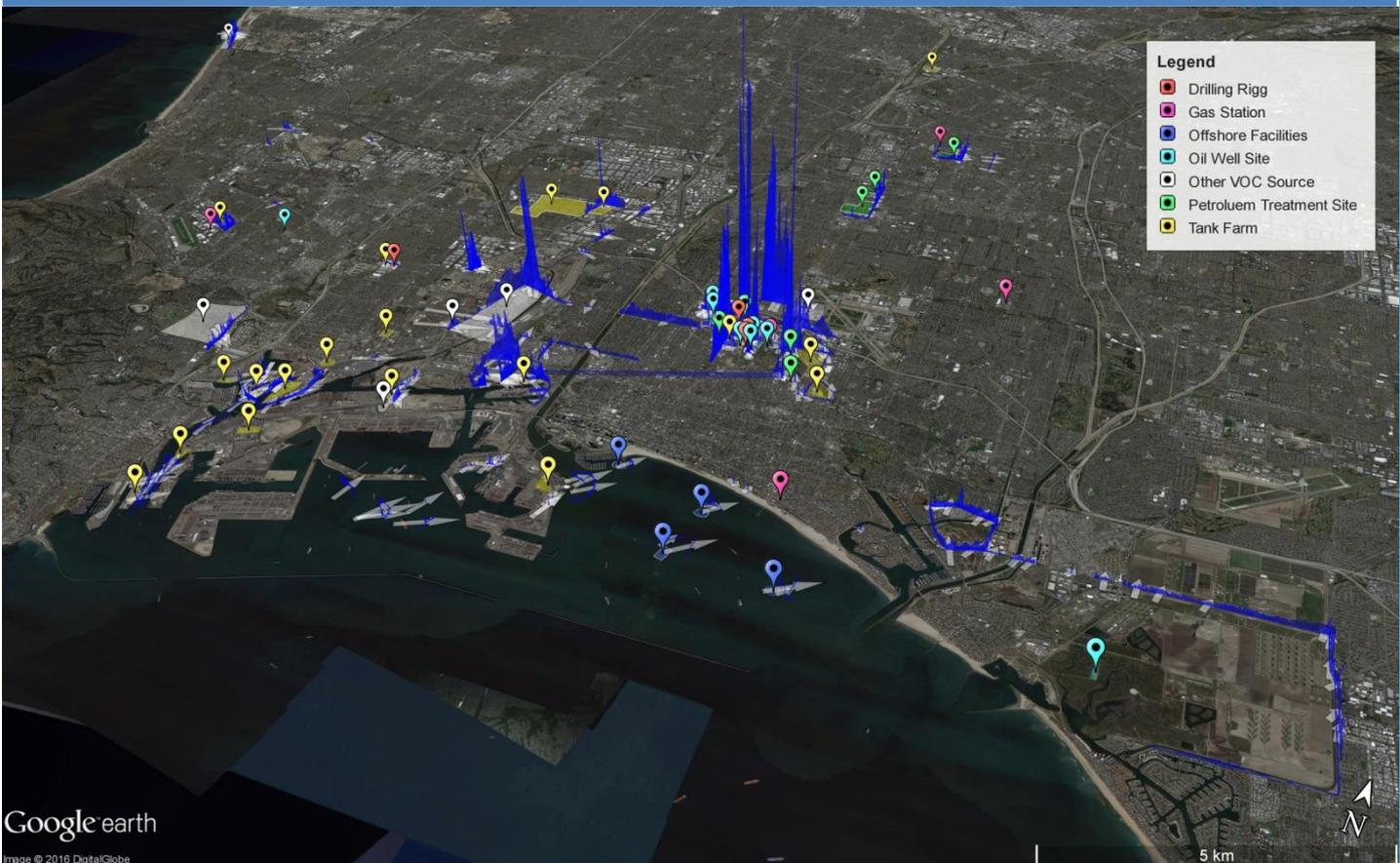


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Using Solar Occultation Flux and other Optical Remote Sensing Methods to measure VOC emissions from a variety of stationary sources in the South Coast Air Basin



FINAL REPORT

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Title: Using Solar Occultation Flux and other Optical Remote Sensing Methods to measure VOC emissions from a variety of stationary sources in the South Coast Air Basin.

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FluxSense Inc. is subsidiary of FluxSense AB (www.fluxsense.se; San Diego, CA). FluxSense started as a spin-off company from research conducted at Chalmers University of Technology in Sweden and has been active for more than 10 years. FluxSense has carried out more than 70 industrial site surveillances in Austria, Belgium, Denmark, France, Middle East, Netherlands, Norway, Sweden and the US.

[Cover: Visualization of alkane (blue curves) plume transects from multiple SOF measurements conducted at selected locations during this study (not a complete data set). Note that data was generated from multiple days and various wind conditions. The apparent height of the blue line is proportional to the integrated vertical column concentration expressed in mg/m^2 . The white arrow indicates approximate wind direction and speed during the measurements. Image mapped on Google Earth © 2016.]

Executive summary

BACKGROUND

Industrial emissions of volatile organic compounds (VOC) contribute to the formation of ground level ozone, which constitutes a public health concern especially in urban areas. To better characterize such emissions in the South Coast Air Basin (SCAB) and to assess their impact on ambient pollution levels, the South Coast Air Quality Management District (SCAQMD) has promoted and sponsored a series of measurement projects using optical remote sensing methods. These projects include experimental studies of emissions from refineries, oil depots, treatment facilities, oil wells, gas stations, fuel islands and barges. Investigations of various types of sources were separated into three projects:

- **Project 1:** 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
- **Project 2:** Using Solar Occultation Flux and other Optical Remote Sensing Methods to measure VOC emissions from a variety of stationary sources in the South Coast Air Basin
- **Project 3:** Remote Quantification of Stack Emissions from Marine Vessels in the South Coast Air Basin

In addition, SCAQMD has sponsored technology demonstration and validation studies to assess uncertainties associated with different optical techniques through side-by-side measurements of actual sources and controlled source gas releases.

Several research studies, including a FluxSense 2013 pilot project (also sponsored by SCAQMD) suggest that emissions of VOCs from industrial activities are substantially underestimated compared to emission inventories. Systematic underestimation of VOC emissions from the petroleum industry, such as large refineries, has been observed in various areas of the US and around the world during multiple measurement surveys. The project described herein studied emissions from smaller sources such as oil wells, intermediate storage tanks and gas stations. In Los Angeles, these small sources are spread out over the entire Basin and many are located in the immediate proximity of residential areas. Overall, these sources are likely to contribute substantially to smog formation and negatively impact air quality in the region. Thus, a systematic and quantitative assessment of such emissions is required to take appropriate and effective actions, reduce the VOC burden and better understand the extent of any related VOC exposure issues.

METHODOLOGY

This report covers studies of gas emission measurements of alkanes, BTEX (i.e. benzene, toluene, ethyl-benzene and xylenes), methane and, in some cases, ammonia from 62 separate sites belonging to eight different source categories in the SCAB (Table ES. 1). The measurements described in this document stretched from the beginning of September to middle November 2015 and included over 900 individual surveys.

Given the large number of industrial sites in the SCAB and the difficulty to appropriately assess their emission contributions, it is very important to utilize state-of-the-art mobile measurement methods for measuring such emissions in real-time. In this study, emission fluxes (kg/h) of alkanes were quantified using mobile optical Solar Occultation Flux (SOF) measurements.

Furthermore, Mobile White Cell Differential Optical Absorption Spectroscopy (MWDOAS) and Mobile extractive Fourier Transformed Infrared (MeFTIR) techniques were used to measure ground level concentrations of alkanes, BTEX and methane, which allowed us to infer emission fluxes when combined with measured SOF fluxes (see method section for details). In addition, tracer correlation quantification measurements of alkanes and methane, using MeFTIR and N₂O tracer gas release, were performed to obtain emissions from some of the smaller and localized sources. A special study of ammonia emissions from cattle farms using the SOF-technique are also discussed in this report.

Mobile measurements using the FluxSense mobile lab were conducted outside the source site fence-lines along public roads or parking lots. An additional sea-based SOF system was used at sea (Ports of Los Angeles and Long Beach) to assess emissions from fuel islands and off-shore drilling rigs. Background concentrations were subtracted by encircling the sites, when possible, or by checking upwind concentrations, so that only emissions from within the facilities were quantified. Wind data was obtained from a mobile 10 m wind mast or from local met stations, with complementary wind profile information from a Light Detection and Ranging (LIDAR) instrument provided by the SCAQMD. The emission results for each source category are presented as daily and total survey averages and discussed in the context of well-known VOC sources in the SCAB.

SOF is a proven technique that has been developed and applied by FluxSense in over 100 fugitive emission studies around the world. In Europe the SOF technique is considered Best Available Technology (BAT) for measurements of fugitive emission of VOCs from refineries. In Sweden SOF is used together with tracer correlation and optical gas imaging to annually screen all larger refineries and petrochemical industries. The estimated uncertainty for SOF emission measurements is typically $\pm 30\%$ for total site emissions. The estimated measurement uncertainties have been verified in several (blind and non-blind) controlled source gas release experiments (including the one performed during this project and discussed elsewhere) and in side-by-side measurements with other measurement techniques.

Inter-comparison measurements between the SOF method and other optical techniques such as DIAL (Differential Absorption Lidar) and long-path FTIR were also conducted through side-by-side measurements of emissions from tanks inside a refinery, an intermediate oil treatment plant, and storage tanks near oil wells. The agreement of the SOF technique with other optical remote sensing methods was excellent (i.e. 10-20 %). As part of the SOF, DIAL and long-path FTIR technology comparisons, a blind gas release experiment was also carried out using a controlled source emitting 2 to 25 kg/h of odorless propane at the flat open parking lot of the Anaheim baseball stadium in Anaheim, CA. Here the SOF measurements consistently underestimated true emissions by 35%, but showed excellent correlation for the different release rate configurations ($R^2 \sim 98\%$). The results of this technology comparison studies are compiled and presented in a separate document.

RESULTS and DISCUSSION

During this project the Fluxsense mobile laboratory surveyed 61 sites, for a total of 451 individual measurement transects. Emissions flux measurements of alkanes using the SOF method were conducted at all sites. Additionally, emission flux measurements of BTEX (using MWDOAS) and of methane (using MeFTIR) were conducted at 28 and 35 sites, respectively. The total measured emission rates from all surveyed locations was 1318 kg/h for alkanes, 68 kg/h for BTEX (12 kg/h of which was Benzene) and 636 kg/h for methane (Table ES 1).

Furthermore, 483 kg/h of alkanes and 301 kg/h of methane were observed from the area in Carson/Wilmington, which contains a mix of multiple sources which individual contribution could not be apportioned due to the lack of publically assessable roads. Finally, a total of 539 kg/h of methane and 245 kg/h of ammonia were detected from 17 cattle farms in Chino Hills. These last emission results, however, are not presented in table ES.1, since their origin is animal husbandry rather than industrial.

Table ES. 1. Summary of FluxSense VOC emission measurements during the 2015 SCAQMD Project-2 survey. Values from Project 1 (Large Refineries) are also included for comparison (see Project 1 report for details).

Source Category (Project-2)	No. of Units meas.	Unit Type	No. of Units in the SCAB	Tot. sum Alkane Flux [kg/h]	Median BTEX Fraction []*	Median Benzene Fraction []*	Median CH ₄ Fraction []*
Oil & Gas Wells (17 sites)	106	Derricks + small tanks	Over 5000 active wells (DOGGR 2016)	138	0.075	0.012	0.53
Tank Farms, Terminals & Depots (13 sites)	328	Storage tanks	Estimated to 750†	314	0.083	0.010	0.78
Petroleum Treatment Sites & Small Refineries (9 sites)	9	Site	Estimated to 15†	501	0.058	0.014	0.49
Offshore - Facilities & Activities (7 sites)	7	Site	Estimated to 20†	69	n.m.	n.m.	n.m.
Gas Stations (8 sites)	8	Site	Approx. 3140 gasoline - dispensing facilities (SCAQMD, 2016)	10	0.24	0.026	0.25
Other Sources (7 sites)*	7	Site	Unknown	286	n.m.	n.m.	0.38
Sum all Measured Sources and Units (61 Sites)	465	Various	-	1318 [kg/h]	68** [kg/h]	12** [kg/h]	636** [kg/h]
Uncategorized Area Source**	1	Multiple Sites		483	n.m.	n.m.	301
Large Refineries (Project-1)	6	Site	-	1130 [kg/h]	129** [kg/h]	18** [kg/h]	704** [kg/h]

*Fractions are mass relative to alkane mass. **Total flux for BTEX, Benzene and methane are inferred fluxes calculated using median fractions times alkane flux for each category. † Estimation based on visual examination of Google Earth™ maps of the South Coast Air Basin (SCAB). *The category *Other Sources* contains miscellaneous VOC sources. **The *Uncategorized Area Source* is large industrial area in Carson/Wilmington containing several non-separable sites (refineries, tank farm and terminals). n.m.= not measured.

Due to the large number and type of sources in the SCAB and the limited duration of the study, only a subset of sites has been sampled within each source category. Emissions from the measured sources are relevant for understanding their impact on air-quality in the SCAB only if they are scaled-up to the total number of units in the Region. Scaled-up emissions for all source categories / units in the SCAB were derived by multiplying the average emission rates per unit by the estimated number of units within each category.

Based on our measurements, the average emission rates from an *Oil & Gas Wells* unit (Derrick and/or Storage Tank) was 1.3 kg/h of alkanes, 0.1 kg/h of BTEX (including 0.015 kg/h of

Benzene) and 0.3 kg/h of Methane. The average emission for a typical tank within *Tank Farms, Terminals & Depots* was 0.96 kg/h of alkanes and 0.08 kg BTEX (including 0.01 kg/h of Benzene). For the other source categories, each site was treated as a single emission point except for the *Other Sources*, which were too heterogeneous to separate the individual components and, therefore, were treated as one large area source. Obviously, actual emissions from individual components can vary significantly from the presented averages, depending on product handled, working status (e.g. functioning vs malfunctioning units), emission control equipment, etc.

Figure ES. 1 illustrates the relative contribution of each source category to the estimated total alkane emission flux for the stationary sources investigated in this study (Project-2) and from Project-1 (Six Large Refineries). The overall projected alkane emission from the sources investigated during Projects 1 and 2 was estimated to be approximately 12,000 kg/h. According to our calculations gas stations, oil and gas wells, treatment facilities and other small sources contribute to over 85 % of the total value. It should be noted that emissions from Oil & Gas Wells contribute to more than half of the estimated total.

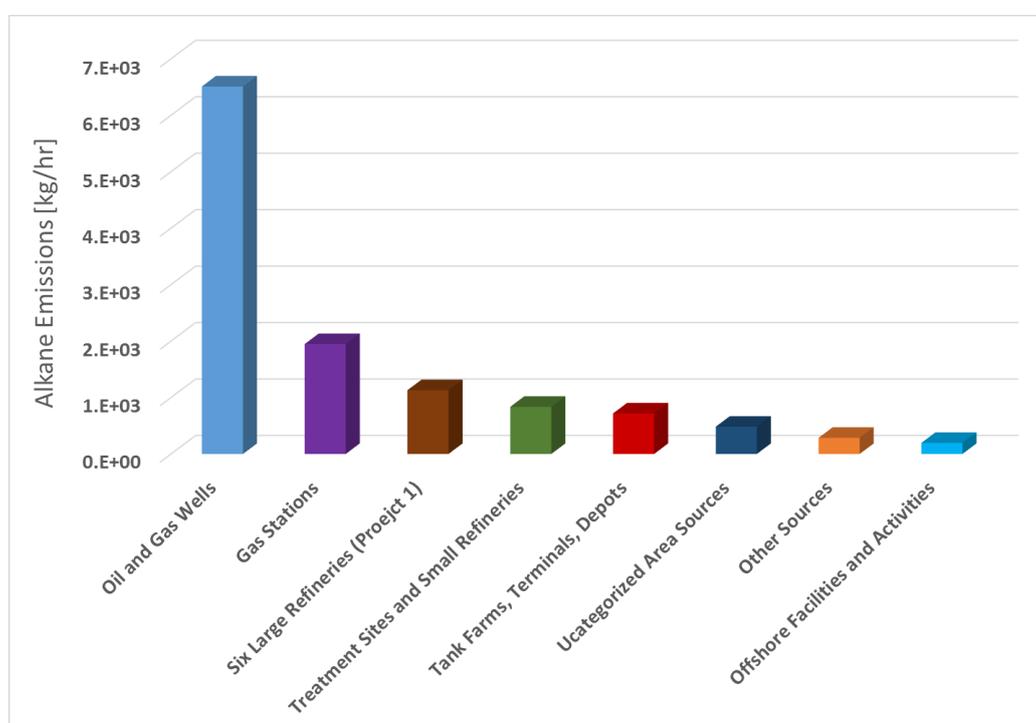


Figure ES. 1. Relative contribution to total **alkane** emissions from the various source categories investigated in Projects 1 and 2. Emission rates for each category were calculated by multiplying the average measured emission per unit by the estimated number of total units. Total alkane emissions are approximately 12,000 kg/h from all included sources.

About 68 kg/h of BTEX (12 kg/h of which was benzene) were directly measured from the subset of sources considered in the project. Scaling-up the observed emissions to account for over 5,000 active oil and gas wells, 3,100 Gas Stations and 750 VOC storage tanks, results in a BTEX load from all measured source categories of around 1,100 kg/h (see Table ES.1). Note that any BTEX emissions from *Offshore Facilities & Activities* and *Other Sources* are excluded here (due to lack of measurements) so the scaled-up value is a conservative value. Despite this limitation, the BTEX emissions from Project-2 sources far surpasses the load from all large refineries in the SCAB (129 kg/h) as measured during Project 1. Considering that a substantial number of sources are located close to residential neighborhoods, these results suggest that further investigation is needed to better quantify the impact of small sources to the total BTEX budget in the Region.

It should be noted that, this scaling-up approach has associated uncertainties because the total number of units has been approximated based on available public information. Additionally, measurements may not be representative for all times of the day and seasons (e.g. gas stations are busier during rush hour traffic, when most of our measurements were made). Total emissions from offshore activities are highly uncertain due to the lack of information on the actual number of fuel barge operations, ship fueling, venting, and other related activities conducted in the Basin. However, at the minimum, this approach provides an indication of the magnitude of all emissions from small stationary sources in the SCAB.

This project also demonstrated the usefulness of conducting mobile survey measurements with optical methods to quickly identify emission and concentration “hot spots” over a large area with multiple emission sources. As such, mobile measurements represent an effective leak detection and repair tool, which can help identify the presence of potential leaks from different parts of a facility. Additionally, mobile measurements provide capability for ground concentration mapping of air toxic pollutants (e.g. BTEX), and as such can be used to assess the health impact of small sources onto neighboring communities.

OUTLOOK

Despite the uncertainties associated with the scaling-up approach adopted here, it is interesting to note that emissions from the six large Refineries (Project-1) only account for a small fraction of the total alkanes and BTEX emissions from stationary sources in the SCAB. Our results suggest that small sources are responsible for the vast majority (over 85 %) of all alkane and BTEX emissions from the stationary sources considered in this study. This finding should motivate further investigation to reconcile measured emission values and estimated emission factors. Additionally, considering the proximity of many of these sources to residential areas, further studies should be conducted to better evaluate potential health impacts on local communities.

The mobile measurement platform and optical methods used in this project allowed for mapping concentrations and measuring fluxes from a large number of sources and source types, and provided very useful information on the relative contribution of small stationary sources to alkane and BTEX emissions in the SCAB. Sources ranged from single oil wells to large tank farms, refineries, and off shore installations. Future studies aimed at improving the emission estimates resulting from this project should include a larger subset of units from all major source categories, and a better characterization of their spatial and temporal variability.

Acronyms, Units and Definitions

Acronyms used in this report

ASOS	Surface Weather Observation Stations
BPD	Barrels per day
BTEX	Sum of Benzene, Toluene, Ethyl Benzene and Xylene
CARB	California Air Resources Board
DOGGR	Division of Oil, Gas & Geothermal Resources, at Department of Conservation CA
DOAS	Differential Optical Absorption Spectroscopy
FTIR	Fourier Transform InfraRed
LDAR	Leak Detection And Repair
LIDAR	Light Detection and Ranging
MWDOAS	Mobile White cell DOAS
MeFTIR	Mobile extractive FTIR
ROG	Reactive Organic Gases
SOF	Solar Occultation Flux
SCAB	South Coast Air Basin
SCAQMD	South Coast Air Quality Management District
VOC	Volatile organic compound, used interchangeably for non-methane VOC

Units

Air temperature	degrees C
Atmospheric Pressure	mbar
Relative Humidity	%
Wind direction	degrees North
Wind speed	m/s
Column	mg/m ²
Concentration	mg/m ³
Flux	kg/h

Unit Conversions

1 lbs = 0.4536 kg
1 kg/h = 52.9 lbs/day
1 bbl = 159 l
1 bbl/day = 5.783 kg/h (crude oil)
1 (short) ton = 907.2 kg
1 kton/year = 104 kg/h
1 klbs/year=0.052 kg/h

Definitions

Alkane or Alkanes are considered to be all non-methane alkane species.

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1 Introduction and Background

Being one of the largest cities in the US and on a global scale, the pollution load to the regional atmosphere of Los Angeles is challenging both for inhabitants getting exposed and for the governing authorities and modelers striving to understand and improve the situation. There are many sources contributing to the air pollution in the South Coast Air Basin (SCAB), both stationary and mobile.

Industrial volatile organic compound (VOC) emissions may contribute to formation of ground level ozone, which is produced through atmospheric chemical reactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in the presence of sunlight, often called photochemical smog. Elevated ozone concentrations are known to reduce crop yields and constitute a public health concern. Larger metropolitan areas in the US, including the SCAB, have trouble meeting ozone standards since anthropogenic sources tend to be concentrated in urban areas, including both mobile and stationary sources. In order to meet current and future more stringent ozone standards in Los Angeles, reductions in VOC emissions are foreseen [Downey et. al. 2015]. VOC emissions from stationary sources, i.e. refineries, storage depots, petrochemical industries etcetera are typically dominated by evaporative losses from storage tanks and process equipment, so-called fugitive emissions. For the SCAB, also fugitive emissions from thousands of active oil and gas wells can contribute to the pollution load. However, actual VOC emissions from distributed sources like oil and gas wells and associated petroleum treatment and intermediate storage installations are uncertain.

Industrial VOC fugitive emissions also contain compounds harmful to human health. For example, aromatic hydrocarbons, including benzene, a known carcinogen, are often found in VOC emissions plumes associated oil and gas extraction. Benzene is also present in gasoline vapors. As a result, a better understanding of sources and magnitudes of fugitive emissions in the SCAB will lead to emission reduction measures leading to potential reduction on health impacts accosted with pollution exposure.

In order to improve our understanding of VOC, NO_2 and SO_2 emissions in the South Coast Air Basin, the South Coast Air Quality Management District (SCAQMD) has promoted and sponsored several measurement projects to study these emissions using optical remote sensing methods. The projects include experimental studies of emissions from refineries, oil depots, treatment facilities, oil & gas wells, gas stations, fuel islands, barges and shipping. In addition, a technology demonstration and validation study was conducted to assess the uncertainties of different optical techniques using side-by-side measurements of real sources and controlled source gas releases.

This report covers the results from the second of three SCAQMD sponsored projects:

- Project 1: 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
- **Project 2: Using Solar Occultation Flux and other Optical Remote Sensing Methods to measure VOC emissions from a variety of stationary sources in the South Coast Air Basin**
- Project 3: Remote Quantification of Stack Emissions from Marine Vessels in the South Coast Air Basin

For Project 2, measurements of alkanes, BTEX and methane emissions from the following six categories of VOC-sources in the SCAB have been conducted:

1. *Oil & Gas wells* (17 sites, 106 units)
2. *Tank Farms, Terminals & Depots* (14 sites, 343 units)
3. *Petroleum Treatment Sites & Small Refineries* (8 sites)
4. *Offshore Facilities & Activities* (7 sites)
5. *Gas Stations* (8 sites)
6. *Other Sources* (7 sites)

In addition to these categories, a large industrial area in Carson/Wilmington was also studied. Since this area contains multiple sites and a large refinery, the results from this area is reported separately as an “*Uncategorized Area Source*”. Another study of emissions from *Cattle Farms* in Chino are also included in this report.

The various result sections in this report further explain the category definitions. We found that the sum of all these sources distributed over the entire SCAB, many of which are located in the immediate proximity of residential areas, is one of the major contributors to VOC-emissions and consequently smog formation in the region.

Emission fluxes of alkanes were measured by mobile optical Solar Occultation Flux (SOF) measurements, for the Cattle Farms ammonia (NH₃) fluxes were also quantified. Emission fluxes of NO₂ and SO₂ were measured using zenith-looking a Differential Optical Absorption Spectrometer (DOAS). The remote sensing techniques were complemented by mobile extractive optical methods, i.e. MeFTIR (Mobile extractive Fourier Transformed Infrared spectrometer) and MWDOAS (Mobile White cell DOAS) to map ground concentrations of alkanes, methane and aromatic VOCs and to calculate inferred fluxes of methane and BTEX when combined with measured SOF fluxes. Direct flux measurements of alkanes and methane, using MeFTIR and tracer gas release (N₂O), were also conducted for some of the smaller and localized sources. A wind-profiling Light Detection and Ranging (LIDAR) instrument supplied by SCAQMD allowed for the continuous measurements of vertical wind profiles. Wind data was also obtained from a mobile 10 m wind mast and from local meteorological stations. Measurements were conducted on land from the FluxSense mobile laboratory, and on water from a research vessel. See Figure 1 for example of measurement setups.

SOF is a proven technique employed by FluxSense in over 100 fugitive emission studies around the world. In Europe the SOF technique is considered one of the Best Available Technology [European Commission 2015] for measurements of fugitive emission of VOCs from refineries; and in Sweden it is used together with tracer correlation and optical gas imaging for annual screening of all larger refineries and petrochemical plants. The estimated uncertainty for the SOF emissions measurements is typically 30 % for the total site emissions. This uncertainty has been calculated from several controlled release experiments (blind and non-blind) and side-by-side measurements with other measurement techniques (also as part of the three SCAQMD projects discussed here).

During this study (Project 2) SOF observations of VOC sources were conducted during 43 measurement days between September 1 and November 15, 2015, resulting in more than 450 transects at 42 different sources. In addition, 23 sources were also measured with MeFTIR combined with tracer gas correlation. Measurements were conducted along publicly accessible roads or parking lots with the FluxSense mobile lab; and from the research vessel within Ports of Los Angeles and Long Beach with a sea-based SOF system, see Figure 1.



Figure 1. Measurement set-ups and scenarios for various sources during the SCAQMD 2015 survey.

For all sources, background concentrations were subtracted by encircling facilities, so that only emissions from within the facilities were quantified. The results are presented as daily and total survey averages, and discussed in the context of our current understanding of magnitude of VOC sources in the SCAB. Examples of some measurement configurations are presented in Figure 1.

