VOC column bias due to water vapor interference is a positive bias.

3. Residual Error Treatments

Residual errors are those related to the residual spectrum, which refers to what remains after the calibration spectra have been subtracted (or factored out) from the sample spectra. It is a measurement of instrument line shape from calibration spectra line shape and constitutes what is not quantified or overquantified due to the goodness of fit (Bernardo et al., 2001; Bowman et al., 2000). The instrumental errors for both the SOF and mobile DOAS methods appear to be small compared with the retrieval errors due to uncertainties in the atmospheric characterization and the radiative transfer (forward model), as indicated in the prior sections.

V. Background Collection/Measurement

A. SYNTHETIC OR ACTIVE BACKGROUNDS

Spectral background generation by the FluxSense SOF method is not explicitly discussed in the documentation that was readily available to the Panel. However, the Mellqvist/FluxSense group states that since instrumental spectral backgrounds cannot be measured directly and Planck curves are not used because the IR light source is sunlight transmission through the atmosphere as it exists in nature, a reference spectrum of a different air mass than where emission measurements are taken is used. Presumably, the single beam is inspected for the absence of target analyte spectral features, so as to avoid cancelling out any emission absorbances when processing. However, utilizing a non-coincident and non-co-located sample spectrum (relative to the measured sample spectrum) can possibly present uncertainties in target analyte detection limits and quantitative measurement accuracies. These uncertainties would increase depending upon the differences of atmospheric aerosol scattering/absorption effects and sunlight transmission effects between the sample spectra columns and the background reference column selected. An example of the latter is the complication of the SOF retrieval of a VOC column by the presence of the spectral interference due to water vapor. The water vapor column in the plume downwind can be significantly larger than the upwind column abundance, depending on the types of sources. These uncertainties can also manifest more when processing low-resolution spectra (the FluxSense SOF spectra appear to be collected under 8 cm^{-1} instrumental resolutions as indicated in the FluxSense reports reviewed by the Panel, especially when trying to analyze the broadband absorbances of alkanes; see previous discussion in Section III.C). The Panel identified an underlying question of the FluxSense SOF method regarding determination of the background: How does a single beam hold up against all the sample spectra collected in the field and how can its selection be quality assured and controlled when presenting results to regulators? A background spectrum is only good for an indeterminate period of

time. As atmospheric changes take place over time, the background will not represent a good baseline or instrument line shape to generate sample absorbance spectra; this increases the error significantly. The more stable the instrument, or more often a background is collected or used, the more representative it is for processing sample spectra with flat baselines and low random noise.

1. Empirical a) Upstream

The empirical backgrounds of the FluxSense SOF method are explained in the previous section. Presumably, the spectral backgrounds for the Sky-DOAS method are synthetic, as there is no information in the FluxSense reports reviewed by the Panel to indicate that the DOAS background spectrum is generated from taking a clean sample spectrum. The presumed synthetic method involves “zapping” or artificially removing absorbance peaks in the designated region of quantification, or using algorithms to create a background with a similar line shape that may be used for generating an absorbance spectrum from a sample single beam and a background single beam.

b) External Cell

The points expressed in the previous sections regarding the selection of the methods influence measurement detection limits and uncertainties, especially when taking measurements at low optical densities. It would appear prudent to implement a “calibration cell”, containing known concentrations of target alkanes within the instrumental light path while assumptions are being determined to gauge the spectral baseline anomalies. This would act as a system calibration Quality Assurance/Quality Control (QA/QC) check. This was not attempted in the South Coast studies. Perhaps an optical path “light wheel” mounted within the FTIR spectrometer bench, with a calibration gas-containing cell and an empty cell (available for switching) could be utilized. This technique is often used in active open-path FTIR measurement studies for spectral validation purposes.

VI. Comparison with Annualized Emission Inventories

In September 2015, the FluxSense system was driven around several refineries in the SoCAB (Mellqvist et al., 2017). Wind speeds and directions were measured on a nearby tower with vertical profiles obtained from a nearby LIDAR remote sensor. This study concluded that “For all major refineries in the SCAB (sic), the ratio between measured and reported emissions for September 2015 is 6.2 for VOCs, 1.5 for SO₂, 0.83 for NO_x, and 34 for benzene, although the total measured benzene emissions were relatively small.”

It is uncertain whether or not comparing these estimates with those reported in annualized inventories is applicable as it is not clear that the same VOCs are being included, nor is it clear where the annual

emission estimates came from. For FluxSense, “VOCs” seem to consist of total alkanes by the SOF method, with BTEX and benzene appearing to be derived from the alkane measurements using ratios from downwind point measurements near the refineries. The alkane substances likely to be measured in the column should correspond to the alkane compounds and abundances in the speciation profiles used for the statewide inventories. Table 1 summarizes these VOC source profiles. It is evident that alkanes (including cycloalkanes) constitute most of the Total Organic Gases (TOG) for overall refinery emissions (composite) and individual emitters. The most abundant alkanes are isomers of pentane, methane, propane,

Table 1.
VOC refinery emission source profiles (percent of Total Organic Gas [TOG]) used by the California Air Resources Board for statewide emission inventories (CARB, 2021).

Compound	Composite	Fug Catalytic Reformer	FCC CO Boiler	Nat Gas Flare	Fug Drainage/ Separation Pits	Fug Pipes, Valves & Flanges	Pump Seals
c7 cycloparaffins	2.27	0.3			16.9	0.2	1.1
c8 cycloparaffins	0.66				5.2		0.1
c9 cycloparaffins	0.11	0.6				0.1	0.8
cyclohexane	0.08	0.2				0.1	0.5
ethane	6.05	16.2		30	1.7	5.8	1.2
hexane	3.86	0.8			11.9	3.4	11
isobutane	2.89	20.7			4.5	7.4	0.8
isomers of decane		2				0.3	1.9
isomers of heptane						0.8	4.1
isomers of hexane		0.8	13		12.2	1.6	5.5
isomers of nonane		2.5				0.5	3.1
isomers of octane		0.7				0.4	2.8
isomers of pentane	16.64	0.9			10.1	7.8	6.6
methane	13.01	0.9	36	20	2.9	28.6	3.3
n-butane	7.99	22.6			14.3	18.3	8.1
n-decane	0.74					0.8	5.1
n-heptane	1.24	0.2				1.4	8.5
n-nonane	0.56	1				0.6	3.9
n-octane	1.73	0.8				1.8	12
n-pentane	4.8	0.2			12	7.7	11.1
propane	19.68	26.7		30	5.9	11.5	3.7
propylene	1.75					0.1	
toluene	0.44	0.8				0.5	3
xylenes (mixed)	0.19	0.8				0.2	1.3
1-butene	0.15						
benzene	0.38	0.3			2.4	0.1	0.5
formaldehyde	8.88		51	20			
Total alkanes	82.31	98.1	49	80	97.6	99.1	95.2
Total TOG	94.1	100	100	100	100	100	100

and ethane. Although the assumption is that refinery VOC emissions are dominated by alkanes, this will not be the case for other VOC emitters. FluxSense data might be more accurately defined as alkanes, BTEX, or benzene, as appropriate, rather than being assumed to represent TOG.

Tables 2 and 3 compare emission estimates for southern California from the FluxSense study, with facility emissions from the Air Resources Board Inventory. Presumably the ARB numbers are determined according to the standard emission estimation methods (RTI, 2015; USEPA, 2015a, b). At first glance, the discrepancies are not overly unreasonable given the differences in definitions of "VOC" and experimental flux vs. annualized emissions. CARB (2009) states that "For each source category, the

ARB derives a value for the Reactive Organic Gases (ROG) by multiplying the reported total organic gases (TOG) by the Fraction of Reactive Organic Gases (FROG). Each source category is keyed to one of the available chemical speciation profiles, a few of which are summarized in Table 1. ARB documentation is not specific about the TOG emission factors and VOC profiles for each facility. For each category, the FROG value is calculated as the weight fraction of those species designated by the ARB as reactive in the speciation profile applicable to the category. CARB (2000) defines ROG as "TOG minus ARB's exempt compounds (e.g., methane, ethane, CFCs, etc.)" It is not clear which compounds are included as "etc."

2017 FluxSense Paper Table 43 - Emissions Converted to Tons per Year				
Refinery	Alkanes + BTEX	SO ₂	NO ₂	Benzene
A - Phillips	2,831	608	635	33
B - Tesoro	780	516	304	11
C - Phillips	2,712	357	556	79
D - Valero	1,746	159	331	16
E - Chevron	2,659	516	608	26
F - Torrance	1,442	357	172	8
Total	12,170	2,513	2,606	173

Table 2.
Emissions (tons/year) by refinery (FluxSense, 2017).

Facility	TOG	ROG	SO _x	NO _x
CHEVRON PRODUCTS CO.	1030.5	614.0	300.1	758.1
EXXONMOBIL OIL CORPORATION	808.6	552.4	333.4	510.5
TESORO REFINING & MARKETING CO, LLC	703.3	455.3	502.6	667.4
PHILLIPS 66 CO/LA REFINERY WILMINGTON PL	401.5	233.8	132.4	493.4
TESORO REFINING AND MARKETING CO	318.4	217.2	163.5	706.5
ULTRAMAR INC (NSR USE ONLY)	271.7	194.3	94.0	308.9
VOPAK TERMINAL LOS ANGELES INC	182.2	181.5	0.0	0.2
EQUILON ENTER. LLC, SHELL OIL PROD. US	124.7	106.5	0.3	4.9
VOPAK TERMINAL LOS ANGELES, INC.	107.2	106.5	0.0	0.1
PHILLIPS 66 COMPANY/LOS ANGELES REFINERY	125.0	96.9	339.8	400.8
KINDER MORGAN LIQUIDS TERMINALS, LLC	101.6	93.8	0.6	2.1
VOPAK TERMINAL LONG BEACH INC., A DELAWARE	75.6	75.4	0.0	1.2
TOTAL	4250.2	2927.7	1866.7	3854.0

Table 3.
2015 ROG emissions (tons/year) from large emitters in the study region (CARB, 2017)."

