Advanced Optical Remote Sensing Technologies to Characterize and Quantify Fugitive Emissions from Refineries In the South Coast Air Basin

Technical Report

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Executive Summary

BACKGROUND

      In September-October 2015, the South Coast Air Quality Management District (SCAQMD) conducted a comprehensive two months study at different refineries in the South Coast Air Basin (SCAB) to characterize and quantify total facility-wide Volatile Organic Compounds (VOCs) emissions using Optical Remote Sensing (ORS) technologies. Atmosfir contributed to this comprehensive study by deploying a D-fenceline system to measure fluxes and concentrations of VOCs continuously (24/7) for four weeks at the fenceline of a refinery tank farm area. The D-fenceline system uses a monostatic, open-path Fourier Transform Infra-Red (OP-FTIR) instrument and multiple retro-reflector mirrors. For this part of the experiment, other contractors participating in the project also conducted emission flux measurements of the same tank farm. Fluxsense conducted mobile Solar Occultation Flux (SOF) measurements at the same refinery as well as at all other refineries in the SCAB. National Physical Laboratory (NPL) operated their Differential Absorption Lidar (DIAL) for one week at the same tank farm. This report presents the results and findings of Atmosfir's portion of the SCAQMD study.

EXPERIMENTAL SETUP AND DATA ANALYSIS

      Figure E1 shows the measurement configuration at the refinery fenceline. The OP-FTIR instrument was installed on an auto-positioner inside a weather-proofed trailer positioned just inside the perimeter of a refinery tank farm. The trailer (yellow square in Figure E1) was also equipped with a weather station. Four retroreflectors were positioned along the fenceline of the facility (labeled north to south M2, M1, M4 and M5 in Figure E1), and the fifth reflector was placed inside the tank farm, nearly perpendicular to the fenceline (see label M3 in Figure E1). The OP-FTIR installation covered approximately 800 m, which is almost the entire length of the tanks farm western boundary. Mirrors 4 and 5 were elevated to create a modified Vertical Radial Plume Mapping (VRPM) beam configuration for direct emission flux calculation on this part of the refinery's fenceline. The distances from the OP-FTIR and heights of the retro-reflecting mirrors are listed in Table E1. Mirror 1 was at the top of a light pole and mirrors 2 and 3 were at the metal staircase of the storage tank.
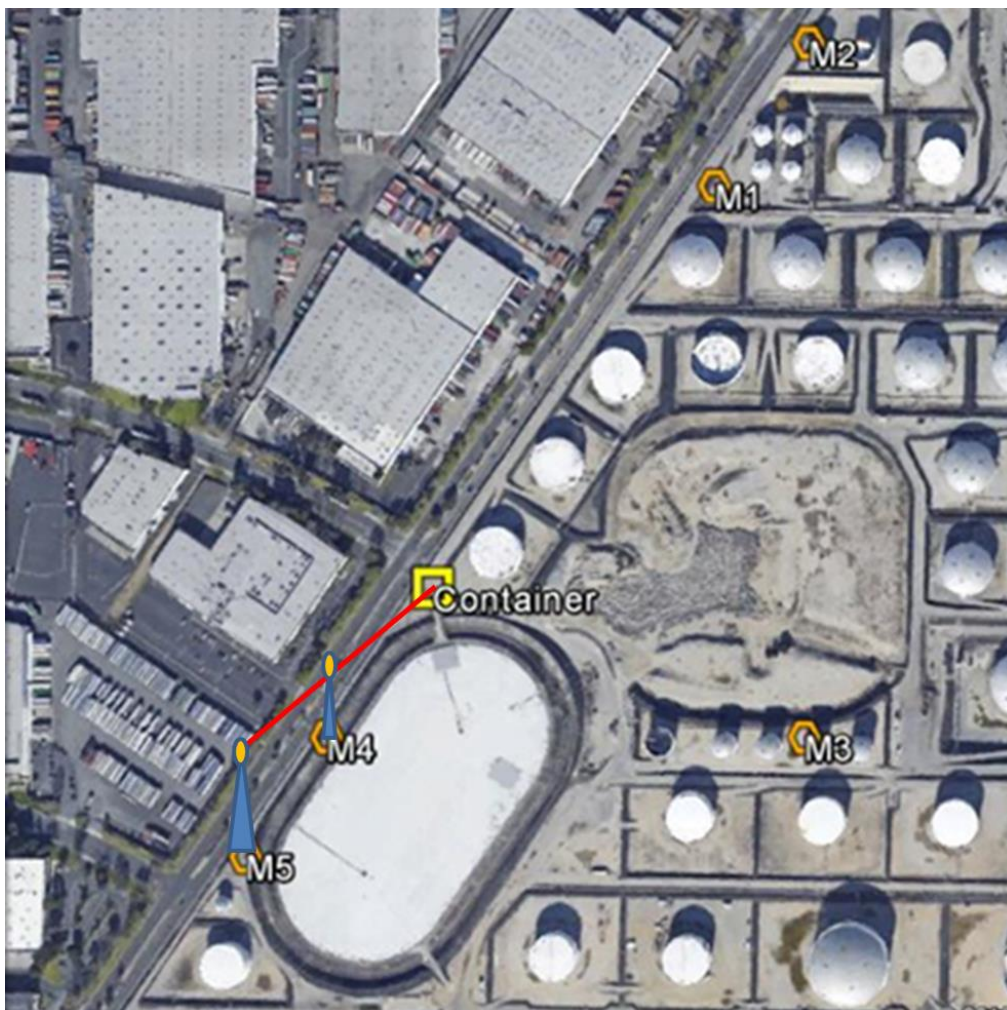
Figure E-1 D-fenceline beam configuration layout.

Table E1 – Distances from the OP-FTIR to the Retroreflectors.

|	M1	M2	M3	M4	M5
Pathlength [m]	400	538	330	147	262
Height [m]	15*	15*	15*	6	10

*estimated height above horizontal direction

The OP-FTIR sequentially scanned to the 5 mirrors. The dwelling time on each mirror was approximately one minute, completing the cycle to the five retroreflectors in less than six minutes. Thus, concentrations of pollutants and emission rate measurements were updated every six minutes. Measurements were performed continuously (24/7) for two 2-week periods (09/25/2015 – 10/09/25015

and 10/15/2015 -10/29/2015). From 10/12/2015 to 10/13/2015 Atmosfir's D-fenceline system participated in a controlled release experiment that was also a part of SCAQMD's funded study.

RESULTS AND DISCUSSION

Figure E2 presents the average total alkane mixture (AM) emission rates measured during six separate time periods during this study. While the average emission flux for the entire study was approximately 40 kg/hr, emission fluxes varied significantly throughout the measurement periods. The lowest average flux of 26 kg/hr was measured from October 06 to October 09, 2015, and the highest average flux of 47 kg/hr was measured between October 15 and October 19, 2015. The second study period (September 29 through October 10, 2015) represents the time when the DIAL and SOF systems performed their detailed short term emission measurements and was characterized by the second largest average flux (45 kg/hr).
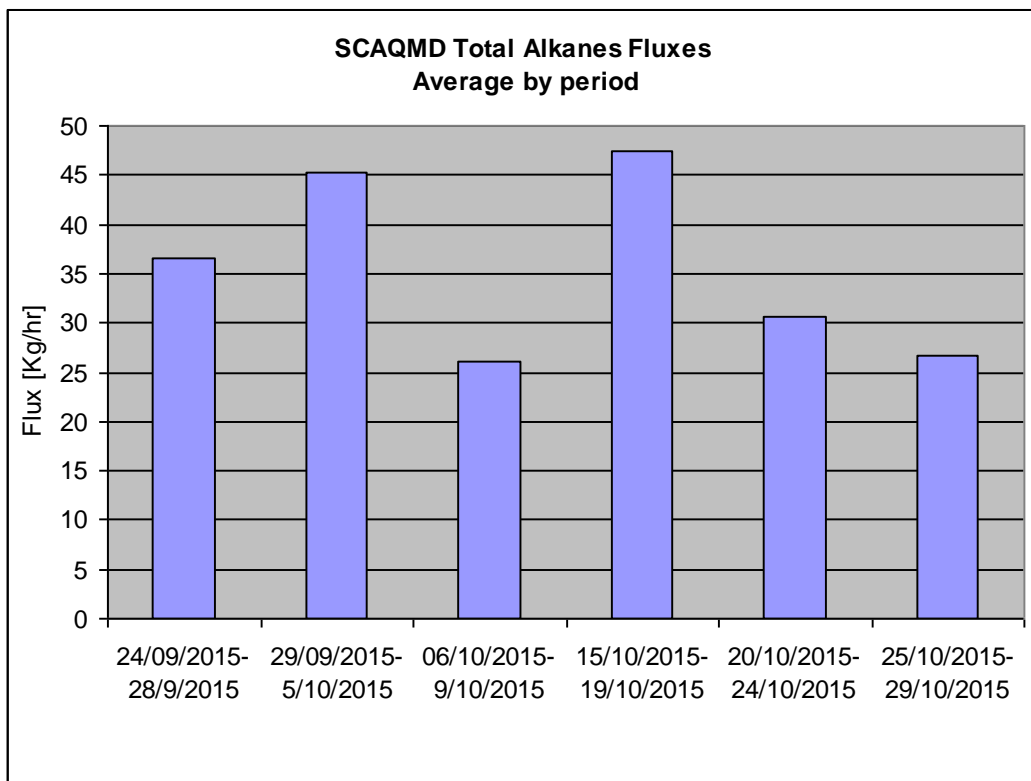
Figure E2 – Total AM average emission rates by period.

Unlike the DIAL and SOF, the D-fenceline system was able to conduct daytime and nighttime measurements and to provide emission data also for time-periods when the DIAL and SOF were not operating. Study-averaged total AM emission fluxes (typical 24-hour average) are presented in Figure

E3. The emission flux averages calculated for daytime, between the hours of 10:00 am through 04:00 pm (here referred to as "Operating" time), and for nighttime, between the hours 4pm through 10 am (here referred to as "Non- Operating" time) are presented in Figure E3 (these hours were chosen according to the actual operating time of the DIAL and SOP). These averages show slightly lower emissions during the "Operating" hours and suggest that emission fluxes extrapolated from "Operating" (10:00 am to 04:00 pm) observations may only be slightly over estimated with respect to daily (24-hr) emissions (6% maximum).
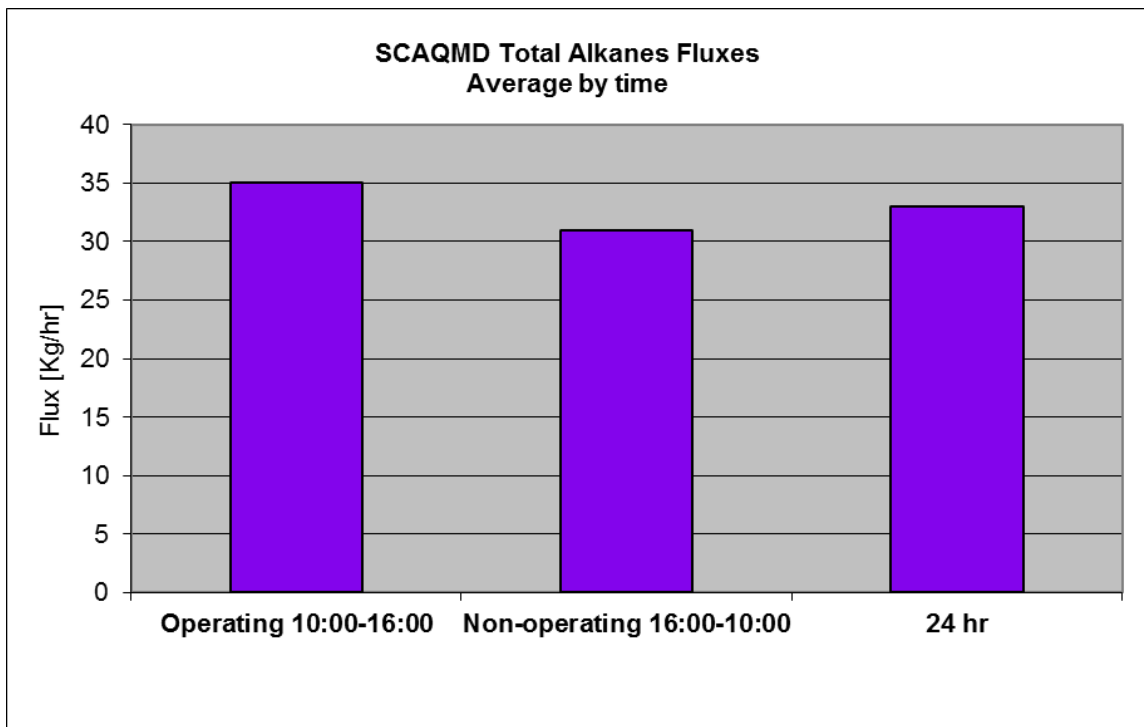
Figure E3 – Total AM average emission rates by time of the day.

