Case Study: Long-Term Remote Sensing of VOC Emissions from a Delayed Coker

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Abstract

A delayed coker is an integral part of many petroleum refineries, especially those that process heavy crude oils. Houston Refining LP operates two, four-drum delayed coking units with a combined capacity of more than 100,000 barrels per day. In an effort to better understand air emissions from the delayed cokers, Houston Refining voluntarily undertook an extensive, year-long volatile organic compound ("VOC") emissions testing and monitoring program. This program included long-term measurement of VOC emissions from one of the delayed cokers using the Vertical Radial Plume Mapping (VRPM) method as described within U.S. EPA Other Test Method 10, *Optical Remote Sensing for Emission Characterization from Non-Point Sources*. The one-year VRPM study involved use of two scanning Open-Path Fourier Transform Infrared instruments and 22 retro-reflector mirror assemblies to measure upwind and downwind concentrations of 18 target VOC compounds that were collectively considered to constitute total VOC. The measurement paths were designed to create a "box" surrounding the unit to determine overall VOC mass flux. On-site meteorological data were also collected and used in the analysis.

This paper presents detailed information on study methodology, observations, analyses, and lessons learned. This paper also includes estimated total VOC emissions from the coker and discusses the variability of those emissions over the course of the one-year study. An analysis related to speciation of the VOC emissions is also presented.

Introduction

A delayed coker is an integral part of many petroleum refineries, especially those that process heavy crude oils. Operation of a delayed coker involves taking residual (bottoms) from crude oil distillation and cooking it at high temperatures in large drums to thermally crack high molecular weight hydrocarbons into lighter hydrocarbons (distillates) that are collected for further processing into refined products for sale. A coker operates in a continuous series of batch cycles where an off-line coke drum vessel is steam-stripped, quenched/cooled, depressurized, de-headed, drilled and emptied of petroleum coke, then re-headed and warmed while an online coke drum is filled with heated feedstock, and vice versa. The solid coke remaining after the coking process is drilled out of the drums, collected, and either sold or burned on-site as fuel. Houston Refining LP ("Houston Refining") currently sells all of its petroleum coke.

Figure 1. Houston Refining 737 Coker Unit

Houston Refining operates two, four-drum delayed coking units: the 736 Unit and the 737 Unit. Per the U.S. Energy Information Administration, Houston Refining has among the highest delayed coking capacities of any refinery in the United States, with total capacity of over 100,000 barrels per day (“bbl/day”). Figure 1 shows the Houston Refining 737 Coker Unit.

Delayed coking has various activities that are potential sources of hydrocarbon emissions including: quench water management, steam venting during depressurization, de-heading, drilling, solid coke handling, and equipment leaks. With the exception of steam venting, hydrocarbon emissions from delayed coking operations are fugitive, meaning they are not released through a stack or vent.

In an effort to better understand air emissions from the delayed cokers, Houston Refining voluntarily undertook an extensive, year-long volatile organic compound (VOC) emissions testing and monitoring program. The methodology and findings of that study are presented in this paper.

System Design and Configuration

OTM 10

A decision was made to use U.S. EPA Other Test Method 10, *Optical Remote Sensing for Emission Characterization from Non-Point Sources* (“OTM 10”), to take long-term measurements of emissions from the 737 Coker Unit. Vertical Radial Plume Mapping (“VRPM”), as described within OTM 10, is used to measure path-integrated concentrations of various pollutants from fugitive and area sources. The path-integrated concentrations from the multiple beam paths are input to an optimization algorithm that maps the concentrations in the vertical plane. The emission flux through the vertical measurement plane is calculated using the product of area-integrated concentrations and the wind speed normal to the plane. This method has been validated in controlled-release studies sponsored by the EPA and the U.S. Department of Defense.

A schematic for a typical vertical-scanning experimental setup is presented in Figure 2. Multiple mirrors are placed on a vertical plane in line with the scanning open-path, path-integrated optical remote sensing (“PI-ORS”) instrument. The location of the vertical plane is selected so that it intersects the mean wind direction as close to perpendicular as is practical.