The FluxSense method assumes that non-refinery sources are easily recognizable, constant emitters at upwind and downwind locations, and can be eliminated. In a complicated region such as the SoCAB, especially in the sub-region where refineries are located, this doesn't appear to be the case. For example, traffic was found to be a large contributor of BTEX in the SoCAB. As shown in Figure 11, BTEX concentrations are generally elevated during the morning and afternoon commutes as compared to other periods of the day. This observation is particularly strong in the winter months. This is an issue common to all upwind/downwind types of integrated measurements. They can be valid in an isolated environment, but as more complexities are introduced and upwind source influences are similar in magnitude to those downwind and are continually changing, more rigor is needed to draw accurate conclusions.

Although the FluxSense method intends to measure transects over several days, a few daytime snapshots of emissions may not be accurately extrapolated to annualized emission rates that are used for regulations and long-term trends, even if they are completely accurate and comparable. Several emissions are temperature-dependent, and nighttime emissions may differ from daytime emissions for some activities. More than five or six measurement periods in different seasons and a variety of meteorological conditions would be needed to estimate annual averages. Refineries may curtail operations for maintenance and when changing from winter to summer fuel formulations.

In spite of the FluxSense limitations, as well as those of the ARB emissions inventory, the factor

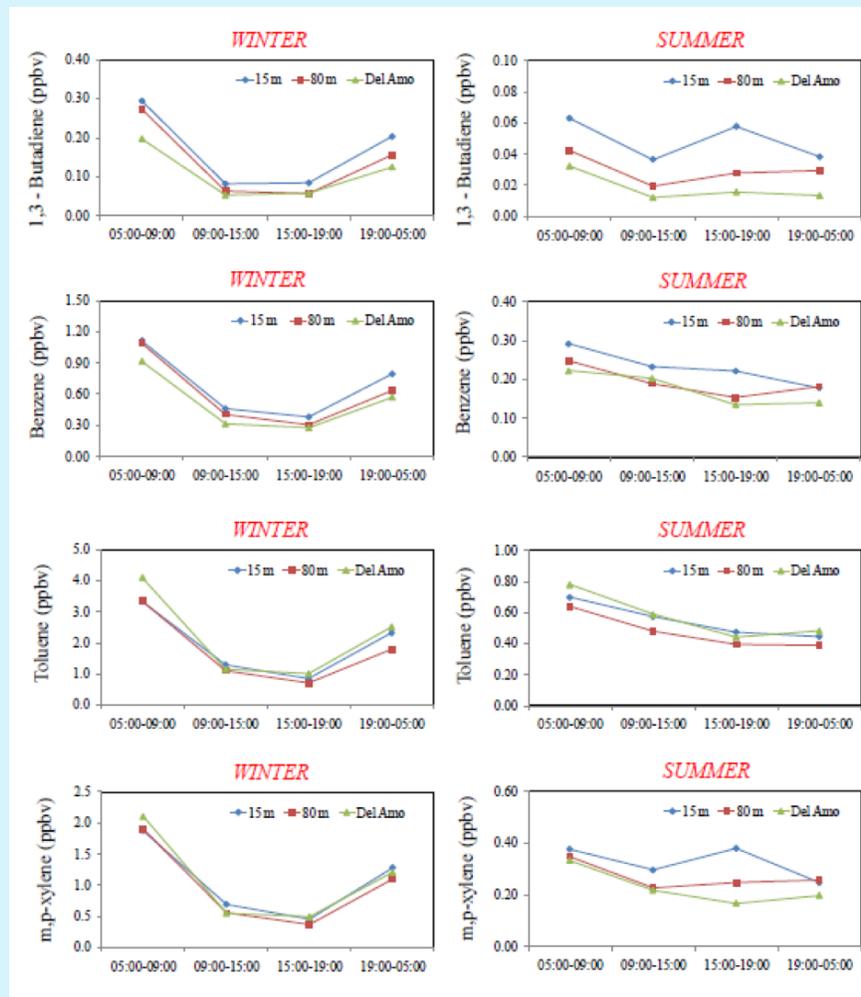


Figure 11. Time-averaged concentrations of benzene, 1,3-butadiene, toluene, and m,p-xylene at three different sites during summer and winter (SCAQMD, 2012).

of six increase in VOC emissions with respect to undocumented emission estimates is a large overestimation. Tables 2 and 3 indicate much closer agreement between the extrapolation of FluxSense measurements to an annual average for all of the pollutants considered. Most of these are probably fugitive emissions from low level sources rather than ducted emissions for which stringent pollution controls are applied, and factors of 2 or 3 uncertainties are common for fugitive VOC measurements.

FluxSense measurements could be useful as a complementary method for emission inventory improvement when coupled with more detailed, source-oriented measurements to obtain improved emission factors and VOC source profiles.

VII. Conclusions

A. LIMITATIONS OF THE FLUXSENSE APPROACH

The limitations of optical methods for remote measurements of VOCs have been discussed in the literature for decades. For example, in their report for CONCAWE entitled Optical Methods for Remote Measurement of Diffuse VOCs, Benassy et al. (2008) listed the limitations of the SOF method, most of which also apply to the SkyDOAS method. The following is a summary of Benassy's list of technical limitations of the FluxSense approach as applied to SCAQMD refineries, with supplementary information added by the Panel:

1. The method provides only short-term horizontal flux emission estimates. Extrapolation of these estimates to an annual period can lead to errors due to the temporal variability of refinery emissions.
2. Flux estimates made where complexities in the wind field exist are susceptible to larger errors. Accuracy is poorer in the complex flow situations (such as near Southern California and Bay Area refineries), where wind profiles are very different from those in smooth open-field conditions.
3. Measurements conducted near source complexes are associated with larger uncertainties than measurements made at some distance from the facilities. It has been argued that emissions are over-estimated when measurements are made in close proximity to sources and are lower than those estimated in open terrain.
4. Retrievals of VOC column content experience spectral interferences due primarily to the water vapor absorbance. The upwind water vapor column content can be significantly different from the downwind (in-plume) column content. Small uncertainties in the estimation of the water vapor column absorbance can result in large VOC retrieval errors. There is an iterative process to the data retrieval which begins by removing the absorbance of interfering species using either a modelled reference spectrum or an upwind spectrum. There is likely a residual spectrum generated during this process, which can be quite large but this is not discussed in the FluxSense reports. The way in which the extraction of this residual is performed is not clearly documented. It is important to determine if there is a subjective component in the retrieval process by making the algorithms and operating procedures and residual spectra available. Additionally, visual inspection of the residual spectra may be a good indicator of error by examining what was not quantified.
5. Several validation experiments of the SOF technique have been conducted with sulfur hexafluoride (SF_6) tracer gas. The retrieved average emission value differed by 11%, but much larger discrepancies were obtained for single measurements.
6. When a refinery is surrounded by other sources, a far-field measurement strategy may not be possible. Fence line measurements can be made as long as there are no sources close by. Measurement scans undertaken close to external emission sources can produce overestimates of the emission fluxes.
7. It is not possible to measure both upwind and downwind simultaneously, so the air parcels sampled upwind of the facility are not necessarily the same parcels sampled on the downwind passes. Intermittent or extraneous emission sources may influence results.
8. The method requires sunny (i.e., cloud-free, daytime) conditions. Emissions from refinery operations tend to be higher during the daytime working hours and solar radiation increases some VOC emissions.
9. The method provides column-averaged concentrations, but no information about concentration variations along the column.
10. Plume depth (or width) and height are not directly measured, so the average wind velocity at the "plume height" is uncertain and may lead to serious errors in mass flux calculations.
11. There is restricted availability, i.e., there is only one company providing SOF measurements.

1. Wind Field Variability

Several of the limitations described above derive primarily from assuming homogeneous meteorological conditions. Significant horizontal wind speed and direction variations are common in the SCAQMD due to the complex terrain of the Palos Verdes peninsula, complex land-sea breeze circulations, irregularly shaped coastline, local variations in ground temperatures, and frequent decoupling of the surface and aloft wind flows. Atmospheric flow, even near the ground, is three-dimensional in nature. Convergence and divergence of low-level winds often produce vertical velocities, and vertical winds can move pollutant mass into and out of higher levels, where wind directions can be completely different than those near the ground. Ambient air in higher layers may derive from upwind sources in a completely different direction from those in the lower levels.

The eight figures presented in Appendix A show wind roses from eight surface METs in the vicinities of the S. CA refineries. These illustrate some nuances of the surface wind convergence patterns in relevant coastal areas of S. CA. The two stations furthest north (Lennox and LAX) reveal the dominance of the westerly winds from the El Segundo area where the coastline is oriented roughly north-south, and where flow is diverted around the elevated terrain on the Palos Verdes peninsula to the south. The two Long Beach stations and the Los Alamitos station are relatively close to one another and show indications of the southerly onshore flow from the east-west oriented shoreline near Long Beach and diversion of flows by high terrain to the west. The two Long Beach and Los Alamitos stations also reveal flow dissimilarities despite their relative proximity to one another. Toward the northeast, the Compton station plot shows that westerly winds dominate, suggesting the Compton station is located northeast of the typical surface flow convergence zones. Taken together, the figures reveal that most of these S. CA refineries studied by FluxSense are in a convergence zone where complex, three-dimensional wind patterns often exist.

2. Ambient Concentrations in the SoCAB

FluxSense vehicle routes along their “upwind” legs may not correctly represent the upwind ambient air at all levels of the sampled columns, which can lead to either over- or under-estimation of emissions fluxes. Comprehensive studies in the SoCAB have

described complex spatial and temporal variations of ambient air concentrations. These are due to the complex interactions between meteorological and emissions patterns. Emissions of VOC, NO_x, and SO₂ in the SoCAB emanate from a diverse spectrum of closely-spaced and intermixed source types. These include mobile, industrial, residential, consumer products, pipelines, power generation, evaporative, and natural sources. The relative importance of each of these source types varies by time and location. For example, a recent study by McDonald et al. (2018) suggested that VOC emissions from volatile chemical consumer products currently comprise a significant, underreported fraction of urban emissions inventories, and therefore may be important and variable sources of VOC in densely populated areas of the SoCAB.

Multiple layers of polluted air from prior days’ emissions along with transport from distant source regions have been measured in the SoCAB. These layers are often evidence of decoupled surface and aloft winds. For example, Wong et al. (2016) reported their measurements of air pollutants from the Mt. Wilson Observatory using ground- and satellite-based FTIRs that revealed significant variability and potential aloft transport of air pollutant emissions from distant sources into the SoCAB. Wunch et al. (2016) discussed their open-path Fourier transform spectrometer measurements of concentrations with unique emissions/dispersion histories, noting that observed aloft air quality concentrations are highly variable across the SoCAB.

