## Gaseous Emissions from Small Sources in the LA Basin measured by OP-FTIR

SCAQMD Request for Proposal #P2015-07 Project 2: Quantification of Gaseous Emissions from Gas Stations, Oil Wells, and Other Small Point Sources

Submitted to SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT 21865 Copley Drive Diamond Bar, California 91765

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### **EXECUTIVE SUMMARY**

During September and October of 2015, KASSAY Field Services, Inc. (Kassay) conducted a fiveweek field study to characterize and quantify emissions of volatile organic compounds (VOC) from gas stations, oil wells, and other small point sources in the Southern California Air Basin (SCAB). For this purpose, Kassay deployed an Open–path Fourier Transform Infrared spectrometer (OP-FTIR) to directly measure the VOC concentration downwind from each measured source. OP-FTIR data, combined with simultaneously collected meteorological measurements then served as an input for E-Calc reverse plume modeling software to calculate the emission rate for each source. All measurements were conducted from a mobile van that was stationed on public access roads and parking lots near the emission sources property lines. Kassay's OP-FTIR emission study was funded by the South Coast Air Quality Management District (SCAQMD), and was a part of the Optical Remote Sensing (ORS) project #2:"Quantification of Gaseous Emissions from Gas Stations, Oil Well, and Other Small Point Sources."

#### **OBJECTIVES**

The primary objective of the small sources study was to utilize various ORS techniques to accurately measure VOC emissions from small point sources such as oil wells, gas stations, and cattle farms, and other small emission sources in the South Coast Air Basin (SCAB). Additionally, VOC emission results generated by Kassay using OP-FTIR technology can be compared to emission results generated from other ORS methods. Kassay's ORS approach used OP-FTIR technology in conformance to United States Environmental Protection Agency (USEPA) Compendium Method TO-16 and emissions computations based on AERMOD modeling software developed by the USEPA. Additionally, since Kassay's hardware is mobile and software is automated, a secondary objective was to demonstrate the ease, practicality, and effectiveness of deploying this ORS technique on multiple small sources types. Ultimately, emission result generated by Kassay can be used to quantify actual emissions from the small sources in the SCAB and help the SCAQMD establish ORS monitoring guidelines.

#### **BACKGROUND**

Despite decades of pollution reduction, the SCAB still faces serious challenges in attainment of air quality standards. One of the keys aspects for improving air quality is to fully characterize and quantify emission sources. There are close to three thousand gasoline filling stations and as many oil wells in the SCAB. SCAQMD has a set of rules aimed to minimize emissions from such sources, but in actuality, magnitude of such emissions is highly uncertain. Two earlier studies conducted by SCAQMD demonstrated that ORS techniques have unique capabilities that allow to measure actual emissions from a variety of sources, and can supply results in near-real time. Therefore, In October of 2014, SCAQMD released a request for proposal (RFP #P2015-07) "Application and Development of Advanced Optical Remote Sensing Technologies to Characterize and Quantify Fugitive and Stack Emissions from Refineries and Other Sources." One of the projects covered by this RFP, Project #2, was to measure emissions from small point sources. In February of 2015, SCAQMD selected Fluxsense Inc. to be the primary qualified contractor for all projects listed in the RFP #P2015-07 solicitation. The review panel recommended that other contractors provide independent ORS measurements to compare with Fluxsenses measurements. Kassay was selected as one of the

independent contractors for the comparative measurements for Project #2. This report includes Kassay's monitoring results for Project #2 and supports SCAQMD's continued investigation of optical remote sensing (ORS) technology as it is applied to small emission sources.

Kassay approach relies on USEPA Compendium Method TO-16: "Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases," for the VOC concentration measurements. To calculate emission rates, Kassay used E-calc, a custom software package based on AERMOD. Since both TO-16 and AERMOD are tools recognized by the USEPA, Kassay's data can be considered a reasonable ORS technique to be used for inter comparison and validation of other ORS monitoring approaches.

For the past 20 years, Kassay has conducted numerous OP-FTIR monitoring projects for fence line monitoring, LDAR, regulatory compliance, and nuisance odor investigation. Kassay is also the supplier of the RAM2000 spectrometer which is distinguished as the only OP-FTIR instrument accredited through USEPA's Technology Verification Program (ETV). Kassay RAM2000 spectrometers have been employed on more than 20 projects with Gaussian dispersion models as well as Radial Plume mapping as described by OTM-10. More recently, Kassay has been working with Minnich & Scotto Inc. to deploy a turn-key software product called 'E-calc' that generates real time emission estimates based on the AERMOD. 'E-calc' is specifically configured to accept path integrated data that is generated by the RAM2000 OP-FTIR. For this project, the combination of the RAM2000 path-averaged concentration data and the E-calc reverse plume modeling software was used to calculate emissions from selected sources in the SCAB.

#### RESULTS AND DISCUSSION

During the study, Kassay conducted twenty eight (28) days of OP-FTIR measurements of three types of small sources in the SCAB: active oil wells, gas stations, and cattle farms. Some sites were visited more than once in order to better characterize the source, or to conduct co-located observations with the other ORS contractors. Although thousands of individual OP-FTIR measurement spectra were collected, only those with valid meteorological data were modeled for emission rates. In total, unique emission measurements were performed on seventeen (17) gas stations, sixteen (16) oil wells, and two (2) cattle farms. The following VOC's were measured during the study: methane, ethane, propane and other non-methane hydrocarbons (referred to as NMHC-balance, which includes the balance of all C2+ - C12+ species not already identified), ammonia, methanol and ethanol. Many other compounds were uniquely spectated, including aromatics such as benzene, toluene, and xylenes. Table ES.1 provides an overview of which types of sources were observed to emit which substances and observed magnitudes of these of emissions. Table ES.2 presents minimum detection limits (MDL's) for the target chemicals of interest for a typical small source based on 3-sigma determination. MDL's from each small source would vary depending on atmospheric conditions, beam path length, and interferences present.

	Summing of + 0 0 chassions rates ranges for the 0 soler (or small source 1)pes										
		Emission Rate Ranges (kg /h) for valid monitoring conditions									
QTY/	Ammonia	Benzene	iso-	n-	Ethane	Ethanol	n-	NMHC	Methane	Propane	Toluene
Туре			butane	butane			hexane	balance			
16 /	Not	0.044-	0.21 -	0.16 -	0.005-	0.008 -	0.076 -	0.015 -	0.013 -	0.26 -	0.0724 -
Oil	detected	5.7	9.9	14.6	5.3	2.8	23.1	16.5	16.3	23.3	4.6
Wells											
17 /	Not detected	Not	Not	0.018-	0.01 -	0.004 -	0.041 -	0.001 -	Not	0.014 -	0.099-
Gas		detected	detected	0.27	1.0	0.87	3.1	3.86	detected	0.6	2.79
Station											
2 /	5.3 -	Not	Not	Not	Not	Not	Not	Not	0.36 -	Not	Not
Cattle	11.2	detected	detected	detected	detected	detected	detected	detected	6.27	detected	detected
Farms											

 Table ES.1:

 Summary of VOC emissions Rates Ranges for the Observed Small Source Types

Table ES.2:

#### Typical Path Average Minimum Detection Limit (MDLs) for VOC's with OP-FTIR

	MDL*(ppm*m) for valid monitoring conditions									
Ammonia	Benzene	iso-butane	n-butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Propane	Toluene
							balance			
0.21	6.4	0.92	3.4	1.8	0.77	3.1	0.63	2.8	2.2	3.9

\* MDL determined using 3-sigma value of CLS processing results from representative data set

Overall, for all observed types of small sources and for all pollutants, measured emission fluxes varied by orders of magnitude. Emissions measured from each source also showed large temporal variations. Emissions of all targeted chemicals listed in Table ES.1, except ammonia, were observed from oil wells sampled during the study. Magnitude of the emissions measured from oil wells varied greatly, for example, different oil wells were found to generate emissions of 0.013- 16.3 kg/hr of methane as well as 0.04 - 5.7 kg/hr and 0.07 - 4.6 kg/hr benzene and toluene respectively. Detection of benzene and toluene emissions from some of oil wells is particularly interesting. Benzene is a known carcinogen with no safe levels. Because oil wells in SCAB are often located within or near residential neighborhoods, BTEX exposure of resident of such communities can be a concern. Gas stations sampled during the study were found not to generate methane or benzene emissions above the detection limits of the method (2.8 & 6.4 ppm\*m) respectfully, but emissions of 0.1 - 2.8 kg/hr of toluene were detected. Significant emissions of ammonia (between 5.3 and 11.2 kg/hr) and methane (between 0.4 - 6.3 kg/hr) were measured from the two cattle farms.

#### INSTRUMENT PERFORMANCE

The performance of the hardware and software used during the experiment was excellent. At no time during the five week study did any portion of the hardware, or data analysis and modeling software fail. The small footprint of the monitoring van allowed for discreet setup in tight areas, often as small as single parking lot spaces. Kassay measurement approach used a single OP-FTIR, single reflector, and single weather station, therefore minimizing overall complexity of the experimental setup. A field crew of 2 -persons were capable of deploying the instrumentation and collecting reliable data within 1-hour of arriving at each monitoring location. The quality of the OP-FTIR data was considered excellent based on good signal to noise and good detection limits for

#### target chemicals. *FUTURE IMPROVEMENTS*

Computer algorithms to process OP-FTIR data are continuously improving. The software algorithms used to process the OP-FTIR data worked reliably, however further improvements, for example to better handle the atmospheric water vapor, can increase sensitivity of OP-FTIR even more. The area in need of the most is the E-calc model integration. Although the algorithms used to generate the emission fluxes were highly developed, the OP-FTIR and GPS data entry needs to be automated. Additionally, the models reliance on certain input parameters, such as surface roughness, could be improved so as better guide the user for proper selection.

#### CONCLUSIONS AND OUTLOOK

Emission measurements from a limited sample of small sources were performed by Kassay using OP-FTIR coupled with reverse plume modeling during September – October 2015. Investigated sources within the SCAB consisted of 17 gas stations, 16 oil well, 2 cattle farms, and one rendering plant. Our measurements revealed that sampled sources emit a variety of VOC and BTEX compounds. Emission fluxes varied temporally and in-between sources. For example, among the same types of sources, emissions varied by orders of magnitude. Small sources in the SCAB are highly non-uniformed: for instance, gas stations vary in sizes and throughput; different operators of gas stations and oil wells might adapt different work practices; additionally, sources may be sampled in different modes of operation. Combination of these and other factors can lead to variations in emissions. Nonetheless, results of our study suggest that small sources can make a significant contribution to SCAB air quality problems. In order to fully ascertain the magnitude of emissions from such sources and how they are affecting air quality, a systematic, statistically significant sampling for each source type has to be performed. Optical Remote Sensing methods are appropriate tools for such future survey(s).

### **SECTION 1 – INTRODUCTION**

This report presents results of emission-rate measurements from small sources, in fulfillment of requirements set forth by the South Coast Air Quality Management District (SCAQMD) in its R&D field project, "Application and Development of Advanced Optical Remote Sensing Technologies to Characterize and Quantify Fugitive and Stack Emissions from Refineries and Other Sources, Project #2- "Quantification of Gaseous Emissions from Gas Stations, Oil Wells, and Other Small Sources").

Kassay Field Services (Kassay) was one of three firms jointly awarded this contract, in response to the SCAQMD Request for Proposals P2015-07, issued September 5, 2014.

#### 1.1 Statement of Need

In recent years small and often not well-regulated sources have come under scrutiny from the public about the unknown nature of their emissions [Rassenfoss, 2015; Wong et al., 2015; Macey et al., 2014, USEPA 2001]. For example, in January of 2015, a study published in the journal of *Atmospheric Chemistry and Physics* warns that official emissions inventories of greenhouse gases are being underestimated [Barboza, 2015]. In fact, the study reported that methane emissions could be up to 61% higher than previously estimated.

Limited background information is available for methane, and non-methane VOC emissions from small sources. Emissions from small sources such as oil wells, intermediate storage tanks, and cattle farms in the South Coast Air Basin (SCAB) are largely determined using estimates from empirical information or sporadic sampling.

Based on 2012 data, the USEPA reported that nearly 29% of all methane emission can be attributed to the oil and gas industry [Rassenfoss, 2015; Macey et al., 2014]. This is amount is followed by the digestive process of grazing animals (enteric fermentation) at 25%. Further speciation of other VOC's are lesser known overall. Even though the air emissions from oil and gas operations are generally understood, evidence exists that new emissions categories are being discovered as the life cycle of a well progresses from drilling through abandonment. In fact, if well emissions are measured at a time when a drilling activity hits a pocket of gas, the VOC's released to the atmosphere can be unpredictable.[Macey et al., 2014] Measurements made at those times could corrupt the accuracy of emissions inventories.

Continuous monitoring of small emissions sources like oil wells and gas stations requires monitoring devices that can measure a wide range of chemicals over periods of time in costly manner. A key challenge for small source emission monitoring is the temporal resolution of the air measurements. Snap-shot air samples may not necessarily characterize the emission source if measured at the wrong time or for a short time duration. Air surrounding small emission sources can contain elevated levels of the same target chemicals that are being measured. Therefore, employing technology that can separate the emission plume from the background is also desirable.

#### **1.2 ORS Technologies**

Optical Remote Sensing (ORS) technologies are capable of real or near real-time monitoring over a long distance while the data can be obtained that has better spacial and temporal resolution. ORS technologies such as Fourier Transform Infrared Spectroscopy (FTIR), Differential Absorption Lidar (DIAL), and Differential Absorption Spectroscopy (DOAS) can be used to characterize small source emissions. Additionally, each one of those technologies can be deployed using a different mode of operation, such as: in a fence line mode (e.g. Open Path FTIR (OP-FTIR) or Long Path DOAS (LP-DOAS)), radial plume mapping mode, solar occultation flux mode (SOF), or reverse Gaussian modeling modes.

In this project, Kassay employed the OP-FTIR method, which offers ORS solution to improve chemical speciation for different VOC's from small sources. With an OP-FTIR, an absorbance spectrum is measured over a wavelength frequency from approximately 2-14 um and individual absorbance peaks can be identified (speciated) during the same time domain.

Another benefit of OP-FTIR is that it is a non-destructive sampling technique. Direct infrared spectra are recorded by the OP-FTIR spectrometer while the plume passes through the optical beam. This is unlike conventional sampling techniques that require air to be collected and sent to a laboratory for analysis. In laboratory analysis, the volume of air collected, sample time, and sample conditions must be carefully recorded so that the concentration can be correctly calculated. Additionally, the sample tubing, container, and the laboratory analysis must be free from contamination and the sample must be safely transported to the lab. Finally, the laboratory method must be capable of injecting the air sample into the analyzer properly without corrupting it. Often the sample must be heated, concentrated or diluted.

Therefore, use of OP-FTIR technology could allow for better identification of different VOC compounds and present real time concentration trends of those chemicals. In combination with the specialized model (E-Calc), near real time emission rates could be determined. Finally, OP-FTIR collects a whole spectrum which can later be re-analyzed for quality assurance or to search for and quantify different chemicals.

#### **1.3 Small Source Project #2**

During September and October of 2015, KASSAY Field Services, Inc. (Kassay) conducted a fiveweek air study to determine the VOC emission rates from gas stations, oil wells, and other small point sources in the SCAB using OP-FTIR technology. Two other contractors Fluxsense Inc. (Fluxsense), and National Physical Laboratory (NPL) also participated in the same study.

OP-FTIR along with meteorological measurements and E-Calc modeling software were used to calculate the emission rates for a variety of VOC's. The proceeding sections of this report describe the methods, discussion, results and conclusion of Kassay's OP-FTIR emission results.

### SECTION 2 - MEASURMENT APPROACH

In order to address the temporal and spatial challenges described above, the OP-FTIR spectrometer was used to collect path integrated measurements downwind from a number of small sources in the SCAB. The concentration of each VOC target chemical in (ppm\*m) was then combined with meteorological data and entered into a dispersion model to calculate the emission rate (flux) over the sample time.