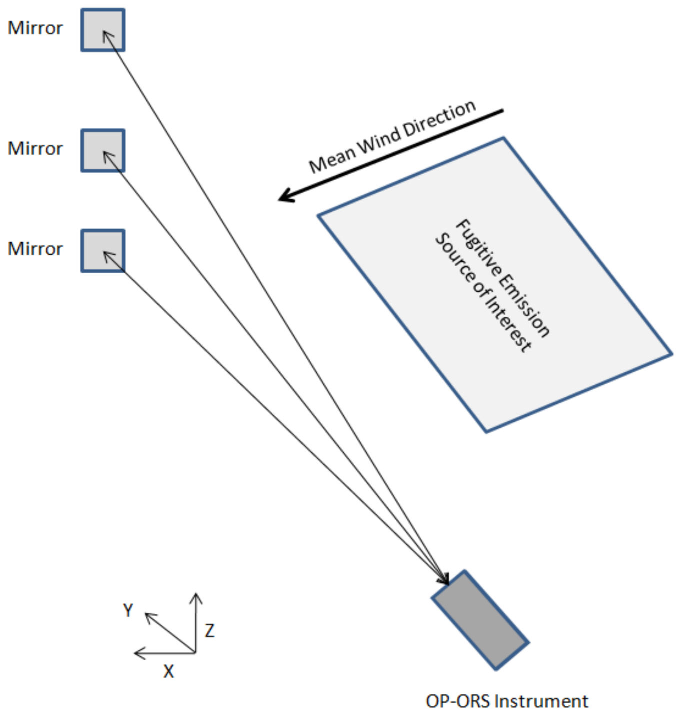

Figure 2: Typical VRPM Configuration

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

$$Q_x = (AIC) \text{ x } (U_x)$$

Measurement Configuration

Two scanning Open-Path Fourier Transform Infrared ("OP-FTIR") units and two meteorological stations located on a single tower were used to gather the information necessary to calculate VOC emission flux (using OTM 10) across four sides of a quadrilateral surrounding the bottom of 737 Coker Unit. The difference between the calculated flux into the quadrilateral (on the upwind side) and out of the quadrilateral (on the downwind side) produces a measurement-based emission rate estimate of VOC from the 737 Coker Unit. Another two internal VRPM planes were devoted for measuring the emissions from the top of the coker unit.

Figure 3 shows the VRPM configuration used for the 737 Coker Unit. The two OP-FTIRs were installed at the locations indicated by the white squares. The "736" instrument was installed to the northwest of the 737 Coker Unit and the "737" instrument was installed to the southeast of the 737 Coker Unit. Twenty-two (22) retro-reflector mirror assemblies were mounted at the locations depicted by the yellow circles. The two meteorological data stations were installed on a single tower (at heights of approximately 50 feet and 100 feet) at the location depicted by the green triangle.

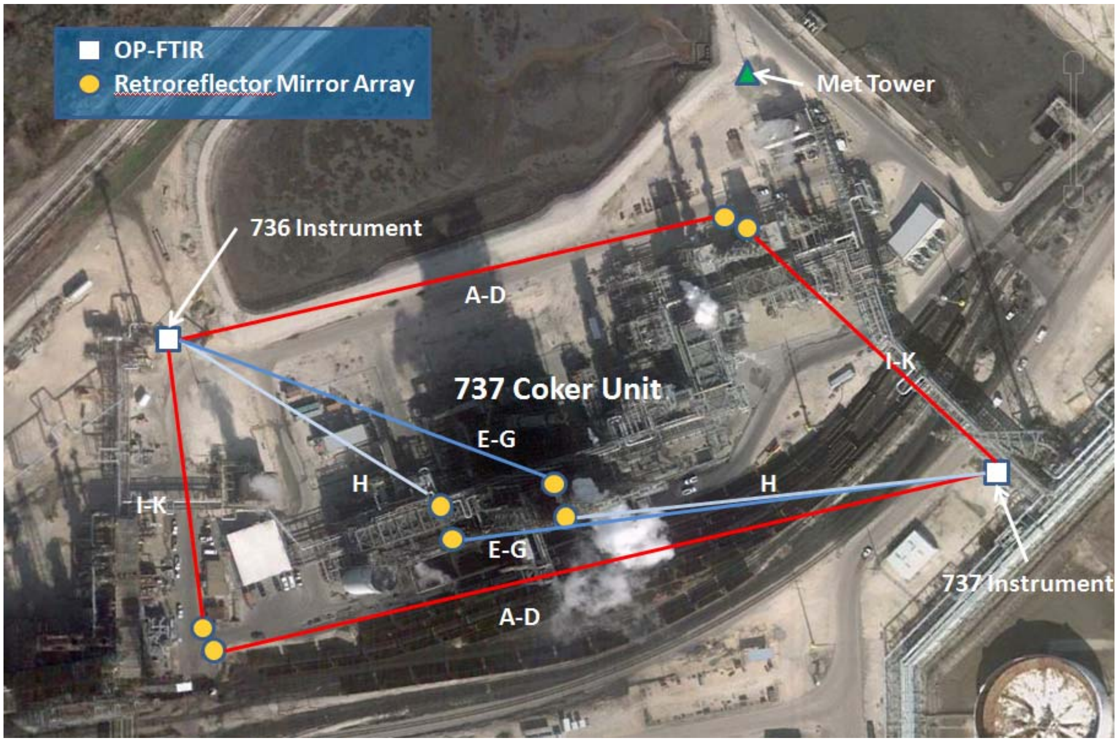

Figure 3: 737 Coker Unit VRPM Configuration
(Image created using Google Earth)