Variable emissions sources located in close proximity are ubiquitous in the SoCAB and present obvious challenges for the FluxSense method as applied to SCAQMD refineries.

B. SCIENTIFIC EVALUATION OF FLUXSENSE EMISSION MASS FLUX ESTIMATES

There have not been extensive scientific evaluations of FluxSense emission mass flux estimates that support FluxSense’s ability to provide consistent, compelling evidence of quantitative reliability.

FluxSense reports that, since 2006, the SOF method has been used during several large air measurement campaigns and for more than 60 individual plant surveys in Europe, the U.S., and

Mexico. In several cases, it has also undergone performance evaluation against other measurement methods using known tracer gas releases. In Sweden, SOF has been used in combination with SF₆ tracer gas release measurements and FLIR gas imaging for annual plant surveys. According to FluxSense, the performance tests suggest that SOF typically has an uncertainty of 30%, but these uncertainties are not addressed mathematically in any of the documents provided in the FluxSense reports. Systematic errors due to FluxSense flux estimation methodology or wind speed assumptions are difficult to separate from random variations in actual source emissions fluxes. A detailed description of the stated 30% uncertainty should be provided or expressed mathematically for each step of the calculation process or procedure.

Based on FluxSense's statement that the SOF method has undergone widespread use and performance evaluation, FluxSense concludes that SOF is a "proven" method. However, FluxSense reports the largest source of SOF uncertainties derive from uncertainties about the wind field. Uncertainties can be much larger than the quoted 30% value in areas with complex, three-dimensional, time-varying wind fields that cannot be well-characterized on the scales of SOF measurements. Thus, it seems more appropriate to characterize the SOF method as frequently-used but, as yet, unevaluated for many situations.

The tracer tests conducted for the SCAQMD at the Anaheim stadium demonstrate potential errors in the FluxSense emissions estimation approach (FluxSense, 2017). SOF consistently underestimated actual propane trace release rates at Anaheim (~40% of actual emissions, meaning actual propane emissions rates were factors of 2 or more greater than FluxSense estimates). This is in contrast to FluxSense's reported SOF uncertainty of 30%. FluxSense suggests that close proximity to the source in the Anaheim tests may have caused the under-predictions (FluxSense, 2017). This suggestion contradicts the prior FluxSense guidance that near-source flux estimates are likely overestimated. Plume height was well known in the Anaheim tests, and the flux calculations based on the differential absorption LIDAR (DIAL) and FTIR methods used the same measured wind data, yet did not have the same consistent under-prediction tendency. Given the large inaccuracies of SOF-derived mass fluxes under the well-documented conditions of the Anaheim tests, method reliability under complex field scenarios may be more uncertain.

C. FLUXSENSE ASSUMPTION OF WELL-MIXED PLUMES

The FluxSense method assumes that daytime refinery plumes are usually vertically "well-mixed" and in contact with the ground. This leads FluxSense to the conclusion that their ground-level MeFTIR and MWDOAS concentration measurements are good indications of average plume concentrations. Based on this assumption, they calculate plume depths (m) by dividing their column-averaged SOF and SkyDOAS concentrations (mg/m²) by their ground-level concentrations (mg/m³). FluxSense then uses their calculated plume depths to select appropriate measurements of aloft wind speeds for their flux calculations.

These assumptions and data processing steps imply that SOF and SkyDOAS are usually needed only to estimate plume depths. If FluxSense assumptions about vertical plume mixing are correct, an alternative to mobile instruments would be establishment of a network of fixed ground-based open-path instruments. There are a number of scientifically established means to estimating plume rise and plume depths. A fixed measurement network would provide long-term averages that are more compatible with regulatory time frames than FluxSense's mobile, short-term snap-shots. If the "well-mixed" assumption is often not applicable, then it seems reasonable to conclude that the FluxSense plume depth estimates and subsequent flux calculations are often questionable.

D. POTENTIAL FOR REGULATORY CERTIFICATION OF THE FLUXSENSE METHOD

In principle, the path for regulatory use of a test method is based on tracing its use back to the appropriate legal authority. The National Ambient Air Quality Standards includes a series of federal reference methods (FRM) that are the "gold standard" for monitoring methods. For the FluxSense system, the driving regulations appear to be a combination of 40 CFR Parts 70 and 71 that determine if a facility will become subject to Title V requirements, various subparts of 40 CFR Parts 60, 61, 63, and 65 (USEPA, 2014), and SCAQMD Rule 1173 (SCAQMD, 2009). All of these focus on fugitive emissions.

Technical advances in measurement technology are incorporated into the regulations through procedures under 40 CFR Parts 53 and 58 that allow a method to be designated as a federal equivalent method (FEM), thus allowing it to be included in the official list of “designated” EPA methods (USEPA, 2017a). Alternatively, for other pollutants under 40 CFR Parts 59, 60, 61, 63, or 65, Method 301 is utilized (USEPA, 2018). All of these approaches for establishing equivalence cite the use of performance metrics such as precision and accuracy. The formal term for these metrics is “figures of merit”, which are specific measures of performance that are used to evaluate capability in comparison to a previously established and validated method, i.e., the reference method.

In practice, there is considerable leeway in the specifications of a reference method. This approach is termed a “performance-based measurement system” (PBMS)”, which focuses on what needs to be measured rather than how to measure it. In essence, a method can be used under this approach so long as the constituent of concern is being measured in the matrix of concern at the concentration level of concern and at the degree of accuracy identified as necessary to address the site decision (USEPA, 2001). At the state and local levels, there are fewer formal processes for establishing a new method as equivalent to existing methods. New methods are evaluated on the basis of the requirements of the application. If reference methods or performance criteria from existing established programs exist, then the new methods are determined against the established applicable methods and/or performance criteria for the application (Katzenstein, 2018).

Within the context of the regulations cited, typical minimum performance metrics for a field method are a precision of $\pm 30\%$ and an accuracy of $\pm 30\%$ agreement with a standard. However, most performance specifications for continuous analyzers are more stringent, along the lines of a 10% agreement (USEPA, 2017b).

The results of field validation tests conducted at several locations and times, cited throughout this report, suggest that the FluxSense system may not meet even those less stringent requirements. A comparison of the noted performance in the FluxSense field studies with typical performance of other methodologies to determine fugitive emissions suggests a lower level of accuracy and precision. All

these indications suggest it would be difficult to obtain a specific designation of equivalence for the FluxSense measurement approach. However, it should be noted that this limitation would not apply to special projects, including for research and survey purposes. Many other new technologies have been employed in a similar manner for non-compliance purposes.

E. POTENTIAL USES AND BENEFITS OF THE FLUXSENSE APPROACH

It is widely believed that VOC emissions are underestimated in the S. CA area by using conventional AP-42 emissions factors, activity levels, and emissions models. Further, photochemical model sensitivity studies over the past few decades have suggested the possibility that VOC emissions inventories for the SoCAB underestimate actual VOC emissions and/or their photochemical reactivity. VOC emission estimates for refineries are particularly suspect given their large numbers of potential fugitive VOC sources (e.g., seals, valves, flanges, storage tanks, reaction vessels, pumps, etc.).

In principal, mobile, open-path concentration measurements, such as those made by FluxSense, may offer advantages over conventional air pollution detection technologies for fugitive emissions. SOF produces column-averaged concentrations that are representative of larger sample volumes. These measurements can also provide information about plumes that may be inaccessible to fixed, ground-based monitors. Their mobility also provides short-term, facility-wide, snap-shots of relative emissions. The SOF has been widely used internationally so it can be viewed as an established (yet not generally “proven”) method. The FluxSense SkyDOAS complements the SOF by allowing the measurement of gases that do not absorb IR light or have too many interferences to measure low detection limits.

It has been demonstrated that the FluxSense method may produce reasonable emission flux estimates under ideal meteorological conditions for relatively isolated air pollutant sources, though such ideal conditions may be rare in the vicinity of refineries within the SCAQMD. So, quantification of regulated refinery emissions mass fluxes in the SoCAB using the FluxSense method remains a subject of debate (as previously discussed).

However, it seems that the FluxSense method may still provide qualitatively useful, short-term information about relative VOC emissions levels. It may be useful for revealing previously unidentified emissions hot-spots, process leaks, or other abnormal fugitive VOC sources within refineries. It may also be useful as part of a comprehensive fugitive VOC emissions control program. To comprise an effective VOC emissions quantification and control program, it may be sensible to combine FluxSense information with data from fixed fence line networks comprised of conventional and open-path or extractive cell FTIR and DOAS systems, and hand-held sniffers and FLIR cameras. Even though they are expensive, occasional short-term, mobile FluxSense surveys can supplement long-term averaged data from permanent measurement systems installed around refineries.

Bibliographies/References

- Angström, A., (1964). The parameters of atmospheric turbidity. *Tellus*, 16, 64-75.
- Bernardo, Cirilo, J.H., (2001). Measurement of instrument line shape functions of high-resolution FTIR spectrometers and their application to the analysis of spectra. Doctor of Philosophy thesis, Department of Chemistry, University of Wollongong.
- Bowman KW, Worden HM, Beer R, (2000). Instrument line-shape modeling and correction for off-axis detectors in Fourier-transform spectrometry. *Appl Opt.* 2000;39(21):3765-3773. doi:10.1364/ao.39.003765
- CARB, (2000). Fact sheet #1: Development of organic emission estimates for California's emission inventory and air quality models. California Air Resources Board, Sacramento, CA. Available at: https://www.arb.ca.gov/ei/speciate/factsheets_model_ei_speciation_tog_8_00.pdf
- CARB, (2009). Definitions of VOC and ROG. California Air Resources Board, Sacramento, CA.
- CARB, (2017). Facility search engine. California Air Resources Board, Sacramento, CA.
- CARB, (2021). Speciation profiles used in ARB modeling. California Air Resources Board, Sacramento, CA. Available at: <http://arb.ca.gov/ei/speciate/speciate.htm>
- Chen, D., B. Zhou, S. Beirle, L. M. Chen, and T. Wagner (2009), Tropospheric NO₂ column densities deduced from zenith-sky DOAS measurements in Shanghai, China, and their application to satellite validation, *Atmos. Chem. Phys.* vol. 9, pp. 3641-3662.
- Chiu, K.H., Sree, U., Tseng, S.H., Wu, C.H., Lo, J.G., (2005). Differential optical absorption spectrometer measurement of NO₂, SO₂, O₃, HCHO and aromatic volatile organics in ambient air of Kaohsiung petroleum refinery in Taiwan. *Atmospheric Environment*, 39, 941-955.
- Chiu, K.H., Sree, U., Tseng, S.H., Wu, C.H., Lo, J.G., (2005). Differential optical absorption spectrometer measurement of NO₂, SO₂, O₃, HCHO and aromatic volatile organics in ambient air of Kaohsiung Petroleum Refinery in Taiwan (vol 39, pg 929, 2005). *Atmospheric Environment*, 39, 3001-3001.
- De Gouw, J.A., Hekkert, S.T.L., Mellqvist, J., Warneke, C., Atlas, E.L., Fehsenfeld, F.C., Fried, A., Frost, G.J., Harren, F.J.M., Holloway, J.S., Lefer, B., Lueb, R., Meagher, J.F., Parrish, D.D., Patel, M., Pope, L., Richter, D., Rivera, C., Ryerson, T.B., Samuelsson, J., Walega, J., Washenfelder, R.A., Weibring, P., Zhu, X., (2009). Airborne measurements of ethene from industrial sources using laser photo-acoustic spectroscopy. *Environmental Science & Technology*, 43, 2437-2442. 10.1021/es802701a.