#### 2.1 Concentration Measurements

OP-FTIR technology measures a complete path average concentrations of many gases over a long distance in real time. The resulting measurement can be expressed as either a path-average (ppm) or path integrated (ppm\*m) concentration. Since the OP-FTIR measurement is concentration along the distance (ppm\*m) the concentration value can be inserted into a Gaussian dispersion model as a direct expression of sigma-x, the dispersion coefficient representing the cross-plume concentration. Figure 2-1 presents a typical depiction of OP-FTIR when used to measure downwind of a Gaussian plume.

The benefit of the OP-FTIR technique is that the Gaussian parameter sigma-x is directly measured as a full spatial integration as opposed to a discreet point measurement that only yields the concentration at a single point location. Therefore, when the majority of the plume is contained by the OP-FTIR beam path, the emission rate calculation can have a higher degree of confidence then reliance on fewer point measurements.



Figure 2-1: Depiction of OP-FTIR Gaussian Plume Measurement.

OP-FTIR equipment was furnished by KASSAY the exclusive supplier of the RAM2000<sup>(TM)</sup> product

line. The RAM2000<sup>(TM)</sup> is the only OP-FTIR system that has completed the USEPA's Environmental Technology Verification (ETV) program. All Equipment was shipped from Mohrsville PA in advance of the field program.



Figure 2-2: Picture of the Kassay Van during deployment in the SCAB.

The RAM2000<sup>(TM)</sup> G2 OP-FTIR was installed in a <sup>1</sup>/<sub>2</sub> ton Ford monitoring van. The OP-FTIR beam was directed out of the side or rear doors. A table mounted inside the van allowed the two person field crew to process and monitor the data from inside the van. The small size of the monitoring van provided the flexibility to park in conventional sized parking spaces in public lots. Figure 2-2 is a picture of the monitoring van at a well site in Carson, CA.

The RAM2000<sup>(TM)</sup> OP-FTIR is a 0.5cm-1 resolution spectral analyzer configured in an active optical arrangement with the infrared source and detector housed in the same instrument cabinet. Figure 2-3 shows the OP-FTIR installed in the monitoring van.

The spectrometer was powered by an external power controller that requires input of 110/120 AC line energy. Power was supplied by a portable generator that would be set outside the van at a location away from the beam path.

The RAM2000<sup>(TM)</sup> G2 propagates the infrared energy to a remotely stationed reflector called a retroreflector. Energy is returned and recorded by the super cooled mercury cadmium telluride detector. The returned signal intensity forms a spectrum that is analyzed for target chemicals. Two retroreflector arrays were supplied for the field project. Each array consists of thirty-seven 2.5-inch hollow retro cubes that will return enough energy for a path up to 400 meters. Individual retro reflector cubes are created by three square flat mirrors that are assembled in a cube configuration that returns the incoming infrared energy at the same angle of incident as the entry. This allows imperfect alignment to reflect adequate energy back to the spectrometer. Figure 2-4 depicts retroreflectors used in the study.



Figure 2-3: Picture of RAM2000<sup>(TM)</sup> OP-FTIR.



Figure 2-4: Picture of Retro-reflectors.

A Climatronics F460 meteorological tower was daily set up at a 3-meter sensor height at each small source location. The weather parameters recorded were as follows: wind speed, direction, temperature, barometric pressure, vertical wind speed. Both the horizontal and vertical standard deviation of the wind was also calculated by the data logger. Figure 2-5 shows the mast of the weather station and sensors.

All of the RAM2000(TM) G2 hardware is controlled by the custom continuous monitoring software

RMMSoft. The software is a user friendly graphical user interface (GUI) used to automatically collect and analyze the infrared spectrum for per-selected target chemicals.



Figure 2-5: Picture of Meteorological Tower.

The software presents the measured concentrations as well as the raw interferogram and the absorbance spectrum. Figure 2-6 presents the RMMSoft display screen.



Figure 2-6 – Screen Shot of RMMSoft GUI.

#### 2.2 Emission Rate Modeling

Kassay was supported in the field by the consulting firm of Minnich and Scotto, Inc. (MSI) and their emissions-calculation software, E-Calc, to generate 15-minute-averaged emission rates for each monitored source and selected contaminants of concern, in real time (see Appendix B for emission rate details). The E-Calc software incorporates USEPA's regulatory version of AERMOD in order to maintain its legal status as a Guideline model. E-Calc employs the area-source technique to generate valid back-calculated gaseous contaminant emission rates. This process is sometimes referred to as inverse modeling.

E-Calc requires the user to enter the path integrated concentration in ppm\*m of the target chemical as measured by the OP-FTIR. During the same time interval, the weather parameters such as wind speed, wind direction, solar insolation, and the standard deviation of the wind direction are measured. Those meteorological values are also entered into E-calc to simulate plume dispersion and transport and ultimately generate all emission rates. See Appendix D for a complete technique description.

#### 2.3 Site Monitoring Strategy

To meet the monitoring objective to measure flux (emission rates) the OP-FTIR beam path was always positioned down-wind of the emission source so that the Gaussian dispersion could be properly modeled. The three emission source types that were monitored for were oil wells & tanks, gas stations and cattle farms.

<u>Oil wells & tanks:</u> Almost all of the observed oil wells and tanks consisted of at the minimum an oil derrick, transport piping, sometimes an intermediate tank storage was also present at the site. The source was therefore considered as a small area that contained all components. Typical oil well sites in the LA Basin are 10-50 square meters in area. Since the sampled oil wells were often located within parking lots, the OP-FTIR van could be positioned in almost any configuration downwind of the area.

<u>Gas stations</u>: The gas stations sources consisted of the fuel island areas where refueling was active. The vents for the underground gas storage were also part of the small area source. Since gas refueling areas were always busy with active traffic, it was typical to set the OP-FTIR on the adjacent property and the retro reflector on the other adjacent property. The beam path would then extend downwind of the entire gas station in order to capture the whole plume.

<u>Cattle farms</u>: The cattle farms feed lots were very large (more than 500 x 500 meters) and consisted of the feed lot shelter and the solid and liquid waste storage. Two cattle farms sampled had road side access perpendicular to the wind direction for the entire feed lot and waste storage. In both

cases measured, the OP-FTIR was located on one corner of the property and the retro reflector was located on the other corner down wind of the process.

Prior to deploying the equipment, the meteorological forecast and on-site weather conditions were considered to determine the prevailing wind direction. Once determined, the Kassay team would drive to a pre-selected source location to determine if there was appropriate site access to set the OP-FTIR and retro-reflector in a potion to be down wind of the emission source. If the configuration was not suitable, the field crew would move to another potential source location.

The following measurement strategy was applied at each monitoring location: collect an upwind background, then set up down wind of the source in a way to fully contain the plume within the OP-FTIR beam path. Prior to beginning of the measurements, the OP-FTIR equipment had to be thermally stabilized over the first 15-30 minutes. During that time, the instrument was not stable and the data quality was poor. When the data was stable, the software was set to continually collect and record back to back spectrum files to be automatically analyzed for the target chemicals.

OP-FTIR data collection would proceeded uninterrupted from the time of data stability until there were at least three (3) 15-minute time intervals that met the criteria of having valid meteorology. Valid meteorology was determined using following criteria: the wind speed must be at least greater than 1 m/s and the plume capture (based on wind direction) above 70%. Below are the sequence of steps for the OP-FTIR monitoring at each small source site.

- ▲ Check wind forecast and select potential sites
- ▲ Daily on-Site planning/ strategy, and safety discussion
- ▲ Stage RAM2000 G2 in van: Power on (allow time for warm up)
- ▲ Setup retro reflectors and met-tower on tripod
- A Measure & record beam path length & orientation
- ▲ Collect up-wind/off wind (before or after data)
- ▲ Setup RMMSoft Collection Analysis
- ▲ Coordinate start time with other contractors
- Command RMMSoft to begin the collect & analyze
- ▲ Maintain/monitor system to confirm data collection
- ▲ Back up all data
- ▲ Break down and secure all equipment

In addition to measuring the three small source types (gas stations, oil wells, cattle farms) the field work included participation in a formal controlled tracer-gas release study on October 12 and 13. The tracer study included propane releases at varying (blind) emission rates, from a small area source at different release heights. All three Project 2 contractors participated in the controlled release study. Results from the controlled-release study are summarized in a separate report by Pikelnaya et al. [2016]. Kassay's results for the controlled propane release are presented in section 3.8 of this report.

Additionally, a controlled tracer-gas release using nitrous oxide (N2O) was performed while

simultaneous VOC measurements by other ORS contractors participating in the project were being collected at actual small source sites on three different dates. The dates for the  $N_2O$  tracer releases were: October 8, October 16, and October 19. The controlled release of  $N_2O$  allows for further intercomparison of emission rates between Kassay's OP-FTIR technique and Fluxsense's SOF technique.

Finally, emissions from a large oil well and tank cluster (October 15) and two rendering plants (October 19) were also characterized for VOC concentrations. Unfortunately, footprints of these sources were too large for valid emission rates to be calculated.

#### 2.4 Analysis of the OP-FTIR Data

Prior to all on-site activities, an analysis method file (script file) was prepared by Kassay. The analysis file included target chemicals that were believed to be present and spectral interferences between those chemicals and the atmosphere. Previous data showed that the emissions form the small sources were laden with non-methane hydrocarbons (NMHC) and other VOC's. The method file prepared for the OP-FTIR included the following target chemicals: ammonia, benzene, ethanol, ethane, iso-butane, n-butane, n-hexane, propane, toluene and non-methane hydrocarbon balance (NMHC-balance – total of C2-C12 unspeciated hydrocarbons – see explanation below).

Spectral analysis of OP-FTIR data is a differential technique, meaning that the target chemical concentration is actually represented as a value in contrast to the background. Hence, in order to properly analyze each spectrum, an on-site background spectrum was recorded. A background spectrum is identical to the data spectrum but free of the target chemicals [Perry et. al., 2016]. At each site, a background spectrum was collected by measuring upwind of the source of the emission.

The OP-FTIR spectrometer collects an infrared spectrum by a user selected time interval. The minimum time for the RAM2000G2 to collect one spectrum is approximately two seconds. Therefore, every two-seconds the spectrometers moving mirrors, detector, and data acquisition system complete a cycle. Co-adding individual two-second scans improves the measurement signal to noise, thus lowering the minimum detection limit. In order to match the meteorological time frame, the RAM2000G2 was set up to co-add individual scans for a 1-minute duration that would be then averaged for a 15 minute meteorological time interval. Every 15 minutes the average VOC concentration recorded and a valid the E-Calc emission-Rate was determined.

Due to the overlapping nature of the infrared absorbance peaks, it is not always possible to individually speciate all hydrocarbons using OP-FTIR. However, a number of the chemicals have unique spectral features allowing their detection. These chemicals include benzene, toluene, isobutane, n-butane, n-hexane, propane. The remaining (C2-C12) hydrocarbons were identified as a single chemical group named "NMHC-balance" due to the strong absorption features in 2800-3200 cm-1spectral region shared by all non-methane hydrocarbons.

Figure 2.7 shows the example of field measured absorbance spectra (top) compared to the hydrocarbon references for C2-C8 (middle) and the C9-C12+ reference (bottom). The total NMHC-balance C2-C12+ was quantified using the mixture reference hcont-2.spc, a unique spectrum to



represent all the NMHC chemicals that absorb in the IR spectral region.

Figure 2-7 – NMHC Balance Abs. Spectra

### **SECTION 3 – RESULTS & DISCUSSION**

Overall, Kassay collected OP-FTIR emission data for twenty eight days in the SCAB. Two of those days were committed to the blind tracer release study (October 12<sup>th</sup> & 13<sup>th</sup>) and the remaining twenty six days were actual small source measurement locations. Eight sites were revisited more than once in order to perform monitoring alongside of other ORS contractors, or to collect additional measurements. One well & Tank site in the Signal Hill section of Long Beach was measured more than four times due to the high concentrations of methane and NMHC that were detected.

#### 3.1 Monitoring Locations

A total of thirty-seven valid measurements were processed during the twenty-eight day field experiment, which included 16 Oil Wells, 17 Gas Stations, 2 cattle farms, 2 rendering plants. The locations of those sites were selected from a larger list small sources provided to Kassay by SCAQMD staff. Choice of locations was based on based on accessibility, wind direction and scheduling availability with the other contractors.

For the sixteen unique oil well sites, the monitoring van usually had to be located on the street corner, sidewalk or adjacent property. Each of the seventeen gas stations site were selected based on the access on adjoining properties, since the van usually could not be oriented on the same property being monitored. For the two cattle farms, the main selection criteria was that the property have a clear line of site up to 400 meters. Figure 3-1 shows the small source location for each source type in the LA Basin.



Figure 3-1: Map of small sources measured by Kassay.

#### **3.2 Target Chemicals**

Twelve VOC chemicals plus one representative NMHC-balance were measured during the field campaign. The NMHC-balance was a single surrogate chemical that represented the total the remaining C2-C12+ hydrocarbons that had absorbance features in the 2800-3200 cm-1 region of the spectrum. Nineteen target compounds were initial monitored for by the OP-FTIR, but only thirteen were detected in concentrations above the method detection limit. Therefore, all OP-FTIR results and emission rate calculations were based on those thirteen VOC's. Table 3-1 presents the universe of target compounds monitored, and depicts which compounds were detected, during at least one monitoring event, for each of the three source types.

	Ī		Source	Detected	
Target Compound	MDL (ppm * m)	Gas Stations	Oil Wells	Cattle Farms	Rendering Plants*
ammonia				х	х
benzene			х		
iso-butane			х		
n-butane		X	х		
ethane		x	x		
ethanol		x	x		x
ethylene					
n-hexane		x	x		
non-methane hydrocarbons (NMHC)**		x	X		
methane			x	х	x
methanol					
naphthalene			x		
n-octane		x			
propane		x	x		
propylene					
toluene		x	x		
m-xylene					
o-xylene					
p-xylene					

Table 3-1:Target compounds and detections by source

\*The rendering plant sources were too large for emission rates to be calculated.

\*\*NMHC are defined as the total C4 hydrocarbons and higher, but excluding any which are detected individually.

#### **3.3** Minimum Detection Limits (MDLs)

The minimum detection limit (MDL) for each target chemical measured by OP-FTIR was calculated using the classical least squares (CLS) statistical analysis. The MDL is the 3-sigma value computed from the standard deviation of the fit between the reference absorbance spectrum and the measurement absorbance spectrum. For the project, the MDL ranged from less then 1 ppb to 50 ppb for most VOC's and NMHC-balance. Target chemicals were identified when the quantification value was above the MDL. Internally, RMMSoft accepts concentration results based on uses an acceptance criteria. The acceptance criteria is an expression of goodness of fit which is multiplier of the MDL which for this program was two times the 3-sigma MDL value. MDL's from each small source would vary depending on atmospheric conditions, beam path length, and interferences present. Typical MDL's for each chemical in this study are tabulated in table ES.2. A more thorough discussion of OP-FTIR MDLs for this project are presented by Perry et al. [2016].

Not shown in the target chemical list is the interfering chemicals in the spectral analysis which also have to account during spectral evaluation. These interferences include atmospheric water vapor, carbon monoxide, carbon dioxide and ozone. When a target chemical was analyzed, it was statistically determined in an analysis matrix along with any interfering chemical that had an absorbance feature within the same spectral region as that target chemical. These statistical considerations are part of the (CLS) analysis used for chemical quantification as described in TO-16. For example, to analyze for benzene, the analysis considers ozone to be present in the same spectral region. Figure 3-2 shows the benzene reference (top) with ozone reference (bottom.)



Figure 3-2: Example of Spectral Interference between Ozone and Benzene.

#### 3.4 Modeled Emission-Rate Events

A total of 265 individual 15-minute-averaged emission-rate monitoring events were completed covering emission sources in the South Coast Air Basin (SCAB.) Of the 265 completed OP-FTIR measurement events, 80 (30.2%) were deemed invalid due to insufficient plume capture and another 21 events (7.9%) had no detected target compounds (but were still considered valid), leaving 164 events (61.9%) with valid emission rates for at least one target compound. Therefore, 164 valid monitoring events were performed. Of these valid events, 88.6% had at least one detected target compound. This supports the method applicability for calculating emission rates from these source types.