2 Instrumentation and Methods

The FluxSense measurement vehicle or “mobile lab” was equipped with four instruments for gas monitoring during the survey: SOF, SkyDOAS, MeFTIR and MWDOAS. Individual measurement methods are described briefly in the subsections below. SOF and SkyDOAS both measure gas columns through the atmosphere by means of light absorption. SOF utilizes infrared light from the direct sun whereas SkyDOAS measure scattered ultraviolet light from the sky. Note that SkyDOAS was only used for Project-1 and Project-3 and is, henceforth, not described in this report. MeFTIR and MWDOAS both measure ground level concentrations of alkanes and BTEX respectively. Accurate wind data is necessary in order to compute emission fluxes. Wind information for the survey was derived from several different sources as described in detail in Section 2.4. A wind LIDAR was used to measure vertical profiles of wind speed and wind direction from 50-1000 m height. The LIDAR data was combined with data from several wind masts from fixed met network- and mobile stations. Figure 2 gives a general overview of the measurement setup and the data flow and pictures of the FluxSense mobile lab is found in Figure 3.

In order to derive final emission flux estimates, the GPS-tagged gas column measurements by SOF and SkyDOAS are combined with wind data and integrated across plume transects at the various source locations. Gas mass ratio measurements by MeFTIR and MWDOAS are then used to infer emission estimates also for methane and BTEX (which can't be measured directly by SOF and SkyDOAS). Occasionally, tracer gas correlation was used at localized sources to measure emissions directly with MeFTIR. Note that SkyDOAS was not used within the present project, but in two the other projects covering refinery and ship emissions.

During the second half of the survey, a smaller SOF instrument was also deployed. This SOF instrument was operated for seven measurement days on a research vessel for offshore measurements between October 13 and October 26, 2015; and for six measurement days between October 29 and November 9, 2015 from the bed of a pick-up truck. Table 1 summarizes the main features and characteristics of all measurement techniques used for this study.

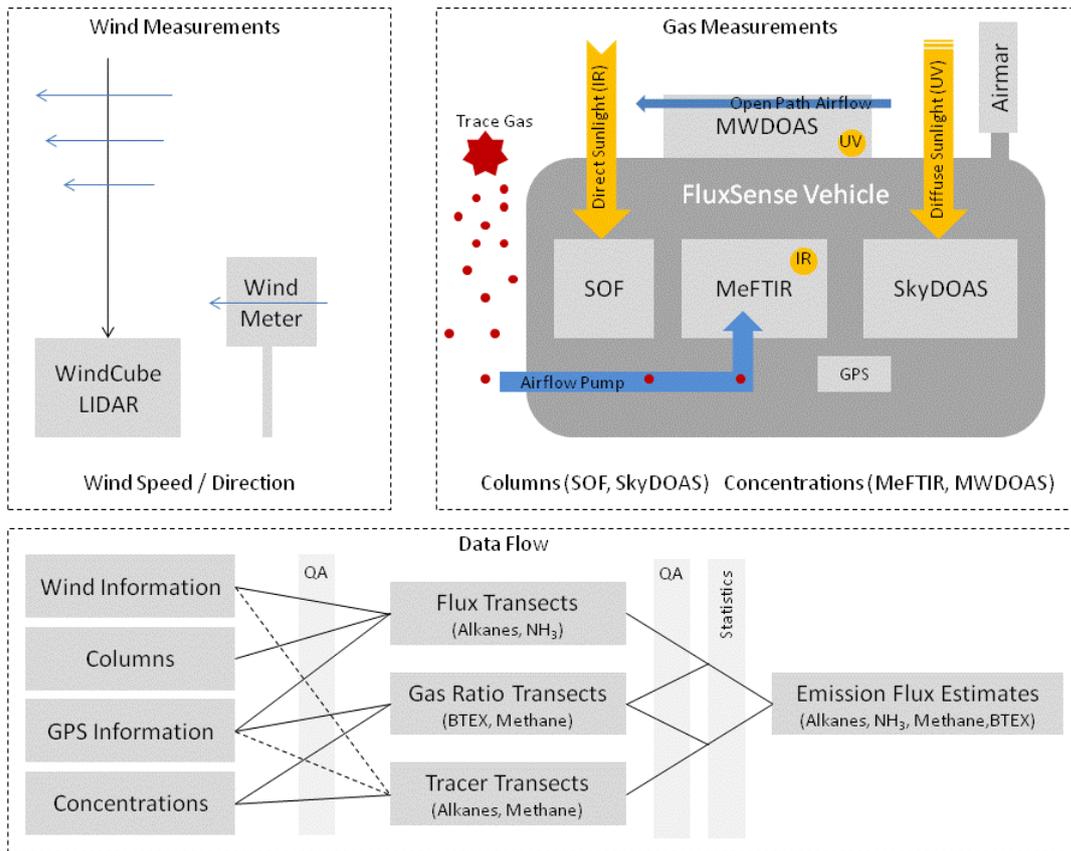


Figure 2. Overview of the FluxSense mobile lab main instruments; SOF, MeFTIR, MWDOAS and SkyDOAS (upper right panel) and wind measurements (upper left panel) and simplified data flow diagram (lower panel). SOF and SkyDOAS are column integrating passive techniques using the Sun as the light source while MeFTIR and SkyDOAS sample local air concentrations using active internal light sources. The data flow describes what information that goes into the flux emission estimates. Direct flux emissions are given from measured columns (SOF and SkyDOAS) of alkanes, SO₂ and NO₂, while inferred fluxes are calculated via gas concentration ratios (MeFTIR and MWDOAS) of BTEX and CH₄. See section 3.2 for principal equations. All emission flux estimates are based on statistical analysis of measured data. Q.C. = Quality Control, S.A.= Statistical Analysis (see Appendix for details). Note that SkyDOAS was not used within Project 2 (this report), but in the other projects covering refinery and ship emissions.



Figure 3. Internal and external view of the FluxSense mobile lab.

Table 1. Summary of FluxSense gas measurement techniques. *For typical wind conditions at an optimal distance from the source. SkyDOAS not used in this project.

Method	SOF	Sky DOAS	MeFTIR	MWDOAS
Compounds	Alkanes: (C _n H _{2n+2}) Alkenes: C ₂ H ₄ , C ₃ H ₆ NH₃	SO₂ NO₂	CH₄ Alkanes: (C _n H _{2n+2}) Alkenes: C ₂ H ₄ , C ₃ H ₆ NH₃ N₂O (tracer)	BTEX
Detection limit Column	0.1-5 mg/m ²	0.1-5 mg/m ²	1-10 ppbv	0.5-3 ppbv
Detection limit Flux*	0.2-1 kg/h	1 kg/h	0.2-2 kg/h	1-2 kg/h
Wind Speed Tolerance	1.5-12 m/s	1.5-12 m/s		
Sampling Time Resolution	1-5 s	1-5 s	5-15 s	8-10 s
Measured Quantity [unit]	Integrated vertical column mass [mg/m ²]	Integrated vertical column mass [mg/m ²]	Mass concentration at Vehicle height [mg/m ³]	Concentration at Vehicle height [mg/m ³]
Inferred Quantity [unit]	Mass Flux [kg/h]	Mass Flux [kg/h]	1) Alkane ratio of ground plume combined with SOF gives mass flux [kg/h] and plume height information [m] 2) Alkane and CH ₄ flux [kg/h] via tracer release	Combined with MeFTIR and SOF gives Mass Flux [kg/h]
Complementary data	Vehicle GPS-coordinates, Plume wind speed and direction	Vehicle GPS-coordinates, Plume wind speed and direction	Vehicle GPS-coordinates Plume wind direction	Vehicle GPS-coordinates, Plume wind direction

2.1 The SOF method

The SOF method [Mellqvist 1999, 2008a, 2008b, 2009, 2010; Kihlman 2005a; Johansson 2014] is based on the recording of broadband infrared spectra of the sun with a Fourier transform infrared spectrometer (FTIR) that is connected to a solar tracker. The latter is a telescope that tracks the sun and reflects the light into the spectrometer independent of the orientation of the vehicle. Using multivariate optimization, it is possible from these solar spectra to retrieve the path-integrated concentrations (referred to as column concentrations), in the unit mg/m², of various species between the sun and the spectrometer. The system used in this project consists of a custom built solar tracker, transfer optics and a Bruker IRCube FTIR spectrometer with a spectral resolution of 0.5 cm⁻¹, equipped with a dual InSb (Indium Antimonide) / MCT (Mercury Cadmium Telluride) detector. A reference spectrum is taken outside the plume so that atmospheric background concentrations are removed. This means that all measured SOF columns are analyzed relative to the background column concentrations.

The system is installed in a measurement vehicle which allows consecutive column concentration measurements to be performed while driving. The flux of a species in a plume from an industry is measured by collecting spectra while driving the vehicle so that the light path from the sun to the instrument gradually cuts through the whole plume, preferably as orthogonally as possible to the wind direction, see Figure 4.

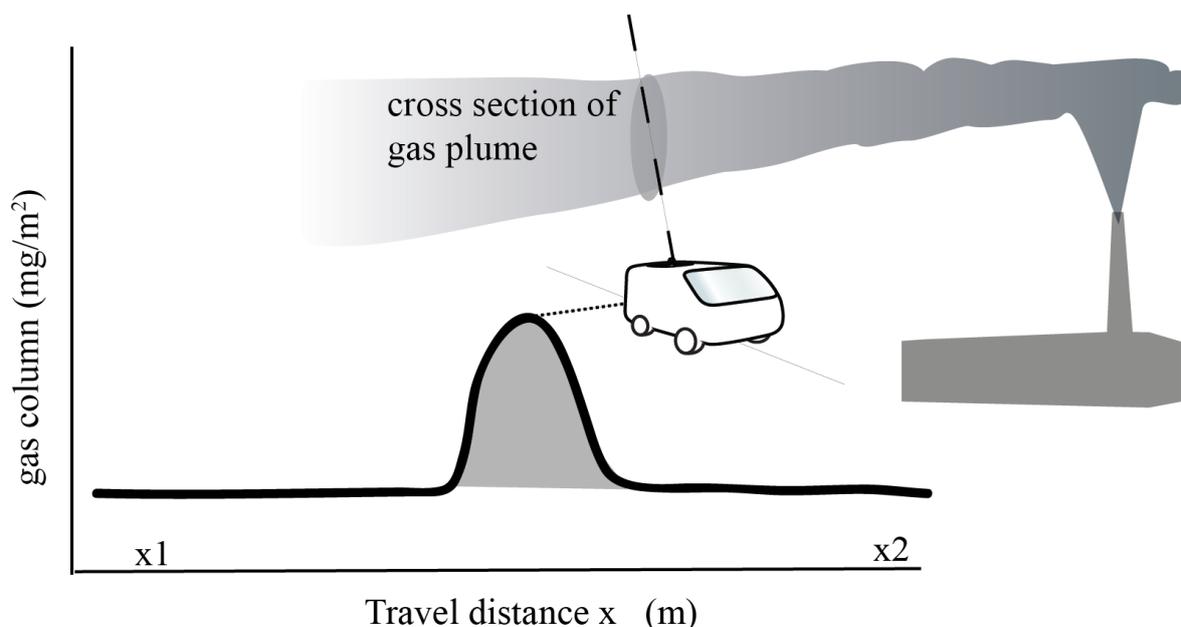


Figure 4. Schematic of the SOF measurement where the vehicle is driven across the prevailing wind so that the solar beam cuts through the emission plume while the sun is locked into the FTIR spectrometer by the solar tracking device on the roof. The VOC mass (or other compound of interest) is integrated through the plume cross section. See section 3.2 for complete equations.

For each spectrum a column concentration of the species is retrieved using custom software (QESOF, i.e. *Quantitative evaluation of SOF*) [Kihlman 2005b]. These column concentrations, together with positions recorded with a GPS (Global Positioning System) receiver and the solar angle calculated from the time of the measurements, are used to calculate the area integrated column of the species in the intersection area between the plume and the light path. The flux of the species is then obtained by multiplying this area integrated concentration with the orthogonal wind speed vector component.

The IR spectra recorded by the SOF instrument are analyzed in QESOF by fitting a set of spectra from the HITRAN infrared database [Rothman 2003] and the PNL database [Sharpe 2004] in a least-squares fitting procedure. Calibration data from the HITRAN database is used to simulate absorption spectra for atmospheric background compounds present in the atmosphere with high enough abundance to have detectable absorption peaks in the wavelength region used by SOF. Spectra, including water vapor, carbon dioxide and methane, are calibrated at the actual pressure and temperature and degraded to the instrumental resolution of the measurements. The same approach is applied for several retrieval codes for high resolution solar spectroscopy developed within Network for the Detection of Atmospheric Composition Change (NDACC) [Rinsland 1991; Griffith 1996] and QESOF has been tested against these with good agreement, better than 3%. For the retrievals, high resolution spectra of ethylene, propene, propane, n-butane and n-octane were obtained from the PNL (Pacific Northwest Laboratory) database and these are degraded to the spectral resolution of the instrument by convolution with the instrument line shape. The uncertainty in the absorption strength of the calibration spectra is about 3.5% for all five species.

In this project, the SOF method was used to measure VOCs in two different modes. Most VOCs with C-H-bonds absorb strongly in the 3.3-3.7 μm (2700-3005 cm^{-1}) spectral region. This region is mainly used for alkane measurements using a spectral resolution of 8 cm^{-1} . Alkenes (including ethylene and propylene) and ammonia are instead measured in the spectral region between 910 and 1000 cm^{-1} using a spectral resolution of 0.5 cm^{-1} . In the alkane mode – the IR

light absorption is essentially sensitive to the total alkane mass (number of alkane C-H bonds) present in the plume. The absorption structures (cross sections) for the various alkane compounds are rather similar, with the absorption strength scaling to the mass of the alkane species. Hence, the actual mix of alkanes in the plume does not affect the retrieved total alkane mass flux much, although only cross sections from a subset of all alkanes (propane, n-butane and octane) are fitted in the spectral analysis. Typically, the rare event of significant absorption from other species in the plume shows up as elevated residuals and is further investigated in the re-analysis. For the alkene mode the specificity of the measurements is good, since the absorption of different species is rather unique in this so called “fingerprint region” and absorption features are often sharp and well separable from each other at 0.5 cm^{-1} resolution.

2.2 Mobile extractive FTIR (MeFTIR)

Mobile Extractive FTIR (MeFTIR) [Galle 2001, Börjesson 2009] in combination with tracers has been used to quantify VOC emissions from refinery and petrochemical sources in Europe and in the U.S. alkanes and alkenes are typically measured, but also methane and other climate gases can be retrieved. MeFTIR is an optical technique capable of monitoring gas concentrations at ppb-sensitivity in mobile field operations. It is used both independently for concentration mapping and flux measurements, but often combined together with simultaneous SOF flux measurements to provide more detailed VOC speciation of plumes and for plume height assessments [Johansson et. al. 2013a]. The plume height can be estimated by dividing measured columns (mg/m^2) with ground concentrations (mg/m^3), assuming that the plume is evenly distributed up to the plume height (and zero above).

The MeFTIR system contains a mid-infrared spectrometer with medium resolution (0.5 cm^{-1}). It utilizes an internal glow bar as an infrared radiation source, and by customized optics this light is transmitted through an optical multi-pass measurement cell with selectable path-length of 9.6-107.2 meters. The system is mounted on a vibration dampening platform to allow for real time plume mapping from a mobile platform, such as a vehicle or boat, see Figure 5.

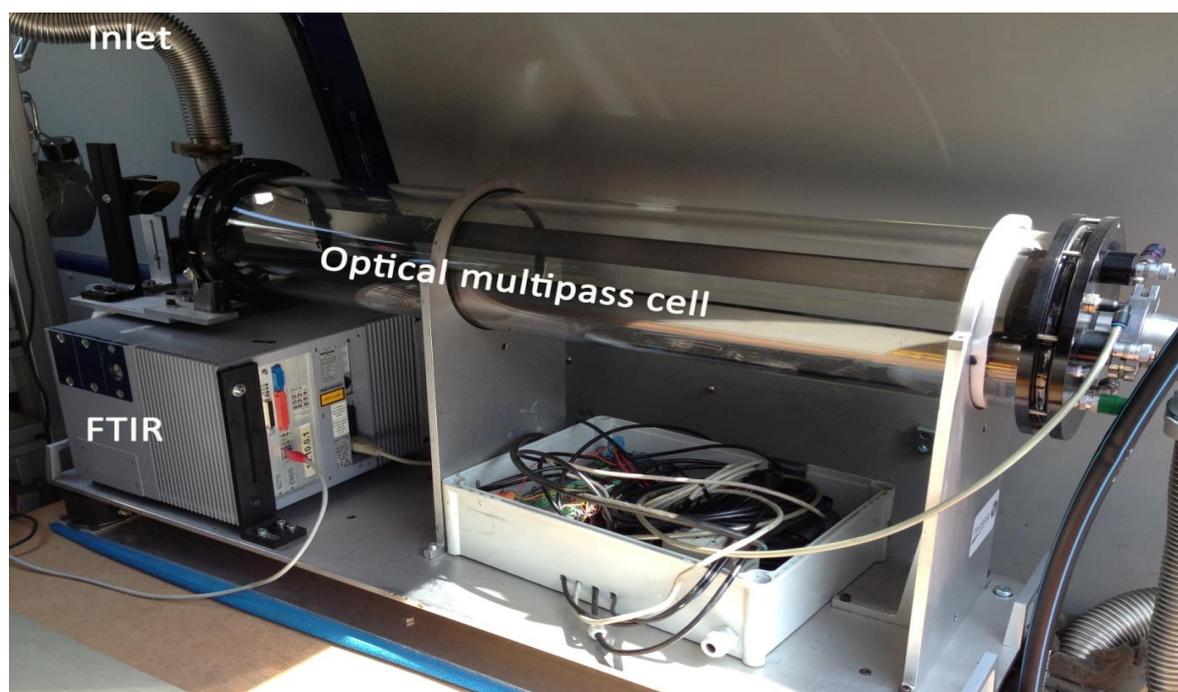


Figure 5. The MeFTIR instrumentation consisting of a Bruker FTIR spectrometer connected to an optical multi-pass cell.

The concentration in the spectra is analyzed in real time by fitting a set of calibrated spectra from the Hitran infrared database [Rothman 2003] and the PNL database [Sharpe 2004] in a least-squares fitting procedure. Compounds being analyzed include ethylene, propylene, total alkane mass (based on fitting cross sections of ethane, propane, n-butane, i-pentane, n-octane), water, methane, CO, CO₂ and N₂O. The analysis routines are very similar to the ones for SOF, but less complex because strong absorption by atmospheric trace gases (water, methane, CO₂) has less consequence at the shorter path length in the MeFTIR measurement cell.

The MeFTIR tracer approach has been tested in a so called gas release “blind test” together with other techniques in U.S. [EREF 2011]. In that test, methane was released from an area-distributed source in four different configurations and flow rates ranging from 1.1-3.3 g/s. At a downwind distance of 400 meters MeFTIR retrieved the fluxes within 6% in 3 cases and 19% in the fourth. This is consistent with other validation experiments, showing a flux estimate accuracy of better than 20%. Concentration measurement by FTIR is a widely used procedure, and the main uncertainties are associated with the absorption cross sections (typically < 3.5%) and spectral retrieval, with an aggregate uncertainty better than 10% in the analysis. Concentrations are monitored in real time in order to detect emission plumes and to judge whether any interfering sources are being sampled. Unwanted signals from local traffic exhaust or from the measurement vehicle itself could be filtered out by looking at the carbon monoxide (typical exhaust compound) concentrations. A stationary source is, on the contrary to any local traffic plumes, characterized by recurrent downwind plumes. Transient and non-repeatable observations are therefore excluded from the results. Furthermore, measurements of ambient concentrations of methane and carbon dioxide (with known atmospheric concentrations) are used for consistency check.

2.3 Mobile White Cell DOAS (MWDOAS)

The ground level mass concentration of Benzene, Toluene, Ethylbenzene, meta- and para-Xylene (BTEX) was measured using a mobile real-time system: Mobile White cell DOAS (MWDOAS). The Mobile White cell DOAS system consists of an open, 2.5 m long optical White cell that is mounted on the roof of the measurement vehicle (see Figure 6). By multiple reflections in the White cell mirror system an overall path length of 210 m is obtained, resulting in low detection limits (ppb). The light from the internal lamp is transmitted through the White cell and then analyzed in a DOAS spectrometer, using the UV wavelength region 255 - 285 nm.

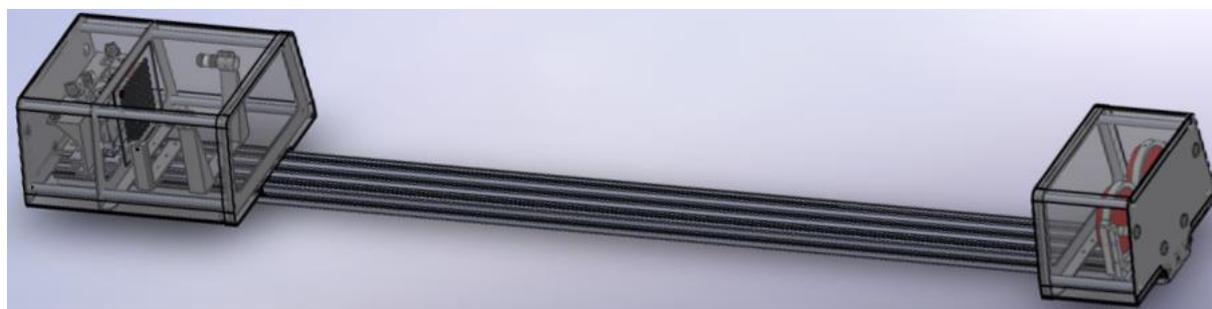


Figure 6. The open path MWDOAS cell having an overall optical path-length of 210 m.

A measurement begins by acquiring a reference spectrum outside the plume, usually upwind of the facility. Spectra are then sampled and averaged continuously while driving through emission plumes. The averaging time is set to around 8 seconds in order to achieve acceptable SNR (see below). This is the lower limit of the temporal sampling between independent

measurements, but the spatial sampling is also dependent by the vehicle's velocity. A typical driving speed for MWDOAS measurements is 10-20 km/h for sufficient plume sampling.

The spectra are geo-tagged and evaluated online using the standard DOAS technique, giving information of plume locations and constituents. Cross-sections included in the evaluation are tabulated in Table 2.

Table 2. The UV-cross-sections used in the evaluation of the MWDOAS spectra.

Chemical compound	Origin of reference spectrum
O ₃	[Burrows 1999]
SO ₂	[Bogumil 2003]
O ₂	[Bogumil 2003]
Toluene	[Fally 2009]
Benzene	[Etz Korn 1999]
1,3,5-Trimethylbenzene	[Etz Korn 1999]
1,2,4-Trimethylbenzene	[Etz Korn 1999]
Styrene	[Etz Korn 1999]
Phenol	[Etz Korn 1999]
p-Xylene	[Etz Korn 1999]
m-Xylene	[Etz Korn 1999]
Ethylbenzene	[Etz Korn 1999]

The MWDOAS data is later post evaluated and merged with the corresponding MeFTIR data to produce a plume specific BTEX/Alkane mass ratio. The mass ratio of BTEX/Alkanes is then used to calculate the aromatic flux from individual sub areas where alkane fluxes have been measured by SOF, assuming they have the same source. Specific area plumes are ideally probed at several times, and an overall average of all plume transect BTEX/Alkane ratios is then made. The method requires in situ access to the plume of the studied source, and as instrumentation typically are mounted on a truck, highly elevated sources with a strong plume lift like hot flares, chimneys and high process towers will not be possible to survey at close distance.

The MWDOAS technique has been validated in various surveys by comparison with canister samples acquired at several different locations and which were subsequently analyzed by gas chromatography (GC-FID). The validation shows that the result from MWDOAS lies well within 10% of the result of the certified canister results for BTEX. Due to an absorption cross-section too weak to be used with reliability in the MWDOAS analysis, the ortho isomer of the Xylene has been omitted in this comparison. When total Xylene is presented in the present survey, the sum of m- and p-Xylenes from the MWDOAS measurement is multiplied by 1.32. This number comes from a ratio comparison of Xylene isomers in 49 canister samples analyzed by GC/FID and taken from eight refineries and tank parks from two countries. The standard deviation in this comparison was 0.07 and adds a 4.5% uncertainty to the total Xylene concentration. Hence, the Xylene concentration from MWDOAS is defined as the sum of the measured m- and p-isomers and the inferred o-isomer.

The MWDOAS system has been used in previous campaigns in USA during 2013 with good results. During the 2013 DISCOVER-AQ campaign [Johansson, 2013b] in Houston, Texas, the system was run in parallel to a mobile Proton Transfer Mass spectrometer (PTrMS) lab as a validation check. The results of Benzene, Toluene and Styrene was compared and showed good agreement, with the PTrMS showing slightly elevated Benzene concentrations compared to the MWDOAS. The sensitivity of MWDOAS is better than 1 ppb for Benzene, better than 3 ppb for Toluene, Ethylbenzene and m-Xylene and as good as 0.5 ppb for p-Xylene.

Since the distribution of the BTEX constituents varies with source we will also present the Benzene to alkane ratio to facilitate the calculation of Benzene flux and identify specific Benzene sources.

Unwanted BTEX signals from local traffic exhausts are generally only significant in congestions (at traffic lights etc.) or in confined spaces, e.g. tunnels. Apart from this, large emitters are also occasionally seen elsewhere. They are generally recognized, partly by their typical gasoline composition signature and partly by their transient nature. A stationary BTEX source is, on the other hand, characterized by recurrent downwind plumes. Transient and non-repeatable BTEX observations are therefore excluded from the result. Note that all concentrations are above the reference/background.

2.4 Wind Measurements and Auxiliary Data

Wind LIDAR

An infrared 3D wind LIDAR provided by SCAQMD was used to measure vertical wind profiles of wind speed and direction. The Leosphere WindCube 100S LIDAR provided wind profiles in the vertical range of 50 m to approximately 1000 m above ground, with 25 m vertical resolution, and wind speed accuracy of 0.5 m/s. The system records 1s data, but 10 minute averages were used for flux calculations in this study. The principle of detection is based on the Doppler shift of the infrared pulse that the instrument sends out and retrieves. Numerous validation surveys attesting the accuracy of the WindCube LIDARs are publically available at www.leosphere.com.



Figure 7. The WindCube 100S (Leosphere) LIDAR used for wind profile measurements in this project.

Wind Masts

Meteorological parameters were measured at selected sites using a portable 3-10 m mast. This mast was equipped with a calibrated RM Young 05108 “prop and vane” anemometer and a Campbell Scientific CR5000 data-logger, see Figure 7. An additional wind mast with a Gill Wind Sonic ultrasonic sensor was occasionally used to measure wind speed and direction.

The weather mast was installed at an open location near the measured source and with unobstructed fetch for wind directions that was used for SOF measurements. The sensor was adjusted to point towards magnetic north but compensated to true north in the post-processing. Wind speed information from the 10-m mast was the main source of wind information for the sources at near distance since plumes are found to be closer to the ground as compared to large refinery plumes. See section 3.4 for a thorough wind analysis.



Figure 8. The FluxSense mobile wind mast used in the 2015 SCAQMD survey with an RM Young anemometer mounted on top. The mast could be erected from 3 to 10 m.