- FluxSense Inc, (2017). Emission Measurements of VOCs, NO₂ and SO₂ from the Refineries in the South Coast Air Basin Using Solar Occultation Flux and Other Optical Remote Sensing Methods. FluxSense AB, Hörsalsvägen 11, SE-41296 Göteborg, Sweden; FluxSense Inc, 113 W G Street # 757, San Diego, CA 92101.
- FluxSense AB, (2014). Pilot study to quantify industrial emissions of VOCs, NO₂ and SO₂ by SOF and mobile DOAS in the Bay Area. FluxSense AB, Hörsalsvägen 11, SE-41296 Göteborg, Sweden; FluxSense Inc, 113 W G Street # 757, San Diego, CA 92101.
- Fransson, K., Mellqvist, J., (2002). Measurements of VOCs at refineries using the solar occultation flux technique. Chalmers University of Technology, Goteborg, Sweden.
- Friedlander, S.K., and J.H. Seinfeld (1969), A dynamic model of photochemical smog, Environ. Science and Technology, vol. 3, pp. 1175-1181.
- Griffiths, P.R., (2017). The early days of commercial FT-IR spectrometry: A personal perspective. Applied Spectroscopy, 71, 329-340. 10.1177/0003702816683529.
- Hanrahan, P.L., (1999), The plume volume molar ratio method for determining NO₂/NO_x ratios in modeling – Part i: methodology, J. Air and Waste Management Assoc. vol. 49, pp. 1324-1331.
- Heckel, A., A. Richter, T. Tarsu, F. Wittrock, C. Hak, I. Pundt, W. Junkermann, and J. P. Burrows, (2005) MAX-DOAS measurements of formaldehyde in the Po-Valley Atmos. Chem. Phys., 5, 909–918. HITRAN, (2012). HITRAN on the Web. Gas Mixture: Atmosphere of Earth. Stick Spectrum at T = 239.79834301 K. High-resolution Transmission Molecular Absorption Database, Atomic and Molecular Physics Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA. Available at: https://commons.wikimedia.org/wiki/File:Synthetic_atmosphere_absorption_spectrum.gif
- Höpfner, M., et al., (2015), Sulfur dioxide (SO₂) from MIPAS in the upper troposphere and lower stratosphere 2002–2012, Atmos. Chem. Phys., vol. 15, pp. 7017–7037.
- Huang, Z., L. Yin, J. Wang, and H. Li (2017), Atmospheric attenuation correction based on a constant reference for high-precision infrared radiometry, Appl. Sciences vol. 7, pp. 1165-1174.
- Jin, L., Gao, M.G., Liu, W.Q., Lu, Y.H., Zhang, Y.J., Wang, Y.P., Zhang, T.S., Xu, L., Liu, Z.M., Chen, J., (2010). Application of SOF-FTIR method to measuring ammonia emission flux of chemical plant. Spectroscopy and Spectral Analysis, 30, 1478-1481. 10.3964/j.issn.1000-0593(2010)06-1478-04.
- Johansson, J.K.E., Mellqvist, J., Samuelsson, J., Offerle, B., Lefer, B., Rappengluck, B., Flynn, J., Yarwood, G., (2014a). Emission measurements of alkenes, alkanes, SO₂, and NO₂ from stationary sources in Southeast Texas over a 5-year period using SOF and mobile DOAS. Journal of Geophysical Research-Atmospheres, 119, 1973-1991. 10.1002/2013jd020485.
- Johansson, J., Mellqvist, J., Samuelsson, J., Offerle, B., Moldanova, J., Rappengluck, B., Lefer, B., & Flynn, J. (2014b). Quantitative measurements and modeling of industrial formaldehyde emissions in the Greater Houston area during campaigns in 2009 and 2011. Journal of Geophysical Research, 119(7), 4303–4322. <https://doi.org/10.1002/2013JD020159>

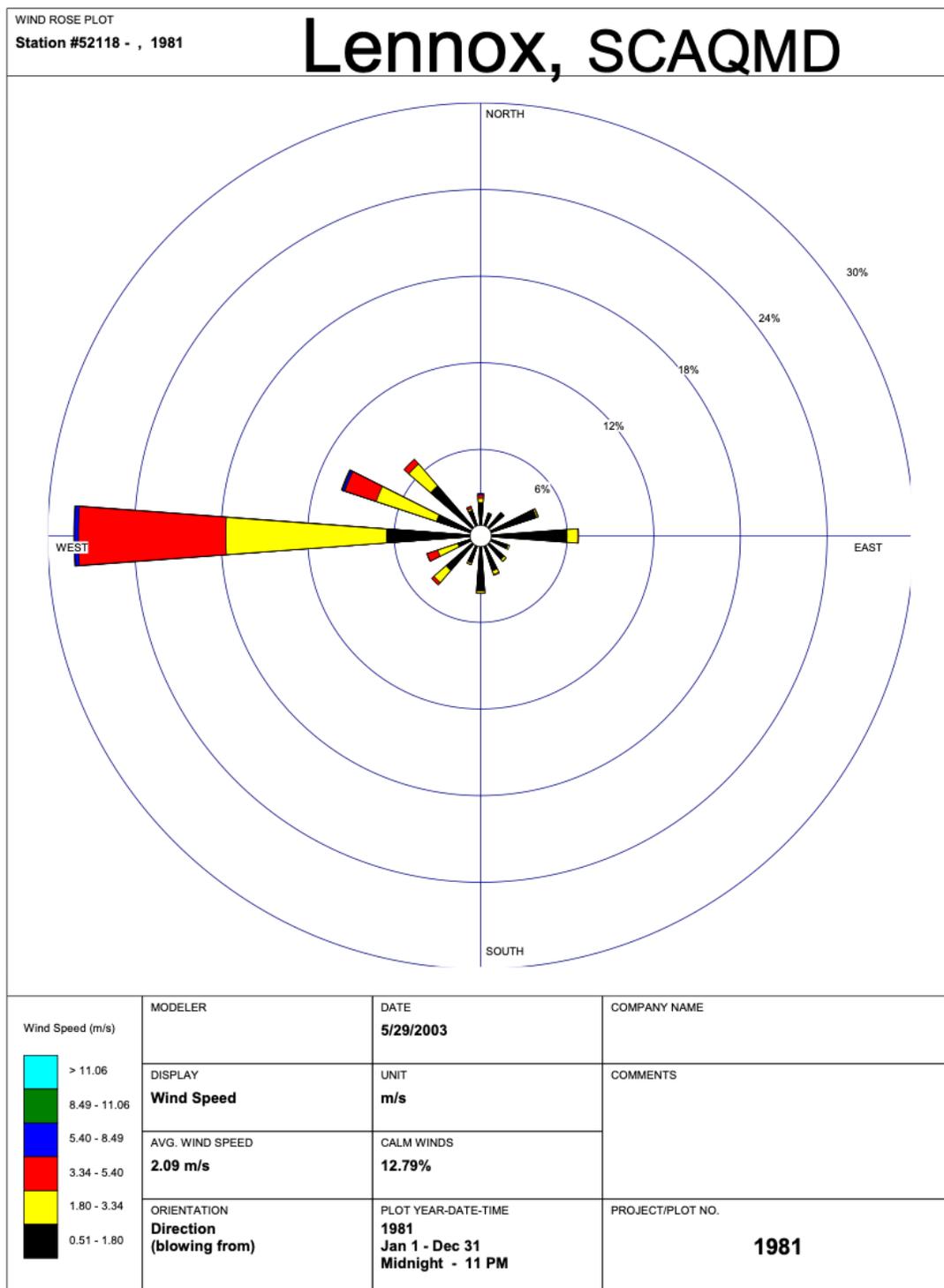
- Katzenstein, (2018). Personal Communication with Aaron Katzenstein of SCAQMD on March 21, 2018. Kihlman, M., (2005). Application of solar FTIR spectroscopy for quantifying gas emissions. M.S. Chalmers University of Technology, Gotenborg, Sweden.
- Kihlman, Manne, (2005). Application of Solar FTIR Spectroscopy for Quantifying Gas Emissions.
- Kim, S.W., McKeen, S.A., Frost, G.J., Lee, S.H., Trainer, M., Richter, A., Angevine, W.M., Atlas, E., Bianco, L., Boersma, K.F., Brioude, J., Burrows, J.P., de Gouw, J., Fried, A., Gleason, J., Hilboll, A., Mellqvist, J., Peischl, J., Richter, D., Rivera, C., Ryerson, T., Hekkert, S.T.L., Walega, J., Warneke, C., Weibring, P., Williams, E., (2011). Evaluations of NO_x and highly reactive VOC emission inventories in Texas and their implications for ozone plume simulations during the Texas Air Quality Study 2006. *Atmospheric Chemistry and Physics*, 11, 11361-11386.
- Lin, T.Y., Sree, U., Tseng, S.H., Chiu, K.H., Wu, C.H., Lo, J.G., (2004). Volatile organic compound concentrations in ambient air of Kaohsiung petroleum refinery in Taiwan. *Atmospheric Environment*, 38, 4111-4122.
- Liu, Z.M., Liu, W.Q., Gao, M.G., Tong, J.J., Zhang, T.S., Xu, L.A., Wei, X.L., Jin, L., Wang, Y.P., Chen, J., (2010). Study of the retrieval algorithm of emission gas spatio-temporal distribution of pollution source using the infrared Solar Occultation Flux (SOF) method (in Chinese). *Acta Physica Sinica*, 59, 5397-5405.
- Mellqvist, J., Ericsson, M., (2016). Data Collection and Interpretation Workshop: Solar Occultation Flux and Other Optical Remote Sensing Techniques to Fully Characterize and Quantify Fugitive Emissions from Refineries in the South Coast Air Basin. FluxSense Inc. San Diego, CA.
- Mellqvist, J., (2002). Ground-based FTIR observations of chlorine activation and ozone depletion inside the Arctic vortex during the winter of 1999/2000. *Journal of Geophysical Research - Atmospheres* D20, no. 107, pp. 2156-2202. DOI: 10.1029/2001JD001080.
- Mellqvist, J., J. Samuelsson, J. Johansson, C. Rivera, B. Lefer, S. Alvarez, and J. Jolly (2010), Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method, *J. Geophys. Res.*, 115, D00F17, doi:10.1029/2008JD011682.
- Mellqvist, J., Kihlman, M., Galle, B., Fransson, K., Samuelsson, J., The Solar Occultation Flux method, a nouvelle technique for quantifying fugitive gas emissions
- Mellqvist, J., Kihlman, M., Samuelsson, J., Galle, B., (2005). The Solar Occultation Flux (SOF) Method, a new technique for the quantification of fugitive emissions of VOCs Proceedings, 98th Annual Meeting of the Air & Waste Management Association, Pittsburgh, PA.
- Mellqvist, J., Samuelsson, J., Isoz, O., Brohede, S., Andersson, P., Ericsson, M., Johansson, J., (2017). Emission measurements of VOCs, NO_2 , and SO_2 from the refineries in the South Coast Air Basin using solar occultation flux and other optical remote sensing methods. FluxSense, Inc., San Diego, CA.