Table 3-2 presents a summary of all emissions-related site visited by Kassay for the small sources. The following monitoring-event distinctions are made:

#### **Completed Monitoring Event**

Any completed monitoring event.

#### **Monitoring Event With Plume Capture < 70%**

Any completed monitoring event having a plume capture less than 70%, regardless of whether target compounds were detected; all such events were deemed invalid.

#### Monitoring Event With No Detects (Plume Capture 70%)

Any completed monitoring event having both a plume capture equal to or greater than 70% and no detected target compounds; all such events were deemed valid, even though no emission rates were derived.

#### Valid Monitoring Event With Calculated Emission Rate(s)

Any completed monitoring event having both a plume capture equal to or greater than 70% and at least one detected target compound; all such events were deemed valid.

Sections 3.5 through 3.10 summarize the results for the gas stations, oil wells and tanks, and cattle farms, respectively. Within each source group, emission rates of all detected target compounds are presented for every valid monitoring event, as well as the mean wind direction, wind speed, and plume capture.

		Site Information		# of Emission-Rate Monitoring Events			
#	Туре	Address	City / Town Completed		w/ Plume Capture < 70%	w/ No Detects (PC 70%)	w/ Valid Emission Rate(s)
		Monitoring Day 1 (Monday, Septer	nber 21, 2015)				
30	oil well and tank	E. Creston Ave. & Walnut Ave.	Signal Hill	9	0	2	7
35	oil well (two)	Brayton Ave. & Gundy Ave.	Signal Hill	4	4	0	0
		Monitoring Day 2 (Tuesday, Septer	nber 22, 2015)				
38	oil well	E. Spring St. & California Ave.	Signal Hill	6	0	4	2
40	oil well	E. Spring St. between California & Orange Ave.	Signal Hill	5	0	2	3
		Monitoring Day 3 (Wednesday, Sept	ember 23, 2015)				
53	cattle farm (Gordon Hay)	Cleveland Ave.	Chino	11	3	0	8
		Monitoring Day 4 (Thursday, Septe	mber 24, 2015)				
4	gas station (Mobil)	E. 2nd St. & Pacific Coast Hwy.	Marina Pacifica	4	4	0	0
1	gas station (Costco #424)	2200 E. Willow St.	Signal Hill	4	4	0	0
		Monitoring Day 5 (Friday, Septem	ber 25, 2015)				
41	oil well (two)	E. Pacific Coast Hwy. (adj. to Trader Joe=s)	Marina Pacifica	8	1	2	5
8	gas station (Costco #1110)	7562 Center Ave.	Huntington Beach	5	0	2	3
		Monitoring Day 6 (Monday, Septer	nber 28, 2015)				
11	gas station (Mobil Circle K)	Pacific Coast Hwy. & Warner Ave.	Sunset Beach	5	0	4	1
42	oil well	S. Atlantic Ave. & E. Spring St.	Signal Hill	4	0	0	4

		Site Information		# of E	mission-Rat	e Monitoring	Events
#	Туре	Address	Address     City / Town     Completed     w/ Plume Capture < 70%		w/ No Detects (PC 70%)	w/ Valid Emission Rate(s)	
		Monitoring Day 7 (Tuesday, Septer	nber 29, 2015)				
43	oil tank	Orange Ave. & E. 29th St.	Signal Hill	4	3	0	1
1	gas station (Costco #424)	2200 E. Willow St.	Signal Hill	4	0	0	4
2	gas station (Vons #1638)	4226 Woodruff Ave.	Lakewood	4	0	0	4
	-	Monitoring Day 8 (Wednesday, Sept	ember 30, 2015)				
6	gas station (Costco #748)	Katella Ave. & Walker St.	Cypress	3	0	1	2
44	oil well	S. Atlantic Ave. & 33rd St.	Signal Hill 3 1 0		0	2	
		Monitoring Day 9 (Thursday, Oct	ober 1, 2015)				
5	gas station (Costco #476)	Skypark Dr. & Garnier St.	Torrance	5	2	1	2
45	oil well	Vermont Ave. (600m north of Sepulveda Blvd.)	Carson	4	0	0	4
	-	Monitoring Day 10 (Friday, Octo	ober 2, 2015)				
54	cattle farm (owner unknown)	Carpenter Ave. & Eucalyptus Ave.	Chino	4	0	0	4
		Monitoring Day 11 (Saturday, Oct	tober 3, 2015)				
46	oil well (two)	Vermont Ave. & Sepulveda Blvd.	Carson	4	3	0	1
		Monitoring Day 12 (Monday, Oct	ober 5, 2015)				
39	oil well and tank	E. 35th St. & Lime Ave.	Signal Hill	4	0	0	4
9	gas station (7-11)	Ball Rd. & S. Brookhurst St.	Anaheim	4	0	0	4

		Site Information		# of E	mission-Rate	e Monitoring	Events
#	Туре	Address	Address     City / Town     Completed     w/ Plume       Capture     < 70%		w/ No Detects (PC 70%)	w/ Valid Emission Rate(s)	
		Monitoring Day 13 (Tuesday, Oct	ober 6, 2015)				
37	oil well	33rd St. & Pasadena Ave.	Signal Hill	4	0	0	4
33	oil well (two)	Orange Ave. (near E. 29th St.)	Signal Hill	6	0	0	6
		Monitoring Day 14 (Wednesday, O	ctober 7, 2015)				
7	gas station (Arco)	E. Livingston Dr. & Termino Ave.	Long Beach	5	0	0	5
3	gas station (Chevron)	Broadway Ave. & Alemetos Ave.	Long Beach	3 0		0	3
10	gas station (Mobil)	E. Livingston Dr. & Termino Ave.	o Ave. Long Beach 4 2 C		0	2	
		Monitoring Day 15 (Thursday, Oc	tober 8, 2015)				
30	oil well and tank	E. Creston Ave. & Walnut Ave.	Signal Hill	12	0	0	12
		Monitoring Day 16 (Friday, Octo	ber 9, 2015)				
43	oil tank	Orange Ave. & E. 29th St.	Signal Hill	18	18	0	0
		Monitoring Day 17 (Saturday, Oct	ober 10, 2015)				
12	gas station (Mobil)	Warner Ave. & Springdale St.	Huntington Beach	3	1	1	1
13	gas station (Arco)	Warner Ave. & Springdale St.	Huntington Beach	4	0	0	4
		Monitoring Day 18 (Sunday, Octo	ber 11, 2015)				
14	gas station (76)	Ball Rd. & State College Blvd.	Anaheim	3	0	0	3

		Site Information		# of E	mission-Rate	e Monitoring	Events		
#	Туре	Address	City / Town	Completed	w/ Plume Capture < 70%	w/ No Detects (PC 70%)	w/ Valid Emission Rate(s)		
		Monitoring Day 21 (Wednesday, Oc	tober 14, 2015)						
15	gas station (76)	N. Studebaker Rd. & E. Spring St.	Long Beach	4	0	1	3		
31	oil well (two)	E. Burnett St. & Gardena Ave.	Signal Hill	8	2	5			
	-	Monitoring Day 22 (Thursday, Oct	ober 15, 2015)						
NA	oil well and tank (cluster of each)	Atlantic Ave. (near Home Depot)	Signal Hill	source chara	source characterization only (no emission rates)				
	Monitoring Day 23 (Friday, October 16, 2015)								
32	oil well rework	Crescent Hts. St. btwn. Walnut & Cherry Aves.	Signal Hill	16	9	0	7		
		Monitoring Day 24 (Saturday, Oct	ober 17, 2015)						
43	oil tank (eight)	Orange Ave. & E. 29th St.	Signal Hill	33	23	0	10		
		Monitoring Day 25 (Sunday, Octo	ber 18, 2015)						
34	oil well (three)	E. Willow St. between Lewis & Lemon Aves.	Signal Hill	4	0	0	4		
		Monitoring Day 26 (Monday, Octo	ober 19, 2015)						
2	gas station (Vons #1638)	4226 Woodruff Ave.	Lakewood	6	0	0	6		
NA	rendering plant (Farmer John=s)	3163 E. Vernon Ave.	Vernon	source chara	acterization of	only (no emiss	ion rates)		
NA	rendering plant (Baker Commodities)	4020 Bandini Blvd.	Vernon	source chara	acterization of	only (no emiss	ion rates)		

		Site Information					# of Emission-Rate Monitoring Events			
#	Туре	Address	City / Town Completed		w/ Plume Capture < 70%	w/ No Detects (PC 70%)	w/ Valid Emission Rate(s)			
	Monitoring Day 27 (Tuesday, October 20, 2015)									
16	gas station (Mobil)	Del Amo Blvd. & State Rd.	Lakewood	3	0	0	3			
17	gas station (76)	La Palma Ave. & Walker St.	La Palma	6	0	0	6			
		Monitoring Day 28 (Wednesday, Oc	tober 21, 2015)							
18	gas station (Shell)	N. Lakewood Blvd. & E. Willow St.	Signal Hill	4	0	0	4			
34	oil well (three)	E. Willow St. between Lewis & Lemon Aves.	Signal Hill	11	0	0	11			
			Total	265	80	21	164			

\* Not included in Table 3-2 are results from: (a) the tracer-gas release studies; and (b) the characterization of source emissions from the cluster of oil wells and tanks, and from the two rendering plants.

#### 3.5 Gas Stations

Valid emission rates were obtained from a total of seventeen gas stations. Table 3-3 summarizes the range of emission rates that were measured. Seven chemical species were detected in concentrations above the MDL.

		0		ίų γ			
QTY/Type	N-butane	Ethane	Ethanol	N-Hexane	NMHC-Balance	Propane	Toluene
	(kg/hr)	(kg/hr)	(kg/hr)	(kg/hr)	(kg/hr)	(kg/hr)	(kg/hr)
17 / Gas Stations	0.018-	0.01 -	0.004 -	0.041 -	0.001 -	0.014 -	0.099-
	0.27	1.0	0.87	3.1	3.86	0.6	2.79
# of Source detected	2	9	15	6	13	4	5

Table 3-3: Range of Emissions (kg/h) from Gas Stations.

Gas station sites selected for measurement were public access vehicle refueling locations that had ongoing activities during the measurement event. The emission source for modeling purposes was designated as the fuel islands, which included emissions from vents from the underground storage tanks, gas pumps, and automobiles being refueled.

The highest concentrations of chemicals measured were the NMHC-balance, followed by n-hexane, toluene, ethane, ethanol, propane and butane. As seen from Table 3-3, the emission results show that the BTEX chemicals were not detected in as much abundance as the strait chain hydrocarbons. Since evaporative emissions are different from combustion, this may be an indication that some emissions are from vehicles rather then actual gas station itself. Furthermore, the highest detection of the NMHC-Balance was during times when there was no ethanol detected.

In one case, the measurement of propane was during the time when a propane cylinder (grill size) was being refilled by the station operator. (SITE 13: ARCO B Warner Ave. & Springdale St., Huntington Beach (Monitoring Day 17). In another case, a high hydrocarbon concentration was measured at the same time that an old model car was being refueled. (Site 2: VONS (#1638), 4226 Woodruff Ave., Lakewood (Monitoring Day 7). In both cases the emissions spiked during the event, then dropped back to pre-condition levels.

#### 3.5.1 Gas Station Monitoring Example

A typical example of monitoring at a gas station was conducted on monitoring day 7 at the Vons gas station on 1638 Woodruff Ave in Lakewood. Figure 3-3 shows the monitoring configuration for Tuesday, September 9<sup>th</sup> monitoring at Vons from 14:00 - 15:00. The Kassay OP-FTIR van arrived at 2:00 pm and positioned the monitoring van in a parking space so that the OP-FTIR beam path was directed across the north side of the fuel islands.

The OP-FTIR was rotated to shoot the IR beam through the back door out to a tripod based retro reflector that was staged about 45 meters away. The meteorological tower was deployed onto the sidewalk. A background was collected, then the monitoring was collected over the next hour.

During that time, the wind continued to drift from the south, moving the emission plume though the OP-FTIR beam. During this deployment, emissions of ethanol, toluene and NMHC-balance were detected by the OP-FTIR while vehicles were refueling. The E-Calc emission model was run on three subsequent 15-minute time averages to generate emission rates. The maximum 15-minute emission rate for ethanol (189.4 mg/s), NMHC-balance (50.3 mg/s), and toluene (752 mg/s) were measured from 14:30-14:45pm.

Compared to the other gas stations measured, the Vons site detected elevated levels of Toluene. Since Toluene was not detected at other sites, Vons was measured again on October 19<sup>th</sup>. Under similar wind conditions, a slightly different (longer) monitoring path was configured. Similar to the previous observations, the same chemicals were detected including Toluene. This suggests that measured Toluene emission was not due to specific vehicles present, but likely originated from the gas station itself. Figure 3.3 shows the monitoring configuration for the Vons fuel station.



Figure 3-3: Example of Gas Station Monitoring Setup.

#### 3.5.2 Summary of Gas Stations

The seventeen gas stations monitored are listed below with their addresses. All measurements were performed similarly to the aforementioned VONS example. Table 3-4 shows the emission results for each gas station.

- **Costco #1110 B** 7562 Center Ave., Huntington Beach (Day 5)
- Mobil Circle K B Pacific Coast Highway & Warner Ave., Sunset Beach (Day 6)
- Costco #424 B 2200 E. Willow St., Signal Hill (Day 7)
- Vons #1638 B 4226 Woodruff Ave., Lakewood (Days 7 and 26)
- Costco #748 B Katella Ave. & Walker St., Cypress (Day 8)
- Costco #476 B Skypark Dr. & Garnier St., Torrance (Day 9)
- **7-11** B Ball Rd. & S. Brookhurst St., Anaheim (Day 12)
- Arco B E. Livingston Dr. & Termino Ave., Long Beach (Day 14)
- Chevron B Broadway Ave. & Alemetos Ave., Long Beach (Day 14)
- **Mobil B** E. Livingston Dr. & Termino Ave., Long Beach (Day 14)
- **Mobil** B Warner Ave. & Springdale St., Huntington Beach (Day 17)
- Arco B Warner Ave. & Springdale St., Huntington Beach (Day 17)
- **76** B Ball Rd. & State College Blvd., Anaheim (Day 18)
- **76** B N. Studebaker Rd. & E. Spring St., Long Beach (Day 21)
- Mobil B Del Amo Blvd. & State Rd., Lakewood (Day 27)
- **76** B La Palma Ave. & Walker St., La Palma (Day 27)
- Shell B N. Lakewood Blvd. & E. Willow St., Signal Hill (Day 28)

Table 3-4 presents, for the gas station sources, results of all valid emission-rate events for all detected target compounds. Sixty 15-minute-averaged monitoring events, resulting in valid emission-rate measurements for at least one compound, were achieved. Overall, a total of eight target compounds were detected.