The horizontal projection of the beam paths depicted by the red lines form a quadrilateral with sides that range from approximately 130 to 380 meters (approximately 425 to 1,250 feet). Each OP-FTIR sequentially scanned 11 retro-reflector assemblies located along three different vertical planes:

1. Four retro-reflectors (identified as A, B, C and D) were located along the north and south of the unit (longer red lines). The purpose of these paths was to measure upwind and downwind path-average concentrations for use in estimating emissions from the bottom of the coker structure. These paths were placed so that they would be near perpendicular to the most common wind direction for the area over the course of a year: from the south-southeast. Retro-reflector "A" was placed close to ground-level to capture very close to the ground emission sources. However, due to interference from physical obstructions, the measurements taken along both path "As" (736 and 737 OP-FTIR instruments) were not used in the flux calculations. However, the data collected by these lower beams was used to evaluate the "leakage" of emissions below the VRPM plane (typically below the height of major obstructions for free flow) as described in the EPA mercury report (EPA 2007).

2. Four retro-reflectors (identified as E, F, G and H) were located in the coker structure, above the tops of the coke drums (dark blue line). The purpose of the E-G paths was to measure upwind and downwind path-average concentrations for use in estimating emissions from the top of the coker structure. One retro-reflector (identified as H) located at the top of the coker structure was used for determination of background concentrations (light blue line). Specifically, the concentration measured by the H path was subtracted from the E, F and G path-average concentrations before calculating mass flux. Due to the difference in path-length between the 736 E-G paths and the 736 H path as well as the large angle between E-G and H (ideally, the background measurements are taken along the same path as other measurements), it was subsequently determined that the 736 H path did not provide a good, representative background concentration. Therefore, measurements taken by the 736 instrument were not used in estimating emissions from the top of the coker structure.
3. Three retro-reflectors (identified as I, J and K) were located along the east and west of the unit (shorter red lines). These paths were used in combination with the A-D paths to measure upwind and downwind concentrations for use in estimating emissions from the bottom of the coker structure.

The OP-FTIR dwell time on each retroreflector mirror array was approximately one minute. Completion of each measurement cycle (11 mirrors for each OP-FTIR) took approximately 13 minutes.

Equipment

OP-FTIR is an accepted quantitative technique to measure gaseous air toxics and volatile organic compounds (USEPA TO-16 1999, ASTM 1997, ASTM 1998). The OP-FTIR instruments pass infrared light along an open beam path to identify and measure any absorbing chemical in the beam path. The two OP-FTIRs used in this project were monostatic: single transmitter/receiver telescopes transmit the IR beams to a corner-cube retro-reflector array that returns the respective beam back to the transmitter/receiver for detection and processing. Since most molecular vapors and gases are infrared active, the OP-FTIR sensors are capable of detecting and measuring a large number of atmospheric species and contaminants simultaneously including:

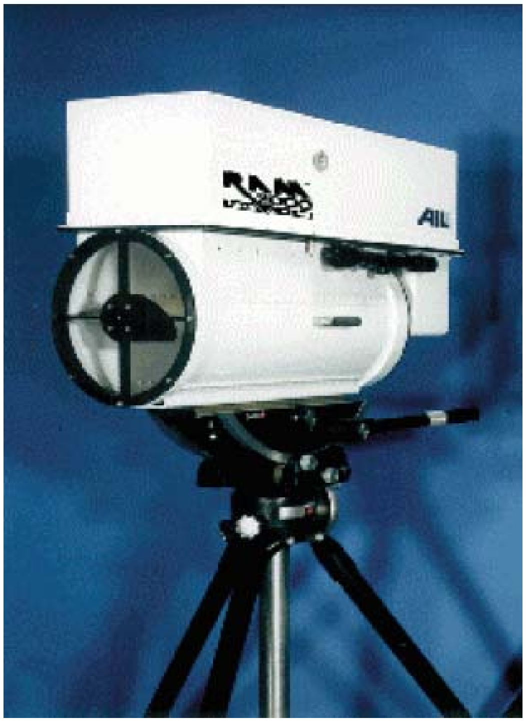

Figure 4. RAM2000 OP-FTIR
(Source: Kassay Field Services, Inc.)