- Mellqvist, J., Samuelsson, J., Johansson, J., Rivera, C., Lefer, B., Alvarez, S., Jolly, J., (2010). Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method. *Journal of Geophysical Research-Atmospheres*, 115,
- Mellqvist, J., Samuelsson, J., Rivera, C., Lefer, B., Patel, M., (2007). Measurements of industrial emissions of VOCs, NH₃, NO₂ and SO₂ in Texas using the Solar Occultation Flux method and mobile DOAS. Chalmers University of Technology, Goteborg, Sweden.
- Menzies, R.T. and R.M. Hardesty (1989), Coherent Doppler lidar for measurements of wind fields, *Proc. IEEE* vol. 77, no. 3, pp. 449-462.
- Noxon, J.F. (1975), Nitrogen dioxide in the stratosphere and troposphere measured by ground-based absorption spectroscopy, *Science* vol. 189, pp. 547-549.
- Noxon, J.F., E. C. Whipple Jr. and R.S. Hyde (1979), Stratospheric NO₂: 1. Observational method and behavior at mid-latitude, *J. Geophys. Res.* vol. 84, C8, pp. 5047-5065.
- Olaguer, E.P., (2013). Application of an adjoint neighborhood-scale chemistry transport model to the attribution of primary formaldehyde at Lynchburg Ferry during TexAQS II. *Journal of Geophysical Research-Atmospheres*, 118, 4936-4946. 10.1002/jgrd.50406.
- Pasquill, F., (1971), Wind structure in the atmospheric boundary layer, *Phil. Tran. Royal Soc. London A*, vol. 269 # 1199, pp. 439-456.
- Piccot, S.D., Masemore, S.S., Ringler, E.S., Srinivasan, S., Kirchgessner, D.A., Herget, W.F., (1994). Validation of a method for estimating pollution emission rates from area sources using open-path FTIR spectroscopy and dispersion modeling techniques. *Journal of the Air & Waste Management Association*, 44, 271-279.
- Claudia Rivera, Jose Antonio García, Bo Galle et al, (2009). Validation of optical remote sensing measurement strategies applied to industrial gas emissions. *International Journal of Remote Sensing*. Vol. 30 (12), p. 3191-3204.
Journal article
- Rinsland, C.P., et al., (1998), Northern and southern hemisphere ground-based infrared spectroscopic measurements of tropospheric carbon monoxide and ethane, *J. Geophys. Res.*, 103 (D21), pp. 28197-28217.
- "Rothman, L.S., Barbe, A., Benner, D., Brown, L.R., Camy-Peyret, Claude, Carleer, M.R., Chance, Kelly, Clerbaux, Cathy, Dana, V., Devi, V.M., Fayt, A., Flaud, J.-M, Gamache, Robert, Goldman, A., Jacquemart, D., Jucks, K.W., Lafferty, W.J., Mandin, J.-Y, Massie, S.T., Yoshino, K., (2003). The HITRAN molecular spectroscopic database: Edition of 2000 including updates through 2001. *Journal of Quantitative Spectroscopy and Radiative Transfer*. 82. 5-44. 10.1016/S0022-4073(03)00146-8.
- RTI, (2015). Emissions estimation protocol for petroleum refineries, version 3. RTI International, Research Triangle Park, NC.

- SCAQMD, (2009). Rule 1173: Control of Volatile Organic Compound Leaks and Releases from Components at Petroleum Facilities and Chemical Plants. South Coast Air Management District, Diamond Bar, CA.
- SCAQMD, (2012). Ambient concentrations of criteria and air toxic pollutants in close proximity to a freeway with heavy duty diesel traffic. South Coast Air Management District, Diamond Bar, CA.
- Seinfeld, J.H., and S.N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, (Wiley-Interscience, Hoboken, NJ, 2006) ISBN 9781118591369.
- Sharpe, S. W., T. J. Johnson, R. L. Sams, P. M. Chu, G. C. Rhoderick, and P. A. Johnson (2004), Gas-phase databases for quantitative infrared spectroscopy, *Appl. Spectrosc.*, 58(12), 1452–1461, doi:10.1366/0003702042641281
- Smith, T.E.L, M. J. Wooster, M. Tattaris, and D. W. T. Griffith (2011), Absolute accuracy and sensitivity analysis of OP-FTIR retrievals of CO₂, CH₄ and CO over concentrations representative of “clean air” and “polluted plumes”, *Atmos. Meas. Tech.*, 4, pp. 97–116.
- Stutz, J., Hurlock, S.C., Colosimo, S.F., Tsai, C., Cheung, R., Festa, J., Pikelnaya, O., Alvarez, S., Flynn, J.H., Erickson, M.H., Olaguer, E.P., (2016). A novel dual-LED based long-path DOAS instrument for the measurement of aromatic hydrocarbons. *Atmospheric Environment*, 147, 121-132. 10.1016/j.atmosenv.2016.09.054.
- Theys, N. et al., (2015), Sulfur dioxide vertical column DOAS retrievals from the Ozone Monitoring Instrument: Global observations and comparison to ground-based and satellite data, *J. Geophys. Res. Atmos.*, vol. 120, pp. 2470–2491. doi:10.1002/2014JD022657.
- Thoma, E.D., Brantley, H.L., Oliver, K.D., Whitaker, D.A., Mukerjee, S., Mitchell, B., Wu, T., Squier, B., Escobar, E., Cousett, T.A., Gross-Davis, C.A., Schmidt, H., Sosna, D., Weiss, H., (2016). South Philadelphia passive sampler and sensor study. *Journal of the Air & Waste Management Association*, 66, 959-970. 10.1080/10962247.2016.1184724.
- Tisopulos, L., Polidori, A., Pikelnaya, O., Mellqvist, J., Samuelsson, J., Ericsson, M., Robinson, R., Innocenti, F., Finlayson, A., Hashmonay, R., Hashmonay, O., (2016). Monitoring of Emissions from a Refinery Tank Farm Using a Combination of Optical Remote Sensing Techniques. Collaborative effort between SCAQMD, FluxSense Inc., National Physical Laboratory, and Atmosfir Optics Ltd.
- USEPA, (2001). The Relationship Between SW-846, PBMS, and Innovative Analytical Techniques. Office of Solid Waste and Emergency Response. U.S. Environmental Protection Agency.
- USEPA, (2014). Leak Detection and Repair – A Best Practices Guide. U.S. Environmental Protection Agency, Washington, DC.
- US EPA, (2015a). Air emissions factors and quantification background document. U.S. Environmental Protection Agency, Research Triangle Park, NC.

- US EPA, (2015b). Emissions estimation protocol for petroleum refineries, Version 3. U.S. Environmental Protection Agency, Research Triangle Park, NC.
- USEPA, (2017a). List of Designated Reference and Equivalent Methods (Issue Date: June 16, 2017). U.S. Environmental Protection Agency, Research Triangle Park, NC.
- USEPA, (2017b). Performance Specification 9 – Specifications and Test Procedures for Gas Chromatographic Continuous Emission Monitoring Systems in Stationary Sources. U.S. Environmental Protection Agency.
- USEPA, (2018). Method 301--Field Validation of Pollutant Measurement Methods from Various Waste Media. U.S. Environmental Protection Agency.
- Wei, W., Lv, Z.F., Yang, G., Cheng, S.Y., Li, Y., Wang, L.T., (2016). VOCs emission rate estimate for complicated industrial area source using an inverse-dispersion calculation method: A case study on a petroleum refinery in Northern China. *Environmental Pollution*, 218, 681-688.
- Wenig, M., S. Kuhl, S. Beirle, E. Bucsela, B. Jahne, U. Platt, J. Gleason, and T. Wagner (2004), Retrieval and analysis of stratospheric NO₂ from the Global Ozone Monitoring Experiment, *J. Geophys. Res.* Vol. 109, D04315. doi:10.1029/2003JD003652