Table 3-4:
<b>Results of Valid Emission-Rate Measurements for Detected Compounds: Gas Stations</b>

E	lvent	Mean V	Vind	Discourse				Emission 1	Rate (mg/s)			
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	n-Octane	Propane	Toluene
	SITE 8: COSTCO (#1110) B 7562 Center Ave., Huntington Beach (Monitoring Day 5)											
10	13:30	218.6	1.241	97.4			14.3		49.5			
12	14:00	223.1	1.183	81.9					136.3			
13	14:15	217.2	1.249	82.6					63.1			
	SITE 11: MOBIL CIRCLE K B Pacific Coast Highway & Warner Ave., Sunset Beach (Monitoring Day 6)											
1	09:45	213.9	1.151	100.0					44.6			
		SITE	1: COS	ГСО (#424	I) B 2200 E	. Willow St.	, Signal Hi	ll (Monitori	ng Day 7) (	Second Tin	ne)	
5	11:30	189.4	1.804	85.2		12.8	6.6	16.2				
6	11:45	182.7	1.856	89.3			6.8	37.8	41.1			
7	12:00	202.5	2.009	73.6		2.5	51.3	510.0				
8	12:15	182.7	1.918	89.3			9.7	90.4	32.2			
			SITE	2: VONS	(#1638), 42	26 Woodru	ff Ave., Lal	kewood (Mo	onitoring D	ay 7)		
9	14:00	175.1	2.152	90.7			47.3					275.3
10	14:15	169.0	2.436	87.5			155.9		42.7			775.7
11	14:30	159.9	2.283	76.7			189.4		50.3			752.0
12	14:45	177.5	2.030	89.9			95.8					237.8

F	Event	Mean V	Vind	DI		Emission Rate (mg/s)						
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	n-Octane	Propane	Toluene
	-		SITE 6:	COSTCO	(#748) B K	atella Ave &	& Walker S	t., Cypress	(Monitorin	g Day 8)		
1	12:45	185.6	2.255	98.2					167.9			
3	13:15	183.2	2.478	99.4					69.1			
SITE 5: COSTCO (#476) B Skypark Dr. & Garnier St., Torrance (Monitoring Day 9)												
3	11:45	173.6	1.966	93.7			39.2					
4	12:00	162.4	1.833	96.4			56.6					
SITE 9: 7-11 B Ball Rd. & S. Brookhurst St., Anaheim (Monitoring Day 12)												
5	14:15	203.1	2.367	100.0			14.7		131.3			
6	14:30	199.4	2.357	100.0			15.2		136.5			
7	14:45	195.9	2.064	100.0			5.0		46.4			
8	15:00	204.7	1.985	100.0			1.7		34.1			
		SI	TE 7: A	RCO B E.	Livingston	Dr. & Terr	nino Ave., I	Long Beach	(Monitoria	ng Day 14)		
1	11:15	162.6	1.928	99.9					6.8			
2	11:30	169.1	1.938	100.0			2.9	59.7			5.1	
3	11:45	171.3	1.869	100.0			1.1	20.3				
4	12:00	189.4	1.769	98.4		4.5						
5	12:15	196.4	1.849	95.5		9.0	2.6	11.4				

F	Event	Mean V	Vind	Discourse		Emission Rate (mg/s)						
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	n-Octane	Propane	Toluene
	SITE 3: CHEVRON B Broadway Ave. & Alemetos Ave., Long Beach (Monitoring Day 14)											
6	13:30	199.3	2.164	71.5			10.9					
7	13:45	216.8	1.727	83.4			11.8	37.2	1.2			27.4
8	14:00	207.2	1.684	78.7			9.6	176.9				152.6
	SITE 10: MOBIL B E. Livingston Dr. & Termino Ave., Long Beach (Monitoring Day 14)											
9	15:00	220.0	2.171	76.8	9.0					10.1		
11	15:30	225.4	2.506	70.3	74.1		1.4				26.8	
		SIT	Ъ 12: М	obil B Wa	rner Ave. <b>8</b>	k Springdal	e St., Hunt	ington Beac	h (Monitor	ring Day 17	)	
3	12:00	221.6	1.555	70.5		52.0	7.0					
		SIT	E 13: AF	RCO B Wa	rner Ave. &	& Springda	le St., Hunt	ington Bea	ch (Monito	ring Day 17	)	
4	12:45	229.6	2.172	98.2		369.7	69.5	859.4			166.9	
5	13:00	246.3	2.463	99.5					221.5			
6	13:15	231.9	2.472	99.3					386.2			
7	13:30	240.0	2.696	99.8					1,070.7	20.8		

E	vent	Mean V	Vind	Discourse	Emission Rate (mg/s)									
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	n-Octane	Propane	Toluene		
SITE 14: 76 B Ball Rd. & State College Blvd., Anaheim (Monitoring Day 18)														
1	14:30	251.3	3.126	94.9					25.8					
2	14:45	244.9	2.992	88.2					7.3					
3	15:00	253.5	3.460	97.1		15.8								
	SITE 15: 76 B N. Studebaker Rd. & E. Spring St., Long Beach (Monitoring Day 21)													
1	11:00	223.9	0.940	93.5		15.1	0.4							
2	11:15	213.8	0.964	96.9	4.9	277.9								
3	11:30	215.3	0.976	96.5		20.7								
			SITE 2	2: VONS (#	#1638) B 42	26 Woodru	ıff Ave., La	kewood (M	onitoring D	ay 26)				
1	10:45	180.2	1.556	90.5		101.0								
2	11:00	172.4	1.681	87.7		45.7	2.8							
3	11:15	177.8	2.004	89.5		14.4								
4	11:30	166.5	1.900	86.1		11.4			18.8			27.6		
5	11:45	175.3	1.798	88.6			5.5		0.3			22.8		
6	12:15	162.1	2.230	84.2			3.5					58.1		

ŀ	Event	Mean V	Vind	Dimensio		Emission Rate (mg/s)						
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	n-Octane	Propane	Toluene
			SITE 1	6: MOBIL	B Del Amo	o Blvd. & S	tate Rd., La	nkewood (M	lonitoring I	Day 27)		
1	11:15	155.3	1.183	96.6		3.3	1.1			3.5		
2	11:30	207.4	1.284	95.2		7.5						
3	11:45	247.1	1.326	76.9		8.7	2.0	49.5			3.8	
	SITE 17: 76 B La Palma Ave. & Walker St., La Palma (Monitoring Day 27)											
4	14:00	160.3	0.986	99.5		37.4	86.2					
5	14:15	200.2	2.213	88.0			191.0		12.6	13.6		
6	14:30	190.7	2.586	91.7		14.7	204.5					
7	14:45	187.0	2.426	93.4		9.1	204.8		1.7			
8	15:00	188.3	2.798	92.9		6.2	243.4			24.3		
9	15:15	198.3	3.008	88.8			179.7			34.0		
		SIT	TE 18: SI	HELL B N	. Lakewood	l Blvd. & E	. Willow St	., Signal Hi	ll (Monitori	ing Day 28)		
1	11:15	169.8	1.125	95.9			119.0					513.7
2	11:30	140.4	1.259	88.6			127.0	32.1	38.1			471.3
3	11:45	152.5	1.866	95.5			181.2					735.2
4	12:00	142.5	1.490	91.2			128.1					499.8

#### 3.6 Oil Wells and Tanks

Valid emission rates were obtained from a total of sixteen (16) oil wells and storage tanks. Table 3-5 presents the range of emission rates that were measured. Ten chemical species were detected in concentrations above the MDL.

Tuste e et Runge et Emissions (ng/m) from en (tens und Storage Tumist													
QTY/ Type		Benzene (kg/hr)	ISO- butane (kg/hr)	N-butane (kg/hr)	Ethane (kg/hr)	Ethanol (kg/hr)	N-Hexane (kg/hr)	NMHC- Balance (kg/hr)	Methane (kg/hr)	Propane (kg/hr)	Toluene (kg/hr)		
16 / Oil Wells		12.2 - 1585	5.9 - 2744	43 - 4044`	1.4 - 1463	2.2 - 783	21.3 - 6425	4.2 - 4598	3.5 - 4514	73 - 6475	20 - 1273		
# of sources detected		2	7	2	5	14	6	13	16	3	7		

Table 3-5: Range of Emissions (kg/hr) from Oil Wells and Storage Tanks.

Oil well & tank sites selected for measurement were those that could be seen to have active motion of the oil derrick, and access for the monitoring van. Each emission source for modeling purposes was area that included the moving oil derrick, the piping, and tank storage.

The individual highest concentrations of chemicals measured was propane followed by n-hexane, NMHC-balance, methane, n-butane, iso-butane, benzene, ethane, toluene, and ethanol. The emission results show that aromatics such as benzene were detected less often then strait chain hydrocarbons. (1 of 16 vs 13 of 16 events) Methane was relatively proportional in emission flux to NMHC hydrocarbons (methane emission 4514 kg/hr vs NMHC-balance 4598 kg/hr). The highest emissions were measured at sites with storage tanks. At one site (Creston & Walnut on October 8<sup>th</sup>, monitoring day 15.), it was noted that as the storage tank was filled the concentration of methane increased up to 820 ppb. But, as the tank was being was emptied the level dropped back to less then 50 ppb. This indicates that the emissions were more a function of the storage operation then of the actual derrick pumping. This site was measured twice, once with other contractors.

At another site (Orange Ave and E. 29<sup>th</sup> St) there were multiple tanks and equipment. It appeared that large tank was the main source of emission due. This site was measured three different occasions, one of those times with other contractors. The details of the third long term monitoring event are presented in the example of section 3.6.1.

#### 3.6.1 Oil Well & Tank Monitoring Example

A typical monitoring example for an oil well and tank source was the site located at Orange Ave and E. 29<sup>th</sup> street in Signal Hill. This site included multiple oil derricks and tank storage. Since there was significant concentrations of VOC's measured, the site was visited more than three times. The first two monitoring days revealed a cycle nature of VOC emissions from the site, resulting in 'puffs' of elevated VOC plumes. However, it was hard to determine if this was a result of meteorological factors, process factors, or changes in some upwind process.
On Saturday October 17, (monitoring of the measurement day # 24) the Kassay field team set up the OP-FTIR monitoring van on the eastern side of the property bounded by Orange Ave and E. 29<sup>th</sup> Street, and conducted a day-long monitoring of the source (from 10:00am to 19:00 PDT). Figure 3.4 shows the monitoring configuration used for data collection.

The Kassay OP-FTIR van arrived at 10:00am and received permission from the Honda Dealer to use their parking lot throughout the day. The OP-FTIR was turned to direct the IR beam out of the back door of the van to a tripod based retro reflector that was staged 166 meters away. The meteorological tower was deployed in the parking lot near the monitoring van. A background was collected, then downwind monitoring continued over the next 8 hours. During that time, the wind was incredibly stable and continued to blow from the direction oil well and tank located on the adjacent property west of the beam path

Concentrations of methane, ethane, propane, iso-butane, n-butane, n-hexane, toluene, ethanol, and NMHC-Balance were measured in cyclical concentrations. The E-Calc emission model was run on 10 subsequent 15-minute time averages to generate emission rates. The maximum 15-minute emission rates measured were as follows: iso-butane (2745 mg/s), n-butane (4043 mg/s), n-hexane (6425 mg/s), NMHC-Balance (4598 mg/s) (6475 mg/s), ethane (72 mg/s) methane (4514 mg/s), ethanol (189.4 mg/s), NMHC-Balance (50.3 mg/s), and toluene (356 mg/s).

Compared to the other two times that this site was measured, the mixture of target chemicals detected remained the same. Like the prior measurements at this site, there was definitely a clear cycle of emission 'puffs' that were identified throughout the day. However, the long term monitoring showed that the strait chain hydrocarbons (n-butane, isobutane, propane, hexane, NMHC-Balance) did not present their highest concentrations at the same time as methane. The methane concentration generally tracked the hydrocarbons concentration, but the overall methane concentration increased throughout the day. This suggests that concentration of methane increased was likely ambient, and not attributed to the source. And since methane was also being emitted from this site, one must be careful not 'over attribute' the source of methane.

#### 43 (Path B) - oil tank (eight), Orange Ave. & 29th St., Signal Hill



Figure 3-4: Oil Well and Tank Monitoring Site.

#### 3.6.2 Summary of Oil Wells Monitored

The sixteen unique oil wells monitored are listed below with their addresses. All measurements were performed similarly to the aforementioned example.

- Well and tank B E. Creston Ave. & Walnut Ave., Signal Hill (Days 1 and 15)
- Well B E. Spring St. & California Ave., Signal Hill (Day 2)
- Well B E. Spring St. between California Ave. and Orange Ave., Signal Hill (Day 2)
- Well (two) B E. Pacific Coast Hwy. (adjacent to Trader Joe=s), Marina Pacifica (Day 5)
- Well B S. Atlantic Ave. & E. Spring St., Signal Hill (Day 6)
- **Tank B** Orange Ave. & E. 29th St., Signal Hill (Day 7)
- Well B S. Atlantic Ave. & 33rd St., Signal Hill (Day 8)
- Well B Vermont Ave. (600m north of Sepulveda Blvd.), Carson (Day 9)
- Well (two) B Vermont Ave. & Sepulveda Blvd., Carson (Day 11)
- Well and tank B E. 35th St. & Lime Ave., Signal Hill (Day 12)
- Well (two) B 33rd St. & Pasadena Ave., Signal Hill (Day 13)
- Well B Orange Ave. (near E. 29th St.), Signal Hill (Day 13)
- Well (two) B E. Burnett St. & Gardena Ave., Signal Hill (Day 21)
- Well rework B Crescent Heights St., between Walnut Ave. & Cherry Ave., Signal Hill (Day 23)
- **Tank (eight)** B Orange Ave. & E. 29th St., Signal Hill (Day 24)
- Well (three) B E. Willow St., between Lewis Ave. & Lemon Ave., Signal Hill (Days 25 and 28)

Table 3-6 presents, for the sources comprising oil wells and/or tanks, results of all valid emissionrate events for all detected target compounds.\* Ninety-two 15-minute-averaged monitoring events, resulting in a valid emission-rate measurement for at least one compound, were achieved. Overall, a total of eleven target compounds were detected.

\* The three controlled N<sub>2</sub>O release studies were performed on Monitoring Day 15 (October 8), Monitoring Day 23 (October 16), and Monitoring Day 26 (October 19).

Comparative testing was performed with FluxSense and NPL on Monitoring Day 15 (October 8), and with NPL alone on Monitoring Day 21 (October 14).

Extended monitoring was requested by SCAQMD on Monitoring Day 24 (October 17) and Monitoring Day 28 (October 21).

 Table 3-6:

 Results of Valid Emission-Rate Measurements for Detected Compounds: Oil Wells and Tanks

I	lvent	Mean V	Vind	DI					Emi	ssion Rate (	(mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butane	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphthal ene	Propane	Toluene
			S	SITE 30: C	OIL WELL	AND TAN	K B E. Cres	ston Ave. &	Walnut Av	ve., Signal H	Hill (Monito	oring Day 1	)		
2	10:00	118.2	4.065	78.3							807.0	901.5			
3	10:15	114.3	4.388	74.4							456.5	785.5			
5	10:45	123.1	3.691	82.3		292.1					672.3				
6	11:00	133.8	3.406	89.4							636.1				
7	11:15	134.5	3.235	89.1							535.0				
8	11:30	118.1	2.981	78.3							685.5				
9	11:45	118.6	3.037	79.3							702.9				
				SIT	E 38: OIL V	VELL B E.	Spring St.	& Californi	ia Ave., Sig	nal Hill (M	onitoring D	ay 2)			
2	10:00	119.8	1.621	74.1		27.8				115.6	38.4				
4	10:45	166.2	1.721	99.9					12.7						
		•	SITE	40: OIL W	ELL B E.	Spring St. b	between Cal	lifornia Ave	e. and Oran	ige Ave., Sig	gnal Hill (M	Ionitoring I	Day 2)		
9	13:15	198.8	2.265	96.9				19.3							
10	13:30	181.6	2.309	99.8								216.8			
11	13:45	203.1	2.599	99.2								172.1			

F	lvent	Mean V	Vind	DI					Emi	ssion Rate (	mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butene	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphtha- lene	Propane	Toluene
	-	_	SITE 41	: OIL WE	LL (TWO)	B E. Pacifi	c Coast Hw	y. (adjacen	t to Trader	Joe=s), Su	nset Beach	(Monitorin	g Day 5)		
1	09:30	230.3	1.496	88.0								334.4			
2	09:45	235.4	1.285	93.6				580.6							
3	10:00	228.2	1.764	89.0				1,463.3							
6	10:45	209.5	1.518	70.8								482.4			
8	11:15	209.3	3.004	70.8					219.3						
		·		SITI	E 42: OIL V	VELL B S.	Atlantic Av	ve. & E. Spr	ing St., Sig	nal Hill (M	onitoring D	ay 6)			
7	15:45	272.9	3.622	98.2					280.1			316.9			
8	16:00	292.1	3.630	81.9					282.5			355.4			
9	16:15	276.2	3.450	92.0					266.2			332.6			
10	16:30	262.6	3.760	99.8					209.0			361.2			
				S	TE 43: OI	L TANK B	Orange Av	e. & E. 29tl	n St., Signal	l Hill (Moni	toring Day	7)			
1	09:30	103.4	0.934	73.7		1,091.3						2,952.9		1,726.3	

