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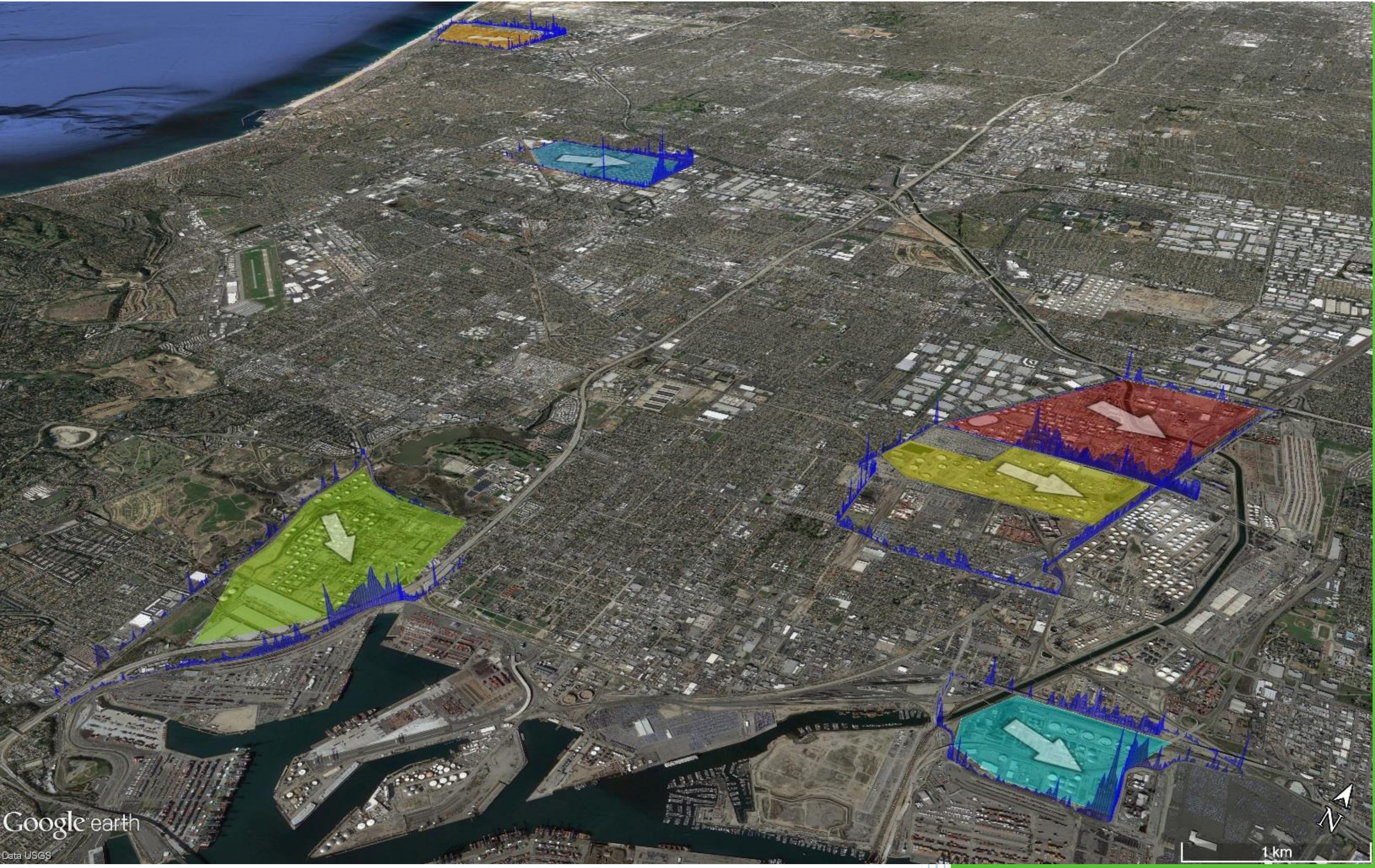
Emission Measurements of VOCs, NO_2 and SO_2 from the Refineries in the South Coast Air Basin Using Solar Occultation Flux and Other Optical Remote Sensing Methods



FluxSense

FINAL REPORT

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Title: 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

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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 100 industrial site surveillances in Austria, Belgium, Denmark, France, Middle East, Netherlands, Norway, Sweden and the US.

[Cover: Visualization of alkane plume transects (blue curves) from Solar Occultation Flux (SOF) measurements conducted at the six refineries for this study during similar wind conditions. The apparent height of the blue line is proportional to the integrated vertical column concentration expressed in mg/m^2. White arrows indicate wind directions during these measurements. Image mapped on Google Earth © 2016.]

Executive summary

BACKGROUND

Accurate characterization of facility-wide emissions from industrial sources on a real or near-real time basis is critical for developing effective control strategies to improve regional air quality, promoting compliance, and reducing exposure for nearby communities. To improve the understanding of such emissions in the South Coast Air Basin (SCAB), the South Coast Air Quality Management District (SCAQMD) has sponsored a series of measurement projects to study industrial emissions using Optical Remote Sensing (ORS) methods. The projects include experimental studies of emissions from refineries, oil depots, treatment facilities, oil wells, gas stations, fuel islands and barges. In addition, SCAQMD has sponsored technology demonstration and validation studies to assess potential uncertainties of different optical techniques through side-by-side measurements of real sources and controlled source gas releases.

Numerous research studies using ORS conducted in the US and worldwide (including a 2013 pilot project sponsored by SCAQMD) suggest that measured emissions of VOCs from industrial facilities are larger compared to emission inventory estimates developed based on accepted reporting conventions. Given the large number of refineries and other industrial activities in the SCAB, it is therefore very important to evaluate novel measurement methods for detecting and quantifying industrial emissions directly.

This report presents the results of a two and a half month long measurement campaign aimed at characterizing and quantifying emissions of VOCs, NOx, and SO_2 from six major refineries in the SCAB. The measurements spanned from August 28 to November 11 2015, with up to 15 individual measurement days at each site. Additionally, a detailed eight day long measurement study inside the tank farm of one of the refineries was conducted to quantify emissions from the tank farm, locate potential leak sources, and validate the SOF technique by comparative measurements to other ORS methods.

Mobile surveys using two ORS techniques, namely SOF (Solar Occultation Flux) and Mobile SkyDOAS (Differential Optical Absorption Spectroscopy), were conducted around the refineries' perimeters to estimate facility-wide emission fluxes of VOCs, SO_2 and NO_2. These ORS techniques were complemented by extractive optical methods, including MeFTIR (Mobile extractive Fourier Transform Infra-Red spectroscopy) and MWDOAS (Mobile White cell DOAS) to map ground concentrations of alkanes, methane and aromatic VOCs and to calculate inferred fluxes for methane and aromatics. The required wind information was collected using a stationary wind-LIDAR (LIght Detection and Ranging; which provides vertical wind profiles) and conventional wind mast measurements.

SOF is a proven technique employed 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 (Barthe *et al.* 2015), and in Sweden it is used together with tracer correlation and optical gas imaging to annually screen all larger refineries and petrochemical industries. In Swedish facilities, ORS emission measurements are conducted annually for at least ten days, during different seasons, in order to obtain a good representation of the annual mean. These measurements represent the total emission flux coming from the entire refinery, divided into sub parts such as process areas, crude oil storage, product storage tanks, water treatment facilities, flares, and loading operations. In the study presented here, such sub-area measurements were demonstrated for the tank farm of Refinery A.

The estimated uncertainty for the SOF emission measurements is typically 30 % for total site emissions, and usually slightly higher for individual sub-parts. The estimated measurement uncertainties have been verified in several (blind and non-blind) controlled source gas release experiments (including the one performed during this study and discussed elsewhere) and in side-by-side measurements with other techniques. The uncertainties in the total refinery emissions of BTEX and CH_4 obtained from inferred fluxes are larger than for the direct flux measurements of alkanes. Ideally, the gases should be well mixed in the plume for this method to work the best, but in reality there will be a stronger weighting towards low elevated sources (tanks) compared to higher elevated ones (process units) depending on the measurement geometry. Based on canister samples collected in several European refineries in the past, we know that typically the BTEX fraction is higher in the process units (10-15 % of total VOCs) compared to tank farms (5-10 % of total VOCs). The inferred BTEX flux will consequently be a low estimate of actual BTEX emissions because plumes from tanks are usually located closer to the surface, while plumes from process areas can extend further up into the atmosphere. In this study the overall BTEX to alkane ratio was 0.11.

RESULTS

Table ES.1 shows the measured hourly emission rates (kg/h) of various gaseous species from the refineries investigated during this study. The emissions presented in table ES 1 represent median values of all valid transects obtained during the two and a half month study period. The BTEX and CH_4 emission values have been extrapolated from concentration ratios of these species to alkanes measured at ground level and scaled with direct alkane emission measurements by SOF. It should be noted that, rather consistently for all the refineries, the BTEX emissions are typically one tenth of the total VOC emissions, while CH_4 emissions are on average two thirds of the alkane emissions.

Table ES.1. Median values of all measured site emissions during the 2015 SCAQMD survey. The fluxes of alkanes, SO_2 and NO_2 are obtained from direct measurements, while BTEX and CH_4 are inferred from gas ratio measurements. Note that benzene is part of BTEX.

Measured Refinery SCAQMD Survey 2015	**N Days**	**Alkane Flux** [kg/h]	**SO_2 Flux** [kg/h]	**NO_2 Flux** [kg/h]	**BTEX Flux** [kg/h]	*Benzene Flux [kg/h]*	**CH_4 Flux** [kg/h]
Refinery A	15	269	62	66	24	*3.4*	167
Refinery B	5	70	53	31	11	*1.1*	53
Refinery C	4	244	37	57	37	*8.2*	142
Refinery D	7	164	17	34	16	*1.6*	79
Refinery E	7	244	53	63	31	*2.7*	207
Refinery F	4	139	37	18	10	*0.8*	57
Sum		**1130**	**259**	**269**	**129**	*18*	**705**

In Table ES.2 the measured emission data for the various sites has been normalized by the corresponding crude oil capacity for each facility and compared to the reported emission inventories. The table shows that the measured VOC emission factors for the studied refineries range from 0.017 % to 0.045 % (mass emission per mass capacity of crude). SOF measurements carried out in other well-run refineries typically show average VOC emission factors of 0.03 % to 0.1 %. Thus, according to this data, the refineries in the SCAB are generally performing well, with relatively low emission compared to their capacity. However, as highlighted in Table ES.2, significant differences exist between measured and reported inventory emissions for VOCs and, for all refineries combined, the overall discrepancy between measured and reported inventory values was a factor of 6.2. For benzene the corresponding overall discrepancy ratio was about 34, although the magnitude of BTEX emissions was relatively small. Refinery C stands out with a measured benzene emission being more than twice as high as the next refinery in order. The measured SO_2 and NO_2 emissions are much closer to, and in some instances lower than, those reported in the inventories. In Table ES 2, the reported annual emissions have been divided by 12 to obtain a monthly inventory value to compare to the measured monthly median emissions from this survey. Hence, the discrepancies and emissions factors are representative for September 2015 (the time-period when the majority of the ORS measurements were performed).

Table ES.2. VOC emission factors normalized by the corresponding crude oil capacity for the various sites, and ratios between measured values and reported inventories for the 2015 SCAQMD survey.

Measured Refinery	**Crude capacity 2015***		**Measured Monthly**	**Emission Factor****	**Discrepancy factor (Measured/Reported^2)**			
Representative of September			**Emission for Sept. 2015**					
2015	**bbl/day**	**Tons^1/mo**	**Alkanes+BTEX Tons^1/mo**	**Alkanes+BTEX %**	**Alkanes+ BTEX**	**SO_2**	**NO_2**	**Benzene**
Refinery A	257300	1086215	214	0.020 %	6.4	1.2	1.0	43
Refinery B***	139000	586801	59	0.045 %	8.3	1.5	0.8	33
Refinery C***			205		11.8	2.7	1.1	202
Refinery D	104500	441156	132	0.030 %	10.5	1.7	1.1	39
Refinery E	269000	1135608	201	0.018 %	5.4	1.7	0.8	38
Refinery F	149500	631128	109	0.017 %	2.7	1.1	0.3	3.2
Overall****	**919300**	**3880908**	**919**	**0.024 %**	**6.2**	**1.5**	**0.83**	**34**

* Crude capacity data is obtained from the 2016 California Energy Commission report.

** Mass emission per mass capacity of crude oil.

*** Crude capacity for Refinery B and Refinery C are reported together since Refinery B processes the crude oil and the Refinery C upgrades intermediate products to finished products.

**** The overall discrepancy values are calculated from the total sum of reported and measured emissions, respectively. The overall emission factor is based on the sum of measured emissions for all refineries relative to the total capacity. Reported annual values have been divided by 12 to obtain a monthly inventory value to compare to the measured monthly average emissions from this survey. The comparisons are representative for September 2015 (the time-period when most of the measurements were performed).

[1] metric tons.

[2] Note that total nitrogen oxides (NO_x) are reported while only the NO_2 fraction was measured by SkyDOAS.

ORS measurements were also conducted for eight days inside the tank farm of one of the refineries listed above. The objective of this part of the study was to demonstrate the capability of real time ORS techniques to identify and quantify emissions and potential gas leak sources inside a refinery. Several storage and crude oil tanks were identified as VOC emitters, including a large underground reservoir containing vacuum gas oil (VGO).

While conducting measurements inside one of the refineries, our mobile optical methods identified an area characterized by elevated alkane concentrations of about 70,000 ppb, in contrast to the ten to a few hundred ppb normally measured downwind of similar sources. An infrared gas imaging camera (FLIR) was used to visualize and confirm alkane gas emissions through a shallow pool of water on the ground. Once the leak was discovered, the refinery staff took swift action to investigate and repair the source of the leak. The investigation discovered a pinhole-size leak in a pipeline buried 30 cm below the ground. After the leak was repaired additional ORS measurements were conducted to verify that the problem was resolved. This event illustrates how mobile ORS measurements combined with conventional gas imaging can quickly identify an unknown leak and allow it to be fixed before any serious complications may occur.

Within this project we also conducted a separate study to compare the SOF readings to those of other ORS techniques such as DIAL (Differential Absorption Lidar) and long-path FTIR through side-by-side measurements on various tanks inside one of the refineries. The agreement between emissions from different tanks and reservoirs inside the refinery measured by SOF and DIAL was excellent (within 10-20 %). As part of the SOF, DIAL and long-path FTIR technology comparison and validation, a blind gas release experiment was also carried out using a controlled source emitting 2-25 kg/h of odorless propane at the flat open parking lot of the Angels stadium in Anaheim, CA. In this study, the SOF measurements consistently underestimated the true emissions by 35%, but showed excellent correlation for the different release rate configurations (R^2 ~98%). The detailed results of this technology inter-comparison study are compiled and presented in a separate report.

DISCUSSION

A common concern when comparing measured emissions with those reported in the inventories is that the reported data are calculated for a full year while measurements are typically conducted over a limited time period. This may impact uncertainties when translating measured emission rates to annualized values, as external environmental parameters such as wind, temperature and solar insolation, affect tank emissions. An additional concern is whether a sufficient number of measurements (and measurement days) have been sampled to eliminate the influence of any intermittent emissions due to tank cleaning, maintenance, flaring, etc. To address these concerns, we carefully analyzed the frequency distributions (histograms) of the measured emissions and wind data, and studied how they may be impacted by seasonal variations in meteorological conditions. In addition, the effect of ambient temperature and wind speed on tank emissions was investigated. For this study we concluded that variations in emissions resulting from environmental changes are relatively small and within the uncertainties of the SOF and SkyDOAS measurements.

The observed differences between measured emissions and reported inventories (based on the US EPA AP-42 standard) are considerably higher than what can be explained by measurement uncertainties alone, or incomplete diurnal and seasonal sampling. Refineries and tank farms are complex environments with a large number of components and numerous potential leak sources (e.g. tank seals, valves, gauges, flares, vapor recovery units, etc.). Many of these components can show degrading performance over time, and to appropriately account for the impact of non-ideal performance in emission inventory reporting is, we believe, an impossible task. Nevertheless, EPA’s AP-42 system provides valuable insights for a specific facility on the production and abatement techniques applied and on what emission level the site could reach given ideal performance of all installations. Comparing measured emissions to ideal performance levels could therefore provide a basis for benchmarking of different refineries or sites.

OUTLOOK

Studies conducted in the SCAB, the Bay Area, Texas, and other places worldwide, show that field measurements provide a reliable way to determine actual emissions of VOCs and other pollutants from refineries and various industrial sites. Accurate estimates of VOC and other pollutant emissions from industrial sources are crucial for improving air quality models, to guide air pollution mitigation strategies, promote successful compliance strategies, and reduce exposure for nearby communities.

In our experience, the observed difference in fugitive VOC emissions between measured and inventory estimates is a general issue for the petroleum industry worldwide. We believe that a possible path forward could be to conduct monitoring in parallel with continued AP 42 based reporting, and to use the measurements to guide and verify the efficiency of the emission reduction efforts at the industrial sites.

Future longer-term ORS studies spanning over different seasons can be conducted in order to alleviate concerns stemming from comparison of emissions measured over limited-time to annual emissions reported through the inventories. Additionally, future studies could combine ORS measurements and site-specific emission modeling performed for inventory calculations. A better dialog between scientists conducting the measurements and the facility operators could also be crucial to improve our understanding of how site activities may affect measured emissions.

Traditional Leak Detection and Repair (LDAR) is an important practice to control and limit unplanned VOC emissions from refineries and to identify potential leak sources. The ORS techniques used in this study have demonstrated their ability to quickly quantify and map refinery emissions and to identify potential air pollution sources within a facility. Using real time measurements, refinery personnel and air quality regulators can enhance LDAR programs by prioritizing LDAR activities. Addressing the most concerning issues first is important to reduce occupational risks for refinery workers, avoid public hazard exposures, and limit the economic losses due to unplanned evaporation of refinery products.

A continued path towards improved air quality involves a good understanding of current emission levels and sources. Repeated and systematic emission measurements will be an important tool for benchmarking industry’s environmental performance as well as for sustaining and verifying efficient emission improvement plans, ultimately resulting in cleaner air and a better environment.

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
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
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

Industrial volatile organic compound (VOC) emissions contribute to significant formation of ground level ozone which is formed through atmospheric chemical reactions of volatile organic compounds (VOCs) and nitrogen oxides NO_x in the presence of sunlight, often called photo chemical smog. Elevated ozone concentrations are known to reduce crop yields and constitute a public health concern.

Larger metropolitan areas in the US, including the South Coast Air Basin, have trouble meeting ozone standards since anthropogenic sources tend to be concentrated in urban areas, including both mobile and stationary sources. VOC emissions from the latter category, i.e. refineries, petrochemical industries and solvent use, are typically dominated by evaporative losses from storage tanks and process equipment, so called fugitive emissions. Industrial NO_x and SO_2 emissions, on the other hand, occur primarily from external combustion sources. These channeled emissions are quite well understood since they come from relatively few places in an industrial site and since they can be monitored using conventional technology. Evaporative losses of VOCs can potentially occur in every unit in which petroleum products are stored, processed or transported. Units that are malfunctioning, in need of maintenance, or irregularly operated can have drastically elevated emissions without giving any indication. These types of irregular emissions can remain unnoticed if measurements of diffuse emissions are not made.

The industries typically estimate their emissions with emission factors calculated using methods and formulas described in AP-42, Compilation of Air Pollutant Emission Factors (US-EPA 2013). New Technologies for quantitatively measuring these types of VOC emissions exist but have so far only been applied at limited facilities. Estimates of VOC emissions from refineries and petrochemical are therefore rarely verified by quantitative measurements. Since reported total VOC emissions from a facility are typically a very small fraction (typically in the order of 0.01-0.10 %) of its crude oil capacity, emissions would remain insignificant in any type of mass balance even if they were many times larger than reported.

Measurements during the 2000 TexAQS (Texas Air Quality Study) and the 2006 TexAQS II indicated that current emission inventories significantly underestimate industrial VOC emissions in Houston (Kleinman *et al.* 2002; Ryerson 2003; Wert *et al.* 2003; Jobson 2004; Mellqvist *et al.* 2010; Karl 2003; De Gouw, J. A. de *et al.* 2009; Washenfelder *et al.* 2010; Parrish *et al.* 2009). Similar conclusions have also been drawn from international studies elsewhere such as Sweden (Kihlman 2005; Kihlman *et al.* 2005), The Netherlands (Mellqvist *et al.* 2009), France (INERIS 2010) and Belgium (Samuelsson *et al.* 2011). Several studies have concluded that industrial VOC emissions contribute significantly to ozone formation (Kleinman *et al.* 2002; Ryerson 2003; Jobson 2004; Gilman *et al.* 2009; Kim *et al.* 2011; Wert *et al.* 2003; Kim *et al.* 2011).

In order to improve the understanding of VOC, NO_2 and SO_2 emissions in the South Coast Air Basin (SCAB) and to assess whether they impact the ground level ozone in a significant way, 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 wells, gas stations, fuel islands, barges and shipping. In addition, a technology demonstration and validation study was carried out to assess the uncertainties of different optical techniques using side-by-side measurements of real sources and controlled source gas releases. This work is an extension of a pilot study that was carried out by FluxSense in Los Angeles area in September/October 2013 (Mellqvist *et al.* 2013a, 2013b).

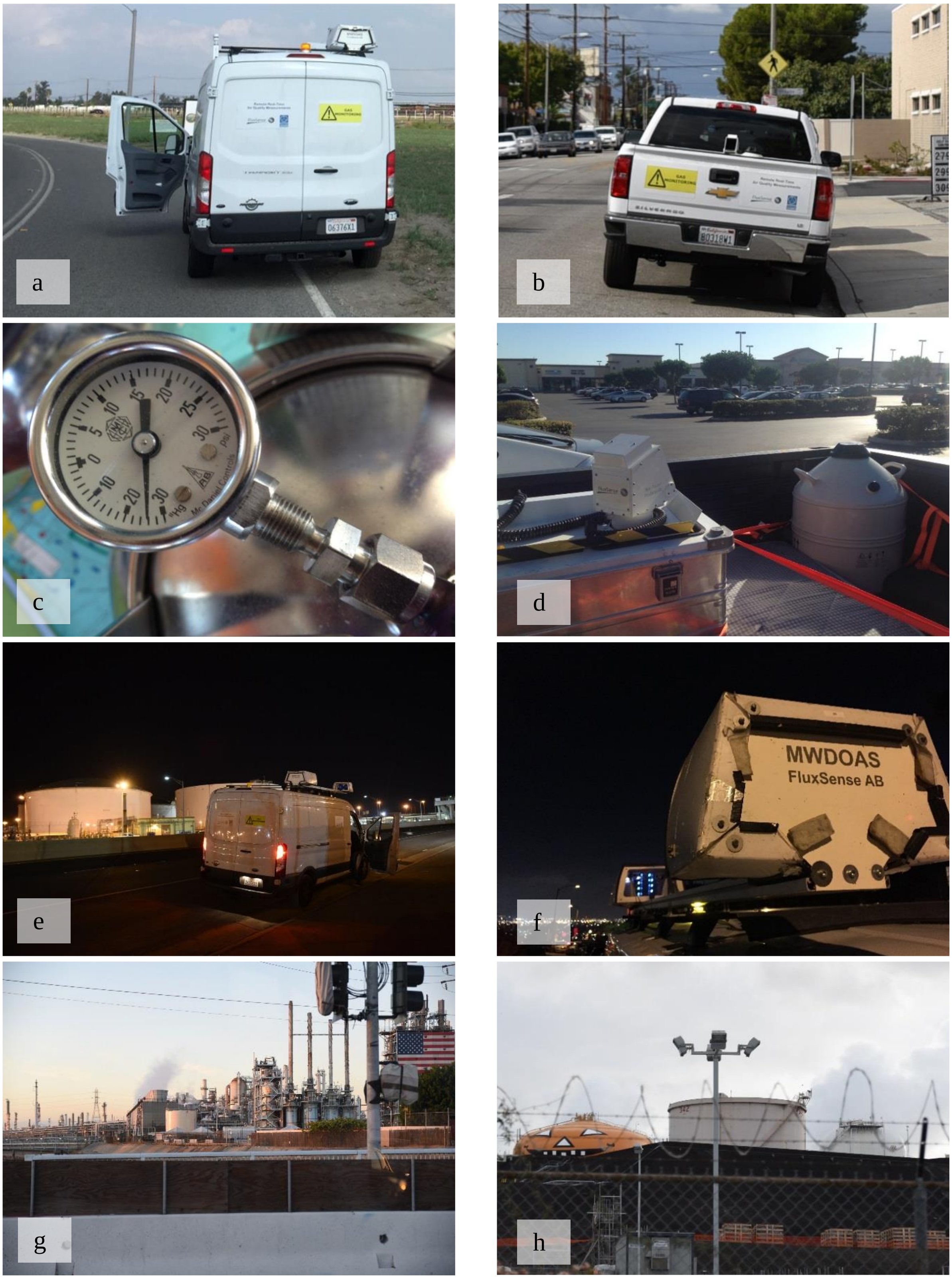

Figure 1. Example images from the 2015 SCAQMD measurement survey. a) FluxSense Mobile lab, b) secondary SOF vehicle, c) Canister sampling, d) Secondary SOF system, e) Night-time MeFTIR measurements, f) MWDOAS measurement, g) Refinery view, h) Tank park view.

This report covers the results from the first of three SCAQMD projects. This project studied emissions of VOCs, CH_4, SO_2 and NO_x from the six main refineries in the SCAB over several months and to compare these to current inventories. This report is one of several other reports describing measurements of smaller emission sources, ship emissions and validation activities. The refineries are denoted Refinery A, Refinery B, Refinery C, Refinery D, Refinery E, and Refinery F respectively. These refineries have a total reported crude oil capacity of more than 900,000 bbl/day (California Energy Commission 2016) and are major contributors of VOC-emissions and, consequently, smog formation in the region.

Two mobile remote gas sensing techniques, SOF (Solar Occultation Flux) and Mobile Sky-DOAS (Differential Optical Absorption Spectroscopy) were operated around the perimeter of the six selected refineries for estimation of facility-wide mass emission fluxes of VOCs, SO_2 and NO_2. The remote gas sensing techniques were complemented by mobile extractive optical methods, i.e. MeFTIR (Mobile extractive FTIR) and MWDOAS (Mobile White cell DOAS) to map ground concentrations of alkanes, methane and aromatic VOCs to calculate inferred fluxes. A mobile wind LIDAR station supplied by SCAQMD allowed for the continuous measurements of vertical wind profiles. Wind data was also obtained from local meteorological stations to complement the LIDAR results. See Figure 1 for example of measurement situations.

SOF is a proven technique employed by FluxSense in over 100 fugitive emission studies around the world. In Europe the SOF technique is 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 to screen all larger refineries and petrochemical industries annually. The Swedish facilities are visited during at least 10 days per year, spread out over the different seasons, to give a good representation of annual mean conditions. The measurements represent the total emission coming from the entire refinery, divided into sub parts such as process areas, crude oil storage, product storage tanks, water treatment facilities, flares and loading operations. The estimated uncertainty for the emissions is typically 30 % for the total site emissions, and somewhat higher for the individual parts. This has been concluded from several controlled source gas release experiments (blind and non-blind) and side-by-side measurements with other measurement techniques.

The measurements were carried out in the period August 28 to November 11 2015, with up to 15 individual measurements days at the individual sites, and up to 40 individual measurements. Representative statistics of measured emissions (e.g. average, standard deviation, median, etc.) were determined for this time period. Measurements were generally conducted outside the facilities fence-lines along public roads measuring both upwind and downwind the refineries to account for inflow of pollutants from the background. During a week and a half (September 28 to 7 October), measurements were also conducted inside the Refinery A at the main eastern tank farm. The aim was to quantify and to locate leaking tanks and components and to validate the technique by comparative measurements.

In this report, the results from these refinery measurements are compared to the reported annual emission inventories. Discrepancies between reported annual inventories and measured emissions are discussed and further investigated.

In parallel to this project an additional study was carried out in which the SOF method was compared to other optical techniques, DIAL (Differential Absorption LIDAR) and long-path FTIR using side-by-side measurements on various tanks inside a refinery, a treatment plant and an oil well cistern; here the agreement with the other methods was excellent, i.e. 10-20 %. As part of the same study, a blind gas release experiment was carried out, using a controlled source releasing 2-25 kg/h of propane at the parking lot of the Angels of Anaheim baseball stadium, Anaheim, CA. Here the SOF measurements consistently underestimating the true emission by 35% but with a good correlation (R^2 ~98%). This study is compiled in a separate paper.

2 Instrumentation and Methods

The FluxSense mobile laboratory 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. 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 2.5. A wind LIDAR was used to measure vertical profiles of wind speed and wind direction from 50-1000 m height. The LIDAR data was supported with complimentary data from several wind masts at 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.

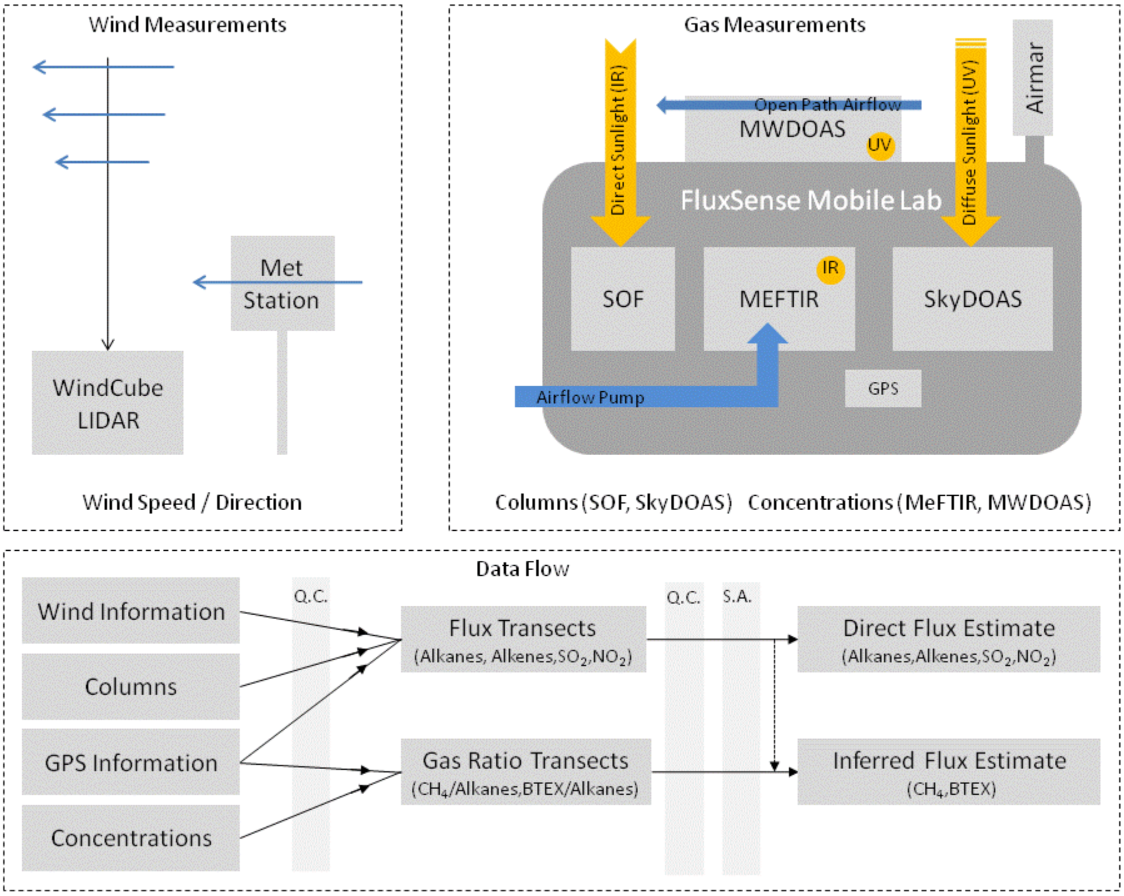

Figure 2. Overview of the FluxSense mobile lab main instruments; SOF, MeFTIR, MWDOAS and SkyDOAS (upper right panel) and wind measurements (upper left panel) and simplified data flow diagram (lower panel). SOF and SkyDOAS are column integrating passive techniques using the Sun as the light source while 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, SO_2 and $NO_{2,}$ while inferred fluxes are calculated via gas concentration ratios (MeFTIR and MWDOAS) of BTEX and CH_4. 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).

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).

During some of the measurement days at the end of the survey (29 October to 9 November), a second SOF instrument was also used. This additional SOF platform was placed on the bed of a pick-up truck (see Figure 1b) and operated independently of the FluxSense mobile lab, but with a similar optical setup. The second instrument made it possible cover more objects within the survey time frame.

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

A table summarizing the main features and characteristics of all measurement techniques used for this study is found in Table 1.

Table 1. Summary of FluxSense gas measurement techniques. *For typical wind conditions at an optimal distance from the source.

Method	**SOF**	**SkyDOAS**	**MeFTIR**	**MWDOAS**
Compounds	**Alkanes**: (C_nH_{2n+2}) **Alkenes:**C_2H_4, C_3H_6	**SO_2** **NO_2**, **HCHO**	**CH_4** **Alkanes:** (C_nH_{2n+2}) **Alkenes:** C_2H_4, C_3H_6	**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]	Alkane ratio of ground plume combined with SOF gives mass flux [kg/h] and plume height information [m]	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; Mellqvist *et al.* 2008b; Mellqvist *et al.* 2008a; Mellqvist *et al.* 2009; Mellqvist *et al.* 2010; EPA 2011) 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. From these solar spectra, it is possible to use multivariate optimization to retrieve the path-integrated concentrations (referred to as column concentrations) of various species between the sun and the spectrometer (in the unit mg/m^2). 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 can be 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.

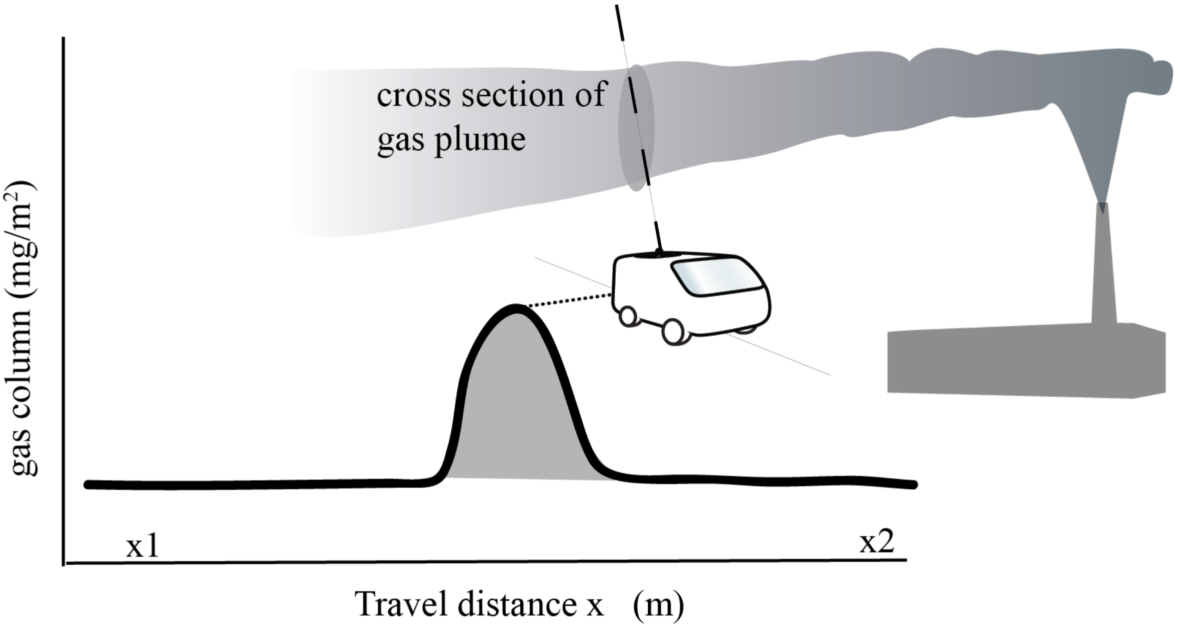

Figure 4. Schematic of the SOF measurement where the vehicle is driven across the prevailing wind so that the solar beam cuts through the emission plume while the sun is locked into the FTIR spectrometer by the solar tracking device on the roof. The VOC mass (or other compound of interest) is integrated 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 *et al.* 2005). 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 *et al.* 2003) and the PNNL database (Sharpe *et al.* 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 *et al.* 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 PNNL (Pacific Northwest National 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) 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 SkyDOAS

The principle for Mobile SkyDOAS (Mobile Differential Optical Absorption Spectroscopy) measurements is very similar to that of SOF. Instead of measuring direct sun light in the infrared region, scattered light in the UV and visible region is measured in zenith angle with a telescope connected with an optical fiber to a Czerny-Turner spectrometer with a CCD camera. Column concentrations are retrieved from spectra in a similar way as with the SOF, although absorption is generally weaker. The system that was used for this project consists of a quartz telescope (20 mrad field of view, diameter 7.5 cm) connected with an optical fiber (liquid guide, diameter 3 mm) to a 303 mm focal length Czerny-Turner spectrometer with a 1024 by 255 pixels, thermoelectrically cooled CCD camera, see Figure 5.

Figure 5. The mobile Sky-DOAS system: Telescope, optical fibre, spectrometer and control computer.

The system was installed in the same measurement vehicle as the SOF system. Plumes were transected in the same way as with the SOF system and the retrieved column concentrations used to calculate fluxes exactly the same way, except that the SkyDOAS measurement direction is always zenith.

In this project, mobile SkyDOAS was used to measure SO_2, NO_2 and HCHO. NO_2 is retrieved in the wavelength region between 324 and 350 nm and SO_2 in the region 310-325 nm. HCHO is measured in the region 322-350 nm. It was however never found above detection limit in any repeatable measurement during the campaign and is therefore not included in the result section. Apart from SO_2, NO_2 and HCHO the spectral analysis also includes other atmospheric compounds such as O_3 and O_4. The rare event of significant absorption from other species in the plume than those included in the spectral fit shows up as elevated residuals and is further investigated in the re-analysis. The absorption line parameters of the retrieved compounds are well established in published databases, stating an uncertainty of 4% (Vandaele *et al.* 1998) for the UV cross section of NO_2 and less than 2% for the SO_2 cross sections (Bogumil *et al.* 2003).

The DOAS technique was introduced in the 1970's (Platt *et al.* 1979) and has since then become an increasingly important tool in atmospheric research and monitoring both with artificial light sources and in passive mode utilizing the scattered solar light. In recent time the multi axis DOAS technique (scanning passive DOAS) has been applied in tropospheric research for instance measuring formaldehyde (Heckel *et al.* 2005; Pikelnaya *et al.* 2007).

Passive DOAS spectroscopy from mobile platforms has also been quite extensively applied in volcanic gas monitoring (Galle *et al.* 2003) for SO_2 flux measurements and for mapping of formaldehyde flux measurements in megacities (Johansson *et al.* 2009), . Mobile SkyDOAS has been used in several studies for measurements of industries i.e. SO_2, NO_2 and HCHO for several campaigns in Texas including NO_2 measurements at Longview in 2012 (Johansson *et al.* 2014a; Johansson & Mellqvist 2013). (Rivera 2009) did SO_2 measurements on a power plant in Spain for validation purposes. They also made measurements at an industrial conglomerate in Tula in Mexico (Rivera *et al.* 2009a) and measurements of SO_2, NO_2 and HCHO during the TexAQS 2006 campaign (Rivera *et al.* 2009b; Rivera *et al.* 2010). There are also groups in both China and Spain working with mobile mini DOAS.