Airmar (Mobile Weather Station)

An Airmar WeatherStation (200 WX) sensor was installed on the roof of the measurement vehicle to complement the other wind measurements and give local ground winds at the vehicle. An additional Airmar Weather Station was also mounted on the top of the research vessel during offshore measurements.

The wind information from the car-based Airmar was not used for flux calculation since the wind field at street level can be heavily disturbed and turbulent. The Airmar was only used as a real-time aid to keep track of the plume directions when making the gas emission measurements. The vessel-based Airmar, on the other hand, was used for flux calculations.

The Airmar provides wind speed and direction relative to true north (compensating for vehicle position), as well as air temperature, pressure and relative humidity. It also provides GPS positions that may be used as a backup for the other GPS-antenna.

GPS

The FluxSense vehicle is equipped with two standard USB GPS-L1 receivers (GlobalSat BU-353S4) hooked up to the SOF and MWDOAS-computers. They are placed horizontally by the windscreens and at the sun-roof for optimal reception. The receivers give the position at a rate of 1 Hz.

3 Measurement Methodology

Typically, the main instruments in the FluxSense mobile lab are operated during favorable meteorological conditions. SOF and Sky-DOAS are mainly used during solar/daytime measurements and MWDOAS and MeFTIR for gas ratio measurements during day or cloudy/nighttime conditions. Plume height calculations are dependent on simultaneous SOF and MeFTIR measurements of alkanes, so MeFTIR was typically running during solar/daytime conditions, when feasible. MWDOAS and SkyDOAS were sharing the same spectrometer in this survey. Hence, time sharing between two different techniques was necessary. In addition to the gas mass ratio measurements by MWDOAS and MeFTIR, canister samples were taken when measuring selected plumes for VOC speciation and complimentary data.

SOF was the primary flux emission measurement technique for this study, but some sources with very small footprint were measured using MeFTIR and tracer gas release. This approach was found to be more favorable for small localized sources and was used for all gas stations and for a few wells- and petroleum treatment sites.

3.1 Survey Setup

The project objective was to quantify the gas emissions of alkanes (non-methane), BTEX and methane from a variety of stationary sources distributed in the SCAB, see Figure 9, in order to obtain a better understanding of the overall VOC load to the Los Angeles atmosphere. For some “organic” sources, such as cattle farms, NH₃ fluxes were also measured. In addition, emissions from “special events” such as flaring and fracking were monitored during the study. The observations were mainly done by fence-line measurements along accessible roads outside the facilities using SOF but also with MeFTIR using N₂O as tracer gas when feasible. In this case the tracer gas was released as close to the source as possible. Furthermore, ground concentration measurements were carried out with mobile MWDOAS and MeFTIR instruments to infer emissions of methane, BTEX and specifically benzene.

The gas measurements were combined with wind data, primarily from a mobile 10 m wind mast but also from adjacent stationary meteorological stations, to calculate fluxes and identify sources. The locations of the small sources are shown as colored flags in Figure 9. Area sources are also noted as colored regions. Locations of meteorological stations are shown in Figure 10. Note that individual sources vary in physical size, number of units (e.g. number of tanks, wells, derricks, etc.) or capacity, but each category represents an ensemble of typical sources.

To be able to get a good selection of sources during the time-frame of the project, several sources were covered during each measurement day. For statistical reasons, the aim was to get more than one transect of each source for each time. Some of the sources, however, were discovered accidentally while passing by and, therefore, have less statistical significance. Furthermore, many of the sources were revisited on several days in order to understand the day-to-day variability of emissions.

Plume separation from different sources were performed by encircling the source and subtracting incoming plumes from the outgoing. When encircling the source was not possible (e.g. lack of accessible roads), relevant upwind measurement transects were instead made in close proximity in space and time.

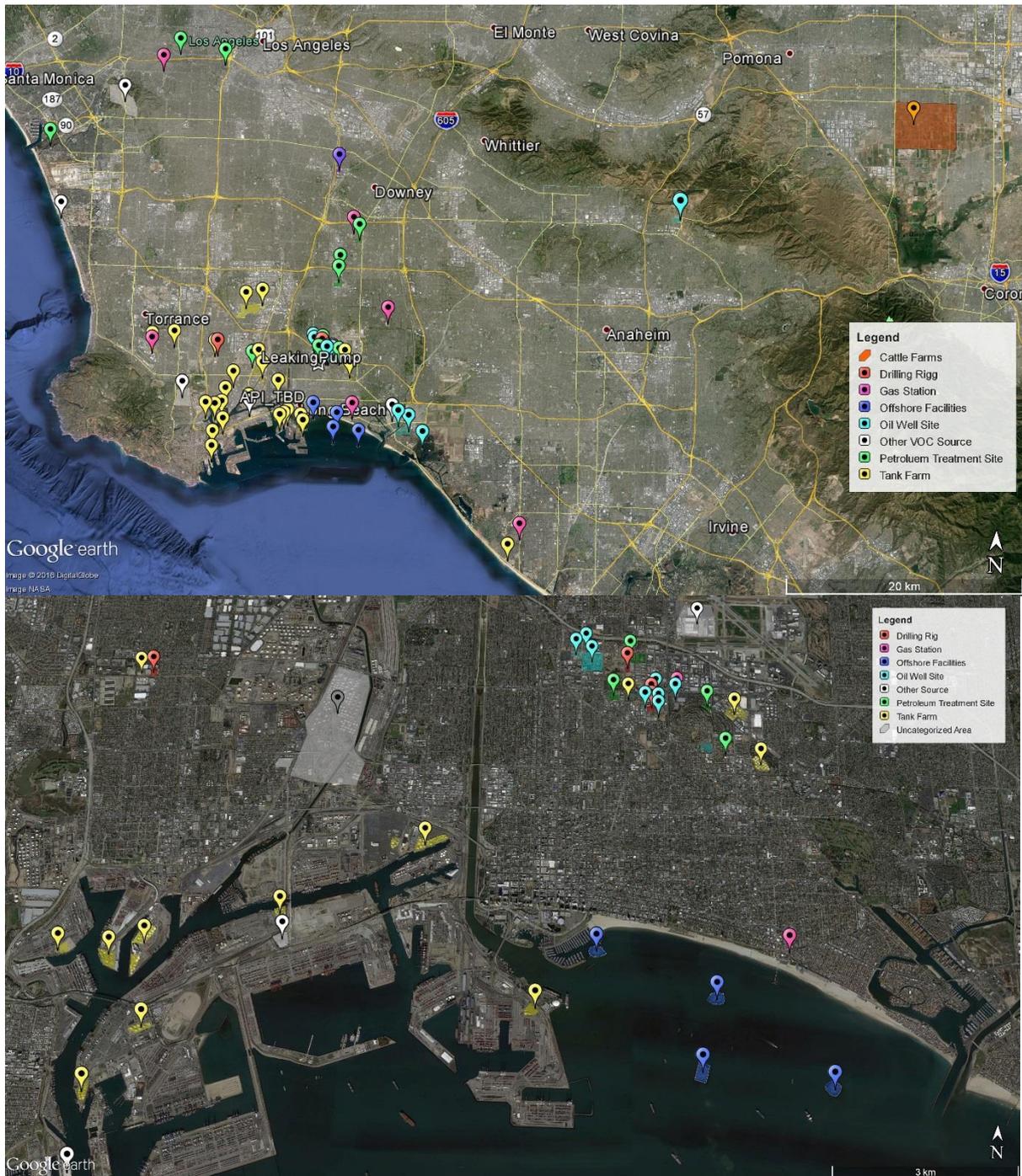


Figure 9. Overview of the measured small sources in the SCAQMD survey 2015. Entire Los Angeles basin (top) and zoomed in at Long Beach/Signal Hill (bottom). Map from Google Earth © 2016.

Observations of sources were made during 43 measurement days between September 1 and November 11, 2015, resulting in more than 450 successful transects of 62 different sources. Of these measurement objects, 42 were made with SOF and 23 sources with MeFTIR + tracer correlation. The number of successful measurements varied substantially from day to day and from source to source depending on weather conditions, local measurement conditions (accessibility, state of the roads, obstacles etc.) and time sharing between different projects, objects and instruments.

Statistical estimates of the flux emissions (kg/h) from the various sources were computed for each measurement day and for the entire survey. This data is compared within and between categories and to the measured emissions from the six largest refineries (Project-1). Extreme events area also identified specifically in the report.

All sources are categorized and assigned names based on the type of source, followed by the closest road intersection and by location of the source relative to that intersection. Table 3 provides a complete list of sources characterized during this project.

Table 3. Overview of all measured sources in SCAQMD 2015, Project-2. Latitude and longitude links refer to Google Maps. Source are identified as following: Source type_Closest road intersection,_Direction to the source from the intersection. Number of units noted, where applicable.

Source Name (Intersection) and Category	No of Units	Latitude, Longitude
Oil & Gas Wells (Derricks, Tanks and Drilling Rigs)	Derricks and Tanks	
Wells_AtlanticAve_ESpringSt_SE	31	33.810703, -118.182837
Wells_WalnutAve_CrescentHeightsSt_NE*	5	33.803406, -118.169738
Wells_AtlanticAve_ESpringSt_SW	16	33.811014, -118.185985
Wells_MarbellaAve_ESepulvedaBlvd_SSW	7	33.808440, -118.175760
Wells_OrangeAve_E28thSt_NW	1	33.806331, -118.272040
Wells_RoseAve_CrestonAve_SW	4	33.799705, -118.169604
Wells_TempleAve_E21stSt_SW	17	33.794458, -118.160333
Wells_ValenciaAve_ELambertRd_NW	8	33.925451, -117.851639
Wells_WalnutSt_W236thSt_SW	4	33.811055, -118.312400
Wells_AtlanticAve_ESpringSt_NW	1	33.812020, -118.184205
Wells_RoseAve_EWillowSt_S	1	33.803759, -118.170132
Wells_GardenaAve_EBurnettSt_NW	2	33.801084, -118.169583
Wells_NOrizabz_E20th_SE	1	33.793222, -118.156420
Wells_PuertoNatalesDr_VinaDelMarAve_SE	2	33.882638, -117.839950
Wells_RoseAve_CrestonAve_SW	4	33.799682, -118.169546
Wells_JeffersonBlvd_BudlongAve_W	1	34.026293, -118.296273
Wells_TonnerCanyonRd_W	1	33.932614, -117.860209
	Sum 106	
Tank Farms, Terminals & Depots	Tanks	
TankFarm_HarbourPlaza_SHarborScenicDr_SE	28	33.750290, -118.192666
TankFarm_PierASt_PierAPI_SW	24	33.756409, -118.272007
TankFarm_RedondoAve_EPacificCoastHwy_NE	24	33.791695, -118.149814
TankFarm_SHenryFordAve_DockSt_NW	54	33.763783, -118.240870
TankFarm_SanClementeAve_SLaPalomaAve_W	43	33.758410, -118.265735
TankFarm_RedondoAve_EWillowSt_SW	24	33.801228, -118.154506
TankFarm_NParamountBlvd_ESouthSt_NW	30	33.865179, -118.163399
TankFarm_WEdisonWay_LuggerWay_SW	10	33.775727, -118.220775
TankFarm_WarfSt_SeasideAve_SW	19	33.735570, -118.272952
TankFarm_FerrySt_PilchardSt_W	7	33.745416, -118.264016
TankFarm_OrangeAve_E25thSt_NE*	12	33.802769, -118.175764
TankFarm_EdisonAve_PierBSt_SE	35	33.776690, -118.213158
TankFarm_JohnSGibsonBlvd_E	18	33.756741, -118.281578
	Sum 328	

Petroleum Treatment Sites & Small Refineries		
TreatmentSite_WilmingtonAve_EDelAmoBlvd_SE	n.a.	33.845094, -118.232228
TreatmentSite_TempelAve_CombellackDr_SW	n.a.	33.801815, -118.159817
TreatmentSite_StJamesPark_W23rdSt_SE	n.a.	34.032084, -118.278116
TreatmentSite_OrangeAve_ESpringSt_SE	n.a.	33.810722, -118.174118
TreatmentSite_LewisAve_EWillowSt_SE	n.a.	33.803451, -118.178492
TreatmentSite_GreenwichCir_RumsonSt_E	n.a.	33.880558, -117.840767
TreatmentSite_SMainSt_WSepulvedaBlvd_SSE	n.a.	33.804931, -118.274477
Refinery_LakewoodBlvd_SomersetBlvd_NW	n.a.	33.898365, -118.147114
Refinery_NParamountBlvd_EArtesiaBlvd_SW	n.a.	33.873691, -118.162155
Offshore Facilities & Activities		
OffShore_FuellIsland_Chaffet	n.a.	33.739580, -118.138958
OffShore_FuellIsland_Freeman	n.a.	33.741482, -118.162368
OffShore_FuellIsland_Grissom	n.a.	33.759425, -118.181594
OffShore_FuellIsland_White	n.a.	33.752502, -118.159479
OffShore_FuelBarges_PortLA	n.a.	variable
OffShore_ShipVenting	n.a.	variable
OffShore_ShipFueling	n.a.	variable
Other Sources		
FuelSupply_SWesternAve_PalosVerdesDrN_SE	n.a.	33.773836, -118.301677
Seaside_45thSt_VistaDelMarBlvd	n.a.	33.907980, -118.423985
Industry_area_CherryAve_EWardlowRd_SE	n.a.	33.816891, -118.162508
PowerPlant_TerminalIslandFwy_SeasideFwy_NW	n.a.	33.759775, -118.240113
OtherSite_AlamedaSt_PacificCoastHighwaySt_SO	n.a.	33.789433, -118.243065
Old_TankFarm_SignalSt_E22St_SE	n.a.	33.724073, -118.273188
Source_Valencie_Lambert_Brea_olinda	n.a.	33.924553, -117.848440
Gas Stations		
	Average # of fueling cars at gas station	
GasStation_CherryAve_EWillowSt_SE	8.1	33.804102, -118.165788
GasStation_DowneyAve_RosecransAve_SE	2.9	33.903581, -118.151222
GasStation_GoldenwestSt_YorktownAve_NE	2.2	33.679586, -118.005702
GasStation_BeachBlvd_AdamsAve_NE	2	33.672554, -117.989038
GasStation_CrenshawBlvd_SkyparkDr_NW	15	33.805578, -118.332870
GasStation_CrenshawBlvd_WJeffersonBlvd_NW	2.6	34.025814, -118.335617
GasStation_EOceanBlvd_ELivingstonDr_E	1	33.760373, -118.145459
GasStation_WoodruffAve_HarveyWay_SE	2.9	33.834452, -118.116030
Uncategorized Area Source		
TankFarm&Refineries_Sepulveda_Alameda_SE	n.a.	33.802607, -118.233229

3.2 Principal Equations

This report includes three different techniques to measure emission mass fluxes as specified below. The primary method in this project is the direct flux measurements of alkanes from SOF. Secondary method (for small and confined sources) is tracer gas measurements from MeFTIR using N₂O as tracer gas. BTEX and methane fluxes are calculated using inferred fluxes from MWDOAS/MeFTIR gas mass ratios.

3.2.1 DIRECT FLUX MEASUREMENTS:

The emission mass flux (Q) of species (j) measured by SOF for a single transect (T) across the plume (P) along path (l) can be expressed by the following integral (SI-units in gray brackets):

$$Q_T^j [\text{kg/s}] = \bar{v}_T [\text{m/s}] \cdot \int_P C_l^j [\text{kg/m}^2] \cdot \cos(\theta_l) \cdot \sin(\alpha_l) dl [\text{m}]$$

Where,

\bar{v}_T = the average wind speed at plume height for the transect,

C_l^j = the measured slant column densities for the species j as measured by SOF or SkyDOAS,

θ_l = the angles of the light path from zenith ($\cos(\theta_l)$ gives vertical columns),

α_l = the angles between the wind directions and driving directions

dl = the driving distance across the plume

Note that SOF and SkyDOAS have different light paths, where the SkyDOAS telescope is always looking in the zenith direction while the SOF solar tracker is pointing toward the Sun. Hence, the measured SOF slant column densities will vary with latitude, season and time of day.

To isolate emissions from a specific source, the incoming/upwind background flux must be either insignificant or subtracted. If the source is encircled or “boxed”, the integral along l is a closed loop and the flux calculations are done with sign. This is taken care of by the FluxSense software.

3.2.2 INFERRED FLUX MEASUREMENTS:

Inferred flux is computed using a combination of SOF and MeFTIR/MWDOAS measurements.

The inferred mass flux (\hat{Q}^i) for species (i) are calculated from MeFTIR and/or MWDOAS ground level gas ratios integrated over the plume (P) along path (l) are given by (SI-units in gray brackets):

$$\hat{Q}^i [\text{kg/s}] = \bar{Q}^j [\text{kg/s}] \cdot \frac{1}{k} \sum_k \frac{\int_P N_l^i [\text{kg/m}^3] dl [\text{m}]}{\int_P N_l^j [\text{kg/m}^3] dl [\text{m}]}$$

Where,

\bar{Q}^j = the average flux of species j from multiple transects as measured by SOF,

N_l^i = the number density concentrations of species i as measured by MWDOAS or MeFTIR,

N_l^j = the number density concentrations of species j as measured by MeFTIR,

k = the number of gas ratio measurements

Note that the inferred flux calculation operates on average values since simultaneous SOF, MWDOAS and MeFTIR measurements are generally not performed and because individual gas ratios are more uncertain than the average. Although not necessarily simultaneously measured, SOF and MeFTIR/MWDOAS measurements must represent the same source plume. Note also that gas ratios do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume is well mixed at the sampling distance.

3.2.3 TRACER GAS FLUX MEASUREMENTS:

The third method to conduct flux measurements is by tracer correlations using only MeFTIR measurements or simultaneous MeFTIR and MWDOAS measurement and a known tracer gas release. These fluxes are given for each transect (T) by the following equation (SI-units in gray brackets):

$$Q_T^j [\text{kg/s}] = Q^{\text{tracer}} [\text{kg/s}] \frac{\int_P N_l^j [\text{kg/m}^3] dl [\text{m}]}{\int_P N_l^{\text{tracer}} [\text{kg/m}^3] dl [\text{m}]}$$

Where,

Q^{tracer} = the release mass flux of the tracer gas from bottle,

N_l^{tracer} = the number density concentrations of the tracer as measured by MeFTIR,

N_l^j = the number density concentrations of species j from MeFTIR or MWDOAS,

Note that tracer gas correlation fluxes do not intrinsically depend on complete plume transects (like for direct flux methods) as long as the emission plume and the tracer gas is well mixed at the sampling distance. Complete plume transects are, however, recommended since the tracer gas release point might not completely match at the sampling distance.

3.3 Uncertainties and Error Budget

A summary of the performance of the FluxSense measurements is presented in Table 4.

Table 4. Performance overview of FluxSense measurement methods.

Measurement Parameter	Analysis Method	Accuracy	Precision	Completeness*
SOF column concentrations alkanes, alkenes, NH ₃	QESOF spectral retrieval	±10%	±5%	70-90%
SkyDOAS column concentrations NO ₂ , SO ₂	DOAS spectral retrieval	±10%	±5%	70-90%
MeFTIR concentrations CH ₄ , VOC, NH ₃ , N ₂ O	QESOF spectral retrieval	±10%	±5%	95%
MWDOAS concentrations BTEX, Benzene	MWDOAS spectral retrieval	±10%	±5%	90%
Wind Speed (5 m)	R.M. Young Wind monitor	±0.3 m/s or 1%	±0.3 m/s	95%
Wind Direction (5 m)	R.M. Young Wind monitor	±5°	±3°	95%
Wind Speed (10 m)	Gill WindSonic	±2%	-	95%
Wind Direction (10 m)	Gill WindSonic	±3°	-	95%
LIDAR Wind Direction (50-1000m)	Leosphere Windcube 100S	-	-	>90% except in heavy fog
LIDAR Wind Speed (50-1000 m)	Leosphere Windcube 100S	±0.5 m/s	-	
GPS position	USB GPS receiver	±2m	±2m	100%
SOF mass flux Alkanes, alkenes, NH ₃	SOF-Report flux calculations	±30%	±10%	80% (in suitable weather conditions)
MeFTIR+tracer mass flux Alkanes	SOF-Report MeFTIR+tracer flux calculations	±25%	±10%	95%
SkyDOAS mass flux NO ₂ , SO ₂	SkyDOAS flux calculations	±30%	±10%	80% (in suitable weather conditions)

* For the optical measurements conducted in this project data completeness is difficult to estimate since the measurements are dependent on external parameters such as weather conditions.

Accuracy of measurement parameters is determined by comparing a measured value to a known standard, assessed in terms of % bias using the following equation:

$$\left[1 - \left(\frac{\text{Measurement}}{\text{Standard}} \right) \right] \times 100$$

Precision is a measure of the repeatability of the results. The precision for the SOF and mobile DOAS system is difficult to measure when inside the gas plumes. However, it is assumed that the precision of the instrument corresponds to the 1-sigma noise when measuring in clean air background. The precision of each instrument used in the project is listed in Table 4.

Data completeness is calculated on the basis of the number of valid samples collected out of the total possible number of measurements. Data completeness is calculated as follows:

$$\% \text{ Completeness} = \left(\frac{\text{Number of valid measurements}}{\text{Total possible measurements}} \right) \times 100$$

3.4 Wind Measurements

The main source of wind information for this project was the FluxSense mobile 3-10 m wind mast equipped with a calibrated RM Young anemometer. The mast was, most of time, mounted on the bed of a pick-up truck and erected from 3 to 10 m depending on the studied object, see Figure 11. An open spot close to the source was chosen for the wind meter. For measurements with no relevant wind mast data available, wind data from an adjacent met station (SCAQMD, ASOS or internal Tesoro/Carson) was used, see Figure 10. For sea-based measurements, data from the AIRMAR sonic sensor, mounted on the top of the vessel (approximately 5 m above sea level), was used, see Figure 12.

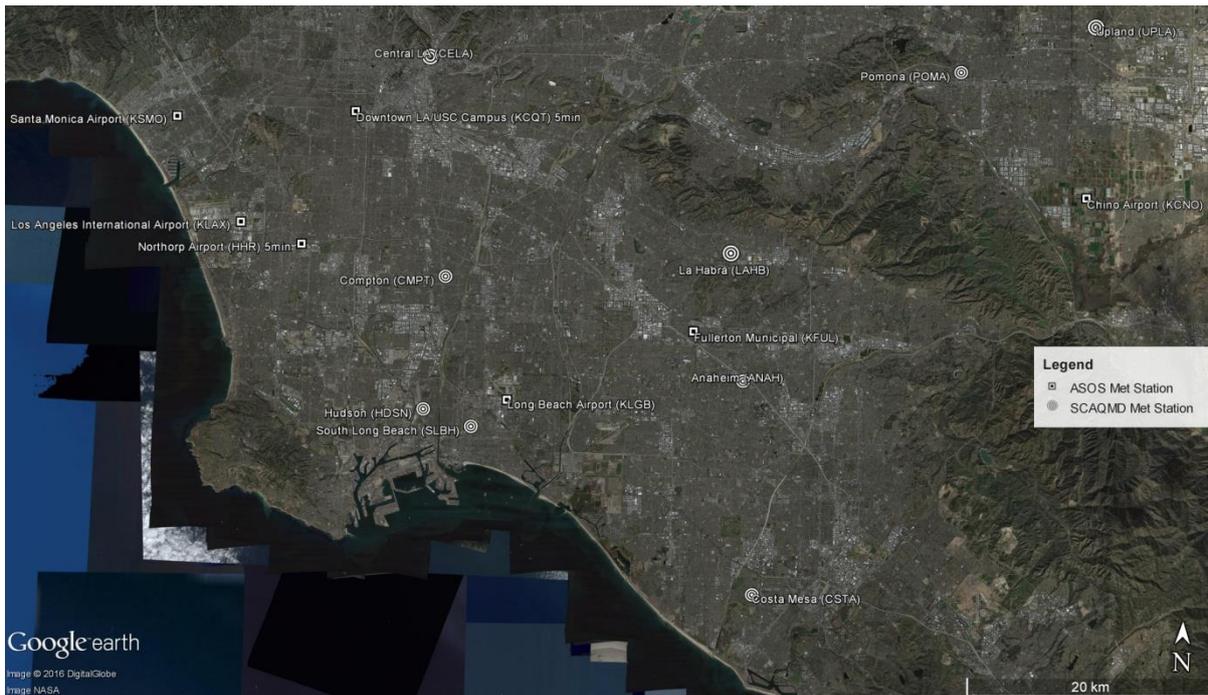


Figure 10. SCAQMD and ASOS Met Stations in the Los Angeles basin. Map from Google Earth © 2016.

The largest source of error in SOF measurements of emission fluxes is typically the wind measurements. The flux is directly proportional to the wind speed (at average plume height) and to the cosine of the wind direction relative to the driving direction. The wind error is a combination of errors in the wind measurements themselves (see Table 4) and errors due to the assumption that the wind velocity measured in a particular way is representative of the average plume velocity. Note that MeFTIR+tracer flux calculations do not include any wind information (only indirectly dependence via wind turbulence mixing) and that the wind field uncertainty consequently can be ignored for these measurements.

Wind profile data, as supplied by a LIDAR, has the major advantage of allowing an average wind for an arbitrary height interval to be calculated. Given some approximate information about the mixing height of the plume, a suitable averaging interval can be chosen, and the LIDAR data can also be used to estimate the sensitivity of the wind error to the error in the mixing height. Hence, LIDAR data was main source of wind information for the refineries in Project-1 with extensive plumes, sampled several hundred meters downwind the facilities. For small sources in this project (Project-2) measured at a closer distance, the wind-LIDAR is typically not as suitable since its lowest sampling altitude of the LIDAR is 50 m.



Figure 11. FluxSense mobile wind mast mounted on the bed of pick-up truck. An RM Young anemometer is used throughout the project. The mast could be erected from 3 to 10 m.

First order estimates of the plume mixing height estimates can be retrieved by simultaneous concentration and column measurements with SOF and MeFTIR as described in Section 2.2. The method assumes homogeneous plume concentrations from ground level to the plume height and zero above, and results are used to indicate if the plume is close to ground or aloft where the wind speed changes less rapidly with height compared to close to ground. Results for some different small sources are found in Table 5. The results indicate a plume height of 13-150 m or 13-80 m if excluding the small refinery. This is considerably lower than for the large refineries in Project-1 which had an overall median plume height of around 400 m. Based on these plume height estimates, wind information from 10 m altitude has been used for all small sources (rather than using 50-400 m, as measured by the wind LIDAR).

The wind information from the car-based Airmar is not used for flux calculation since the wind field at street level can be quite disturbed and turbulent. This Airmar only acts as a real-time aid to keep track of the plume directions when making the gas emission measurements. The vessel-based Airmar (See Figure 12), on the other hand, is also used for flux calculations since the marine wind field is much less disturbed and the wind meter on the vessel is located immediately at the plume (land based met stations not applicable).



Figure 12. The research vessel for sea-based SOF measurements during the SCAQMD 2015 survey. The sonic wind sensor encircled in red at the top.