A similar emission rate analysis was performed for methane and is presented in the full report. Methane emission rates diurnal and long term trends did not always correlate with total AM trends, suggesting that methane and AM may not necessarily be emitted from the same sources(s).

On October 05, 2016 the D-fenceline system was able to detect fugitive emissions from a leaking tank inside the refinery. The data showed that both total AM and methane where emitted from the same source (Tank 16). This leak episode was monitored until and after it was resolved and was also observed by the SOF and DIAL technologies. The strong correlation between total alkanes and

methane observed during this event is probably caused by the use of methane as a "blanket" gas in the identified leaking tank (information provided by site personnel).

In addition to measure total AM fluxes, the advanced OP-FTIR technology deployed by Atmosfir was able to reliably measure, with real time spectral validation, a wide range of compounds including benzene and other aromatic hydrocarbons. When detected, typically during calm atmospheric and low wind speed conditions, hourly benzene levels at the fenceline were about 13 ppb. It is impossible to derive emission information from such low frequency and low wind speed data. Typical minimum quantification limit (MQL) for benzene was around 3 ppb. Two more compounds were detected at low frequency, m-Xylene and p-Xylene. Also in this case, hourly concentrations for these two compounds were only detected at low wind speed and were about 6 and 7 ppb, respectively. Typical MQL for m-Xylene and p-Xylene was around 2 ppb for both. Toluene and o-Xylene were measured more frequently and their average hourly concentrations when detected were about 14 and 6 ppb, respectively. Typical MQL for toluene and o-Xylene was 4 and 2 ppb respectively. Generally, aromatic compounds were present at very low hourly concentrations at the facility fenceline. Acetylene and ethylene were detected frequently at very low levels of around 1 ppb.

CONCLUSIONS AND OUTLOOK

During this study, Atmosfir's D-fenceline OP-FTIR system automatically and continuously (24/7) measured fenceline concentrations of pollutants at a refinery fenceline for four weeks. Multiple compounds important for air quality and photochemical smog formation were measured simultaneously demonstrating that OP-FTIR is well-suited for long-term fenceline monitoring. In addition to fenceline concentrations, emission fluxes of total alkanes and methane were calculated using the OP-FTIR and modified VRPM methodology. The resulting emissions accounted for fluxes crossing the lowest 15 meters of the refinery fenceline (corresponding to the approximate elevation of the highest retro-reflector). Thus, although these fluxes are indicative of overall refinery emissions and can assist with assessing long-term variability, they are likely to under-estimate total emissions. This information is helpful when translating emission data collected during short-term ORS emission studies by SOF and DIAL technologies to annual emissions.

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1. Introduction

Optical Remote Sensing (ORS)Technologies have been used for measuring total Volatile Organic Compounds (VOC's) and other air toxics' emissions since late 1980's. Typically, these studies were short term (about a month) and provided a clear picture that a large portion of the refinery's VOC emissions are left unaccounted in the annual emission inventory reporting. However, one may argue that measurements from these short term flux studies may not be extrapolated to calculate long term annual emission rates, and that short term results do not take into account process and season changes throughout the year. This created the need to develop a monitoring approach for tracking such long term variations and calculate more accurately the annual total emission rate. Such model was initially outlined in 2010 and later adopted in 2011 in the EPA's Optical Remote Sensing Handbook[1]. Figure 1 illustrates the synergy between short and long-time measurements in order to achieve reliable long term emission monitoring and efficient emission reductions. The base of this triangle is the continuous fenceline monitoring, such as open path FTIR (OP-FTIR) technology, which can put the results from the detailed short term emission studies, such as differential absorption lidar (DIAL) and solar occultation flux (SOF) technologies, in context of annual emission measurements. Furthermore, the OP-FTIR D-fenceline monitoring can provide critical information needed to guide emission reduction efforts: 1. when the emission event occurs; 2. what the compound(s) emitted is; 3. where this compound comes from; and 4. how significant the emission event is.
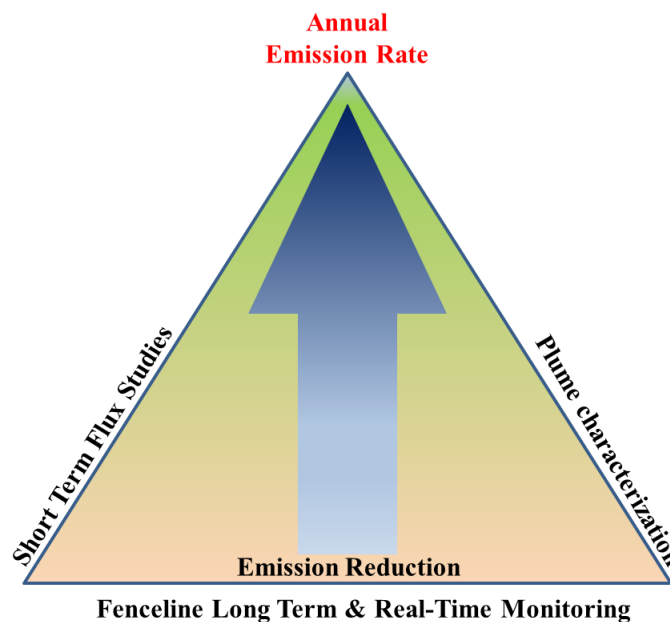
Figure 1 – Schematic triangle for emission long term monitoring and emission reduction.

In September-October 2015 the South Coast Air Quality Management District (SCAQMD) conducted a comprehensive five-week study at different refineries in the South Coast Air Basin (SCAB) to characterize and quantify total facility-wide VOCs emissions using ORS technologies. To our knowledge, the current study was the first one to conduct simultaneous observations using multiple ORS technologies, therefore allowing to put emissions derived from short-term measurements conducted by Fluxsense and National Physical Laboratory (NPL) into context of long term emission monitoring using D-fenceline system. Fluxsense used a SOF technique on a mobile platform to measure emissions around all major refineries in the SCAB. During the same study NPL operated their DIAL technique for one week to provide detailed VOCs emission data in the tank farm area of a selected refinery. During that week, the SOF system collected emission data in the same area as the DIAL conducted its emission data collection. Similarly, Atmosfir used a monostatic, OP-FTIR instrument and multiple retro-reflecting mirrors to measure continuous VOCs concentrations and fluxes in the vicinity of the same storage tank farm for a total period of four weeks including the week of the detailed data collection by the other two ORS technologies. Wind data was also collected as part of Atmosfir's D-fenceline configuration. This OP-FTIR technique has been thoroughly validated by the U.S. EPA[2,3,4]. It was used to complement the SOF and DIAL short term emission rate data and to demonstrate its applicability and efficiency as a year around 24/7 fenceline monitoring system for fugitive air toxics.

2. Measurement and Analysis Methods

2.1. Open Path FTIR

OP-FTIR is an accepted quantitative technique to measure gaseous air toxics and VOCs[2,3,4]. The OP-FTIR instrument passes infrared light along an open beam path to identify and measure any absorbing chemical in the beam path. The OP- FTIR used in this project was monostatic, where a single transmitter/receiver telescope transmits the IR beams to a corner-cube retro-reflector array that returns the respective beam back to the transmitter/receiver for detection and processing. Since most molecular vapors and gases are infrared active, the OP-FTIR sensors are capable of detecting and measuring a large number of atmospheric species and contaminants simultaneously including:

• Alkanes such as methane, and for example butane/octane as a total alkane mixture (OP-FTIR is not capable of speciating individual alkanes at the required low level concentrations);
• Aromatics including benzene, toluene, ethylbenzene and xylenes ("BTEX");
• Highly-reactive VOCs ("HRVOCs") such as ethylene and propylene; and
• Air toxics such as 1,3-butadiene, formaldehyde, and styrene.

2.2. Spectral Analysis

OP-FTIR spectra are analyzed using a multi-variant regression fit to quantitatively calibrated spectra to determine the path-integrated concentrations of any absorbing gas. Most of the IR spectral references were created by Pacific Northwest National Laboratory ("PNNL") in collaboration with the National Institute of Standards and Technology ("NIST"). Recent advancements in OP-FTIR data processing developed by Atmosfir Optics allow for reliable, real-time analysis and presentation of multiple pollutant concentrations along with real time QA/QC procedures such as spectral validation. These spectral validation images also demonstrate the unprecedented low detection levels (unique to Atmosfir Optics proprietary algorithm) which increase the reliability of the measurement with OP-FTIR monitoring technology. The analysis was done using the time-averaging method (TAM), which is a real-time technique for determining concentration averages at lower detection limits using averaging several spectra over a longer period than the data collection period[5]. The method can produce significantly lower instrument detection limits. For the emission analysis, a moving time averaging method of 5 single beam spectra was used to generate the sample averaged single-beam spectrum. Each of the resulting data points therefore represents average concentration for the last five scans and is updated with every scan. For the air quality TAM analysis, the sample single beam spectra were averaged for an hour and data was reported every 15 minutes. For the background single beam spectrum, the most recent averaged single beam with no target compound present in it was used. Since the background single beam spectrum is updated constantly, the TAM algorithm has the property of quantifying automatically the fast fluctuating near source plumes and screening out the slow changing background (or constant in case of methane, carbon dioxide, and nitrous oxide). Therefore, all concentrations considered for the emission analysis in this emission study are background subtracted and (with wind direction data) may be attributed to the nearby target emission source.

The next step involves performing a Classical Least Squares analysis on the averaged absorbance spectrum created from the sample and background averaged single-beam spectra. The resulting concentration determination is the time-averaged result, and the detection limit is determined from the standard error of the regression fit as described in TO-16[4].