- Alkanes such as methane, and butane/octanes as a total alkane mixture (OP-FTIR is not capable of speciating individual alkanes at the required low level concentrations);
- Aromatics including benzene, toluene,

ethylbenzene and xylenes ("BTEX");

- Highly-reactive VOCs ("HRVOCs") such as ethylene and propylene; and
- Air toxics such as 1,3-butadiene, formaldehyde, and styrene.

The two OP-FTIR instruments used during testing were the RAM2000 provided by Kassay Field Services, Inc. (www.kassay.com), as shown in Figure 4.

The RAM 2000 is an active OP-FTIR technology that uses light from a silicon carbide glower within the monitor to project a modulated infrared light beam to a retro-reflector. The retro-reflector directs the modulated beam back to a mercury cadmium telluride detector within the monitor. The projected infrared beam is modulated by a Michelson interferometer that allows for elimination of contributions from any stray background source of infrared light. The return signal is analyzed for absorbed frequencies that act as fingerprints for any chemical species present. The OP-FTIR measures path average absorbance of infrared light in the range of 700 to 4,000 cm^{-1}. OP-FTIR spectra are analyzed using a multi-variant regression fit (Haaland and Easterling 1982) to quantitatively calibrated spectra to determine the path-integrated concentrations of any absorbing gas. Most of the IR spectral references were created by Pacific Northwest National Laboratory ("PNNL") in collaboration with the National Institute of Standards and Technology ("NIST").

Integral to the RAM2000 is a cryocooler that keeps the detector very cold and allows it to detect the infrared return signal. Other equipment included:

- 2 RAM2000 power controllers:
- 2 RAM2000 Instrument computers;
- 2 Integrated positioners (for moving and pointing the OP-FTIR sequentially at each of the retro-reflector mirror assemblies);
- 2 Positioner controllers;
- 2 HUB computers with air cards for transmitting data;
- 2 Climatronics Tacmet weather sensors;
- 2 Climatronics (Campbell) data loggers;
- 2 antenna repeaters for weather stations;
- 2 shelters with electric and AC;
- 2 industrial BPS (back-up power supplies); and
- 1 pole for mounting weather sensors.

The OP-FTIR and supporting equipment was housed in buildings specifically constructed by Houston Refining for the coker study. Photographs of one of these structures are shown in Figure 5.

Figure 5. OP-FTIR Instrument Shed

As noted previously, the system included 22 retro-reflector mirror assemblies. Shown in Figure 6 is an assembly containing 37 retro-reflector mirrors. The mirrors are mounted in a housing fitted with a fan and filtered air supply as well as a heat source to keep particulates and condensates off the mirrors. This assembly is typical of the 22 assemblies.

Figure 6. Retro-reflector Mirror Assembly, Front and Rear Views

Figure 7 shows the positioning of retro-reflector mirror assemblies A, B and C associated with the 736 OP-FTIR instrument as mounted on the absorber tower superstructure.