ŀ	lvent	Mean V	Vind	DI					Emi	ssion Rate (	mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butene	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphtha- lene	Propane	Toluene
				SI	TE 44: OII	WELL B	S. Atlantic	Ave. & 33r	d St., Signa	l Hill (Mon	itoring Day	8)			
4	14:45	178.1	1.289	95.9					71.0		4.2	88.8			95.1
5	15:00	188.6	1.169	94.7					99.2		25.9	128.6			
				SITE 45: (	OIL WELL	B Vermon	t Ave. (600r	n north of S	Sepulveda H	Blvd.), Cars	on (Monito	ring Day 9)	)		
6	14:15	288.2	2.604	87.6					8.7						34.4
7	14:30	271.6	3.157	95.4				23.0	16.8						
8	14:45	262.8	2.764	90.9					3.3						20.0
9	15:00	274.3	2.719	96.4					2.2		4.8	3.5			
				SITE 46	: OIL WEI	L (TWO)	B Vermont	Ave. & Sep	ulveda Blv	d., Carson (	Monitoring	g Day 11)			
6	12:45	164.6	2.531	71.2					7,328.0			5,074.7	519.9		1,273.1
				SITE 39	: OIL WE	LL AND TA	ANK B E. 3	5th St. & L	ime Ave., S	ignal Hill (1	Monitoring	Day 12)			
1	11:30	173.1	0.860	99.0					116.4		125.2	88.5			
2	11:45	176.3	1.497	98.8		34.5			280.4		367.9	132.1			348.4
3	12:00	173.6	1.560	99.0		54.0			283.1	25.6	223.1	84.5			276.5
4	12:15	182.5	1.543	95.8		20.6			326.6		197.8	97.4			570.8

F	Event	Mean V	Vind	Diama					Emi	ssion Rate (	mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butene	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphtha- lene	Propane	Toluene
				SI	TE 37: OII	L WELL B	33rd St. &	Pasadena A	ve., Signal	Hill (Monit	oring Day	13)			
1	11:15	269.0	1.462	82.3			133.9					50.7			
2	11:30	287.1	1.544	74.8			184.4					98.1			
3	11:45	279.8	1.837	78.1			43.1				21.1	31.2			
4	12:00	288.5	1.767	73.7					12.1		80.2	18.6			
				SITE 33	: OIL WEL	L (TWO)	3 Orange A	ve. (Near E	. 29th St.),	Signal Hill	(Monitorin	g Day 13)			
5	13:45	296.7	2.961	94.8								8.2			
6	14:00	291.8	2.894	99.0		5.9						6.5			33.7
7	14:15	314.5	2.728	84.5				10.6							
8	14:30	303.1	3.029	92.9				8.1	3.4			419.6			
9	14:45	299.0	3.252	96.8							529.8	795.8			
10	15:00	302.4	3.392	93.2							331.1	507.6			

E	vent	Mean V	Vind	Diama					Emi	ssion Rate (	mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butene	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphtha- lene	Propane	Toluene
			S	ITE 30: O	IL WELL A	AND TANK	B E. Crest	ton Ave. &	Walnut Av	e., Signal H	ill (Monito	ring Day 15	5)		
1	11:45	154.3	2.016	90.0		75.8			9.6		667.8	159.5			
2	12:00	164.6	2.105	99.2					23.8						
3	12:15	156.1	2.301	99.3		187.7					2,248.1				
4	12:30	150.1	2.608	94.8		351.9					3,324.3				
5	12:45	155.1	2.570	96.0		239.7					2,444.5				
6	13:00	149.8	2.741	89.8		473.7				352.9	3,705.3	158.5			
7	13:15	148.3	3.075	94.5		517.1				741.9	2,763.0	340.6			
8	13:30	163.1	2.525	99.1		507.2				734.0	1,861.9	261.4			171.2
9	13:45	148.1	2.044	85.3		169.8					824.9				
10	14:00	156.4	1.727	90.6		116.8			27.9	252.7	319.9	148.2			
11	14:15	164.0	1.938	95.5		403.2				981.4	1,364.6	400.6			90.5
12	14:30	187.4	1.661	99.9		82.4		1.4	5.9	248.6	532.9	132.3			

F	Event	Mean V	Vind	DI					Emi	ssion Rate (	(mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butene	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphtha- lene	Propane	Toluene
	-			SITE 31:	OIL WEL	L (TWO) E	B E. Burnet	t St. & Gar	dena Ave.,	Signal Hill	(Monitorin	g Day 21)			
6	14:15	283.6	1.786	82.1							91.1	69.2			
8	14:45	284.2	1.591	83.2	1,546.6				109.2		222.9	597.3			
9	15:00	283.2	1.557	71.1	1,345.3				196.8		438.8	722.6			
10	15:15	290.0	1.440	72.3	1,585.8				264.8		73.3	659.4			
12	15:45	286.8	1.258	73.9	402.7				88.9		142.7	309.1			
	-	SITE	32: OIL V	WELL RE	WORK B	Crescent H	eights St., b	etween Wa	lnut Ave. a	nd Cherry A	Ave., Signal	l Hill (Mon	itoring Day	23)	
1	10:15	211.5	1.294	86.6					52.5		1,237.3	360.5			
2	10:30	203.0	1.210	82.3					650.2		1,904.3	572.9			
3	10:45	211.4	1.241	76.8					783.3		2,116.6	437.6			
4	11:00	199.4	1.366	86.7					455.9		2,260.3	149.6			
7	11:45	190.0	0.923	77.6	12.2				618.1		2,205.7	303.2			
14	13:45	242.1	1.444	76.6							1,472.3	1,043.5			
15	14:00	237.6	1.461	72.9							820.2	934.4			

F	Event	Mean V	Vind	Diserse					Emi	ssion Rate (	mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butene	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphtha- lene	Propane	Toluene
	-		-	SITE 4	3: OIL TAN	NK (EIGH)	() <b>B Orang</b>	e Ave. & E.	29th St., Si	ignal Hill (N	Aonitoring	Day 24)	_		
4	11:45	275.0	1.575	70.1		2,744.9	4,043.9	480.6	71.8	6,425.1		2,837.1		6,475.1	
5	12:00	278.2	1.756	70.9		2,157.7	2,659.5		31.8	5,336.0	1,325.7	1,864.0		4,966.9	315.2
8	12:45	280.2	2.291	75.1		856.2	2,058.3	286.1			3,808.5	1,937.0		3,705.3	258.2
10	13:15	278.3	2.429	74.0		1,255.3	2,485.9	114.0	33.7	1,317.5	2,832.2	2,167.4		4,470.6	
11	13:30	282.7	2.470	71.1		1,216.2	830.5			1,342.2		1,468.4		3,891.1	356.0
21	16:00	283.4	2.713	74.4		66.6				438.8	3,278.1	1,236.8		1,141.1	
26	17:15	286.3	2.715	71.2		288.3					3,475.6	3,026.3		832.7	
27	17:30	279.6	2.430	76.8		680.5					4,278.2	3,355.4		1,565.2	
28	17:45	280.4	2.696	74.1		472.1					4,598.1	4,278.3		838.1	
29	18:00	283.0	2.586	74.7		206.3	505.3				3,768.4	4,514.2		473.1	
	-	S	ITE 34: (	OIL WEL	LS (THREE	E) <b>B E. Wi</b> l	low St. (bet	ween Lewis	Ave. & Le	mon Ave.),	Signal Hill	(Monitorin	ng Day 25)		
1	12:30	192.4	2.128	98.5						51.3	196.5	123.5			60.5
2	12:45	186.1	2.331	99.6							91.4	21.6			
3	13:00	192.6	2.514	98.5						141.8		27.7			
4	13:15	193.3	2.372	98.6							103.1	7.9			

E	vent	Mean V	Vind	DI					Emi	ssion Rate (	mg/s)				
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Capture (%)	Benzene	iso- Butene	n-Butane	Ethane	Ethanol	n-Hexane	NMHC	Methane	Naphtha- lene	Propane	Toluene
		SITE 34:	OIL WI	ELLS (TH	REE) B E.	Willow St.	(between L	ewis Ave. &	Lemon Av	ve.), Signal l	Hill (Monit	oring Day 2	8) (Second	Time)	
5	13:45	156.5	1.715	99.9					269.9		512.4	633.9		188.9	
6	14:00	153.7	2.120	99.7					316.4	27.5	398.0	278.7		73.2	
7	14:15	164.2	2.273	99.3					372.2		141.4	77.0			
8	14:30	163.1	2.122	99.6					349.2		87.3	59.1			
9	14:45	151.5	1.207	99.6					227.6		263.0	186.9			
10	15:00	149.3	1.711	99.5					293.9	32.9	212.6	141.2			
11	15:15	148.6	1.561	99.4					278.0	21.3	241.3	180.2			
12	15:30	148.0	1.566	99.2					251.5	52.8	230.2	115.8			
13	15:45	134.3	1.297	91.3					241.1		180.7	18.6			
14	16:00	125.5	1.493	86.6					241.7		163.6				
15	16:15	145.1	1.285	98.8					172.5		82.5				

#### 3.7 Cattle Farms

Two cattle farm measurements were made, both within the city of Chino. There were many agricultural farms and cattle (feed lot) farms located within the same vicinity. The cattle farms selected for measurement were ones with long roads that were perpendicular to the feed lots.

Although VOC hydrocarbons were measured, there was hardly and detections above the background level. The main elevated chemicals were ammonia (53 - 112 kg/hr) and methane (0.36 - 6.27 kg/hr). Since there were so many cattle farms within the small area, the ambient air upwind had a higher concentration of methane and ammonia then measured in non-agricultural areas closer to the city of Signal Hill.

Valid emission rates were obtained from a total of two cattle farms:

- Gordon Hay B Cleveland Ave., Chino (Day 3)
- (owner unknown) B Carpenter Ave. & Eucalyptus Ave., Chino (Day 10)

#### 3.7.1 Cattle Farm Monitoring Example

A typical example of monitoring at cattle farm feed lot operation was conducted on monitoring day 10 at an unnamed farm on Carpenter & Eucalyptus Avenue in Chino. Figure 3-5 shows the monitoring configuration used east of the feed lot on Friday October 2<sup>nd</sup>, from 12:00 to 13:30.

The Kassay OP-FTIR van was positioned along the shoulder of the road bordering the farm. The OP-FTIR was directed to shot the IR beam through the back door out to a tripod based retro reflector that was staged 272 meters away. The meteorological tower was deployed on the shoulder of the road near the road. A background was collected, and then monitoring continued over the next two hours. During that time, the wind continued to blow from the west, through the feedlot, moving the emission plume though the OP-FTIR beam.

Initially, since the entire area had high concentrations of ammonia and methane a known clean background was used from another site. However, this resulted in over attributing upwind emissions to the farm. Therefore, immediately afterward, the van was moved to the road west of the farm and an upwind background was collected. Since the upwind included the overall local ambient concentration of methane and ammonia, the data was reprocessed so that the emission rates were attributed just to the farm.

The highest 15-minute emission measured at the farm was ammonia 3121 mg/s and methane 651 mg/s. The emissions trend between the two chemicals tracked well and seemed to indicate that both of these emissions were from the source. Figure 3-5 shows the monitoring configuration for the cattle farm on Carpenter and Eucalyptus Ave.



#### 54 - Cattle Farm (E of Carpenter Ave, & Eucalyptus Ave.)

Figure 3-5: Depiction of the Cattle Farm Monitoring Site.

#### 3.7.2 Summary of Cattle Farms

The other cattle farm measured was very similar in configuration and operation. Table 3-7 presents all the valid emission-rate events for all detected target compounds. Twelve 15-minute-averaged monitoring events, resulting in valid emission-rate measurements for at least one compound, were achieved.

Overall, only ammonia and methane were detected along with very low trace amounts of hydrocarbons.

 Table 3-7:

 Results of Valid Emission-Rate Measurements for Detected Compounds: Cattle Farms

]	Event	Mean W	ind		Emission	Rate (mg/s)
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Plume Capture (%)	Ammonia	Methane

#### SITE 53: GORDON HAY B Cleveland Ave., Chino (Monitoring Day 3)

	1			1	1	
1	12:45	258.3	1.856	77.1	1,999.6	2,385.6
2	13:00	304.1	1.777	81.6	1,831.3	2,257.3
3	13:15	282.8	1.918	87.9	1,932.3	1,868.0
4	13:30	285.1	2.099	86.4	1,473.4	1,086.7
6	14:00	250.4	2.461	71.6	2,170.5	2,495.6
7	14:15	293.8	2.713	86.6	2,104.4	2,387.0
8	14:30	272.7	2.626	84.3	1,827.5	1,500.9
9	11:45	272.7	2.779	84.8	1,992.7	1,740.6

SITE 54: (UNKNOWN) B Carpenter Ave. & Eucalyptus Ave., Chino (Monitoring Day 10)

1	12:30	234.6	3.081	89.8	2,582.6	99.8
2	12:45	260.2	2.809	92.5	2,071.0	413.7
3	13:00	246.5	3.242	87.2	2,812.9	651.3
4	13:15	255.7	3.779	91.7	3,120.9	171.

#### 3.8 Controlled Release Results

In order to establish a baseline for comparison of ORS techniques, KASSAY participated in a formal blind propane tracer release study and N2O release with other contractors. The formal propane release was conducted on Angel's stadium of Anaheim parking lot under controlled conditions. The N2O tracer release was conducted with FluxSense and NPL at an oil well and gas station small sources while quantifying those actual emissions. Sections 3.8.1 and 3.8.2 present results of the formal (propane) and informal (N<sub>2</sub>O) controlled tracer-gas release studies, respectively.

#### **Results for propane releases:**

Comparing E-Calcs calculated emission rate with the known release emission rate, a total percent error for the two days was 28%. Upon further review as described below, the surface roughness parameter was changed to a smoother value. This improved the percent error to 2%. The 'R squared' value for both cases was 0.72 and 0.77 respectively.

#### Discussion of propane release study

The process to measure the propane release was the same as used to monitor the other small sources. The OP-FTIR and meteorological tower was set up down wind of the emission source; in this case the tracer release point. A total of forty-two 15-minute measurements were made over two test days. During that time, the SCAQMD released the tracer at blind release rates. KASSAY only processed the release from the lowest elevation point since E-calc model is not applicable for elevated sources.

Figures 3-6 and 3-7 depict the FTIR measurement configurations for the first and second days of the controlled propane release, respectively. Also depicted are the locations of the release and the on-site meteorological tower.

On October 12 (first day, also overall Monitoring Day 19), the beam path was oriented normal to a wind blowing from 230 degrees (a southwest wind direction), and the acceptable wind-direction range was between 185 and 275 degrees; the path length was 136 meters (downwind normal distance of 33 meters). On October 13 (second day, also overall Monitoring Day 20), the beam-path orientation and acceptable wind-direction range were the same as Day 1; the path length was 153 meters (downwind normal distance of 23 meters). On both days, the beam height was about 1.0 meter above ground on both days.

Tables 3-8 and 3-9 present Kassays' results of the controlled propane release on October 12 and 13, respectively. An important parameter in AERMOD (and, thus, e-Calc) is the surface roughness length ( $z_o$ ), which is related to the height of the obstacles to the wind flow. The surface roughness length can be defined as the maximum height at which the mean horizontal wind speed is zero. Values range from less than 0.001 meter over a calm water surface to 1 meter or more over a forest or urban area.

Representative  $z_o$  values in the upwind area of interest can be determined by: (a) employing the procedure based on surrounding land use per AERMET, AERMODs meteorological pre-processor; or (b) assigning an appropriate value from look-up tables. In general, it is preferable to use the AERMET option (herein referred to as producing the unadjusted  $z_o$  value) when the upwind area of influence acting upon the source is large, e.g., where stack emissions from a power plant are modeled. Conversely, use of the second option (assign  $z_o$  value –referred here as adjusted value) may lead to more accurate results when the upwind area of influence is more limited, as is the case in these two studies.

Predicted emission rates based on both adjusted and unadjusted  $z_o$  values are presented for each day. Depending on the actual wind direction and the upwind terrain, the unadjusted  $z_o$  values calculated by AERMET ranged between 0.380 and 0.556 meter. Predicted emission rates resulting from adjusted  $z_o$  values of 0.1 meter, 0.05 meter, and 0.01 meter are also shown, this selection was based on published literature compiled by the Texas Commission on Air Quality (TCEQ) for similar surfaces (see <u>http://www.cabq.gov/airquality/documents/pdf/tceqstcroughnessguidance.pdf</u>).