2.3 Mobile extractive FTIR

Mobile Extractive FTIR (MeFTIR) (Galle *et al.* 2001; Börjesson *et al.* 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.* 2014b). 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 6.

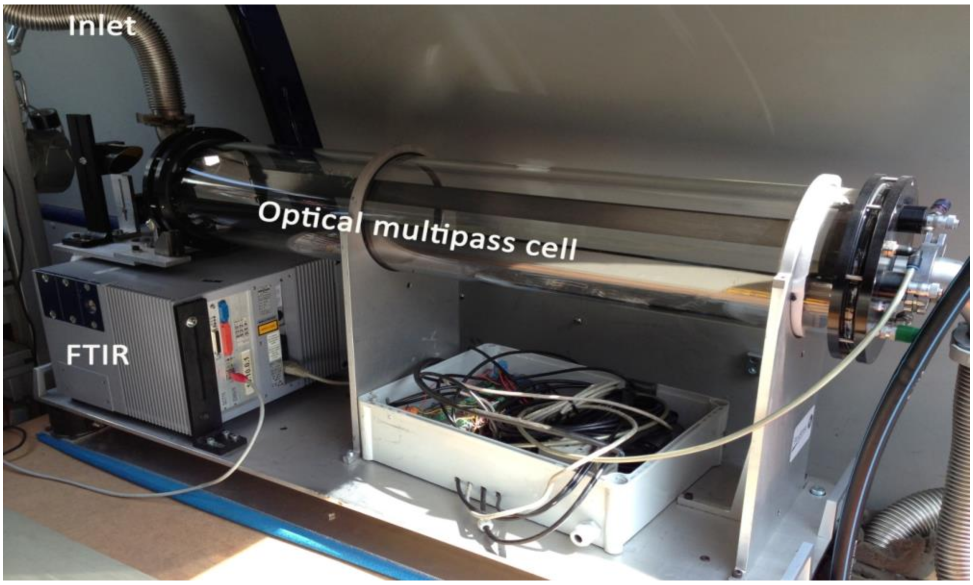

Figure 6. The MeFTIR instrumentation consisting of a Bruker FTIR spectrometer connected to an optical multi-pass cell.

The transmitted light is detected simultaneously with an InSb-detector (Indium Antimonide) in the 2.5–5.5 µm (1800–4000 cm^{-1}) region and a MCT (Mercury Cadmium Telluride) detector in the 8.3–14.3 µm (700–1200 cm^{-1}) region. Temperature and pressure in the cell are averaged over the duration of each measurement. Atmospheric air is continuously pumped at high flow rate through the optical cell from the outside, taking in plume air from the roof of the vehicle (2.5 m height) through a Teflon tube. A high flow pump is used to ensure that the gas volume in the cell is fully replaced within a few seconds. Spectra are typically recorded with an integration time of 10 seconds. A GPS-receiver is used to register the position of the vehicle every second.

The concentration in the spectra is analyzed in real time by fitting a set of calibrated spectra from the Hitran infrared database (Rothman *et al.* 2003) and the PNNL database (Sharpe *et al.* 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, CO_2 and N_2O. The analysis routines are very similar to the ones for SOF, but less complex because strong absorption by atmospheric trace gases (water, methane, CO_2) 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. (Babilotte 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.

2.4 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 7). 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.

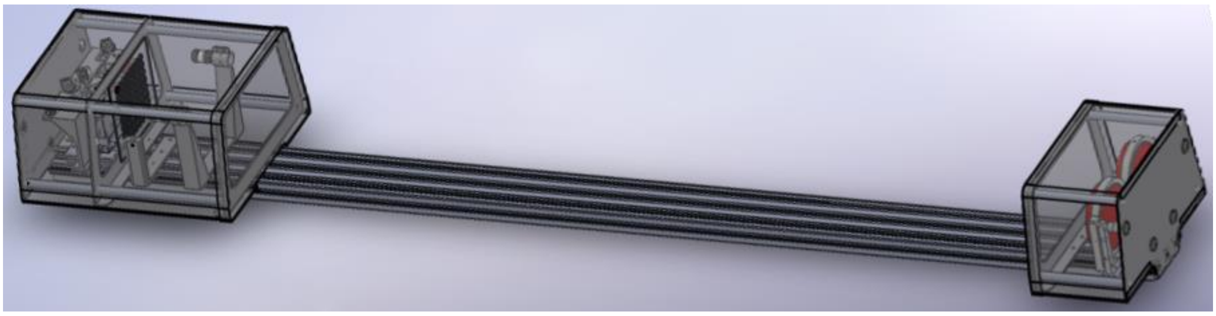

Figure 7. The open path MWDOAS cell having an overall optical path-length of 210 m.

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 *et al.* 1999)
SO_2	(Bogumil *et al.* 2003)
O_2	(Bogumil *et al.* 2003)
Toluene	(Fally *et al.* 2009)
Benzene	(Etzkorn *et al.* 1999)
1,3,5-Trimethylbenzene	(Etzkorn *et al.* 1999)
1,2,4-Trimethylbenzene	(Etzkorn *et al.* 1999)
Styrene	(Etzkorn *et al.* 1999)
Phenol	(Etzkorn *et al.* 1999)
p-xylene	(Etzkorn *et al.* 1999)
m-xylene	(Etzkorn *et al.* 1999)
Ethylbenzene	(Etzkorn *et al.* 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 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.

2.5 Wind Measurements and Auxiliary Data

Wind LIDAR

An infrared 3D wind LIDAR provided by the SCAQMD (shown in Figure 8) was used to measure vertical wind profiles of wind speed and wind direction. The unit used for this study (i.e. model WindCube 100S) produced by Leosphere (France) provides wind profiles in the vertical range 50 to around 1000 m above surface level, or even further if atmospheric conditions allow it. Within this range data can be retrieved in 25 m vertical resolution. Stated wind speed accuracy is 0.5 m/s. Applicable radial wind speed range is -30 to 30 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 through: www.leosphere.com.

Figure 8. The WindCube 100S (Leosphere) LIDAR used for wind profile measurements in this project.

Wind Mast

Meteorological parameters were measured at selected sites using a portable 10 m mast, see Figure 9. This mast was equipped with a calibrated RM Young 05108 “prop and vane” anemometer and a Campbell Scientific CR200 data logger.

The weather mast was installed at an open location near the refinery of interest 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 or other wind stations in the area is used to fill in the gap of the lowest 40 m of the atmosphere where no LIDAR data exists. Since the plume heights from petrochemical facilities generally are several hundred meters during sunny conditions (some hundred meters downwind where SOF measurements are done), the wind speed information below 40 m does not influence the flux calculations substantially (typically a few percent).

Figure 9. 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. The wind information from the Airmar is not used for flux calculation but acts as a real-time aid to keep track of the plume directions when making the gas emission measurements.

The Airmar provides wind speed and direction relative to true north (compensating for vehicle position), air temperature, pressure and relative humidity. It also provides GPS positions which may be used as back-up to the other GPS-receiver.

GPS

The FluxSense vehicle is equipped with two standard USB GPS-L1 receivers (GlobalSat BU-353S4) hooked up to the SOF and DOAS-computers. They are placed horizontally by the windscreen and on the 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 for each individual instrument. SOF and SkyDOAS 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 these two different techniques was necessary. In addition to the gas mass ratio measurements by MWDOAS and MeFTIR, some canisters were also sampled in selected plumes for further VOC speciation and complimentary data.

By keeping track of wind directions and avoiding strong upwind sources, the same plumes were essentially sampled during solar/daytime and cloudy/nighttime measurements so that representative gas ratios were collected. Only MeFTIR and MWDOAS measurements with repeated plume signature and high correlation between target and alkane concentrations were accepted. Canister sampling was only performed during cloudy/nighttime measurements when ground plumes are generally present and monitored in real-time.

3.1 Survey Setup

The main objective of this study was to quantify the total gas emissions of non-methane VOCs (alkanes and BTEX), NO_2, SO_2 and methane from six major refineries in the Los Angeles Basin denoted Refinery A, Refinery B, Refinery C, Refinery D, Refinery E and Refinery F respectively (see Figure 10). This was done by conducting fence-line measurements along accessible roads outside the facilities using mobile optical measurements (SOF and mobile DOAS) to obtain total gas emission fluxes from the refineries. Furthermore, ground concentration measurements were carried out with mobile MWDOAS and MeFTIR instruments to infer emission of methane, BTEX and specifically benzene.

Gas measurements were combined with wind data, primarily from SCAQMD's wind LIDAR system, but also from meteorological stations and from a mobile 10 m wind mast, to calculate fluxes and identify sources. Throughout the study the wind LIDAR was moved between four different locations (L1-L4, see Figure 10) depending on the facilities measured. The geographical positions of the refineries are noted as colored areas in Figure 10 along with various meteorological sites and wind LIDAR positions. In general, each measurement day was dedicated to one specific refinery except for Refinery B and Refinery C which were both surveyed within the same time frame.

Emissions from each refinery were calculated by driving around the targeted facility to capture the entire downwind plume and then subtracting potential contributions from emissions deriving from upwind sources. This approach is referred to as “box-measuring” in this report. When complete upwind plume measurement was not possible (e.g. lack of accessible roads), relevant upwind measurement transects were made in close proximity in space and time. The aim was to make multiple measurements during several days over the entire duration of the study (from 28 August to 10 November 2015) in order to map detected plumes at different times, during variable wind conditions, and from different distances from the sites to better understand emission variability, plume dispersion, and the potential for local community exposure.

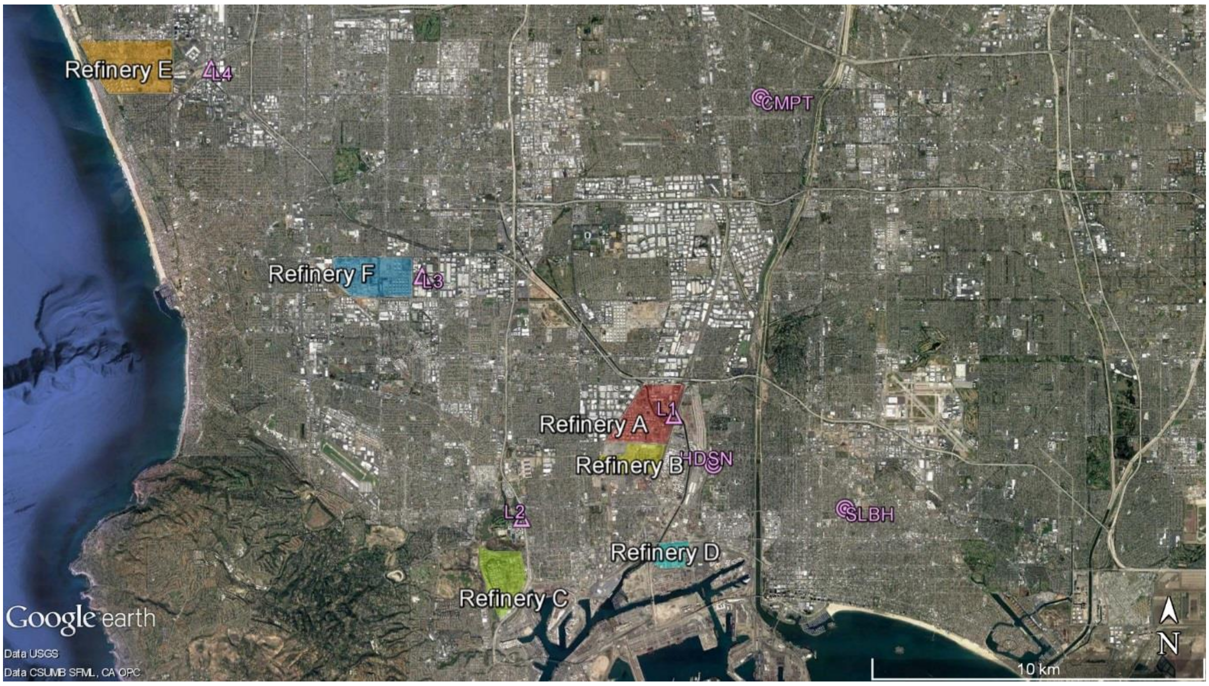

Figure 10. Map showing the locations of the six refineries that were targeted for this study. Also shown are meteorological sites and LIDAR positions. Map from Google Earth © 2016.

Altogether, measurements were carried out during 40 days, however the number of successful and quality assured measurements varied substantially from day to day and from facility to facility depending on weather conditions, local measurement conditions (e.g. road accessibility), and time sharing between different refineries and instruments.

Refinery A is the largest refinery in the Southern California Air Basin (along with Refinery E) and it has been collaborating with SCAQMD to support this campaign and making it possible to carry out 7 days of onsite measurements. In addition, 15 measurement days of total emissions were carried out on refinery fenceline. A statistical estimate of flux emissions (kg/h) was computed for each measurement day at each refinery. Total mean and median values for the entire survey period were calculated in parallel. This data was compared to the reported annual emission inventories. Extreme events (beyond 1.5 times the inter-quartile range) and possible point sources within a refinery were also noted in the report.

3.2 Principal Equations

This report includes two 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. BTEX and methane fluxes are calculated using inferred fluxes from MWDOAS/MeFTIR gas mass ratios.

DIRECT FLUX MEASUREMENTS:

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

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

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 “box-measured”, 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.

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):

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

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/SkyDOAS, 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.

The uncertainties in the total refinery emissions of BTEX and CH_4 obtained from inferred fluxes are larger than for the direct flux measurements of alkanes. Ideally the gases should be well mixed in the plume for this method to work the best, but in reality there will be a stronger weighting towards low elevated sources (tanks) compared to higher elevated ones (process units) depending on the measurement geometry. In the past we have done canister sampling in several European refineries, and typically the BTEX fraction is higher in the process units (10-15 %) compared to tank farms (5-10 %). The inferred emission flux of BTEX will consequently be a low estimate of the BTEX emission. For smaller, more isolated sources we estimate that the uncertainty of the inferred fluxes is only slightly higher than the direct flux measurement.

PLUME HEIGHT ESTIMATES:

This is a method to calculate approximate plume heights from simultaneous SOF slant columns and MeFTIR ground level concentrations, measured across an emission plume. The plume height, h_T , for a transect, *T*, across a plume, P, along the path, *l*, is given by the following equation (Si-units in gray brackets):

$$h_T^j[\mathrm{m}] = \frac{\int_P \ C_l^j[\mathrm{kg/m^2}] \cdot \cos(\theta_l) \ dl[\mathrm{m}]}{\int_P \ N_l^j[\mathrm{kg/m^3}] \ dl[\mathrm{m}]}$$

Where,

C_l^j = the slant column density of species j as measured by SOF,
θ_l = the angle of the light path from zenith ($\cos(\theta_l)$ gives vertical columns),
N_l^j = the number density concentrations of species j from MeFTIR,

This method distributes the plume homogeneously from the ground to the plume height (and zero above). In reality, however, emission plumes have a vertical gradient controlled by wind shear, turbulence, atmospheric lapse rate, release altitude etc. Hence, the plume height as calculated using the equation above, is only a first order approximation. In this report, plume heights have consistently been calculated using alkane measurements (i.e. j=*alkane*). Median values of multiple plume height estimates are used to decrease uncertainties.

3.3 Uncertainties and Error Budget

Table 3 summarizes the accuracy, precision, and data completeness for measurements from each instrument employed during this field campaign.

Table 3. Accuracy, precision, and data completeness for measurements from each of FluxSense's measurement methods.* 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.

Measurement Parameter	Analysis Method	Accuracy	Precision	Completeness*
SOF column concentrations alkanes, alkenes	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,	QESOF spectral retrieval	±10%	±5%	95%
MWDOAS concentrations BTEX, Benzene	MWDOAS spectral retrieval	±10%	±5%	90%
Wind Speed (5m)	R.M. Young Wind monitor	±0.3 m/s or 1%	±0.3 m/s	95%
Wind Direction (5m)	R.M. Young Wind monitor	±5°	±3°	95%
Wind Speed (10m)	Gill WindSonic	±2%	-	95%
Wind Direction (10m)	Gill WindSonic	±3°	-	95%
LIDAR Wind Direction (50-1000m)	Leosphere Windcube 100S	-	-	>90% except in heavy fog
LIDAR Wind Speed (50-1000m)	Leosphere Windcube 100S	±0.5 m/s	-	
GPS position	USB GPS receiver	±2m	±2m	100%
SOF mass flux Alkanes, alkenes	SOF flux calculations	±30%	±10%	80% (in suitable weather conditions)
SkyDOAS mass flux NO_2, SO_2	SkyDOAS flux calculations	±30%	±10%	80% (in suitable 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:

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

Precision is a measure of the repeatability of the results. The precision for the SOF and mobile SkyDOAS 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 this project is listed in Table 3.

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:

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

3.4 Wind Statistics and Plume Heights

The largest source of error in SOF and SkyDOAS emission flux calculations is typically determined by the quality of the collected 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 total wind uncertainty results from a combination of wind measurements errors (see Table 3) and errors due to the assumption that the measured wind velocity measured is representative of the average plume velocity. 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. Estimates of the plume mixing height estimates can in turn be retrieved by simultaneous concentration and column measurements with SOF and MeFTIR as described in section 3.2. The method assumes homogeneous plume concentrations from ground level to the plume height. Plume height results for the different refineries in this study are found in Table 4 and Figure 11.

Table 4. Summary of plume height (median values) estimations for all refineries surveyed during this study. Wind information used for flux calculations is also reported (all non-LIDAR winds scaled to LIDAR 0-400m with the given scaling factors). *Measurements at Refinery D were conducted during a flaring event with high elevated plumes.

Refinery	Number of Measurements	Median Plume Height [m]	Primary Wind (0-400m)	Secondary Wind (Scaling factor)
Refinery A	19	475	LIDAR L1	Refinery A Mast (1.34)
Refinery B	3	514	LIDAR L1	Refinery A Mast (1.34)
Refinery C	5	464	LIDAR L2	AQMD-SLBH (1.0)
Refinery D*	2	835	LIDAR L1	ASOS-KLGB (1.17)
Refinery E	11	239	LIDAR L4	ASOS-KLAX (0.83)
Refinery F	6	292	LIDAR L3	LIDAR L1 (1.0)
All Refineries	**46**	**413**		

These results indicate a plume height of 250-500 m with an overall median for all refineries of around 400m. The high values at Refinery D were estimated during a flaring event on November 1, 2015, with non-typical elevated emissions and should be treated cautiously. Based on these estimates, the average wind for the interval 50-400 m, as measured by the wind LIDAR, has been used for flux calculations in this survey. Wind information from Refinery A's 10 m mast during the calibration period (October 2-6, 2015) was used to account for the lowest 50 m of the air column. In this compensation, the 10 m wind data was used from 0 to 20 m and a linear interpolation was applied between the 10 m wind and the LIDAR wind between 20 and 50 m. Although this compensation had a very small effect (~2%) on the total wind speed as provided by the LIDAR between 50 and 400m, it was applied to all flux calculations for consistency.

Note that plumes of different gases may behave differently. Plumes originating from combustion sources (e.g. SO_2 and NO_2), are generally stack releases. As such, they are released at a high altitude and more buoyant (hotter) than fugitive and cold VOC emissions. Hence, SO_2 and NO_2 are expected to be found at a slightly higher altitude than alkanes when measuring refinery emissions at a fence-line distance like in this survey. Plume height estimations are, however, not possible for SO_2 and NO_2 (no simultaneous concentrations measurements). But since the wind gradient with height was weak during the survey and with the emissions confined within in the boundary layer (see discussion below), the effect on the calculated fluxes are small and well within the measurement uncertainty.

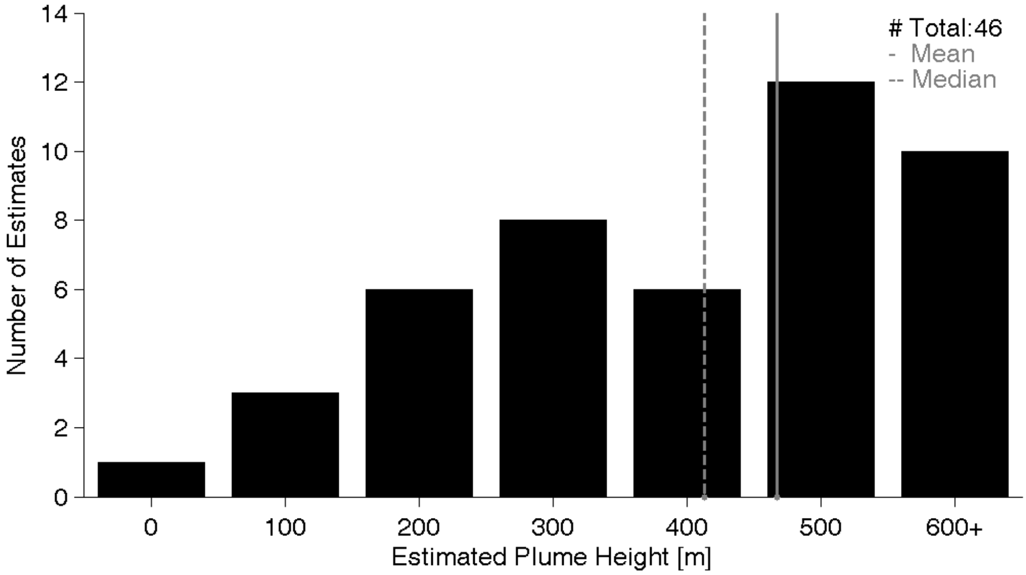

Figure 11. Plume height estimations for all refineries during the 2015 SCAQMD survey. The last bin, denoted '600+', contains all data points above 600 m. The median and average values are indicated as dashed and solid gray lines, respectively.

Wind LIDAR data has always been used as the primary wind information for flux calculations in this survey. The different LIDAR locations/sites are specified in Figure 10. For cases where no LIDAR information was available (e.g. LIDAR malfunction or data collected at non-representative sites) an appropriate secondary wind source was used based on its proximity to the measured refinery. Secondary wind data was scaled to match the 50-400 m LIDAR wind at a location closest to the measurement site using the slope of a linear least-squares-fit, see *Scaling Factors* in Table 4 and plots in Appendix B.

In order to assess the sensitivity of the flux calculations to deviations from the assumed plume mixing height, wind LIDAR data (10 min average) for different altitude ranges (i.e. 50-100 m, 50-200 m, 50-300 m, 50-400 m, and 50-500 m) were compared to the reference LIDAR wind (50-400 m) during the two calibration periods (October 2-6, 2015 at LIDAR site L1 and October 9-16, 2015, at site L3; see Figure 10). For both calibration periods, the wind speed comparisons show that the systematic difference for the alternative height intervals is less 4% compared to the reference interval (50-400 m) and that the vast majority of data points are within 30% of the reference wind (50-400 m) (see example in Figure 12 and the complete data set in Appendix B). For the wind direction, the same comparisons showed a systematic difference of less than 5° to the reference wind and a total spread of the random differences of less than 30° for almost all data points.

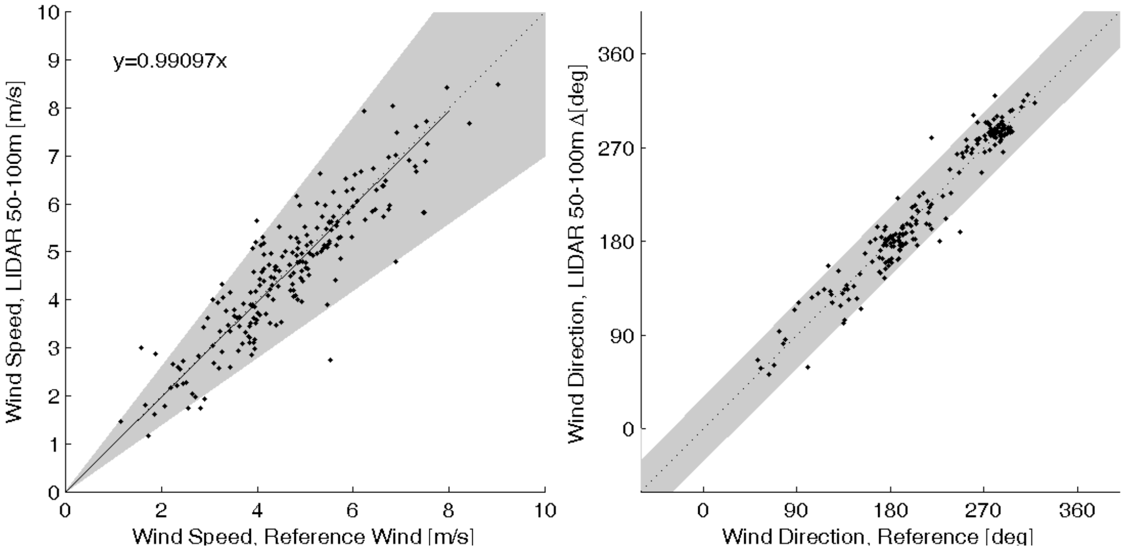

Figure 12. Wind LIDAR data (10 min average from 10AM to 5PM) for 50-100 m versus the reference LIDAR wind (50-400 m) during the calibration period (October 2-6, 2015) at LIDAR site L1. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as a solid line. See Appendix B for the complete data set.

The variability of the wind with height and time is further illustrated in Figure 13. The two upper panels show the average wind (solid lines) at each height level relative to the 50-400 m reference average as well as the average standard deviation (±1σ; dashed lines). These profiles show that the wind does not systematically deviate more than 15% or 5° at any height level and that the standard deviation of the random deviations are generally less than 20% in wind speed and 20° in wind direction, except for the highest levels in the interval. The two lower panels in Figure 13 show the results of comparison between the reference wind and the same reference wind a few minutes earlier. These plots also show the average wind deviation as a function of the time difference (solid lines), as well as the average standard deviation (±1σ; dashed lines). As expected, the random deviations increase with the time difference, while the systematic deviations are close to zero. The reason why the average deviation is not actually zero is that the prevailing wind conditions during the study featured a distinct pattern of winds increasing throughout the day while also shifting direction in a recurring pattern.

Two examples of the evolution of the wind profile over the course of a day are shown in Figure 14. Both of them show clear signs of the prevailing wind pattern throughout the study, with weak winds in the morning that increase in magnitude from approximately 10:00 AM to 12:00 PM and forward while also shifting direction. Since a wind speed of at least 1-2 m/s is typically needed in order to accurately calculate flux, useful data could normally not be collected before 10:00 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 often varies dramatically. This altitude range coincides very well with the typical plume mixing height estimates in Table 4 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 was on average weaker and more variable in the uppermost levels of the 50-400 m height interval, as seen in Figure 13. The convective boundary layer simply does not always extend above this height level.

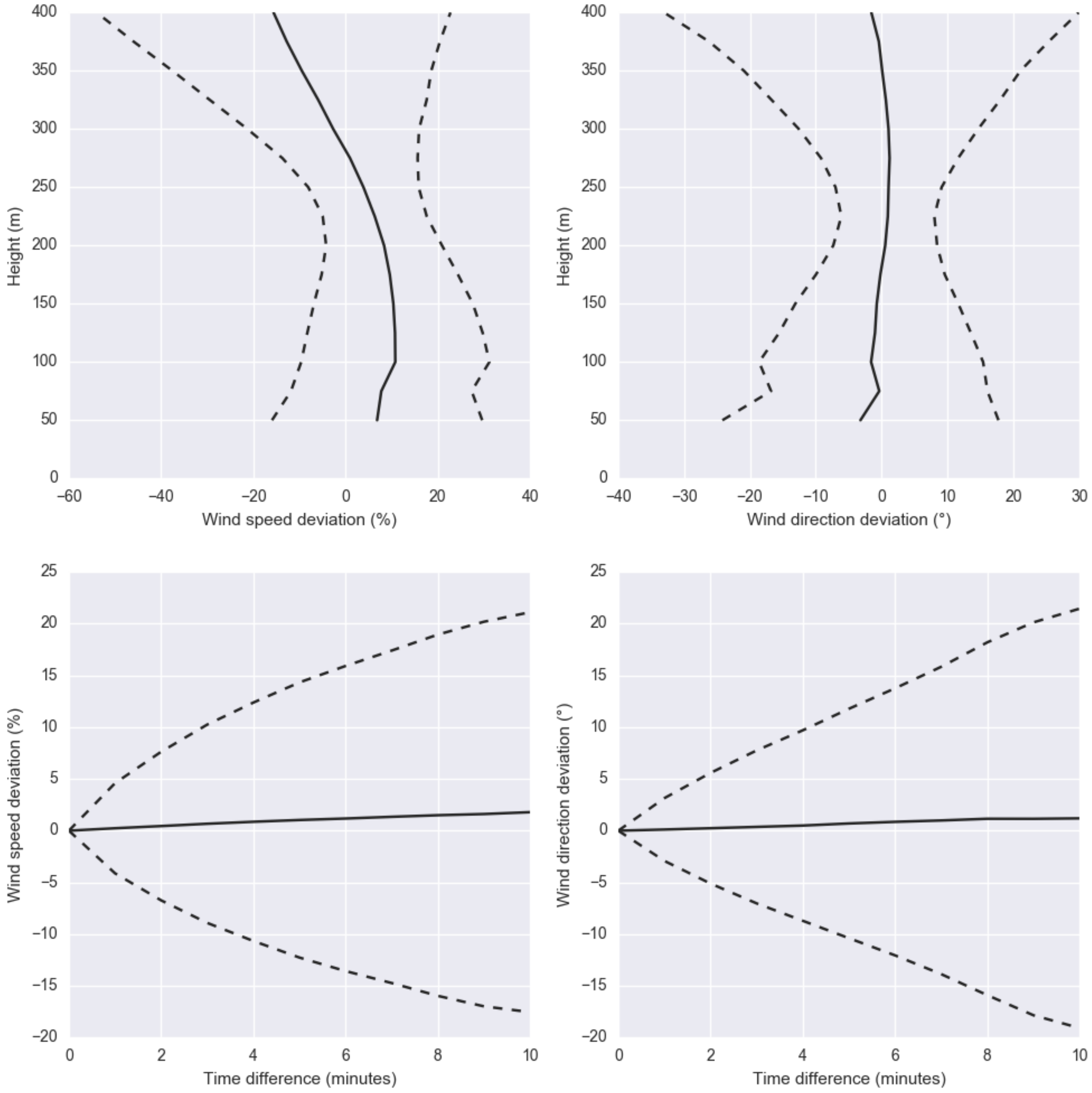

Figure 13. 10-min wind LIDAR data for the entire 2015 SCAQMD survey. Average (solid lines) and standard deviation (±1σ; dashed lines). Top row panels show altitude information and the lower row panels show time dependence (see Appendix B for additional plots).

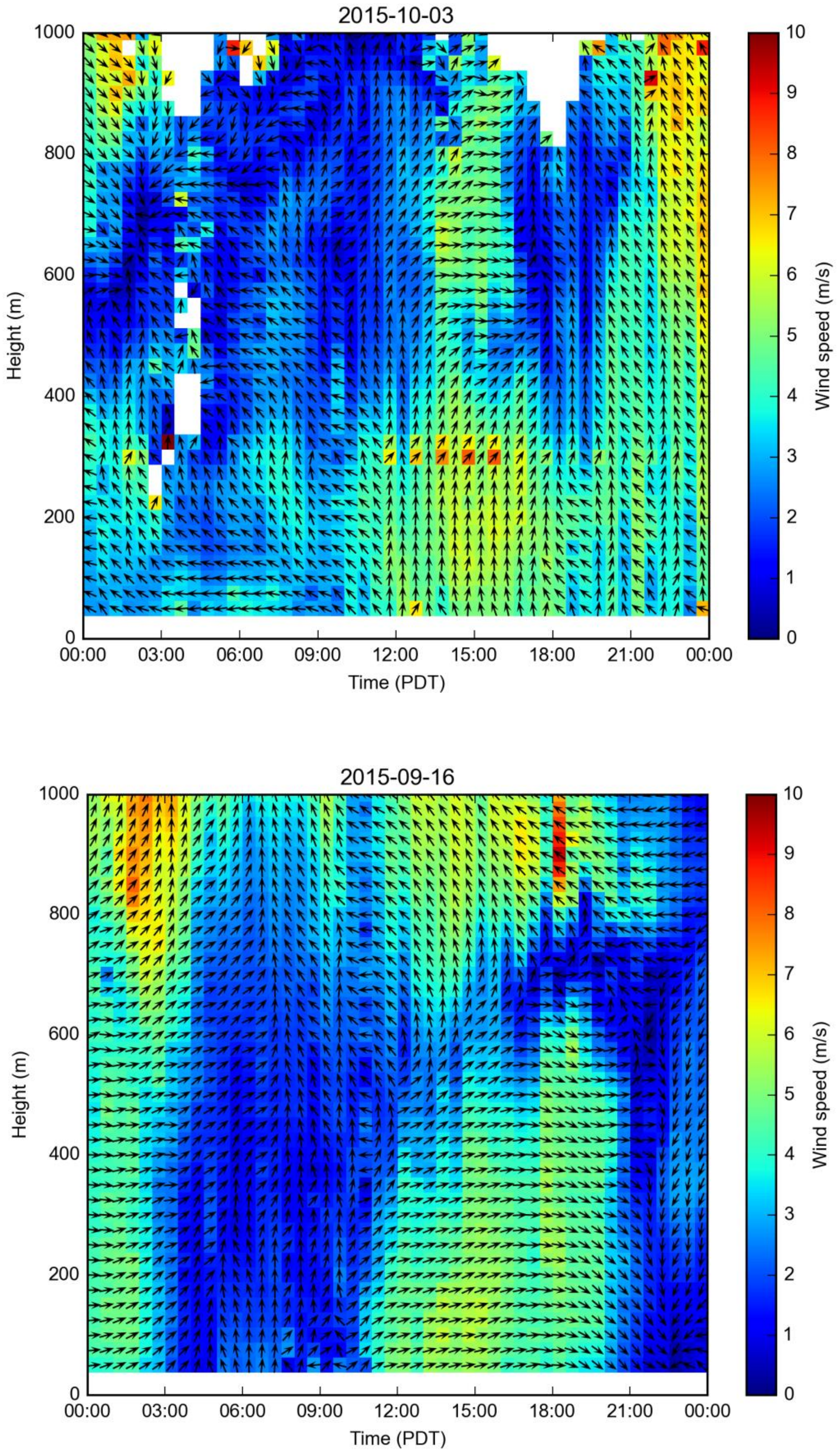

Figure 14. Wind LIDAR raw data at the L1 and L4 site. 30 min averages from 50 to 1000 m measured on October 3, 2015 at the L1 site (upper panel) and on September 16, 2015 at the L4 site (lower panel). The color scale gives the magnitude of the wind speed and the black arrows show the wind direction. Both plots show typical low wind speeds during night-time conditions and stable winds with little altitude variation (wind shear) from 50 to 400m from noon to sunset. See Appendix B for additional data.

4 Results - Total Refinery Measurements

Emission flux measurement results (median values) for the six refineries surveyed during this study are summarized in Table 5. Figure 15 through Figure 17 present graphical representations of measured emissions of alkanes, SO_2, and NO_2. Collectively, refineries in the South Coast Air Basin were found to emit 1130 kg/h of alkanes, 259 kg/h SO_2, 269 kg/h NO_2, 129 kg/h BTEX (of which 18 kg/h is Benzene) and 705 kg/h methane. Section 4.1 through 4.6 below provides detailed description of measured emissions from each studied refinery in the South Coast Air Basin.

Table 5. Summary of emission flux measurements during the 2015 SCAQMD survey. SOF and SkyDOAS results are reported here as median values of all quality assured transects to reduce sensitivity to outliers. *MWDOAS and MeFTIR are inferred values through measured ground level gas mass concentration ratios (See section 2.3 and 2.4). †Excluding eastern tank park that is not owned by Refinery B.

	SOF			*SkyDOAS*				*MWDOAS*		*MeFTIR*
Refinery	**N Days**	**N Meas**	**Alkane Flux** [kg/h]	**N Days**	**N Meas**	**SO_2 Flux** [kg/h]	**NO_2 Flux** [kg/h]	**BTEX Flux*** [kg/h]	**Benzene Flux*** [kg/h]	**CH_4 Flux*** [kg/h]
Refinery A	15	40	269	10	39/34	62	66	24	3.4	167
Refinery B†	5	15	70	10	35	53	31	11	1.1	53
Refinery C	4	15	244	3	9	37	57	37	8.2	142
Refinery D	7	33	164	4	20	17	34	16	1.6	79
Refinery E	7	35	244	7	29/19	53	63	31	2.7	207
Refinery F	4	16	139	2	3	37	18	10	0.8	57
Sum			**1130**			**259**	**269**	**129**	**18**	**705**

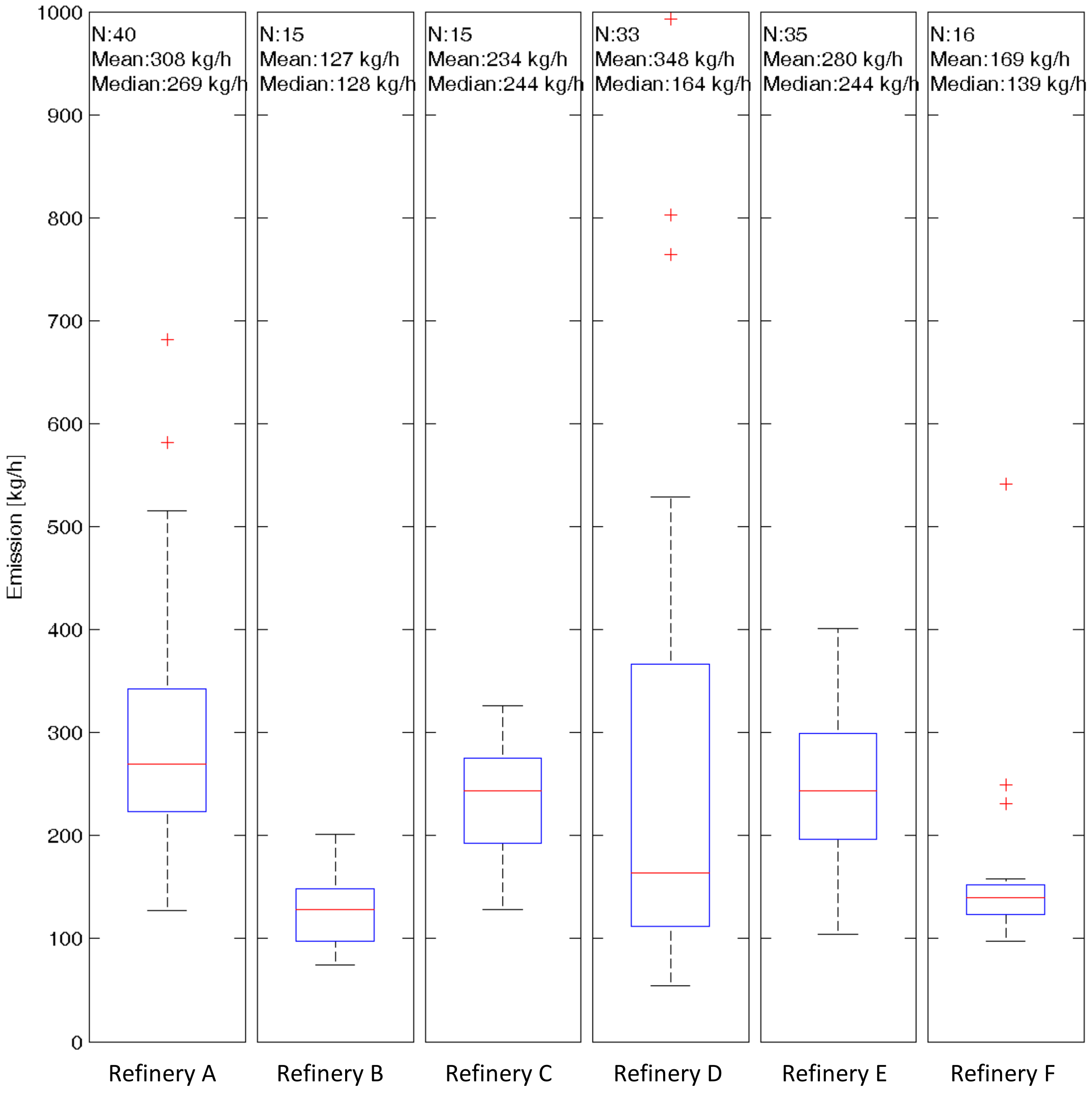

Figure 15. Box-plots of measured alkane emissions (kg/h) from the six refineries surveyed during the 2015 SCAQMD study. Median (50-percentile) values are presented as red bars and upper and lower quartiles as blue boxes with dashed whiskers extending to 1.5 times the inter-quartile range. Outliers beyond the whisker lengths are indicated by red crosses.