The advanced OP-FTIR technology was demonstrated to measure reliably, with real time spectral validation, a wide range of compounds in unprecedented sensitivity including benzene and other aromatics. Figure 2 shows an example of the detection-validation feature in Atmosfir's software package. In this measurement, o-Xylene was detected in the path to M5 with a concentration of 2.1ppb. The detection limit for this particular measurement was 1.04 ppb.

o-Xylene | M5 | 10/24/2015, 13:10:55 | 2.07ppb | MQL: 1.04 | Path-Length: 262m
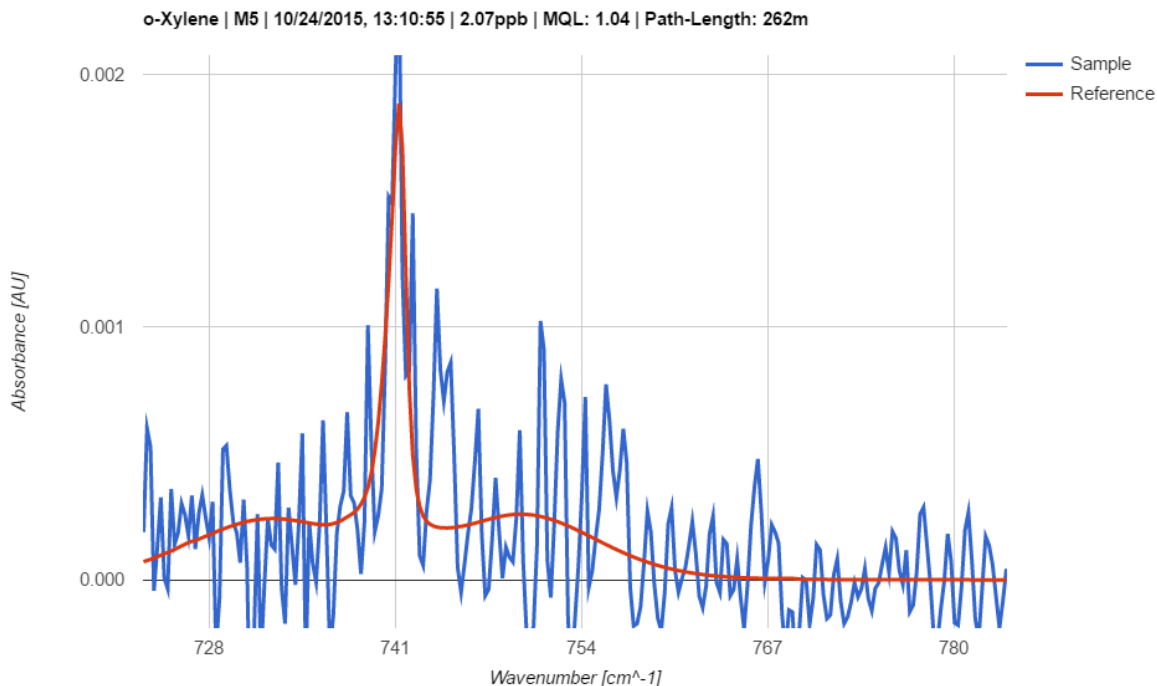
Figure 2 - Example of spectral validation of o-Xylene at 2.1 ppb.

2.2.1. Total Alkanes Mixture

In the infrared region absorption features of many hydrocarbon species in the C-H stretch region are relatively similar. For the n-butane to n-octane series, the similarity is greatest between the components with consecutive carbon numbers (e.g. butane and pentane) and the similarities decrease for components with greater difference in carbon numbers (e.g. C-4 and C-8, butane and octane). The overlapping absorptions and the similarity in band shapes of these and other hydrocarbons with significant C-H stretch signal makes it impossible to determine the concentration of the individual compounds of the mixture in the classic least squares (CLS) regression fit of measured absorbance. Consequently, US-EPA has developed and validated an analysis procedure for total alkane mixture (AM) using OP-FTIR technique[5,7]. The central assumption of the AM procedure is that the complex mix of hydrocarbons emitted from the source can be approximated by the previously described two-component estimation which utilizes for example n-butane and n-octane as bounding surrogate pair. This procedure provides total AM concentration and equivalent molecular weight which allows the conversion to mass concentrations and subsequently to mass fluxes of total AM. The procedure and its validation are described in details in Appendix A5 and in Appendix F6 in references 5 and 7 respectively. The total AM concentration C_V(Total AM) by volume (in ppb v) is simply the sum of the two surrogates' volume concentration $C_V(A_1)$ and $C_V(A_2)$, e.g. C_V(nButane) and C_V(nOctane) as the two surrogates in most previous studies. The equivalent molecular weight (EMW) is required for conversion

of the concentration by volume C_V(Total AM) to concentration by mass C_M(Total AM). The EMW is given by:

$$EMW = \frac{C_V(A_1)MW(A_1) + C_V(A_2)MW(A_2)}{C_V(Total\ AM)}$$ (Equation 1)

Where $MW(A_1)$ and $MW(A_2)$ are the molecular weights of the two surrogates in g/mol. The total AM mass concentration C_M (Total AM) in $\mu g/m^3$ is given by:

$$C_M(Total\ AM) = \frac{C_V(Total\ AM) \times EMW}{24.5}$$ (Equation 2)

In previous studies[5,7] n-Butane and n-Octane were chosen as the bounding surrogate pair for various petroleum based emission sources. As a part of this study, tests were conducted to determine the appropriateness of use of this pair for the monitored area in the refinery. The results of this test confirmed that n-Butane and n-Octane are the most suitable Total AM surrogate pair with the least mass residuals in the CLS fit and presented in section 4.3.1 of this report.

The three spectral validation images given in Figure 3 demonstrate the combined reconstruction of absorbance spectrum for different equivalent molecular weight plumes crossing the OP-FTIR beam from various sub-areas of the monitored refinery.

The three total alkanes mixture (63 g/mol, 73 g/mol, and 92 g/mol EMW respectively from top to bottom) spectral validation images presented in Figure 3 were collected on the same path on 10/05/2015 at different times of the day when wind direction was different or the emission rate of the various type of sources was changing during the day. In addition to the spatial and wind information collected by the D-fenceline monitoring system (multiple paths), the information on the equivalent molecular weight of detected hydrocarbon mixture can be used to identify and localize the emission or leaking source.
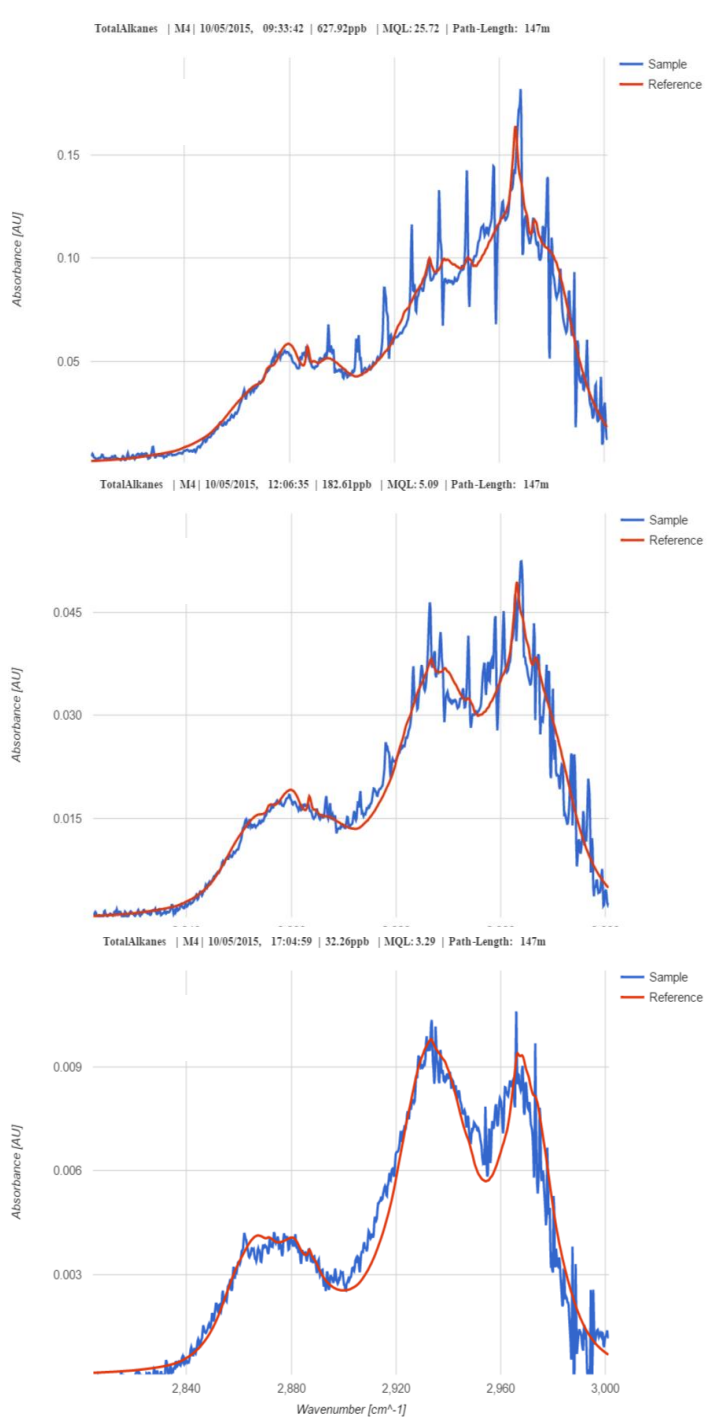
Figure 3 - Three total alkanes mixture spectral validation images collected on the path on 10/05/2015 (a) 63 g/mol (b) 73 g/mol (c) 92 g/mol EMW.

2.3. Emission Rates Calculation Methods

2.3.1. Vertical Radial Plume Mapping

In order to conduct long-term measurements of emissions from the part of the refinery, Vertical Radial Plume Mapping (VRPM) method was employed, as outlined in U.S. EPA Other Test Method 10 (OTM-10)[6]. The Radial Plume Mapping method (RPM) was developed at the University of Washington in the mid-1990s. The method uses positional scanning or multiple single beam-path open path instruments to collect path-integrated concentration data along multiple beam paths in the configuration deployed in the survey area. The beam paths can be configured in a vertical plane deployed downwind of the survey area (VRPM methodology) to map the downwind plume from the site. By including meteorological data collected concurrently with the ORS measurements, the VRPM methodology can be used to calculate the downwind emission flux from the site. This leads to a direct, measurement-based estimate of the emission rate from the survey area. A more detailed discussion of the RPM methodology and of the VRPM configuration can be found in EPA's OTM-10[6]. This method has been validated in controlled-release studies sponsored by the EPA and the U.S. Department of Defense.

Several different beam configurations of the VRPM methodology are recommended. The minimum required is two mirrors, one of which should be on the ground defining the full length of the setup, and one on the vertical structure. However, site limitations forced us to use a slightly modified VRPM methodology. The modified VRPM includes two beams shining in about the same direction where the long beam is directed to a mirror on tall tower (about 10 meters in this study) and the short beam is directed to a mirror at about half the height and about half the distance. The measurement is therefore divided into two segments and the ratio between the path-averaged concentration at the far and elevated segment and concentration at the near less elevated segment are calculated for each concentration determination. A ratio larger than 1 indicates a poor vertical plume capture, presumably due to elevated sources located upwind from the measurement plane. Normally, poor vertical plume capture leads to severe underestimation of emission flux. As a part of this study, a controlled-release experiment involving release of a known quantity of propane from elevated points was conducted. Data collected during the controlled-release was used to calibrate beam flux to a more accurate emission flux for the entire study. The tradeoffs between the traditional and modified VRPM beam configuration were evaluated in the controlled release study and is discussed in details in section 4.3.2 of this report.

A schematic for an example of a typical vertical-scanning experimental setup is presented in Figure 4. Multiple mirrors are placed on a vertical plane in line with the scanning open-path, path-integrated ORS instrument. The location of the vertical plane is selected so that it intersects the mean wind direction as close to perpendicular as is practical.
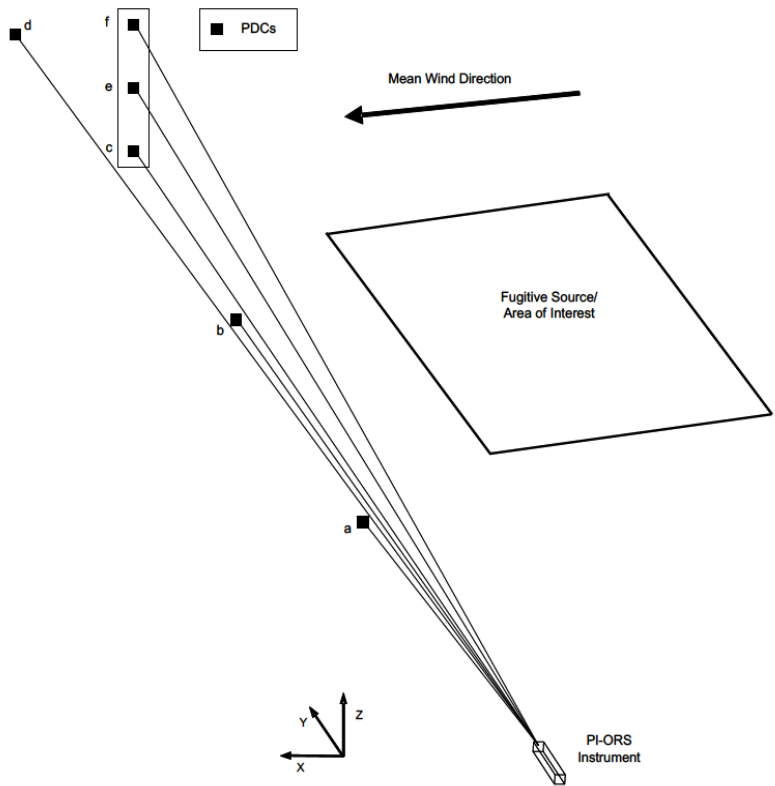
Figure 4 – Example of a VRPM configuration setup.