Table 5. Summary of plume height (median values) estimations from some typical small sources in the SCAQMD survey 2015 and used wind information. FS=FluxSense

Refinery	Number of Meas.	Median Plume Height [m]	Primary Wind	Secondary Wind
Refineries (Proj-1)	46	413	LIDAR 0-400m	ASOS/SCAQMD/Tesoro
Wells (Drilling Rigg)	2	13	FS Wind Mast	ASOS/SCAQMD/Tesoro
Wells (Derricks)	35	16	FS Wind Mast	ASOS/SCAQMD/Tesoro
Treatment Facility	16	37	FS Wind Mast	ASOS/SCAQMD/Tesoro
Small Refinery	15	152	FS Wind Mast	ASOS/SCAQMD/Tesoro
Tank Farm (large)	13	80	FS Wind Mast	ASOS/SCAQMD/Tesoro
Big Reservoir Tank	54	28	FS Wind Mast	ASOS/SCAQMD/Tesoro
Small Tank	27	43	FS Wind Mast	ASOS/SCAQMD/Tesoro
Offshore	-	-	FS Airmar	-

The FluxSense 10 m mobile wind mast was always the primary wind information for flux calculations in this survey. For cases where no relevant primary wind mast data was available, a secondary wind source was used, see Table 5. The secondary wind source was selected based on the proximity to the measured site and correlation.

In order to assess the sensitivity of the flux calculations to deviations from the assumed plume mixing height, wind LIDAR data (10 min average) from 50-100 m have been compared to the reference FluxSense 10 m wind mast during the calibration periods 2-6 October 2015 at site Tesoro Carson (see Figure 9). For this calibration period, the wind speed average at 50-100 m were systematically 20% higher than the 10 m mast data, see Figure 13, but the majority of data points are still within 30% of the wind mast. The wind direction is generally within 30°. The results from this calibration study gives an indication that the measured SOF fluxes for the largest of the small sources (large Tank Farms and Small Refineries) can be underestimated by a maximum of 20%, and presented fluxes are conservative.

For consistency no individual corrections for plume altitude are applied for the sources in this report because individual source plume height estimates are generally not available (lack of simultaneous SOF and MeFTIR data) and because conditions vary in space and time so that the calibration results from 2-6 October at Carson may not be representative for another particular site.

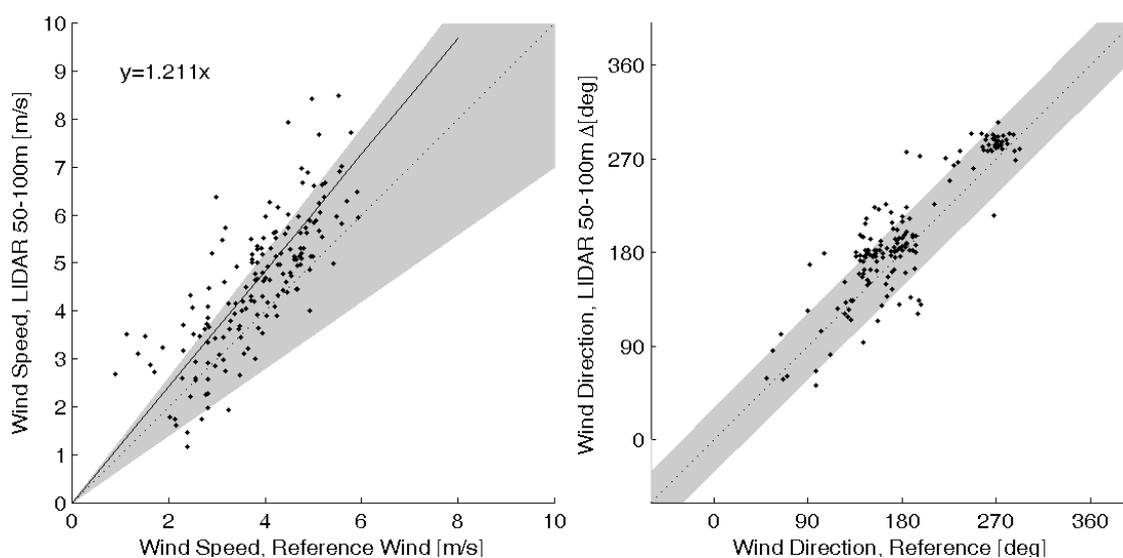


Figure 13. Wind LIDAR data (10 min average from 10AM to 5PM) for 50-100 m versus the reference FluxSense 10m wind mast during the calibration period 2-6 October 2015 at Tesoro Carson. The shaded areas indicate $\pm 30\%$ relative deviation from reference wind speed (left panel) and $\pm 30^\circ$ deviation from reference wind direction (right panel). Fitted least squares are shown as solid line.

An example of the evolution of the wind profile over the course of a day is shown in Figure 14. It shows a clear sign of the prevailing wind pattern throughout the study, with weak winds in the morning that increase in magnitude from approximately 10-12 AM and forward while also rotating clockwise. Since a wind speed of at least 1-2 m/s is typically needed in order to make accurate flux measurements, useful data could normally not be collected before 10 AM. As also seen in these examples, the wind is relatively homogenous within a layer up to 300-500 m, but at higher altitudes, the wind direction is often completely different indicating that this layer of homogenous wind is the convective boundary layer. The exact height of this layer varies throughout the day, and this explains why the wind is on average weaker and more variable in the uppermost levels of the 50-400 m height interval, as seen in Figure 14. The convective boundary layer simply does not always extend above this height level.

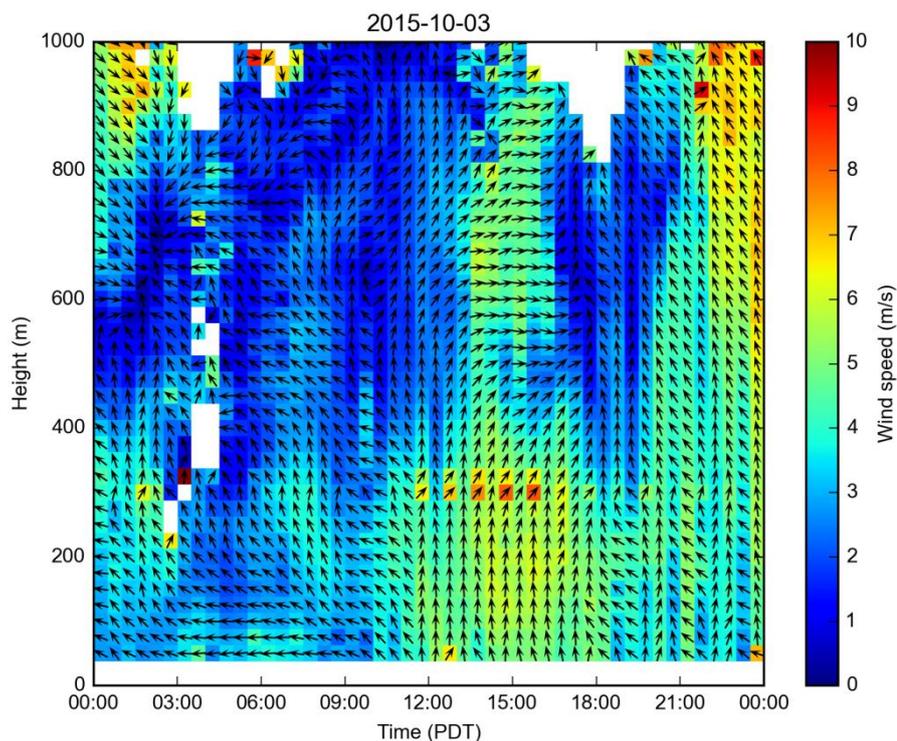


Figure 14. Wind LIDAR Raw data (30 min averages) from 50 to 1000 m at the L1 site in Carson measured on October 3, 2015. The color scale gives the magnitude of the wind speed and the black arrows show the wind direction (north up). The plot shows typical low wind speeds during night-time conditions and stable winds with little altitude variation (wind shear) from 50 to 400m in the period noon to sunset.

4 Results

In order to improve our understanding of emissions of VOC's, BTEX, NO₂, and SO₂ from a variety of stationary sources in the South Coast Air basin, emissions from 465 different units throughout the SCAB have been measured during this project. The studied sources have been categorized as following: *Oil & Gas Wells, Tank Farms, Terminals & Depots, Petroleum Treatment sites & Small Refineries, Gas Stations, Offshore Facilities & Activities* and *Other Sources*. Due to the large number of sources in the SCAB and the limited duration of the study, only a subset of sources has been sampled within each category, with differing statistical coverage between the source categories, see Table 6. For instance, 106 oil and gas wells have been measured, whereas there are over 5000 active wells in the SCAB [DOGGR 2016]. For VOC storage tanks in *Tank Farms, Terminals and Depots*, on the other hand, we estimate that nearly a half of such sources were included in this survey. This estimate is based on visual counting using Google Earth™. Note that any storage tanks in the other categories or in refinery tank parks (Project-1) are not counted here.

Table 6. Number of measured units in each category and total estimated number of units in the SCAB during the SCAQMD 2015 campaign- Project 2.

Source Category	Unit types	Number of Measured Units	Total Number of Units in the SCAB	Percent of Total Units Measured
1) <i>Oil & Gas Wells</i>	Derricks and Storage Tanks	106	5000 [†]	2.1%
2) <i>Tank Farms, Terminals & Depots</i>	Tanks	328	750 [‡]	44%
3) <i>Petroleum Treatment Sites & Small Refineries</i>	Entire site	9	15 [‡]	60%
4) <i>Gas Stations</i>	Entire site	8	3140 [†]	0.3%
5) <i>Offshore Facilities/Activities</i>	Entire site	7	20 [‡]	35%
6) <i>Other Sources</i>	Entire site	7	unknown	unknown
7) <i>Uncategorized Area Source</i>	Various	1	unknown	unknown
Total number of units		465		

[†]Source: DOGGR 2016 database. [‡] Visual counting using Google Earth™.

Results for the different categories of stationary sources in the SCAQMD survey 2015 are presented in separate subsections below and summarized in Table 7. The geographical positions are given in Table 3 and marked as coloured areas and flags in Figure 9. The results in Table 7 are given as survey means per site and as total measured fluxes per category. The daily means and standard deviations are presented in the category subsections below. Average results per unit within each category are presented in Table 8.

Table 7. Average emissions from the sources in the SCAQMD-2015 Project-2 for each source category. N is a number of measurements.

Sources/Sites	SOF or MeFTIR+tracer			MWDOAS		MeFTIR
	N	Alkane Flux [kg/h]	BTEX Flux [kg/h]	Benzene Flux [kg/h]	CH ₄ Flux [kg/h]	
Oil & Gas Wells (consisting of Derricks, Storage Tanks and Drilling Rigs)						
Wells_AtlanticAve_ESpringSt_SE	SOF	7	36	n.m.	n.m.	n.m.
Wells_WalnutAve_CrescentHeightsSt_NE*	SOF/M+T	31	21	n.m.	0.23	3.90
Wells_AtlanticAve_ESpringSt_SW	SOF	11	9.6	n.m.	n.m.	17
Wells_MarbellaAve_ESepulvedaBlvd_SSW	SOF	1	5.2	n.m.	n.m.	2
Wells_OrangeAve_E28thSt_NW	SOF	1	2.8	n.m.	n.m.	n.m.
Wells_RoseAve_CrestonAve_SW	SOF	39	7.8	0.18	0.07	15
Wells_TempleAve_E21stSt_SW	SOF	4	37	4.11	0.45	n.m.
Wells_ValenciaAve_ELambertRd_NW	SOF	1	1.6	n.m.	n.m.	n.m.
Wells_WalnutSt_W236thSt_SW	M+T	11	1.8	0.14	0.03	1.00
Wells_AtlanticAve_ESpringSt_NW	M+T	9	0.37	0.02	0.00	0.03
Wells_RoseAve_EWillowSt_S	M+T	3	0.05	0.01	0.00	0.06
Wells_GardenaAve_EBurnettSt_NW	M+T	4	2.3	n.m.	n.m.	0.51
Wells_NOrizaba_E20th_SE	M+T	7	0.17	n.m.	n.m.	0.07
Wells_PuertoNatalesDr_VinaDelMarAve_SE	M+T	11	1.4	0.10	0.01	0.82
Wells_RoseAve_CrestonAve_SW	M+T	4	3.4	0.08	0.03	1.80
Wells_JeffersonBlvd_BudlongAve_W	M+T	9	2.6	0.62	0.07	2.30
Wells_TonnerCanyonRd_W	M+T	21	5.5	n.m.	n.m.	n.m.
Total for "Wells" Category	17	174	138	5.3	0.9	44
Tank Farms, Terminals & Depots						
TankFarm_HarbourPlaza_SHarborScenicDr_SE	SOF	3	15	n.m.	n.m.	n.m.
TankFarm_PierASt_PierAPI_SW	SOF	5	13	n.m.	n.m.	n.m.
TankFarm_RedondoAve_EPacificCoastHwy_NE	SOF	1	7.1	0.59	0.07	6
TankFarm_SHenryFordAve_DockSt_NW	SOF	7	6.9	n.m.	n.m.	n.m.
TankFarm_SanClementeAve_SLaPalomaAve_W	SOF	7	39	n.m.	n.m.	n.m.
TankFarm_RedondoAve_EWillowSt_SW	SOF	3	24	n.m.	n.m.	n.m.
TankFarm_NParamountBlvd_ESouthSt_NW	SOF	9	43	6.71	0.65	n.m.
TankFarm_WEdisonWay_LuggerWay_SW	SOF	10	46	n.m.	n.m.	24
TankFarm_WarfSt_SeasideAve_SW	SOF	2	8.3	n.m.	n.m.	n.m.
TankFarm_FerrySt_PilchardSt_W	SOF	2	10	n.m.	n.m.	n.m.
TankFarm_OrangeAve_E25thSt_NE*	SOF/M+T	11	12	0.15	0.06	11
TankFarm_EdisonAve_PierBSt_SE	SOF	4	59	n.m.	n.m.	n.m.
TankFarm_JohnSGibsonBlvd_E	SOF	2	29	n.m.	n.m.	n.m.
Total for "Tank Farms, Terminals and Depots" Category	13	66	314	7.4	0.8	41
Petroleum Treatment Sites & Small Refineries						
TreatmentSite_WilmingtonAve_EDelAmoBlvd_SE	SOF	4	76	n.m.	n.m.	9
TreatmentSite_TempelAve_CombellackDr_SW	SOF	9	196	2.30	n.d.	37
TreatmentSite_StJamesPark_W23rdSt_SE	M+T	3	0.20	n.m.	n.m.	0.09
TreatmentSite_OrangeAve_ESpringSt_SE	SOF	24	170	3.50	0.81	125
TreatmentSite_LewisAve_EWillowSt_SE	SOF/M+T	13	14	1.29	0.34	13

TreatmentSite_GreenwichCir_RumsonSt_E	M+T	8	2	0.02	0.01	0.96	
TreatmentSite_SMainSt_WSepulvedaBlvd_SSE	SOF	3	3.1	n.m.	n.m.	21	
Refinery_LakewoodBlvd_SomersetBlvd_NW	SOF	7	24	2.84	0.34	n.m.	
Refinery_NParamountBlvd_EArtesiaBlvd_SW	SOF	5	16	1.81	0.23	n.m.	
Total for "Petroleum Treatment Sites & Small Refineries" Category		9	76	501	12	1.7	205
Offshore Facilities & Activities							
OffShore_FuellIsland_Chaffet	SOF	2	12	n.m.	n.m.	n.m.	
OffShore_FuellIsland_Freeman	SOF	2	8.2	n.m.	n.m.	n.m.	
OffShore_FuellIsland_Grissom	SOF	1	3.98	n.m.	n.m.	n.m.	
OffShore_FuellIsland_White	SOF	3	5.94	n.m.	n.m.	n.m.	
OffShore_FuelBarges_PortLA	SOF	7	7.1	n.m.	n.m.	n.m.	
OffShore_ShipVenting	SOF	2	27	n.m.	n.m.	n.m.	
OffShore_ShipFueling	SOF	4	5.2	n.m.	n.m.	n.m.	
Total for "Offshore Facilities & Activities" Category		7	21	69	n.m.	n.m.	n.m.
Gas Stations							
GasStation_CherryAve_EWillowSt_SE	M+T	13	2.24	0.51	0.06	0.48	
GasStation_DowneyAve_RosecransAve_SE	M+T	15	0.57	0.10	0.01	0.47	
GasStation_GoldenwestSt_YorktownAve_NE	M+T	7	1.71	0.62	0.07	0.50	
GasStation_BeachBlvd_AdamsAve_NE	M+T	6	1.26	0.31	0.03	1.10	
GasStation_CrenshawBlvd_SkyparkDr_NW	M+T	11	0.73	n.m.	n.m.	0.33	
GasStation_CrenshawBlvd_WJeffersonBlvd_NW	M+T	8	2.58	0.68	0.07	0.35	
GasStation_EOceanBlvd_ELivingstonDr_E	M+T	11	0.38	n.m.	n.m.	0.08	
GasStation_WoodruffAve_HarveyWay_SE	M+T	5	0.45	0.10	0.01	0.03	
Total for "Gas Stations" Category		8	76	9.9	2.3	0.2	3.3
Other Sources							
FuelSupply_SWesternAve_PalosVerdesDrN_SE	SOF	4	52	n.m.	n.m.	23	
Seaside_45thSt_VistaDelMarBlvd	SOF	23	41	n.m.	n.m.	n.m.	
Airport_CherryAve_EWardlowRd_SE	SOF	3	60	25.9	n.d.	23	
PowerPlant_TerminalIslandFwy_SeasideFwy_NW	SOF	1	30	n.m.	n.m.	n.m.	
OtherSite_AlamedaSt_PacificCoastHighwaySt_SO	SOF	2	74	n.m.	n.m.	5	
Old_TankFarm_SignalSt_E22St_SE	SOF	5	29	n.m.	n.m.	n.m.	
Source_Valencie_Lambert_Brea_olinda	M+T	n.m.	n.m.	n.m.	n.m.	12	
Total for "Other Sources" Category		7	38	286	26	n.m.	62
Total Sum all Measured Sources		61	451	1318	53†	3.7†	355†
Uncategorized Area Source							
TankFarm&Refineries_Sepulveda_Alameda_SE	SOF	6	483	n.m.	n.m.	301	

*Average of SOF and MeFTIR+tracer measurements (M+T). †Only sources where actual BTEX and CH₄ measurements were carried out are summed up here, leaving out any contributions from the ones not quantified. n.m. = not measured. n.d. = not detected (below detection limit).

Summing up emissions from all the 61 different measured sites/sources (including more than 450 units of wells, tanks etc.) and 451 SOF and MeFTIR+tracer transects resulted in a flux of 1318 kg/h of alkanes. Some of these sources (28) were also measured with MWDOAS and 35 with MeFTIR giving a sum of 53 kg/h of BTEX (3.7 kg/h of which were Benzene) and 355 kg/h of methane. Note that BTEX and methane measurements were not performed at all sites and, thus, these values are likely underestimated with respect to actual emissions from all

sources. In addition, 483 kg/h of alkanes and 301 kg/h of methane were found from the uncategorized area source in Carson/Wilmington.

The category with largest measured emissions is *Petroleum Treatment Sites & Small Refineries* with 501 kg/h and followed by (in falling order) *Tank Farms, Tank Groups, Terminals & Depots* with 314 kg/h of alkanes; *Oil & Gas Wells* with 138 kg/h; *Offshore Facilities & Activities* with 69 kg/h; and *Gas Stations* with 9.9 kg/h. The order is similar when considering BTEX or Methane emissions, with the exception that these measurements were not performed for *Offshore Facilities & Activities* (the MWDOAS and MeFTIR instruments were not operated from the research vessel).

Average emissions of alkanes, BTEX and methane per unit source of each source category derived from this measurement campaign are presented in Table 8. Median BTEX and Methane fractions have been used to calculate emission fluxes but note that these measurements have not been performed for all sites (see Table 7). The average emissions from an *Oil & Gas Wells* unit (Storage Tank and/or Derrick) is 1.3 kg/h of alkanes, 0.1 kg/h of BTEX (of which 0.015 kg/h Benzene) and 0.3 kg/h of Methane. The emission for an average *Tank Farm* tank is 0.96 kg/h of alkanes and 0.08 kg BTEX (of which 0.01 kg/h Benzene).

Table 8. Average emission rates per unit in the different categories.

Source Category	Unit Types	Number of Measured Units	Average Emissions per Unit			
			Alkanes [kg/h]	BTEX [kg/h] [†]	Benzene [kg/h] [†]	CH ₄ [kg/h] [†]
Oil & Gas Wells	Derricks and Tanks	106	1.30	0.097	0.015	0.31
Tank Farms, Terminals & Depots	Tanks	328	0.96	0.079	0.0097	0.75
Petroleum Treatment Sites & Small Refineries	Entire Sites	9	55.7	3.23	0.77	27.4
Gas Stations	Entire Sites	8	1.24	0.31	0.033	0.31
Offshore Facilities/Activities	Entire Sites	7	9.79	n.m.	n.m.	n.m.
Other Sources	Entire Sites	7	40.9	n.m.	n.m.	15.5
Total Measured Units		465				

[†]Average emission fluxes of BTEX and CH₄ per unit are calculated by multiplying the average alkane flux per unit by the median BTEX or methane ratios within each category.

4.1 Oil & Gas Wells (Derricks, Tanks, Drilling Rigs)

Seventeen (17) different *Oil & Gas Wells* sites were observed during the survey, of which eight (8) with SOF and ten (10) with MeFTIR+tracer correlation (see cyan coloured flags and areas in Figure 9). Summing up all the measured sites gives 106 single units (Derricks and Storage tanks). The characteristics of the sites vary considerably as they contain different number of derricks, storage tanks and occasionally drilling rigs. Some sites comprise just a single derrick. The emissions varied considerably between sites (see Table 9 and Table 10), from a few grams per hour (RoseAve_EWillowSt_S) to over 60 kg/h of alkanes for individual transects (AtlanticAve_ESpringSt_SE). Higher emissions were observed during drilling events, and storage tanks at well sites were generally larger emitters than the derricks.

In total, based on 174 measurements, 138 kg/h of alkanes were detected from the observed Oil and Gas Wells sites. Examples of a typical SOF-transect and a MWDOAS/MeFTIR measurement are presented in Figure 16 and Figure 16, respectively. On average, 1.3 kg/h of alkanes per unit was measured; however the site-to-site variability was large, ranging from 0.05 kg/h/unit (Wells_RoseAve_EWillowSt_S) to 5.5 kg/h/unit (Wells_TonnerCanyonRd_W).

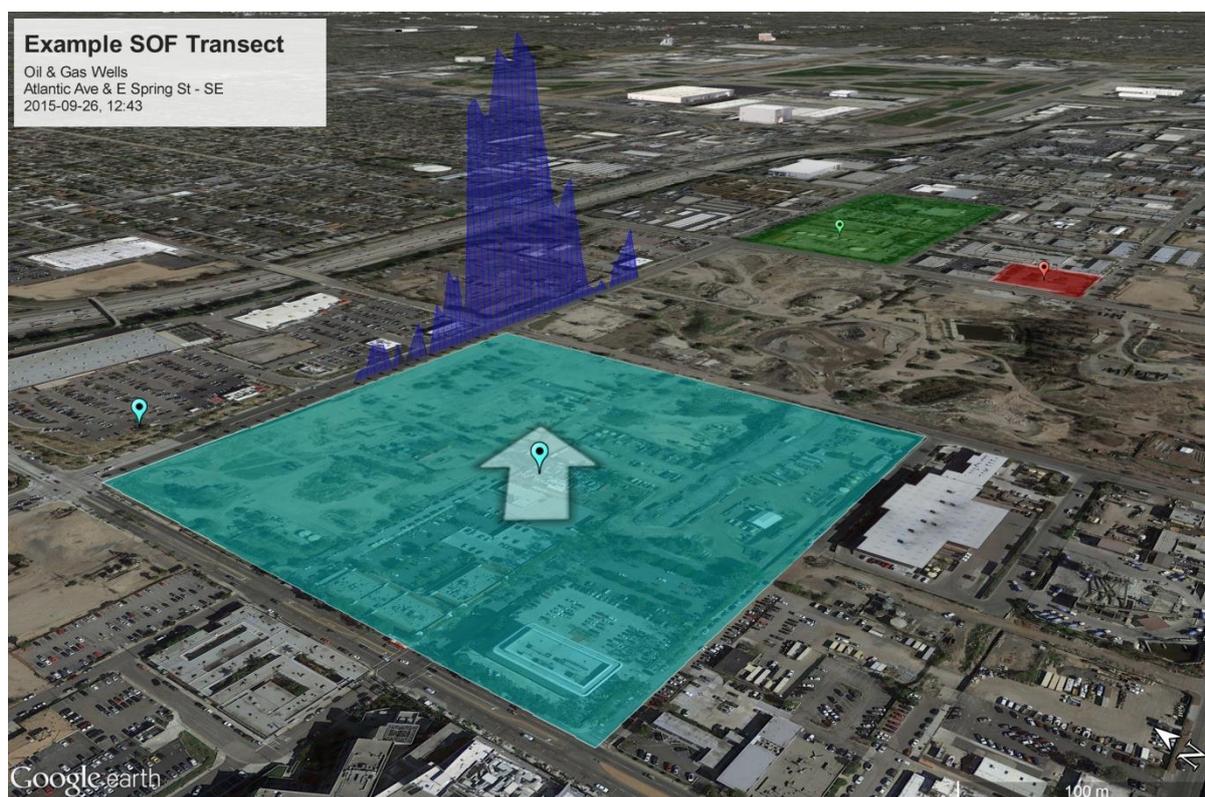


Figure 15. Example of a SOF measurement of Oil & Gas Wells at Atlantic Ave and E Spring St, Signal Hill, 26 October 2015, 12:43. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m², max 25 mg/m²). Wind direction during the measurement is indicated by the white arrow, measured with the FluxSense 10m wind mast. Map from Google Earth™ 2016.

Table 9. Summary of alkane SOF measurements of *Oil and Gas Wells*. *N* is equal to number of measurement transects.

Source Oil & Gas Wells	Day [yyymmdd]	Timespan [hhmmss- hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
AtlanticAve_ESpringSt_SE	150926	124337 -124529	1	26	2.8	214
	151003	101714 -130549	4	45±21	3.1-4.8	150-174
	151008	160012 -160207	1	24	3.4	283
	151009	160735 -160917	1	20	4.7	301
WalnutAve_CrescentHeightsSt_NE	151003	121252 -121341	1	20	4.2	177
	151015†	131401 -152522	6	46±11	2.4-3.4	171-209
AtlanticAve_ESpringSt_SW	150926	123149 -135152	5	13±3.9	2.7-3.5	150-215
	151003	101813 -130418	5	6.8±4.9	2.8-4.1	152-187
	151008	154624 -154655	1	4.7	3.2	289
MarbellaAve_ESepulvedaBlvd_SS	151022	125709 -125840	1	5.2	2.4	170
OrangeAve_E28thSt_NW	151009	141949 -142038	1	2.8	2.9	281
RoseAve_CrestonAve_SW	151008	122003 -135335	39	7.8±3.5	1.4-2.9	135-198
TempleAve_E21stSt_SW	151003	92926 -93119	1	39	2.8	206
	151111	134427 -135027	3	36±40	1.9-2.4	284-329
ValenciaAve_ELambertRd_NW	151105	101647 -101725	1	1.6	1.8	120

† Ongoing drilling (see 4.1.1)

Table 10. Summary of alkane MeFTIR+tracer correlation measurements of *Oil and Gas Wells*. *N* is equal to number of measurement transects.