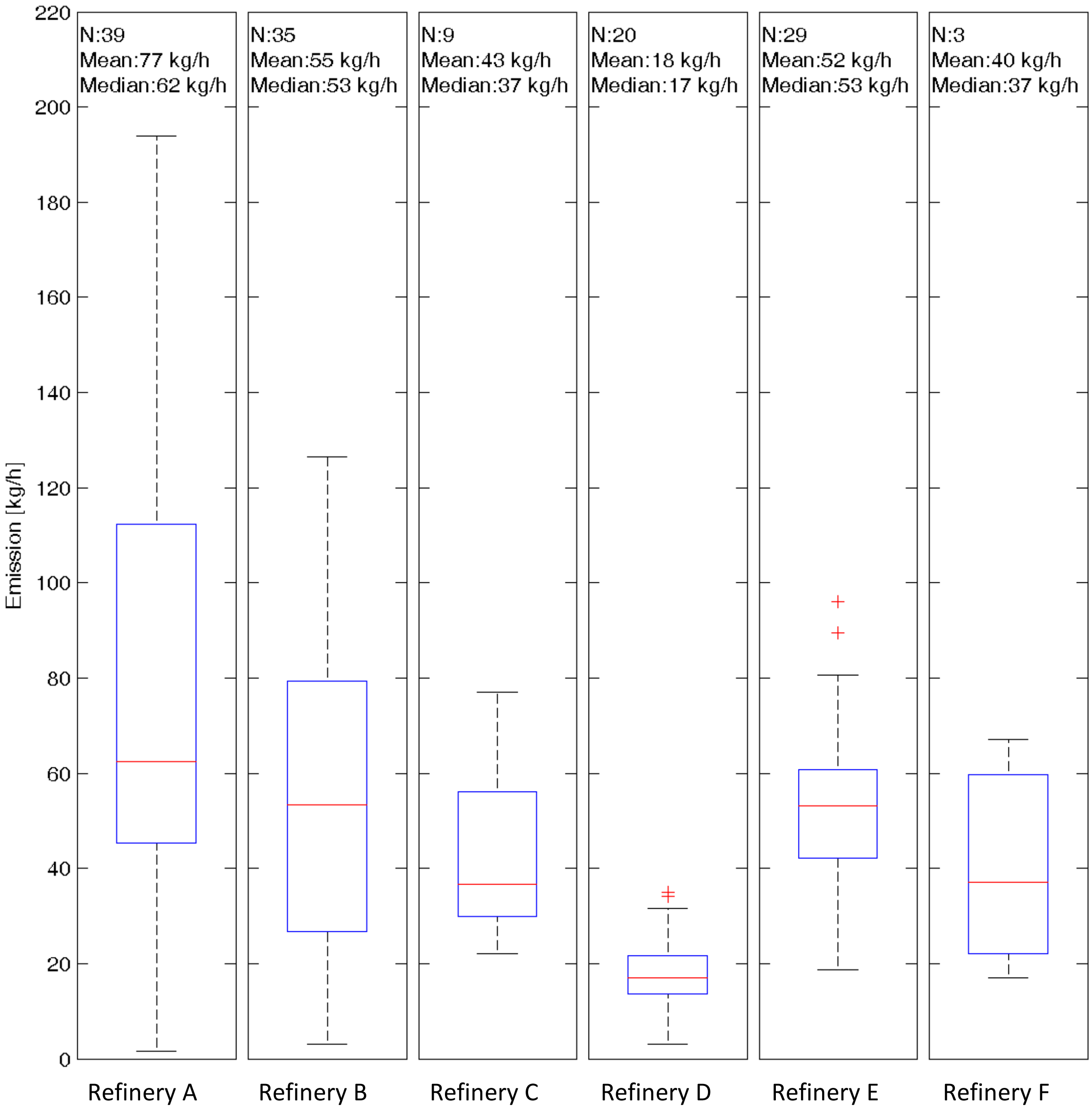

Figure 16. Box-plots of measured SO_2 emissions (kg/h) from the six refineries surveyed during the 2015 SCAQMD study. Median (50-percentile) values are presented as red bars and upper and lower quartiles as blue boxes with dashed whiskers extending to 1.5 times the inter-quartile range. Outliers beyond the whisker lengths are indicated by red crosses.

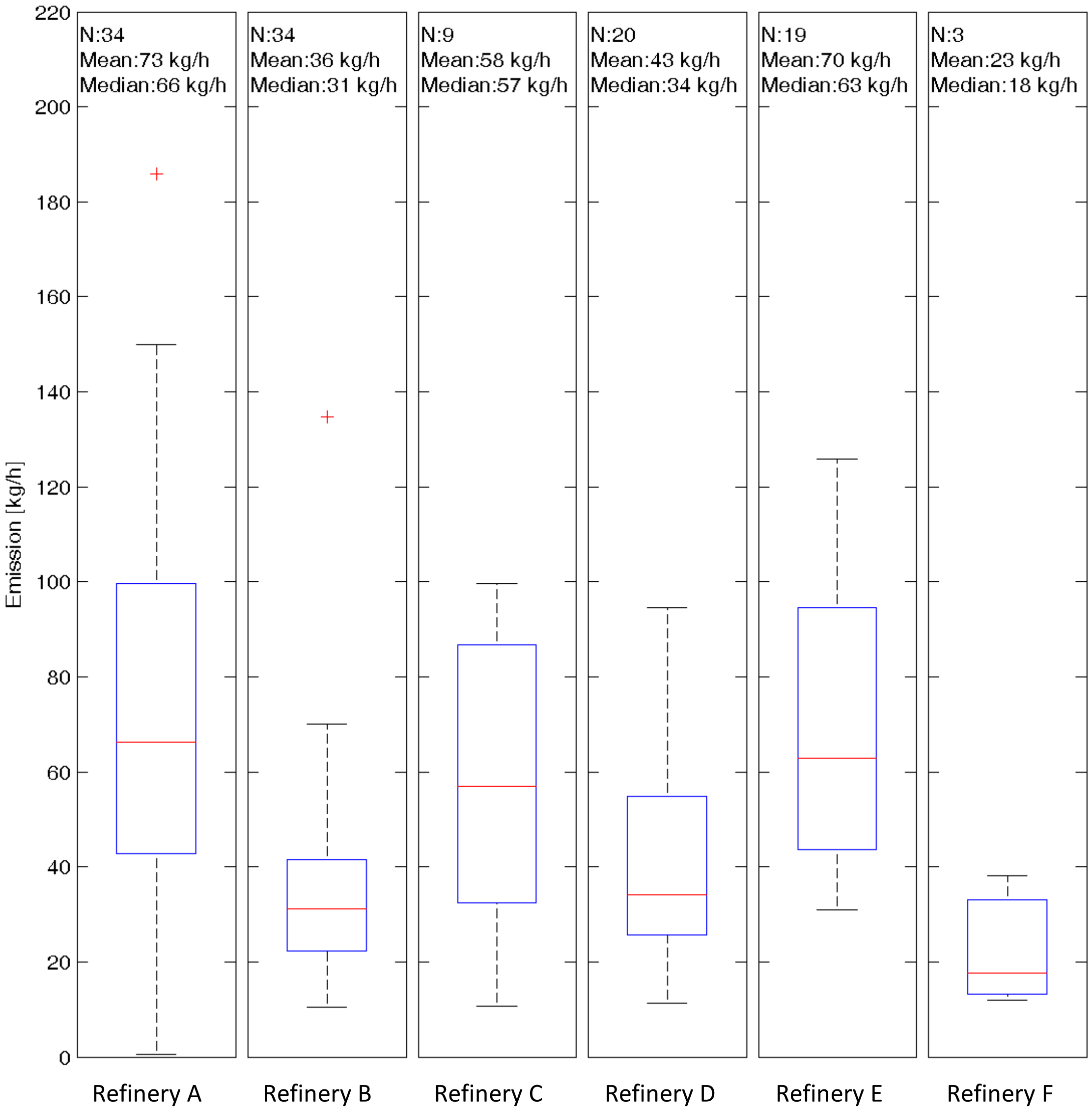

Figure 17. Box-plots of measured NO_2 emissions (kg/h) from the six refineries surveyed during the 2015 SCAQMD study. Median (50-percentile) values are presented as red bars and upper and lower quartiles as blue boxes with dashed whiskers extending to 1.5 times the inter-quartile range. Outliers beyond the whisker lengths are indicated by red crosses.

4.1 Refinery A

At Refinery A (crude oil capacity 257 kBPD (California Energy Commission 2016)) 15 measurement days of total emissions have been carried out and additionally one week of measurements inside the facility (see Section 5) through a collaboration between the refinery and SCAQMD.

The measurements were conducted over a period of eleven weeks, stretching from August 28 to November 10. Note that, typically, the number of successful measurements for each day varies considerably depending on acceptable solar- and wind conditions, interfering background levels and instrument availability. To accurately compensate for incoming background plumes, it was necessary to drive around the targeted facility for multiple times (see example in Figure 18), which is time-consuming.

Wind information for flux calculations were provided by a wind LIDAR (50-400 m average) right across the refinery's fence-line. This wind data was complemented with information collected by a 10 m wind station (scaled to match 50-400 m LIDAR) operated inside Refinery A. Typical wind velocities and direction at these locations were 4-5 m/s and 300°N, respectively (see Figure 19).

4.1.1 Alkanes (non-methane)

Alkane emissions from Refinery A were measured with the SOF during 15 different days from August 29 to November 10, 2015 (see Table 6). Daily means varied from 215 kg/h (September 5) to over 800 kg/h (October 29). The grand total average and standard deviation of all 40 quality assured transects amount to 308±113 kg/h. The median value was 269 kg/h. Histograms of all transects (Figure 20) show a sharp peak at around 250 kg/h and a "tail" of measurements above 500 kg/h. Most transects show a typical column peak directly downwind of the southern tank park (especially downwind of the large reservoir and tank-16) and of the process area (Figure 18).

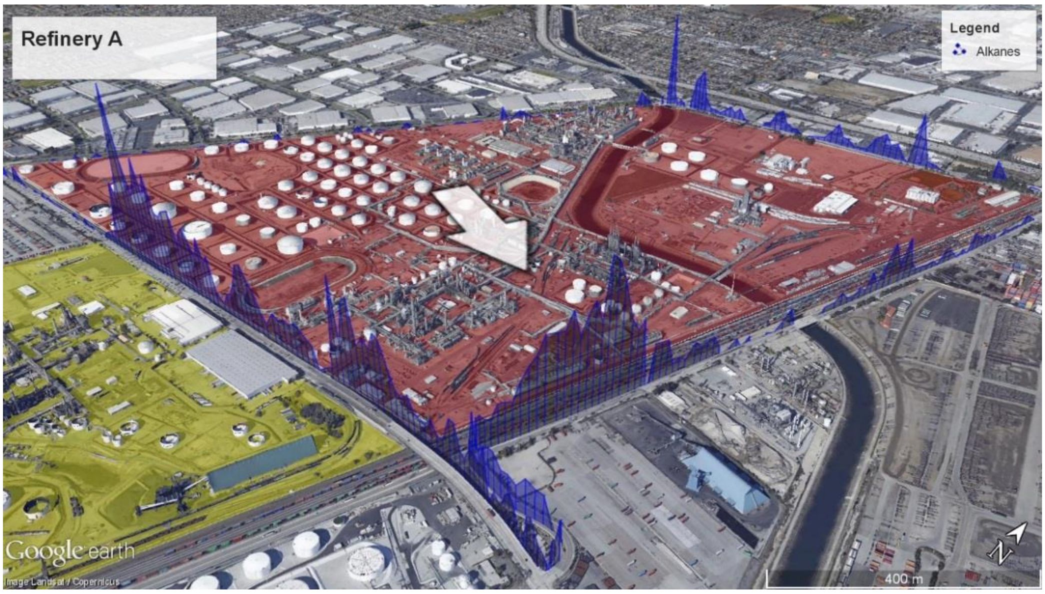

Figure 18. Example of SOF measurements around Refinery A (red area) conducted on September 5, 2015, from 15:20 to 15:37. The height of the blue line is proportional to the amount of alkanes in the gas column (i.e. 10 m is equivalent to 1 mg/m^2; max measured value was 64 mg/m^2). The wind direction is indicated by the white arrow. Average wind speed during this measurement was 6 m/s. Emissions on the upwind side of the facility were subtracted from the downwind side in order to obtain emissions from within the measured area. This particular transect measured 267 kg/h of Alkanes from Refinery A.

Table 6. Summary of SOF alkane measurements for Refinery A. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	144942 -173531	3	413.1±88.6	5.4-7.4	289-295
150902	142535 -154524	3	319.2±74.7	4.7-5.4	305-310
150903*	130746 -131654	1	271.8	3.8	136
150904	134638 -154706	3	226.8±45.2	3.9-5.0	193-199
150905	112732 -165808	7	214.9±84.2	3.1-6.0	181-295
150906	135041 -160653	3	304.7±76.8	2.7-5.5	262-299
150907	142422 -164733	3	223.8±85.7	3.9-7.0	284-285
150908	111515 -123733	2	322.0±223.7	2.6-2.6	272-323
151003	135421 -151958	2	281.8±70.9	4.9-5.2	174-191
151010*	100622 -102546	1	220.8	2.2	65
151018*	143919 -145556	1	281.5	3.7	188
151020	142108 -154446	4	333.5±165.7	4.2-6.0	276-298
151029	110714 -115044	2	866.0±260.3	7.3-7.3	313-316
151107	103907 -114442	3	265.5±38.6	2.7-4.1	17-38
151110	142726 -145648	2	260.6±29.7	9.8-10.1	253-263
Average±SD	**-**	**(total 40)**	**308±113 (37%)**	**-**	**-**
Median	**-**	**(total 40)**	**269**	**-**	**-**

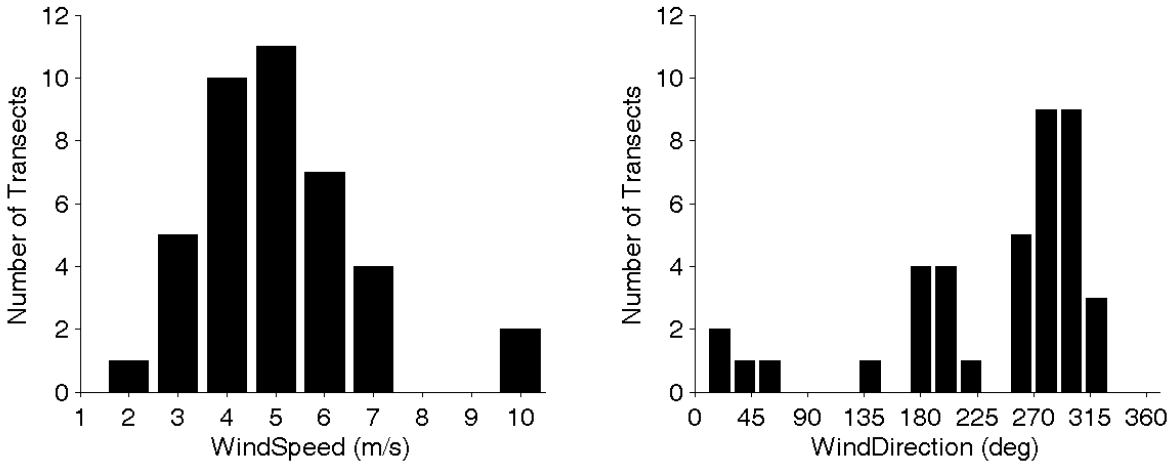

Figure 19. Histograms of wind speed (left) and wind direction (right) for all SOF measurements at Refinery A during the 2015 SCAQMD survey.

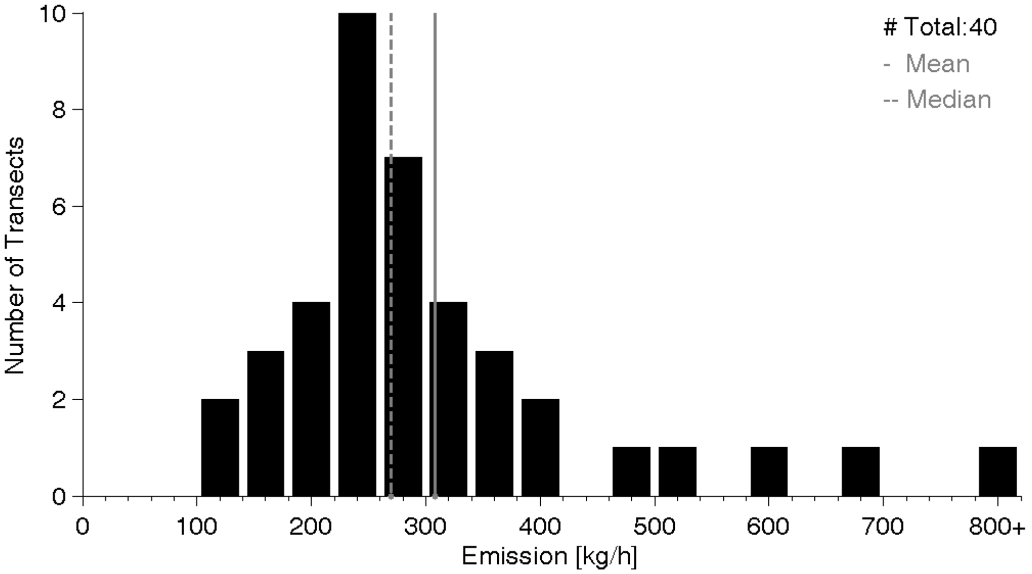

Figure 20. Histogram of all SOF measurements at Refinery A during the 2015 SCAQMD study. The last bin, denoted ‘800+’, contains all data points above 800 kg/h. The median and average values are indicated as dashed and solid gray lines, respectively.

4.1.2 SO_2 and NO_2

SO_2 and NO_2 emissions from Refinery A facility were measured for 10 measurement days during the campaign, from August 29 to November 30 2015 (some of the transects can be seen in Figure 21). Summaries and histograms of SkyDOAS emission measurements are presented in Table 7, Table 8, Figure 22 and Figure 23. Emissions averaged 73 and 77 kg/h for NO_2 and SO_2, respectively. Median values for these two gaseous pollutants were 66 (NO_2) and 62 kg/h (SO_2). The precise origins of the plumes cannot be decided from these measurements, although the Cogen-plant seems to be a matching source for some of the NO_2 plumes.

Figure 21. Transects of plumes originating from Refinery A. NO_2 (pink line) and SO_2 (brown line) were impacted by westerly winds. Conversely, BTEX (blue line) and alkane (yellow line) plumes were measured in the presence of northerly winds. The column thickness for both NO_2 and SO_2 is reported on the same scale (max NO_2 = 3 mg/m^2 flux NO_2 = 114 kg/h, max SO_2 = 11 mg/m^2 flux SO_2 = 46 kg/h). Alkanes and BTEX columns are scaled separately for better visibility (max BTEX = 0.25 mg/m^3, max alkanes = 1.95 mg/m^3). The examples presented here are single transects made on September 2 and on September 19, 2015.

Table 7. Summary of Refinery A NO_2 measurements.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	144857 -172703	3	57.0±69.3	5.4-7.6	285-296
150902	140707 -151247	3	59.3±49.8	4.4-6.5	300-314
150903	125302 -134150	2	119.7±42.8	4.1-4.5	115-131
150904	134011 -154225	4	76.2±26.5	4.3-4.9	185-200
150905	113143 -161302	5	67.9±22.9	3.5-6.0	180-295
150906	111801 -165522	5	54.3±18.8	1.8-4.3	266-302
150907*	151830 -152142	1	49.6	5.0	286
150908	113158 -123350	2	26.8±2.1	2.5-2.7	258-323
151029	105412 -150635	7	105.3±49.9	7.0-11.0	275-324
151030	112454 -161144	2	65.7±92.3	2.7-5.0	142-199
Average±SD	**-**	**(total 34)**	**72.8±45.1 (61.9%)**	**-**	**-**
Median	**-**	**(total 34)**	**66.3**	**-**	**-**

Table 8. Summary of Refinery A SO_2 measurements.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	144857 -173037	3	114.5±69.1	5.4-7.6	285-296
150902	140726 -154429	4	59.4±40.2	4.4-6.5	298-314
150903	125302 -134150	3	44.2±37.0	2.4-4.5	116-133
150904	134011 -154225	4	66.5±34.2	4.3-4.8	185-200
150905	104604 -161046	7	41.4±28.3	2.1-6.0	103-295
150906	111801 -165332	5	73.2±35.1	1.8-4.4	266-301
150907	134339 -152051	2	54.0±44.8	3.8-5.0	264-286
150908	113244 -123504	2	60.6±11.5	2.6-2.7	259-318
151029	105412 -150635	6	125.5±36.3	6.9-11.0	275-325
151030	112531 -161409	3	129.9±67.3	2.7-5.0	142-202
Average±SD	**-**	**(total 39)**	**77.1±42.0**	**-**	**-**
Median	**-**	**(total 39)**	**62.4**	**-**	**-**

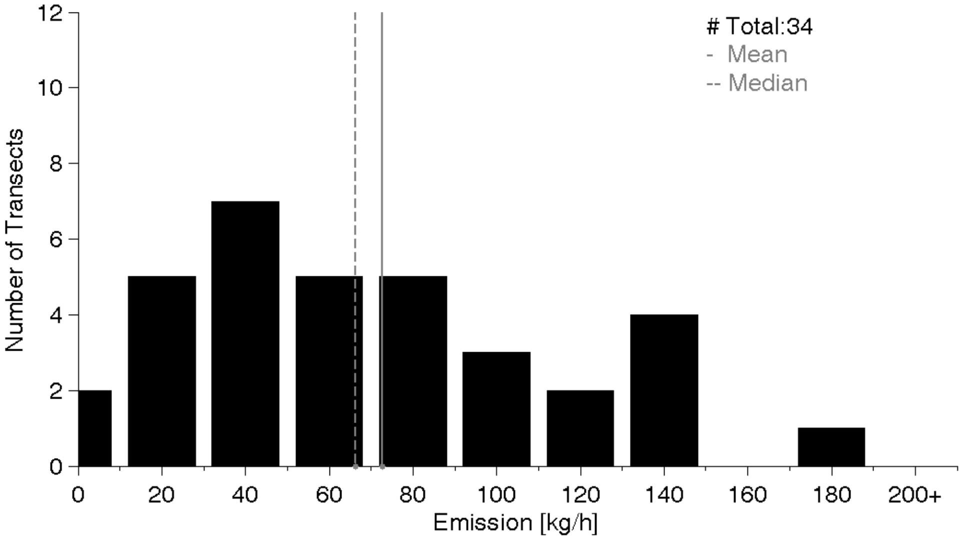

Figure 22. Histogram of all SkyDOAS NO_2 measurements at the Refinery A during the 2015 SCAQMD survey. The last bin, denoted ‘200+’, contains all data points above 200 kg/h. The median and average values are indicated as dashed and solid gray lines, respectively.

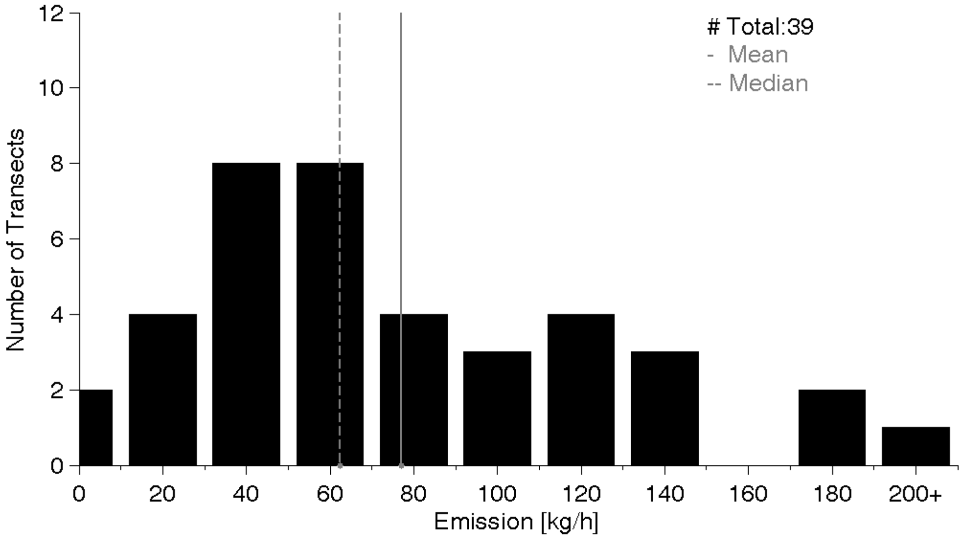

Figure 23. Histogram of all SkyDOAS SO_2 measurements at Refinery A during the 2015 SCAQMD survey. The last bin, denoted '200+', contains all data points above 200 kg/h. The median and average values are indicated as dashed and solid gray lines, respectively.

4.1.3 BTEX

The fraction of BTEX compounds present in the measured alkane plumes emitted from Refinery A was measured either in the late evening or early morning when plumes are closer to the ground. This fraction is calculated by combining BTEX measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured along two roads depending on wind direction. Results for these measurements are shown in Table 9. The average mass fraction of BTEX to alkanes was 0.087 or 8.7%. The average flux of BTEX can be calculated by multiplying this value by the total alkane flux as measured by the SOF-technique. The average mass fraction of benzene to alkanes was 1.3% and the benzene flux can be calculated in the same way as above.

Table 9. Summary of MWDOAS BTEX measurements at Refinery A. *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	221347-221949	7.8	0.98	2.3	323
150919	231317-231938	5.4	0.92	1.5	329
150921	051934-052525	12.8	1.7	1.8	73
150922	062223-063032	13.4	1.7	2.4	110
150922	073305-074108	6.8	0.65	1.9	81
150922	051356-051759	3.6	0.21	2.1	83
150922	183651-184148	11.2	2.7	2.1	181
Average±SD	-	**8.7±3.8**	**1.3±0.8**	-	-

4.1.4 Methane

The average fraction of methane to total non-methane alkanes in the plume originating from Refinery A was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). Methane measurements were conducted during different times of the day and a summary of these results is shown in Table 10. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux as measured by SOF provides an estimate of the methane flux from the refinery. The average methane-to-alkanes mass fraction for Refinery A was 0.62.

Table 10. Summary of MeFTIR methane measurements at the Refinery A. *Methane/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction* [%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	221206 -231956	2	44	1.6-2.2	332-347
150922	062220 -063024	1	41	1.9	88
151018	144244 -145057	1	64	3.4	177
151020	122426 -154604	6	71	2.4-5.7	135-312
151029	105144 -150803	6	67	4.0-11.3	285-328
151030	113932 -155450	3	57	1.3-4.0	186-289
Average±SD	**-**	**(total 19)**	**62±25**	**-**	**-**

4.2 Refinery B

Refinery B (crude oil capacity (together with Refinery C) 139 kBPD (California Energy Commission 2016)) is located just south of Refinery A, see Figure 24. This site was frequently surveyed in combination with the Refinery A facility. However, due to the proximity to other sources, such as Tank Farm G and Refinery A, there is an increased possibility of interference depending on wind direction and therefore there were fewer valid emissions measurements. Note that the surveyed area also included a crude tank park on the west side that is not owned by Refinery B. Emission contributions from this crude tank park have been accounted for in the data post-processing (see below).

Wind information from the wind LIDAR (L1, 0-400 m average) was mainly used for the flux calculations. This was complemented by Refinery A's 10 m wind station data (scaled to match 0-400 m LIDAR) when needed. Typical wind directions and velocities during the measurements were 4 m/s and 180 or 270°N, see Figure 25.

4.2.1 Alkanes (non-methane)

Alkane emissions from Refinery B were measured with SOF during five non-consecutive days from September 4 to November 10, 2015, see Table 11 and discussion above. Daily means varied from 83 kg/h (September 6) to 173 kg/h (September 7). The grand total average and median for all 15 quality assured transects were 127±23 kg/h and 128 kg/h, respectively. Histogram of all transects shows a "compact" distribution at around 130 kg/h with no outliers, see Figure 26.

Measurement transects typically showed the presence of two peaks, one downwind the western side and another downwind the eastern side, see Figure 24. Based on transects where a complete separation between the two sides/peaks was possible (during S to SW winds), 45% of the emissions were attributed to the western side and 55% to the eastern side. The 55 correction factor has been applied in the survey mean/median calculations (e.g. Table 5), but not for daily means (e.g. Table 11) or individual measurements (e.g. Figure 26). The correction was done in order to exclude the emissions that should not be attributed to Refinery B when inter-comparing the different refineries in this report.

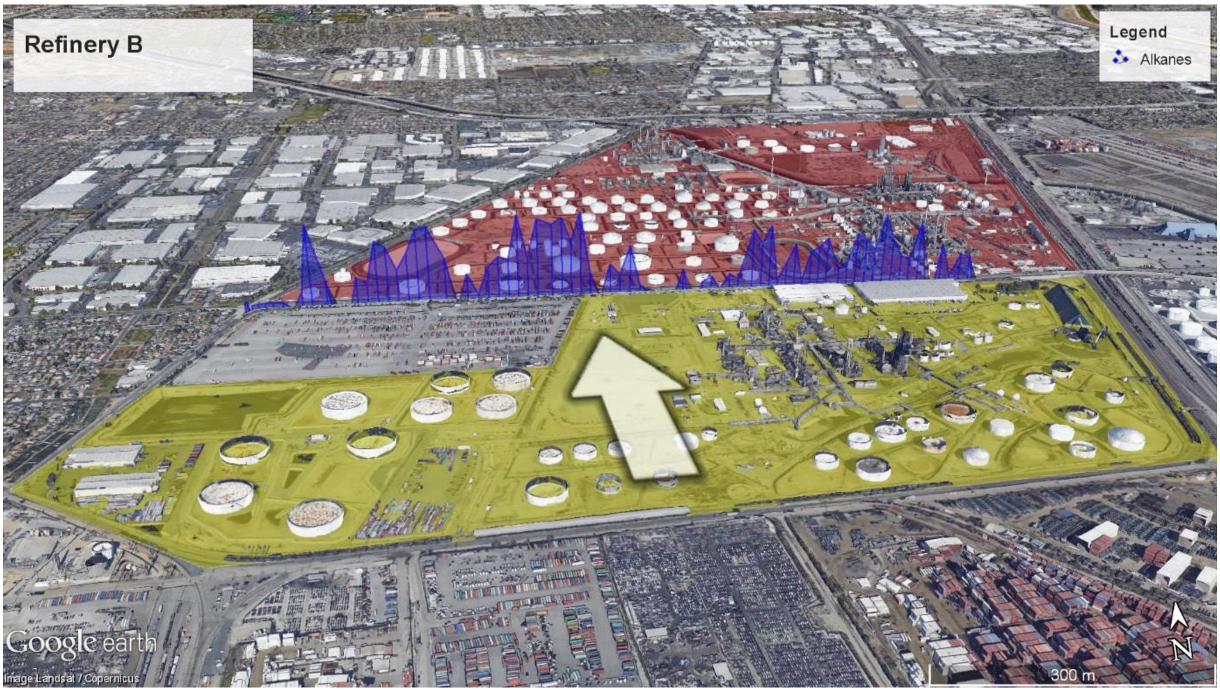

Figure 24. Example of SOF measurements conducted at Refinery B (yellow area) on September 4, 2015, 16:10-16:13. The alkane column is shown as a blue line with apparent height proportional to the gas column (10 m equivalent to 1 mg/m^2, max 32 mg/m^2). Wind direction during the measurements is indicated by the white arrow. The average wind speed during these particular measurements was 3.2 m/s. Emissions on the upwind side are insignificant and not shown in this figure. Emissions resulting from this particular transect were estimated at 107 kg/h.

Table 11. Summary of SOF alkane measurements for Refinery B (including the crude tank park west of the refinery).

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150904	134712 -165939	6	116.3±23.6	3.2-5.5	178-253
150905	153737 -171908	3	121.9±7.4	5.8-6.1	268-279
150906	124744 -163755	2	83.2±13.0	3.4-3.7	165-279
150907	140251 -150726	2	172.8±39.8	3.9-4.3	284-285
151110	143118 -145107	2	161.5±17.6	9.4-10.2	255-255
Average±SD	**-**	**(total 15)**	**127±23 (18%)**	**-**	**-**
Median	**-**	**(total 15)**	**128**	**-**	**-**

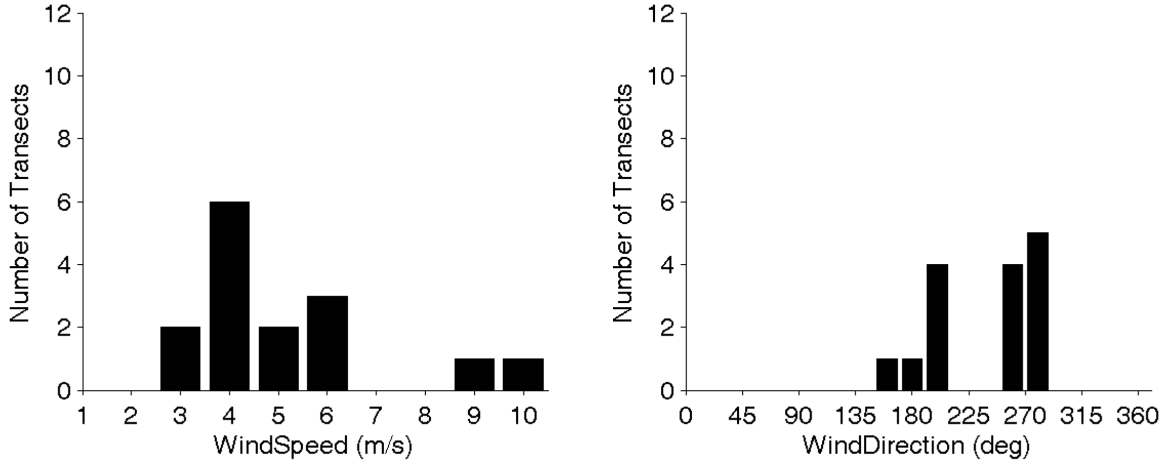

Figure 25. Wind histograms at Refinery B summarizing all wind speed (left) and wind direction (right) measurements conducted during the 2015 SCAQMD study.

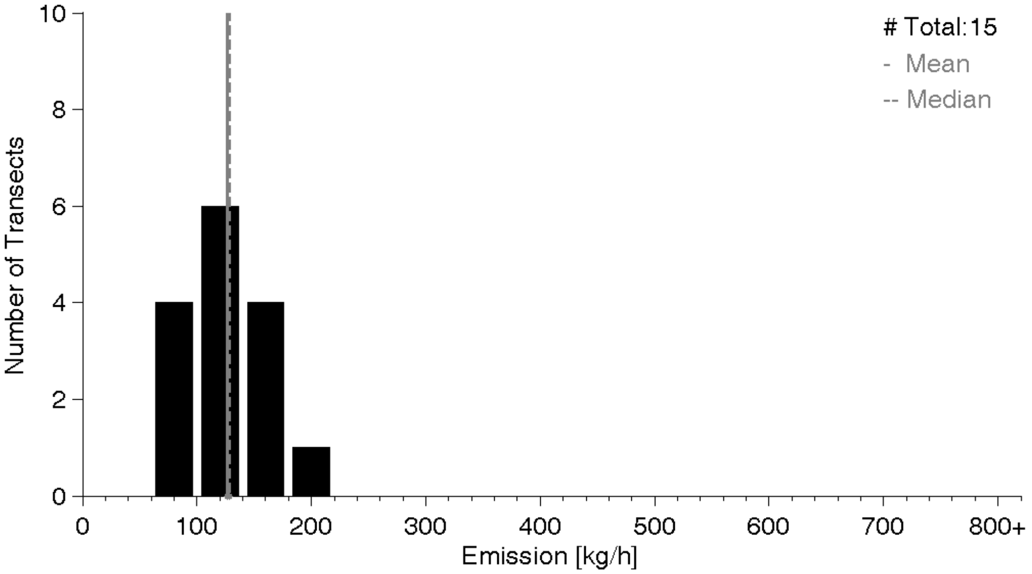

Figure 26. Histogram of all SOF measurements conducted at Refinery B (including crude tank park west of the refinery) during the 2015 SCAQMD study. The median and average values are shown as dashed and solid gray lines, respectively.

4.2.2 SO_2 and NO_2

SO_2 and NO_2 emissions were measured for 10 measurement days during the campaign, from August to October, 2015. Figure 27 shows examples of measurement transects conducted on September 2 and September 19, 2015. Summaries and histograms of SkyDOAS emission measurements are presented in Table 12, Table 13, Figure 28 and Figure 29. In this case NO_2 emissions averaged 36 kg/h and SO_2 55 kg/h. Median values for these two gaseous pollutants were 31 (NO_2) and 53 kg/h (SO_2).