Propane was released, at varying emission rates, over the two-day study from pre-designated heights (3.0m, 6.4m, and 7.9m) from a scissors-type lift. Kassay and the other contractors\*, however, did not know the emission-rate values.

In addition to presenting the wind and emissions data for each monitoring event (per tables in Section 2 for the small sources), the following additional event-specific information is presented in the controlled release tables:

- standard deviation of the horizontal wind direction (sigma theta or  $\sigma_{\theta}$ );
- the measured path-integrated propane concentration; and
- a judgment on the quality of the e-Cal-derived propane emissions data, based on the existing meteorology.

On October 12, propane emission rates for a total of sixteen monitoring events (15-minute) were derived, all from a release height of 3.0 meters (Table 3-8).

On October 13, propane emission rates were derived for a total of 26 monitoring events (15-minutes): seven events with a release height of 3.0m, three events with a release height of 6.4m, and sixteen events with a release height of 7.9m (Table 3-9).

\*Other Project 2 contractors who participated in the controlled release study were National Physics Laboratory (NPL) of Great Britain (LIDAR method) and FluxSense of Sweden (Solar Occultation Flux method). A fourth firm, awarded another ORS project by SCAQMD, also participated in the controlled release study: Atmosfir (Vertical Radial Plume Mapping method).

Following is a discussion of the results by release height for the elevated measurements.

#### 6.4m and 7.9m Release Height

The area-source technique is not intended to be applied to elevated releases, as most or all of the plume mass is likely to pass over the FTIR beam, under most circumstances.

The spectrometer did, however, measure low concentrations of propane for each monitoring event performed with the 6.4m and 7.9m release heights (see Table 3-8), but these measurements clearly traversed the underside of the three-dimensional plume. This is evidenced by the fact that e-Calc produced emission rates that were increasingly absurd as the surface roughness length approached 0.01m (emission rates not shown), which was a clear indication that the model was attempting to reconstruct the plume based on an increasingly nominal plume capture in the vertical dimension.

No emissions data from the 6.4m and the 7.9m release heights are considered valid, and, as such, results from these release heights are not discussed further.

#### 3.0m Release Height

Even though the propane release height (3.0m) was greater than the FTIR beam (about 1.0m), the plume center line, in this case, could reasonably be anticipated to be brought close to the ground immediately. This is because the fully collapsed scissors-lift structure from which the propane was released formed a solid volume, thereby causing the air to flow up over it and then down the other side, as opposed to passing right through it (as was the case when the lift was extended for the other releases). Air flow over and down a solid structure is commonly known as plume downwash, a phenomenon addressed in AERMOD (and e-Calc).

Upon examination, the quality of the emissions data was better on October 13 than on October 12. On October 12, only one of sixteen events had emissions data judged very good, with the emissions data from the remainder of the events judged as either good (four events), fair (six events), or poor (three events). Two events were not valid, due to an unacceptable plume capture, well less than the 70 percent criterion for valid data.

In contrast, on October 13, one of seven events had emissions data judged good, with emissions data for the remainder of the events judged as either excellent (three events), or very good (three events).

In general, the meteorology for applying the area-source technique was much better on October 13 than on October 12, and this was the primary reason for the difference in the quality of the emissions data. The principal meteorological conditions affecting data quality were wind speed, atmospheric turbulence, and, to a lesser degree, wind direction. Under typical meteorological conditions, wind speeds greater than about 0.8 m/s are generally sufficient to yield acceptable emissions data (assuming sufficient plume capture). However, when the atmosphere is very unstable, the occurrence of thermal eddies can affect the quality of the emissions data.

On the first day, the strong heating of the asphalt parking lot likely resulted in the establishment of a very steep temperature lapse rate near the ground, resulting in a highly unstable atmosphere through the vertical extent of the propane plume. Even though the mean wind speed was greater than 0.8 m/s and the mean wind direction was generally acceptable, the wind was light enough to allow these highly unstable conditions to persist, resulting in the creation of turbulent eddies and shifting winds. This is supported by the high sigma-theta values for several events that day, which evidences that the wind blew some of the time outside the acceptable range for those events. As a general rule, the emissions data is somewhat suspect for events in which sigma-theta values are greater than 35 degrees B the AERMOD sigma-theta upper-limit default value.

On the second day, the mean wind speed was greater, which decreased an air parcel=s residence time over the hot asphalt, thus inhibiting the very steep lapse rate. This explains the lower sigma-theta values and the corresponding higher quality of the emissions data.

In terms of the surface roughness length, the otherwise empty asphalt parking lot had, scattered in the upwind direction beyond about 50 or 100 meters from the measurements (depending on the event-specific wind direction), concrete traffic barriers (:-meter height) and parked cars. Based upon our professional judgment, the  $z_o$  value which best represents this situation is 0.05 meter. Therefore, the entries in the two tables which correspond to a  $z_o$  value of 0.05 meter represent our preferred emission rates (bolded entries) for each 15-minute monitoring event (Provided under separate cover is our best estimate of the propane emission rate for each release period, as determined by the SCAQMD (units of kilograms per hour), and taking into account the judged quality of the meteorological data for each 15-minute monitoring event).



Figure 3-6: Measurement configuration for the controlled propane release: October 12, 2015.



Figure 3-7: Measurement configuration for the controlled propane release: October 13, 2015.

## Table 3-8:Results of All Emission-Rate Measurements for the Controlled Release of Propane: October 12, 2015Acceptable Wind-Direction Range = 185 B 275 degrees

E	vent	N	Iean Wir	nd	Path-Int Concen	tegrated tration	Plume	Emi	ission Rate a (m	s Function g/s)	of zo	Judged
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	AERMET	<i>z</i> <sub>0</sub> = <b>0.10m</b>	$z_o = 0.05 \mathrm{m}$	$z_o = 0.01 \mathrm{m}$	Quality of Data
					Pr	opane Relea	se Height = 3	3.0m				
1	13:00	266.7	1.722	41.9	53.32	96.17	85.5	1,909.1	1,303.2	1,179.1	882.9	fair
2	13:15	280.3	1.460	79.5	28.17	50.81	76.7	1,040.0	718.9	645.7	362.7	poor
3	13:30	281.9	1.581	62.1	44.34	79.98	75.2	1,814.7	1,248.5	1,118.1	617.4	poor
4	13:45	235.8	1.400	87.3	42.12	75.97	99.9	1,212.4	755.9	692.0	809.0	poor
5	14:00	226.0	1.824	33.2	134.22	242.09	99.1	4,606.8	2,975.2	2,762.2	3,607.0	good
6	14:15	213.3	2.106	32.5	118.76	214.21	93.9	4,845.4	3,099.6	2,868.2	3,305.2	good
7	14:30	235.5	2.158	16.9	164.36	296.45	100.0	6,424.0	4,177.0	3,904.2	5,674.0	very good
8*	14:45	232.9	1.226	49.8	100.37	181.04	100.0	2,525.5	1,607.7	1,471.9	1,662.0	fair
9	15:00	230.3	1.767	34.2	143.11	258.12	99.7	4,674.8	3,035.6	2,829.1	3,905.5	good
10	15:15	242.4	1.689	29.3	216.16	389.88	99.6	6,168.1	4,335.6	4,027.6	5,435.1	good
11	15:30	237.7	1.139	69.7	169.83	306.32	99.8	3,694.2	2,456.7	2,254.5	2,674.1	fair
12*	15:45	262.1	1.400	38.8	242.20	436.85	88.2	6,299.3	4,329.1	3,966.6	3,726.3	fair
13	16:00	251.0	1.400	44.8	26.78	48.30	95.6	653.0	453.5	419.7	496.5	fair

FTIR Pathlength = 136m

## Table 3-8 (Cont'd):Results of All Emission-Rate Measurements for the Controlled Release of Propane: October 12, 2015Acceptable Wind-Direction Range = 185 B 275 degreesFTIR Pathlength = 136m

Event Mean Wind		nd	Path-Integrated Concentration		Plume	Em	ission Rate a (m	as Function g/s)	of zo	Judged		
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	AERMET	$z_o = 0.10 \mathrm{m}$	$z_o = 0.05 \mathrm{m}$	$z_o = 0.01 \mathrm{m}$	Quality of Data
					Propan	e Release H	eight = 3.0m	(Cont=d)				
14	16:15	261.5	1.232	34.2	30.10	54.29	89.0	704.7	483.8	440.9	392.5	fair
15	16:30	315.8	2.067	17.3	15.24	27.49	28.4	3,033.9	2,577.3	2,377.7	331.9	not valid
16	16:45	311.3	2.018	20.1	19.51	35.19	40.8	2,221.9	1,731.4	1,570.2	356.1	not valid

#### Note:

\* The emission rates for Events 8 and 12 were derived based on truncated 1-minute FTIR measurements. It appears that the propane was shut off prior to completion of each 15-minute event (7 and 3 minutes before event completion, respectively), as evidenced by: (a) verbal communication in the field that NPL had changed the emission rates at those times; and (b) examination of the 1-minute FTIR measured concentration data, which dropped to or near the instrument=s minimum detection level (MDL).

If we were to assume the propane release had, in fact, continued throughout these events and that these low measurements were real, the respective emission rates for Events 8 and 12 would be: 1,581.4 and 5,039.5 mg/s for the AERMET treatment of  $z_o$ ; 1,006.6 and 3,463.3 mg/s for  $z_o = 0.10$ ; 921.6 and 3,173.2 mg/s for  $z_o = 0.05$ ; and 1,040.6 and 2,981.0 mg/s for  $z_o = 0.01$ .

## Table 3-9:Results of All Emission-Rate Measurements for the Controlled Release of Propane: October 13, 2015Acceptable Wind-Direction Range = 185 B 275 degreesFTIR Pathlength = 153m

E	vent	Ν	Iean Wir	nd	Path-Int Concen	tegrated tration	Plume	Em	ission Rate a (m	as Function g/s)	of zo	Judged
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	AERME T	$z_o = 0.10 \mathrm{m}$	$z_o = 0.05 \mathrm{m}$	$z_o = 0.01 \mathrm{m}$	Quality of Data
					Р	ropane Rele	ease Height =	3.0m				
1	10:45	217.6	2.161	46.6	211.57	381.60	99.6	5,006.7	4,579.3	4,968.5	8,529.3	good
2	11:00	205.5	3.086	21.4	208.35	375.80	99.2	5,952.5	5,952.5	6,414.7	8,312.4	very good
3	11:15	189.8	3.001	16.1	173.44	312.83	95.2	4,620.6	4,054.3	4,110.6	4,676.9	very good
4*	11:30	200.7	3.826	15.0	159.79	288.21	99.7	5,409.7	5,360.7	5,781.5	7,516.6	very good
					Pr	opane Relea	se Height = (	6.4m**				
5	11:45	214.2	3.488	18.8	19.23	34.68	100.0					not applicable
6	12:00	208.7	3.204	23.5	18.77	33.86	99.8					not applicable
7	12:15	224.8	3.507	21.5	18.13	32.70	100.0					not applicable
					Pr	opane Relea	se Height = 7	7.9m**				
8	12:30	219.9	3.055	24.1	20.36	36.72	100.0					not applicable
9	12:45	215.1	2.419	24.7	60.32	108.80	100.0					not applicable
10	13:00	211.9	2.730	26.8	45.09	81.33	100.0					not applicable
11	13:15	213.1	3.314	29.7	23.16	41.77	100.0					not applicable

# Table 3-9 (Cont'd):Results of All Emission-Rate Measurements for the Controlled Release of Propane: October 13, 2015Acceptable Wind-Direction Range = 185 B 275 degreesFTIR Pathlength = 153m

E	vent	Μ	lean Wir	nd	Path-Int Concen	egrated tration	Plume	Emi	ission Rate a (m	ns Function g/s)	of zo	Judged
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	AERME T	$z_o = 0.10 \mathrm{m}$	$z_o = 0.05 \mathrm{m}$	$z_o = 0.01 \mathrm{m}$	Quality of Data
					Propan	e Release H	eight = 7.9m*	** (Cont=d)				
12	13:30	224.2	3.124	16.3	26.14	47.15	100.0					not applicable
13	13:45	219.2	3.935	20.6	19.20	34.63	100.0					not applicable
14	14:00	223.7	3.966	16.4	29.63	53.44	100.0					not applicable
15	14:15	220.2	4.186	20.6	34.71	62.61	100.0					not applicable
16	14:30	224.2	3.732	21.8	34.85	62.86	100.0					not applicable
17	14:45	224.9	4.179	19.7	40.67	73.36	100.0					not applicable
18	15:00	225.7	4.165	18.6	38.43	69.32	100.0					not applicable
19	15:15	216.6	3.676	18.5	39.13	70.58	100.0					not applicable
20	15:30	238.8	3.685	17.9	34.25	61.78	100.0					not applicable
21	15:45	215.8	4.260	16.7	0.53	0.96	100.0					not applicable
22	16:00	211.5	3.757	15.2	2.77	5.00	100.0					not applicable
23	16:15	213.9	4.211	18.3	0.65	1.17	100.0					not applicable

# Table 3-9 (Cont'd):Results of All Emission-Rate Measurements for the Controlled Release of Propane: October 13, 2015Acceptable Wind-Direction Range = 185 B 275 degreesFTIR Pathlength = 153m

Event		Mean Wind			Path-Integrated Concentration		Plume	Em	ission Rate a (ma	s Function g/s)	of zo	Judged	
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	AERME T	<i>z</i> <sub>0</sub> = <b>0.10m</b>	$z_o = 0.05 \mathrm{m}$	$z_o = 0.01 \mathrm{m}$	Quality of Data	
					Р	ropane Rele	ease Height =	3.0m					
24*	16:30	220.1	4.016	18.4	274.39	494.91	100.0	11,308.7	11,986.8	14,055.5	22,602.6	excellent	
25	16:45	224.6	3.924	15.8	276.49	498.70	100.0	11,175.7	12,128.2	14,357.4	23,712.9	excellent	
26	17:00	228.3	3.597	18.4	318.22	573.97	100.0	11,823.9	12,914.4	15,336.6	25,668.1	excellent	

Notes:

The emission rates for Events 4 and 24 were derived based on truncated 1-minute FTIR measurements. For Event 4, It appears that the propane was shut off 3 minutes prior to event completion. For Event 24, it appears that the propane was shut off sometime prior to event initiation, and resumed after 3 minutes into the event. As in the first day of the formal controlled release (Table 3-1), the propane shut-offs are evidenced by: (a) verbal communication in the field that NPL had changed the emission rates at those times; and (b) examination of the 1-minute FTIR measured concentration data, which dropped to or near the instrument=s minimum detection level (MDL).

If we were to assume the propane release had, in fact, continued throughout these events and that these low measurements were real, the respective emission rates for Events 4 and 24 would be: 4,434.5 and 9,110.6 mg/s for the AERMET treatment of  $z_o$ ; 4,394.3 and 9,656.9 mg/s for  $z_o = 0.10$ , 4,739.3 and 11,323.5 mg/s for  $z_o = 0.05$ ; and 6,161.5 and 18,209.3 mg/s for  $z_o = 0.01$ .

\*\* As discussed on page 3-2, the area-source technique is not intended to be applied to elevated releases.

#### 3.9 Informal Nitrous Oxide Releases

Kassay participated in three informal controlled  $N_2O$  release studies: October 8, October 16, and October 19, 2015.

#### October 8 (Monitoring Day 15)

On October 8, Kassay participated in an informal controlled release study with FluxSense and NPL at the oil well and tank located at E. Creston Ave. and Walnut Ave., in Signal Hill (Kassay Site #30). N<sub>2</sub>O was released in a controlled manner during Kassay=s final four events at this site on this day (Monitoring Day 15 per Table 3-10). Kassay, however, was not privy to the emission-rate values or when (or if) the emission rate was changed.