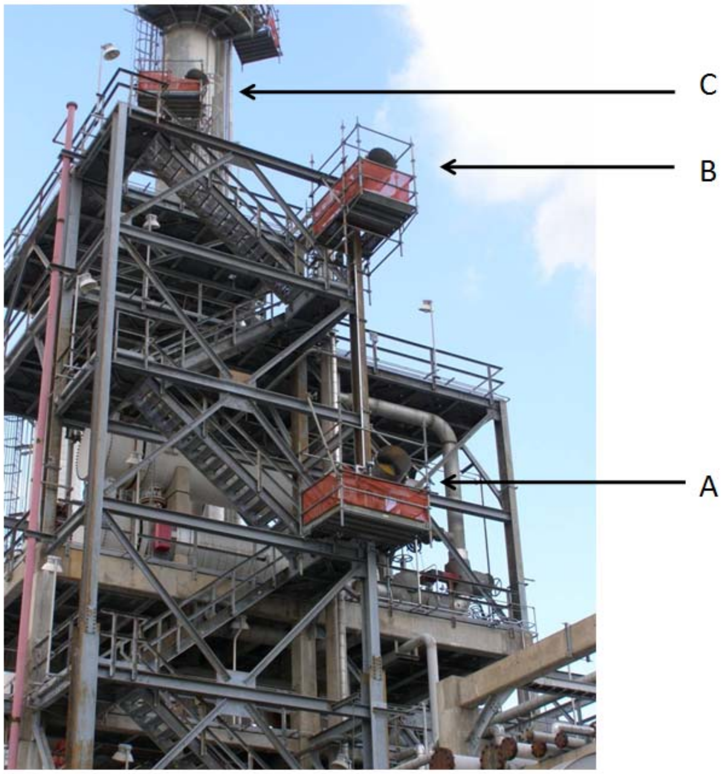

Figure 7. Retro-reflector Mirror Assemblies Mounted on Absorber Tower

Presented as Figure 8 is a schematic of the data collection system. This is typical of both systems.

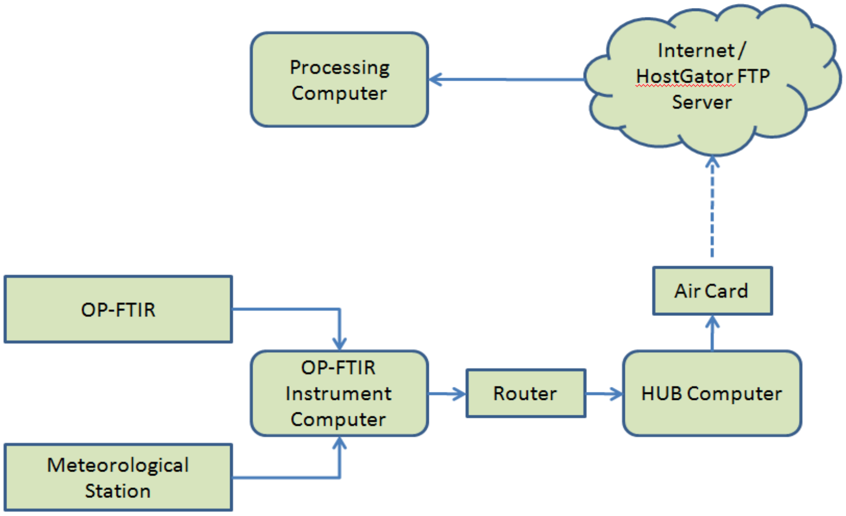

Figure 8. Data Collection System Schematic

Data Collection and Analysis Procedures

Spectral Analysis

This analysis was conducted in accordance with EPA Compendium Method TO-16, ASTM Standard E 1865 -97, and ASTM Standard E 1982 – 98. The spectral analysis was done according to the following steps:

- For each reflector beam grouping shown in Figure 3, single beam ("SB") spectra were averaged for five cycles (a cycle is defined as a full scan of the configuration plane) providing a sample SB spectrum for a certain time interval (approximately 60-70 minutes) spanning 5 measurement cycles.

- For each sample SB spectrum, a sample absorbance was calculated using the respective (same beam) daily averaged background SB spectrum. To further improve sensitivity, only "good" quality SB spectra consisting of a signal level of at least 80% of the maximum signal level for that day were averaged to provide low noise background SB spectra for each beam.

- Each sample absorbance was fitted to a known concentration compound reference absorbance spectra using the classical least squares ("CLS") algorithm available through the FTIR software, RMMSoft.

- The results produced were the path-average concentration and corresponding error for each compound. The background SB spectra were evaluated for the concentration of each compound within the background, typically very close to zero. As a result of this evaluation, the concentration values for each compound were corrected to include the amount in the background for the reported concentrations.

- An error corresponding to 3 times the standard deviation, or 3σ, was reported for each compound as an indication of goodness-of-fit in the CLS analysis. The error for each compound is indicative of the signal-to-noise ratio and was used for calculating the minimum detection level (MDL) and the minimum quantification level (MQL) for each concentration CLS determination. MDL and MQL are equal to twice the error (6σ) and three times the error (9σ), respectively.

- In addition, for all compounds other than butane and octane (the surrogates for the total alkane mixture), a data quality indicator was verified; specifically, whether the error associated with each detected compound was more than twice of the daily minimum error. An increase in error is typically indicative of a potential false positive, and therefore these values were screened out as unquantifiable [EPA 2009]. This is not the case for butane and octane, which were fitted as surrogates for a much larger group of alkanes. For butane and octane, an increase in concentration error may occur due to a mismatch of the compounds and is not indicative of a false positive. Therefore, any determination of butane or octane that was larger than 9 σ was verified as a reliably quantified concentration value unless the spectrum was "corrupted" by the ethylene filter described below. The following compounds were quantified: butane, octane, 1,3-butadiene, acetylene, benzene, cyclohexane, ethane, ethylene, formaldehyde, m-xylene, o-xylene, p-xylene, methanol, MTBE, naphthalene, propylene, styrene, and toluene.