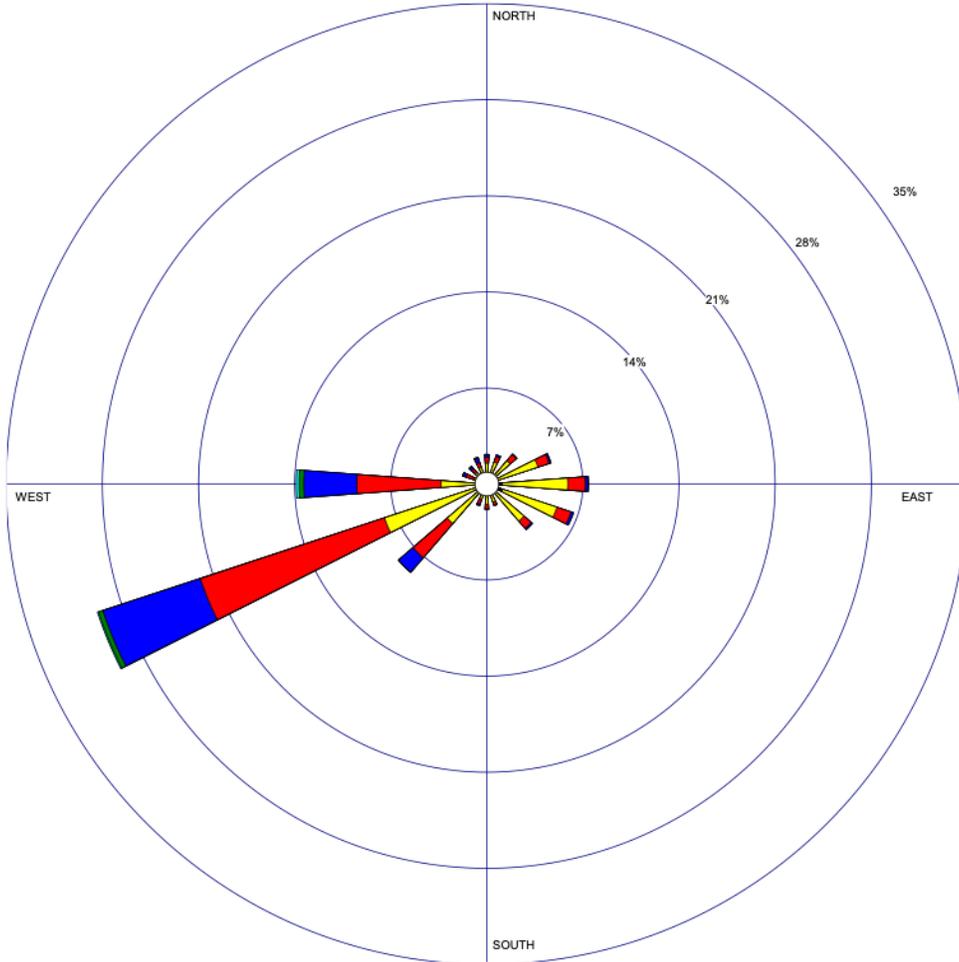
Appendix A: Wind Roses from Surface Meteorological Stations near Refineries in Southern CA"



WIND ROSE PLOT

Station #23174 - LOS ANGELES/INT'L ARPT, CA 1985-1989

Los Angeles

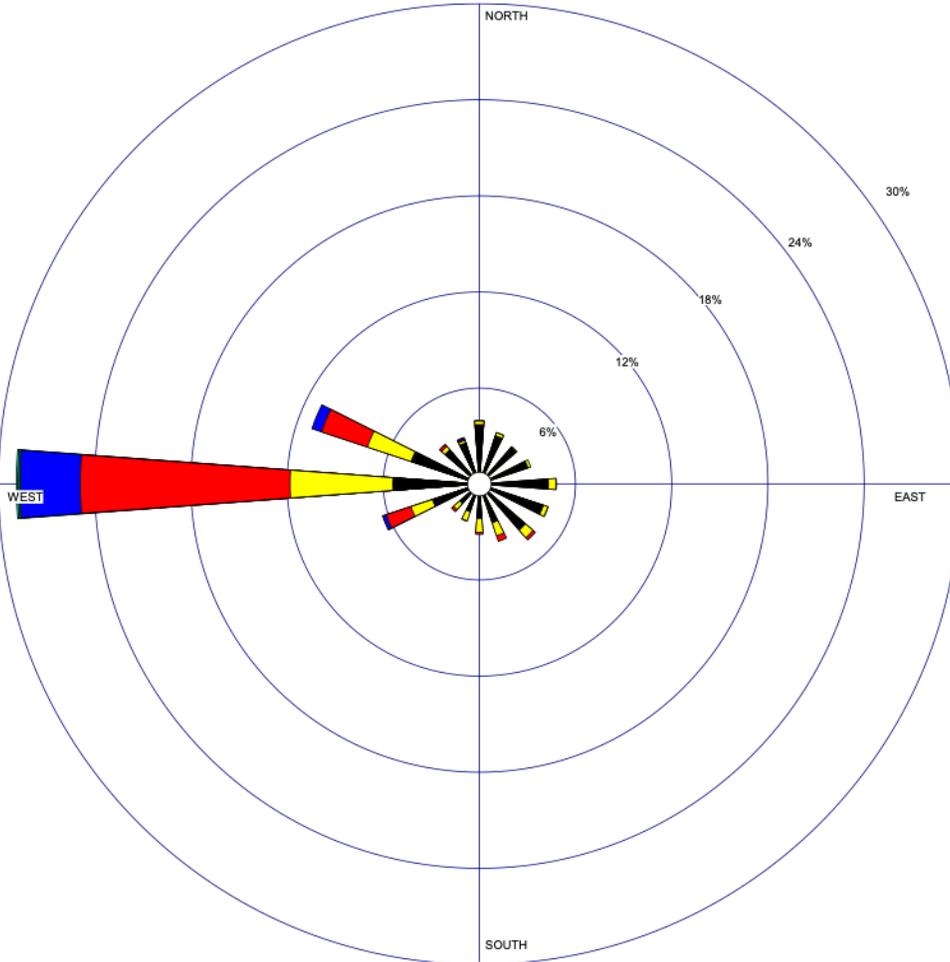


<p>Wind Speed (m/s)</p> <ul style="list-style-type: none"> > 11.06 8.49 - 11.06 5.40 - 8.49 3.34 - 5.40 1.80 - 3.34 0.51 - 1.80 	<p>MODELER</p>	<p>DATE</p> <p>5/28/2003</p>	<p>COMPANY NAME</p>
	<p>DISPLAY</p> <p>Wind Speed</p>	<p>UNIT</p> <p>m/s</p>	<p>COMMENTS</p>
	<p>AVG. WIND SPEED</p> <p>3.75 m/s</p>	<p>CALM WINDS</p> <p>6.11%</p>	
	<p>ORIENTATION</p> <p>Direction (blowing from)</p>	<p>PLOT YEAR-DATE-TIME</p> <p>1985 Jan 1 - Dec 31 Midnight - 11 PM</p>	<p>PROJECT/PLOT NO.</p> <p>1985-1989</p>

WRPLOT View 3.5 by Lakes Environmental Software - www.lakes-environmental.com

WIND ROSE PLOT
 Station #53112 - , 1981

Compton, SCAQMD

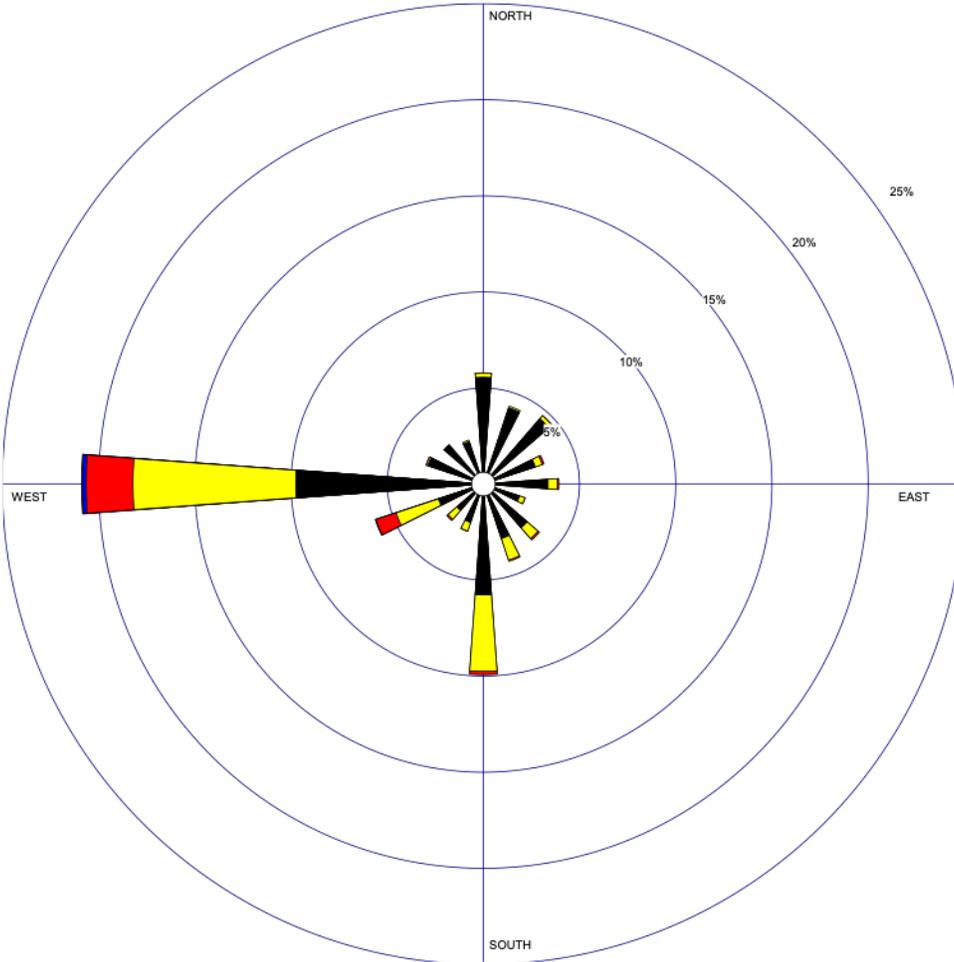


Wind Speed (m/s) 	MODELER 	DATE 5/29/2003	COMPANY NAME
	DISPLAY Wind Speed	UNIT m/s	COMMENTS
	AVG. WIND SPEED 2.39 m/s	CALM WINDS 7.92%	
	ORIENTATION Direction (blowing from)	PLOT YEAR-DATE-TIME 1981 Jan 1 - Dec 31 Midnight - 11 PM	PROJECT/PLOT NO. 1981