Figure 3-8 depicts the FTIR measurement configuration. Also depicted are the locations of the  $N_2O$  release and the on-site meteorological tower. The beam path was oriented normal to a wind blowing from 180 degrees (a southerly wind direction), and the acceptable wind-direction range was between 135 and 225 degrees. The path length was 134 meters, and the shortest (normal) distance between the source and the beam path was 27 meters.

 $N_2O$  was released continually by FluxSense from a funnel atop a tripod-mounted pole, at a release height of 5.5 meters, positioned adjacent to the top of the oil tank (from which a FLIR camera showed emissions to be emanating, intermittently).

Tables 3-10 presents results of the controlled  $N_2O$  release as determined via the area-source technique using AERMOD (e-Calc). The format is similar to the tables for the formal controlled propane release (Tables 3-8 and 3-9).

The quality of all emissions data was judged either very good (two events) or good (two events). The lesser quality was due to the sigma-theta values being above 35 degrees. Even though the  $N_2O$  release height was 5.5 meters, we believe that down wash caused the plume center line to be brought to (or near) the ground, owing mainly to the presence of the large tank in close lateral proximity. This, and the fact that the terrain was hilly and grassy (not asphalt-covered like the formal controlled release study) supported the very **good** data quality judgments.

Examination of the 1-minute FTIR data (not provided) showed that the measured concentration went to zero prior to 14:45, indicating that the  $N_2O$  either was shut off or had run out and explaining the marked drop in the 15-minute-averaged emission rate.



Figure 3-8: Measurement configuration for the controlled nitrous oxide release: October 08, 2015

#### **Table 3-10:**

#### Results of All Emission-Rate Measurements for the Controlled Release of Nitrous Oxide: October 8, 2015

		-				0		0	
Event		Mean Wind			Path-In Concer	tegrated itration	Plume	Emission	Judged
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	Rate (mg/s)	Quality of Data

#### Acceptable Wind-Direction Range = 135 B 225 degrees

9	13:45	148.1	2.044	27.1	40.61	73.10	97.2	1,595.6	very good
10	14:00	156.4	1.727	37.9	53.30	95.94	99.6	2,149.0	good
11	14:15	164.0	1.938	25.8	39.18	70.52	100.0	1,994.5	very good
12	14:30	187.4	1.661	43.3	9.69	17.44	100.0	424.9	good

#### October 16 (Monitoring Day 23)

On October 16, Kassay participated in an informal controlled release study with FluxSense at the oil well re-work site located on Crescent Heights St. (between Walnut Ave. and Cherry Ave.), in Signal Hill (Kassay Site #32). N<sub>2</sub>O was released in a controlled manner during Kassay=s final four events at this site on this day (Monitoring Day 23 per Table 3-2). As with the October 8 controlled N<sub>2</sub>O release, Kassay was not privy to the emission-rate values or when (or if) the emission rate was changed.

Figure 3-9 depicts the FTIR measurement configuration for the informal controlled release study on October 16. Also depicted are the locations of the N<sub>2</sub>O release and the on-site meteorological tower. The beam path was oriented normal to a wind blowing from 270 degrees (a west wind direction), and the acceptable wind-direction range was between 225 and 270 degrees. The path length was 113 meters, and the shortest (normal) distance between the source and the beam path was 96 meters.

 $N_2O$  was released continually by FluxSense from a funnel positioned out their vehicle window, at a release height of 2.0 meters.

Tables 3-11 presents results of the controlled  $N_2O$  release on October 23 as determined via the areasource technique using AERMOD (e-Calc). The format is similar to the earlier informal  $N_2O$  release (Table 3-3).

The quality of all emissions data was judged poor for the four events. Sigma-theta values were all above 35 degrees, and the plume capture for the first event was below the 70 percent criterion.

1 able 5-11.
Results of All Emission-Rate Measurements for the Controlled Release of Nitrous Oxide:
October 16, 2015
Acceptable Wind-Direction Range = 225 B 270 degrees

Table 2 11.

Event		Μ	Mean Wind			tegrated itration	Plume	Emission	Judged
#	Start Time (PDT)	Direction (degrees)	Speed (m/s)	Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	Rate (mg/s)	Quality of Data

	JII 11 52.				cint mergines		in energy riv	c. a wannu	
13	13:30	287.6	1.447	60.2	7.76	13.97	48.1	605.1	poor
14	13:45	242.1	1.444	50.7	11.23	20.21	80.1	700.7	poor
15	14:00	237.6	1.461	50.3	4.65	8.37	77.5	304.4	poor
16	14:15	258.9	1.091	55.8	6.45	11.61	80.8	312.6	poor

#### SITE 32: OIL WELL REWORK B Crescent Heights St. (between Cherry Ave. & Walnut Ave.),



Figure 3-9: Measurement configuration for the controlled nitrous oxide release: October 16, 2015.

#### October 19 (Monitoring Day 26)

On October 19, Kassay participated in an informal controlled release study with FluxSense and NPL at Vons gas station (#1638), located at 4226 Woodruff Ave., in Lakewood (Kassay Site #2). N<sub>2</sub>O was released in a controlled manner during Kassay=s six events at this site on this day (Monitoring Day 26 per Table 3-2). As with the earlier controlled N<sub>2</sub>O releases, Kassay was not privy to the emission-rate values or when (or if) the emission rate was changed.

Figure 3-5 depicts the FTIR measurement configuration. Also depicted are the locations of the  $N_2O$  release and the on-site meteorological tower. The beam path was oriented normal to a wind blowing from 235 degrees (a southwest wind direction), and the acceptable wind-direction range was between 180 and 290 degrees. The path length was 132 meters, and the shortest (normal) distance between the source and the beam path was 19 meters.  $N_2O$  was released continually by FluxSense within 1 meter of the ground.

Tables 3-5 presents results of the controlled  $N_2O$  release as determined via the area-source technique using AERMOD (e-Calc). The format is similar to the earlier informal  $N_2O$  releases (Table 3-3 and 3-4).

The quality of all emissions data was judged poor for four events, and fair for only one. The main problem was the fact that the wind was generally not within the acceptable wind-direction range, thus causing the plume to impact the beam path at an oblique angle.

## Table 3-12:Results of All Emission-Rate Measurements for the Controlled Release of Nitrous Oxide:<br/>October 19, 2015October 19, 2015Acceptable Wind-Direction Range = 180 B 290 degrees

Event		Μ	lean Wir	ıd	Path-Int Concen	tegrated tration	Plume	Emission	Judged
#	Start Time (PDT)Direction (degrees)Speed (m/s)		Sigma Theta (degrees)	ppm-m	mg/m <sup>2</sup>	Capture (%)	Rate (mg/s)	Quality of Data	
SITE 2: VONS GA		AS STATION	N (#1638) B	4226 Wood	ruff Ave., La	kewood			
1	10:45	180.2	1.556	38.5	41.89	75.40	90.9	523.2	fair
2	11:00	172.4	1.681	29.3	49.77	89.59	87.7	580.5	poor
3	11:15	177.8	2.004	37.1	68.88	123.98	90.1	859.2	poor
4	11:30	166.5	1.900	29.3	69.76	125.57	86.6	1,024.6	poor
5	11:45	175.3	1.798	42.7	77.40	139.32	89.2	936.3	poor
6	12:15	162.1	2.230	33.4	61.23	110.21	84.6	1,144.0	poor

 Acceptable WD Window = 180° to 290°

 Betrorellector

 Betrorellector

Figure 3-10: Measurement configuration for the controlled nitrous oxide release: October 19, 201

#### 3.10 Miscellaneous Source characterizations.

Sections 3.10.1 and 3.10.2 present results of the source emission characterizations for the oil well and tank cluster (Monitoring Day 22) and the rendering plants (Monitoring Day 26), respectively.

#### 3.10.1 Cluster of Oil Wells and Tanks

Table 3-13 presents characterization results for the oil well and tank cluster. In addition to the compounds shown, trace amounts of ethylene were detected during Event 25 (0.47 ppm-m, 1.8 ppb), and trace amounts of methanol were detected during Events 9 and 14 (0.52 ppm-m, 2.0 ppb and 0.53 ppm-m, 2.03 ppb, respectively).

	womoring Day 22 (Thursday, October 15, 2015)											
Event Downwind Concentration												
#	Start	n-butane		ethanol		NM	NMHC		Methane		Toluene	
	Time (PDT)	ppm-m	ppb	ppm-m	ppb	ppm-m	ppb	ppm-m	ppb	ppm-m	ppb	

Table 3-13: Characterization Results for the Oil Well and Tank Cluster Monitoring Day 22 (Thursday, October 15, 2015)

Atlantic Ave. (near Home Depot), Signal Hil
One-Way Pathlength = 260.0m

1	10:00	3.88	14.9								
2	10:15			0.63	2.4			4.64	17.8		
3	10:30										
4	10:45					4.60	17.7				
5	11:00					1.55	6.0				
6	11:15									5.58	21.5
7	11:30					0.69	2.7				
8	11:45					1.98	7.6	2.95	11.3		
9	12:00					7.96	30.6				
10	12:15					0.76	2.9				
11	12:30					0.78	3.0				
12	12:45					1.02	3.9				
13	13:00					1.95	7.5				
14	13:15					1.20	4.6				
15	13:30					3.05	11.7				
16	13:45					2.21	8.5				
17	14:00										
18	14:15					0.90	3.5				

19	14:30			0.40	1.5				
20	14:45			0.72	2.8	3.57	13.7		
21	15:00			3.63	14.0				
22	15:15			0.58	2.2				
23	15:30			9.18	35.3	7.12	27.4	4.83	18.6
24	15:45			8.55	32.9	36.75	141.3	4.73	18.2
25	16:00			5.30	20.4	7.00	26.9		
26	16:15			3.08	11.8	51.98	199.9		

#### **3.10.2 Rendering Plants**

In the LA Basin there are some rendering plants that have been a concern for local residents due to the offensive odor of the processes. On October 26th, KASSAY deployed the monitoring van to the area and collected OP-FTIR data. Due to the very large size of the plants, the emission model was invalid.

Review of the OP-FTIR data showed low amounts of methane, ammonia, and ethanol. Table 3.10.2 presents characterization results for the two rendering plants.

<b>Table 3-14:</b>
<b>Characterization Results for the Rendering Plants</b>
Monitoring Day 26 (Monday, October 19, 2015)

Event		<b>Downwind Concentration</b>						
	Start Time (PDT)	Start Ammon		Eth	anol	Methane		
#		ppm-m	ppb	ppm-m	ppb	ppm-m	ppb	

Farmer John=s, 3163 E. Vernon Ave., Vernon

One-Way	Pathlength = 72.0n	n
---------	--------------------	---

7	13:45			0.37	5.1		
8	14:00	0.11	1.5	6.26	86.9	5.48	76.1
9	14:15	0.47	6.5	10.40	144.4	9.89	137.4
10	14:30	0.43	6.0	7.83	108.8	14.89	206.8

Baker Commodities, 4020 Bandini Blvd., Vernon One-Way Pathlength = 107.0m

				-		
11	15:15	7.22	67.5	0.51	4.8	

#### **SECTION 4 - CONCLUSION**

KASSAY ORS technique using the OP-FTIR and E-Calc was applicable to the small source and performed well in the field. The OP-FTIR was able to identify significant VOC concentrations above the instrument MDL's. The E-Calc model was able determine emission rates and based upon the blind study was able to clearly demonstrate a worse case average percent error of 28% or better. When adjusted for surface roughness factors in the model, the percent error improved to only 2%.

All three types of small sources had appreciable VOC emission above the backgrounds. Measured concentrations of the methane and NMHC-balance were in most cases several factors higher then the MDLs that ranged from 1-50 ppb (with acceptation of BTEX chemicals which were close to the MDL).

The emissions at all small sources were not constant. In all source types measured, the VOC emission would rise and fall over the monitoring time period. In almost no cases was a chemical detected at a concentration that remained for the same for more then 15 minutes. This demonstrates the need for ORS technologies which can provide continuous measurements over a longer time period.

The emissions results were similar to those presented by other contractors. At the time of this writing, comparative ORS data from the DAIL and SOF measurements are not available. However, discussions and general comparisons during the field tests showed similar VOC types and concentrations during the same time interval. This confirms that the OP-FTIR technique will have some degree of agreement with the SOF and DAIL techniques. Specifically, at the co-measured oil well and gas station sites, Fluxsenses and NPL measured elevated emissions of the methane, and NMHC gases that were measured by Kassay. The emissions at all three source types were significant enough to demonstrate need to better monitor or even possibly regulate small sources.

#### **Gas Stations**

The gas stations showed a mixture of VOC's that are consistent with the blends of fuels expected and with published finding of gas station emissions. This study showed that other VOCs such as strait chain hydrocarbons were shown to be present in significant abundance. In fact, although benzene was only measured a few times at gas stations, other hydrocarbons like n-hexane and NMHC were often present. The ASTDR minimal risk level for n-hexane (often a surrogate for all strait chain hydrocarbons) is 2,115 ug/m^3. One gas stations measured in this study released n-hexane at a rate of up to 859 mg/s, making the potential for exceeding that risk level significant. Since the OP-FTIR can measure BTEX chemicals as well as other hydrocarbons, it demonstrates that this ORS technology can be helpful in better characterizing emissions inventories for gas stations.

#### Oil Wells

The oil wells consistently showed VOC's emissions of methane and NMHC's. Much of the published research for well emissions focus on the study of methane. Our OP-FTIR measurements

confirmed that methane is perhaps the most significant emission from the oil wells. However, our OP-FTIR measurements of emissions show that other VOC's including aromatic and NMHC are emitting at the same time. Most significant of this study was the finding that emissions from the oil well sites were highest when there were storage tank present. This indicates that control of on-site storage of tanks (vents, flanges, transferring) is a key aspect of emission reduction.

#### **Cattle Farms:**

The cattle farms showed elevated concentration of ammonia and methane. Ammonia is found in the microbial breakdown of manure and urine and methane is produced when organic matter is digested. Kassay's measurements at the cattle farms agrees with USEPA's findings that both of those chemicals are significantly emitted from the feed lots and manure handling.

The OP-FTIR ammonia and methane concentrations trended with each other at both cattle farms. This demonstrates that some relationship exists, but more study will need to be done to determine if the changes were a function of atmospheric conditions or actual source strength. The concentration of hydrocarbons at the cattle farms were low and most non-detects.

#### **Rendering Plants**

Despite have the most repugnant odor of any sites that Kassay measured, the gases detected at the two rendering plants (Baker Industries, Farmer Johns) did not show any appreciable amount of VOC's. Only methane, ammonia and ethanol were detected in low PPB concentrations.

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#### APPENDIX A-3

#### **AREA-SOURCE TECHNIQUE**

#### **Overview**

The area-source technique is a mass-balance method for measuring gaseous contaminant emissions from ground-level, non-buoyant area-type (or point) sources, such as lagoons and ponds, landfills, and hazardous waste sites. Intended for use with optical remote sensing (ORS), the method utilizes open-path spectroscopy – either FTIR, ultraviolet (UV), or tunable diode laser (TDL) – to generate a path-integrated concentration (PIC) in the cross-plume dimension, i.e., a "whole-plume" approach. It offers a rapid and inexpensive direct means of reliably assessing emissions from area sources (leaking gas station pumps and oil well components, in this case). Parameterization of vertical dispersion within the microscale region between the source and the downwind measurement path, via sophisticated surface-based meteorological monitoring, obviates the need for measuring contaminant concentrations or meteorological parameters in the vertical dimension.<sup>1</sup>

The analysis reduces to one of conservation of mass, as the extent of the pollutant's lateral and vertical dispersion is taken into account (i.e., plume dilution is directly measured). The area-source technique involves the time-averaged, cross-plume measurement of source attribution, and the subsequent back-calculation of a coincident emission rate based on Gaussian dispersion relationships inherent in most EPA air dispersion models (in this case, AERMOD – EPA's Guideline Gaussian air dispersion model). The method is applicable to all types of area sources, i.e., homogeneous (uniformly emitting) and heterogeneous (having "hot spots"); it was developed by the EPA's National Environmental Response Team (ERT) in the early 1990s and has been well-documented.<sup>2-10</sup>

Source attribution is represented as a path-integrated concentration, obtained by subtracting the upwind PIC value, when significant, from the downwind PIC value. A path-integrated concentration (units of  $mg/m^2$ ) is derived by integrating a concentration at a point ( $mg/m^3$ ) across the width (crosswind direction) of the contaminant plume (m). The benefit of working with path-integrated, or cross-plume, concentration data lies in its inherent spatial representativeness.