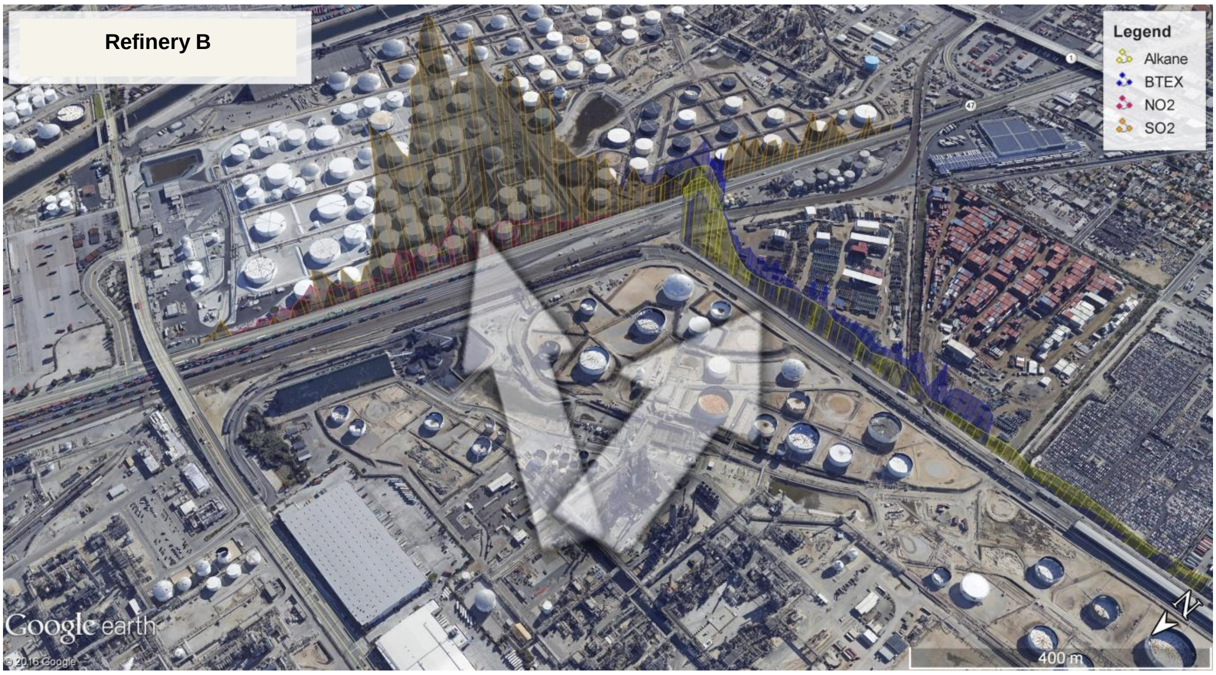

Figure 27. Transects of plumes originating from Refinery B. NO_2 (pink line) and SO_2 (brown line) were impacted by westerly winds (4.3 m/s). Conversely, BTEX (blue line) and alkane (yellow line) plumes were measured in the presence of northerly winds. The column thickness for both NO_2 and SO_2 is reported on the same scale (max NO_2 = 5.6 mg/m^2, flux NO_2 = 11.7 kg/h, max SO_2=25 mg/m^2, flux SO_2 = 68.2 kg/h). Alkanes and BTEX columns are scaled separately for better visibility (max BTEX = 0.03 mg/m^3, max alkanes = 0.36 mg/m^3). The examples shown here were collected on September 8 and on September 19, 2015.

Table 12. Summary of NO_2 measurements at Refinery B.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	152225 -152509	1	31.8	7.0	295
150902	132957 -141007	2	21.8±0.7	5.0-6.3	303-315
150903	130123 -133346	2	30.7±15.3	3.9-4.9	106-148
150904	134837 -152937	4	41.2±8.3	3.7-4.9	193-203
150905	103515 -171321	11	27.7±9.2	1.0-6.2	112-286
150906	130316 -163207	4	52.6±12.9	2.6-4.5	162-286
150907	132433 -161506	4	28.5±8.9	3.5-6.1	242-285
150908	110353 -124134	3	57.7±67.2	2.0-8.8	313-327
151029	121217 -121936	1	67.9	7.3	312
151030	114718 -153206	2	19.3±12.6	2.0-4.5	112-193
Average±SD	**-**	**(total 34)**	**35.6±22.4 (62.8%)**	**-**	**-**
Median	**-**	**(total 34)**	**31.2**	**-**	**-**

Table 13. Summary of SO_2 measurements at Refinery B.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150829	152225 -152509	1	126.5	7.0	295
150902	133006 -141007	2	17.9±0.8	5.1-6.3	303-316
150903	130123 -133323	3	34.0±8.6	3.9-4.9	105-150
150904	134828 -152937	4	37.5±20.1	3.7-4.9	193-203
150905	103537 -171321	11	56.1±28.7	1.0-6.2	111-287
150906	130316 -163207	4	78.3±13.5	2.6-4.5	162-286
150907	132433 -161506	4	79.9±18.3	3.5-6.1	242-285
150908	110353 -124134	3	68.9±26.9	2.0-8.8	314-327
151029	121150 -133517	2	14.7±16.5	7.1-7.3	311-313
151030	114718 -115224	1	9.0	2.2	114
Average±SD	**-**	**(total 35)**	**54.5±21.5 (39.3%)**	**-**	**-**
Median	**-**	**(total 35)**	**53.4**	**-**	**-**

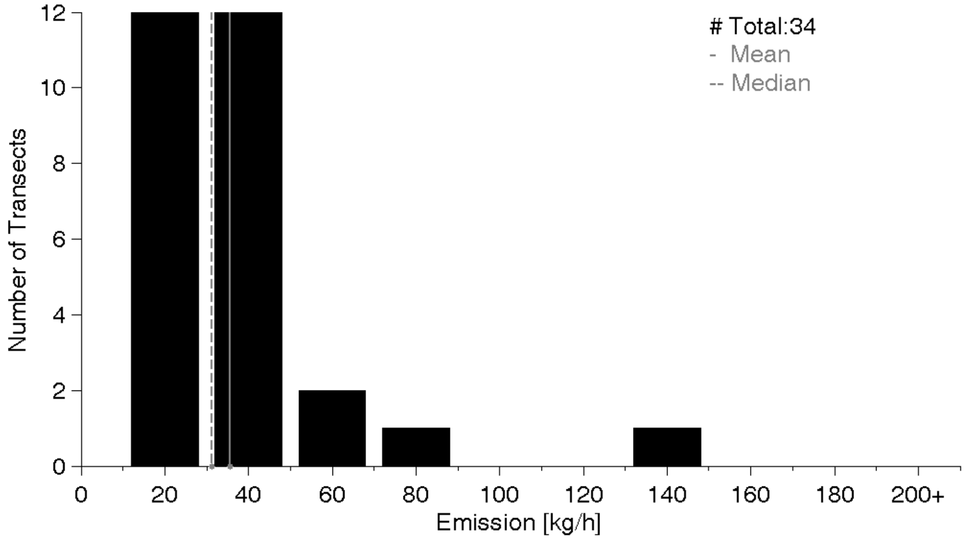

Figure 28. Histogram of all SkyDOAS NO_2 measurements at the Refinery B during the 2015 SCAQMD study. The median and average values are indicated as dashed and solid gray lines, respectively.

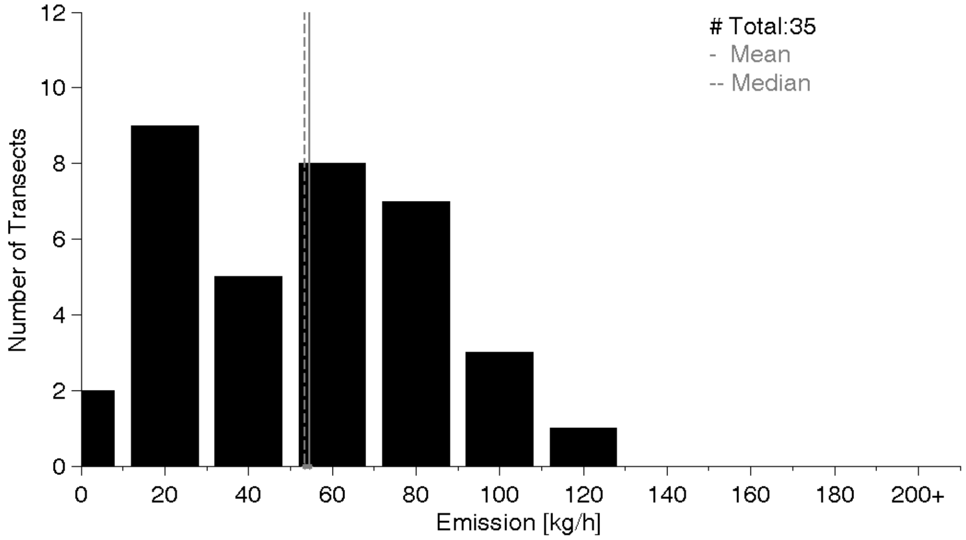

Figure 29. Histogram of all SkyDOAS SO_2 measurements taken at Refinery B during the 2015 SCAQMD study. The median and average values are indicated as dashed and solid gray lines, respectively.

4.2.3 BTEX

The fraction of BTEX compounds present in the measured alkane plumes emitted from Refinery B was measured either in the late evening or early morning when the plume was closer to the ground. This fraction is calculated by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured along two roads depending on wind direction. A summary of these measurements is shown in Table 14 and an example of a plume transect illustrated in Figure 27.

The average mass fraction of BTEX to alkanes was 0.084 or 8.4%. The average flux of BTEX can be calculated by multiplying this value by the total alkane flux as measured by the SOF-technique. The average mass fraction of benzene to alkanes was 0.9% and the benzene flux can be calculated in the same way as above.

Table 14. Summary of MWDOAS BTEX measurements at Refinery B. *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	222903-223809	11.3	0.18	2.5	345
150919	232406-232758	5.5	0.75	2	325
150919	220447-220915	7.3	0.71	2	302
150921	053955-054412	6.5	1.9	0.9	64
150922	070636-071237	11.4	0.9	1.5	64
Average±SD		**8.4±2.8**	**0.9±0.6**		

4.2.4 Methane

The average fraction of methane to total non-methane alkanes in the plume originating from Refinery B was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes. To determine the source of the plume, wind directions from Refinery A's 10 m mast were used (wind speed is irrelevant for these measurements). Methane measurements were conducted during different times of the day and a summary of these results is shown in Table 15. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux as measured by SOF provides an estimate of the methane flux from the refinery. The average methane-to-alkanes mass fraction for Refinery B was 0.75.

Table 15. Summary of MeFTIR methane measurements at Refinery B. *Methane/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction* [%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	222929 -232735	2	73	2.0-2.6	325-346
151018	145106 -145455	1	91	3.1	171
151020	134959 -162614	3	110	1.6-5.4	163-295
151029	121145 -122309	1	23	4.9	317
151030	112324 -155949	3	53	2.1-4.1	121-188
Average±SD	**-**	**(total 10)**	**75±36**	**-**	**-**

4.3 Refinery C

Refinery C, (crude oil capacity together with Refinery B 139 kBPD, (California Energy Commission 2016)) is located north of the Los Angeles port, see Figure 10. Significant upwind background plumes from the port and oil wells on the west side must be compensated for in the flux calculations. This is done by encircling (‘box-measuring’) the facility when possible (see example in Figure 18).

Wind information for the flux calculations on September 18, 2015 came from the wind LIDAR (0-400 m average) at position L2, located at the golf course parking lot north of the refinery, see Figure 30. For the other days, wind information from the SCAQMD met station at South Long Beach (SLBH) was used (scaled to match 0-400m LIDAR). See section 3.4 for additional wind analysis. Typical wind speeds and wind directions during the measurements are 3 m/s and 130-320°N, see Figure 31. Winds are generally weak at this site due to the hills on the west side.

4.3.1 Alkanes (non-methane)

Alkane emissions from Refinery C was measured with SOF during four days in the period September 7 to November 4, see Table 16. The daily means varied from 128 kg/h (4 November, single measurement) to over 297 kg/h (29 October). The average emission determined from the 15 quality assured transects was 234±36 kg/h and the median emission was 244 kg/h. Histograms of all transects (Figure 32) show a peak at around 230 kg/h and no extreme outliers. Most transects show a typical column peak directly downwind the north-west tank park and the process area, see Figure 30.

Table 16. Summary of SOF alkane measurements for Refinery C. *Single measurement

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150907	104256 -121838	4	296.5±22.4	2.1-2.9	134-163
150918	133231 -165721	5	200.5±47.1	2.6-3.7	301-323
151022	144739 -161143	5	238.4±31.1	2.9-3.9	170-204
151104*	121336 -122731	1	128.2	2.9	239
Average±SD	**-**	**(total 15)**	**234±36 (15%)**	**-**	**-**
Median	**-**	**(total 15)**	**244**	**-**	**-**

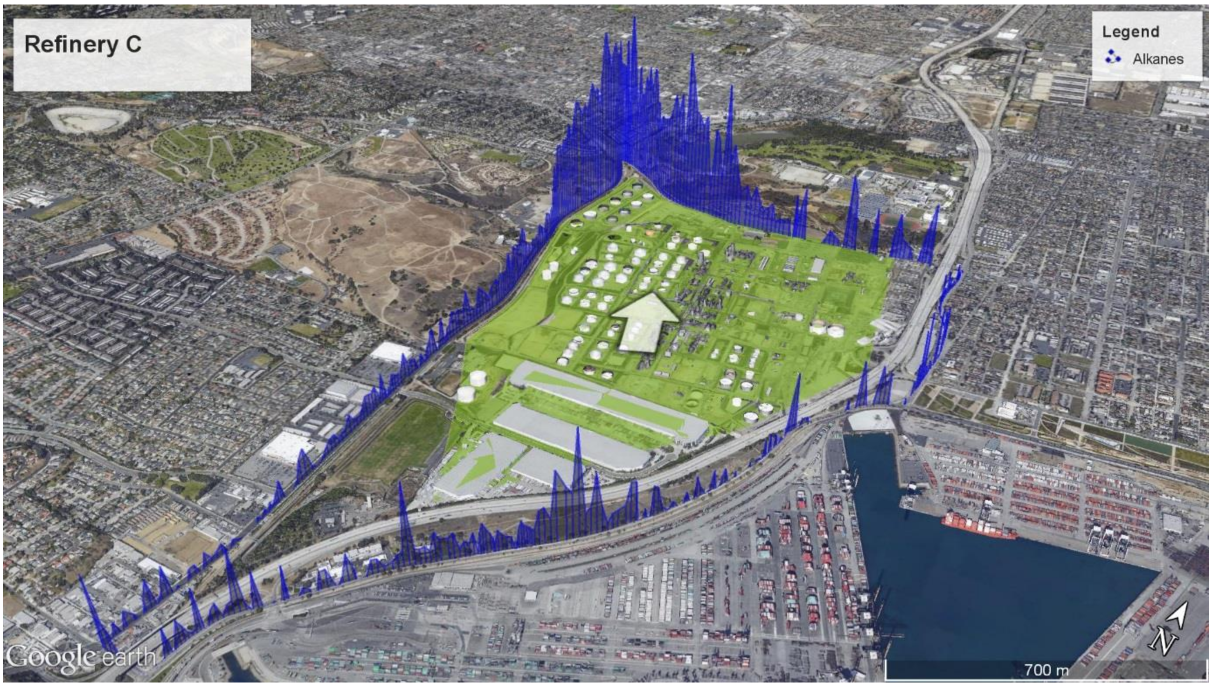

Figure 30. Example of a SOF 'box' measurement of the Refinery C (green area) 7 September 2015, 11:57-12:18. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 76 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed was 2.9 m/s for this particular measurement. Emissions on the upwind side (from LA harbor) are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 285 kg/h from Refinery C.

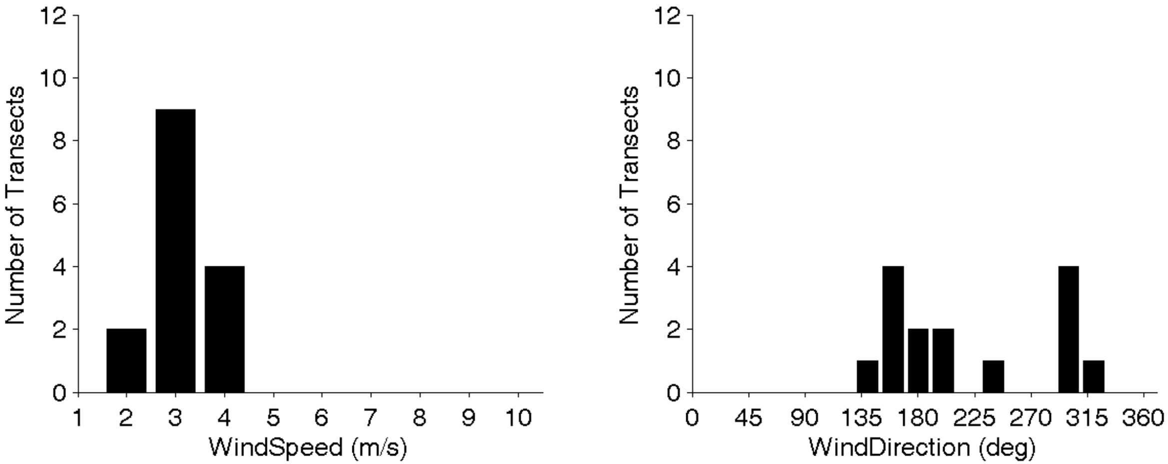

Figure 31. Wind histograms at Refinery C of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

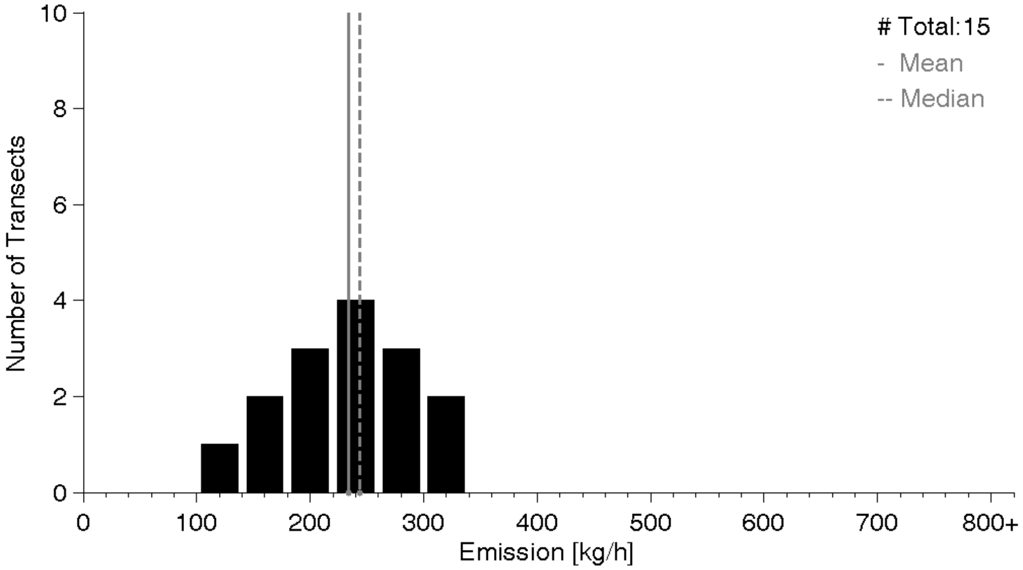

Figure 32. Histogram of all SOF measurements at Refinery C during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.3.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured for three measurement days during the campaign, twice in September and once in November. Summaries and histograms of SkyDOAS emission measurements are presented in Table 17, Table 18, Figure 34 and Figure 35. An example of a measurement is shown in Figure 33. Emissions averaged 58 and 43 kg/h and medians were 57 and 37 kg/h for NO_2 and SO_2 respectively.

Table 17. Summary of NO_2 measurements at Refinery C.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150907	95140 -121752	4	44.7±38.6	1.5-4.0	167-320
150918	134001 -153244	4	78.0±14.4	2.1-3.9	309-329
151104	121533 -122359	1	34.1	4.1	265
Average±SD	**-**	**(total 9)**	**58±29 (50%)**	**-**	**-**
Median	**-**	**(total 9)**	**57**	**-**	**-**

Table 18. Summary of SO_2 measurements at Refinery C.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150907	95122 -121752	4	48.7±21.9	1.4-4.2	166-310
150918	134212 -153244	4	39.5±16.4	1.9-3.9	309-331
151104	121405 -122616	1	30.7	4.1	271
Average±SD	**-**	**(total 9)**	**43±19 (45.4%)**	**-**	**-**
Median	**-**	**(total 9)**	**37**	**-**	**-**

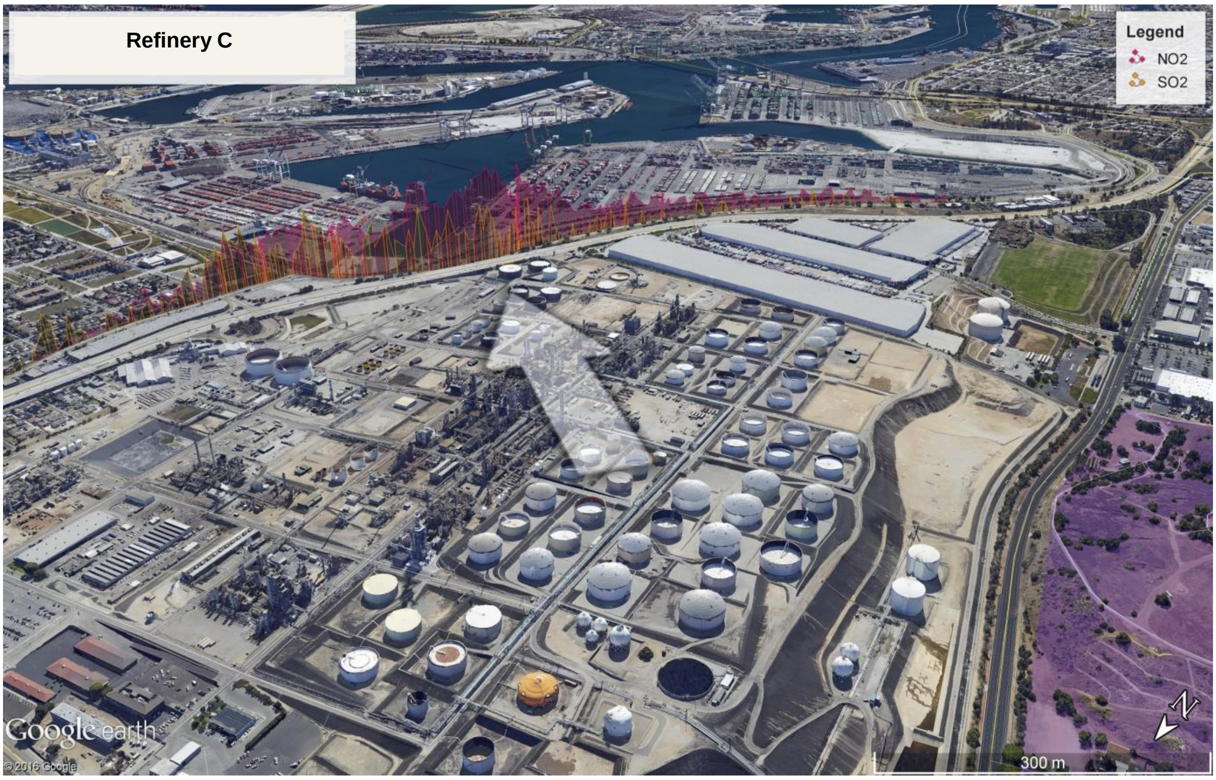

Figure 33. Transects of plumes originating from Refinery C. the NO_2 (pink) and SO_2 (brown) plume from Refinery C in north-westerly wind (3.7 m/s). Max NO_2 = 9.5 mg/m^2, flux NO_2 = 81 kg/h, max SO_2=5.6 mg/m^2, flux SO_2 = 37.5 kg/h Data from September 18 2:59 PM.

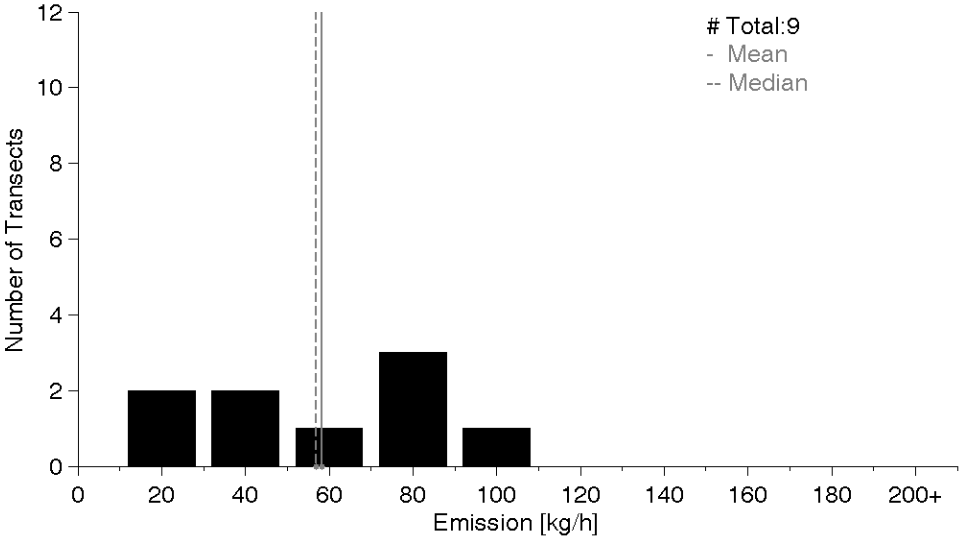

Figure 34. Histogram of all SkyDOAS NO_2 measurements at Refinery C during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

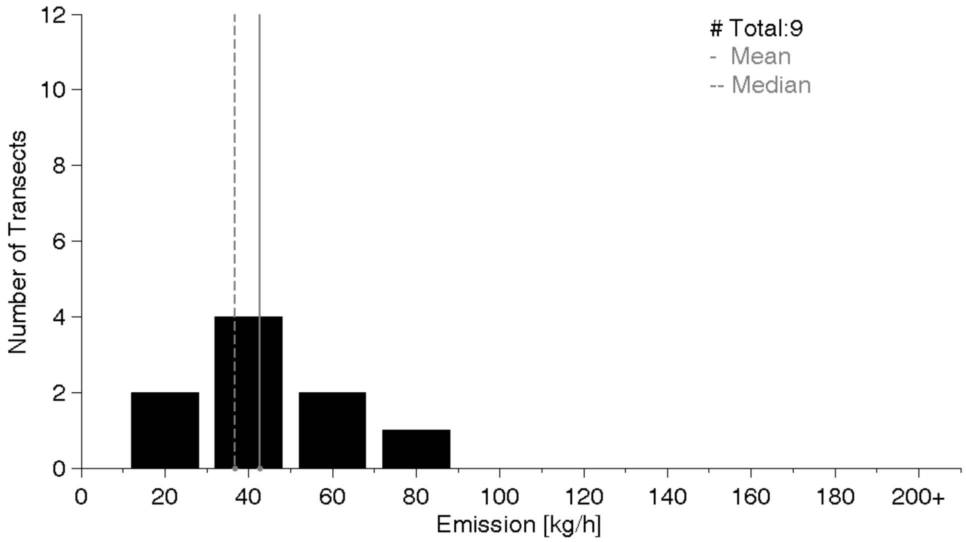

Figure 35. Histogram of all SkyDOAS SO_2 measurements at Refinery C during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.3.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery C were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from the SCAQMD-SLBH wind station were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured on different public roads surrounding the facility, depending on wind direction. The measurements are shown in Table 19.

The average mass fraction of BTEX to alkanes was 15.1%. The average flux of BTEX can be calculated by multiplying this figure with the total alkane flux as measured by the SOF-technique. The average fraction of benzene to alkanes was 3.4% and the benzene flux can be calculated in the same way as above. The plumes sampled during the measurement at Refinery C were weak and the low levels of both alkanes and BTEX causes a higher degree of uncertainty than usual in the mass ratio determination.

Table 19. Summary of MWDOAS BTEX measurements at Refinery C . *BTEX/alkane fraction.

Day [yymmdd]	Time span [hhmmss-hhmmss]	BTEX Fraction* [%]	Benzene Fraction* [%]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150918	220402-221009	12.6	1.4	2.5	323
151102	155155-155401	8.3	3.2	3.4	235
151102	150946-152855	13.8	2.4	3.5	254
151102	154248-154634	16.1	3.1	3.2	246
151104	160717-162206	24.8	6.7	3.3	275
Average±SD	-	**15.1±6.1**	**3.4±2.0**		

4.3.4 Methane

The average fraction of methane to total non-methane alkanes in the plume originating from Refinery C was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes measured simultaneously. Wind information from either LIDAR in position L2 or SCAQMD-SLBH was used, only wind direction, not wind speed matters for these measurements. Measurements were made both during the day and in late evenings and are shown in Table 20. Applying the measured fence-line ground level methane-to-alkane mass fraction to the by SOF measured alkane flux, gives an estimate of the methane flux from the refinery. The average methane-to alkane-mass fraction for Refinery C was 0.58.

Table 20. Summary of MeFTIR methane measurements at Refinery C. *Methane/alkane mass fraction.

Day [yymmdd]	**Timespan** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction*** **[%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150918	213422 -225735	2	61	2.9-3.0	321-327
151022	150050 -161331	5	49	3.1-5.2	182-193
151102	150921 -164835	3	68	2.8-3.8	243-279
151104	144900 -161529	2	62	4.0-12.0	230-262
Average±SD	**-**	**(total 12)**	**58±31**	**-**	**-**

4.4 Refinery D

Refinery D, (crude oil capacity: 105 kBPD (California Energy Commission 2016)) is located north of the Long Beach port, about 4 kilometers south of Refinery A, see Figure 10. To accurately compensate for incoming background plumes, it is necessary to make ‘box’ measurements (see example in Figure 36) which was easily done using public roads. Some measurements were however excluded since the incoming fluxes were comparable in size to the outgoing fluxes (adding too much uncertainty to the calculated flux). This was especially true for northerly and westerly winds carrying VOC-rich air from Refinery A and Refinery B.

Wind information for the flux calculations comes from the wind LIDAR (0-400 m average) at position L1 - (see Figure 10) or the Long Beach Airport ASOS station (scaled to match 0-400m LIDAR) or SCAQMD South Long Beach (SLBH) (scaled to match 0-400 m LIDAR). See section 3.4 for additional wind analysis. Typical wind directions and velocities during the measurements are 2-5 m/s and around 180°N or 270 degrees, see Figure 37.

4.4.1 Alkanes (non-methane)

Alkane emissions from Refinery D were measured with SOF during 7 days in the period September 3 to November 9, see Table 21. The daily means varied substantially from 90 kg/h (6 September) to an extreme of almost 1000 kg/h (1 November). A flaring event occurred 1 November which explains the large deviation for this day. The grand total average and standard deviation of all the 33 quality assured transects amounts to 348±253 kg/h and the median 164 kg/h. Histogram of all transects, Figure 38, show a gathered distribution at around 120 kg/h and some extreme outliers above 500 kg/h (which exclusively emanate from 1 November). Most transects show a typical column peak directly downwind the process area, see Figure 36. On November 1, significant VOC columns were detected directly downwind the flares in the west corner.

Table 21. Summary of SOF alkane measurements for Refinery D. *Single measurement. †Significantly deviating results due to flaring event.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150903*	140059 -140320	1	191.6	4.3	204
150906	171235 -180214	2	90.3±20.2	3.9-4.2	289-300
150907*	170803 -172210	1	125.6	6.6	269
150908	132545 -173630	9	192.0±66.9	4.0-7.8	274-296
150919	113306 -143232	10	116.7±47.1	2.2-2.6	160-198
151101†	104629 -150057	8	974.7±497.0	2.1-5.3	183-206
151109	135330 -144219	2	141.7±31.2	6.8-7.9	245-256
Average±SD	**-**	**(total 33)**	**348±253 (73%)**	**-**	**-**
Median	**-**	**(total 33)**	**164**	**-**	**-**

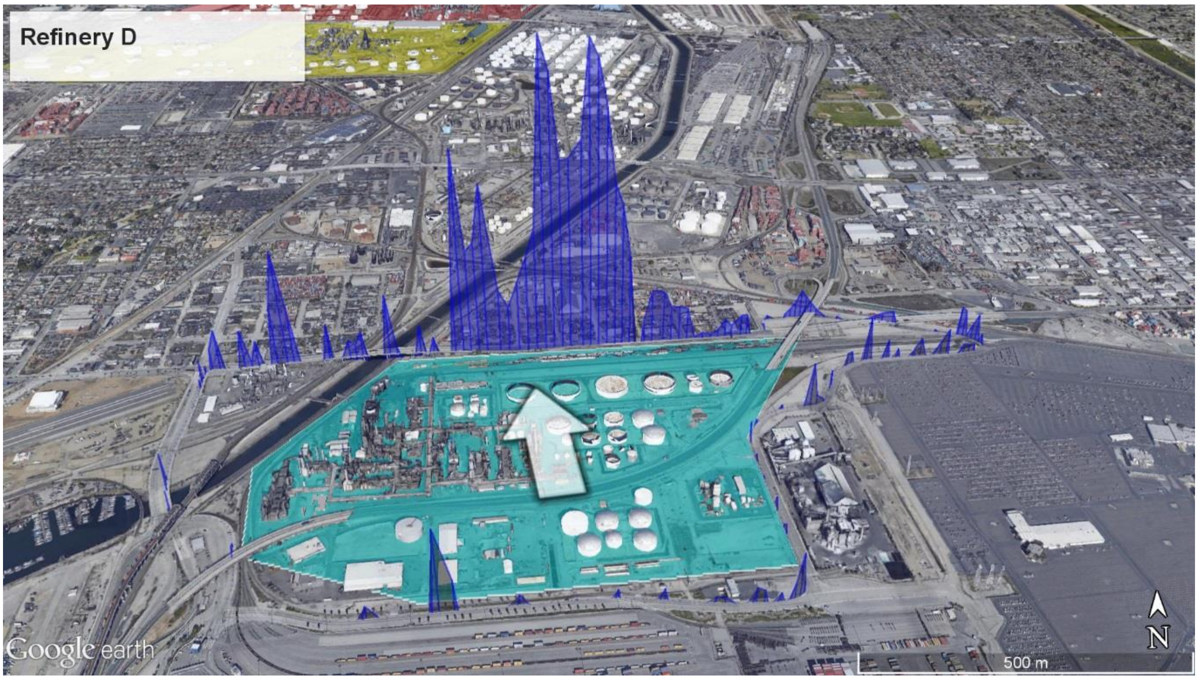

Figure 36. Example of a SOF ‘box’ measurement of Refinery D (cyan area) 19 September 2015, 13:08-13:20. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 80 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed during was 2.5 m/s. Emissions on the upwind side are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 185 kg/h from Refinery D.

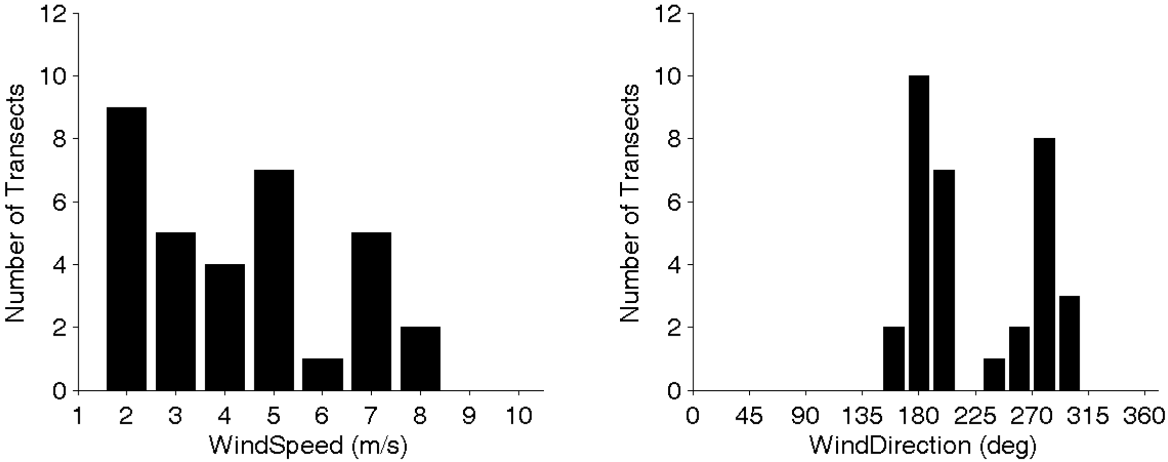

Figure 37. Wind histograms at Refinery D of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

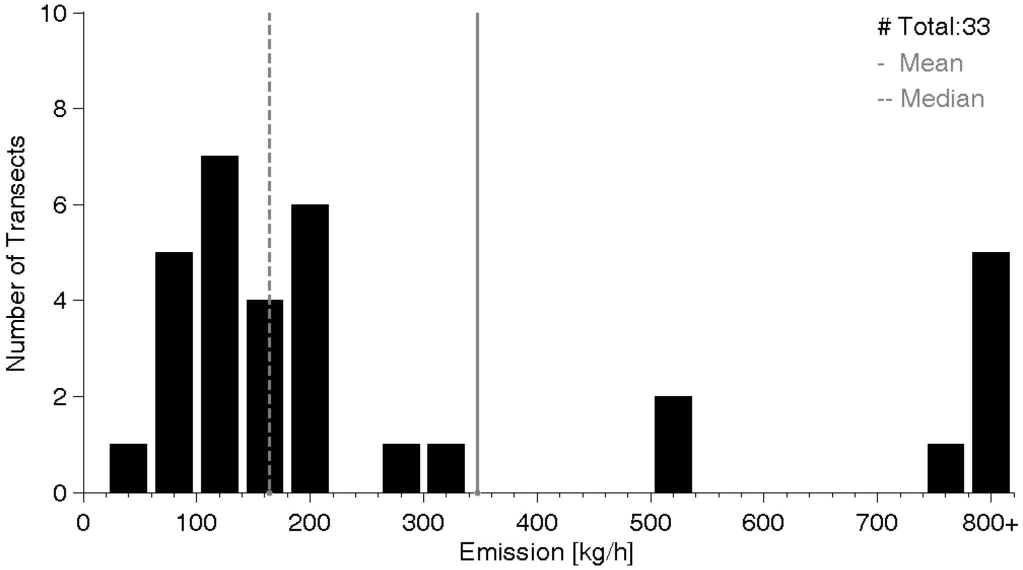

Figure 38. Histogram of all SOF measurements at Refinery D during the SCAQMD survey 2015. The last bin, denoted '+', contains all data points above 800 kg/h. The median and average values are indicated as dashed and solid gray lines.

4.4.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured for four measurement days in September during the campaign, example of a measurement is shown in Figure 39. Summaries and histograms of SkyDOAS emission measurements are presented in Table 22, Table 23, Figure 40 and Figure 41. Emissions averaged 43 and 18 kg/h and medians were 34 and 17 kg/h for NO_2 and SO_2 respectively.

Table 22. Summary of NO_2 measurements at Refinery D. *Single measurement.

Day [yymmdd]	**Timespan** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150902 *	160645 -160817	1	52.0	4.0	229
150906 *	100048 -100200	1	11.4	2.2	322
150908	132935 -152837	6	42.4±25.9	4.0-6.6	290-324
150919	114002 -142810	12	44.4±23.2	3.7-5.6	156-201
Average±SD	**-**	**(total 20)**	**43±24 (55%)**	**-**	**-**
Median	**-**	**(total 20)**	**34**	**-**	**-**

Table 23. Summary of SO_2 measurements at Refinery D . *Single measurement.