Source Oil & Gas Wells	Day [yyymmdd]	Timespan [hhmmss- hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
WalnutSt_W236thSt_SW	151025	124244 -133422	11	1.7±1.5	0.0-0.6	72-174
AtlanticAve_ESpringSt_NW	150926	141633 -143538	9	0.37±0.34	2.6-3.1	166-190
RoseAve_EWillowSt_S	151015	184252 -185050	3	0.05±0.05	0.5-1.1	291-326
GardenaAve_EBurnettSt_NW	151016	144950 -145639	4	2.2±2.5	2.2-2.7	263-305
WalnutAve_CrescentHeightsSt_NE	151016†	131452 -142845	18	12±10	0.5-4.0	45-327
	151022	205834 -212041	6	8.3±4.2	0.3-0.9	309-326
Jefferson_Budlong	151103	152830 -155933	9	2.6±2.2	0.0-4.0	1-353
PuertoNatalesDr_VinaDelMarAve_SE	151028	141643 -145659	11	1.4±1.3	1.1-1.6	172-227
RoseAve_CrestonAve_SW	151008	141416 -143119	4	3.4±2.2	0.8-1.9	173-227
TonnerCanyonRd_Brea*	150923	123131 -163259	21	5.5±2.2	1.7-3.9	172-257

† Ongoing drilling (see Section 4.1.1).

*Fracking event (see Section 4.1.2).

The fluxes of CH₄ and BTEX were measured either directly using MeFTIR+tracer correlation, or as an inferred flux based on the ratio of BTEX or CH₄ to alkanes. This ratio was then multiplied by the alkane flux measured from the same site using SOF. Both the CH₄ and the BTEX fluxes varied considerably between different well sites. Table 11 shows the fluxes for all measured single and groups of wells. The median fraction of CH₄ over alkanes including calculated fractions from the MeFTIR+tracegas measurements is 0.53. The median BTEX fraction for all 8 measured wells and well sites is 0.075 with variations from 0.02 to 0.27 as can be seen in Table 12. Also the internal BTEX composition showed large variations and was

essentially all benzene during the drilling event described below. Examples of the measured BTEX and benzene plumes are presented in the chapter 4.9.

Table 11. Summary of MeFTIR CH₄ /Alkane mass ratio and CH₄ MeFTIR+tracer correlation measurements for *Oil and Gas Wells*. *N* is equal to number of measurement transects.

Source Oil & Gas Wells	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	CH ₄ /alkane mass ratio [%]	Tracer gas meas. CH ₄ flux [kg/h]
Wells_AtlanticAve_ESpringSt_SW	150926	134820 -135218	2	37	
	151003	110727 -110819	1	66	
Wells_MarbellaAve_ESepulvedaBlvd_SSW	151022	125833 -131933	2	43±7	
Wells_RoseAve_CrestonAve_SW	151003	122808 -122910	1	190	
Wells_WalnutSt_W236thSt_SW	151025	124244 -133422	11		1.0±0.7
Wells_AtlanticAve_ESpringSt_NW	150926	141633 -143538	9		0.03±0.02
Wells_RoseAve_EWillowSt_S	151015	184252 -185050	3		0.06±0.08
Wells_GardenaAve_EBurnettSt_NW	151016	144921 -145704	3		0.51±0.52
Wells_NOrizabz_E20th_SE	150922	191932 -203007	7		0.07±0.05
Wells_PuertoNatalesDr_VinaDelMarAve_S	151028	141643 -145659	11		0.82±0.61
Wells_RoseAve_CrestonAve_SW	151008	141416 -143119	4		1.8±1.5
Wells_JeffersonBlvd_BudlongAve_W	151103†	152830 -155933	8		2.3±0.9
Wells_WalnutAve_CrescentHeightsSt_NE	151016†	131426 -142845	18		4.4±3.7
	151022	205834 -212041	6		3.4±1.4

† Ongoing drilling.

Table 12. Summary of MWDOAS/MeFTIR ratio measurements of *Oil and Gas Wells*. *N* is equal to number of measurement transects.

Source Oil & Gas Wells	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	BTEX/alkane ratio [%]	Benzene/alkane ratio [%]
WalnutSt_W236thSt_SW	151025	124255 -134024	11	7.9±4.2	1.6±1.2
AtlanticAve_ESpringSt_NW	150926	141644 -143433	9	5.3±4.7	1.1±1.7
RoseAve_EWillowSt_S	151015	184335 -185554	4	27.8±10.1	3.9±2.4
Jefferson_Budlong	151103	152322 -160146	7	23.6±18.0	2.7±2.0
PuertoNatalesDr_VinaDelMarAve_SE	151028	125945 -130432	2	7.1±9.1	0.67±1.11
RoseAve_CrestonAve_SW	151008	121740 -142323	15	2.3±0.7	0.88±0.23
WalnutAve_CrescentHeightsSt_NE	151015†	135132 -154623	8	2.7±0.5	2.7±0.3
	151016†	131314 -142834	10	3.1±3.3	1.2±0.2
TempleAve_E21stSt_SW	151003	93025 -93057	1	22.6	1.7
	151111	135238 -135303	2	5.5±3.1	0.98±0.73

† Ongoing drilling

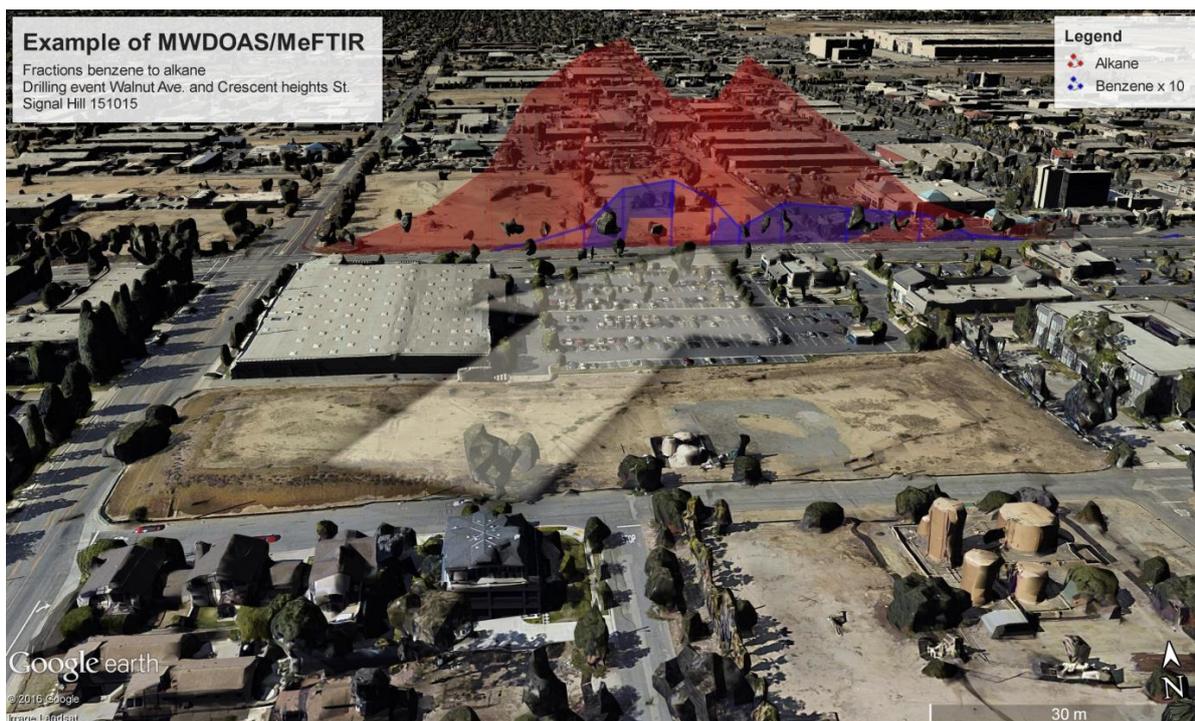


Figure 16. Example of a MWDOAS/MeFTIR measurement of Oil & Gas Wells at Walnut Ave. and Crescent Heights St., Signal Hill, 15 October 2015, 13:59. Alkane concentration is shown as a red curve and the BTEX (in this specific case the only present BTEX was benzene) is shown as a blue curve. The BTEX have been magnified x 10 for visibility. Wind direction during the measurement, indicated by the white arrow, was measured with the FluxSense 10m wind mast. Map from Google Earth™ 2016.

4.1.1 Drilling Event

Different stages of an oil well drilling event were captured during this measurement campaign. On the field bordered by Walnut Avenue, Crescent Heights St., the Ocean Crest Credit Union building and the Food 4 Less parking lot, a well drilling was observed on October 3, 15-16. The drilling rig was later replaced by a derrick which also was measured on October 22, 2015. The results from measurements conducted during drilling and oil pumping are presented in Table 13. The highest emissions (12 to 46 kg/h) was found during days of ongoing drilling and the lowest (8.3 kg/h) when the drilling rig had been replaced by a Derrick. The BTEX flux measured during drilling on October 15 and 16 consisted often almost entirely of benzene as can be seen in Figure 31. The BTEX to alkane fraction can be found in Table 12.

Table 13. Measured alkanes emissions of drilling event at well site WalnutAve_CrescentHeightSt_NE, Signal Hill. The drilling rig had been replaced by a Derrick for the last measurement day.

Source	Day	Timespan	N	Alkane Emission	Wind Speed	Wind Dir
WalnutAve_CrescentHeightSt_NE	[yyymmdd]	[hhmmss-hhmmss]		Mean±SD [kg/h]	Min-Max [m/s]	Min-Max [deg]
Drilling rig (SOF)	151003	121252 -121341	1	20	4.2	177
Drilling rig (SOF)	151015	131401 -152522	6	46±11	2.4-3.4	171-209
Drilling rig (MeFTIR)	151016	131452 -142845	18	12±10	0.5-4.0	45-327
Derrick (MeFTIR)	151022	205834 -212041	6	8.3±4.2	0.3-0.9	309-326

4.1.2 Hydraulic Fracturing Event

A stimulation of an established well (API: 0405921759) by hydraulic fracturing (fracking) took place in the Tonner Road Canyon, Brea, on September 23, 2015. MeFTIR and MWDOAS measurements of both alkanes and BTEX using tracer gas were performed before, during and after the fracking event. Measurements started during the preparation phase at 13:30 and ended at 16:57. Emissions of alkanes of about 5.4 kg/h and a BTEX emission of ~0.23 kg/h was found throughout the entire measured period, with no significant difference in emissions detected before or after relative time of the fracking event. Details of the measurements are presented in Table 14.

Table 14. MeFTIR+tracer correlation measurements of fracking event at well site Tonner Canyon Rd, Brea (fracking commenced at 16:35).

Source TonnerCanyonRd	Day [yyymmdd]	Timespan [hhmmss- hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
Before 16:35	150923	123131 -163259	21	5.5±2.2	1.7-3.9	172-257
After 16:35	150923	163604 -165744	5	5.4±0.9	2.9-3.4	211-251

4.2 Tank Farms, Terminals & Depots

Fourteen (14) different *Tank Farms, Terminals & Depots* sites were observed during the survey, 13 of which with SOF and 1 with MeFTIR+tracer correlation (see yellow coloured flags and areas in Figure 9). The sizes of the sites vary considerably with different number of tanks and on-site activities. The alkane emissions also vary considerably between sites and from day to day (see in Table 15 and

Table 16) from 5 kg/h (FerrySt_PilchardSt_W) to 60 kg/h (EdisonAve_PierBSt_SE).

In total, alkane emissions of 314 kg/h were measured from the observed sites based on 66 measurements. Example of typical SOF-transects for different wind directions and measurement days for the same site is shown in Figure 17. On average 0.96 kg/h of alkanes per unit was measured, however, emissions varied from site to site, from 0.13 kg/h/unit (TankFarm_SHenry FordAve_DockSt_NW) to 4.63 kg/h/unit (TankFarm_WEdisonWay_LuggerWay_SW).

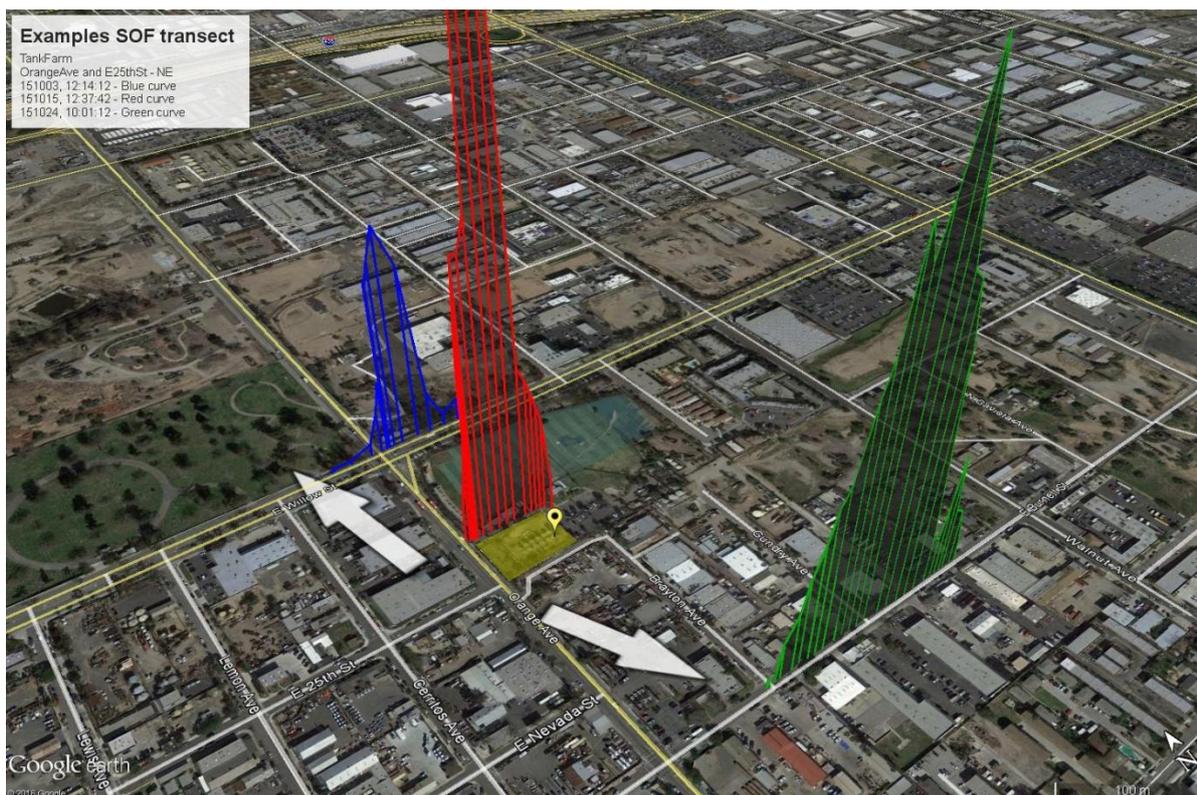


Figure 17. Example of a SOF measurement of a Tank Farm at Orange Ave and E 25th, Signal Hill. The figure shows measurements from the 3rd October 2015 12:14 (blue curve), 15th October 12:37 (red curve) and the 24th October 10:01. The apparent height of the curve is proportional to the measured alkane column (10 m equivalent to 1 mg/m²). Both the red and blue measurement had similar wind direction. Map from Google Earth™ 2016.

Table 15. Summary of SOF measurements of Tank Farms, Terminals & Depots.

Source Tank Farms	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
HarbourPlaza_SHarborScenicDr_SE	151015	151220 -154938	3	15±5.1	2.7-4.9	218-233
PierASt_PierAPI_SW	151020	145357 -152458	3	7.9±0.4	2.3-4.2	207-241
	151021	113343 -113757	1	3.6	3.1	167
	151026	160221 -160617	1	39.8	4.0	335
RedondoAve_EPacificCoastHwy_N	151003	113036 -113706	1	7.1	3.0	167
SHenryFordAve_DockSt_NW	150902	161552 -162626	3	6.1±2.2	2.3-2.7	208-231
	150906	173642 -174002	2	11±13	3.6-4.1	313-327
	151101	110538 -120024	2	4.4±3.2	3.3-4.0	186-202
SanClementeAve_SLaPalomaAve_	151020	152834 -161936	2	48±11	3.9-4.1	225-228
	151021	144744 -160709	4	36±19	2.8-4.4	177-212
	151026	133748 -134231	1	28.8	3.0	187
WEdisonWay_LuggerWay_SW	151101	114611 -114834	1	67	2.9	184
	151109	132035 -152947	9	44±18	3.3-6.2	249-316
WarfSt_SeasideAve_SW	151019	144434 -144856	1	7.9	4.0	184
	151021	112416 -113024	1	8.7	3.6	181
FerrySt_PilchardSt_W	151019	144928 -145331	1	15.6	3.3	175
	151021	121004 -121426	1	5.4	3.4	180
OrangeAve_E25thSt_NE	151003	121412 -121518	1	12.8	3.7	170
	151015	123742 -135034	4	13±8.5	2.1-4.7	161-221

	151024	100112 -105808	2	20±15	2.3-2.3	4-336
EdisonAve_PierBSt_SE	151101	115014 -142911	4	59.1±6.0	2.4-4.0	175-193
JohnSGibsonBlvd_E	151020	142902 -144147	2	29±2.8	3.5-4.6	225-242
NParamountBlvd_ESouthSt_NW	151023	111314 -142610	9	43±10	1.4-3.5	197-295

Table 16. Summary of MeFTIR+tracer measurements of Tank Farms.

Source Tank Farms	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
OrangeAve_E25thSt_NE	151015	130611 -132744	4	9.5±3.9	2.8-4.0	168-195

CH₄ and BTEX was measured as inferred fluxes using the ratio to alkane measured with MeFTIR and MWDOAS. The results are shown in

Table 17 and Table 18, respectively. For all tank farms the CH₄ fraction was below 100%. Only one tank farm was measured with MWDOAS which showed a rather low fraction of 1.2% for BTEX.

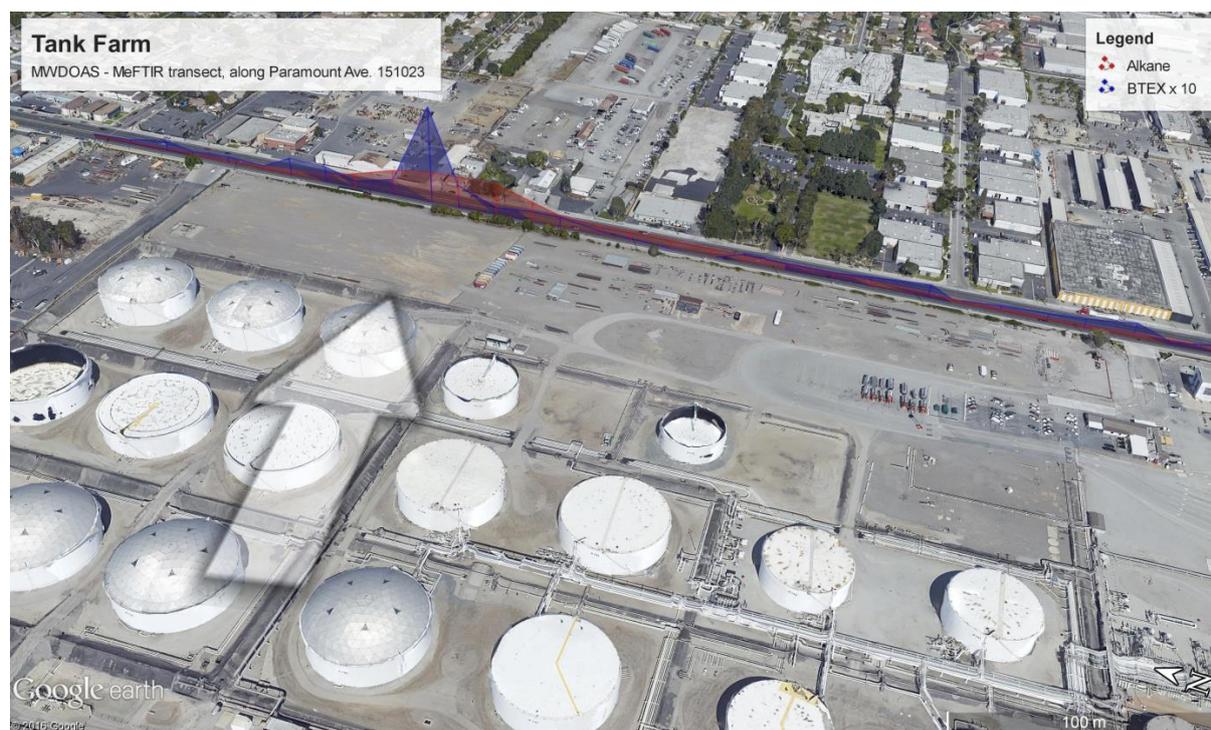


Figure 18. Example of a MWDOAS/MeFTIR measurement of a Tank Farm along Paramount Ave, Paramount 23 October 2015, 12:17. Alkane concentration is shown as a red curve and the BTEX is shown as a blue curve. The BTEX have been magnified x 10 for visibility. Wind direction during the measurement, indicated by the white arrow, was measured with the FluxSense 10m wind mast. Map from Google Earth™ 2016.

Table 17. Summary of MeFTIR CH₄ /Alkane mass ratio and CH₄ MeFTIR+tracer of Tank Farms, Terminals & Depots.

Source Tank Farms	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	CH ₄ /alkane mass ratio [%]	Tracer gas meas. flux [kg/h]
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RedondoAve_EPacificCoastHwy_NE	151003	113018 -113704	1	78
WEdisonWay_LuggerWay_SW	151104	165341 -165757	1	26
	151109	133858 -154923	9	55±20
OrangeAve_E25thSt_NE	151015	113616 -134815	10	92±49

Table 18. Summary of MWDOAS/MeFTIR mass ratio measurements of *Tank Farms, Terminals & Depots*.

Source	Day	Timespan	N	BTEX/alkane mass ratio	Benzene/alkane mass ratio
Tank Farms	[yyymmdd]	[hhmmss-hhmmss]		[%]	[%]
OrangeAve_E25thSt_NE	151015	133739 -134805	2	1.2±0.1	0.50±0.18

4.3 Petroleum Treatment Sites & Small Refineries

Nine (9) different *Petroleum Treatment Sites & Small Refineries* were observed during the survey, of which 7 with SOF and 3 with MeFTIR+tracer correlation (see green coloured flags and areas in Figure 9). A Petroleum Treatment site was typically identified as a site where product inflow from several wells is handled and also intermediately stored in storage tanks. Similarly to other sources, the size and emissions varied considerably between sites and from day to day (see

Table 19 and Table 20) from 0.2 (TreatmentSite_StJamesPark_W23rdSt_SE) kg/h to almost 200 kg/h (TreatmentSite_TempelAve_CombellackDr_SW). In total, 501 kg/h of alkanes were detected from the observed sites, based on 76 measurements. An example of a typical SOF-transect of a small asphalt refinery is presented in Figure 19.

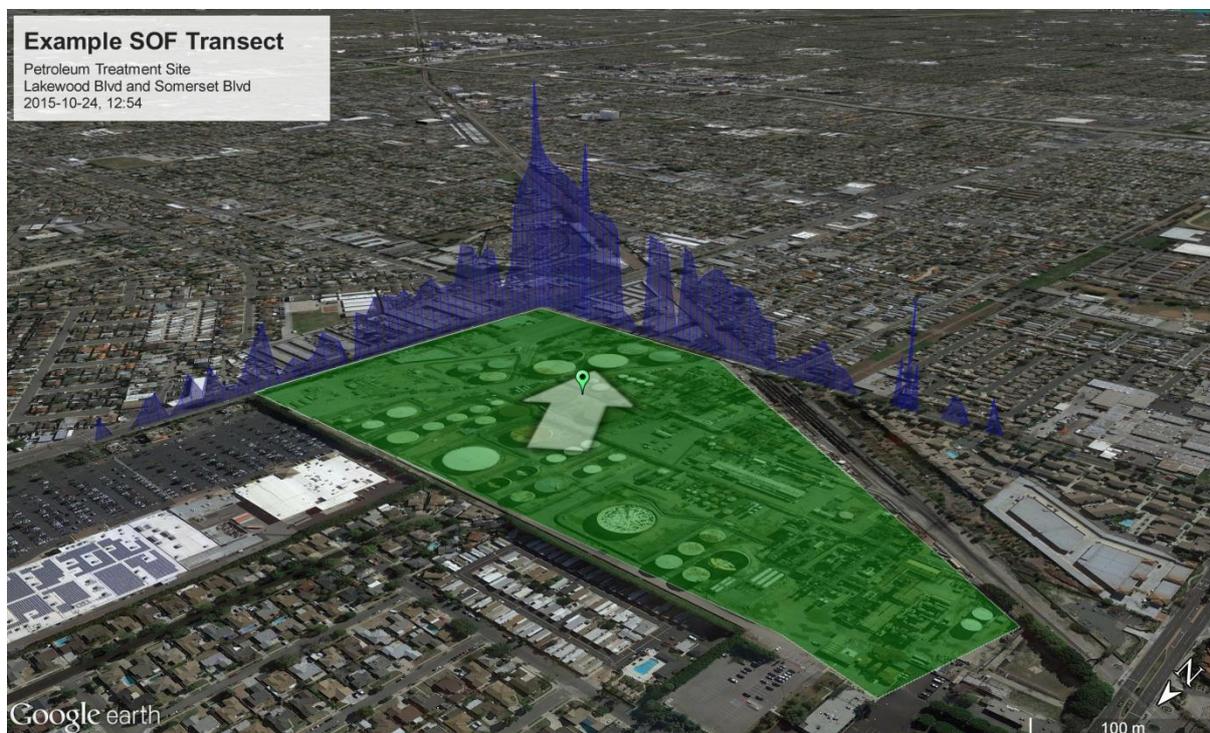


Figure 19. Example of a SOF measurement of an asphalt refinery at Lakewood Blvd and Somerset Blvd, Paramount, 24 October 2015, 12:54. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m², max 25 mg/m²). Wind direction during the measurement is indicated by the white arrow, measured with the FluxSense 10m wind mast. Map from Google Earth™ 2016.

Table 19. Summary of SOF measurements of *Petroleum Treatment Sites & Small Refineries*.