Employment of the area-source technique offers several significant advantages over other approaches: (a) the capability to make continuous, time-averaged emission-rate measurements for little or no additional cost, as all analyses are performed *in situ* – i.e., there is no associated lab cost; (b) the capability to discern small changes in emission rates over time; (c) the capability to re-analyze the PIC measurements at any later time, as all analyses are performed (and retained) electronically; and (d) the simplicity of the method, as all measurements are ground-based (1- to 2-meter height), without the need for employment of expensive and cumbersome towers or lifts.
## **Three-Step Approach**

Following is the three-step approach for use with EPA Method TO-16 (employed for this project).

# 1. <u>Identify Source Attribution</u>

The attribution from each source (e.g., gas station or oil well component) involves a series of 15minute-averaged monitoring events, in which near-ground-level measurements are made. Meteorological forecasting is employed to identify configurations which minimize the contribution from upwind sources, where significant.

The open-path spectrometer is positioned immediately downwind of a given source, with the beam oriented in the crosswind direction. The beam path must be of a length sufficient to ensure maximum plume capture of the source emissions (see below). The mean wind direction should be normal (or nearly so) to the beam path, but departures of up to 40 or 50 degrees from normal may be acceptable.

Coincident meteorological measurements are made using an appropriately configured portable meteorological tower, placed at a location judged representative of the microscale conditions between the source and the downwind measurement path. The height of the meteorological measurements should be the same as the beam-path height above the source (generally, about 2 meters).

# 2. Predict the Relative Path-Integrated Concentration Along the Measurement Path

AERMOD (<u>A</u>merican Meteorological Society / <u>E</u>PA <u>R</u>egulatory <u>Mod</u>el) is used to predict the relative path-integrated concentration along the downwind measurement path (Step 1).<sup>11,12</sup> This is accomplished by: (a) predicting the point concentration (mg/m<sup>3</sup>) at every meter along the measurement path based on a "unity" emission rate (e.g., 1 mg/m<sup>3</sup>) and on the actual meteorology and source configuration; (b) determining the arithmetic average of the predicted point concentrations (mg/m<sup>3</sup>); and (c) multiplying the average point concentration by the downwind pathlength (m).

The predicted unity-based, path-integrated concentration can be thought of as the concentration that the open-path spectrometer would see if the entire source were emitting at a constant emission rate (i.e., homogeneous, or uniformly emitting). If a source is known not to be emitting uniformly, the relative emission strength across each source needs to be represented in the unity modeling (discussed below).

3. <u>Scale Unity Modeling Results to Calculate Emission Rate</u>

For a given contaminant, the actual emission rate, Q, is determined in accordance with the following equation:

$$\mathbf{C} / \mathbf{Q} = \mathbf{C}_{\mathrm{U}} / \mathbf{Q}_{\mathrm{U}}$$
 (Equation 1)

where:

С	=	measured path-integrated concentration (attribution) (mg/m <sup>2</sup> )
Q	=	actual emission rate (mg/s)
C <sub>U</sub>	=	predicted unity-based path-integrated concentration along the measurement path $(mg/m^2)$
$\mathbf{Q}_{\mathrm{U}}$	=	unity-based emission rate (mg/s)

**Equation 1** describes the relationship inherent between: (a) the unity-based dispersion modeling; and (b) the actual emission rate and downwind measurements. The cornerstone of the area-source technique, this relationship states that the measured path-integrated concentration is to the actual emission rate as the unity-based, path-integrated (modeled) concentration is to *its* unity-based emission rate. The only unknown term in this equation is the actual emission rate (Q).

AERMOD generates unique values of  $C_U$  for each monitoring event, based on the continually changing on-site meteorology.

As mentioned in Step 2 above, characterization of the relative source strength across the source surface for each contaminant is required in order to support the unity-based modeling. The term "relative source strength" simply refers to how the emissions vary across a source, relative from one "subarea" to the next, and not the actual emission rates.\*

#### **Required Meteorological Data**

Contemporaneous meteorological data to support the area-source technique are measured and/or calculated, in precise 15-minute blocks of time (coinciding with each monitoring event), and recorded onto a PC-accessible data logger.

Measured data consists of wind direction, horizontal and vertical wind speed, and temperature. Calculated data consists of standard deviation of the horizontal wind direction (sigma theta or  $\sigma_{\theta}$ ) and standard deviation of the vertical wind speed (sigma W or  $\sigma_{w}$ ).

For each monitoring event, horizontal and vertical dispersion coefficients, as well as the wind velocity profile, are derived for use in AERMOD and, together with the source-attribution data, used to generate emission rates and assess the degree of plume capture (see below).

<sup>\*</sup> Because all Project #2 sources were measured from a "stand-off" position, individual gas station pumps and oil well components were assumed to be of equal strength, and each such source was necessarily assumed to be a uniformly emitting small area source; this assumption is judged reasonable for these sources.

#### **Assessment of Plume Capture**

An important feature of the area-source technique is its ability to generate accurate emission rates without the need to capture the entire downwind cross-plume mass. Despite measuring only a portion of this mass, an emission rate for the entire source is generated, as the total unity-based emission rate inherently accounts for the emission variability across the entire source surface.

The plume-capture equation is used to assess the percentage of the crosswind plume capture:

$$PC = (C_U / C_{UE}) \times 100$$
 (Equation 2)

where, for any given pollutant:

PC =	plume capture (crosswind) (%)
C <sub>U</sub> =	predicted unity-based path-integrated concentration along the measurement
	path (mg/m <sup>2</sup> )
$C_{UE}$ =	predicted unity-based path-integrated concentration along the extended
	measurement path (mg $/m^2$ )

The "extended" measurement path encompasses the actual FTIR measurement path; for modeling purposes, however, it is extended laterally (each direction, from the measurement path endpoints) to distances beyond which there is, essentially, a zero predicted impact.

A plume capture on the order of 60 to 80 percent is the criterion generally applied to determine monitoring event validity.

### References

Following are references supporting application of the area-source technique.

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#### APPENDIX A-4

## **E-CALC<sup>®</sup> DESCRIPTION**

Minnich and Scotto, Inc. (<u>www.msiair.net</u>) is the architect of e-Calc<sup>®</sup> – an <u>e</u>missions-<u>calc</u>ulation software package developed primarily for use with Kassay Field Service's RAM2000 G2 open-path FTIR spectrometer.

### What Are the Benefits of Open-Path Monitoring for Calculating an Emission Rate?

The difference between a source emission rate (mass per time) and an ambient air concentration (mass per volume) is often poorly understood. Further, few investigators appreciate the full utility of the path-integrated concentration when coupled with on-site meteorology and air dispersion modeling for deriving emission rates. When properly applied, open-path FTIR spectroscopy eliminates the spatial data-representativeness problem inherent in emission approaches which rely solely on point-sampling techniques. This path-integrated "whole-plume" measurement approach offers perhaps the only means of fully employing the U.S. EPA's data quality objective process for generating emission rates, thereby ensuring that end-user needs are always met.

Point-type monitors typically report gaseous concentrations as the mass of contaminant per volume of air, such as milligrams per cubic meter (mg/m<sup>3</sup>), or the volume of contaminant per volume of air, such as parts per million (ppmv). Although path-integrated concentrations are often reported as parts-per-million times meter (ppm-m), it is often desirable to convert from ppm-m to milligrams per square meter (mg/m<sup>3</sup> x m, or mg/m<sup>2</sup>) in order to avoid having to consider the compound's molecular weight explicitly in calculating emission rates.

Emission rates derived from point monitoring data are frequently underestimated, as there is no way of knowing the proximity of a hand-held monitor (or Summa canister) to the plume centerline, especially given the fact that wind direction is never constant; in fact, it is generally not possible to ensure that the sample isn't inadvertently collected completely outside the downwind plume. This fundamental sampling design flaw explains, at least in part, the wide variability in reported emission factors for the same process components – particularly in the oil and gas industry.

**Figure 1** illustrates how the pollutant concentration at a location downwind of a small source drops off rapidly as one moves away from the plume centerline.





**Figure 2** illustrates how the entire crosswind plume is sampled using open-path FTIR spectroscopy. The spectrometer collects path-integrated concentration data, meaning that contaminant concentrations are measured downwind of the source along the entire crosswind dimension of the plume. The spectrometer, in essence, counts the molecules of each pollutant, thus ensuring that concentrations are not "missed" anywhere along the IR beam path (which can extend upwards of 300 meters, depending on the application).





Open-path FTIR spectroscopy (U.S. EPA Toxic Organic Compendium Method 16, or Method TO-16) is identical to laboratory FTIR spectroscopy – itself a "reference" method since the 1970s – except that the "sample" is measured in the open atmosphere rather than from a cell. Because analyses are performed *in situ* (i.e., there is no sample *per se*), all "sample handling" errors are eliminated (another source of negative bias), and re-analysis can be performed at any time in the future – *even for compounds not monitored for originally*.

This is an extraordinary benefit, as unknown compounds can be identified and quantified once a library absorption spectra is created. And because all analyses are performed on-site, there is never a wait-time to receive information from the laboratory. Method TO-16 can see hundreds of individual compounds in real time, as well as each greenhouse gas and VOC (volatile organic compound) from oil and natural gas production, which is a potential concern.

Using dispersion modeling relationships, a source emission rate is "back-calculated" for a given pollutant based on the downwind (cross-plume) path-integrated concentration and the on-site meteorology representative of the precise monitoring event duration (sometimes referred to as "inverse" modeling).

### What Exactly is e-Calc?

E-Calc<sup>®</sup> is MSI's proprietary, Windows-based client-server software for calculating, in real time, contaminant emission rates – precise 15-minute-averaged snapshots – from individual ground-based (or near-ground-based) sources. Originally created to help municipal solid waste landfill owners comply with mandated emissions reporting and permitting requirements for methane and other greenhouse gases, e-Calc<sup>®</sup> is designed for automated use with Kassay's RAM2000 G2 unit. The software is based on AERMOD (<u>A</u>merican Meteorological Society / <u>EPA R</u>egulatory <u>Mod</u>el) – the U.S. EPA's Guideline air dispersion model for regulatory application. It incorporates path-integrated output from the spectrometer with coincident on-site meteorological data and other information.

E-Calc<sup>®</sup> employs the U.S. EPA regulatory version of AERMOD in order to maintain the model's legal Guideline status. For each monitoring event, generation of input files requires meteorological data together with emissions-characterization and monitoring configuration data. E-Calc<sup>®</sup> currently assigns dispersion coefficients based on wind speed, land use, solar insolation, and statistical data treatments such as the standard deviations of the horizontal wind direction and vertical wind speed.

**Figure 3** illustrates the e-Calc<sup>®</sup> measurement system. Most input data is directly measured and entered into the software program automatically. Pre-identified source locations together with FTIR beam-path coordinates are manually entered into simple data input screens (not shown). The e-Calc<sup>®</sup> analysis screen is utilized for entry of event-specific meteorological data leading to emissions calculations via AERMOD, as well as the subsequent generation of a hard-copy report for each monitoring event (discussed below).

FIGURE 3. E-CALC MEASUREMENT SYSTEM



#### How Does e-Calc Work?

Figure 4 depicts the functional logic for e-Calc<sup>®</sup>.

Measured data consist of:

- the 15-minute-averaged <u>open-path concentration data</u> downwind of the source; and
- the <u>on-site meteorology</u> collected from the portable tower, as well as other parameters such as solar elevation angle and temperature.

Simulated data include:

- <u>boundary-layer data</u> which is pre-processed by AERMET;
- <u>surface characterization information</u> from the NLCD (National Land Cover Data) database and pre-processed by AERSFC; and
- <u>source and beam path location</u> using site plans and USGS coordinate imagery.

Measured data	FTIR meteorology
Simulated data	boundary layer surface characterization and beam path (orthoimagery)
Pre-processing software	AERMET (modified)
AERMOD-ready input data	met files control file "pfl" data ("sfc" data
Unity modeling	AERMOD
Emission-rate calculation	measured PIC emission rate

FIGURE 4. E-CALC FUNCTIONAL LOGIC

**Figure 5** presents an example e-Calc<sup>®</sup> analysis screen. The AERMOD output file includes all input data, a model set-up summary, and unity-modeling results for each 15-minute monitoring event.





#### How Exactly Are Emissions Derived?

Emission rates of each target compound (pollutant) are calculated in accordance with the *area-source technique*, in which the following relationship holds:

$$C / Q = C_U / Q_U$$
 (Equation 1)

where:

=	measured path-integrated concentration (attribution) (mg/m <sup>2</sup> );
=	actual emission rate (mg/s);
=	predicted unity-based path-integrated concentration along the measurement
	path $(mg/m^2)$ ; and
=	unity-based emission rate (mg/s).
	= = =

**Equation 1** describes the inherent relationship between: (a) the unity-based dispersion modeling; and (b) the actual emission rate and downwind measurements. The cornerstone of the *area-source technique*, this ratio states that the measured path-integrated concentration is to the actual emission rate as the unity-based path-integrated (modeled) concentration is to *its* unity-based emission rate. The only unknown term in this equation is the actual emission rate (Q).

The spectrometer generates the measured path-integrated concentration (C). AERMOD is configured to yield a predicted concentration for each meter along the beam path; these predictions are summed to derive the predicted unity-based path-integrated concentration ( $C_U$ ).

Assignment of the unity-based emission rate  $(Q_U)$  is straightforward (i.e., simply set to 1 mg/s), unless the source includes multiple emission "subareas" of varying magnitude; in such a case, multiples of unity are assigned to each subarea based either on determination of *relative source strengths* or on best professional judgement.

### What Does an e-Calc Monitoring Event Report Look Like?

**Figure 6** presents an actual e-Calc<sup>®</sup> monitoring event report for a large (1 square kilometer) process pond in support of an Alabama paper mill, against which a nuisance lawsuit was brought by the nearby community.

E-	CALC MONITOR	ING EVENT REPORT	
	EVENT SU	<b>MMARY</b>	
EVENT # (E) SOURCE HYDROGEN SULFIDE EMISSIO PLUME CAPTURE	7 Polishing DN RATE 9.6 lb/hr 77.5 %	Pond	
аколорости Project Info	**************************************	Event Information	
CLIENT International Pa SOURCE Polishing Pond PROJECT # 538.01	per	EVENT#(E) 7 MONITORING DAY 2 DATE 06/30/2011 START TIME 11:00 E-CALC INPUT FILE P12-0207	
Meteorological I	nformation	Emissions Information	
WIND DIRECTION WIND SPEED SIGMA THETA SIGMA W TEMPERATURE SOLAR ELEVATION ANGLE CLOUD COVER	<ul> <li>340.1 degrees</li> <li>2.643 m/s</li> <li>28.14 degrees</li> <li>0.242 m/s</li> <li>32.2 degrees C</li> <li>64.99 degrees</li> <li>0 tenths</li> </ul>	Q = Qu x (C / Cu)           EMISSION RATE (Q)         1,207.7 mg/s         9.6 lb/hr           UNITY EMISSION RATE (Qv)         68,772.49 mg/s           CONCENTRATION (C)         30.3 mg/m           UNITY CONCENTRATION (Cv)         1,725.41 mg/m	
	Plume-Ca	pture Results	
	$\mathbf{PC} = (\mathbf{C}\mathbf{U})$	/ Cue) x 100%	
PLUME CA UNITY CON EXTENDED	PTURE (PC) CENTRATION (Cv) PATH UNITY CONCENTRA	77.5 % 1,725.41 mg/m2 ATION (Cve) 2,226.80 mg/m2	
PLUME CA UNITY CON EXTENDED	PTURE (PC) CENTRATION (Cv) PATH UNITY CONCENTR/	77.5 % 1,725.41 mg/m2 XTION (Cue) 2,226.80 mg/m2	

FIGURE 6. E-CALC MONITORING EVENT REPORT