Day [yymmdd]	Timespan [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150902*	160645 -160817	1	19.4	4.0	229
150906*	100048 -100205	1	13.6	2.2	322
150908	132935 -152823	6	26.8±8.3	4.0-6.6	289-322
150919	114057 -142758	12	14.0±5.6	3.5-5.7	166-204
Average±SD	**-**	**(total 20)**	**18±6.5 (36%)**	**-**	**-**
Median	**-**	**(total 20)**	**17**	**-**	**-**

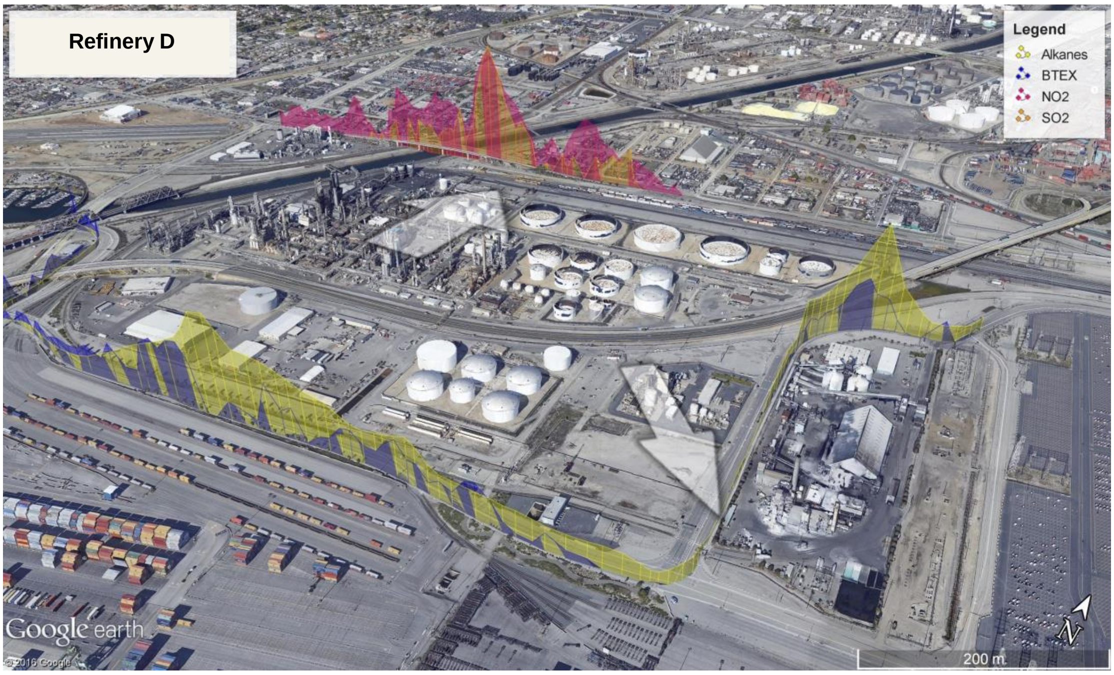

Figure 39. Transects of plumes originating from Refinery D: NO_2 (pink), SO_2 (brown) in south wind and BTEX (blue) and alkane (yellow) in north-westerly winds. NO_2 and SO_2 show column thickness and are both on the same scale (max SO_2 = 10.1 mg/m^2, flux SO_2 = 18.3 kg/h, max NO_2 = 9.8 mg/m^2, flux NO_2 = 39.3 kg/h), alkanes and BTEX show concentrations and are scaled independently for visibility (max BTEX =0.02 mg/m^3, max alkanes = 0.29 mg/m^3). Data from September 19, 12:42 PM and 8:32 PM.

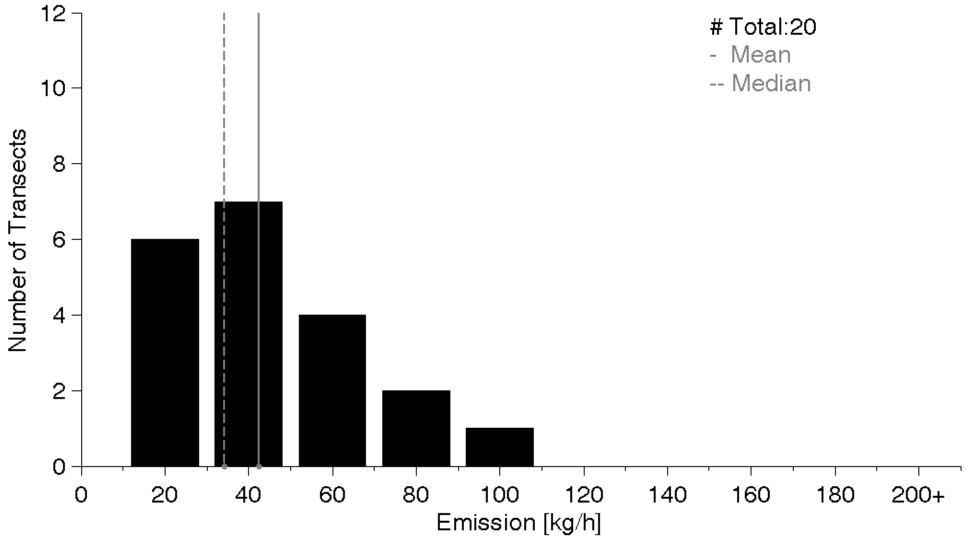

Figure 40. Histogram of all SkyDOAS NO_2 measurements at Refinery D during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

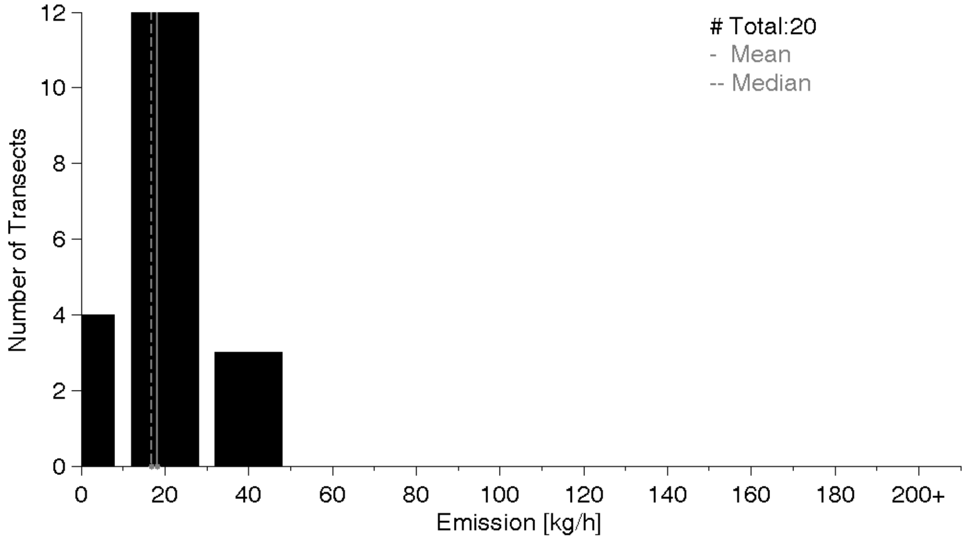

Figure 41. Histogram of all SkyDOAS SO_2 measurements at Refinery D during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.4.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery D were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. A measurement example is shown in Figure 39. To determine the source of the plume, wind directions from the LIDAR positioned at L1 or the SCAQMD-HDSN wind station were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured on different public roads surrounding the facility, depending on wind direction. The measurements are shown in Table 24.

The average fraction of BTEX to alkanes was 0.099 or 9.9%. The average flux of BTEX can be calculated by multiplying this figure with the total alkane flux as measured by the SOF-technique.

The average fraction of benzene to alkanes was 1.0% and the benzene flux can be calculated in the same way as above.

Table 24. Summary of MWDOAS BTEX measurements at Refinery D. *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	200817-201303	6.3	0.81	3.4	309
150919	205012-205749	16.2	0.93	1.8	330
150919	203234-204133	5.1	1.3	3	331
150919	214233-215112	4.1	0.33	1.2	320
151104	170956-171120	20.7	2.5	2.2	266
151104	171422-171457	11.9	0.7	2.6	273
151104	171504-171546	4.7	0.46	3.8	295
Average±SD		**9.9±6.5**	**1.0±0.7**		

4.4.4 Methane

The average fraction of methane to total non-methane alkanes in the plume from Refinery D was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume were compared to the average concentration of correlating alkanes measured simultaneously. Wind information from ASOS_KLGB was used, though only wind direction, not accurate wind speed matters for these measurements. Measurements were made during daytime and are shown in Table 25. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux measured by SOF, gives an estimate of the methane flux from the refinery. The average methane-to-alkane fraction for Refinery D was 0.48.

Table 25. Summary of MeFTIR methane measurements at Refinery D. *Methane/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction*** **[%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150919	115502 -234019	10	46	0.5-4.5	41-345
151101	102640 -121744	3	55	0.8-3.9	141-190
Average±SD	**-**	**(total 13)**	**48±20**	**-**	**-**

4.5 Refinery E

Refinery E (crude oil capacity: 269 kBPD, (California Energy Commission 2016)) is located at the Pacific coast, around 20 kilometers northwest of Refinery A (Figure 10). This refinery is totally isolated from the other refineries in this study. There are however, other significant background plumes from the oil wells and power plants along the coast line that must be compensated for in the flux calculations. This is done by encircling (‘boxing’) the facility when possible (see example in Figure 42). No prevailing night-time VOC-rich air masses during AM were present in this coastal location (as compared to the other refineries in this survey).

Wind information for the flux calculations comes from the wind LIDAR (0-400 m average) at position L4 located around 1 km east of the refinery (see Figure 42) for the period 9-16 September. For the other days, wind information from the Los Angeles International Airport (KLAX) ASOS met station, 3 km north of the refinery, was used (scaled to match 0-400 m LIDAR). See section 3.4 for additional wind analysis. Typical wind directions and velocities during the measurements are 4-7 m/s and 270°N, see Figure 43. Winds were generally steady at this site due the sea breeze.

4.5.1 Alkanes (non-methane)

Alkane emissions from Refinery E were measured with SOF during seven days in the period September 9 to November 6, see Table 26. The daily means varied from 185 kg/h (13 September) to over 700 kg/h (11 September). The increased emissions 11 September points toward the tank park in the northwest corner. The grand total average and standard deviation of all the 35 quality assured transects amounts to 280±223 kg/h and the median 244 kg/h. Histograms of all transects (Figure 44) show a peak at around 240 kg/h and one extreme outlier (from 11 September). Most transects show a broad column peak downwind the core of the facility, see Figure 42.

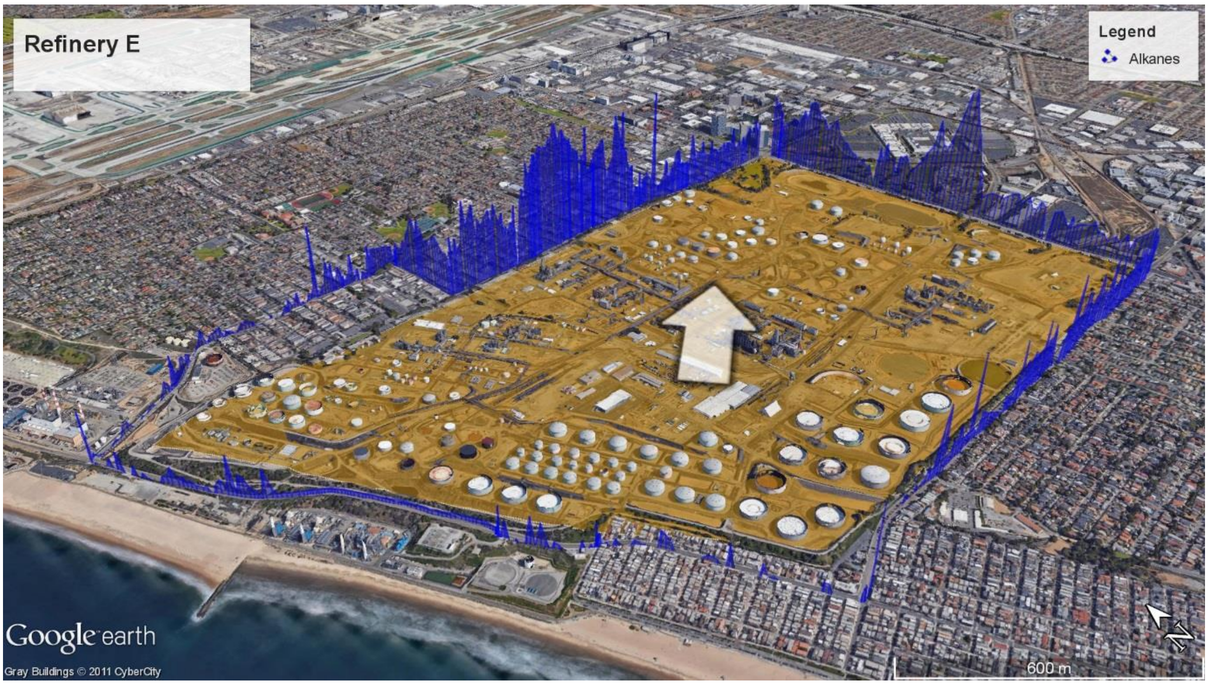

Figure 42. Example of a SOF 'box' measurement of Refinery E (orange area) 6 November 2015, 10:47-11:22. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 55 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed during this particular measurement was 1.8 m/s. Emissions on the upwind side are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 229 kg/h from Refinery E.

Table 26. Summary of SOF alkane measurements at Refinery E. *Single measurement. †Extremely deviating results due to (likely) tank park event.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150909	120735 -152659	5	242.2±83.3	4.6-6.7	266-279
150911†	110544 -133021	3	701.9±718.8	2.3-5.3	240-252
150913	112120 -144848	4	185.0±62.3	1.9-6.4	239-261
150916	145339 -160447	2	206.1±96.9	4.9-5.3	253-254
150920	105011 -143901	7	302.7±75.6	4.2-6.0	265-270
150927	120435 -152615	9	218.9±44.8	3.4-4.9	257-270
151106	104724 -140220	5	249.1±41.5	1.8-4.2	235-255
Average±SD	**-**	**(total 35)**	**280±223 (80%)**	**-**	**-**
Median	**-**	**(total 35)**	**244**	**-**	**-**

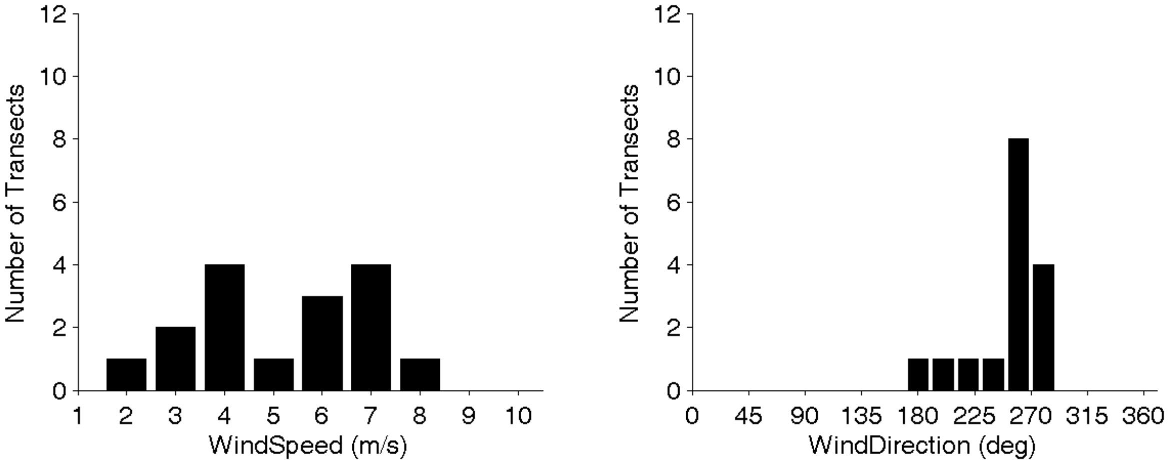

Figure 43. Wind histograms at Refinery E of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

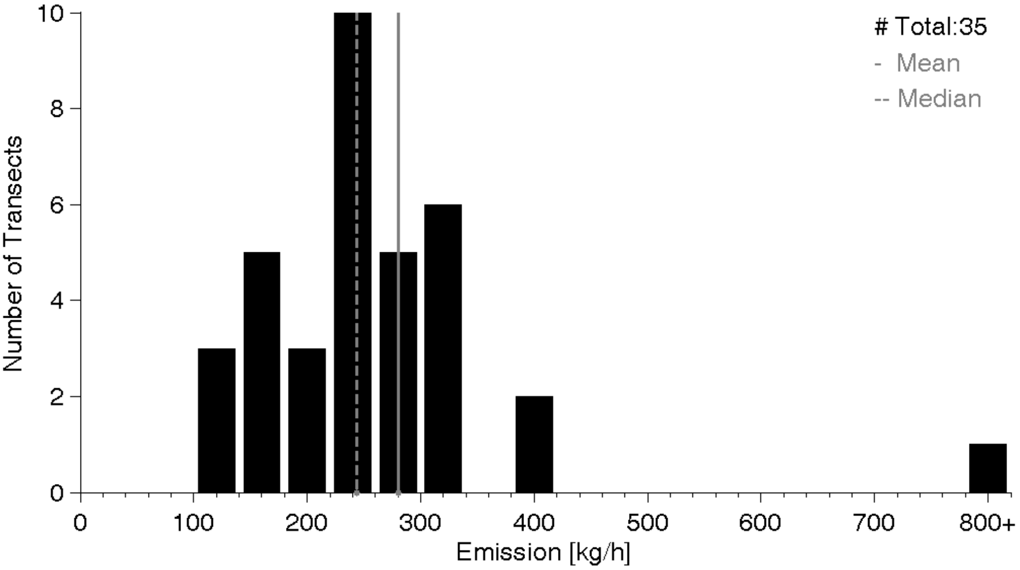

Figure 44. Histogram of all SOF measurements at Refinery E during the SCAQMD survey 2015. The last bin, denoted '+', contains all data points above 800 kg/h. The median and average values are indicated as dashed and solid gray lines.

4.5.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured during 7 measurement days in September and November during the campaign, examples of such measurements can be seen in Figure 45. As these plumes are from combustion sources and presumably stack releases, the plumes are expected to be at a higher altitude than the VOC plume when measuring near the facility, as in nearly all the measurements. Summaries of SkyDOAS emission measurements are presented in Figure 46, Figure 47, Table 27 and Table 28. Emissions were determined using LIDAR-wind, measured at position L4 or scaled KLAX ASOS met station. Typically, baselines were corrected for background (vehicle and other sources for NO_2) thus setting inflow to zero. Emissions averaged 70 and 52 kg/h and medians were 63 and 53 kg/h for NO_2 and SO_2 respectively.

Table 27. Summary of NO_2 measurements at Refinery E. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150909	114049 -145759	5	99.1±19.9	4.6-5.0	260-268
150911	111924 -132450	2	67.2±47.0	3.6-5.0	259-270
150913	112658 -144342	4	60.4±13.9	4.0-5.9	245-258
150916	145850 -163249	3	45.5±16.2	3.7-4.5	249-265
150920	110103 -114007	2	101.3±29.2	4.4-4.8	263-268
150927	140555 -144335	2	44.3±6.3	4.2-4.9	254-264
151106 *	123305 -124620	1	35.9	2.9	251
Average±SD	**-**	**(total 19)**	**70±23 (33%)**	**-**	**-**
Median	**-**	**(total 19)**	**63**	**-**	**-**

Table 28. Summary of SO_2 measurements at Refinery E. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150909	114700 -152537	6	40.5±20.4	4.0-5.2	258-272
150910 *	154026 -155223	1	42.1	4.4	266
150911	103551 -132450	4	49.3±25.7	3.5-5.0	252-270
150913	091458 -144342	7	47.4±11.7	2.3-5.9	242-258
150916	145850 -163249	3	55.6±9.8	3.8-4.7	249-268
150920	105910 -113707	2	76.4±27.7	4.5-4.9	261-271
150927	140555 -151747	4	61.7±9.4	4.2-4.9	254-264
151106	114611 -124623	2	70.7±26.6	2.5-2.8	250-252
Average±SD	**-**	**(total 29)**	**52±19 (35%)**	**-**	**-**
Median	**-**	**(total 29)**	**53**	**-**	**-**

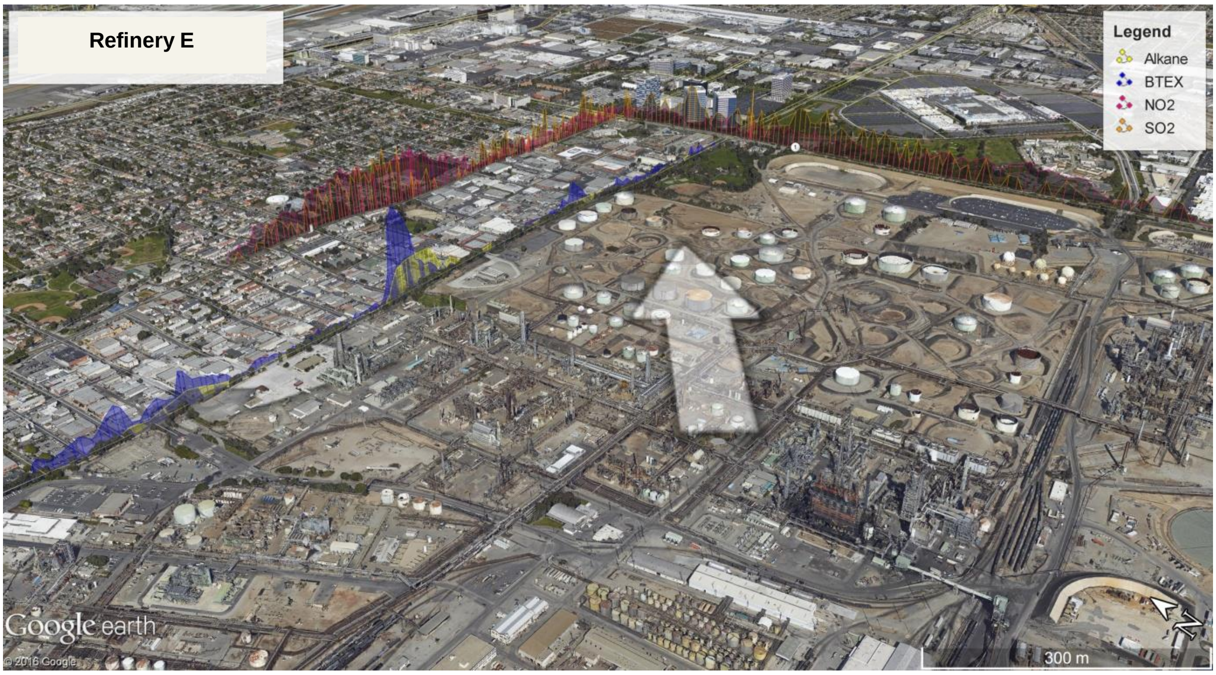

Figure 45. Transects of plumes originating from Refinery E: NO_2 (pink), SO_2 (brown), BTEX (blue) and alkane (yellow). NO_2 and SO_2 show column thickness and are both on the same scale (max NO_2 = 5.9 mg/m^2, flux NO_2 = 42.5 kg/h, max SO_2 = 6.4 mg/m^2, flux SO_2 = 48.9 kg/h), alkanes and BTEX show concentrations and are scaled independently for visibility (max BTEX = 0.04 mg/m^3, max alkanes = 0.13 mg/m^3). Example transects from September 16, 4:23 PM and 9:07 PM.

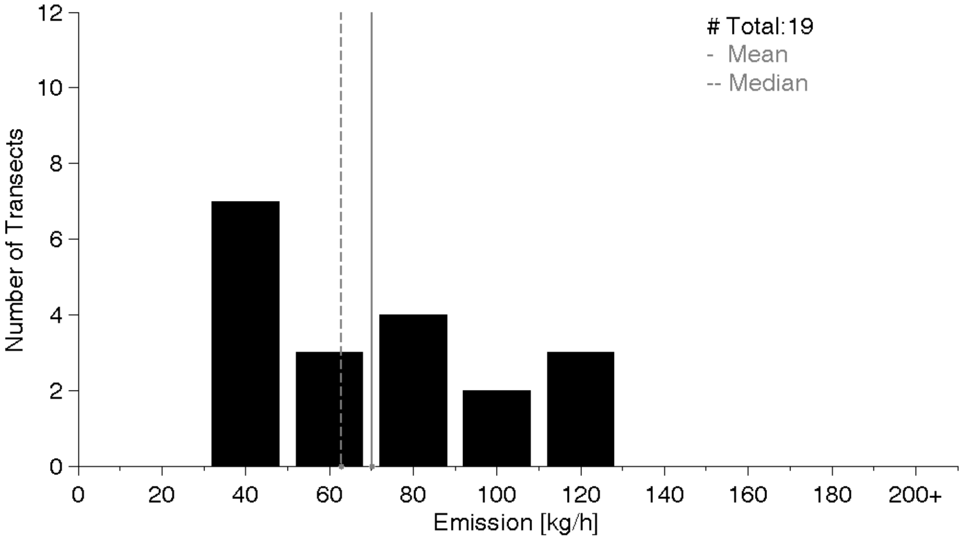

Figure 46. Histogram of all SkyDOAS NO_2 measurements at Refinery E during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

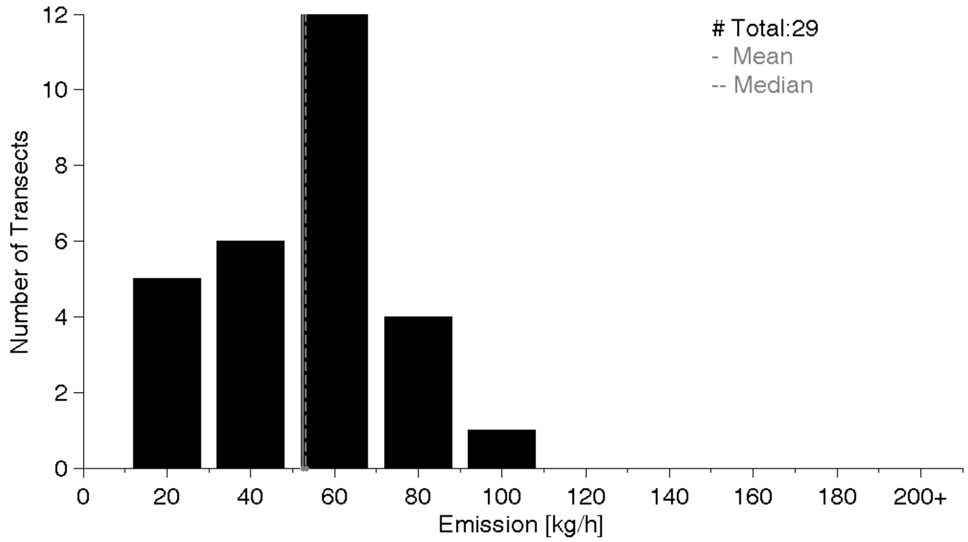

Figure 47. Histogram of all SkyDOAS SO_2 measurements at Refinery E during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.5.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery E were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX level measurements from MWDOAS and alkane measurements from MeFTIR. Figure 45 shows an example of a measurement. To determine the source of the plume, wind directions from the LIDAR positioned at L4 or the ASOS-KLAX wind station were used (wind speed is irrelevant for these measurements). The total BTEX ratio was measured north of the facility. The measurements are shown in Table 29.

The average mass fraction of BTEX to alkanes was 0.13 or 13.0%. The average flux of BTEX can be calculated by multiplying this figure with the total alkane flux as measured by the SOF-technique. The average mass fraction of benzene to alkanes was 1.1% and the benzene flux can be calculated in the same way as above.

Table 29. Summary of MWDOAS BTEX measurements at Refinery E. *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150916	112732 -165808	12	0.53	0.8	353
150916	130746 -131654	13.5	0.71	1.3	330
150916	134638 -154706	2.1	1	1	331
150916	142535 -154524	20	2	2	320
150916	144942 -173531	17.2	1.4	2.1	317
Average±SD	**-**	**13±6.8**	**1.1±0.6**	**-**	**-**

4.5.4 Methane

The average fraction of methane to total non-methane alkanes in the plume from Refinery E was measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of correlating alkanes measured simultaneously.

Wind information from ASOS_KLAX was used, only wind direction, not wind speed matters for these measurements. Measurements were made during daytime and late evening and are shown in Table 30. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux measured by SOF, gives an estimate of the methane flux from the refinery. The average methane-to-alkane fraction for Refinery E was unusually high on the night of September 19 and might have been affected by some temporary release source. Therefore the measurements from September 19 will not be used in the result. When measured on September 27 the fraction was no longer extreme and the average from that day, 0.85 will represent the resulting fraction for Refinery E.

Table 30. Summary of MeFTIR Methane measurements at Refinery E. *Methane/alkane mass fraction. †Extremely deviating results likely due to other non-identified temporal source.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150916†	170318 -224508	5	180	4.0-5.1	230-268
150927	112103 -151358	5	85	4.0-4.0	230-230
Average±SD	**-**	**(total 10)**	**85±7**	**-**	**-**

4.6 Refinery F

Refinery F (crude oil capacity 150 kBPD, (California Energy Commission 2016)) is located around 10 kilometers northwest of Refinery A, see Figure 10. Emission plumes from other refineries in this study or other large emitters do not interfere directly with plumes from Refinery F with the prevailing wind directions. But there are some minor oil wells and storage tanks west of the refinery which must be compensated for in the flux calculations by ‘boxing’ the facility during westerly winds (see example in Figure 48).

Wind information for the flux calculations comes from the wind LIDAR (0-400 m average) at position L3 located 300 m east of the refinery (see Figure 48) 17 September. For the other days, wind information from the L1 LIDAR site was used. See section 3.4 for additional wind analysis. Typical wind directions and velocities during the measurements are around 4 m/s and around 180 or 270°N, see Figure 49.

4.6.1 Alkanes (non-methane)

Alkane emissions from Refinery F were measured with SOF during four days: 9, 13 and 17 September and 7 November, see Table 31. The daily means varied from 117 kg/h (13 September) to 219 kg/h (17 September). The grand total average and standard deviation of all the 16 quality assured transects amounts to 169±105 kg/h and the median 140 kg/h. Histograms of all transects (Figure 50) show a peak at around 120 kg/h and one extreme outlier (from 17 September). Transects show a column peak downwind the southeast tank park and the process area, see Figure 48.

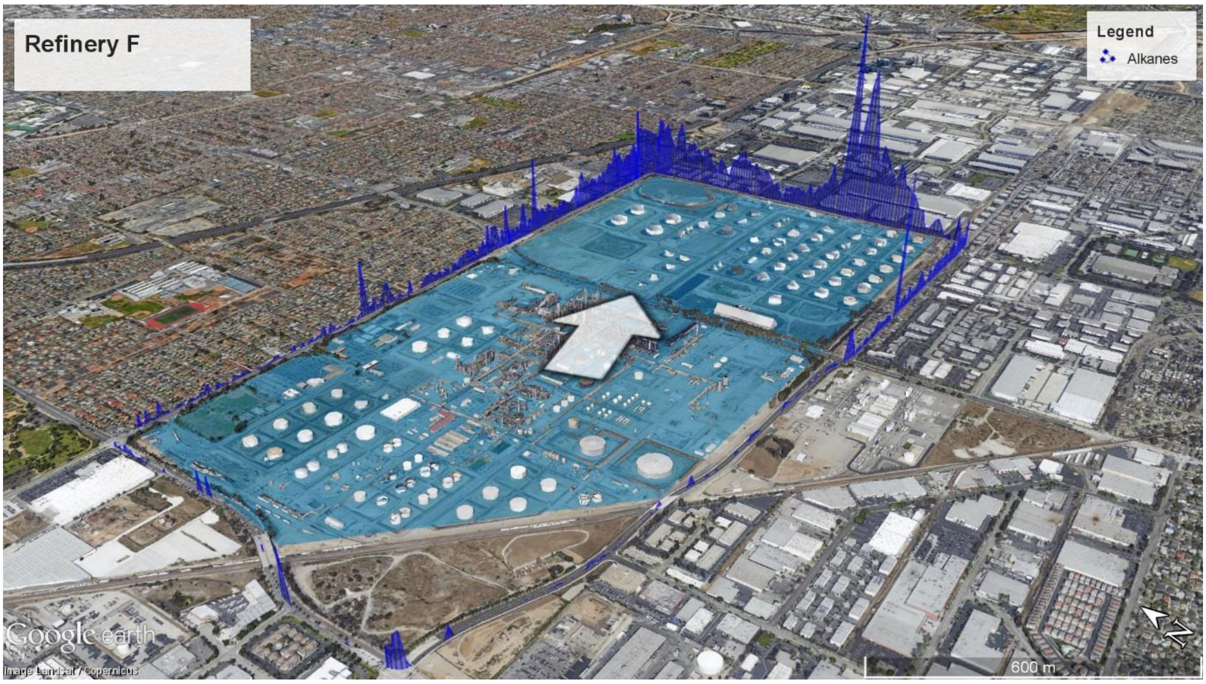

Figure 48. Example of a SOF ‘box’ measurement of the Refinery F (light blue area) 17 September 2015, 12:39-13:04. Alkane column is shown as a blue curve with apparent height proportional to gas column (10 m equivalent to 1 mg/m^2, max 83 mg/m^2). Wind direction during the measurement is indicated by the white arrow. Average wind speed during was 3.1 m/s. Emissions on the upwind side are subtracted from the downwind side in order to get emissions from within the box. This particular transect measured 230 kg/h from Refinery F.

Table 31. Summary of SOF alkane measurements for Refinery F. *Single measurement.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150909*	164857 -165755	1	157.7	3.6	226
150913	153509 -170800	4	117.1±18.0	6.2-7.1	270-277
150917	120844 -161940	7	219.4±152.4	3.1-7.6	251-261
151107	133217 -145646	4	135.3±6.5	2.5-4.5	189-277
Average±SD	**-**	**(total 16)**	**169±105 (62%)**	**-**	**-**
Median	**-**	**(total 16)**	**140**	**-**	**-**

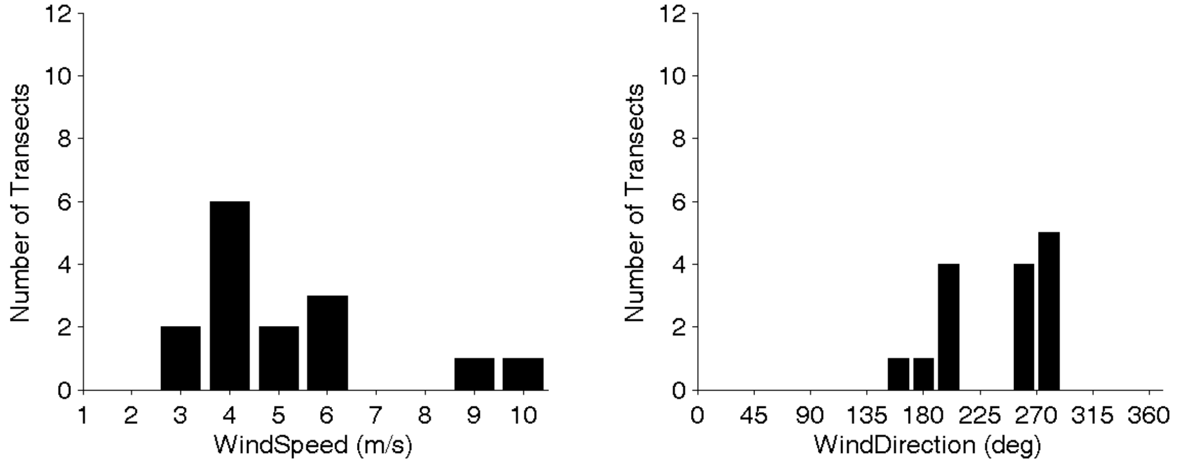

Figure 49. Wind histograms at Refinery F of wind speed (left) and wind direction (right) for the SOF measurements during the SCAQMD survey 2015.

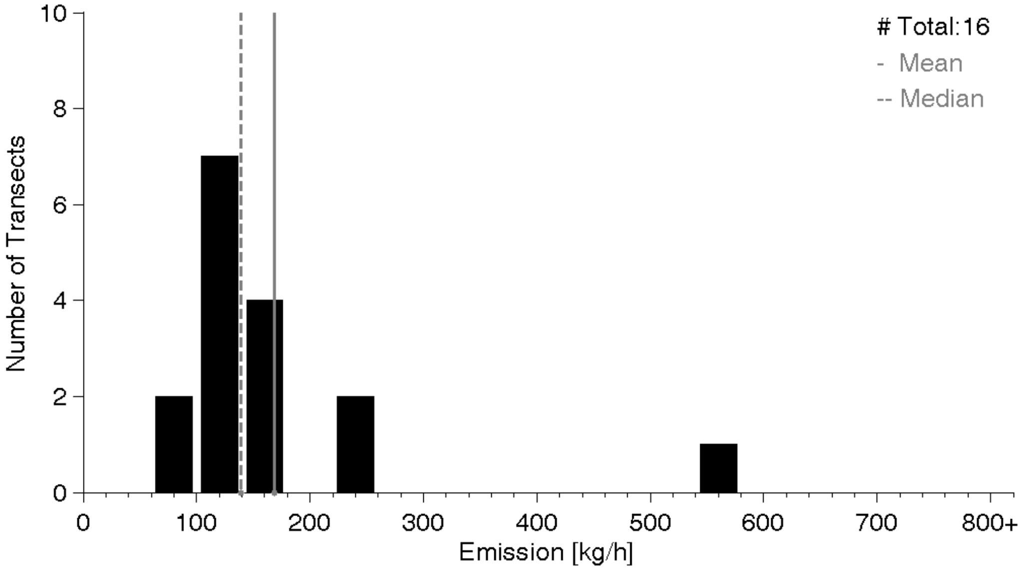

Figure 50. Histogram of all SOF measurements at Refinery F during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

4.6.2 SO_2 and NO_2

SO_2 and NO_2 emissions from the facilities were measured for 2 measurement days in September. Summaries of SkyDOAS emission measurements are presented in Table 32 and Table 33. An example of a measurement is shown in Figure 51. For Refinery F the number of measurements is very low and the result may therefore be less reliable as a representation of typical emissions. Emissions averaged 23 and 40 kg/h and medians were 18 and 37 kg/h for NO_2 and SO_2 respectively.

Table 32. Summary of NO_2 measurements at Refinery F. *Single measurement.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150913	153603 -160753	2	14.8±4.1	6.1-6.1	258-273
150917	132227 -132826	1	38.2	5.0	252
Average±SD	**-**	**(total 3)**	**23±4.1 (18%)**	**-**	**-**
Median	**-**	**(total 3)**	**18**	**-**	**-**

Table 33. Summary of SO_2 measurements at Refinery F. *Single measurement.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150913*	153535 -154138	1	67.2	6.2	260
150917	121200 -132803	2	27.0±14.2	3.3-4.9	248-252
Average±SD	**-**	**(total 3)**	**40±14 (35%)**	**-**	**-**
Median	**-**	**(total 3)**	**37**	**-**	**-**

Figure 51. Transects of plumes originating from Refinery F: NO_2 (pink), SO_2 (brown), BTEX (blue) and alkane (yellow). NO_2 and SO_2 show column thickness and are both on the same scale (max NO_2 = 5.0 mg/m^2, flux NO_2 = 38.2 kg/h, max SO_2 = 4.4 mg/m^2, flux SO_2 = 17 kg/h), alkanes and BTEX show concentrations and are scaled independently for visibility (max BTEX = 0.01 mg/m^3, max alkanes = 0.55 mg/m^3). Example transects from September 17, 1:22 PM and 11:36 PM.

4.6.3 BTEX

The BTEX mass fraction to alkane in the plumes emitted from Refinery F were measured either in the late evening or early morning when the plumes were closer to ground. The mass fraction is acquired by combining BTEX ground level measurements from MWDOAS and alkane measurements from MeFTIR. To determine the source of the plume, wind directions from the LIDAR positioned at L3 or the KLAX-ASOS wind station were used (wind speed is irrelevant for these measurements). BTEX mass ratios were measured along one road picking up the plume from the tank park, and along another cutting through the facility and enabling a measurement of the process plume in westerly wind. The measurements are shown in Table 34 and Table 35.

The average mass fraction of BTEX to alkanes was 0.137 or 13.7% and 0.017 or 1.7% for the process and the tank park respectively. The average flux of BTEX can be calculated by multiplying this figure with the alkane flux as measured from these two sources by the SOF-technique. The average mass fraction of benzene to alkanes was 0.9% for the process plume and 0.3% for the tank park plume. Benzene flux can be calculated in the same way as above. Both the total BTEX flux and the benzene flux for Refinery F can be found in Table 5.