The VRPM methodology produces an isopleth map of the chemical concentrations on the vertical plane, from which an area-integrated concentration (AIC) is determined. The emission flux (Q) through the plane is equal to the product of AIC and the component of the wind speed normal to the measurement vertical plane.

2.3.1.1. Vertical Plume Capture

As described in earlier studies, the concordance correlation factor (CCF) was used to represent the level of fit for the reconstruction in the path-integrated domain (predicted versus measured concentrations). CCF is defined as the product of two components:

CCF =rA   (Equation 3)

Where:

r   =   the Pearson correlation coefficient;

A   =   a correction factor for the shift in population and location.

This shift is a function of the relationship between the averages and standard deviations of the measured and predicted concentration vectors. The Pearson correlation coefficient is a good indicator of the quality of fit to the Gaussian mathematical model. In this procedure, typically an r close to 1 will be followed by an A very close to 1. This means that the averages and standard deviations in the two concentration vectors are very similar and the mass is conserved (good flux value). However, when a poor CCF is reported (CCF<0.80) at the end of the fitting procedure it does not directly mean that the mass is not conserved. It could be the case where only a poor fit to the Gaussian function occurred if the correction factor A was still very close to 1 (A>0.90). However, when both r and A are low one can assume that the flux calculation is inaccurate.

In the controlled release study the CCF of the vertical beams was used for evaluation VRPM quality of fit and for assessment the vertical capture. In order to establish good vertical plume capture the concentration C_e of the elevated beam needs to be lower than the concentration C_g of the ground level beam just below. When $C_e<0.9C_g$ the VRPM was run directly and calculated CCF value of the vertical beams is always 1. When $C_e>=0.9C_g$, the concentration of the elevated beam is forced to be equal to 90% of the concentration of the ground concentration ($C_e=0.9C_g$) before running the VRPM algorithm. However, the CCF is calculated with the original C_e and is degraded as the ratio C_e/C_g gets larger. When CCF<0.9 the Ce is approaching the value of Cg and the plume is defined as not captured vertically and flux value is not included as valid. This CCF criteria is more conservative than recommended in OTM-10 (CCF<0.8) however we decided that CCF values between 0.8 and 0.9 represent times of poor vertical plume capture and is defined in this study as not valid fluxes.

2.3.1.2. Horizontal Plume Capture

The horizontal plume capture is typically evaluated by plotting the VRPM fluxes as a function of wind directions (on both sides of the normal to the VRPM plane) for the whole study period[8,9,10]. Then linear regression is performed separately on each side of the normal and the resulted linear equations are used to adjust the VRPM calculated fluxes to actual emission rate from the upwind source.

2.3.2. Emission Rate by Beam Flux method

Beam flux is defined as the calculated flux through the beam width of about 0.25 meters. It is the product of the mass path integrated concentration and the wind speed component normal to the beam direction. This value is multiplied by the beam vertical width and presented in emission rate unit like Kg/hr. Typically, we may use the beam flux method when we have a comparison between beam fluxes at a ground level beam and the corresponding emission fluxes measured in the vertical plane above the beam either by well-designed VRPM methodology or other ORS methodology such as DIAL

or SOF. The slope of a linear regression line in such comparison provides the long term conversion factor between beam fluxes at the fenceline and emission rate crossing that fenceline. In this study we did not have a desired vertical plume capture in the modified VRPM plane (the segment ratio is much larger than 1). Therefore correction factor derived from the data collected in the controlled release study was used to derive a reliable conversion factor despite the poor vertical plume capture.

3. Field Configuration

The Atmosfir Optics' trailer equipped with OP-FTIR, auto-positioner, and wind monitor was positioned just inside the perimeter of a refinery fenceline, and on the west side of the facility. The trailer was connected to the internet via air card and all raw spectral and wind data was transferred in real time to Atmosfir's dedicated server for further analysis and system real-time monitoring.

Figure 5 – Pictures of Study Field Setup.

3.1. Instrumentation

The OP-FTIR instruments used during testing were the Bruker OPS provided by Bruker Optics Germany. The Bruker OPS is an active monostatic OP-FTIR technology that uses light from a silicon carbide glower within the monitor to project a modulated infrared light beam to a retro-reflector. The retro- reflector directs the modulated beam back to a mercury cadmium telluride detector within the monitor. The projected infrared beam is modulated by a Michelson interferometer that allows for elimination of contributions from any stray background source of infrared light. The return signal is analyzed for absorbed frequencies that act as fingerprints for any chemical species present. The OP-FTIR measures path average absorbance of infrared light in the range of 700 to 4,000 cm^{-1}. The auto-

positioner was manufactured by EVPU Systems, Slovakia. The R.M. Young Model 32500 wind monitor was located on the trailer at 7.5 m height. The wind monitor was purchased with EPA calibration certificate a month before the field study, and field calibration in accordance to the instrument manual instructions was conducted prior to use.

3.2. D-fenceline Configuration

Figure 6 depicts the orientation and dimension of the D-fenceline configuration in relation to the refinery's storage tanks. The general azimuth direction of the beams 1 and 2 (M1 and M2) from the container is about 35^0. The azimuth of beam 3 (M3) is about 120^0 and the azimuth of beams 4 and 5 (M4 and M5) is about 215^0 and are the modified VRPM configuration.
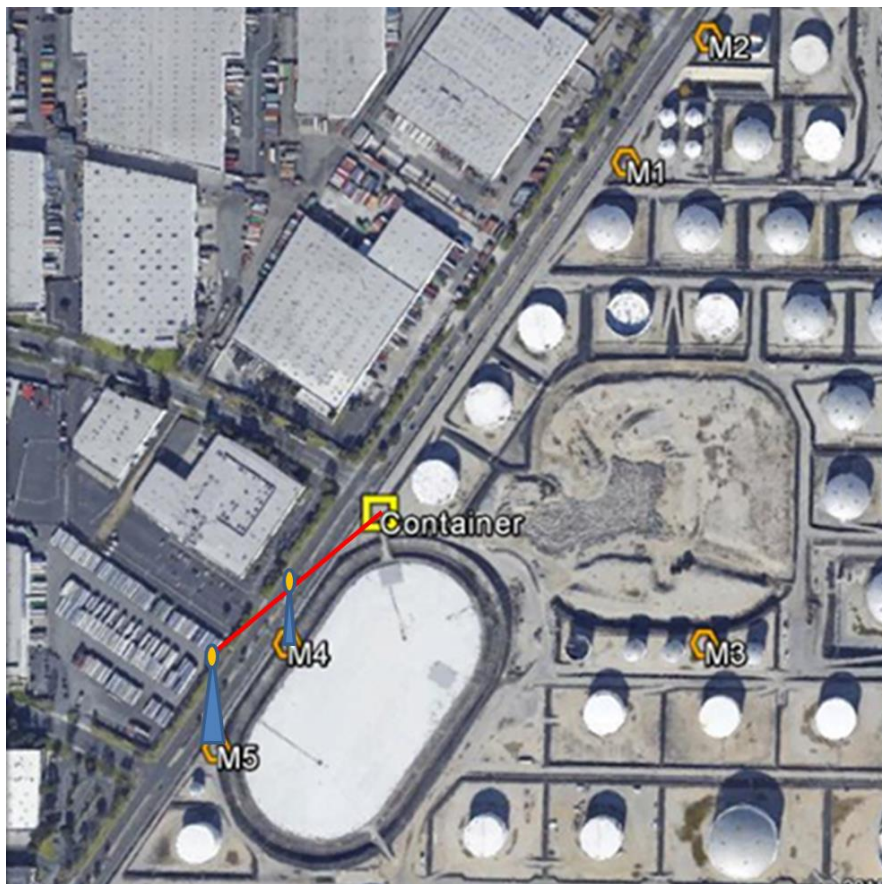
Figure 6 – D-fenceline beam configuration layout.

Table 1 Provides distances to each of the mirrors and heights of mirrors 4 and 5 that are part of the modified VRPM beam configuration. Mirror 1 was at the top of a light pole and mirrors 2 and 3 were

at the metal staircase of the storage tank. Exact heights are not available and the height information for these mirrors is not included in the flux calculations.

Table 1 – Dimensions of field configurations

	M1	M2	M3	M4	M5
Line length [m]	400	538	330	147	262
Height [m]	~15*	~15*	~15*	6	10

*estimated height above horizontal direction

This configuration is also in accordance to the 1-D radial plume mapping methodology in EPA OTM-10 test method[6].

3.3. Data Collection

The OP-FTIR system scanned among the 5 mirrors continuously 24/7 for two 2-week periods (09/25/2015 – 10/09/25015 and 10/15/2015 -10/29/2015). The six day break was for participating in the controlled release study with other groups in the project's team. The dwelling time on each mirror was approximately one minute completing a cycle over the five-beam configuration in less than six minutes (including time between mirrors). The concentration determinations for the flux calculations are with moving average (TAM) procedure of five cycles and therefore concentration and emission rates data represents approximately the last 30-minute intervals updating every 6 minutes.

4. Results and Discussion

We applied our quantification algorithm on many compounds and determined that only total AM and methane were suitable for emission analysis as they originated from the source area and were sufficiently and frequently (10 times as recommended in OTM-10 repeated whenever the wind direction was from the source) above their minimum quantification levels (MQLs) of about 2 ppb and 4 ppb for total AM and methane, respectively. However, a number of other compounds that were detected originated for the source area (see Table 2). Examples of spectral validation images for all compounds detected from the source are given in Appendix 1.

Table 2 below summarizes the other spectrally validated measured compounds with hourly air quality TAM. A complete dataset has been provided to SCAQMD in a separate data package with the final report.

Benzene levels were very low and it was very rarely detected typically at low wind speeds. It is impossible to derive emission information from such low frequency and low wind speed data especially during night time and early morning. Two more compounds were detected at low frequency, m-Xylene and p-Xylene. Toluene and o-Xylene had many more hits. Generally, the aromatics had very low hourly concentrations on the facility fenceline. Acetylene and ethylene were detected frequently at very low levels around 1 ppb and high sub–ppb very low typical MQL.

Table 2 – Summary of spectrally validated measured compounds

Compound	Number of measurements**	Average Concentration [ppb]*	MQL [ppb]	Minimum Determination [ppb]	Maximum Determination [ppb]
Benzene	11	12.5	3.2	4.6	20.8
Toluene	236	14.4	3.8	2.8	81.0
o-Xylene	603	6.4	1.7	1.3	51.7
m-Xylene	34	5.7	1.9	2.5	25.2
p-Xylene	29	7.2	2.6	1.9	34.0
Acetylene	802	1.22	0.38	0.18	9.6
Chlorodifluoromethane	68	0.57	0.11	0.12	2.9
Ethyl Acetate	5	5.2	0.46	3.9	7.3
Ethylene	682	1.38	0.45	0.35	195.0
Propylene	9	4.15	1.08	1.87	5.8

* Average of measurements when detected above the MQL

** Maximum possible measurements = 2700

Sulfur dioxide and nitrogen dioxide were not detected at all and their typical MQL was 2 ppb. All of these compounds are close to their MQL and typically were detected at very low wind speeds during night time and early morning. This does not allow retrieving the sources and their strengths using these low level data.