Source Petroleum Treatment Sites and Small Refineries	Day [yyymmdd]	Timespan [hhmmss- hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
OrangeAve_ESpringSt_SE	150926	131449 -144834	2	361±2.2	3.4-3.6	163-179
	150927	103631 -103824	1	283	2.3	145
	151002	91454 -91542	1	288	2.5	98
	151003	101439 -132149	6	206±72	2.3-4.2	161-181
	151009	132355 -152637	12	124±48.0	2.3-4.7	272-315
	151024	110454 -111124	2	36±24	1.9-2.4	20-338
TempelAve_CombellackDr_SW	150926	151932 -152209	1	124	2.0	212
	151003	120954 -131802	8	205±97.5	3.2-4.3	172-185
LakewoodBlvd_SomersetBlvd_NW	151023	151816 -160054	3	20±7.2	3.0-3.2	254-268
	151024	125445 -142030	4	28±7.1	1.2-2.5	257-339
LewisAve_EWillowSt_SE	150926	132718 -132743	1	18	2.5	169
	151003	121516 -121542	1	16	4.1	173
	151015	132050 -152810	2	25±16	2.6-4.0	195-202
WilmingtonAve_EDelAmoBlvd_SE	151020	124818 -153308	3	77±17	1.9-5.8	140-255
	151030	125235 -125642	1	71	2.2	154
LakewoodBlvd_EArtesiaBlvd_SW	151023	120843 -141036	5	16±4.8	1.6-3.4	248-326
SMainSt_WSepulvedaBlvd_SSE	151022	132820 -134528	3	3.1±0.7	2.0-2.6	140-185

Table 20. Summary of alkane MeFTIR+tracer measurements of *Petroleum Treatment Sites & Small Refineries*.

Source Petroleum Treatment Sites	Day [yyymmdd]	Timespan [hhmmss- hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
StJamesPark_W23rdSt_SE	151019	165352 -170539	3	0.20±0.14	0.4-0.7	201-314
GreenwichCir_RumsonSt_E	151028	123336 -133531	8	2.0±1.2	0.3-2.4	159-219
LewisAve_EWillowSt_SE	151018	124654 -131121	9	5.9±3.1	1.8-2.6	155-221

CH₄ and BTEX fluxes were measured based on their ratio to alkanes. With the exception of a few outliers, the study median value for CH₄/alkane ratio of 0.47 (see Table 21). For BTEX, small refinery sites had the highest BTEX/alkane ratio, which was approximately one order of magnitude higher than that at petroleum treatment sites (see Table 22). The site at LewisAve_EWillowSt_SE was the only exception, having BTEX/alkanes ratio similar to that of a small refinery.

Table 21. Summary of MeFTIR CH₄ /Alkane ratio and CH₄ MeFTIR+tracer measurements of *Petroleum Treatment Sites & Small Refineries*.

Source Petroleum Treatment Sites	Day [yyymmdd]	Timespan [hhmmss- hhmmss]	N	CH ₄ /alkane ratio [%]	Tracer gas meas. flux [kg/h]
WilmingtonAve_EDelAmoBlvd_SE	151020	130139 -131317	2	7±4	
	151030	125139 -125707	1	21	
TempelAve_CombellackDr_SW	151003	95342 -123740	3	19±2	
StJamesPark_W23rdSt_SE	151019	165352 -170539	3		0.09±0.12

OrangeAve_ESpringSt_SE	150926	120808 -164604	8	38±17	
	150927	102925 -103148	1	43	
	151003	100000 -132148	7	180±120	
	151009	123830 -152632	1	46±14	
LewisAve_EWillowSt_SE	150926	132608 -132813	1	39	
	151015	124559 -153510	3	49±8	
	151018	121811 -133538	7	120±80	
GreenwichCir_RumsonSt_E	151028	123336 -133531	8		0.96±0.57
SMainSt_WSepulvedaBlvd_SSE	151022	130342 -134404	4	670±430	

Table 22. Summary of MWDOAS/MeFTIR ratio measurements of *Petroleum Treatment Sites & Small Refineries*.

Source Petroleum Treatment Sites	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	BTEX/alkane ratio [%]	Benzene/alkane ratio [%]
OrangeAve_ESpringSt_SE	150926	120810 -124659	2	0.94±0.01	0.33±0.03
GreenwichCir_RumsonSt_E	151003	100106 -132105	8	2.7±1.4	0.41±0.15
	151009	132403 -155923	1	1.8±0.4	0.53±0.10
	151028	123752 -133517	3	1.2±0.4	0.53±0.08
LewisAve_EWillowSt_SE	151018	123520 -133244	1	9.5±3.8	2.5±1.5
TempelAve_CombellackDr_SW	151003	123409 -123627	2	1.2±1.1	0.41±0.26
LakewoodBlvd_SomersetBlvd_NW	151023	152547-155242	2	11.6±1.2	1.4±0.7
NParamntBlvd_EArtesiaBlvd_SW	151023	115136-142952	8	11.6±7.2	2.0±1.3

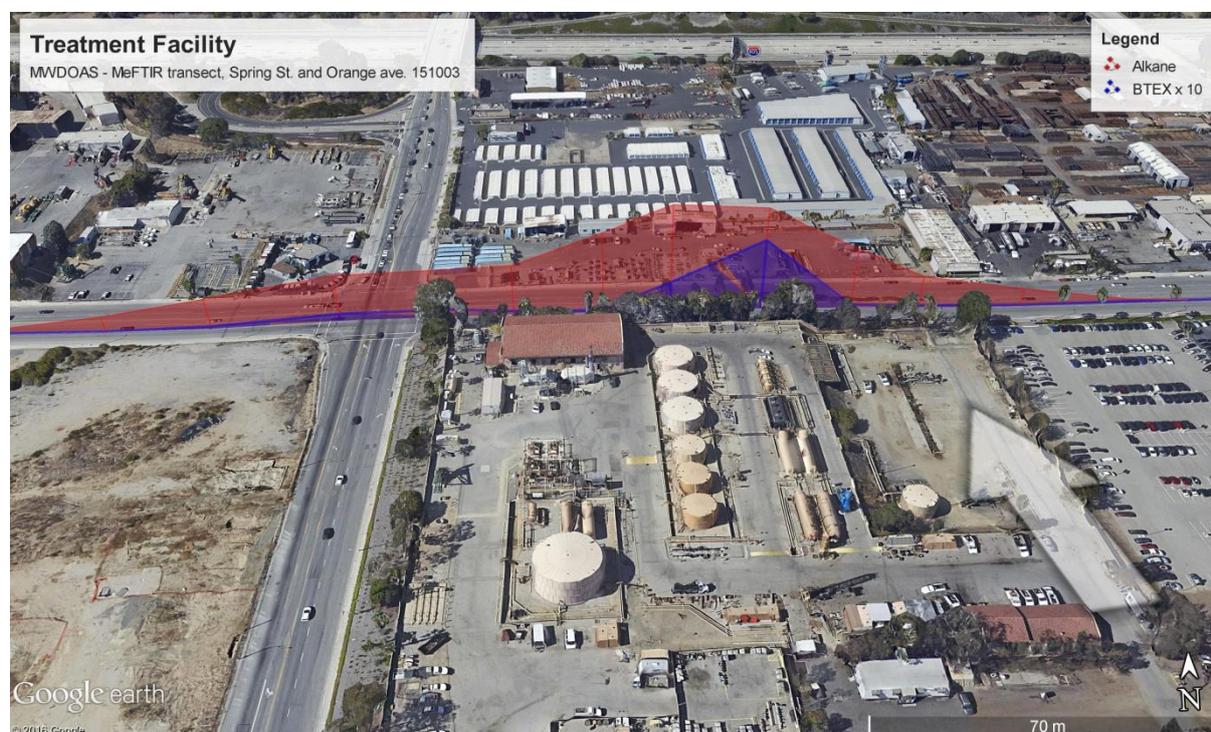


Figure 20. Example of a MWDOAS/MeFTIR measurement of a Treatment Facility at Spring St and Orange Ave, Signal Hill, 3 October 2015, 12:00. Alkane concentration is shown as a red curve and the BTEX is shown as a blue curve. The BTEX have been magnified x 10 for visibility. Wind direction during the measurement, indicated by the white arrow, was measured with the FluxSense 10m wind mast. Map from Google Earth™ 2016.

4.4 Offshore Facilities & Activities

Seven (7) different offshore sites and activities were observed during the survey with SOF (see blue coloured flags and areas in Figure 9). No MWDOAS or MeFTIR measurements were taken for the offshore sites since this instrumentation was operated in the mobile van and not mounted on the research vessel. The alkane emissions varied from 4 kg/h (Fuel Island Grissom) to 27 kg/h (Ship Venting), as seen in Table 23. In total, emissions of 69 kg/h of alkanes were measured from these sources based on 21 measurements. SOF-transects of three Fuel Islands on October 13, 2015 are shown in Figure 21.

Not all offshore emission source types were sampled during this campaign. For example, offshore sources not sampled within the scope of this work include offshore oil platforms located further off Long Beach, towards the Catalina Island. Large uncertainty also exists in a number of fuel barge operations, ship fuelling and venting activities. Therefore, there is a large uncertainty associated with scaling-up measured offshore emissions. A more viable approach would include more measurements to establish typical emission factors for these activities and then scale with data on number of operations within the port area, or handled product volumes where applicable.



Figure 21. Example of SOF measurements of Fuel Islands outside Long Beach, 13 October 2015, 12:50-13:15. Alkane column is shown as a yellow curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m², max 35 mg/m²). Wind direction during the measurement is indicated by the white arrow, measured with the FluxSense 10m wind mast. Map from Google Earth™ 2016.

Table 23. Summary of SOF measurements of *Offshore Facilities and Activities*.

Source Offshore	Day [yymmdd]	Timespan [hhmmss-hhmmss]	N	Alkane Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
Fuel Island White	151013	131421 -132323	2	6.7±2.0	2.3-3.3	218-224
	151015	143335 -143511	1	4.5	4.0	232
Fuel Island Freeman	151013	125038 -125311	1	8.6	3.3	187
	151015	142832 -143049	1	7.9	5.4	232
Fuel Island Chaffee	151013	130322 -130526	1	6.9	1.7	221
	151015	141358 -141609	1	16	5.6	239
Fuel Island Grissom	151015	144825 -145121	1	4.0	3.4	222
Fuel Barges Port LA	151015	132908 -134256	2	8.1±6.7	4.5-6.6	204-244
	151026	122818 -161745	4	5.8±3.3	2.7-5.5	243-345
Ship Venting	151026	121948 -122550	2	27±1.2	5.7-6.3	213-229
Ship Fuelling	151026	131407 -161745	4	5.2±2.8	2.7-5.1	213-345

4.5 Gas Stations

Emissions from eight (8) different *Gas Stations* were measured during the survey with MeFTIR plus tracer (see pink coloured flags and areas in Figure 9). The number of fuel pumps and fuelling vehicles varied from site to site. The measured rates represent total emissions coming from gas station area, including fugitives from gasoline storage tanks, emissions during fuelling, and tail pipe emissions of vehicles driving to and from the station. In general emissions of alkanes were smaller compared to the other source categories and varied from 0.4 kg/h (GasStation_EOceanBlvd_ELivingstonDr_E) to 2.6 kg/h (GasStation_CrenshawBlvd_WJeffersonBlvd_NW) (see Table 24). In total, 10 kg/h of alkanes were measured from the observed sites based on 76 measurements. An example of a typical MeFTIR-transect is given in Figure 22. The average tracer gas flow used was 3.7 kg/h but varied from site to site.

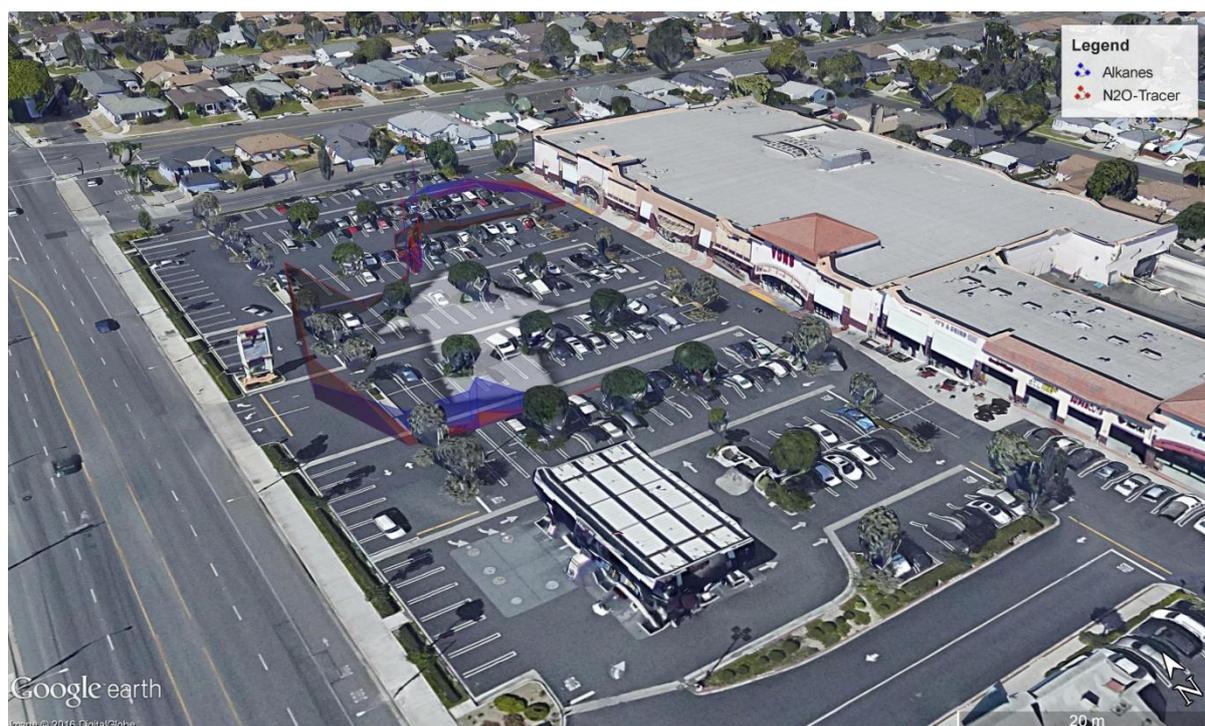


Figure 22. Example of a MeFTIR measurement of Gas station at Woodruff Ave and Harvey Way, Lakewood, 26 October 2015, 12:43. Alkane ground concentration is shown as a blue curve and tracer (N₂O) as a red with apparent height proportional to gas concentration. Wind direction during the measurement is indicated by the white arrow. Map from Google Earth™ 2016.

Table 24. Summary of alkane MeFTIR+tracer correlation measurements of *Gas Stations*.

Source Gas Stations	Day [yymmdd]	Timespan [hhmmss-hhmmss]	N	Alkane Emission Mean±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
BeachBlvd_AdamsAve_NE	151027	145236 -152049	6	1.3±1.8	1.0-1.7	225-249
CherryAve_EWillowSt_SE	151015	162256 -172752	13	2.2±2.2	2.0-4.0	45-304
CrenshawBlvd_SkyparkDr_NW	151029	174737 -184313	11	0.74±0.75	1.1-3.2	292-314
CrenshawBlvd_WJeffersonBlvd_N	151103	170227 -173202	8	2.6±1.1	4.0-4.0	230-230
DowneyAve_RosecransAve_SE	151023	174830 -184414	15	0.57±0.74	0.6-1.7	234-289
EOceanBlvd_ELivingstonDr_E	151101	170151 -180632	11	0.38±0.63	0.0-4.0	45-318
GoldenwestSt_YorktownAve_NE	151027	125724 -132405	7	1.7±1.3	0.2-0.6	255-346
WoodruffAve_HarveyWay_SE	151019	113047 -122626	5	0.44±0.28	1.6-2.3	197-208

BTEX flux was calculated from the measured BTEX/alkane ratio and can be found in Table 25. On average, BTEX to alkane mass fractions did not vary significantly from site to site and averaged at 26 % and 2.8 % for BTEX and benzene, respectively.

Table 25. Summary of MWDOAS/MeFTIR BTEX/alkane mass ratio measurements of *Gas Stations*.

Source Gas Stations	Day [yymmdd]	Timespan [hhmmss-hhmmss]	N	BTEX/alkane ratio [%]	Benzene/alkane ratio [%]
BeachBlvd_AdamsAve_NE	151027	151914 -153112	6	24.6±4.4	2.1±0.6
CherryAve_EWillowSt_SE	151015	162256 -172516	6	22.7±15.5	2.5±1.9
CrenshawBlvd_WJeffersonBlvd_N	151103	170237 -173303	7	26.5±12.0	2.9±2.1
GoldenwestSt_YorktownAve_NE	151027	125739 -134336	6	36.3±13.6	3.9±3.6
DowneyAve_RosecransAve_SE	151023	173531 -183136	6	18.1±9.6	1.9±0.6
WoodruffAve_HarveyWay_SE	151019	110801 -122601	19	22.4±16.8	2.7±2.9

4.6 Other Sources

Seven Other Sources were observed during the survey with SOF and MeFTIR (see white coloured flags and areas in Figure 9). Note that this category is a collection of remaining and unknown sources thus being very inhomogeneous with very different site characteristics.

The alkane emissions vary considerably between sites and from day to day as seen in

Table 26, from 14 kg/h (*Disused Tank Farm/Boat Loading*) to 80 kg/h (*CherryAve_EWardlowRd_SE*). On average, 286 kg/h were seen from all the observed sites based on 38 measurements. An example of a typical SOF-transect is seen in Figure 23.



Figure 23. Example of a SOF measurements of a VOC source west of Vista Del Mar Blvd in Long Beach, 11 September 2015, 11:05. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m², max 30 mg/m²). Wind direction during the measurement is indicated by the white arrow, measured with the FluxSense 10m wind mast. Map from Google Earth™ 2016.

Table 26. Summary of alkane SOF-measurements of Other Sources.

Source Other Sources	Day [yymmdd]	Timespan [hhmmss-hhmmss]	N	Alkane Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
WesternAve_PalosVerdesDrN_SE (Fuel Supply and Storage)	150918	135615 -164251	4	52±15	3.5-5.6	301-324
45thSt_VistaDelMarBlv (Power plant, Wells & Loading)	150909	120758 -151047	5	31±9.0	5.3-5.9	256-274
	150911	110537 -114448	2	41±18	4.6-4.9	233-257
	150913	103832 -142124	5	50±38	3.8-7.1	237-261
	150914	124438 -124748	1	133	4.8	238
	150916	151907 -152320	1	26	5.4	262
	150920	112016 -134936	9	32±19	4.9-6.0	262-286
CherryAve_EWardlowRd_SE (Airport Tanks and Facilities)	150926	131039 -161635	2	80±37	3.6-3.7	201-314
	151111	123133 -123321	1	20	3.6	321
TerminallIslandFwy_SeasideFwy_N (Power Plant)	151101	115847 -115931	1	30	3.5	204
AlamedaSt_PacificCoastHwy St SE (Car Scrap Yard & Painting?)	150902	160210 -160237	1	51	4.2	289
	151110	143615 -143710	1	97	10.3	258
SignalSt_E22St_SE (Disused Tank Farm/Boat Loading)	151019	141833 -142541	1	37	5.9	175
	151020	135300 -170458	2	38±3.7	4.3-4.9	226-230
	151021	124345 -125423	1	14	3.5	183
	151026	130834 -131317	1	20	4.4	235

Table 27. Summary of MeFTIR CH₄ /Alkane ratio and CH₄ MeFTIR+tracer measurements of *Other Sources*.

Source Other Sources	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	CH ₄ /alkane ratio [%]
WesternAve_PalosVerdesDrN_SE	150918	144840 -145111	1	44
CherryAve_EWardlowRd_SE	150926	131056 -131203	1	38

Table 28. Summary of Summary of MWDOAS/MeFTIR ratio measurements of *Other Sources*.

Source Petroleum Treatment Sites	Day [yyymmdd]	Timespan [hhmmss-hhmmss]	N	BTEX/alkane ratio [%]	Benzene/alkane ratio [%]
CherryAve_EWardlowRd_SE	150926	161604 -161625	1	43	3.4

4.7 Uncategorized Area Source

The Sepulveda_Alameda_SE source in Carson/Wilmington is large and diverse industrial area, including several different sites (tank farms, truck loading depots, refineries) which could not be separated using the fence-line measurements (at the prevailing wind direction). Hence, emissions from this area cannot be attributed to any of the categories in this study and is reported separately here. The average alkane emission of 483 kg/h, based on 6 measurements from 4 days (see Table 29), is however not insignificant in terms of the total SCAB emissions. The contribution from this area alone is around 4% of the total alkane emissions in the SCAB which is more than any other single large refinery of Project-1. The daily means varied from 268 kg/h on 29 August 2015 to more than two times that amount, 713 kg/h, on 3 September 2015. No valid BTEX measurements were done on this area source during the survey but a couple of methane measurements indicated a high methane to alkane ratio of 63% (see Table 30).

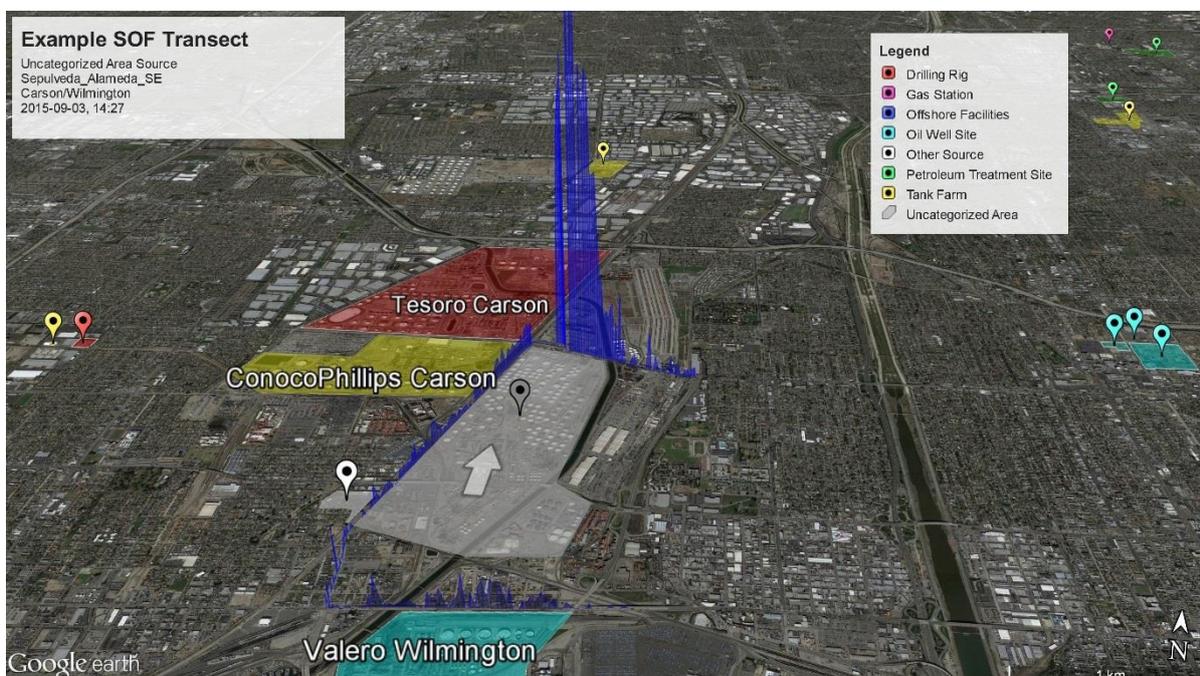


Figure 24. Example of a SOF measurement transect of the *Uncategorized Area Source* (gray shaded area) in Long Beach, 3 September 2015, 14:30. Also noted are large Refineries from Project-1 (names) and other surrounding sources from Project-2. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m², max 400 mg/m²). This particular transect gave 750 kg/h. Wind direction during the measurement is indicated by the white arrow. Map from Google Earth™ 2016.

An example of a measurement transect during southern winds is found in Figure 23. Strong columns were found on the downwind (northern) side and only weak columns on the upwind (southern) side. Note the size of the area and the proximity to other large sources in all directions except on the east side. Measurements during easterly winds would be useful for separating the different sites within the area but were not conducted during the study since this wind direction is rare.

Table 29. Summary of alkane SOF-measurements of an *Uncategorized Area Source* in Carson/Wilmington.

Source Uncategorized Area Source	Day [yymmdd]	Timespan [hhmmss-hhmmss]	N	Alkane Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
Sepulveda_Alameda_SE Tank farm, Terminal & Refineries	150903	142758 -144507	2	713±55	3.5-3.9	156-182
	150904	132219 -133100	1	327	5.0	179
	151003	140703 -143238	2	438±177	5.4-5.4	159-181
	150829	141048 -141744	1	268	3.2	184

Table 30. Summary of MeFTIR CH₄/Alkane mass ratio of an *Uncategorized Area Source* in Carson/Wilmington.

Source Uncategorized Area Source	Day [yymmdd]	Timespan [hhmmss-hhmmss]	N	CH ₄ /alkane ratio [%]
Sepulveda_Alameda_SE	151018	145455 -150436	2	63

4.8 Cattle Farms

NH₃ emissions from *Cattle Farms* in Chino were measured on October 17, 2015 by high resolution (0.5 cm⁻¹) SOF measurements. Total NH₃ emission from the area outlined by the orange rectangle in Figure 25 was 245 kg/h based on three large box measurements (area 4 by 5 km; see Table 31). We estimated 17 cattle farms located within the orange box.

Table 31. Summary of SOF ammonia (NH₃) measurements at *Cattle Farms* in Chino.

Day [yymmdd]	Timespan [hhmmss-hhmmss]	No. of Transects	Ammonia Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
151017	133330 -160319	3	245±19.5	3.8-4.4	234-244

Characterization of the mass concentration ratio of methane to ammonia was performed using MeFTIR in five plume integrations between 14:15-17:44 on October 17, 2015. The plumes of methane and ammonia were co-located, and the integrated cross plume mass ratio of methane to ammonia was on average 2.2±0.3 (± 1 SD), see Table 32. The ammonia flux average of 245±20 kg/h from SOF measurements and the methane to ammonia plume mass ratio of 2.2±0.3 from the MeFTIR measurements infers a methane emission from the sampled area of 540 kg/h.

Table 32. Integrated plume mass ratio of methane to ammonia measured with MeFTIR at *Cattle Farms* in Chino.