Table 34. Summary of MWDOAS BTEX measurements at Refinery F. Tank park plume *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150917	214724-215203	1.9	0.44	1.8	270
150917	232708-232841	1.4	0.19	2.8	251
Average±SD	**-**	**1.7±0.4**	**0.3±0.2**	**-**	**-**

Table 35. Summary of MWDOAS BTEX measurements at Refinery F. Process plume *BTEX/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**BTEX Fraction*** [%]	**Benzene Fraction*** [%]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150917	221740-221813	12.8	0.87	1.7	244
150917	233614-233641	13.3	1	2.6	252
150917	231920-232007	15.1	0.71	4	45
Average±SD		**13.7±1.2**	**0.9±0.3**		

4.6.4 Methane

The average fraction of methane to total non-methane alkanes in the plume from Refinery F were measured at ground level using MeFTIR. The plume was sampled along roads surrounding the facility and the average concentration across the plume was compared to the average concentration of alkanes measured simultaneously. Applying the measured fence-line ground level methane-to-alkane mass fraction to the median alkane flux measured by SOF, gives an estimate of the methane flux from the refinery. Wind information from LIDAR in position L3 was used, only wind direction, not wind speed matters for these measurements. Only three measurements were made on one evening September 17 as shown in Table 36. The average methane-to-alkane fraction for the Refinery F was 0.41.

Table 36. Summary of MeFTIR methane measurements at Refinery F. *Methane/alkane mass fraction.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Methane fraction*** **[%]**	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150917	211536 -233000	3	41	1.9-3.3	251-274
Average±SD	**-**	**(total 3)**	**41±6**	**-**	**-**

5 Results – On-site Measurements in a Refinery Tank Farm

On site measurements in the tank farm of a major refinery in the South Coast Air Basin were carried out for 8 days between 28 September and 7 October 2015 using the mobile optical methods described in the previous sections (i.e. SOF, MWDOAS and MeFTIR). The objective of this activity was to demonstrate the capability of these real time optical techniques to identify and quantify gas leakages inside a refinery and to compare the results with other optical methods used during the same time frame. These include a DIAL (Differential Absorption LIDAR; a laser-based method) operated by NPL (National Physics Laboratory, UK) at different locations within the tank farm, and a stationary long path FTIR system that was operated by Atmosfir in the west part of the tank farm. Here the FTIR coupled to a telescope was automatically pointed towards multiple reflectors put at strategic positions in different parts of the tank farm and at different heights to estimate ground source emissions using the EPA's OTM-10 method (see separate report by Atmosfir). These various methods were used independently but on several occasions side by side measurements were carried out for validation purposes (see report by Pikelnaya et. al. (2016)).

In this study we carried out mobile optical measurements throughout the tank farm on available roads in order to localize potential hot-spot emission areas and quantify emissions from selected tanks and tank groups. The emphasis was to investigate emissions from tank groups and tanks rather than the whole tank farm emissions, although this was also done.

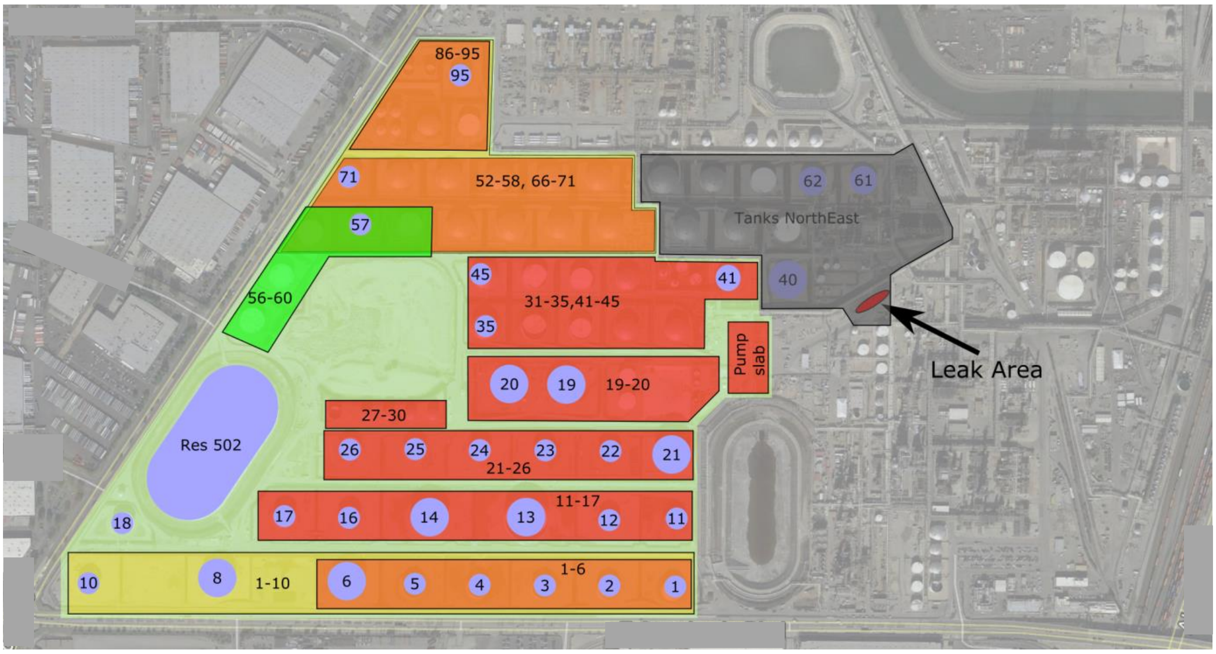

Figure 52. Overview of the tank farm part of the refinery where on site measurements with SOF + MeFTIR + MWDOAS were conducted for about one week in September/October 2015. Tanks, tank groups and specific areas have been given numbers and names respectively for reference to measurement results. North is upwards. Groups of quantified tanks are denoted by coloured rectangles, and individual tanks that have been quantified are indicated by blue shapes/circles. The surveyed part (large light green area) is restricted in the west and south by the site fence-line, and in the east and north by roads going east of tank 1-11-21-Pump slab and then between the “Tanks NorthEast” and tank groups “52-58+66-71” and to the northeast corner of group “86-95”.

This limited study included alkane column measurements and ground concentration measurements of alkanes, methane and aromatic VOCs. A wind meter was positioned on an elevated plateau on a big open field inside the tank farm, thus sampling wind at a height comparable to a typical tank roof height.

The real-time capability and sensitivity of the instruments (2 s sampling time resolution for SOF and MWDOAS, 10 s for MeFTIR) was essential to this work as shown in Figure 53. By observing the geo-tagged emissions in real time, any occurring hot-spots can immediately be investigated further to for example conclude if the sources are intermittent or continuous. By driving on the upwind and downwind side of the tanks and unit areas, any incoming emission fluxes or interfering sources can be identified and accounted for.

Figure 53. A picture from the measurement van showing real time data while passing through a source. The column and concentration data is shown together with the measurements position on a map for fast hotspot identification and interpretation.

Validation between SOF (FluxSense) and DIAL (NPL) was done on tank 16 (crude), tank 13 (crude) and on reservoir 502 (vacuum gas oil).

5.1 Tank Park

Table 37 summarizes the plume transects including the whole tank farm in one run. The median emission of all these complete tank farm emission measurements was 145 kg/h based on 9 measurements distributed over four days. This corresponds to approximately half the total measured refinery emission (see section 4.1.1). The overall tank farm single observations ranged from 104-194 kg/h for the daily averages (4 different days).

Figure 54 shows an example of SOF measurements around the tank farm at the selected refinery. In this transect the highest column (165 mg/m^2) of VOC was measured at the elliptically shaped tank (here referred as tank reservoir no 502) in the lower left corner. This is explained by the pass being close to the source before the release was dispersed by convection and turbulence. It’s evident that reservoir 502 is a substantial source of alkanes. However, when following the measurement transect along the perimeter of the tank farm several extended plume sections are observed, and these add up to emission being several times that of reservoir 502 alone. The contribution from different parts of the tank farm is discussed in the next section.

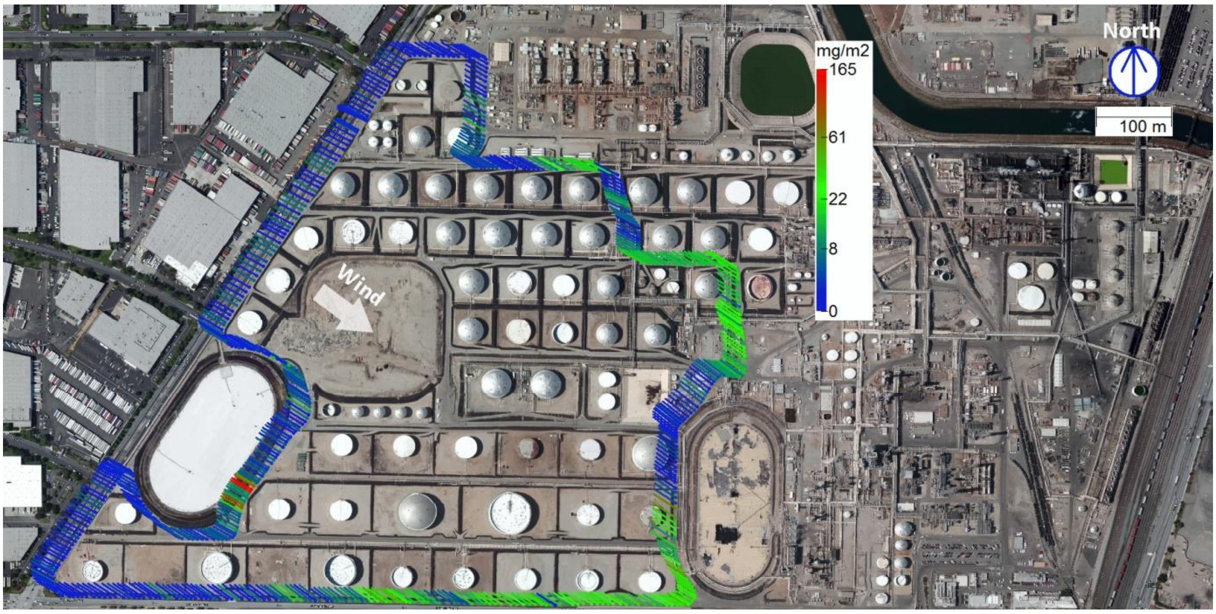

Figure 54. SOF measurement of alkanes around the major body of the tank farm on September 29, 2015 between 2:51 PM and 3:15 PM. Each measured spectrum is represented by a single line, with color indicating the evaluated integrated vertical alkane column. The line orientation indicates the direction from which the wind is blowing. North is upwards and in this case the wind blew from northwest.

Table 37. Summary of SOF alkane measurements for the refinery tank park considered in this study.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150928	143009 -153658	2	187.6±89.2	5.2-5.5	291-299
150929	145455 -150723	2	193.9±33.2	4.7-6.3	302-302
151002	143351 -154352	4	136.5±33.7	4.4-5.5	277-294
151006	140304 -150009	2	104.4±24.7	3.7-5.4	280-285
Average±SD	**-**	**(total 9)**	**153±53 (35%)**	**-**	**-**
Median	**-**	**(total 9)**	**145**	**-**	**-**

5.2 Individual Tanks and Tank groups

Based on 233 measurement transects of different tanks and tank groups, specific tank emissions have been summarized in Table 38. Adding up all the measured tank farm objects give on average 191 kg/h of alkanes. This is in line with the estimate from the SOF measurements for the complete tank farm in one run (153 kg/h, Table 37). Note that these numbers represent two different approaches with varying coverage in time and space. The statistic basis is quite variable among the tank farm objects, ranging from Reservoir 502 having 80 measurements distributed over 8 days to a few objects having only a single observation.

Table 38. Summary of onsite measurements (SOF) of tanks and tank groups. $^{a)}$ For the BTEX emission the average BTEX to alkane mass fraction (6.0 %) has been used for the tanks where the BTEX fraction was not quantified. $^{b)}$ For the benzene emission the average benzene to alkane mass fraction (0.59 %) has been used for the tanks where the benzene fraction was not quantified. *Items in italics and aligned to the right are either subgroups part of other items or not part of the overall Tank farm average.*

Tank_ID	**Average alkane (kg/h)**	**SD (kg/h)**	**No. meas.**	**No. days**	**BTEX to alkane mass fraction (%)**	**BTEX emission a) (kg/h)**	**Benzene to alkane mass fraction (%)**	**Benzene emission b) (kg/h)**
Tank_1	1	0.4	5	3	2	0.02	0.37	0.00
Tank_2	2.8	4.9	3	2	n.m.	0.17	n.m.	0.02
Tank_3	1.3	0.3	4	3	n.m.	0.08	n.m.	0.01
Tank_4	0.6	0.1	4	3	n.m.	0.04	n.m.	0.00
Tank_5	1.7	0.2	4	3	n.m.	0.10	n.m.	0.01
Tank_6	4.2	1.7	8	4	3.3	0.14	0.39	0.02
Tank_8	2.6	1.8	9	3	n.m.	0.16	n.m.	0.02
Tank_11	10.9	5.4	9	4	7.6	0.83	0.65	0.07
Tank_12	2.4	1.7	9	4	5.3	0.13	0.73	0.02
Tank_13	21.6	10.4	32	5	8.9	1.92	0.55	0.12
Tank_14	5.4	4.1	9	4	1.5	0.08	0.48	0.03
Tank_16_all days	*259*	*134*	*55*	*6*	*1.4*	*3.63*	*0.34*	*0.88*
Tank_16_excl. 151005	42	34	13	5	1.4	0.59	0.34	0.14
Tank_17	2.8	1	10	5	0.6	0.02	0.54	0.02
Tank_18	0.7	0.6	2	2	n.m.	0.04	n.m.	0.00
Tanks_19-20	15.8		1	1	n.m.	0.95	n.m.	0.09
Tank_21	6.3	1.4	5	2	12.3	0.77	n.m.	0.04
Tank_22	1.2	0.5	6	2	11.4	0.14	0.25	0.00
Tank_25	2.1		1	1	n.m.	0.13	n.m.	0.01
Tanks_27-30	5.3	0.2	5	4	5.6	0.30	1.5	0.08
Tanks_31-35_42-45	12.6		1	1	n.m.	0.76	n.m.	0.07
Tank_40	*4.5*	*0.1*	*2*	*1*	*n.m.*	*0.27*	*0.48*	*0.02*
Tanks_56-60	*7.6*	*0.6*	*2*	*2*	*n.m.*	*0.46*	*n.m.*	*0.04*
Tank_57	*3.0*		*1*	*1*	*5.6*	*0.17*	*0.24*	*0.01*
Tank_71	*3.7*		*1*	*1*	*5.6*	*0.21*	*0.37*	*0.01*
Tanks_52-58_66-71	13.7		1	1	9.3	1.27	0.88	0.12
Tanks_86-95	8.0	0.7	6	4	4.4	0.35	n.m.	0.05
Reservoir_502	26.1	11.4	80	8	10.7	2.79	1.1	0.29
Total all measured tanks:	**191**		**233**			**12**		**1.2**

As seen in Table 38, Tank 16 had one day (5 October, 2015) where atypical emissions were observed. Including this day would raise the overall average for Tank 16 to 259 kg/h if compared to 42 kg/h if this day is excluded. In the presented grand total average for the tank farm, this atypical event was left out for Tank 16 (42 measurements were conducted on tank 16 this day in a validation experiment with other optical techniques, whereas 13 measurements were done for the other days being included in the average). BTEX to alkane mass fractions were also measured for many of the tanks, and ranged from 1.4 to 12.3 % which is quite normal values for a tank farm containing both crude and refined petroleum product tanks. Last four columns in Table 38 specify measured BTEX fractions, inferred BTEX emissions and corresponding columns for benzene, using the SOF alkane emission and the BTEX and benzene fractions respectively. For tanks where BTEX or benzene were not measured, the average BTEX mass fraction (6.0 %) or benzene average fraction (0.59 %) has been used. Overall a BTEX emission of 12 kg/h is estimated from the tank farm, of which 1.2 kg is estimated to be benzene.

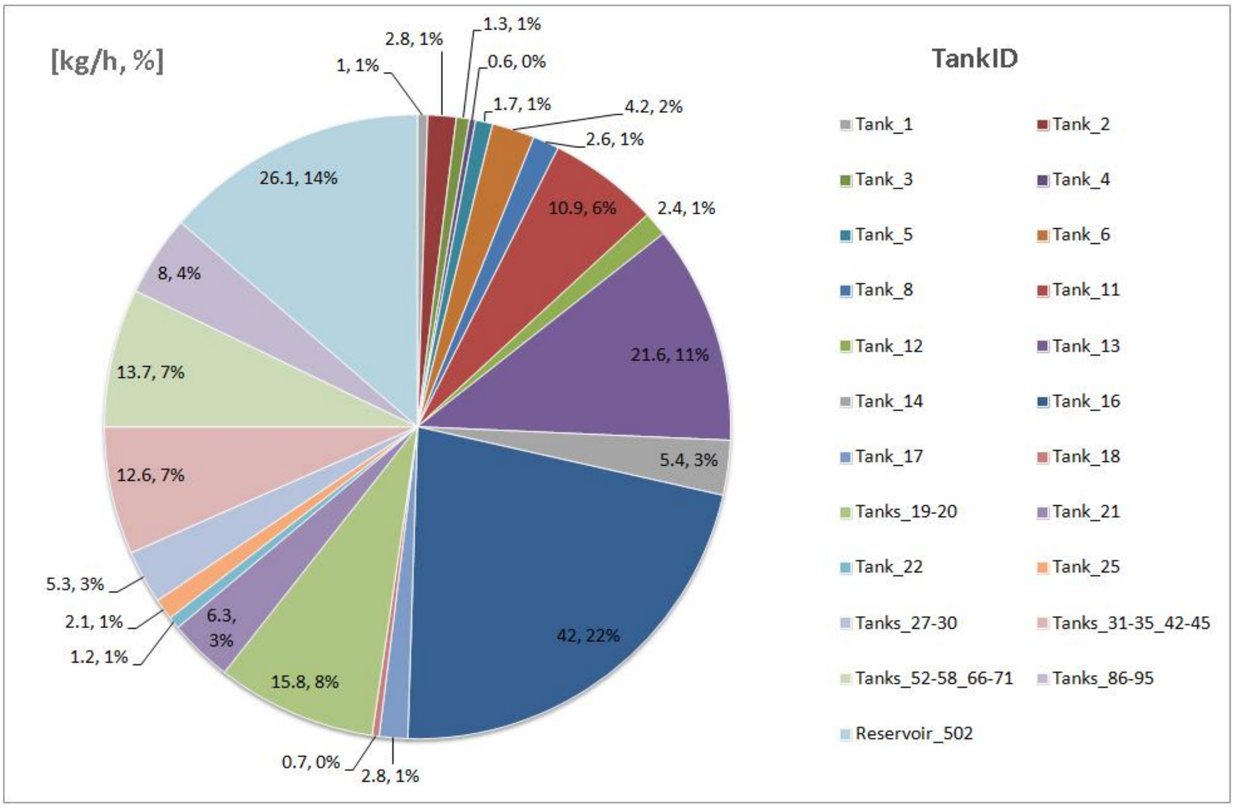

Figure 55. Summary of all measurements on the specified tanks and tank groups and their relative contribution to the total emission of 192 kg/h. The measurements on tank 16 from 5 October were omitted here due an atypical release event.

Figure 55 shows the absolute and relative contribution from all measured tanks and tank groups to the tank farm overall sum of alkanes (191 kg/h). Three tanks stand out with single contributions above 10% each, with Tank_16 being the strongest source (22%, Crude) followed by Reservoir_502 (14%, Vacuum Gas Oil (VGO)) and Tank_13 (11%, Crude). These tanks were also studied in more detail, to obtain better statistics. A validation study between the SOF and DIAL techniques were also done on these tanks with very good agreement of the results (see Pikelnaya et. al. (2016)).

The 502 source is a large covered reservoir which contain vacuum gas oil (VGO). It has two ventilations shafts, one in the north and one in the south. Specific data from tank 502 are found in Table 39 and Figure 56. Histograms of the 80 individual plume transects of this source, from 8 different days, resemble something close to a normal distribution with an average emission of 26 kg/h, very close to the median of 25 kg/h. The observed spread in day to day averages ranged from 20 to 36 kg/h. The emissions from Reservoir 502 were split up on contributions from the north and the south vent respectively, showing that the vast majority of the reservoir emissions originated from the south vent with 90% of the reservoir’s overall emission.

With a BTEX mass fraction of 11%, this was the strongest source of aromatics found in the tank farm, with an estimated emission of 2.8 kg/h BTEX (23% of the overall). Also when considering benzene, Reservoir 502 was the strongest source with 0.3 kg/h. Tank 13 and Tank 16 were found to have a BTEX emission of 1.9 kg/h and 0.6 kg/h respectively. Corresponding benzene emissions were 0.12 kg/h and 0.14 kg/h. The BTEX and benzene results for Tank 13, 16 and Reservoir 502 were based on 8, 57 and 28 observations within each category respectively.

Table 39. Summary of SOF alkane measurements reservoir no 502. *Single measurement.

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150928	140807 -155200	4	27.7±7.4	4.2-6.0	287-294
150929	140318 -151343	2	20.2±7.7	3.4-3.8	272-291
150930	133031 -150355	6	26.1±13.4	2.1-3.6	192-303
151001	100906 -152231	9	28.8±11.5	1.5-4.7	276-295
151002	141403 -143033	7	36.3±15.6	3.8-4.9	262-294
151005*	155251 -155806	1	32.3	3.8	173
151006	121009 -160214	16	20.7±8.6	2.6-6.2	256-324
151007	134310 -153441	35	25.9±11.7	3.0-5.5	264-317
Average±SD	**-**	**(total 80)**	**26.1±11.4 (44%)**	**-**	**-**
Median	**-**	**(total 80)**	**24.7**	**-**	**-**

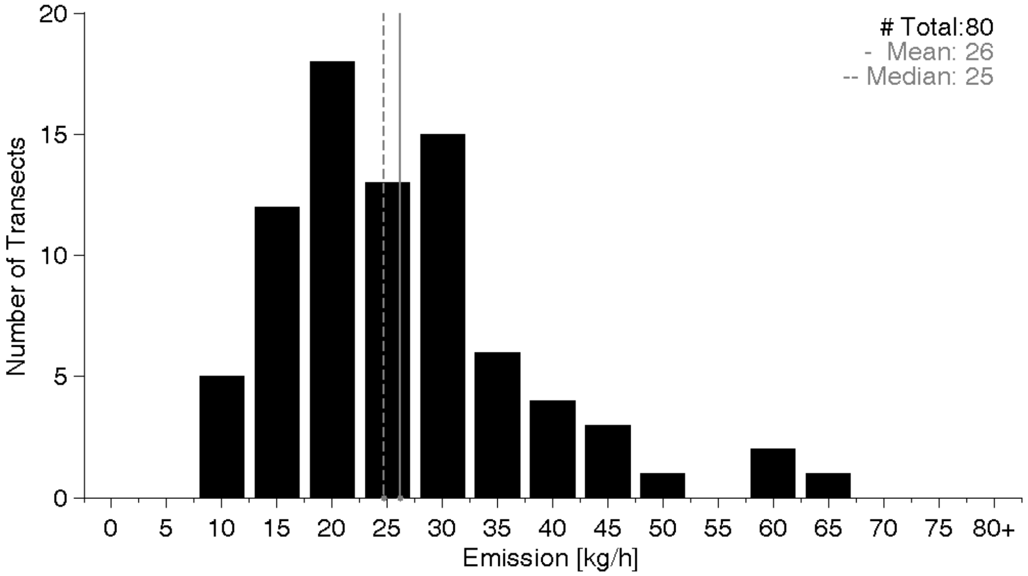

Figure 56. Histogram of all SOF measurements at reservoir 502 during the SCAQMD survey 2015. The median (24.7 kg/h) and average (26.5 kg/h) values are indicated as dashed and solid gray lines.

Figure 57 shows SOF measurements of VOCs in the crude oil part of the tank farm. Here the height of the column corresponds to the measured vertical column of alkanes (non-methane) and the arrow shows the wind direction (south-east in this case). The large columns downwind of the second tank from the left in the middle row (here referred to as tank 16) suggest the presence of a distinct leak at this tank. During the campaign, this tank showed large emissions during several days, see Table 40, and large variability range suggesting a dependence on operations. The refinery personnel and SCAQMD were notified of this finding and service personnel carried out an inspection showing that one of the valves was leaking. When the tank was filled with new product and the floating roof accordingly moved upwards, the displacement of VOC contaminated air between the internal floating roof and the external dome generated the large emissions through the malfunctioning vent gauge. The measurements illustrated in this figure were compared against DIAL measurements with very good agreement (see separate report by Pikelnaya et. al. (2016)).

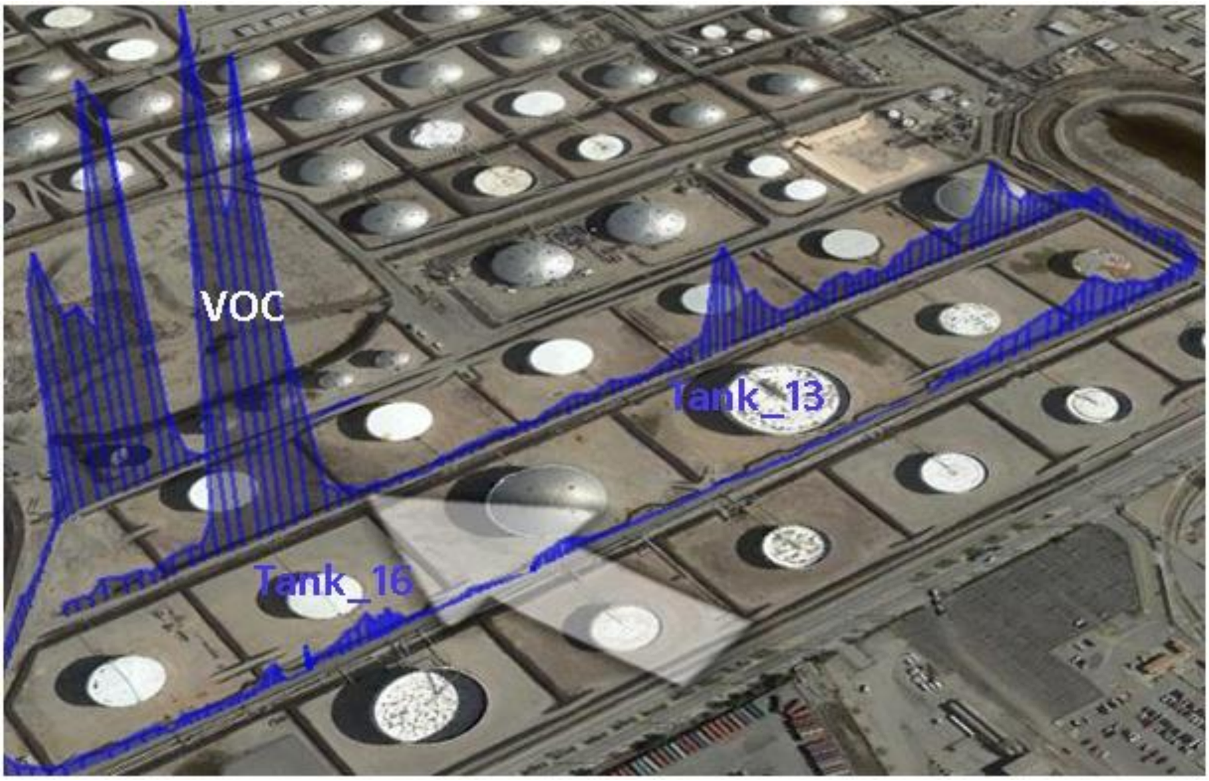

Figure 57. Measurements of VOCs with SOF in the crude oil part of the tank farm. Here the height of the blue columns corresponds to the amount of alkanes present in the column measured by SOF and the white arrow corresponds to the wind direction (south-east in this case).

Figure 57 also shows Tank_13 (two tanks right of tank 16 in the middle row) being a source of emissions – compare the clean upwind columns to the clear VOC plume downwind of tank 13 and 16 respectively. Table 40 and Table 41 include daily average emission data and the total average and median values from SOF measurements at tank 16 and tank 13 respectively.

Table 40. Summary of SOF alkane measurements for tank 16. *Single measurement.† Non-typical event with malfunctioning valve at tank roof on the 5 October 2015.

Day [yymmdd]	Time span [hhmmss-hhmmss]	No. of Transects	Emission Average±SD [kg/h]	Wind Speed Min-Max [m/s]	Wind Dir Min-Max [deg]
150928*	141036 -141127	1	28.0	4.9	294
150930*	135622 -135646	1	0.33	2.8	188
151001	133101 -141133	5	73.6±29.9	3.3-4.9	147-194
151002	123616 -133233	5	29.5±12.9	3.1-5.1	147-194
151005†	113438 -155044	42	326.6±151.4	3.1-6.2	144-204
151006*	151220 -151258	1	2.1	4.8	283
Average±SD	All days	(total 55)	259±134 (52%)	-	-
Median	All days	(total 55)	222	-	-
Average±SD	**Excluding 151005**	**(total 13)**	**42.0±33.6 (80%)**	**-**	**-**
Median	**Excluding 151005**	**(total 13)**	**41.5**	**-**	**-**

Table 41. Summary of SOF alkane measurements for tank 13. * Single measurement

Day [yymmdd]	**Time span** [hhmmss-hhmmss]	**No. of Transects**	**Emission Average±SD** [kg/h]	**Wind Speed Min-Max** [m/s]	**Wind Dir Min-Max** [deg]
150928*	141153 -141257	1	1.1	4.9	292
150930*	135449 -135542	1	12.9	12.9	194
151001	132928 -141655	5	22.9±10.5	3.4-4.9	154-190
151002	112139 -133118	11	16.1±8.5	2.1-5.1	139-194
151005	123245 -160628	14	27.5±12.0	4.0-7.7	166-205
Average±SD	**-**	**(total 32)**	**21.6±10.4 (48%)**	**-**	**-**
Median	**-**	**(total 32)**	**18.1**	**-**	**-**

Figure 58 and Figure 59 show the frequency distribution of the SOF alkane measurements at tank 13 and tank 16 respectively, for the week of on site measurements. As seen in the distributions, tank 16 emissions show a large spread, almost as two source distributions overlay with a secondary maximum and tail of observations above 250 kg/h corresponding to the atypical event with a malfunctioning valve at the tank roof during filling on October 5 as discussed previously. Tank 13 in Figure 58 showed a more typical tank emission distribution.

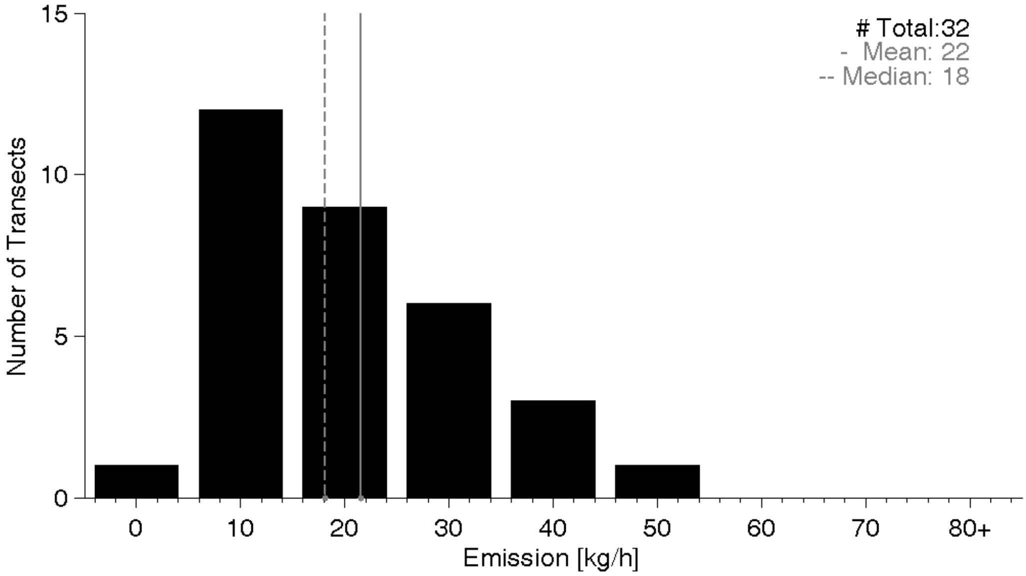

Figure 58. Histogram of all SOF measurements at Tank 13 during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

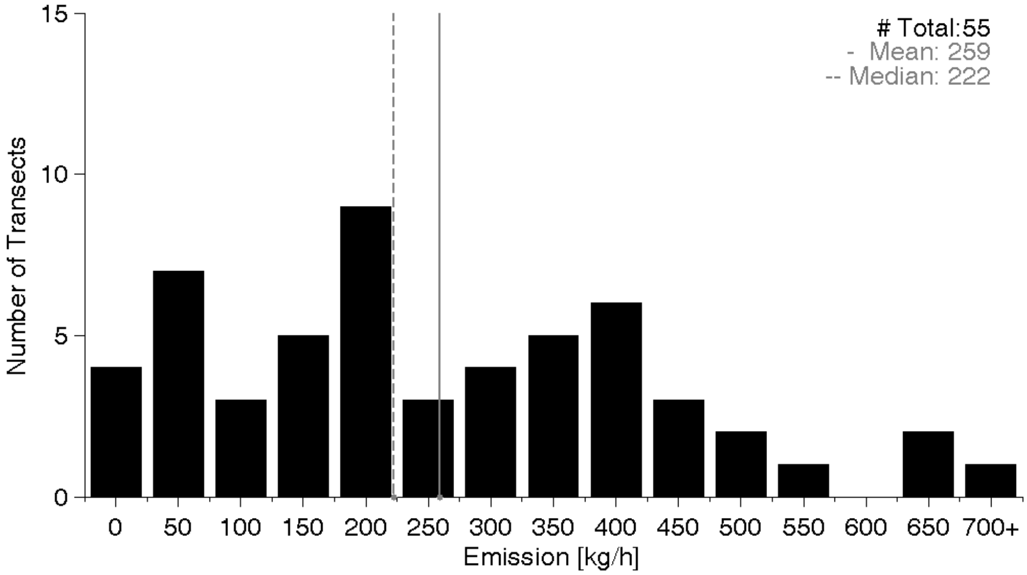

Figure 59. Histogram of all SOF measurements at Tank 16 during the SCAQMD survey 2015. The median and average values are indicated as dashed and solid gray lines.

The ground concentration of aromatic BTEX and alkanes across the refinery tank farm are shown in Figure 60 and Figure 61 respectively. The ratio of aromatics to alkanes was measured using MWDOAS and MeFTIR while driving through the tank park. Measurements were specifically concentrated on tanks 13, 16 and 502.

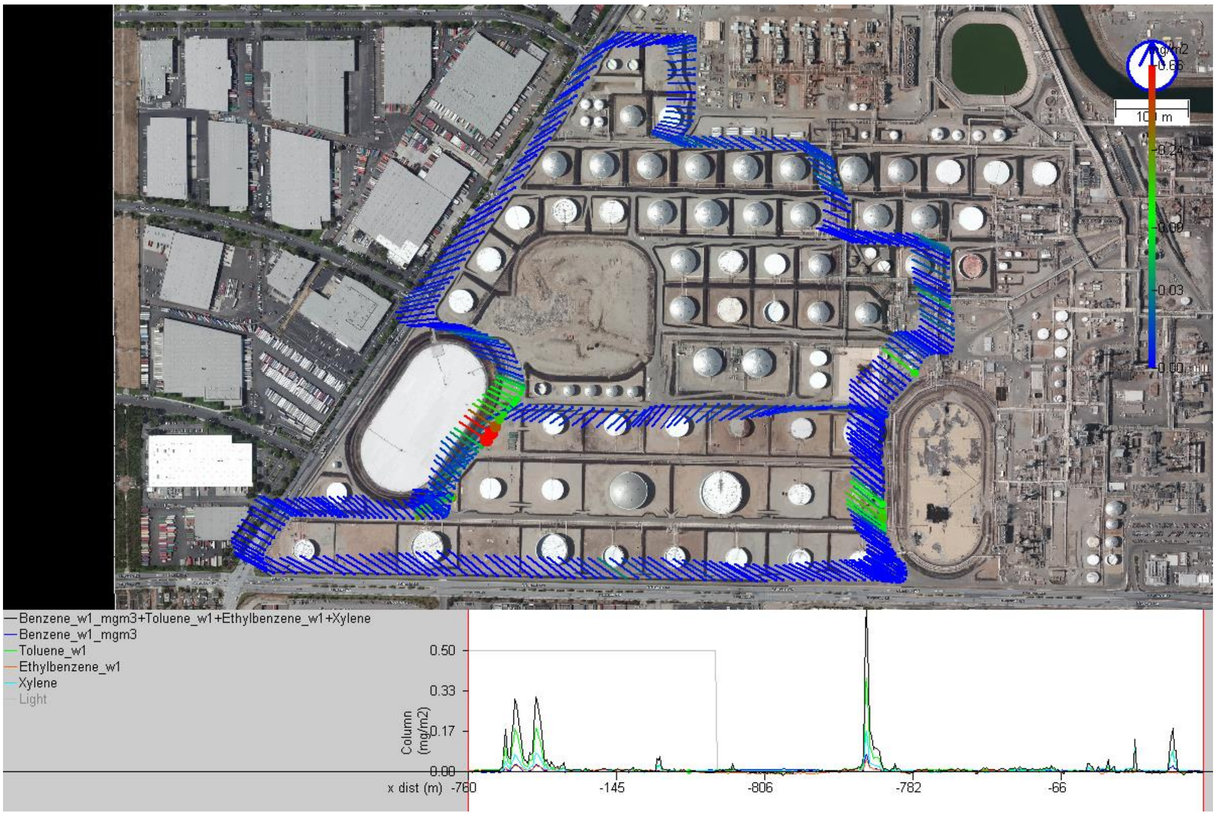

Figure 60. Aromatic VOC concentrations in mg/m^3 across the tank farm measured using MWDOAS. Bars are pointing towards the wind, hence in the direction of the source. North is upwards in the figure.