Figure 7 provides time series of the total AM 6(a) and methane 6(b) concentrations for the first 2-week period on beam path 3. These graphs show also time series of wind directions for the same period on a secondary y-axis. It is apparent that there is some correlation between the two compounds, although that is not always the case. When we have good correlation the concentration spike is originated from sources (e.g. storage tanks) that contain both heavy alkanes and methane. Many storage tanks contain very little methane and this information may help differentiating between sources if the site operator has prior information on tanks content.
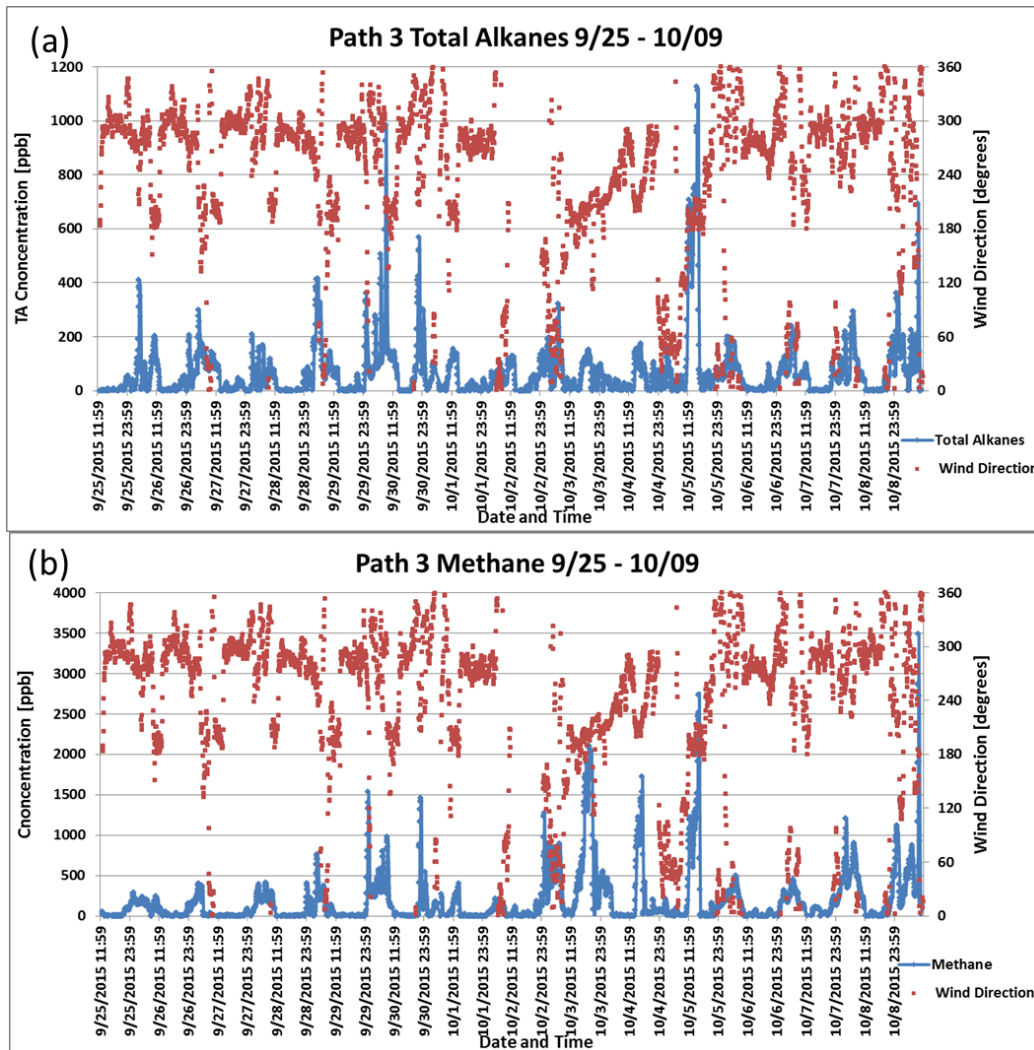
Figure 7 - Time series of the (a) total AM and (b) methane concentrations for the first 2-week period on beam path 3.

4.1.   Example of an Emission Event

Figure 8 shows a time series of a case study for an emission event on October 05, 2015 which was detected and monitored by the D-fenceline system until and after it was resolved. The graphs show that both total AM and methane are emitted from the same source in this event. Elevated AM (see Figure 3 (a) for equivalent molecular weight of this emission event) and methane concentrations were monitored on beam paths 4 and 5 (path 5 not shown) at 9 am when wind direction was from the southeast. At around noon wind direction shifted to the south causing high AM and Methane concentrations to be monitored on beam path 3. At 4:30 pm the facility found the source and terminated this event. This emission source was not detected again at these flux levels for the rest of this demonstration study. This leak event was also observed by the SOF and DIAL technologies. The strong correlation between total alkanes and methane in this event is due to the use of methane as a "blanket" gas in the identified leaking tank (information given by site personnel).
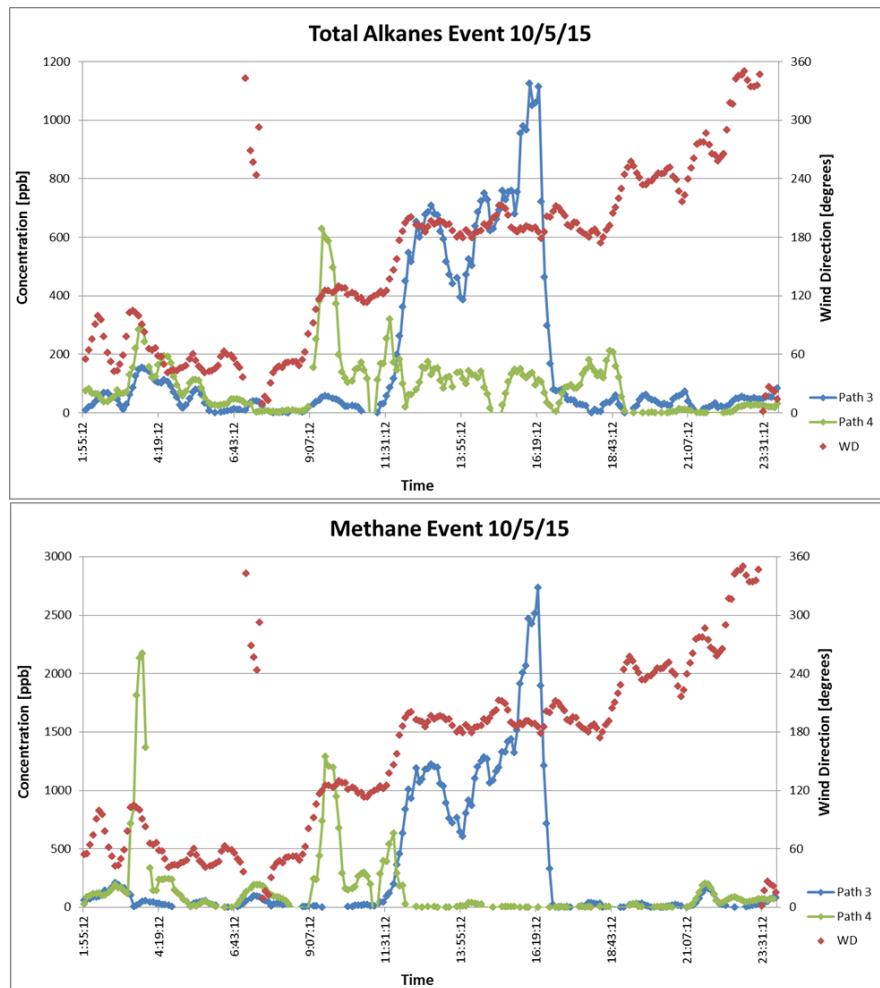
Figure 8 - Time series of (a) the total AM and (b) methane concentrations on beam paths 3 and 4 on 10/05/2015.

4.2. Emission Rate Results

Unadjusted fluxes crossing the facility fenceline were calculated along paths 2 and 5 using mixing height parameter retrieved from the modified VRPM configuration as described in the method section. The sum of these fluxes at any given time represented the minimum total unadjusted flux crossing the 800 m of fenceline (see Table 1). In order to provide an assessment of the horizontal plume capture by the D-fenceline configuration, the project team initially analyzed the calculated total AM flux values for prevailing wind direction, with respect to the orientation of the beam configuration plane, at the time of the measurements. For the horizontal plume capture analysis only total AM flux values during periods when the prevailing wind direction was within ± 90° of perpendicular to the plane of the D-fenceline configuration (wind direction 125°) were considered.

Total AM is the primary target compound of this study as it makes the majority of the VOCs mass emitted from a refinery source. The initial assessment was done by plotting the calculated AM flux values as a function of prevailing wind direction, as depicted in Figure 9.

Figure 9 - Linear regressions of unadjusted total AM flux values for calculating emission rates.

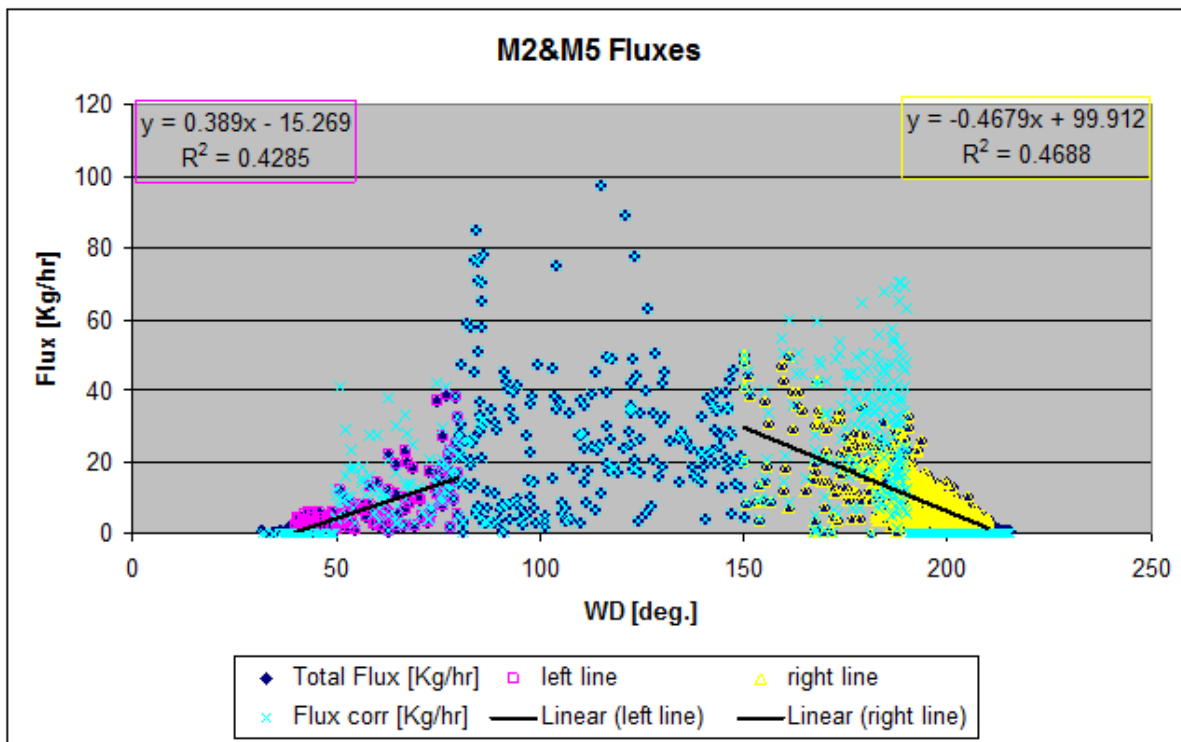As one may observe from the above plot of unadjusted flux values versus wind direction, the linear drop in flux values as the absolute angle from the normal gets larger does not begin in the perpendicular to the measurement plane. Therefore, we excluded the middle range wind directions from the linear regression process and evaluated the conversion factor to emission rates on each side data (yellow and pink markers) separately. After the linear regression was performed on both sides (darker blue unadjusted flux data in Figure 9), each unadjusted was corrected by the slope and y-intercept to retrieve the minimum adjusted total emission rate crossing the D-fenceline configuration (light blue markers in Figure 9).