WRPLOT View 3.5 by Lakes Environmental Software - www.lakes-environmental.com

WIND ROSE PLOT
 Station #53101 - , 1981

Long Beach, SCAQMD

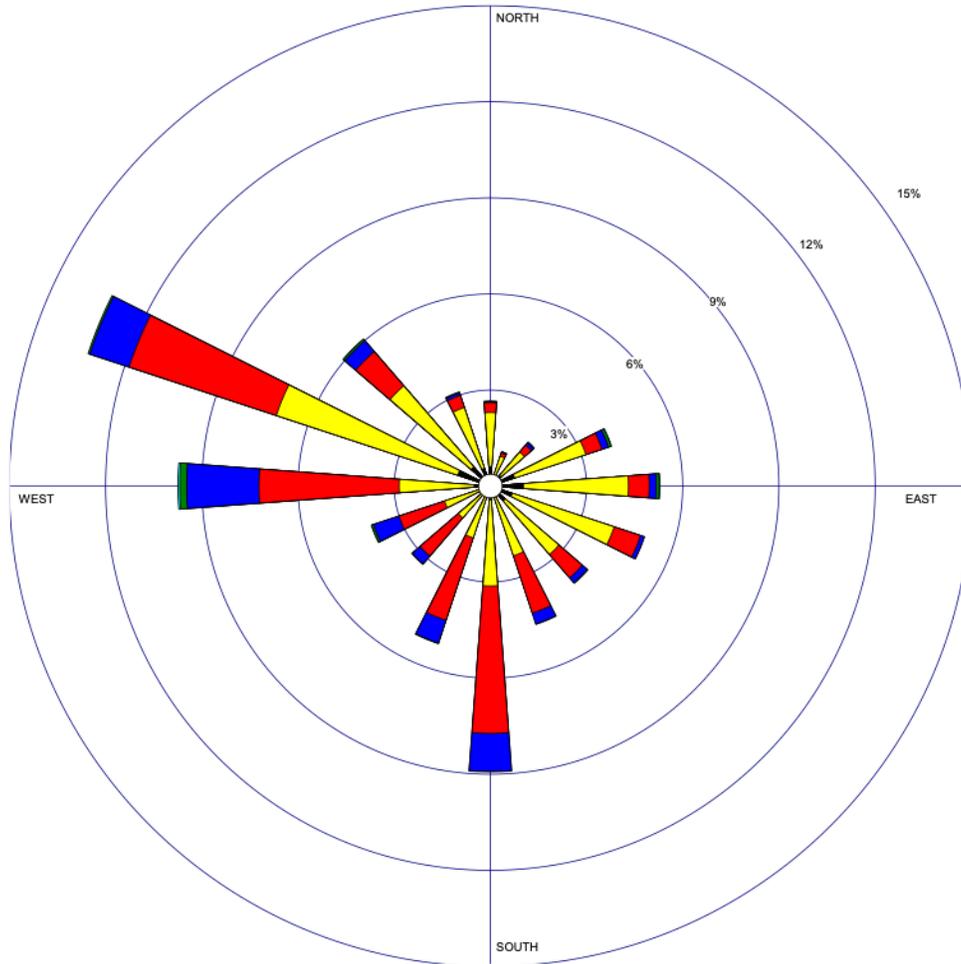


Wind Speed (m/s) 	MODELER	DATE 5/29/2003	COMPANY NAME
	DISPLAY Wind Speed	UNIT m/s	COMMENTS
	AVG. WIND SPEED 1.71 m/s	CALM WINDS 17.48%	
	ORIENTATION Direction (blowing from)	PLOT YEAR-DATE-TIME 1981 Jan 1 - Dec 31 Midnight - 11 PM	PROJECT/PLOT NO. 1981

WRPLOT View 3.5 by Lakes Environmental Software - www.lakes-environmental.com

WIND ROSE PLOT
 Station #23129 - , 1962-1964

Long Beach

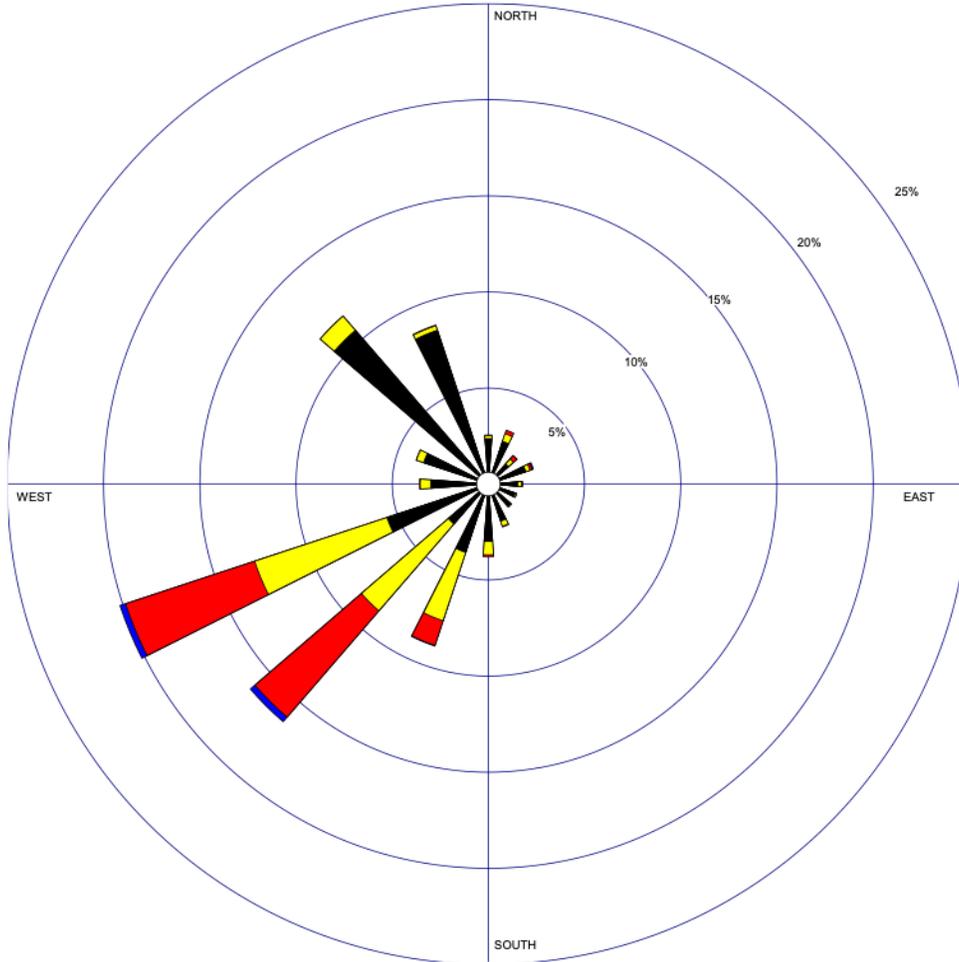


Wind Speed (m/s) > 11.06 8.49 - 11.06 5.40 - 8.49 3.34 - 5.40 1.80 - 3.34 0.51 - 1.80	MODELER 	DATE 5/28/2003	COMPANY NAME
	DISPLAY Wind Speed	UNIT m/s	COMMENTS
	AVG. WIND SPEED 3.46 m/s	CALM WINDS 18.14%	
	ORIENTATION Direction (blowing from)	PLOT YEAR-DATE-TIME 1962 Jan 1 - Dec 31 Midnight - 11 PM	PROJECT/PLOT NO. 1962-1964

WRPLOT View 3.5 by Lakes Environmental Software - www.lakes-environmental.com

WIND ROSE PLOT
 Station #53127 - , 1981

Los Alamitos, SCAQMD



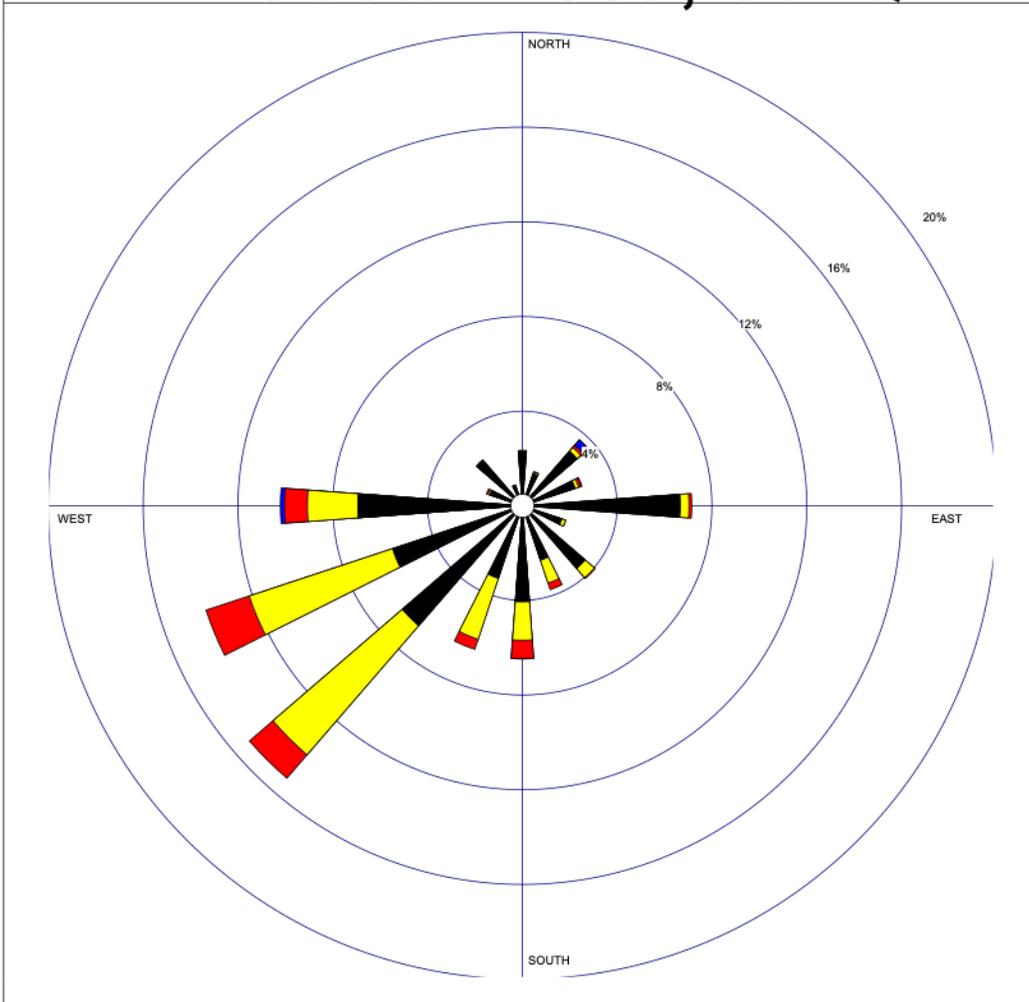
Wind Speed (m/s) 	MODELER 	DATE 5/29/2003	COMPANY NAME
	DISPLAY Wind Speed	UNIT m/s	COMMENTS
	AVG. WIND SPEED 2.18 m/s	CALM WINDS 5.71%	
	ORIENTATION Direction (blowing from)	PLOT YEAR-DATE-TIME 1981 Jan 1 - Dec 31 Midnight - 11 PM	PROJECT/PLOT NO. 1981