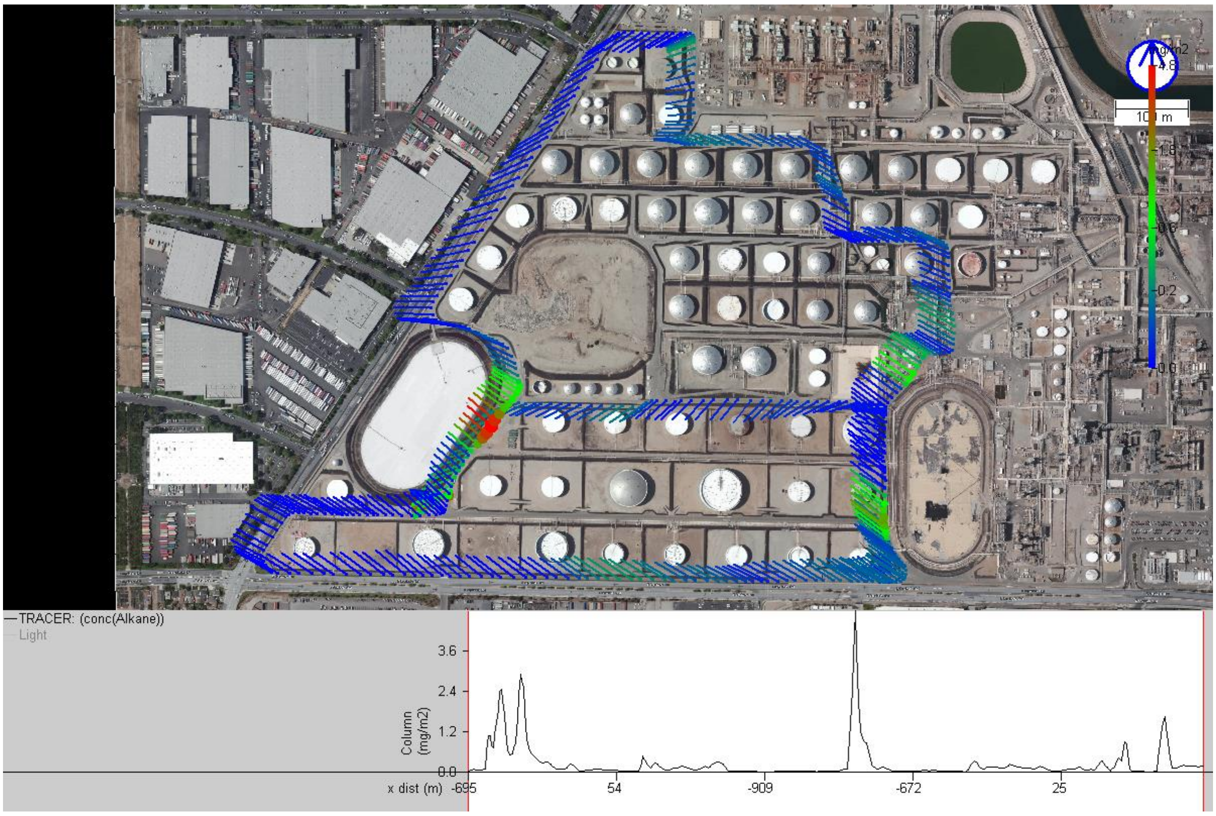

Figure 61. Alkane concentrations in mg/m^3 measured using MeFTIR across the tank farm. Bars are pointing towards the wind, hence in the direction of the source. North is upwards in the figure.

5.3 Further Leak search and Leak Detection

On site measurements with the real time geo-tagged result capabilities of the SOF + MeFTIR + MWDOAS techniques, as described in the previous section, are in a way a continuous leak search task. By driving the mobile lab on accessible roads on the upwind and downwind side of the different sources it’s possible to rather quickly (within hours) build a concentration map of a whole tank farm with located hot spots of elevated concentrations/emissions. Repeating this several times makes it possible to judge whether an observed emission pattern seems recurring or just being an intermittent release (for the time frame of the measurements). Repeated measurements at a site also build confidence in what emission levels that are normally observed, and when an aberration is observed and should be alarmed to the operations department.

During the 8 days of on site measurements between 28 September and 7 October, two major atypical emission events were identified, and reported to the operations and SCAQMD representatives. Tank_16, has already been discussed previously where a malfunctioning vent at the external roof of the crude tank inferred atypical high concentration levels and emission rates downwind of the tank 5 October. This was observed both by the MeFTIR and SOF measurements, and an inspection by operations verified the vent being stuck open.

Another atypical leak was found in the southern part of the so called *Tanks_Northeast* area, see Figure 52. Passing on the road south of the area, elevated alkane concentrations was observed with about 70,000 ppb in contrast to ten to hundred ppb normally observed downwind the various tanks. The leak was discovered late in the day, short before working permits ended as well as the sun setting to low for continued work. SOF and MeFTIR measurements pointed out an area next to the ground in the vicinity of several pipe lines. A gas camera was brought in to visualize that gas was indeed emerging from the soil beneath the pipes. Tubing was also attached to the MeFTIR instrumentation for “walk around” leak search with the tubing sampling air from locations around the pipe lines and at the ground. Figure 62 shows a SOF measurement from the particular site. Six SOF measurements between 4 PM and 5 PM on 30 September estimated the leak to be on average 31 kg/h.

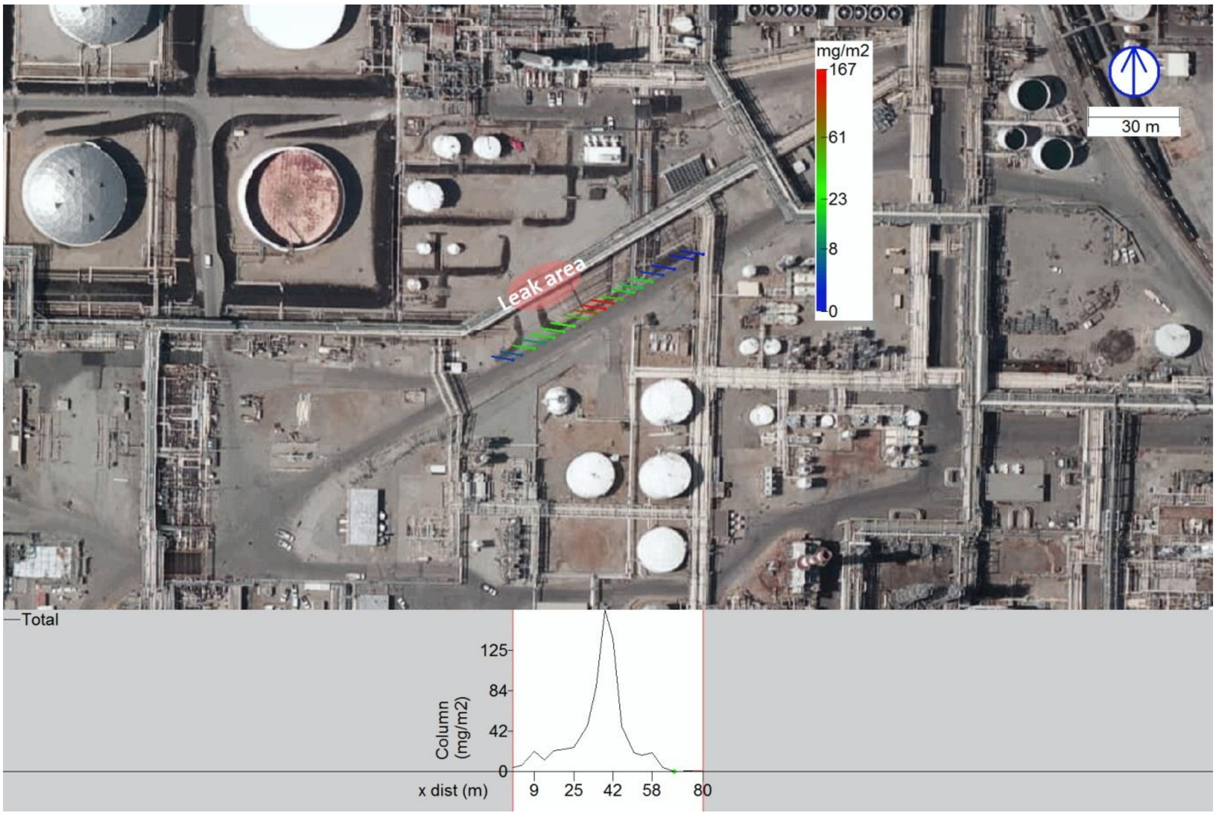

Figure 62. SOF measurement observing an atypical leak from the soil ground near a set of pipe lines. The leak area is indicated by a light-red area. The colored lines show observed alkane column (mg/m^2) with the lines pointing towards the wind and potential source. The graph beneath the picture shows integrated alkane column along the transect through the plume with traversed distance in meters.

Personnel from operations and SCAQMD were notified about the findings at once, and the source of emissions was further investigated by the refinery staff who immediately took appropriate actions. A leak, the size of a pinhole, was found in an alkane pipeline buried 30 cm below the ground. After the leak was repaired additional SOF and MeFTIR measurements were conducted to verify that the issue was resolved.

This case illustrates how mobile optical measurements and gas imaging information can be used to identify unknown leaks, and that immediate call upon and guidance of repair efforts can safely mitigate and suppress the risk of any further, potentially serious, complications. In general during the onsite measurements, working together with the experienced operations staff provided valuable input for interpreting the observed emissions and potential deviations from normal operations.

6 Discussion and Conclusion

Emission measurements of VOCs (alkanes, methane, and BTEX), SO_2 and NO_2 from six major refineries in the SCAB have been carried out by FluxSense Inc. using several state-of-the-art ORS techniques during a two and a half month campaign. The six refineries have a combined capacity of more than 900,000 barrels of crude oil per day and constitute an important stationary source of VOC emissions in Southern California.

For each refinery we compared the measured emission rates to the corresponding emission inventory values obtained by means of the US EPA AP-42 model (US-EPA 2013). The reported annual emissions have been divided by 12 to obtain average monthly emission rates, which were then compared to measured monthly median emissions obtained in this study. Thus, the comparisons are representative for September 2015 (the time-period when most of the measurements were performed).

An analysis of measured monthly emissions from each refinery normalized by the corresponding crude oil capacity is presented in Table 42. The overall alkane emission factor for all refineries in the SCAB (% of total emitted mass of alkanes to total capacity mass of crude oil) is 0.024%, ranging between 0.017 % and 0.045 % for the different facilities. This average emission factor is within 0.03 % and 0.1 %, a range observed from previous measurements conduced at well-run refineries in Europe (Kihlman *et al.* 2005; Mellqvist *et al.* 2009; INERIS 2010; Samuelsson *et al.* 2011). Thus, according to this data, the refineries in the SCAB are characterized by relatively low emissions compared to their capacity.

Table 42. Capacity normalized VOC (Alkanes+BTEX) emission factors * for the 2015 SCAQMD survey.

Measured Refineries 2015 Survey	**Crude Oil Capacity***		**Measured Monthly Emission** Alkanes + BTEX	**Emission Factor** Alkanes + BTEX
	[bbl/day]	Tons[1]/mo	Tons[1]/mo	[%]
Refinery A	257300	1086215	214	0.020%
Refinery B	139000**	586801**	59	0.045%
Refinery C			205	
Refinery D	104500	441156	132	0.030%
Refinery E	269000	1135608	201	0.018%
Refinery F	149500	631128	109	0.017%
Sum of all	**919300**	**3880908**	**919**	**0.024%**

*Crude capacity data is obtained from the 2016 California Energy Commission report. The overall emission factor is based on the sum of measured emissions for all refineries relative to the total capacity.
**Crude capacity for Refinery B and Refinery C are reported together since Refinery B processes the crude oil and Refinery C upgrades intermediate products to finished products.
[1] Metric Tons

A comparison between the measured monthly emissions and the average monthly emissions from the inventories (i.e., annual inventory emission divided by 12) is presented in Table 43. For all major refineries in the SCAB, the ratio between measured and reported emissions for September 2015 (denoted as D in table 43) is 6.2 for VOCs, 1.5 for SO_2, and 0.83 for NO_x. For benzene this ratio is ~34, although the total measured benzene emissions were relatively small. Note that the inventories report NO_x (NO_2+NO), while only NO_2 is measured by the SkyDOAS. However, previous studies have shown that NO_2 typically constitutes 75 % or more of the NO_x found in the air around refineries (Rivera *et al.* 2010).

Table 43. Reported (*Rep*) average monthly emissions [metric tons per month] from the available inventory for the six SCAB refineries and measured emissions (*Meas*) for the 2015 SCAQMD survey. *D* denotes the ratio between measured and reported emissions (Meas/Rep). The overall discrepancy values (last row) are calculated from the total sum of reported and measured emissions, respectively. The comparisons are representative for September 2015.

Refineries	*Total VOC*			*SOx*			*NOx* [1]			*Benzene*		
2015 Survey	**Rep.**	**Meas.**	**D**	**Rep.**	**Meas.**	**D**	**Rep.**	**Meas.**	**D**	**Rep.**	**Meas.**	**D**
	Tot VOC	*Alk+ BTEX*		*SOx*	*SO_2*		*NOx*	*NO_2*				
	tons /mo	tons /mo	[]	tons /mo	tons /mo	[]	tons /mo	tons /mo	[]	tons /mo	tons /mo	[]
Refinery A	33	214	6.4	38	46	1.2	50	48	1.0	0.06	2.5	43
Refinery B	7	59	8.3	26	39	1.5	30	23	0.8	0.03	0.8	33
Refinery C	17	205	12	10	27	2.7	37	42	1.1	0.03	6.0	202
Refinery D	12	132	11	7	12	1.7	23	25	1.1	0.03	1.2	39
Refinery E	37	201	5.4	23	39	1.7	57	46	0.8	0.05	2.0	38
Refinery F	40	109	2.7	25	27	1.1	39	13	0.3	0.19	0.6	3.2
All refineries	**148**	**919**	**6.2**	**129**	**190**	**1.5**	**237**	**197**	**0.8**	**0.38**	**13**	**34**

[1] Nitrogen oxides (NO_x) are reported in inventories while only the NO_2 fraction was measured by SkyDOAS.

The comparison of measured emissions with annual inventory values presents a number of challenges. Firstly, it is important to know whether the studied refineries operated under typical conditions during the measurement campaign. Since operational data from the facilities is not available for this project, we estimated the average monthly emission rate at each site by dividing the reported annual emission inventory value for each facility by 12.

Secondly, it has to be established that a sufficient number of measurements have been conducted during the measurement period to eliminate the risk of disproportional influence from intermittent emissions due to tank cleaning, maintenance, flaring, etc. To address this point the frequency distributions of the measured emission (as shown in Figure 15) have been analyzed and taken into account in our calculations. As a result median measured emissions were used for comparison with inventories instead of average measured emissions, therefore reducing the sensitivity to outliers.

Thirdly, the effects of differences in meteorological conditions between September 2015 and the entire year need to be considered to establish how representative the emissions measured during the study were to the entire year. In our experience, tank emissions contribute approximately 2/3 of the total refinery emissions (Kihlman 2005). At the same time, emissions from tanks are also more affected by environmental parameters such as wind, temperature and solar insolation, than emissions from process units. Therefore, a sensitivity study for two types of crude oil tanks, external floating roof tank (EFRT) and internal floating roof tank (IFRT), utilizing the formulas in the AP-42 model was conducted. A very similar approach has been previously applied to evaluate seasonal variations of refinery emissions (Johansson *et al.* 2014b). During the measurement campaign, the average maximum daytime temperature was 5.4 °C higher than the 2015 average annual temperature of 19.6 °C (data from weatherunderground.com for Torrance Airport), while the 2015 monthly and annual average wind speeds were both 2.2 m/s (data from weatherunderground.com for Long Beach Airport). In addition, the monthly average solar radiation was 22 W/m^2 higher than the annual average of 226 W/m^2 (data from Torrance airport from the National Solar Radiation Database). According to AP-42 model, these differences in meteorology combined resulted in 11 % and 29 % higher modeled emissions for September 2015 than for the annual average for the IFRT and EFRT, respectively. These values are within the uncertainty of the SOF method.

Additionally, no dependency of measured emissions on temperature and wind speed was observed. Figure 63 illustrates that there was no obvious correlation between measured alkane emissions and wind speed or temperature at Refinery A. Therefore, the observed discrepancies between measured emissions and reported inventories (based on the AP-42 standard (US-EPA 2013)) are considerably higher than what can be explained by measurement uncertainties or short-term sampling alone.

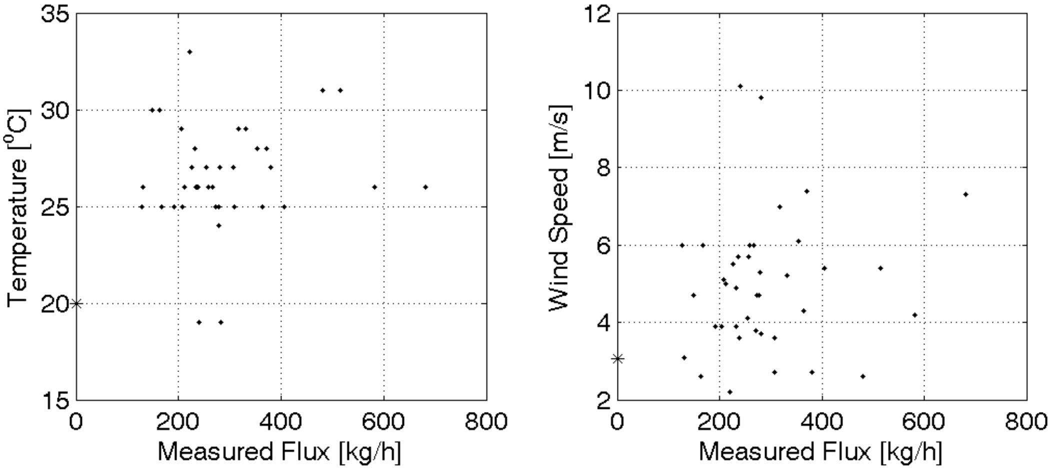

Figure 63. SOF emission data from Refinery A plotted against the corresponding local temperature and wind speed values (left and right plots, respectively). *Annual average values from the meteorological station at Torrance Airport (KTOA) 2015 [www.weatherunderground.com].

Refineries and tank farms are complex environments with a large number of installations and numerous potential emission sources (e.g. tank seals, valves, gauges, flares, vapor recovery units, etc.). Many of these components can show degrading performance over time, and to accurately account for the impact of non-ideal performance in emissions inventory reporting is, we believe, an impossible task. Nevertheless, EPA’s AP-42 system provides valuable insights for a specific facility on the production and abatement techniques applied, and on what emission level the site could reach given ideal performance of all installations. Comparing measured emissions to ideal performance levels established by AP-42 could provide a basis for benchmarking of different refineries or sites.

OUTLOOK

Studies conducted in the SCAB, the Bay Area, Texas, and other places worldwide, show that field measurements provide a reliable way to determine actual emissions of VOCs and other pollutants from refineries and various industrial sites. Accurate estimates of VOC and other pollutant emissions from industrial sources are crucial for improving air quality models, to guide air pollution mitigation strategies, promote successful compliance strategies, and reduce exposure for nearby communities.

In our experience, the observed difference in fugitive VOC emissions between measured and inventory estimates is a general issue for the petroleum industry worldwide. We believe that a possible path forward could be to conduct monitoring in parallel with continued AP 42 based reporting, and to use the measurements to guide and verify the efficiency of the emission reduction efforts at the industrial sites.

Longer-term ORS studies spanning over different seasons could be conducted in order to alleviate concerns stemming from comparison of emissions measured over limited-time to annual emissions reported through the inventories. Additionally, future studies could combine ORS measurements and site-specific emission modeling performed for inventory calculations. A better dialog between scientists conducting the measurements and the facility operators could also be crucial to improve our understanding of how site activities may affect measured emissions.

Traditional Leak Detection and Repair (LDAR) is an important practice to control and limit unplanned VOC emissions from refineries and to identify potential leak sources. The ORS techniques used in this study have demonstrated their ability to quickly quantify and map refinery emissions and to identify potential air pollution sources within a facility. Using real time measurements, refinery personnel and air quality regulators can enhance LDAR programs by prioritizing LDAR activities. Addressing the most concerning issues first is important to reduce occupational risks for refinery workers, avoid public hazard exposures, and limit the economic losses due to unplanned evaporation of refinery products.

A continued path towards improved air quality involves a good understanding of current emission levels and sources. Repeated and systematic emission measurements will be an important tool for benchmarking industry’s environmental performance as well as for sustaining and verifying efficient emission improvement plans, ultimately resulting in cleaner air and a better environment.

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8 Acknowledgements

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9 Appendix A: Quality Assessments

Quality checks and measures are performed at several levels in order as indicated in Figure 2 and given below. On arrival, 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/m^2 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. Put the LIDAR truck on level ground.
6. Check that wind information is available and reasonable.

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

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

Data Analysis, Interpretation, and Management

DATA REPORTING REQUIREMENTS:

A Draft and Final Report will be delivered to SCAQMD electronically (i.e., via file transfer protocol (FTP) or e-mail) in MS-WORD format no later than the established deliverable due date. After post-processing, validation and analysis, the data will be delivered to SCAQMD at the time of the final report.

DATA VALIDATION PROCEDURES:

Project personnel will 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 will be 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 will be 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 kml 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 (see previous section). In the audit procedure the completed transects will be reviewed by an independent experienced SOF-operator that was not involved in the actual data evaluation. At least one of the persons involved in the data processing must have been in the FluxSense mobile lab while the actual measurements were made

STATISTICAL PROCEDURES:

The final data will be presented as daily means and standard deviations for each facility together with histograms showing all individual measurements. The variability of the result will be a combination of measurement uncertainties, wind variability and actual variability in the emissions from the facility.

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

More samples will provide a closer estimate of the actual emissions. In reality, the number of measurement will be a trade-off between acceptable statistics and available time and conditions for making the measurement and time sharing between other measurements. The aim is 3-5 transects with acceptable quality per facility and day during at least four days. If boxing is not performed, at least 1 representative upwind measurement per facility should be made.

DATA SUMMARY AND ANALYSIS:

The data will be post processed with the spectral retrieval programs QESOF (SOF) and QDOAS (mobile DOAS). This will give 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 will be processed using the output from Leosphere WindCube system. Data files are saved as ASCII-files.

The weather mast will be connected to a real time data logger and will be 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 will be 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.

10 Appendix B: Wind Plots

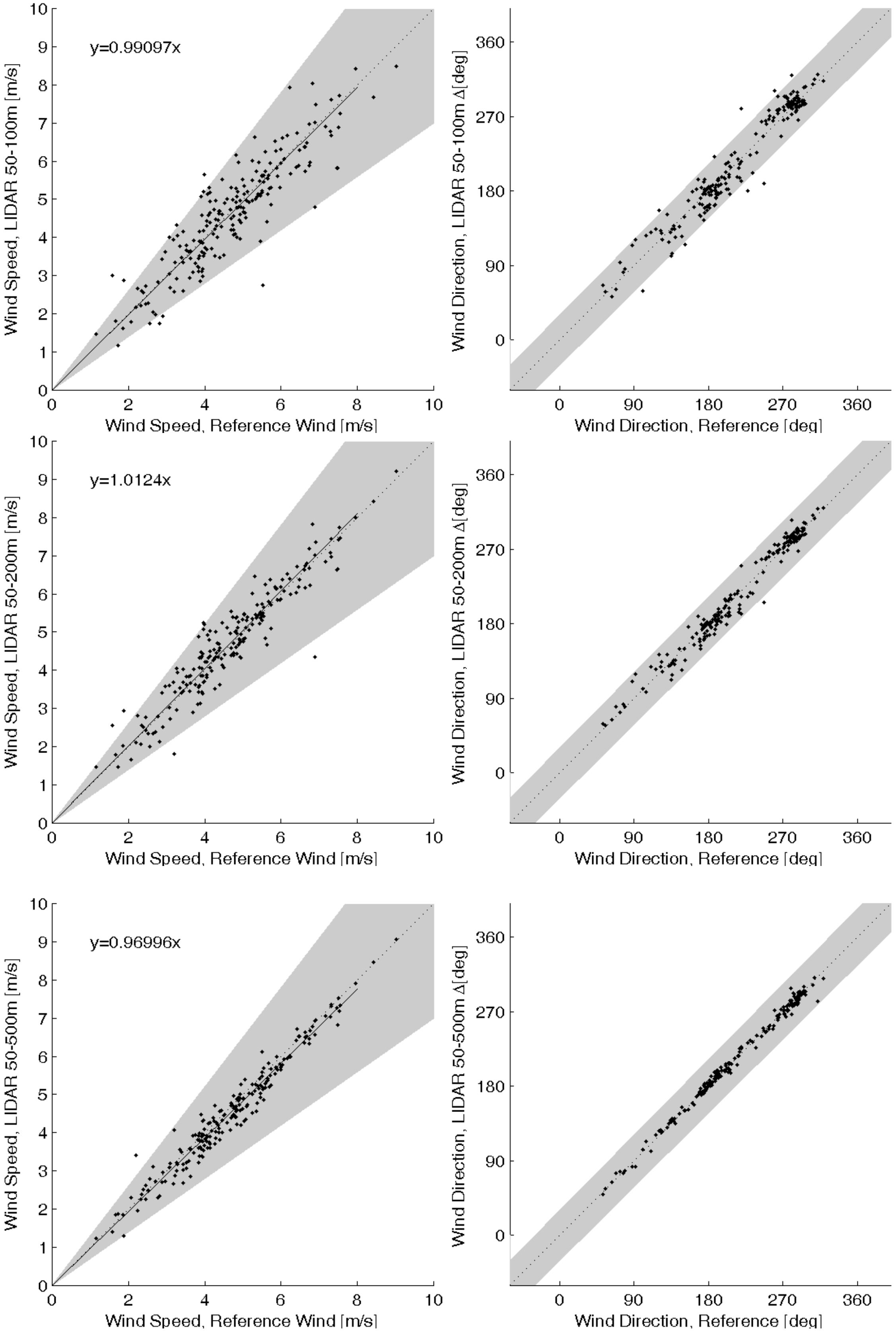


Figure 64. Wind LIDAR data for different altitude ranges versus the reference LIDAR wind (50-400m) during the calibration period 2-6 October 2016 at LIDAR site L1 (10 min average from 10AM to 5PM) . The shaded areas indicate ±30% relative deviation from reference wind speed (left panels) and ±30° deviation from reference wind direction (right panels). Fitted least squares are shown as solid lines.

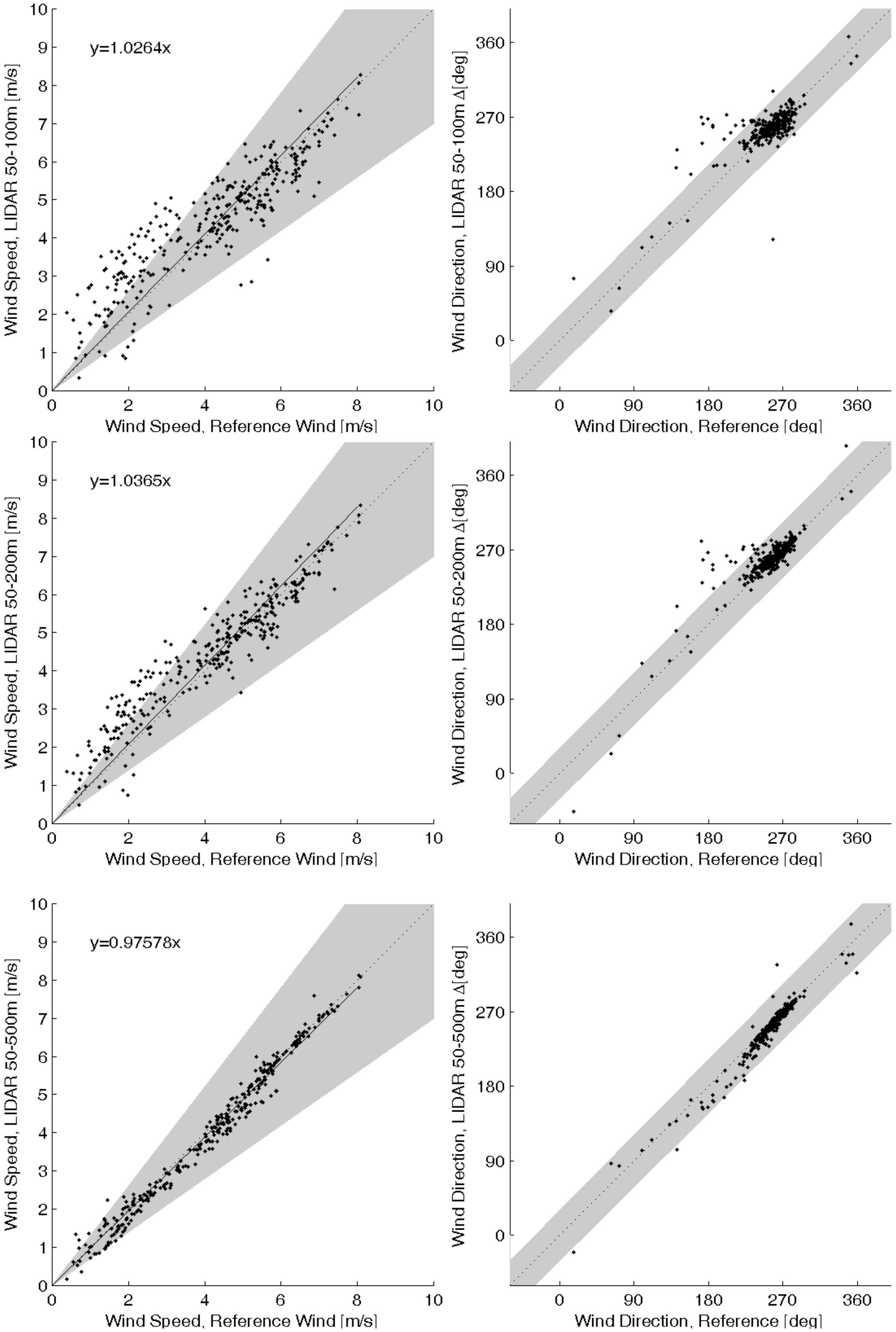


Figure 65. Wind LIDAR data for different altitude ranges versus the reference LIDAR wind (50-400m) during the calibration period 9-16 October 2016 at LIDAR site L4 (10 min average from 10AM to 5PM). The shaded areas indicate ±30% relative deviation from reference wind speed (left panels) and ±30° deviation from reference wind direction (right panels). Fitted least squares are shown as solid lines.

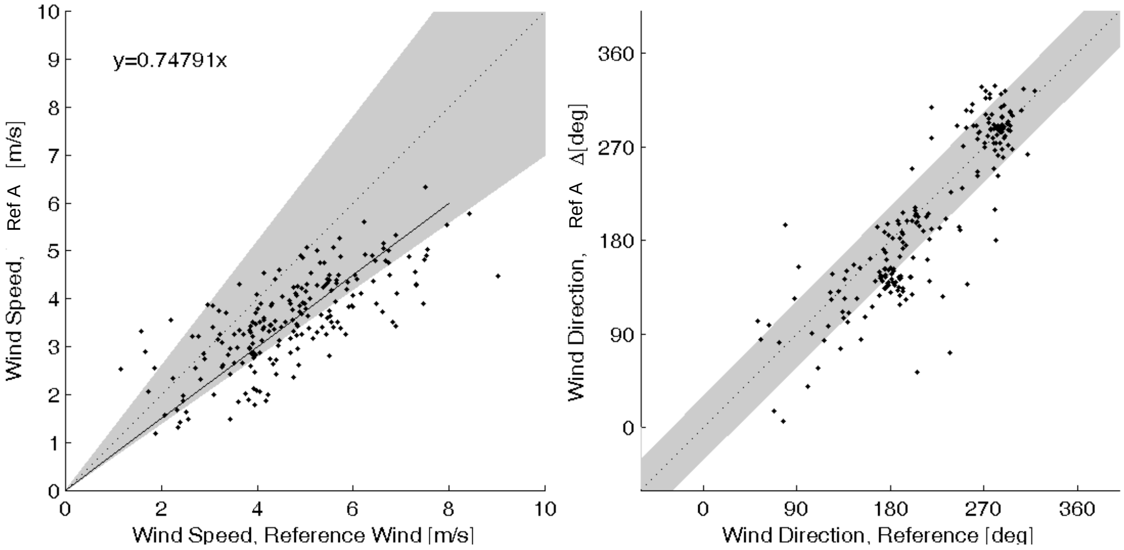


Figure 66. Refinery A´s 10m wind mast data versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM) during the calibration period 2-6 October 2016 at LIDAR site L1. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

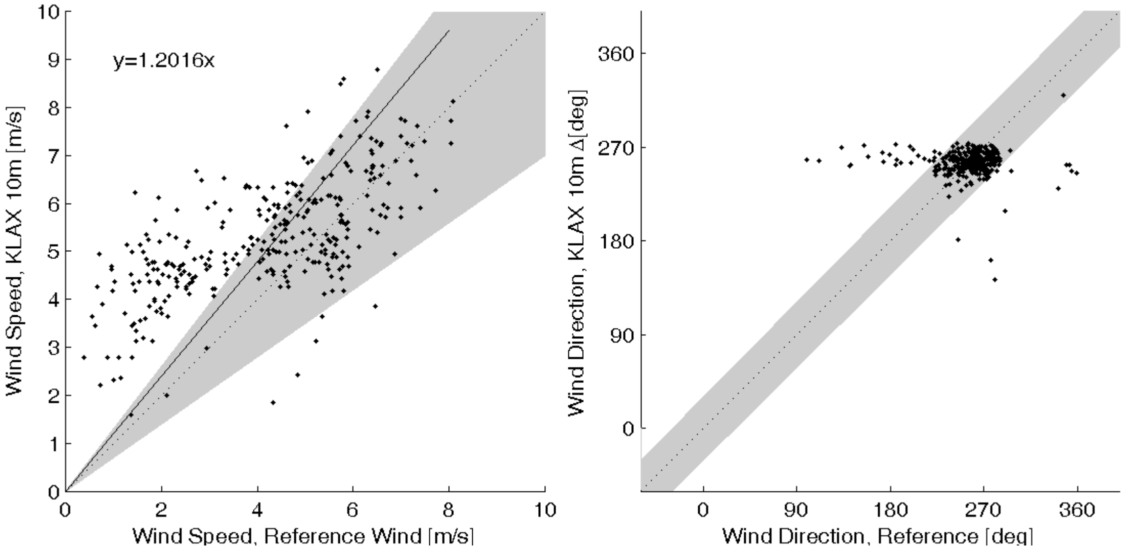


Figure 67. ASOS Met station at Los Angeles International Airport-KLAX versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM)during the calibration period 9-16 October 2016 at LIDAR site L3. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

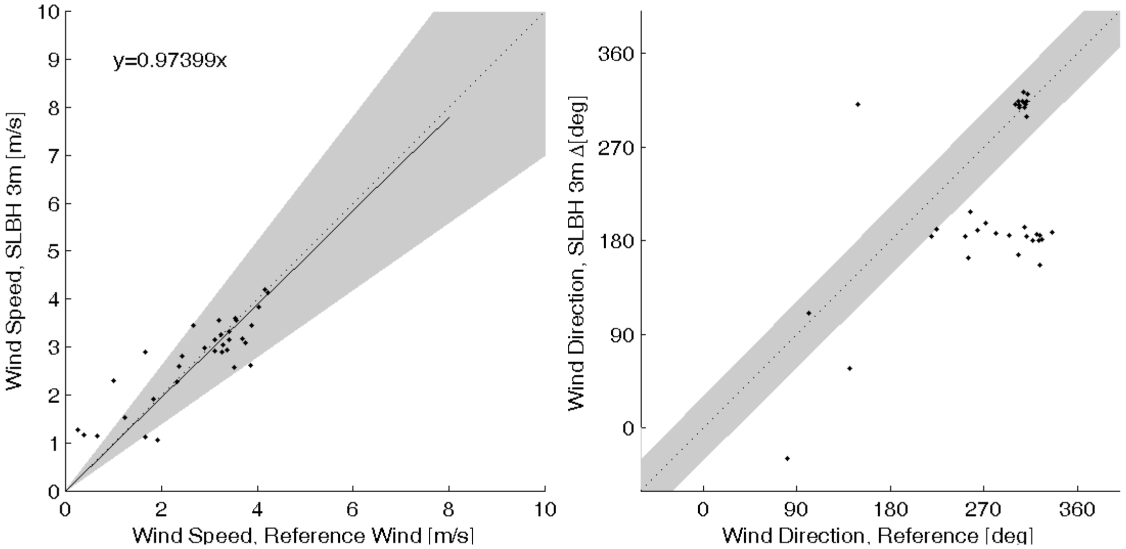


Figure 68. SCAQMD Met station at South Long Beach (SLBH) versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM)during the calibration 18 October 2016 at LIDAR site L2. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

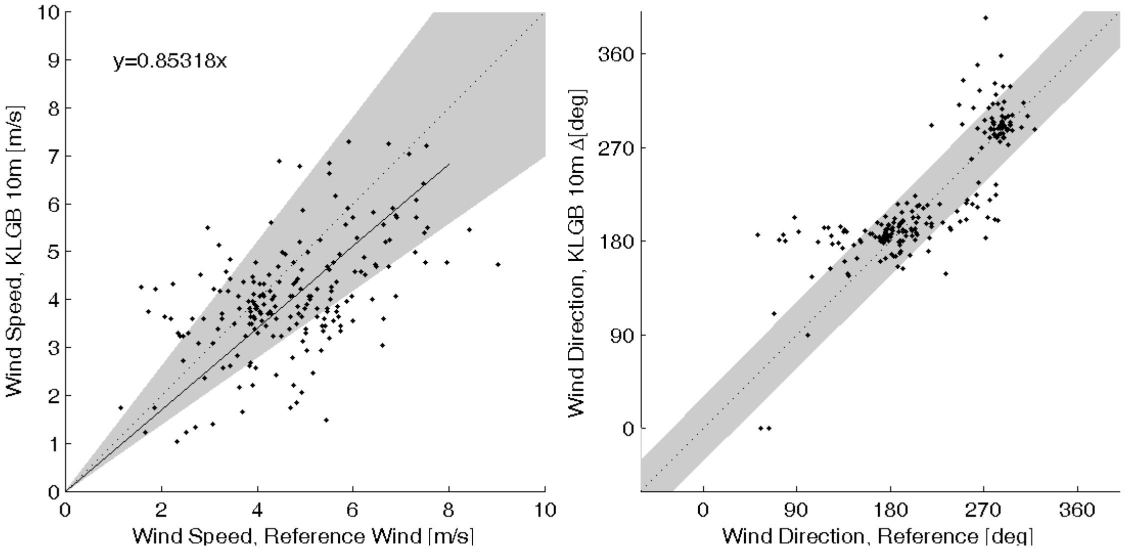


Figure 69. ASOS Met station at Long Beach Airport (KLGB) versus the reference LIDAR wind (50-400m) (10 min average from 10AM to 5PM)during the calibration period 2-6 October 2016 at LIDAR site L1. The shaded areas indicate ±30% relative deviation from reference wind speed (left panel) and ±30° deviation from reference wind direction (right panel). Fitted least squares are shown as solid lines.