In addition to the emission rate values crossing the D-fenceline beam configuration (paths 2+5) the project team has looked the sum of fluxes crossing path 3 from the northeast and from the southwest (in order to calculate the same area as the M2+M5 line calculation).The hypothesis was that this independent approach for calculating the total minimum emission rates should provide slightly lower absolute emission rate (path 3 is only 330 m) and follow over time similar trend of emissions.

Table 3 and Figure 10 provides the average emission rate values along beam 2 and 5 (800 m) of the facility fenceline in six time periods of the long term fenceline portion of the study. Measured AM fluxes varied between 26 and 47 kg/hr for different time periods. For comparison only (we did not have modified VRPM configuration along path 3) we also present the average emission rate values crossing from both side of the beam 3 for the same six periods of the long term fenceline portion of the study. The detailed emission study by the DIAL and SOF technologies was performed mostly during the second period in Figure 10.

This period had second highest emissions based on modified VRPM measurements (see Table 3). This can be explained by a couple of leaks detected by ORS technologies and resolved immediately by the facility (the underground leak discovered by the SOF, and in the leak from tank 16 that was detected by all three ORS technologies; see section 4.1 for details).

Table 3 – Summary results of total AM emission rates

SCAQMD
Total Alkanes

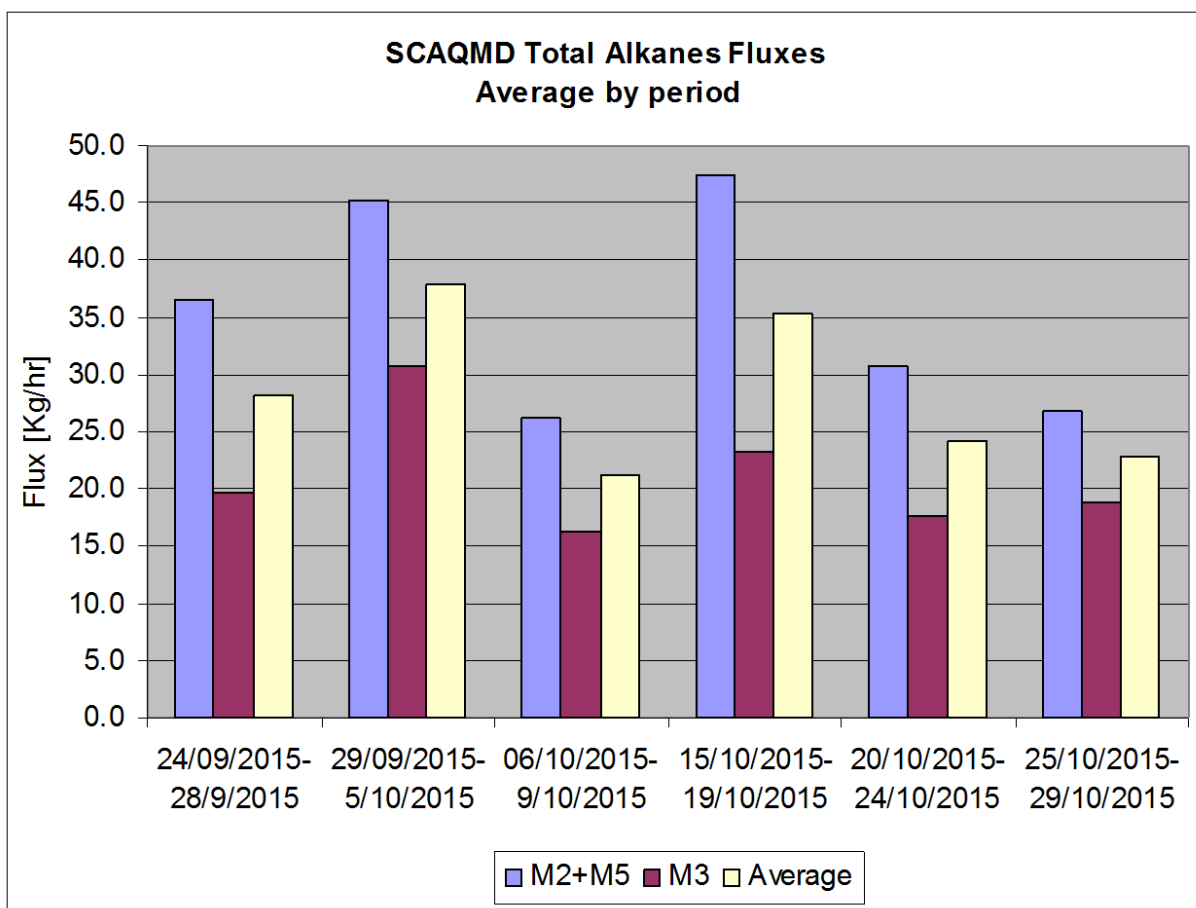| By Period	M2+M5	M3	Average
	Flux [Kg/hr]	Flux [Kg/hr]	Flux [Kg/hr]
24/09/2015-28/9/2015	37	20	28
29/09/2015-5/10/2015	45	31	38
06/10/2015-9/10/2015	26	16	21
15/10/2015-19/10/2015	47	23	35
20/10/2015-24/10/2015	31	18	24
25/10/2015-29/10/2015	27	19	23
All periods	39	28	33

Figure 10 – Total AM emission rate by period in the two independent approaches.

The continuous (24/7) fenceline monitoring also can capture diurnal variations in relative emissions and, therefore, scale the short term detailed daytime only emission rates accordingly. Table 4 and Figure **11** provides average total AM emissions data separated by two time periods. The first time period, designated "Operating" represents period in between 10:00 -16:00, which was typical measurement time for the DIAL and SOF systems. The second time period, designated "Non-Operating", corresponds to the rest of the time period between 16:00 and 10:00 of the following day. For comparison, the emissions from the entire period of measurement for the whole day are also presented (actual 24 hr) and a 24 hour time weighted average calculated from the two periods of the day.

Diurnal relative emissions are important for the extrapolation to annual emission rates of emissions measured in short term studies with day only systems (SOF and DIAL). In our study emissions measured by the modified VRPM between hours of 4pm and 10am were about 15% lower than emissions measured between 10am and 4pm. This corresponds to 6% overestimation in daily (24-hour) alkane emissions when using only the "Operating" (10am and 4pm) data.

Methane is another target compound of this study as it is a potent greenhouse gas emitted from a refinery source. It is important to mention that only the OP-FTIR technology provided direct emission data for methane. As for the total AM, the initial assessment was done by plotting the methane flux values as a function of prevailing wind direction, as depicted in see Figure 12.

Table 4 – Toatl AM Emisson rate by time of the day calculated by two independent methods

Total Alkanes

Diurnal period	M2+M5 Flux [Kg/hr]	M3 Flux [Kg/hr]	Average Flux [Kg/hr]
Operating 10:00-16:00	42	28	35
Non-operating 16:00-10:00	37	26	31
actual 24 hr	39	28	33
24 hr time weighted average	38	27	32
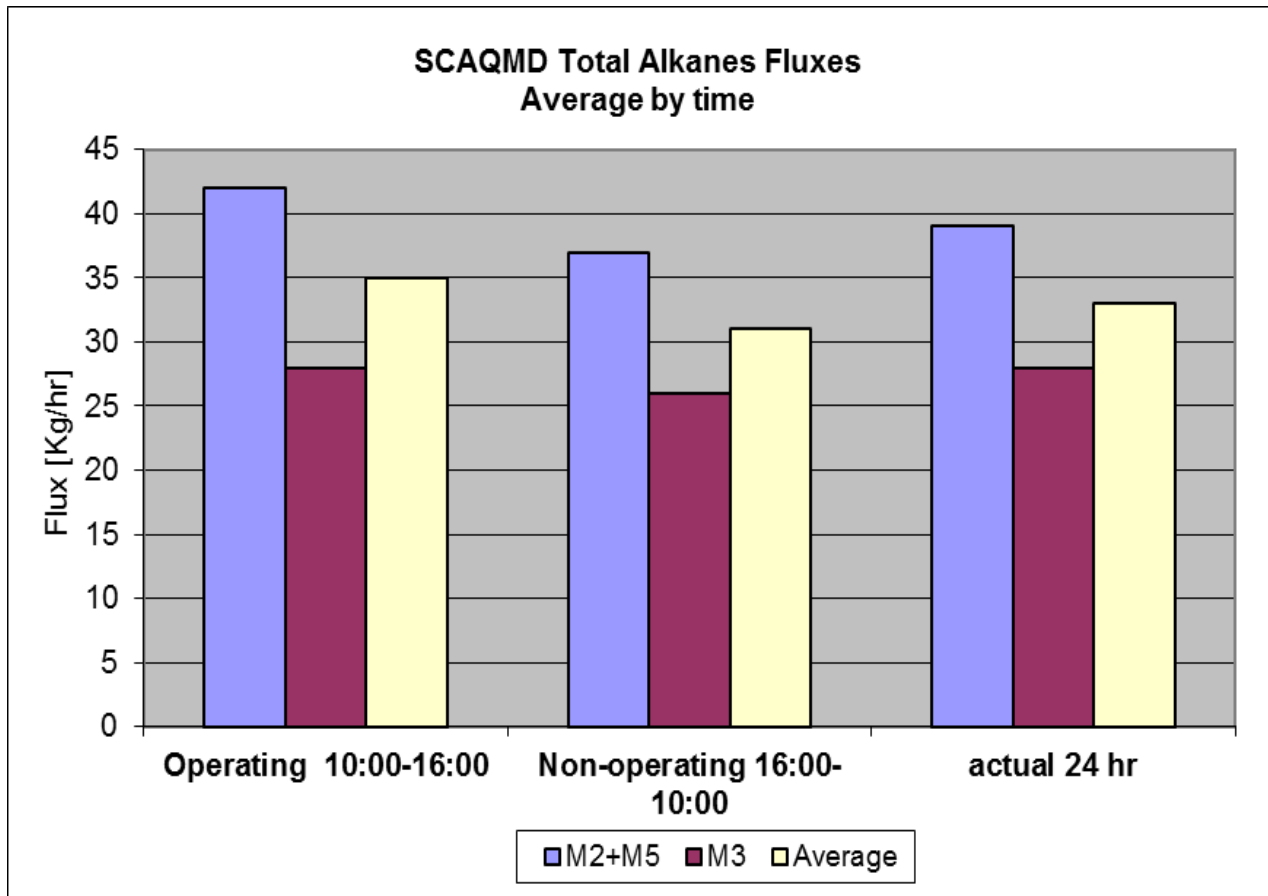
Figure 11 – Total AM average emission rate by time of the day.
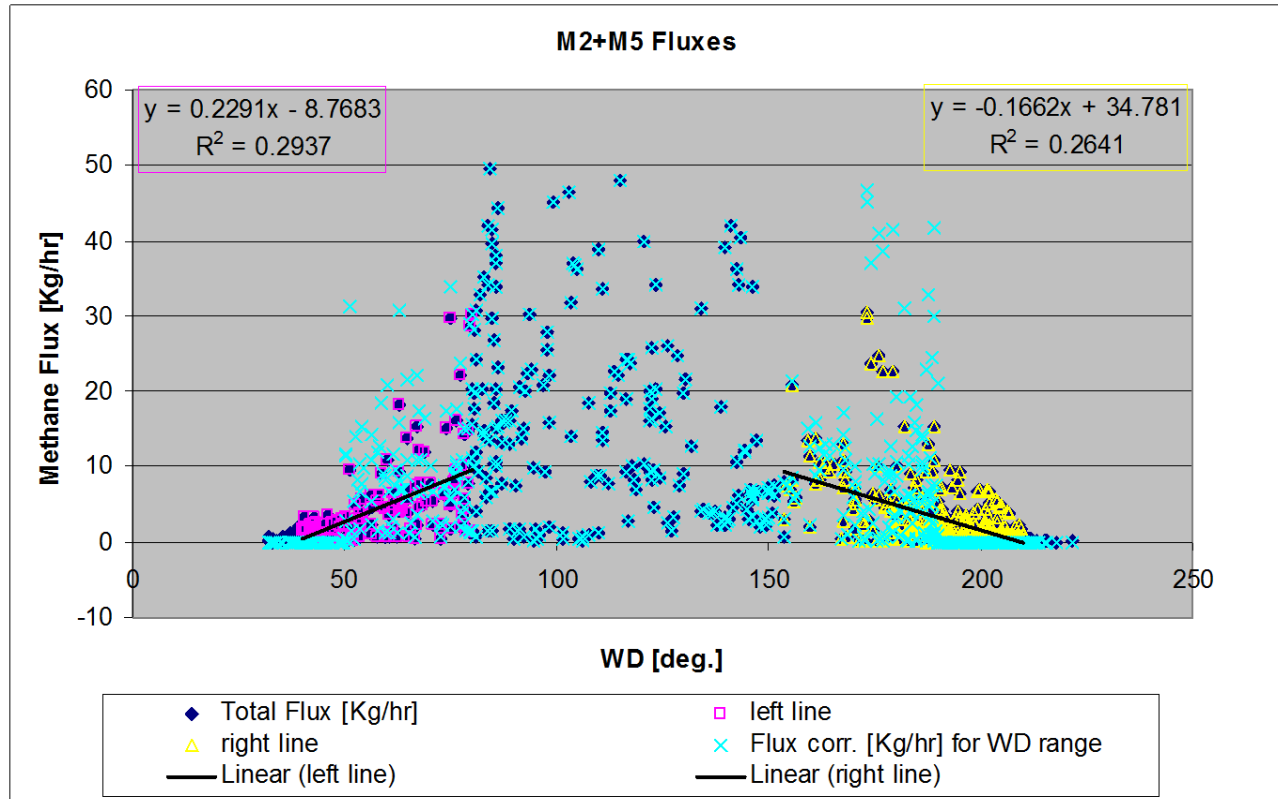
Figure 12 - Linear regressions of unadjusted methane flux values for calculating emission rates.