Day [yymmdd]	Timespan [hhmmss-hhmmss]	No. of Transects	Methane to ammonia mass ratio Average±SD [%]
151017	141506 -174433	5	220±30

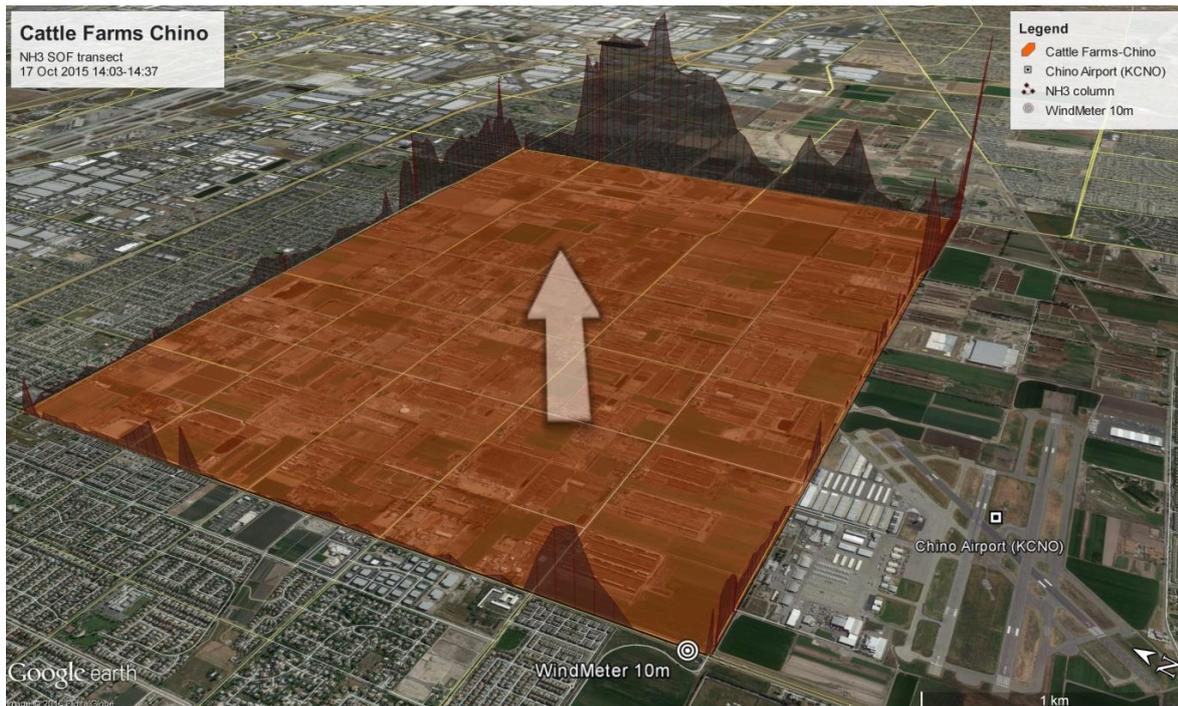


Figure 25. Example of a SOF 'box' measurement of cattle farms in Chino (orange area) refinery 17 October 2015, 14:03-14:37. NH_3 column is shown as a brown curve with apparent height proportional to gas column (100 m equivalent to 1 mg/m^2 , max 22 mg/m^2). Wind direction during the measurement is indicated by the white arrow, measured with the FluxSense 10m wind mast (white circle in the map). Map from Google Earth™ 2016.

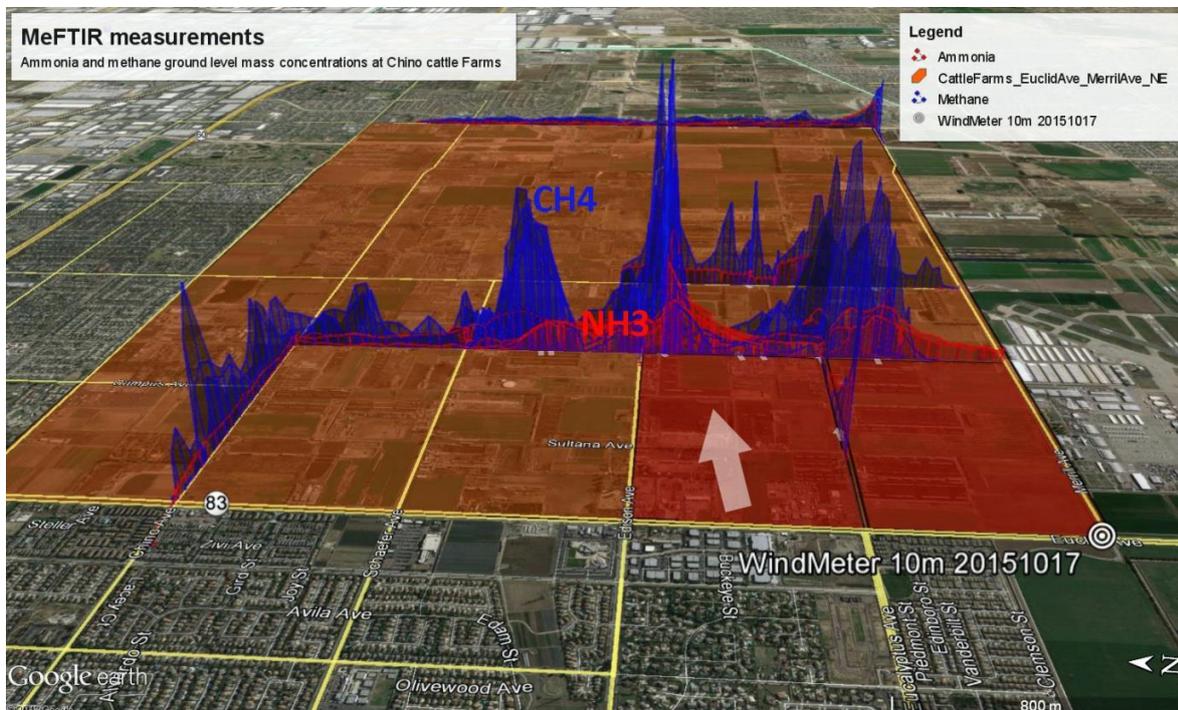


Figure 26. Methane and ammonia ground level concentration measurements with MeFTIR at cattle farms in Chino on October 17. NH_3 concentration is shown as a red curve with apparent height proportional to gas concentration (max $274 \text{ } \mu\text{g/m}^3$). Methane is shown as a blue curve (max $1300 \text{ } \mu\text{g/m}^3$). Wind direction during the measurement is indicated by the white arrow, measured with the FluxSense 10m wind mast (white circle in the map). Map from Google Earth™ 2016.

4.9 Real-time concentration mapping of BTEX and benzene

In addition to locating and quantifying sources of alkanes, BTEX and methane emissions within this project, ground-level concentration mapping of these species were also conducted using MeFTIR and MWDOAS. In some instances, elevated levels of benzene (above 1 ppb over the background) were detected while driving around the known emission source, and the plume was mapped by driving away from that source. Further source identification was performed by detecting a pollution plume(s) and triangulating from the plumes back to the source using the wind direction. Therefore, these mobile surveys can also be used as a tool to assess actual HAP exposure levels in residential areas and sensitive receptors located near the sources. Real-time mobile concentration measurements of BTEX, alkanes and methane, combined with the corresponding SOF alkane flux measurements, were also used to calculate BTEX and methane fluxes.

Figures 27 through 35 show examples of concentration mapping conducted during the project, these examples represent typical sources observed during the study. The total BTEX is shown as a solid black line and the benzene only is shown as a solid blue line; concentrations are presented in [$\mu\text{g}/\text{m}^3$].

On October 25, 2015, FluxSense mobile laboratory measured emissions from an oil well site containing derricks and storage tanks located in a residential area near Sur La Brea Park in Torrance. During this survey, BTEX levels of up to $140 \mu\text{g}/\text{m}^3$ were measured, $45 \mu\text{g}/\text{m}^3$ (or 14.1 ppb) of which were benzene (see Figure 27).



Figure 27. Emission from derricks with associated tanks (main source) at Sur La Brea Park, denoted “Wells_WalnutSt_W236thSt_SW” in the result section, on October 25, 1:35 -1:41 pm. BTEX levels up to $140 \mu\text{g}/\text{m}^3$ was observed on the nearby street, of which $45 \mu\text{g}/\text{m}^3$ was benzene. Wind speeds were low at the time, about 1-2 m/s. Each measured spectrum is represented with a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by distance driven through the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing.

After MWDOAS detected the BTEX plume, an infrared gas camera (FLIR, kindly supported by SCAQMD Long Beach office) was used to visualize the observed emissions, see Figure 28, showing several gas leaks on a couple of tank roofs and pipes.



Figure 28. After MWDOAS detected the BTEX plume at the site by Sur La Brea Park (Figure 27), an infrared gas camera (FLIR) was used to visualize the observed emissions. To the left is a photo of the site, with the gas camera in the foreground. To the right a snapshot from the infrared camera is shown, with emerging gas enhanced by a yellow line here. VOC was being emitted from many leaks on the tank roof and pipes, and the gas is seen as black or white against the grey background.

Figure 29 shows a measurement along E Burnett Street in Signal Hill in the afternoon of October 8, 2015. During this survey, we measured BTEX levels up to $220 \mu\text{g}/\text{m}^3$, of which $40 \mu\text{g}/\text{m}^3$ (12.5 ppb) were benzene.

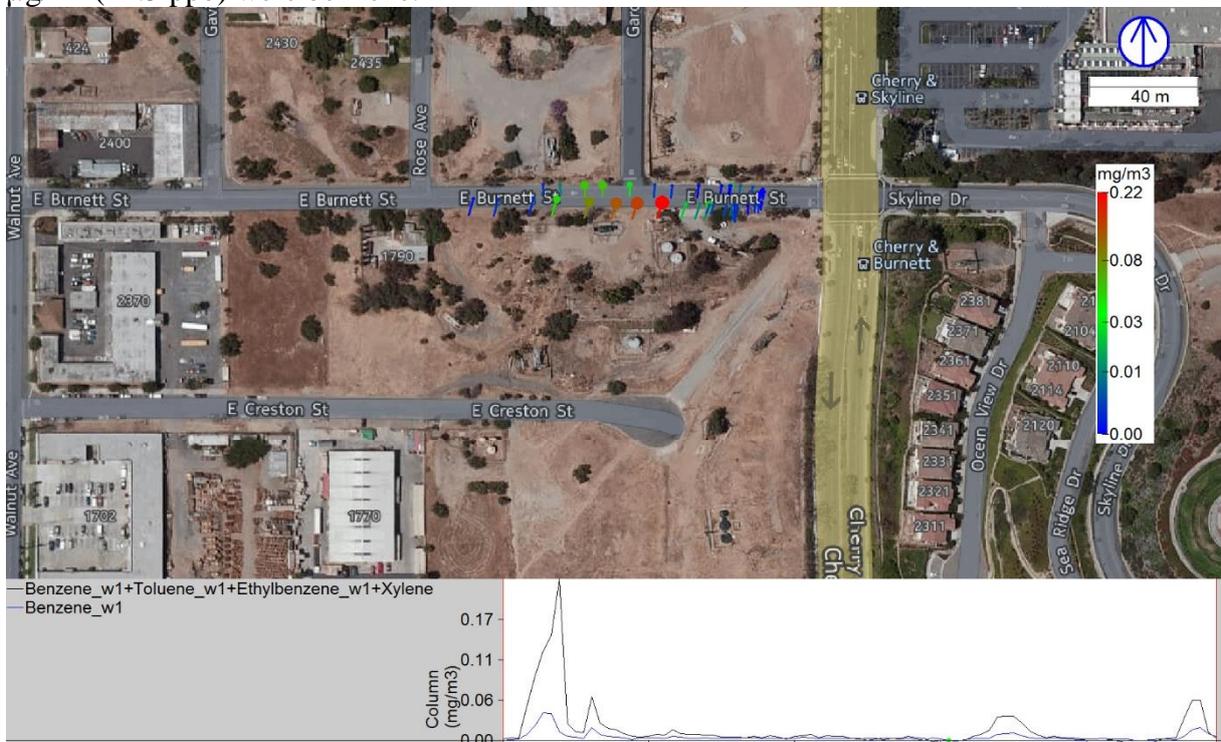


Figure 29. Emission from several wells and tanks measured along E Burnett street in Signal Hill on October 8, 1:58-2:08 pm. Each measured spectrum is represented with a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by distance driven through the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing.

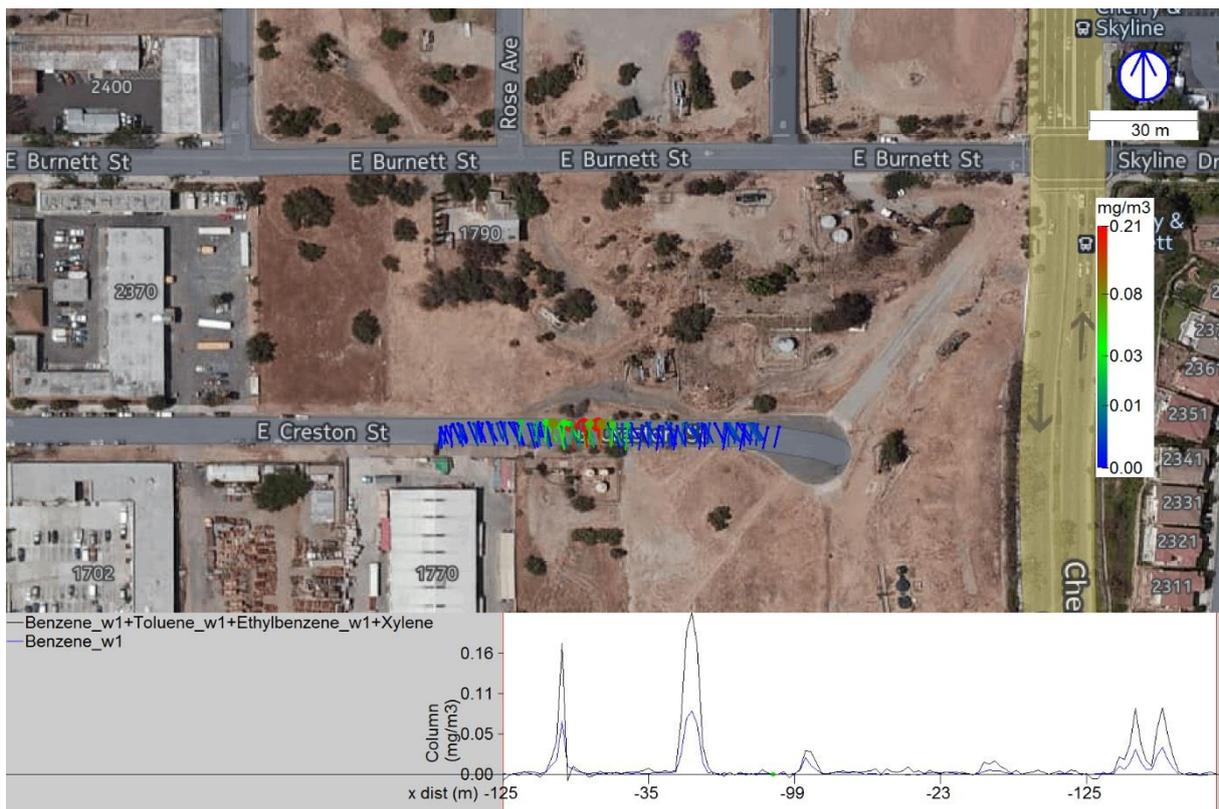


Figure 30. Emission from the well and tanks denoted “Wells_RoseAve_CrestonAve_SW” in the result section, on October 8, 12:31-12:39 am. Each measured spectrum is represented with a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by distance driven through the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing.

Figure 30 shows a measurement in the same area and same day (October 8, 2015 at 12:35 pm), performed in closer proximity to the suspected source on E Creston St, verifying that it was the dominating source of the observed elevated BTEX concentrations. BTEX levels up to $210 \mu\text{g}/\text{m}^3$, of which benzene was $83 \mu\text{g}/\text{m}^3$ (26 ppb), were measured on the street near the source. Winds were blowing from the south at about 2 m/s. Further investigation with a FLIR camera identified a vent of one of the tanks as the main source of emissions.

On October 15 and 16, 2015 flux measurements and BTEX concentration mapping was done at a well site near E 25th Street (also referred to as Crescent Heights Street, see Table 13) in Signal Hill, see Figure 31. During this time period, a drilling rig was active at the site, and increased alkane emissions were observed on 15 October compared to earlier measurements on 3 October when no drilling occurred, see Table 9 and Table 10. High benzene concentrations of up to $180 \mu\text{g}/\text{m}^3$ (56.4 ppb) were detected in the neighbourhood (see Figure 31) during 15 and 16 October.

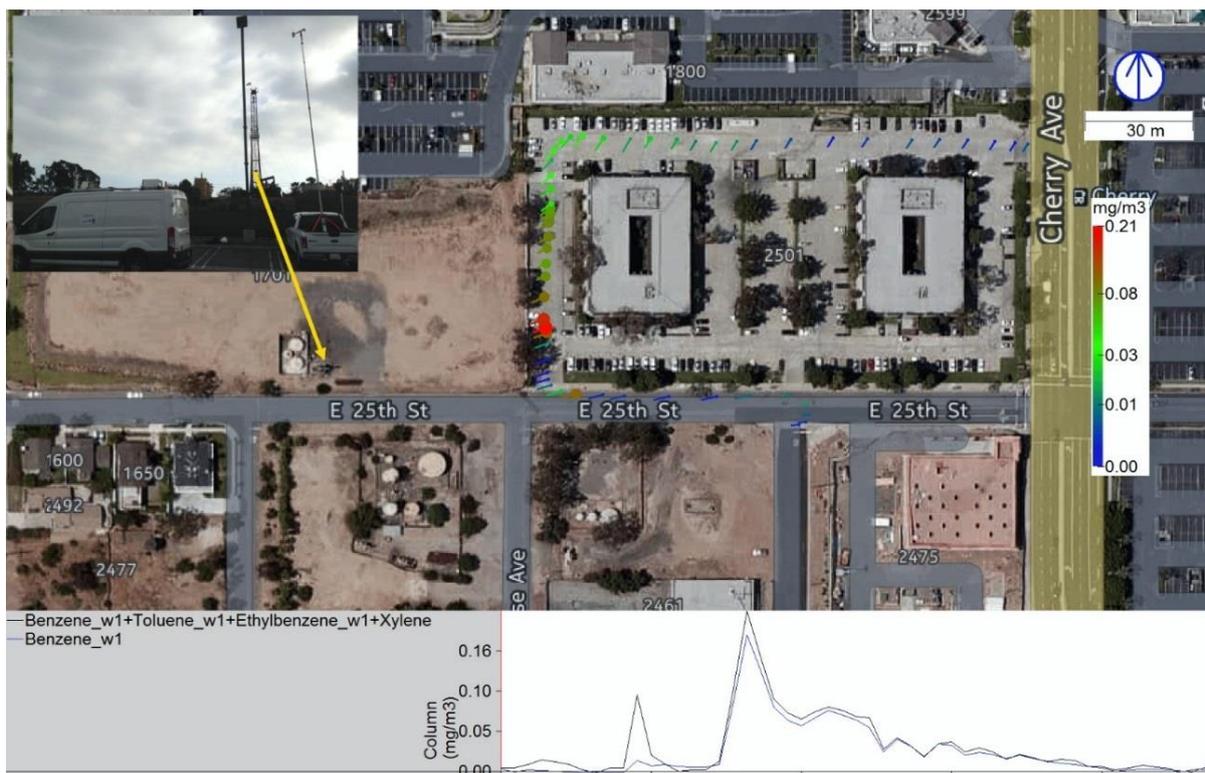


Figure 31. Emission from the drilling site at Walnut Avenue and Crescent Heights on October 16, 12:35-12:41 am. Both on October 15 and 16 high levels of benzene was measured downwind this site. This measurement showed BTEX levels up to $210 \mu\text{g}/\text{m}^3$, of which benzene $180 \mu\text{g}/\text{m}^3$. Wind speed was about 1-1.5 m/s, coming from WSW. Enclosed is a photo of the drilling rig, with the rig position indicated by the orange arrow, and with the FluxSense mobile lab in the foreground. Each measured spectrum is represented with a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by distance driven through the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing.

SOF emission flux measurements as well as BTEX mapping with MWDOAS were carried out on multiple days (see

Table 19), from a petroleum treatment/separation site near the intersection of Orange Ave and E Spring St, in Signal Hill. Figure 32 shows a plume transect on October 3, 2015 at 10:10 AM, depicting BTEX levels of up to $230 \mu\text{g}/\text{m}^3$ on E Spring St, of which benzene was $27 \mu\text{g}/\text{m}^3$ (8.5 ppb). The wind was blowing from south at 3.5 m/s. By means of a FLIR gas imaging camera, the roof of the largest tank on the site (furthest south) was identified as the main emission point.

Figure 33 shows an extended plume transect at a well field and petroleum treatment site located in a residential area in Yorba Linda, near Buena Vista Ave and Greenwich Circle. The measurements were conducted in close proximity to the site as well as while following the plume further away to a distance of 200 m. BTEX levels of up to $110 \mu\text{g}/\text{m}^3$ were measured near the site and of up to $21 \mu\text{g}/\text{m}^3$ at 200 m distance. Corresponding benzene levels were 46 and $3 \mu\text{g}/\text{m}^3$ (14.1 and 1 ppb), respectively. By use of a FLIR camera, a leaky tank roof on the site was identified as the main emission source. The wind speed was about 2 m/s from SSW.

A small tank farm near Orange Ave and E 25 Street in Signal Hill, was measured on October 15, 2015 at 1:45 PM, see Figure 34. A plume of up to $60 \mu\text{g}/\text{m}^3$ BTEX, of which $35 \mu\text{g}/\text{m}^3$ (11 ppb) benzene was observed from the site. Similarly to the other sites, a tank roof vent was identified as a main source of emissions. The wind speed at this occasion was 5 m/s.

Figure 35 shows a measurement at a gas station located at the intersection of Cherry Ave and Willow St, Signal Hill conducted on October 3, 2015. Concentrations of up to $26 \mu\text{g}/\text{m}^3$ BTEX were measured, $4 \mu\text{g}/\text{m}^3$ of which was benzene, at 160 m distance from the source and a wind speed of 2.5 m/s.



Figure 32. Emission on October 3, 10:10-10:12, from the treatment site denoted “TreatmentSite_OrangeAve_ESpringSt_SE” in the result section. Each measured spectrum is represented with a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by distance driven through the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing. The wind was blowing from south at 3.5 m/s.



Figure 33. Emission on October 28, 1:23-1:28 pm, from the treatment site denoted “TreatmentSite_GreenwichCir_RumsonSt_E” in the result section. Each measured spectrum is represented with a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by distance driven through the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing. The wind speed was about 2 m/s from SSW.

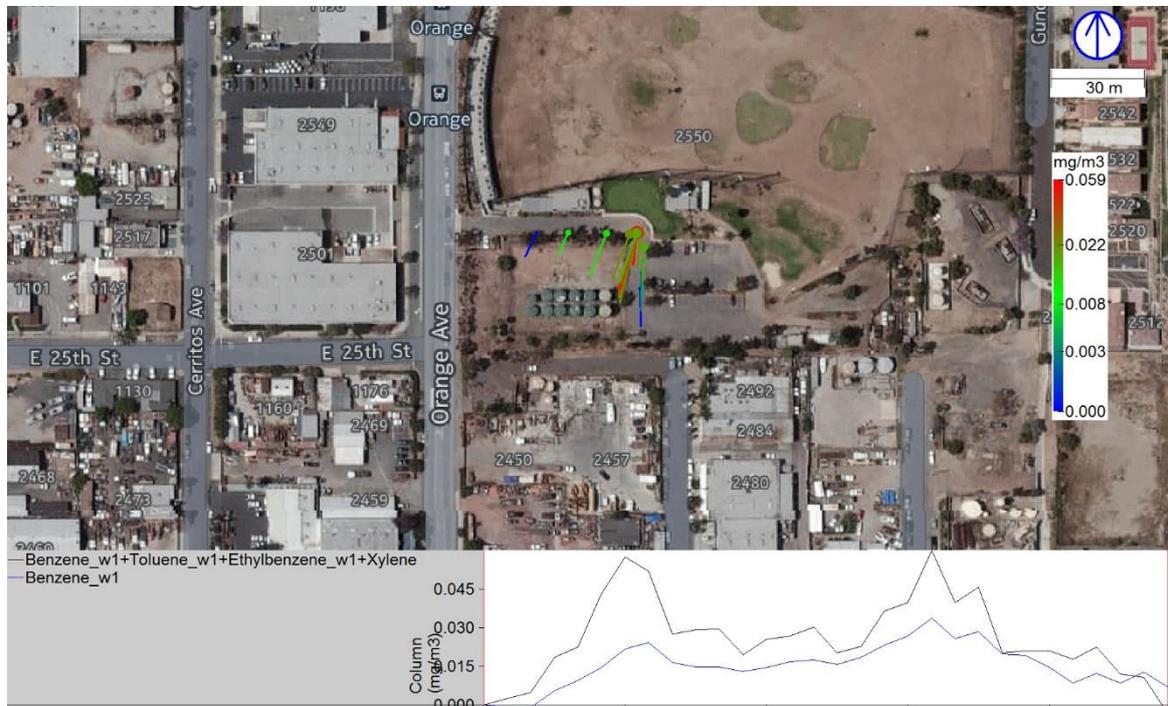


Figure 34. Emission on October 15, 1:46-1:48 pm, from the tank farm denoted “TankFarm_OrangeAve_E25thSt_NE” in the result section. Each measured spectrum is a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by distance driven through the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing. Wind speed was about 5 m/s, coming from SSW.



Figure 35. Emission on Oct 15, 5:02-5:04 pm, from the gas station at Cherry Ave. and E Willow St. in Signal Hill. Each measured spectrum is represented with a point, with color and size indicating the evaluated integrated vertical BTEX column according to the logarithmic color bar. The BTEX (black) and benzene (blue) column by time standing still in the plume is also shown in the lower part of the figure. A line from each point indicates the direction from which the wind is blowing. Wind speed was about 2.5 m/s, coming from W, and the distance from sample position to the source was 160 m.

5 Discussion and Conclusions

Emission measurements of Alkanes, Methane and BTEX in the South Coast Air Basin (SCAB) have been carried out by FluxSense Inc. using several optical remote sensing techniques during a 2-month campaign from September through November, 2015. This report covers Project 2, which focused on small stationary sources of VOCs, in which emissions from 61 sites and six different categories were quantified. Concentration mapping of areas surrounding those sources was also conducted. VOC emissions from an uncategorized area source in Carson/Wilmington, which included multiple unidentified sources, were measured but reported separately due to unfavorable meteorological conditions and lack of accessible roads. A brief study of ammonia and methane emissions from cattle farms in Chino was also conducted.

During Project 2, 451 flux measurement transects and 303 gas mass ratio measurements were performed. The number of measurements for each site varied from a single measurement to more than 30. The final data for each source is presented as daily mean as well as survey mean. When more than one measurement was conducted, the standard deviation is also reported. The reported values are only representative of the time period covered by this study, and the measurement uncertainty depends on the number of samples collected. Single emission values should be considered as snap-shots. Note also that flux measurements of BTEX and methane derived from MWDOAS and MeFTIR measurements have an inherent additional uncertainty due to adding the uncertainties in the gas ratios to the original SOF flux estimate uncertainty. The variability of the result is a combination of measurement uncertainties and actual variability in the emissions generated by these sites. Anomalous emission values, observed in a few occasions/days for some of the facilities, were not excluded since site operations at the time of measurements were unknown and, hence, these values may very well represent a part of the standard operations.

Table 33. Measured and scaled-up emissions for the total SCAB per source category, based on FluxSense measurements during the SCAQMD-2015 campaign, Projects 1 and 2.

Source Category Project-2	No. of Meas. Units	Estimated Number of units in the SCAB	Measured Alkane Emissions [kg/h]	Scaled-up Alkanes Emissions [kg/h]	Scaled-up BTEX [†] Emissions [kg/h]	Scaled-up Benzene [†] Emissions [kg/h]	Scaled-up CH ₄ [†] Emissions [kg/h]
Oil & Gas Wells	106	5000*	138	6510	487	75	1568
Tank Farms, Terminals & Depots	328	750**	314	718	59	7.3	560
Petroleum Treatment Sites & Small Refineries	9	15**	501	835	48	12	411
Gas Stations	8	3140*	10	1947	488	52	492
Offshore Facilities & Activities	7	20**	69	196	<i>n.m.</i>	<i>n.m.</i>	<i>n.m.</i>
Other Sources	7	Unknown	286	286	<i>n.m.</i>	<i>n.m.</i>	109
Uncategorized Area Source	1	Unknown	483	483	<i>n.m.</i>	<i>n.m.</i>	301
Six Large Refineries (Project-1)	6	6	1130	1130	129	18	705
Total SCAB	472	8932	2931	12105	1212	164	4146

[†]Median BTEX and CH₄ fractions within each category have been used to calculate scaled-up fluxes. Also shown are the results for six large refineries (Project-1), which are described in separate report. *[DOGGR 2016] ** Visual Estimations using GoogleEarth™. n.m. = not measured.