Quantified Compounds

Quantified compounds that meet the requirements described above were summed for each time stamp (i.e. span over five cycles) to give a total hydrocarbon volume concentration in ppb. A corresponding equivalent error ("EE") corresponding to the square root of the sum of squared error for all quantified compounds was calculated. A single concentration-weighted average molecular weight and corresponding total mass concentration ("TMC"), in µg/m^3, were calculated for each sample spectrum and time stamp.

The error associated with the measurement of ethylene was used as a filter for verifying the data quality of TMC values equal to zero. If the ethylene error was smaller than 5 times the minimum ethylene error of the day for that beam, the zero TMC value was considered a good quality zero value that should be retained for flux calculations. However, if it was larger, then it was assumed that no compounds were quantified because of poor quality spectral data (rain, steam, particulate matter) at that time frame. These TMC values were "flagged" and not used in the flux calculation. This approach for verifying the data quality of the TMC values equal to zero is based on project team experience.

Time Interval Flux and Wind Data

All TMC concentrations were grouped into beam groupings B-D (low beams), E-G (high beams), and I-K (low beams) in a sequential manner by cycle end-time. The time difference between each grouping was typically no larger than five minutes. The flagged values discussed above were replaced as follows:

- If one of the three TMC values for the beam groups above was not valid, the flagged value was replaced by the average of the other two valid quantified values.
- If two were not valid, both beams were replaced with the third valid quantified value (i.e. all beam groupings will be equal).
- If all three beam groupings were not valid for this time interval, flux was not calculated for that particular time interval.

Wind direction and wind speed data were vector-wise averaged from both wind monitors for the whole time interval it took each OP-FTIR instrument to cycle through once (i.e., collect spectral data) on all beam groupings mentioned above. Total flux (lb/hr) was calculated using the VRPM method for all configuration time intervals with qualified concentration and wind values. An illustration of the VRPM plume reconstruction is shown in Figure 9.

Top of the Coker Background Beam Concentration Subtraction

For each of the OP-FTIR instrument measurements taken from the top of the coker, the TMC of the H beam measured immediately following the measurement of the E-G beams was subtracted from each of the (E-G) beams. This was done to subtract any background source concentrations that may interfere with the measurement of emissions from the top of the coker. If the result of subtraction was negative, the new TMC value was set to zero.

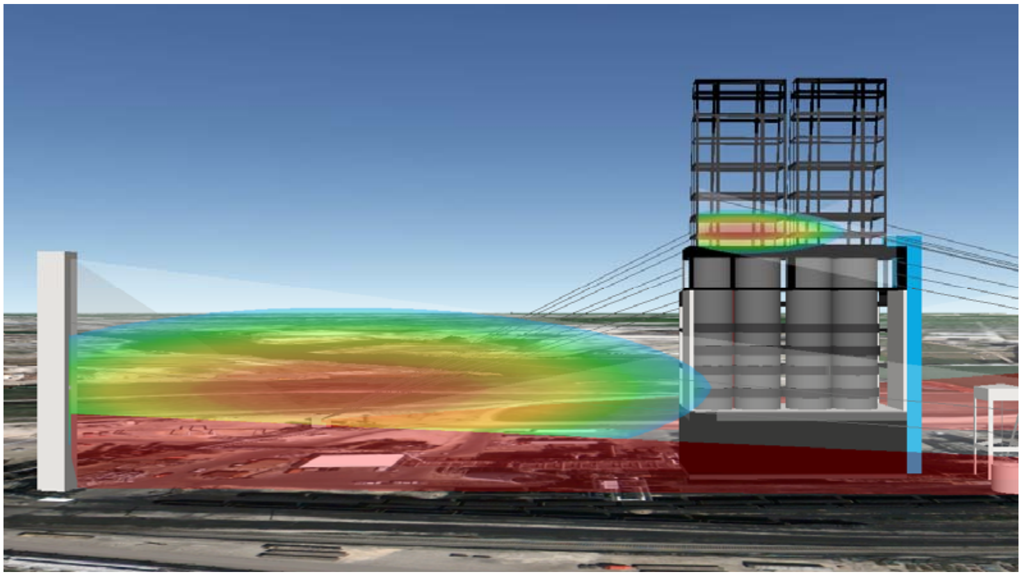

Figure 9. Illustration of VRPM Plume Reconstruction

15-Minute Flux Values

Fifteen (15) minute flux values are the result of averaged flux values per plane (defined by the end time of the last cycle) in a 15 minute block. The 15 minute blocks are defined as shown in Table 1.