Table 5 and Figure 13 provides the average emission rate values along beam 2 and 5 (800 m) of the facility fenceline in six periods of the fenceline portion of the study. Similarly to total AM, we also present the average emission rate values crossing from both side of the beam 3. Again, it is important to mention that the detailed emission study by the DIAL and SOF technologies was performed mostly during the second period in Figure 13. However, the SOF did not measure direct (only inferred with extractive FTIR) flux data for methane and the DIAL was not tuned to methane detection in this study. Like in the total AM case, this period had the second highest emissions as derived from modified VRPM.

Methane emissions measured by OP-FTIR did not correlate with total AM emissions. Furthermore, the correlation between the two independent methods of calculating emission was poorer for methane than for total AM. This may indicate inhomogeneous in time and space of the methane emissions compared to total AM emissions.

Table 5 – Summary results of methane emission rates

SCAQMD Methane By Period	M2+M5	M3	Average
	Flux [Kg/hr]	Flux [Kg/hr]	Flux [Kg/hr]
24/09/2015-28/9/2015	9	4	6
29/09/2015-5/10/2015	19	28	24
06/10/2015-9/10/2015	10	14	12
15/10/2015-19/10/2015	1	2	2
20/10/2015-24/10/2015	22	7	14
25/10/2015-29/10/2015	17	20	18
All periods	18	25	21
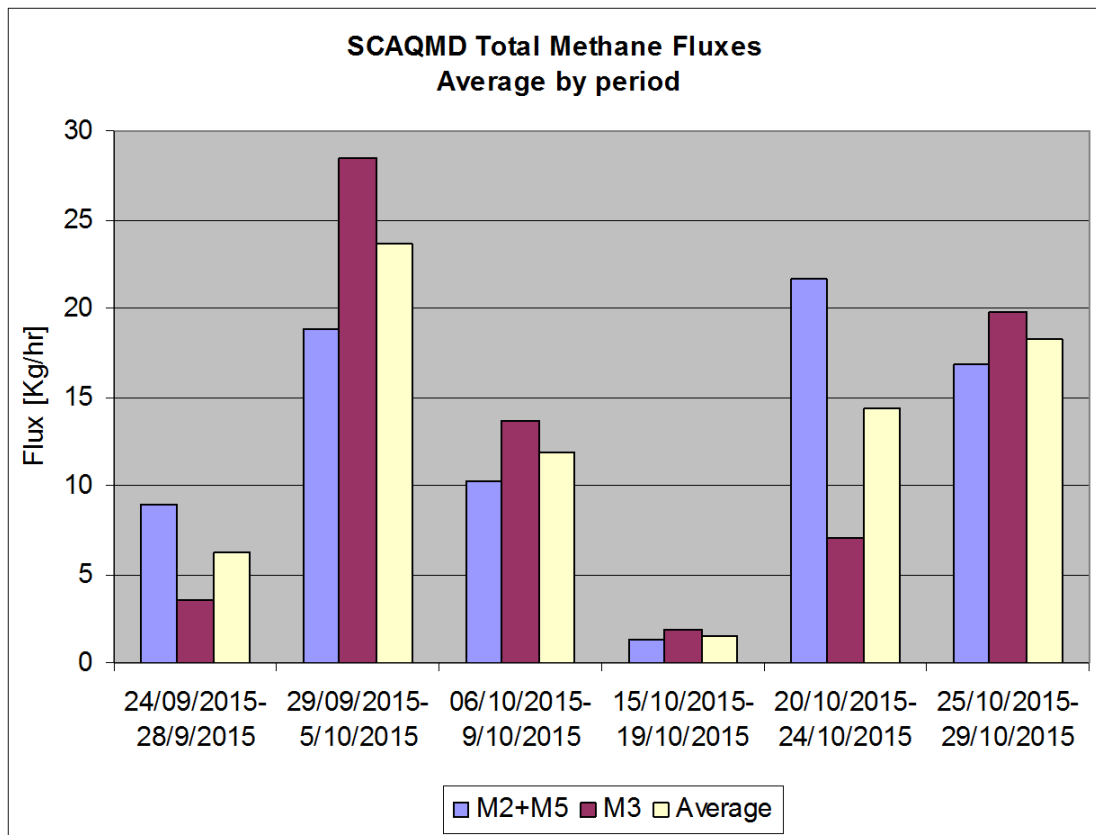
Figure 13 - Methane emission rate by period in the two independent approaches.

Table 6 and Figure 14 present methane emissions data separated by two time periods (as described in the alkanes section above).

Table 6 – Methane emission rate by time of the day calculated by two independent methods

Methane

Diurnal period	M2+M5	M3	Average
	Flux [Kg/hr]	Flux [Kg/hr]	Flux [Kg/hr]
Operating 10:00-16:00	10	17	14
Non-operating 16:00-10:00	23	33	28
actual 24 hr	18	25	21
24 hr time weighted average	20	29	25
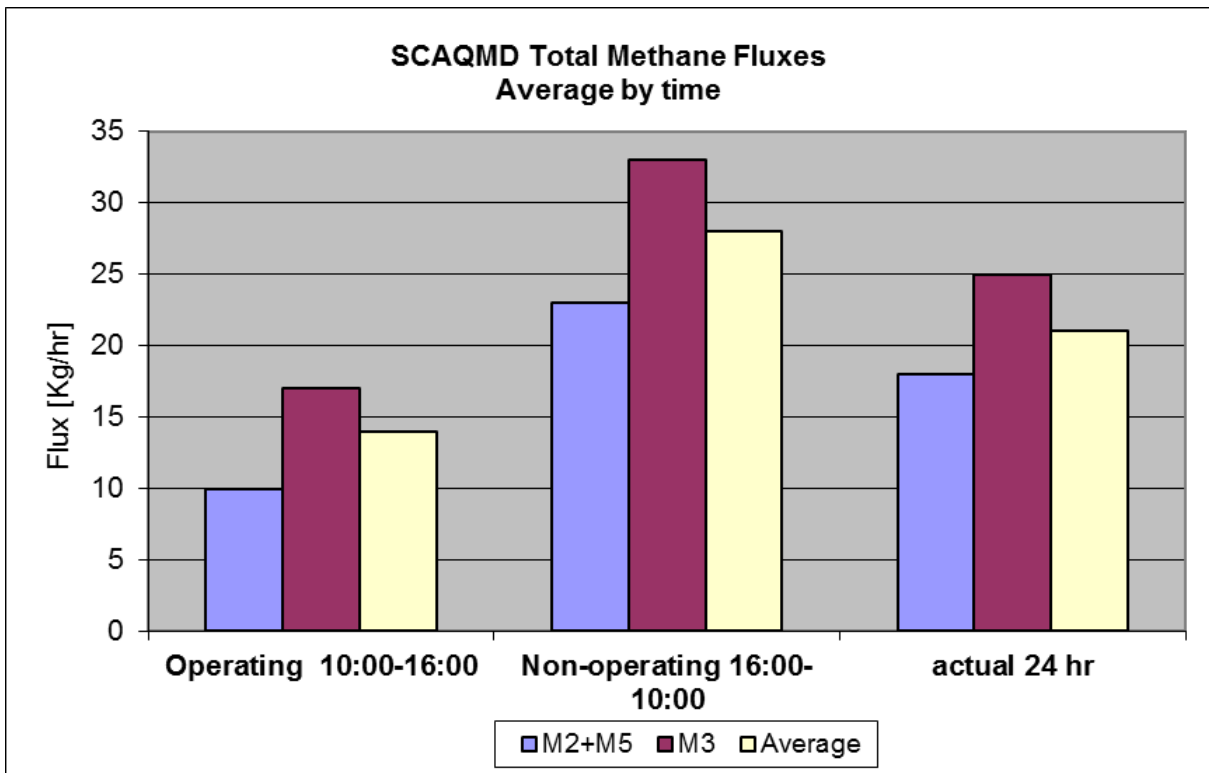
Figure 14 – Methane average emission rate by time of the day.

Unlike the total AM emissions from the "Non-Operating" period which were slightly lower than the "Operating" emissions, the methane emissions from the "Non-Operating" period (4pm to 10 am) were more than twice the methane "Operating" emissions. This corresponds to about 33% underestimation in daily (24-hour) methane emissions when using only "Operating" data. This was a surprising result and may be associated with the inhomogeneous spatial and temporal distribution of methane sources in the tank farm area.

4.3. QA/QC

4.3.1. OP-FTIR

Atmosfir's OP-FTIR analysis algorithm generates automatically spectral validation for every concentration determination. This compares the measured absorbance with normalized (by resulted concentration) reference absorbance measured in known concentration and this is in essence the best performance based calibration of each determination reported.

US EPA TO-16 method recommends using nitrous oxide determinations as a calibration of the OP-FTIR. Table 7 summaries the average determinations of all valid spectra collected in this study. These results are good mostly because we use nitrous oxide CLS analysis on each one minute spectrum to invalidate poor quality spectra before performing CLS analysis for the study target compounds.

Table 7 – Nitrous Oxide QA/QC

		M1	M2	M3	M4	M5
Average	ppb	320.011	319.993	320.001	319.993	320.001
Std	ppb	1.026	1.239	1.284	1.246	1.525
Precision	%	0.321	0.387	0.401	0.389	0.477
Accuracy	%	0.003	-0.002	0.0003	-0.002	0.0003

In Table 8 we present the average mass concentration (in $\mu g/m^3$) of total AM and average error as reported by the CLS algorithm for two assumed pairs associated by wind direction to the area emission source.

Table 8 – Comparison results for total AM surrogate pairs

Pair	Total AM Average Concentration	Total AM Average Error	Error/Concentration
	g/m^3	g/m^3	%
n-Butane & n-Octane	1274	20	1.6
n-Pentane & n-Nonane	1433	60	4.2

As one can observe the relative and absolute residual mass as expressed by the error is far smaller for the n-Butane and n-Octane surrogate pair. This is the reason that all total AM concentrations, fluxes, and emission rates in this study were measured using n-Butane and n-Octane as the surrogate pair.