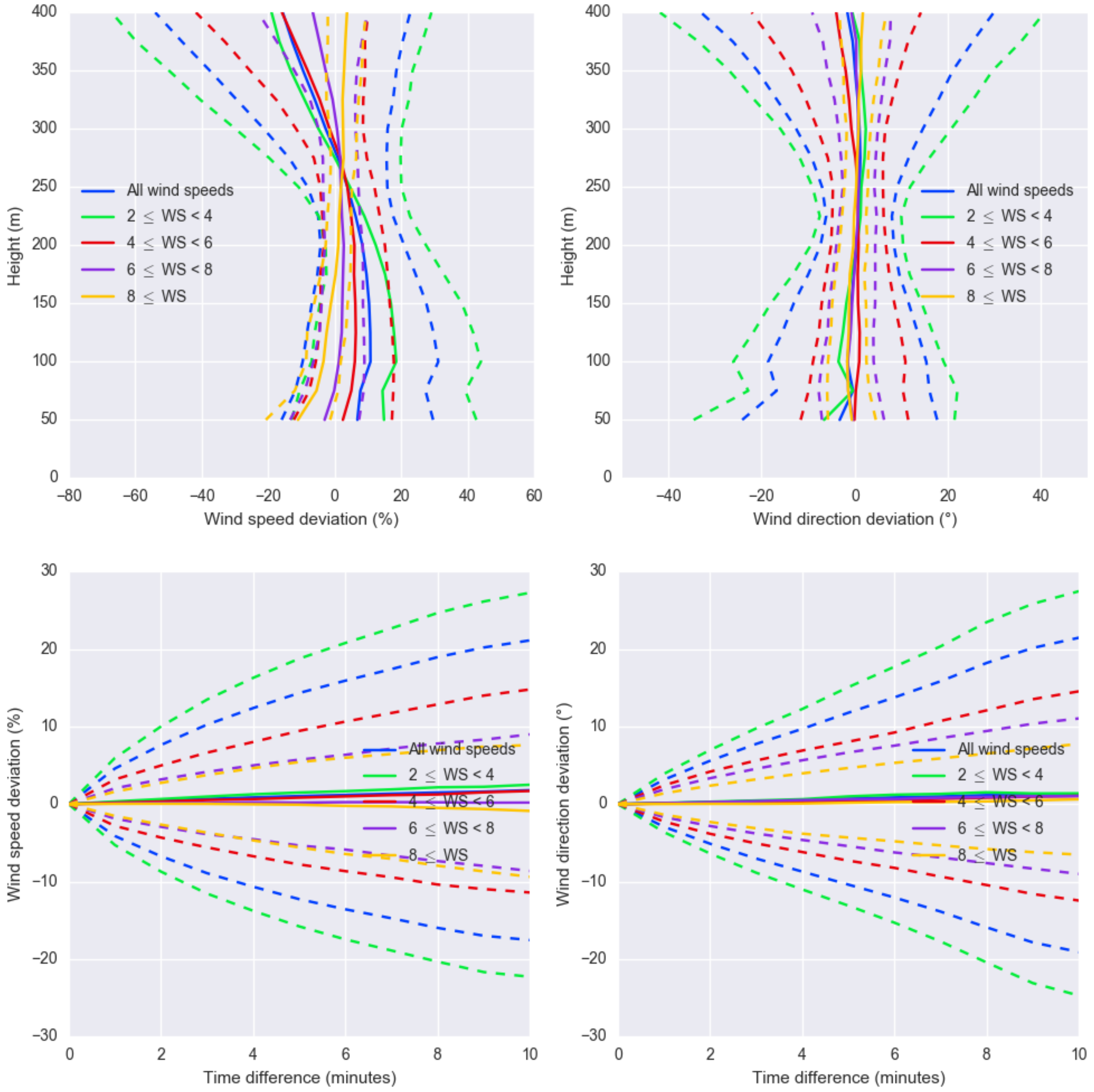


Figure 70. Wind LIDAR 10-min data for the entire SCAQMD survey 2015. Average (solid lines) and 1σ deviations (dashed lines). Top row panels show altitude information and the lower row shows time dependence. Different colors represent different wind speed ranges.

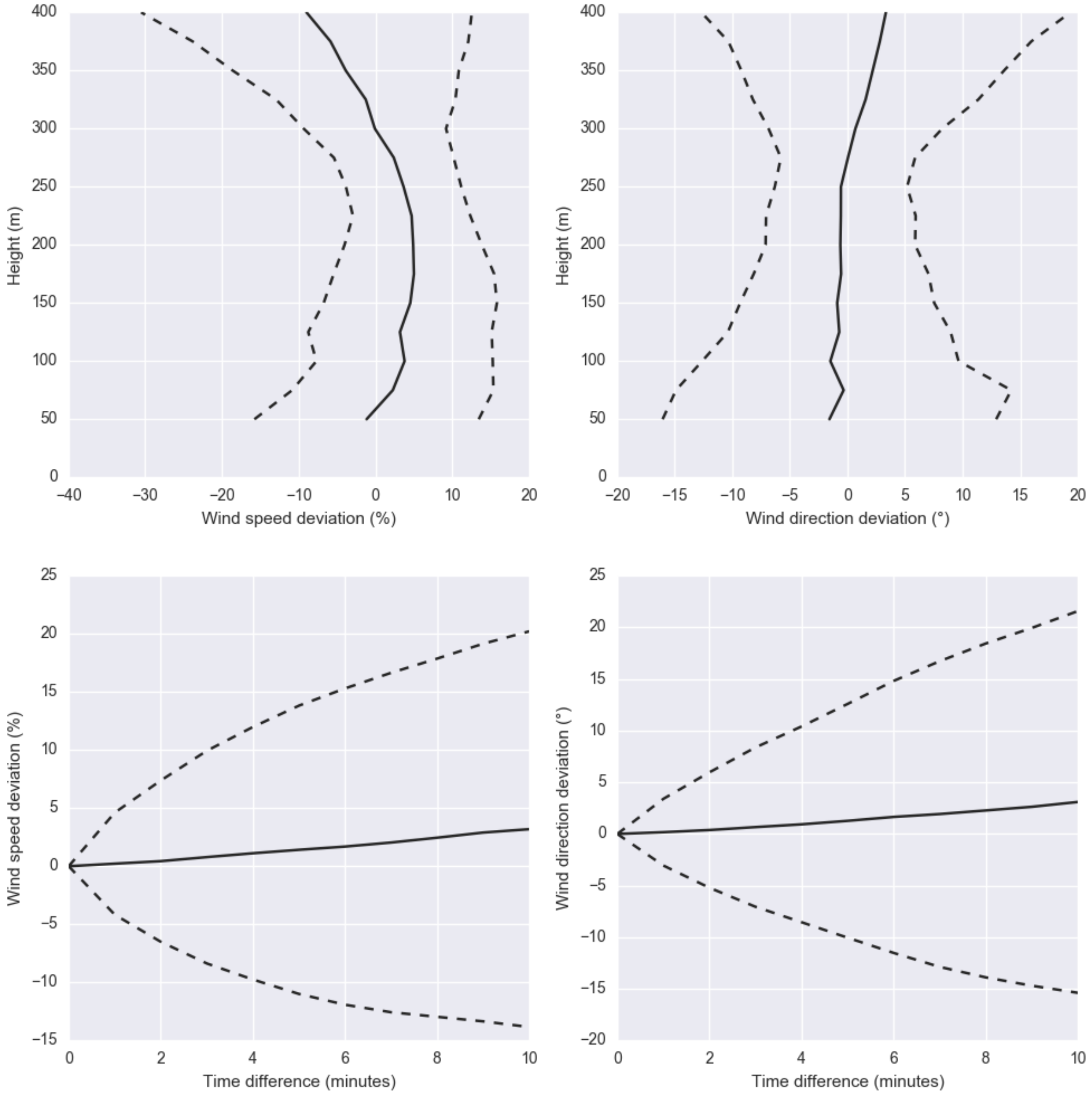


Figure 71. Wind LIDAR 10-min data at L1. Wind data averages (solid lines) and 1σ deviations (dashed lines) for the calibration period (9-16 Oct) during the SCAQMD survey 2015. Top row panels show altitude information and the lower row shows time dependence.

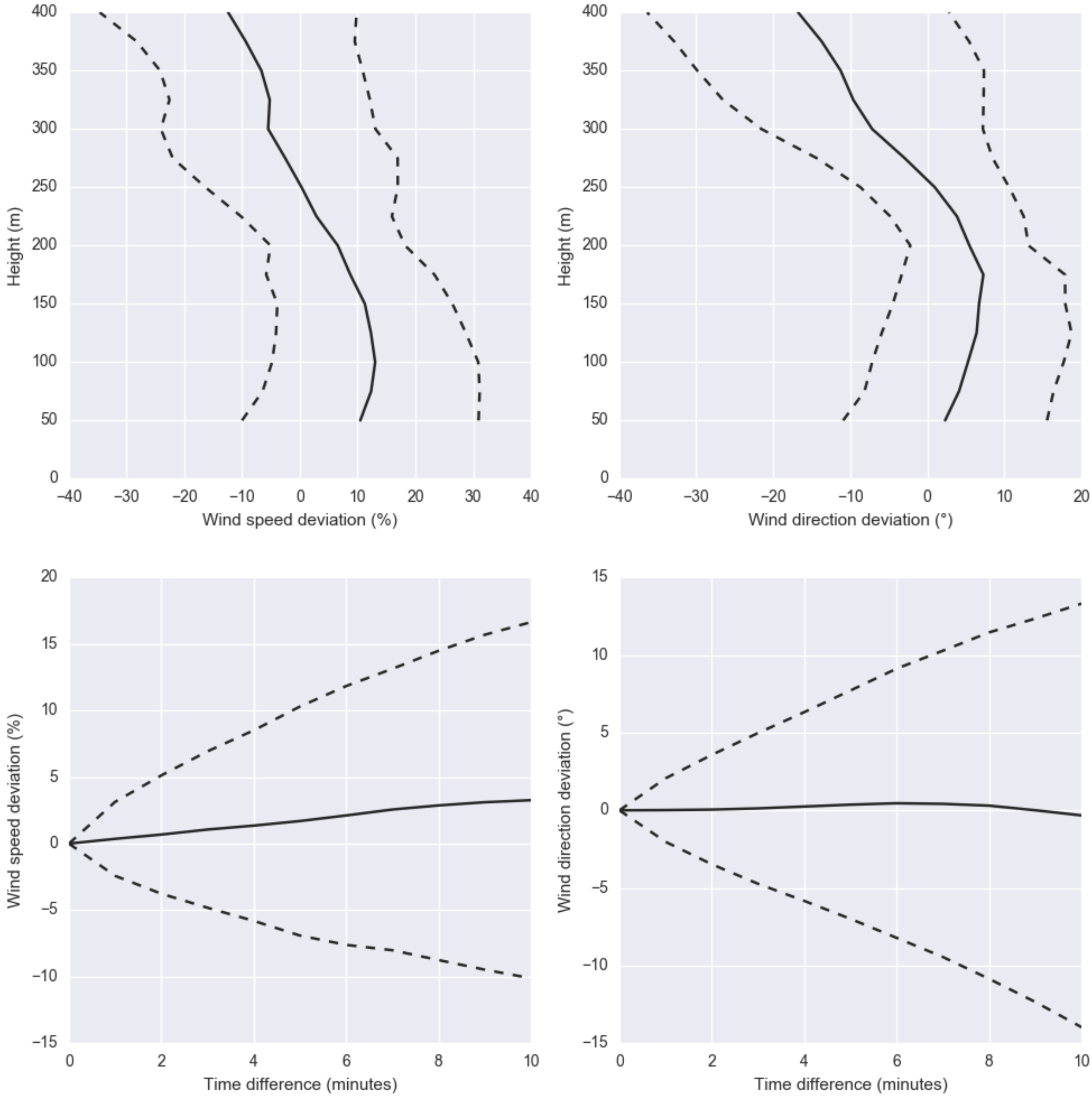
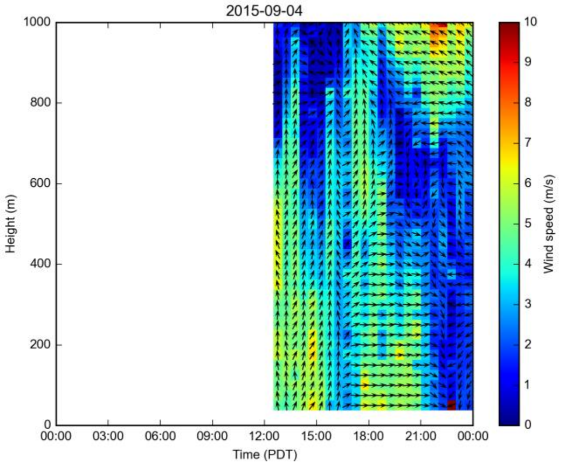


Figure 72. Wind LIDAR 10-min data at L4. Wind data averages (solid lines) and 1σ deviations (dashed lines) for the calibration period (2-6 Oct) during the SCAQMD survey 2015. Top row panels show altitude information and the lower row shows time dependence.

Figure 73. Wind LIDAR data (30 minute averages) from 50 to 1000 m for all measurement daysin this project. Arrows indicate wind direction and color wind speed (0-10 m/s). White gaps when no data available due to limited back scatter signal or other reason. **All panels below**.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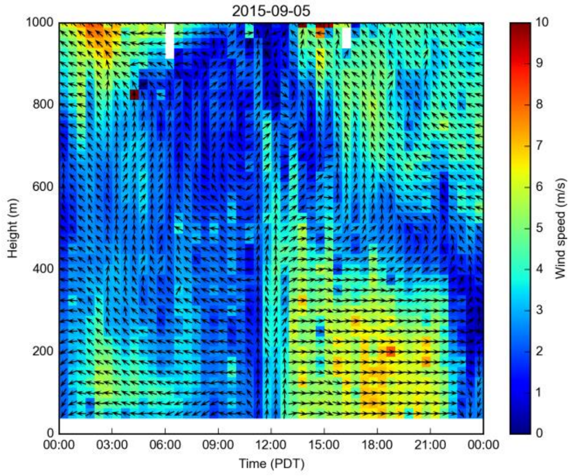
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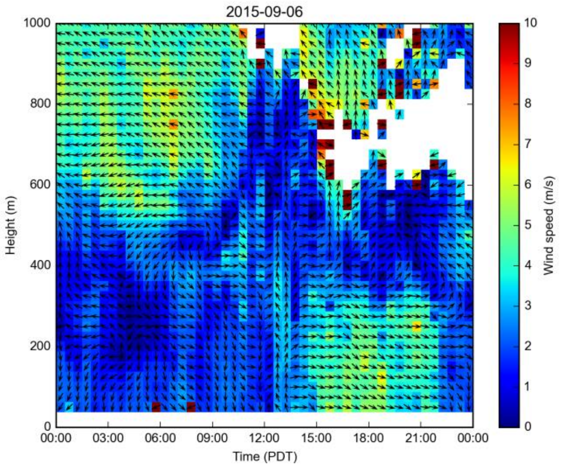
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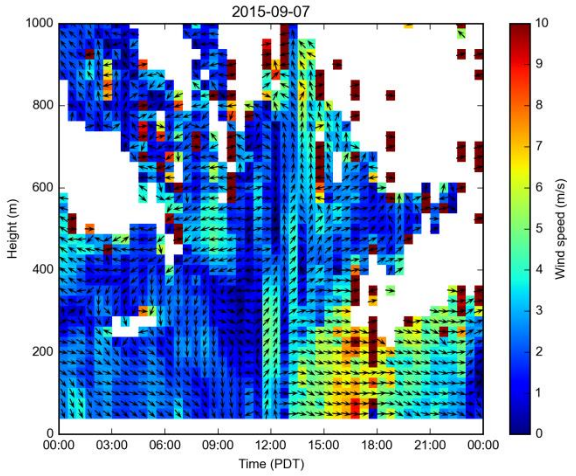
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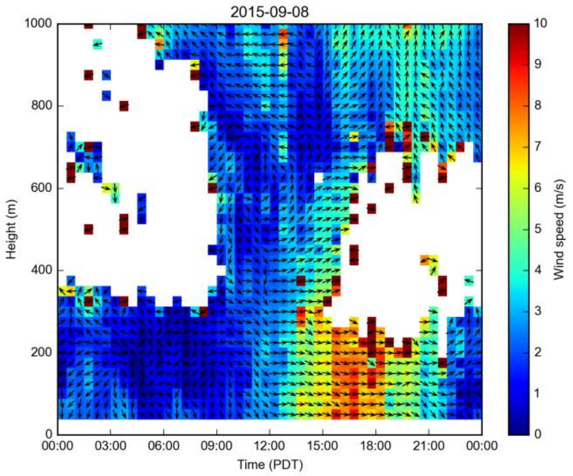
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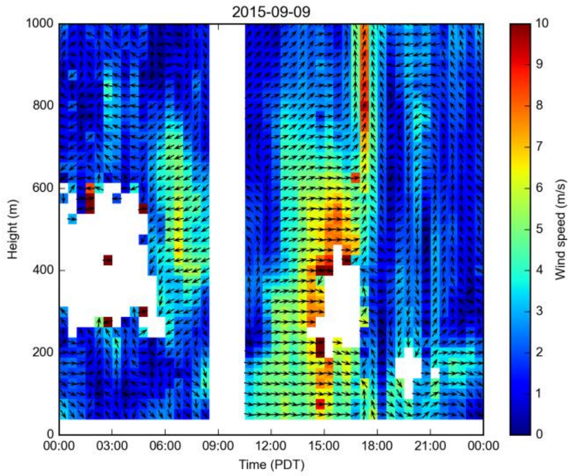
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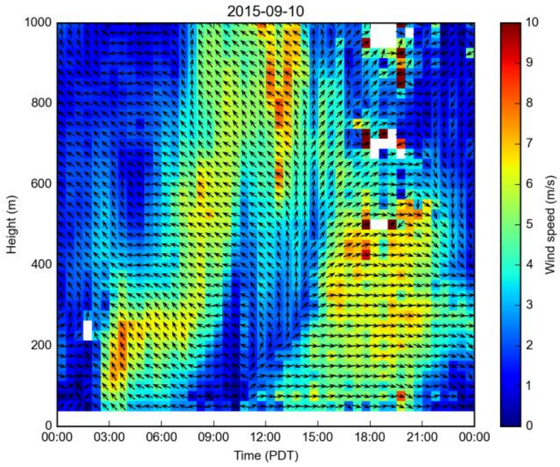
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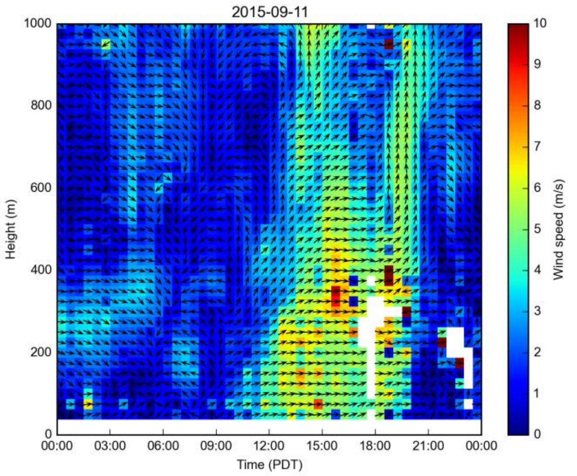
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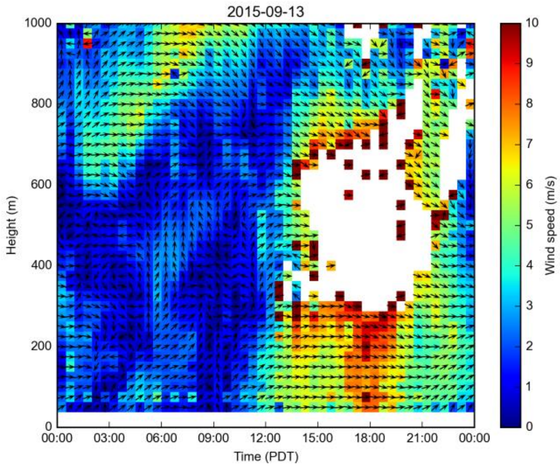
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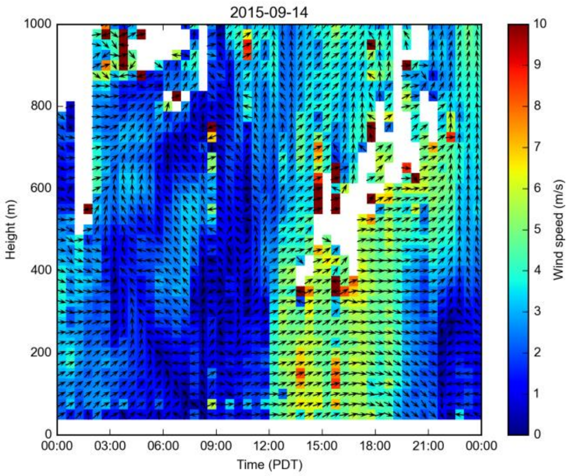
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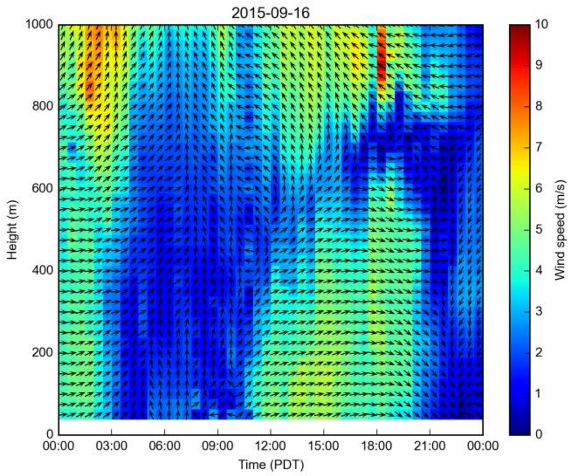
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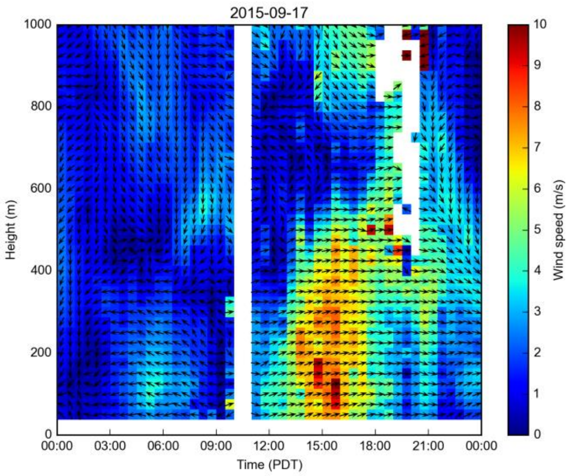
200
400
600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
1
2
3
4
5
6
7
8
9
10


2015-09-17
Height (m)
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200
400
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800
1000
Time (PDT)
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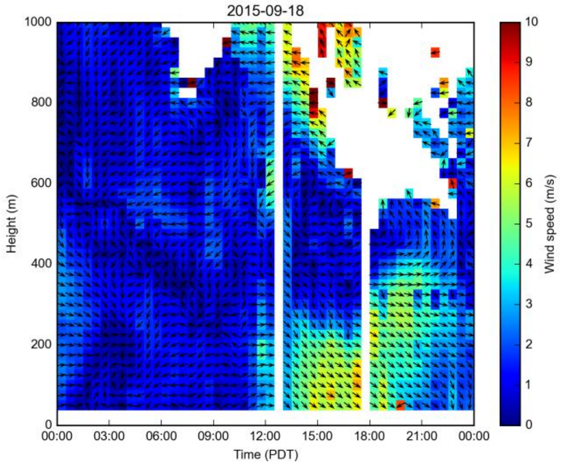
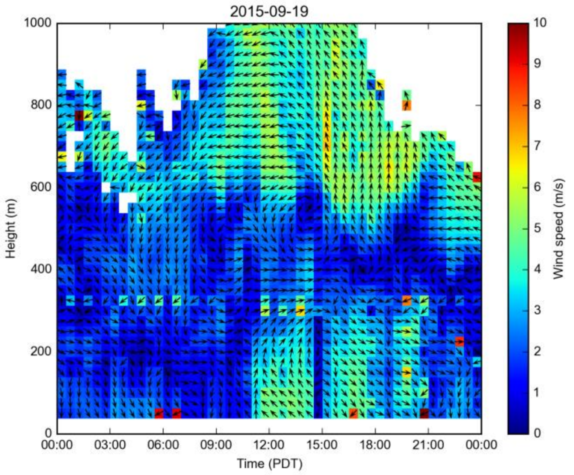
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
1
2
3
4
5
6
7
8
9
10


2015-09-18
Height (m)
1000
800
600
400
200
0
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Time (PDT)
Wind speed (m/s)
10
9
8
7
6
5
4
3
2
1
0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200
0
00:00
03:00
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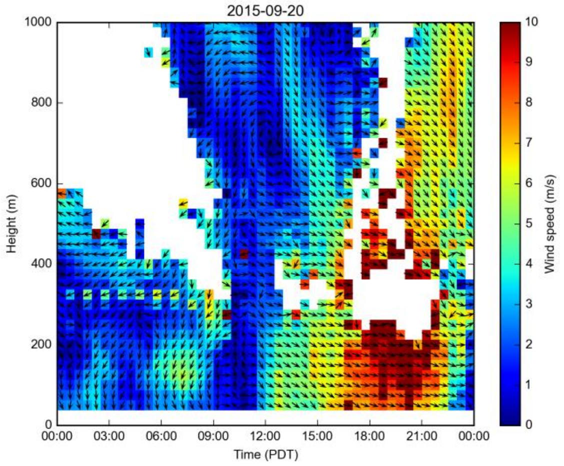
09:00
12:00
15:00
18:00
21:00
00:00
Time (PDT)
Wind speed (m/s)
10
9
8
7
6
5
4
3
2
1
0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200
0
00:00
03:00
06:00
09:00
12:00
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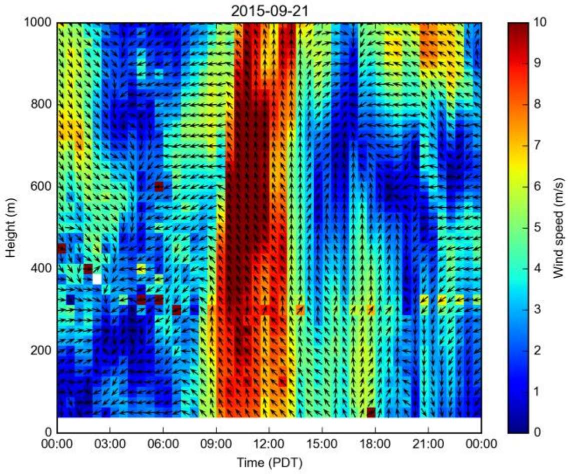
18:00
21:00
00:00
Time (PDT)
Wind speed (m/s)
10
9
8
7
6
5
4
3
2
1
0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200
0
00:00
03:00
06:00
09:00
12:00
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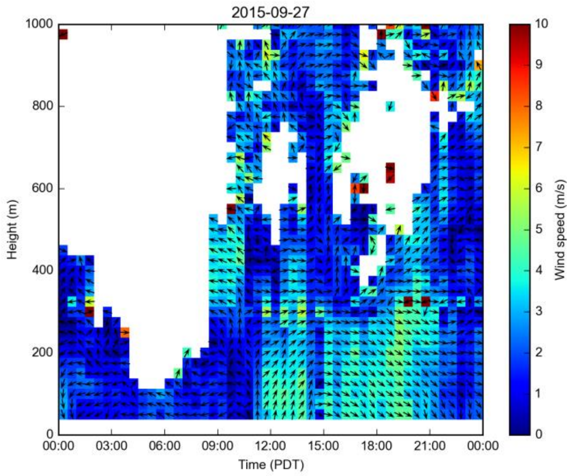
18:00
21:00
00:00
Time (PDT)
Wind speed (m/s)
10
9
8
7
6
5
4
3
2
1
0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200
0
00:00
03:00
06:00
09:00
12:00
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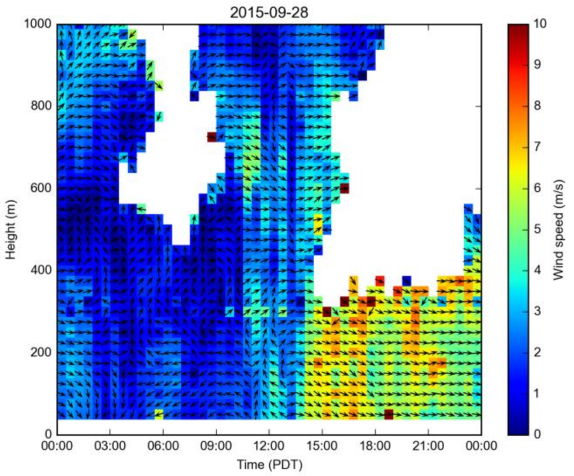
18:00
21:00
00:00
Time (PDT)
Wind speed (m/s)
10
9
8
7
6
5
4
3
2
1
0


2015-09-28
Height (m)
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200
0
00:00
03:00
06:00
09:00
12:00
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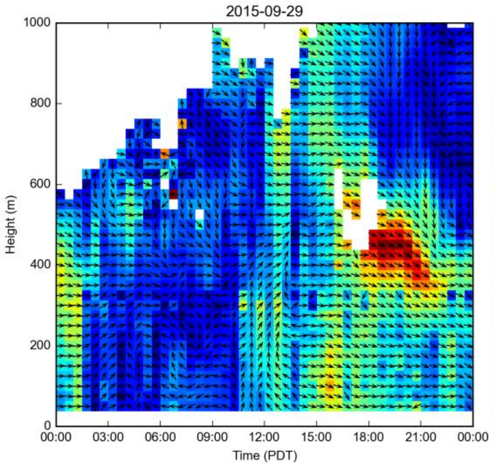
18:00
21:00
00:00
Time (PDT)
Wind speed (m/s)
10
9
8
7
6
5
4
3
2
1
0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Height (m)
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400
600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
1
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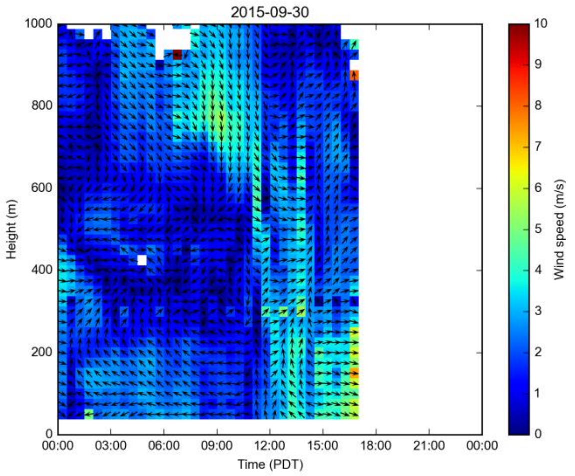
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Height (m)
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400
600
800
1000
Time (PDT)
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03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
1
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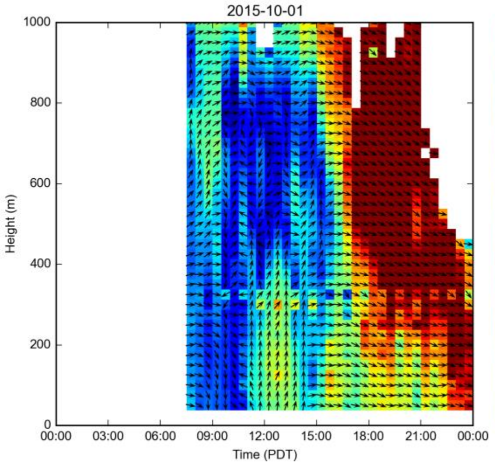
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Height (m)
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400
600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
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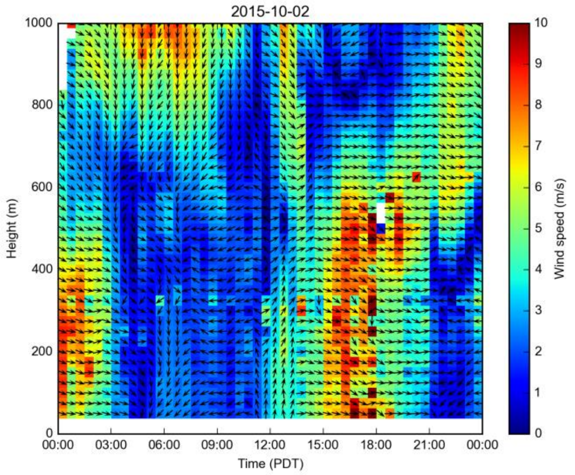
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Height (m)
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400
600
800
1000
Time (PDT)
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03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
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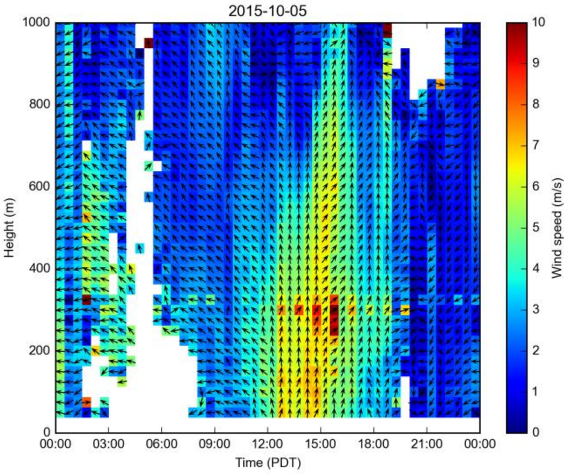
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Height (m)
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800
1000
Time (PDT)
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03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
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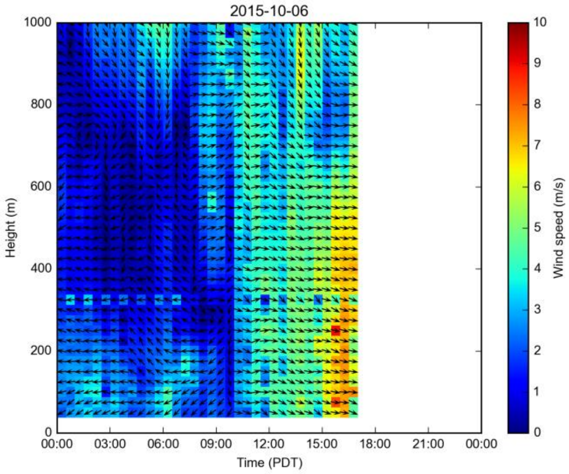
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Height (m)
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200
400
600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
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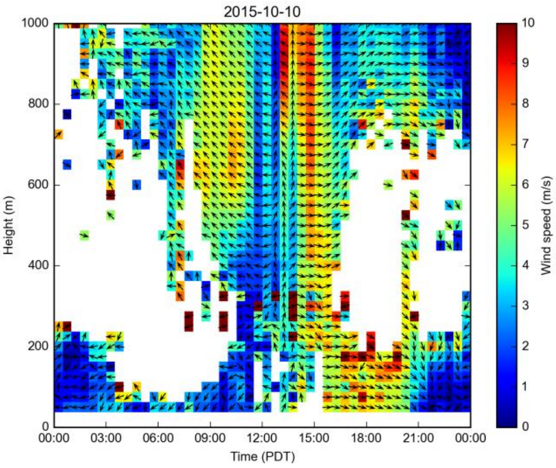
2015-10-10
Height (m)
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600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
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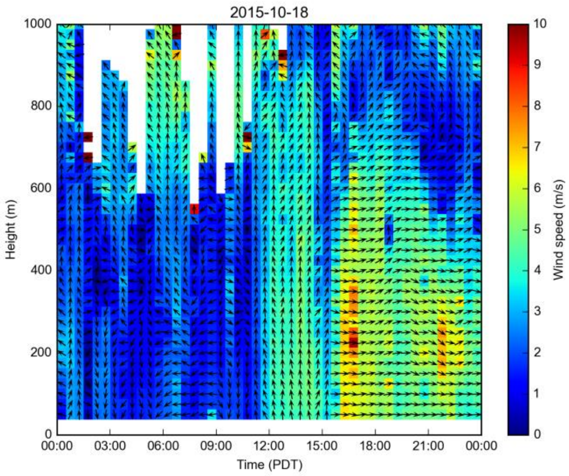
2015-10-18
Height (m)
0
200
400
600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
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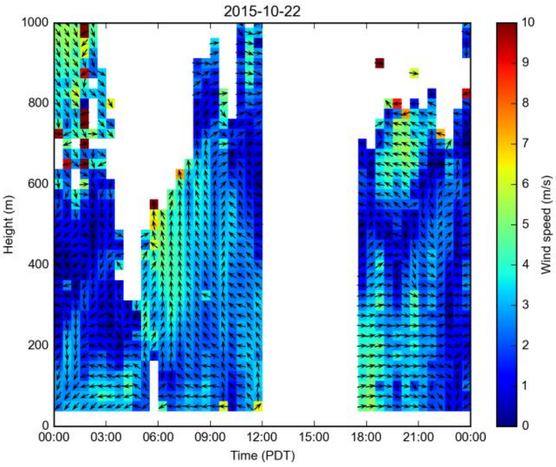
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Height (m)
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200
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600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
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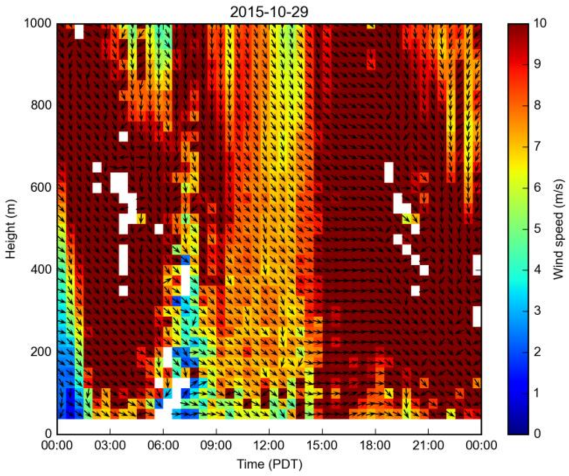
2015-10-29
Height (m)
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200
400
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1000
Time (PDT)
00:00
03:00
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18:00
21:00
00:00
Wind speed (m/s)
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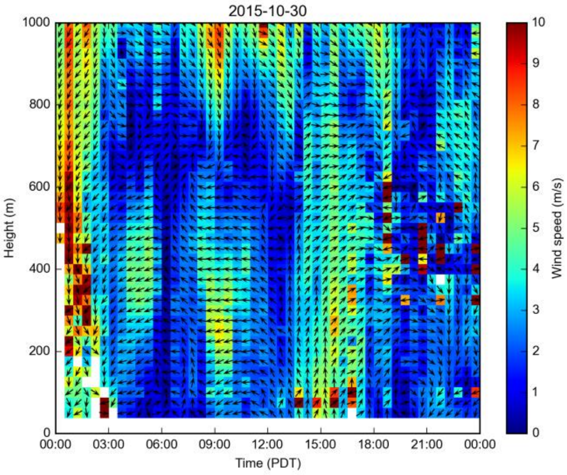
2015-10-30
Height (m)
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200
400
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800
1000
Time (PDT)
00:00
03:00
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09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
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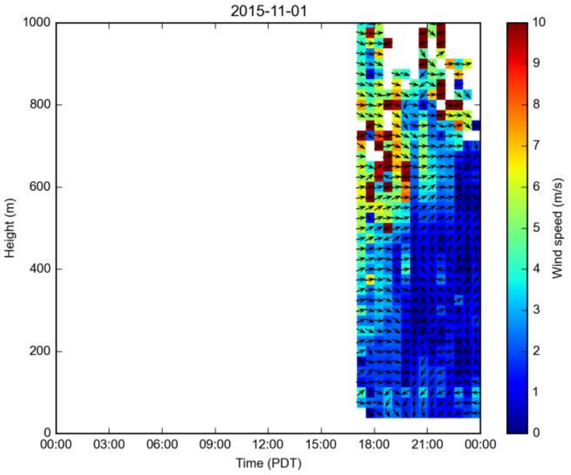
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Height (m)
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200
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600
800
1000
Time (PDT)
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Wind speed (m/s)
0
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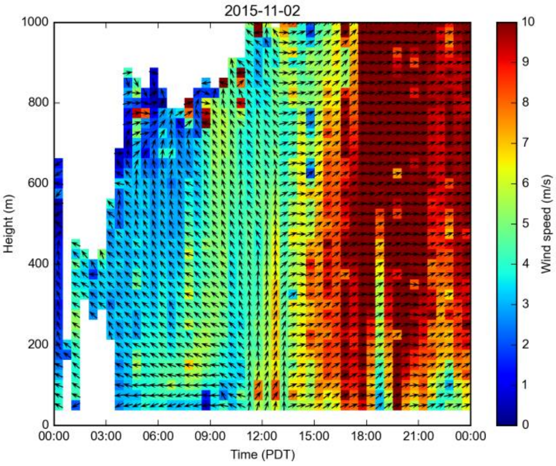
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Height (m)
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800
1000
Time (PDT)
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06:00
09:00
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15:00
18:00
21:00
00:00
Wind speed (m/s)
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