WRPLOT View 3.5 by Lakes Environmental Software - www.lakes-environmental.com

WIND ROSE PLOT

Station #53126 - , 1981

Costa Mesa, SCAQMD



<p>Wind Speed (m/s)</p> <ul style="list-style-type: none"> > 11.06 8.49 - 11.06 5.40 - 8.49 3.34 - 5.40 1.80 - 3.34 0.51 - 1.80 	<p>MODELER</p>	<p>DATE</p> <p>5/29/2003</p>	<p>COMPANY NAME</p>
	<p>DISPLAY</p> <p>Wind Speed</p>	<p>UNIT</p> <p>m/s</p>	<p>COMMENTS</p>
	<p>AVG. WIND SPEED</p> <p>1.82 m/s</p>	<p>CALM WINDS</p> <p>15.48%</p>	
	<p>ORIENTATION</p> <p>Direction (blowing from)</p>	<p>PLOT YEAR-DATE-TIME</p> <p>1981 Jan 1 - Dec 31 Midnight - 11 PM</p>	<p>PROJECT/PLOT NO.</p> <p>1981</p>

WRPLOT View 3.5 by Lakes Environmental Software - www.lakes-environmental.com

Appendix B: Other Sources Accessed By Authors

- Atmosfir Optics Ltd., (2015). Quantification of Fugitive emissions from Large Refineries: Implementation Plan. Ein Iron, Israel
- Bénassy, M-F., Bilinska, K., De Caluwé, G., Ekstrom, L., Leotoing, F., Mares, I., Roberts, P., Smithers, B., White, L., Post, L. (2008). Optical methods for remote measurement of diffuse VOCs: their role in the quantification of annual refinery emissions. CONCAWE. Brussels.
- Cuclis, A. (2016). Introduction to the FluxSense Presentation on Solar Occultation Flux. Houston Advanced Research Center.
- Hashmonay, R., Shpitzer, G., Kagann, R., Hashmonay, O., The Role of Continuous Open Path FTIR Fenceline Monitoring for Estimation of Total Fugitive Emissions from a Large Refinery. Collaborative effort between Atmosfir Optics Ltd. And SCAQMD. Tisopulos, L., Polidori, A., Pikelnaya, O.
- Minnich and Scotto, Inc., (2015). QUALITY ASSURANCE PROJECT PLAN Rev. 0 Application of the Area-Source Technique for Measuring Emission Rates from Small Sources SCAQMD Request for Proposal #P2015-07 Project 2: Quantification of Gaseous Emissions from Gas Stations, Oil Wells, and Other Small Point Sources. Freehold, NJ.
- Mellqvist, J., Ericsson, M., (2016). Data Collection and Interpretation Workshop: Solar Occultation Flux and Other Optical Remote Sensing Techniques to Fully Characterize and Quantify Fugitive Emissions from Refineries in the South Coast Air Basin. FluxSense Inc. San Diego, CA.
- Mellqvist, J., Samuelsson, J., Ericsson, M. (2012). Using Solar Occultation Flux and Other Optical Remote Sensing Techniques to Fully Characterize and Quantify Fugitive Emissions, #79 Air Quality Measurement Methods and Technology. Collaborative effort between FluxSense Inc. and SCAQMD. Tisopulos, L., Polidori, A., Pikelnaya, O. (2012). Chapel Hill, NC.
- Mellqvist, J., Samuelsson, J., Offerle, B., Brohede, S., Andersson, P., Ericsson, M. (2014). Pilot study to quantify industrial emissions of VOCs, NO₂ and SO₂ by SOF and mobile DOAS in the Carson Area. FLuxSense Inc. San Diego, CA.
- Mellqvist, J., Samuelsson, J., Offerle, B., Brohede, S., Andersson, P., Ericsson, M. (2014). Pilot study to quantify industrial emissions of VOCs, NO₂ and SO₂ by SOF and mobile DOAS in the Bay Area. FluxSense Inc. San Diego, CA.
- Mellqvist, J., Samuelsson, J., Ericsson, M., Brohede, S., Anderson, P., Johansson, J., Isoz, O. Using Solar Occultation Flux and Other Optical Remote Sensing Techniques to Fully Characterize and Quantify Fugitive Emissions from Refineries in the LA basin Paper# 948. Collaborative effort between FluxSense Inc., and SCAQMD. Tisopulos, L., Polidori, A., Pikelnaya, O.

- Mellqvist, J., Samuelsson, J., Ericsson, M., Brohede, S., Andersson, P., Johansson, J., Isoz, O. Quantification of Gaseous Emissions from Gas Stations, Oil Wells and Agriculture Using Optical Solar Occultation Flux and Tracer Correlation Methods Paper# 947. Collaborative effort between FluxSense Inc., and SCAQMD. Tisopulos, L., Polidori, A., Pikelnaya, O.
- Perry, S., Kricks, ABS # 996. Use of the Adaptive Background Filtering (ABF) algorithm to improve analysis of open path FTIR gaseous emissions spectra collected from urban oil wells, storage tanks, and other small point sources Based on data from SCAQMD Project #2: Quantification of gaseous emissions from gas stations, oil wells, and other small point sources. Collaborative effort between Kassay Field Services, Inc., RJK Consulting, and SCAQMD. Kricks, R., Pikelnaya, O., Polidori, A., Tisopulos, L.
- Pikelnaya, O., Polidori, A., Tisopulos, L. Use of Multiple Optical Remote Sensing Techniques to Quantify Gaseous Emissions from Urban Oil Wells, Storage Tanks, and Other Small Point Sources. Collaborative effort between SCAQMD, FLuxSense Inc., National Physical Laboratory, Minnich and Scotto Inc., and Kassay Field Services Inc. Mellqvist, J., Samuelsson, J., Brohede, S., Izos, O., Andersson, P., Ericsson, M., Robinson, R., Innocenti, F., Minnich, T., Scotto, R., Perry, S.
- Polidori, A., Tisopulos, L., Pikelnaya, O. Controlled-Release Experiment to Validate Field Measurements from Different Optical Remote Sensing Techniques. Collaborative effort between SCAQMD, National Physical Laboratory, FluxSense Inc., Atmosfir Optics., Kassay Field Services Inc., and Minnich and Scotto Inc.
- Polidori, A., Tisopulos, L., Pikelnaya, O. (2016). Quantification of Emissions from Gas Stations, Urban Oil Wells, and Other Small Point Sources Using Optical Remote Sensing Methods Air Quality Measurement Methods and Technology. Collaborative effort between SCAQMD, FluxSense Inc., National Physical Laboratory, Minnich and Scotto, Inc., and Kassay Field Services, Inc. Mellqvist, J., Samuelsson, J., Ericsson, M., Robinson, R., Innocenti, F., Minnich, T., Scotto, R., Perry, S. (2016). Chappel Hill, NC
- Randall, D., Coburn, J. (2010). Critical Review of DIAL Emission Test Data for BP Petroleum Refinery in Texas City, Texas. RTI International. Research Triangle Park, NC.
- Robinson, R. (2016). The Measurement of Fugitive and Diffuse VOC and GHG Emissions Using DIAL and Validation Using a Controlled Release Facility. A&WMA Air Quality Measurement methods conference. National Physical Laboratory. United Kingdom
- Robinson, R., Innocenti, F., Gardiner, T., Finlayson, A., Connor, A., Few, J., Helmore, J. (2016). Validation of Fugitive Emissions Measurement Techniques Using Differential Absorption Lidar and a Controlled Release System: Talk#916. AWMA. New Orleans, LA.
- Thoma, E.D., Brantley, H.L., Oliver, K.D., Whitaker, D.A., Mukerjee, S., Mitchell, B., Wu, T., Squier, B., Escobar, E., Cousett, T.A., Gross-Davis, C.A., Schmidt, H., Sosna, D., Weiss, H., (2016). South Philadelphia passive sampler and sensor study. Journal of the Air & Waste Management Association, 66, 959-970. 10.1080/10962247.2016.1184724.

Tisopulos, L., Polidori, A., Pikelnaya, O. Monitoring of Emissions From a Refinery Tank Farm Using a Combination of Optical Remote Sensing Technique. Collaborative effort between SCAQMD, FluxSense Inc., National Physical Laboratory, and Atmosfir Optics LTD. Mellqvist, J., Samuelsson, J., Ericsson, M., Robinson, R., Innocenti, F., Finlayson, A., Hashmonay, R., and Hashmonay O

Tisopulos, L., Polidori, A., Pikelnaya, O., Mellqvist, J., Samuelsson, J., Ericsson, M., Robinson, R., Innocenti, F., Finlayson, A., Hashmonay, R., Hashmonay, O., (2016). Monitoring of Emissions from a Refinery Tank Farm Using a Combination of Optical Remote Sensing Techniques. Collaborative effort between SCAQMD, FluxSense Inc., National Physical Laboratory, and Atmosfir Optics Ltd.

Tisopulos, L., Polidori, A., Pikelnaya, O. Quantification of Fugitive Emissions From Large Refineries Using Optical Remote Sensing Methods. Collaborative effort between SCAQMD, FluxSense Inc., National Physical Laboratory, Atmosfir Optics LTD. Mellqvist, J., Samuelsson, J., Ericsson, M., Robinson, R., Innocenti, F., Hashmonay, R., Shpitzer, G.

US EPA (2011). EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Air Quality Analysis Division Measurement Technology Group. U.S. Environmental Protection Agency, Research Triangle Park, NC.