Table 1. 15 Minute Block Average Definitions

15 minute block	Start Time	End Time
0	hh:00:00	hh:14:59
1	hh:15:00	hh:29:59
2	hh:30:00	hh:44:59
3	hh:45:00	hh:59:59

Determination of Total VOC Emission Rates

Bottom of the Coker

Method 1: EPA Produced Water Ponds Study Method

As reported in the “Measurement of Emissions from Produced Water Ponds: Upstream Oil and Gas Study #1,” dated October 2009, EPA used OTM 10 to estimate emissions from produced water ponds at two test sites in Colorado. The testing employed two OP-FTIR instruments in a four-corner configuration – similar to the two OP-FTIR, four-corner configuration used in the Houston Refining coker study.

In conducting the produced water pond study, it was recognized that there was uncertainty as to how much of the mass flux captured by the upwind VRPM plane was also captured by the downwind VRPM plane. The range of uncertainty was between: a) none of the upwind mass flux passing through the downwind flux plane; and b) all of the upwind mass flux passing through the downwind flux plan. As a best-estimate of the net flux, it was assumed that on average, half of the upwind flux was also captured by the downwind VPRM plane with an uncertainty equal to ±50% of the upwind flux. Following is an example:

- The mass flux downwind of the source is 15 lb/hr.
- The mass flux coming from upwind sources is 5 lb/hr. This is also the uncertainty in the analysis.
- The maximum net flux, or emission rate, is 15 lb/hr (15 lb/hr – 0 lb/hr).
- The minimum net flux, or emission rate, is 10 lb/hr (15 lb/hr – 5 lb/hr).
- The average net flux is reported as: {[Downwind Flux (15 lb/hr)] – [0.5 x Upwind Flux (5 lb/hr)]} ± [0.5 x Upwind Flux (5 lb/hr)] = 12.5 lb/hr ± 2.5 lb/hr.

Method 1 for estimating emissions from the bottom of the coker follows this approach.

Method 2: Downwind Flux Minus Upwind Flux

The Houston Refining coker study was conducted under very different conditions than the EPA produced water pond study. Table 2 summarizes some of these differences.

Table 2. Differences Between Houston Refining Coker Study and EPA Produced Water Pond Study

Factor	Houston Refining Coker Study	EPA Produced Water Pond Study
Emission Source	• Three-dimensional • Highly complex facility • Highly variable operations and emissions	• Two-dimensional • Very simple facility • Low variability in operations and emissions
Upwind Sources	• Large number of upwind sources • Emissions from upwind sources can be highly variable over short periods of time • Many elevated sources • Source temperatures ranging from ambient to flame temperature (e.g. flares)	• Fewer upwind sources • Most sources at or near ground-level • Most sources relatively close to ambient temperature
Wind Flow Obstruction	• Measurements taken in close proximity to a very large structure with significant wind flow obstruction – much like a high-rise building	• Measurements taken in flat terrain with minimal physical obstructions.

These factors may introduce more uncertainty into the results of the Houston Refining coker study than existed in the EPA produced water pond study. However, this additional uncertainty, both positive and negative, cannot be quantified using just the information collected as part of this study. Given the "uncertainty" in the uncertainty analysis, as an alternative to Method 1 outlined in Section 3.6.1, a second method that does not take into consideration uncertainty is presented. Method 2 is simply:

Emission Rate = Downwind Mass Flux – Upwind Mass Flux

Mathematically, the difference between the reported results is that Method 1 equals Method 2 plus half of the upwind mass flux (as uncertainty). As upwind source emissions decline, the uncertainty declines and the emission rates estimated using Method 1 approach those estimated using Method 2. In the absence of upwind sources, the emission rates estimated using Method 1 would be equal to those estimated using Method 2. In this study, the difference between Method 1 and Method 2 results was significant because of the high uncertainty introduced from upwind sources.

Top of the Coker

Flux calculations for the top of the coker were done differently than for the bottom of the coker. Specifically, background concentrations measured along path H were subtracted from paths E, F and G prior to performing the VRPM calculations. The emission rate was not determined by subtracting the upwind flux from the downwind flux as was done for the bottom of the coker. Therefore, no uncertainty is calculated or presented for the top of the coker.