Table 33 presents a summary of the measured and estimated scaled-up total hourly emission rates for all different categories in this study and in Project-1. The total measured emission of alkanes from all sources in Project-2 adds up to 1,318 kg/h, which is comparable to the 1,130 kg/h from the six large refineries in Project-1. There is also a contribution of 483 kg/h from the Uncategorized Area Source, resulting in a total measured alkane emission rate of 1801 kg/h. During Project 2 emission measurement were conducted from a very limited subset of small sources, while in Project 1 emissions from nearly all big refineries were quantified. When extrapolated to the total number of estimated small sources in the SCAB, the total hourly alkane emissions add up to around 12,000 kg/h, most of which (over 85 %) emanated from the six source categories considered in Project-2.

Figure 36 shows the relative distribution of alkane+BTEX emissions if the average results from the measured units within each category in Table 33 are used to scale total emission fluxes for all measured types of sources. This gives an overall alkane+BTEX emission of approximately 13,000 kg/h of which 53% from *Oil & Gas Wells*, 18% from *Gas Stations*, 9% from *Large Refineries (Project-1)*, 7% from *Treatment Facilities & Small Refineries*, 6% from *Tank Farms, Terminals & Depots*, and 2% from *Other Sources*. *Off Shore Facilities & Activities* emissions represent only about 1% of the total. However we are of the opinion that the overall emissions from this last source category are higher than calculated if one were to account for oil platform emissions and fuel barge operations which are not included in the Project 2 survey. The category distribution for individual gases (alkanes, BTEX, Benzene and Methane) are found in Figure 37 to

Figure 40. Notable here are the high relative contribution of *Gas stations* for BTEX (40%) and *Oil & Gas Wells* for Methane (38%).

The scaling-up approach has uncertainties due to the assumptions made on the total number of units for each source category. Measurements may also not be representative for all times of the day and seasons (e.g., gas stations tend to be busier during rush hour when most measurements were made). Ideally, the gas station measurements should be assessed relative to the actual loading volumes, establishing an emission factor that can be scaled to the overall gas station loading volumes in the SCAB. On average, there were 4.6 cars fuelling while the gas station measurements were conducted in this project. The gas station measurements include the overall fuelling event, for example lining up prior to accessing the fuel pump, actual fuelling and then starting up to leave the site. In the present scaling for the gas station emissions, a diurnal cycle was used with the established average emission applied for 12 hours, and no emissions for the remaining time.

In terms of scaling emissions to estimate emissions from all offshore activities, there is a large uncertainty in, for example, the average number of active fuel barge operations, ship fuelling and venting activities. For this purpose, a more viable approach would be to include more measurements to establish typical emission factors for these activities and scale with data on number of operations within the port area, or handled product volumes where applicable.

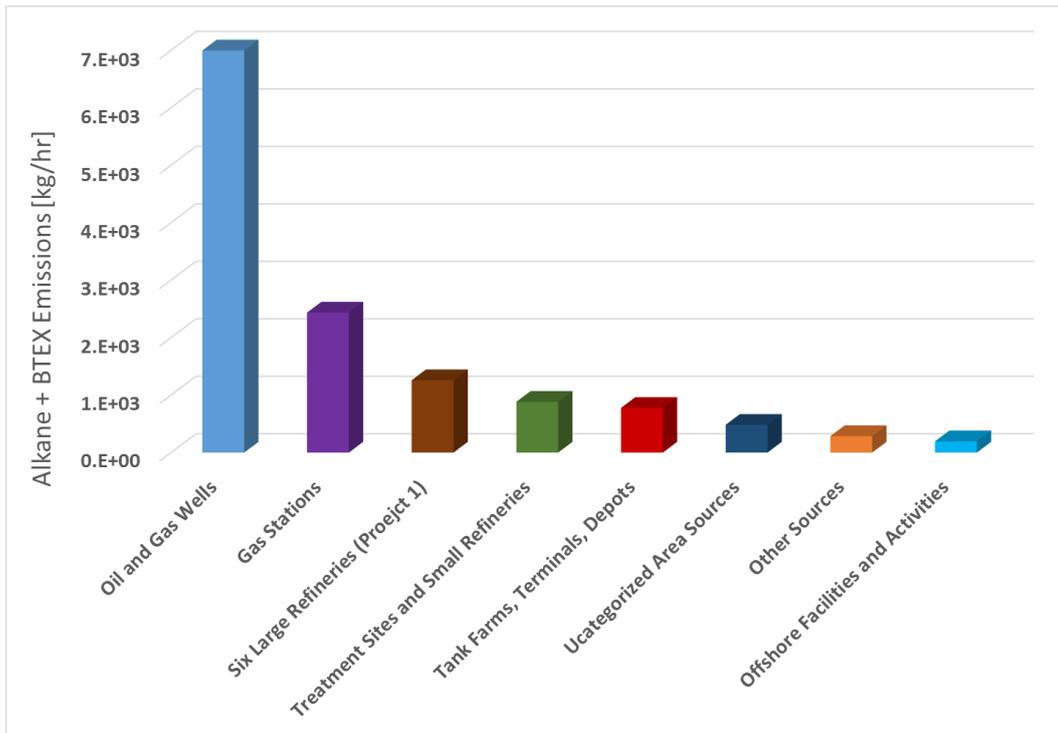


Figure 36. Relative contribution to total **alkane and BTEX** emissions from the various source categories investigated in Projects 1 and 2. Emission rates for each category were calculated by multiplying the average measured emission per unit by the estimated number of total units. Total alkane and BTEX emissions are approximately 13,000 kg/h from all included sources. Note that no BTEX emissions are excluded for *Offshore Facilities*, *Other Sources* or for the *Uncategorized Area Source*, due to lack of measurements.

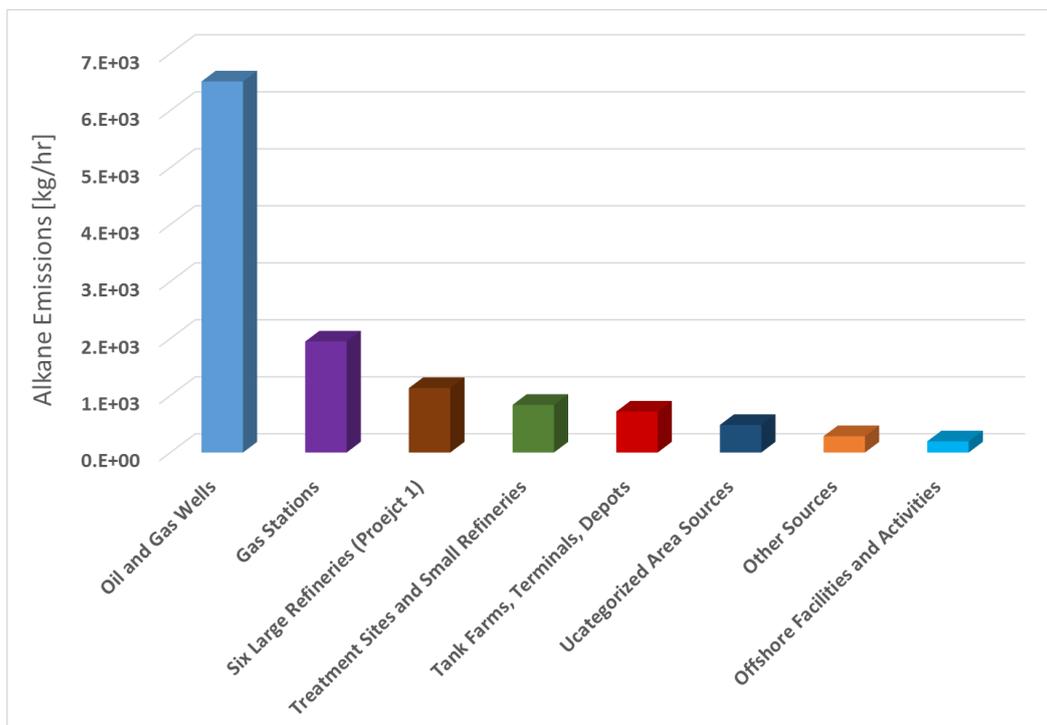


Figure 37. Relative contribution to total **alkane** emissions from the various source categories investigated in Projects 1 and 2. Emission rates for each category were calculated by multiplying the average measured emission per unit by the estimated number of total units. Total alkane emissions are approximately 12,000 kg/h from all included sources.

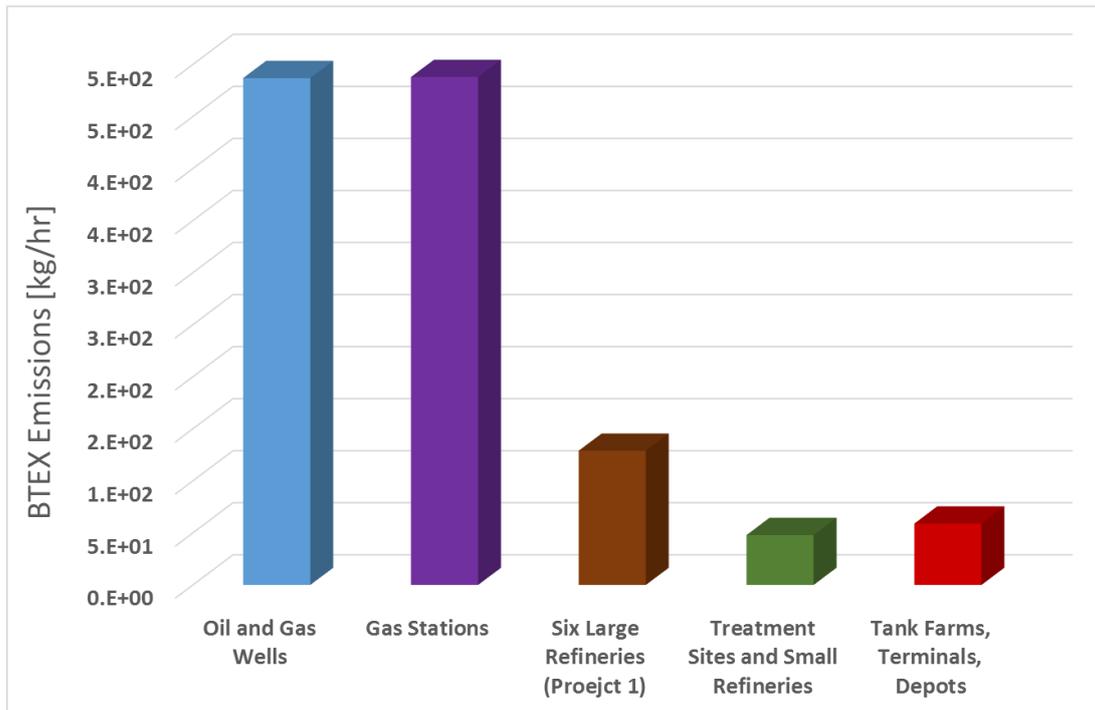


Figure 38. Relative contribution to total **BTEX** emissions from the various source categories investigated in Projects 1 and 2. Emission rates for each category were calculated by multiplying the average measured emission per unit by the estimated number of total units. Total BTEX emissions are approximately 1,200 kg/h from all included sources. Note that BTEX emissions were not included for *Offshore Facilities*, *Other Sources* or for the *Uncategorized Area Source*, due to lack of measurements.

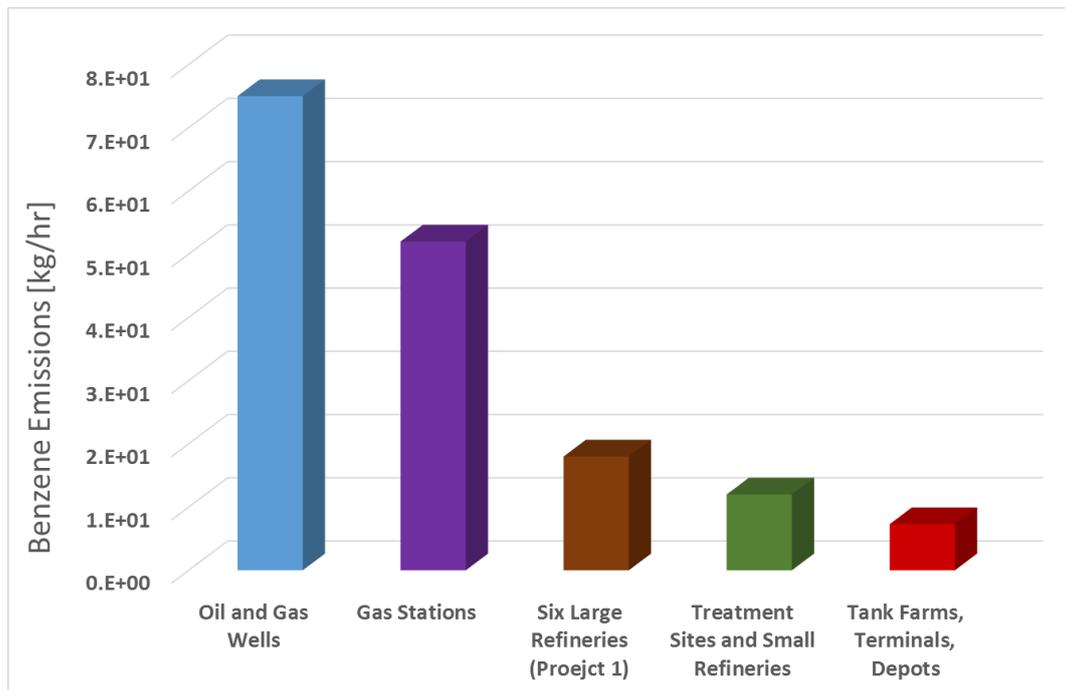


Figure 39. Relative contribution to total **benzene** emissions from the various source categories investigated in Projects 1 and 2. Emission rates for each category were calculated by multiplying the average measured emission per unit by the estimated number of total units. Total benzene emissions are approximately 160 kg/h from all included sources. Note that Benzene emissions from *Offshore Facilities*, *Other Sources* or for the *Uncategorized Area Source* were not included due to lack of measurements.

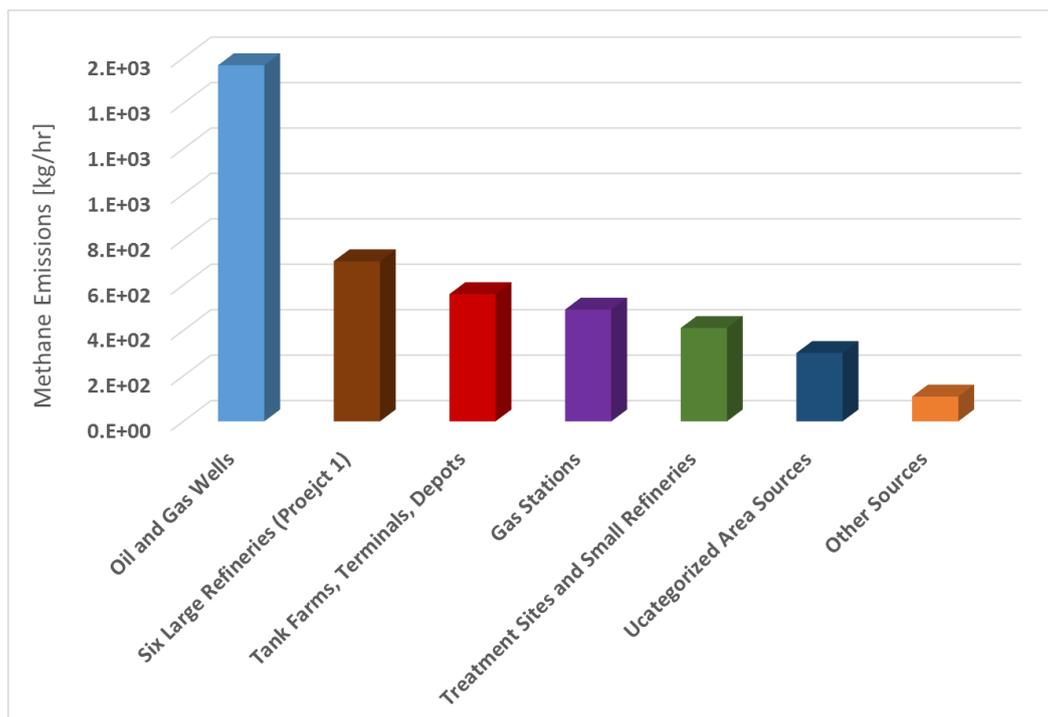


Figure 40. Relative contribution to total **methane** emissions from the various source categories investigated in Projects 1 and 2. Emission rates for each category were calculated by multiplying the average measured emission per unit by the estimated number of total units. Total methane emissions are approximately 4,100 kg/h from all included sources. Note that methane emissions from *Offshore Facilities* were not included due to lack of measurements.

Considerable methane emissions were seen from the various sources in Project-2. The average measured methane to alkanes ratio for the oil and gas wells was 0.53, whereas a much higher value (0.78) was measured for tank farms and depots. Aside from methane being part of the stored or handled product, the presence of methane emissions could be explained common practices such as when tanks are blanked with methane at the top to limit VOC emissions, and methane is leaking into the atmosphere. The overall methane emission rate of 636 kg/h was calculated from the selected sites investigated in Project-2. This value is comparable to the emission rate measured from the large refineries in Project-1 (700 kg/h). However, when emissions measured in Project 2 are scaled-up to account for other small sources in the SCAB, methane emissions from these non-refinery sources become dominant.

Approximately 68 kg/h of BTEX (of which 12 kg/h was benzene) were measured from the various sources surveyed in this project. These emission rates are approximately half of the total BTEX rates measured from all large refineries in the SCAB (see Project 1). Considering the large number of active oil wells and gas stations in the SCAB, the total actual BTEX load from these sources is likely to be substantial.

Large temporal variations in measured emission rates and large variability in emissions from similar sources/sites/units were also observed. This variability highlights the importance to associate the amounts of observed emissions with the type(s) of operations conducted at each site. The drilling event observed on October 15, 2015 (see Section 4.1.1) offers a good example of how emissions can vary over the life cycle of an oil well. More detailed information on the status of each unit and of ongoing activities at each sites will provide useful information on when large emissions may occur and how they could be reduced.

Measured average emissions from the *Uncategorized Area Source* in Carson/Wilmington were 483 kg/h of alkanes and 301 kg/h of methane. Daily measured emissions showed significant variability, with values ranging from over 700 kg/h on 3 September 2015 to less than half this amount for the remaining measurement days (see Table 29). A more detailed survey of this area was not possible due to the complexity of the fence-line configuration and the variable wind patterns experienced during the study. Additional measurements in this area, preferably during easterly winds, could help assign the emissions to the specific sites. If such source identification is successful, emissions from the different sites can be assigned to the appropriate source category, creating a more accurate total emission estimate. BTEX measurements in this area will also help to create a more complete picture of emissions.

Substantial methane and ammonia emissions were measured from *cattle farms* in Chino. On average 245 kg/h NH₃ and 540 kg/h CH₄ (compared to 648 kg/h from the other measured sources) were observed from an area of 5.4 by 4.0 km, including approximately 17 cattle farms. No attempt was made to scale-up these biogenic emissions of NH₃ and CH₄, because of the limited number of measurements taken, the limited knowledge of the sources, and the total number of units (cattle farms or cows) in the SCAB. More extensive measurements are needed to better quantify emissions from this source category and from other biogenic sources such as water treatment plants or landfills.

This project also demonstrated the potential of mobile measurements for community-scale monitoring. Traditionally, such monitoring is conducted by establishing multiple fixed measurement sites near the facility of interest and in a surrounding community. While this strategy is sufficient for surveying emissions from a single facilities, it is nearly impossible to implement for routine community scale monitoring at numerous locations. Therefore, mobile measurements offer a clear progress towards large-scale monitoring of multiple sources and communities.

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8 Appendix: Quality Assurance

Quality checks and measures are performed at several levels in order as indicated in Figure 2 and given below. On arrival on a measurement day, FluxSense personnel will power up the equipment, check operating parameters, and test the instruments. The purpose is to run operational checks to catch problems prior to field deployment and repair all malfunctioning equipment.

Quality Checks and Routines

PRIOR TO MEASUREMENTS:

Vehicle:

1. Checking vehicle status according to safety and performance
2. Mount warning lights and signs
3. Make sure that battery pack is fully charged
4. Make sure any loose items are stowed away securely

Instruments:

1. Turn on instruments and make sure that detectors are properly cooled
2. Optimize signals by optical alignment (SOF, SkyDOAS, MWDOAS, MeFTIR)
3. Cleaning mirrors and optics if necessary (SOF, SkyDOAS, MWDOAS)
4. Rotational alignment (SOF). Tolerance: ± 2 mg/m² in any direction
5. Checking spectral resolution and response (SOF, SkyDOAS, MWDOAS, MeFTIR)
6. Take calibration spectra (SkyDOAS, MWDOAS)

GPS:

1. Checking that GPS information is available and reasonable.
2. Check time synchronization of all instruments and computers.

Wind:

1. Checking that the time difference of logger and computer and synchronize if necessary. Tolerance 1s.
2. Select an open flat surface at a representative location for the measurements
3. Erecting the wind mast vertically and secure it firmly
4. Directing sensor correctly (toward magnetic north) using a compass. Tolerance: ± 5 deg.
5. Check that wind information is available and reasonable

Tracer Measurements:

1. Weigh gas tube without regulator and ensure sufficient amount of trace gas left for the entire measurement period
2. Mount gas regulator and release tube and ensure no leaks.
3. Turn the gas regulator to an appropriate flow rate for the prevailing measurement conditions and note start time.

DURING MEASUREMENTS:

1. Drive slowly and steadily to reduce vibration noise. Around 20-30 km/h for SOF/SkyDOAS and around 10-20 km/h for MWDOAS/MeFTIR (dependent on distance to source and the spatial resolution required)
2. Avoid shadows as far as possible during solar measurements (SOF, SkyDOAS).
3. Try boxing the facilities when possible or make relevant upwind/background measurements continuously.
4. Keep track of wind directions and measured columns/concentrations so that the entire plume from a facility is captured.
5. Always try to start new measurements outside the plume.
6. Aim for 3-5 transects with acceptable quality (See section on data analysis below) per facility and day and at least 1 upwind measurement (if not boxing).
7. Take notes and photos on interesting findings and events
8. Check the wind meter on a regular basis to make sure that it is operational

AFTER MEASUREMENTS:

1. Turn off instruments and download gas measurement data to external hard drive
2. Download data from wind mast logger and save to external hard drive
3. Download data from wind LIDAR and save to external hard drive
4. Dismount wind mast if not in safe location
5. Turn off wind LIDAR and store securely over night
6. Store Airmar data and measurement notes on external hard drive
7. Update survey documents and Google Earth maps accordingly
8. Charge vehicle, LIDAR and data logger batteries over night
9. Make sure that instruments are well protected inside the vehicle from rain/moisture

For Tracer Measurements:

10. Turn off gas regulator and note stop time.
11. Dismount regulator and weigh gas tube

DATA ANALYSIS:

1. Discard transects with noise levels above the detection limits (see Table 1)
2. Discard transects with significant baseline variations
3. Discard transects with significant data gaps in the plume
4. Discard transects with extended vehicle stops
5. If incoming plumes are of significant magnitude compared to the outgoing plume (SOF and SkyDOAS) treat transects with extra care and require further statistics
6. Discard transects with average wind speeds below 1.5 m/s (SOF and SkyDOAS)
7. Discard transects with highly varying wind directions
8. Discard transects with no relevant wind information or opposing results for nearby met stations.

Data Analysis, Interpretation, and Management

DATA REPORTING REQUIREMENTS:

A Draft and Final Report are delivered to SCAQMD electronically (i.e., via file transfer protocol (FTP) or e-mail) in MS-WORD. Raw data and a Google Earth-KMZ file with geo location information of the sites will be delivered to SCAQMD at the time of the final report.

DATA VALIDATION PROCEDURES:

FluxSense maintain records that include sufficient information to reconstruct each final reported measurement from the variables originally gathered in the measurement process. This includes, but is not limited to, information (raw data, electronic files, and/or hard copy printouts) related to sampler calibration, sample collection, measurement instrument calibration, quality control checks of sampling or measurement equipment, "as collected" or "raw" measurement values, an audit trail for any modifications made to the "as collected" or "raw" measurement values, and traceability documentation for reference standards.

Difficulties encountered during sampling or analysis, such as interference between adjacent plumes, large upwind fluxes or highly variable wind fields are documented in narratives that clearly indicate the affected measurements. All electronic versions of data sets should reflect the limitations associated with individual measurement values.

The data collected in the project is made available in electronic format at the time of the final report. For all data we will produce ASCII tables with the geo-positioning and time. In addition, KMZ files will be produced for the most useful data for Google Earth viewing.

To ensure high quality data an internal audit procedure of the data is carried out. In the project, gas columns obtained from SOF and mobile DOAS measurements are used to calculate gas fluxes through a procedure which includes manual checking of each measurement transect and manual choices of baselines etc. In the audit procedure the completed transects will be reviewed by a person that was not involved in the actual data evaluation.

STATISTICAL PROCEDURES:

The final data is presented as daily averages and standard deviations for each facility together and a total survey averages. Note that the variability of the result is a combination of measurement uncertainties, wind variability and actual variability in the emissions from the facilities.

Extreme outliers are generally not excluded, unless non-typical conditions/operations at the site are reported. In this case, the outliers are reported separately so that these conditions/operations can be followed up.

More samples provide a closer estimate of the actual emissions. In reality, the number of measurements will be a trade-off between acceptable statistics and available time and conditions for making the measurement and time sharing between other measurements.

DATA SUMMARY AND ANALYSIS:

The data is post processed with the spectral retrieval programs QESOF (SOF) and QDOAS (mobile DOAS). This gives time series of column concentrations, positions and solar angles stored in ASCII-files. These files are loaded into custom software, SOF-Report, used to calculate fluxes.

Wind LIDAR data are processed using the output from Leosphere WindCube system. Data files are saved as ASCII-files.

The weather mast is connected to a real time data logger and is periodically downloaded to a computer. The data logger samples the input voltage of each instrument at a set time interval, digitizes it, and stores the data sequentially into a record.

ASCII tables with time stamped geo positioned data are produced. In addition, kml files will be produced for viewing the data in Google Earth. The data will also be retained for a minimum of 5 years at FluxSense.

DATA STORAGE REQUIREMENTS:

The spectra from the spectroscopic measurements (SOF, SkyDOAS, MeFTIR, MWDOAS) are directly saved to the hard drive of the computer used to operate these instruments. At the end of each measurement day, all new such data will be copied to an external hard drive by the operator. Approximately 1 GB of data will be produced per measurements day.