4.3.2. Controlled Release Results

Atmosfir participated in the SCAQMD controlled release study in order to evaluate the suitability of a simplified 2-beam VRPM configuration to capture short-term emissions on a facility fenceline. Based on numerous previous controlled release studies, we recognized the following limitations of the VRPM setup:

1. VRPM configuration (when not elevated enough) is designed to measure emissions originating from near ground sources.
2. The VRPM method consistently underestimates the true emissions when wind speed is near the lower boundary of the allowed range by OTM-10 of 1 to 2 m/s.
3. The VRPM methodology performs far better for long term release studies rather than short-term releases because the horizontal plume's capture can be corrected using a large dataset of measured fluxes.

To overcome these challenges, during the controlled-release experiment, we increased the speed of the data collection by a factor of 3 in order to obtain a larger dataset of measured fluxes.

Since we could not apply the traditional VRPM at the refinery, Atmosfir designed a hybrid beam configuration of a 2-beam VRPM configuration and a modified VRPM configuration. The objective of the

modified VRPM configuration is to find a conversion factor between the beam flux and the true flux from elevated sources as a function of segments' ratio in the controlled release study.

4.3.2.1.   Evaluation of the VRPM Methodology

The 2-beam VRPM configuration was 180 meters long where the ground level beam was at approximately 1 m high above the pavement and the elevated beam was at 1 m at the OP-FTIR end and 10 m high at the top of a scissor lift on the far end of the VRPM configuration. The controlled emission source of propane was about 50 m away to the west from the measurement plane and at 3 m high above the ground. The azimuth of the VRPM configuration was 345^0 and therefore the wind directions were perpendicular to the vertical plane at 255^0. Atmosfir tried to produce flux calculations for higher source elevation runs but these run could not produce a required negative vertical gradient of concentrations. Table 9 below provides the results of the 5 valid runs (source height at 3 m) for evaluation of the VRPM study as reported about a month after the study took place.

Table 9 – Reported Controlled Release Results

Local Start Time	Local Stop Time	Release Altitude [m]	Average Wind Speed [m/s]	Average Wind Direction [degrees]	Average Release Rate [kg/hr]	STDEV Release Rate [kg/hr]
13:02	13:56	3	1.2	253	3.0	0.8
14:00	14:55	3	1.8	235	6.1	1.7
15:00	15:58	3	1.5	240	10.8	2.4
16:00	16:45	3	1.2	294	0.6	0.1
10:44	11:43	3	3.3	212	11.7	1.0
11:47	12:40	6.4	VRPM NA	VRPM NA	VRPM NA	VRPM NA
12:48	13:41	7.9	VRPM NA	VRPM NA	VRPM NA	VRPM NA
13:43	14:38	7.9	VRPM NA	VRPM NA	VRPM NA	VRPM NA
14:44	15:39	7.9	VRPM NA	VRPM NA	VRPM NA	VRPM NA
15:44	16:29	7.9	VRPM NA	VRPM NA	VRPM NA	VRPM NA
16:34	17:16	3	4.2	229	18.8	2.6

Figure 15 demonstrates the different performance in the two days of the controlled release study due to the difference in atmospheric stability between the two days. This is very consistent with past findings that the VRPM methodology underestimate in unstable atmospheric conditions (low wind speeds), especially in short-term releases (up to an hour) when there is not sufficient information to

perform plume capture corrections. Over several hours of constant release the VRPM methodology becomes independent of the atmospheric stability condition and performs typically within 10% of the true release rate.
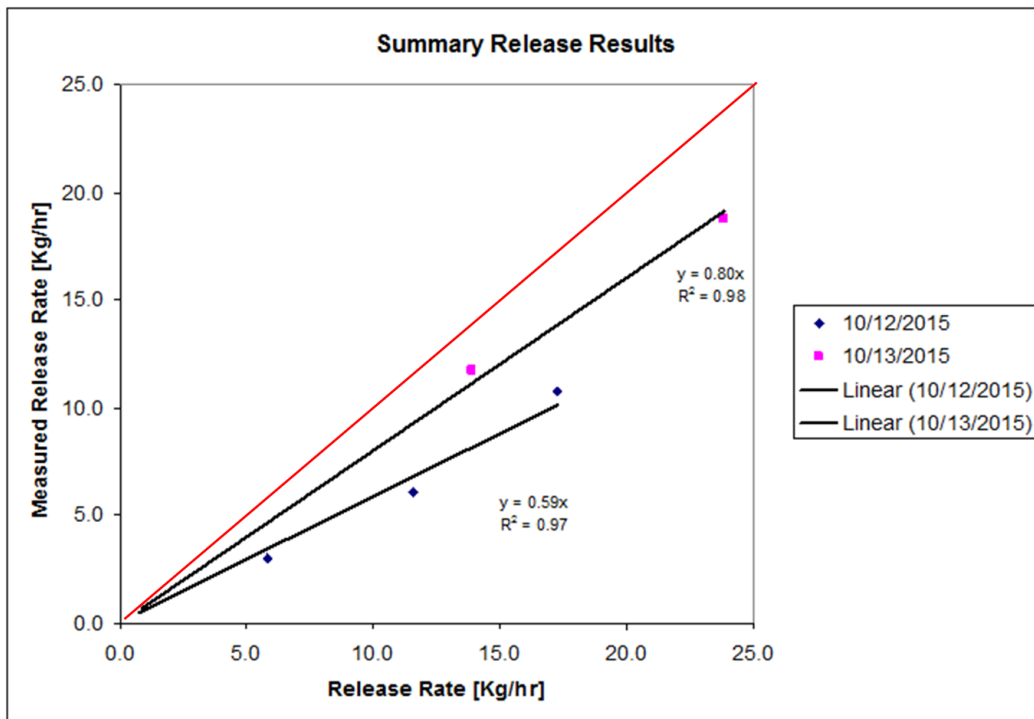

Figure 15 – VRPM performance in the short-term an elevated release study.

4.3.2.2.   Beam Flux Conversion to Flux

Atmosfir used the runs of the elevated sources in the controlled releases study to retrieve conversion factor between beam flux and estimated emission flux crossing the facility fenceline. This multiplicative conversion factor is proportional to an estimated mixing height depends on the beam width in the beam flux calculations. We calculated the ratio of the true emission to the normalized beam flux (by source strength in each run) and plotted these values against the modified VRPM segment ratio (see figure 16 below). The segment ratio is simply the propane concentration of the elevated segment over the propane concentration of the ground segment. As the average ratio on the facility fenceline was above 4, the conversion factor in this study was chosen to be 100 in all beam flux based flux calculations. This selected conversion factor represents a mixing height of constant concentration of 25 m considering that beam width was 0.25 m in the beam flux value determinations.
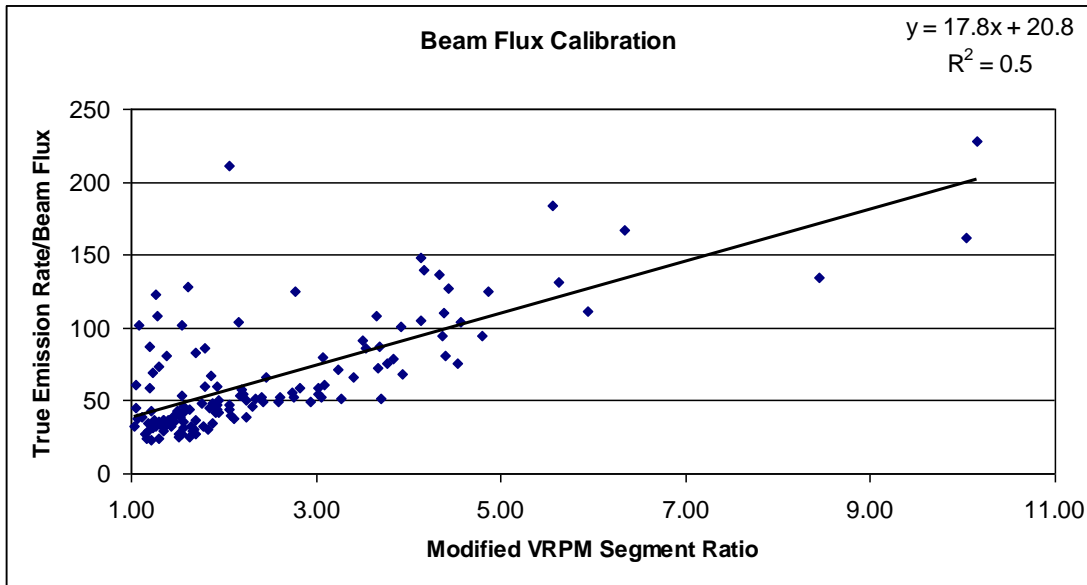
Figure 16 – Beam Flux Calibration graph for estimating a representative mixing height.

5. Conclusions

During this project, Atmosfir's D-fenceline OP-FTIR system automatically and continuously (24/7) measured fenceline concentrations of pollutants at a refinery fenceline for four weeks. Multiple compounds important for air quality and photochemical smog formation were detected during this measurement campaign along the fenceline of the refinery tank farm. Total alkanes and methane, other VOC's and aromatic hydrocarbons were also routinely observed at the tank farm fenceline. Overall, the hourly concentration of aromatic hydrocarbons was in line with what one would expect to find at the refinery fenceline. Benzene, m- and p-xylenes were very rarely detected, and typically observed only at low wind speeds. However, toluene and o-xylene were observed often, with average hourly concentrations when detected of 14.4 ppb and 6.4 ppb, respectively. Acetylene and ethylene were also frequently detected with average concentrations when detected of 1.2 ppb and 1.4 ppb, respectively. Sulfur dioxide and nitrogen dioxide were not detected above their typical OP-FTIR detection limit of 2 ppb.

In addition to fenceline concentrations, emission fluxes of total alkanes and methane were calculated using the OP-FTIR and modified VRPM methodology. The resulting relative emission accounted for fluxes crossing the lowest 15 meters of the refinery fenceline (corresponding to the approximate elevation of the highest retro-reflector). Thus, although these emission fluxes are indicative of overall refinery emissions and can assist with assessing long-term emission variability, they are likely to under-estimate total emissions. During this study, diurnal variations of total alkane

emissions observed by OP-FTIR suggest that estimates relying on day-time measurement (here defined as data collected between 10:00am to 04:00pm) may over-estimate daily (24-hour) emissions, but only by approximately 6%. In contrast, diurnal variations in methane emissions suggest that extrapolations from daytime-only (10:00am to 04:00pm) estimates may result in nearly 33% under-estimation of methane emissions.

In summary, this study demonstrated that OP-FTIR is well-suited for long-term fenceline measurements of VOCs with very little maintenance. Applying VRPM methodology to OP-FTIR fenceline measurements also provided information on diurnal variations of near-ground emissions. This information is helpful when translating emission data collected during short-term ORS emission studies by SOF and DIAL technologies to annual emissions.

6. References

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7. Appendices

Appendix I – Spectral Validation SCAQMD Report

Acetylene | M4 | 10/22/2015, 23:26:01 | 2.00ppb | MQL: 0.28 | Path-Length: 147m

Benzene | M1 | 10/06/2015, 06:29:22 | 12.65ppb | MQL: 7.62 | Path-Length: 400m

Chlorodifluoromethane | M4 | 10/02/2015, 06:53:56 | 2.84ppb | MQL: 0.18 | Path-Length: 147m

Ethylene | M1 | 10/09/2015, 00:40:44 | 1.25ppb | MQL: 0.48 | Path-Length: 400m

Methane | M3 | 10/27/2015, 14:40:19 | 83.98ppb | MQL: 8.18 | Path-Length: 330m

Methanol | M1 | 10/25/2015, 22:13:36 | 5.41ppb | MQL: 0.85 | Path-Length: 400m

m-Xylene | M4 | 10/24/2015, 23:40:58 | 2.53ppb | MQL: 1.69 | Path-Length: 147m

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o-Xylene | M5 | 10/23/2015, 10:58:34 | 4.52ppb | MQL: 1.54 | Path-Length: 262m

Propylene | M1 | 10/06/2015, 05:10:03 | 3.72ppb | MQL: 2.04 | Path-Length: 400m

p-Xylene | M1 | 10/19/2015, 11:28:14 | 6.29ppb | MQL: 5.76 | Path-Length: 400m

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