Determination of Speciated VOC Emission Rates

The following approach was used to construct an average speciation profile for emissions from the 737 Coker Unit.

Step 1. The speciation analysis was performed using spectral data collected on the 737 instrument: beams A-D for the bottom of the coker and beams E-G for the top of the coker. Data from the 737 instrument was used because of the assumed minor contribution of up-wind sources to the path-average concentrations measured on the south side of the 737 Coker Unit. Conversely, measurements taken on the other legs of the configuration (737 instrument beams I-K, and all beams of the 736 instrument) were assumed to have significant contribution from upwind sources. One year's worth of data was screened and selected periods to analyze for individual compounds using the following criteria:

a. The wind had to be out of the north, between 330 and 30 degrees. It is presumed that winds out of the north should typically have the least contribution from upwind sources and, therefore measurements taken downwind of the coker should be relatively free of contribution from other emission sources. This was confirmed by looking at the zero results of specation for the upwind beams collected by the 736 unit. As shown in Figure 10, other emission sources at Houston Refining are located in close proximity to the east and south of the 737 Coker Unit. Sources associated with another refinery are located to the west of the coker. There are relatively fewer emission sources located to the north of the coker and these are located at a greater distance than those in the other directions. The exception is Houston Refining marine loading operations conducted in close proximity to the north. These emissions, however, are intermittent and are accounted for in the analysis (see Step 1.c).

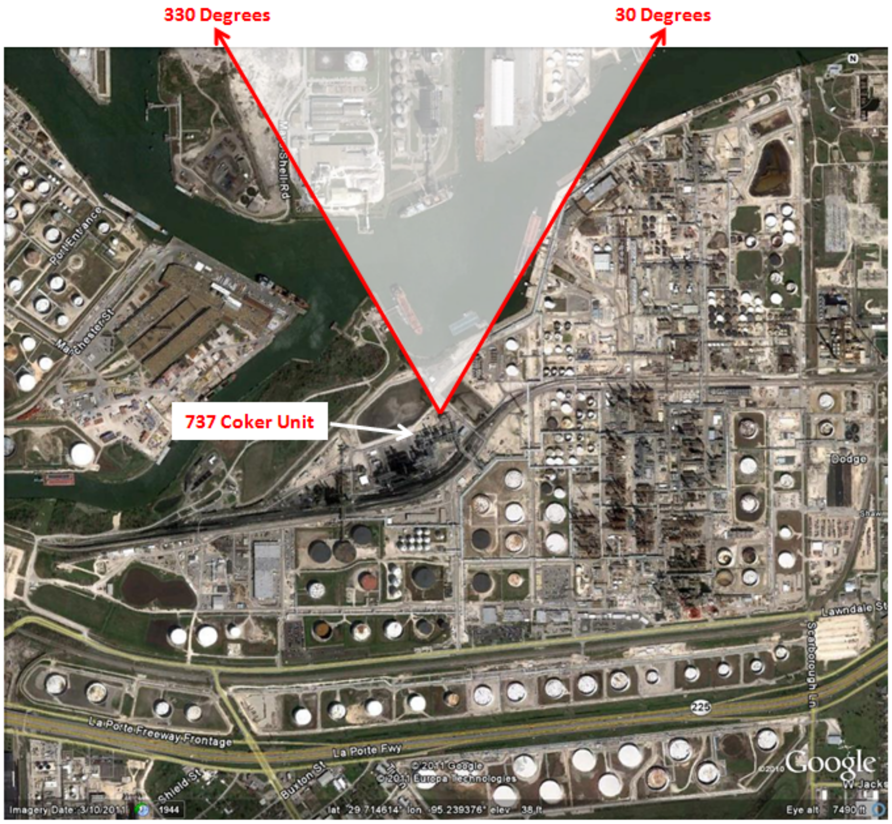

Figure 10: Location of 737 Coker Unit in Relation to Other Emission Sources
(Image Source: Google Earth)

b. Because of the typically-low concentrations of individual compounds other than alkanes, the analysis was conducted for periods of: 1) persistent wind direction, and 2) persistent measurable concentrations of alkanes. The periods selected for analysis were at least two hours in duration and had at least 8 measurement cycles over which the spectra could be averaged.

c. For the bottom configuration (beams A-D), the upwind data from the 736 instrument was analyzed to confirm that there were no or low contributions from upwind sources for each of the periods identified for analysis.

d. For the top configuration (beams E-G), the background beam (beam H) was analyzed to confirm that there were significantly lower contributions (less than 50%) from other sources. Since the H beam almost always measured alkanes, most likely contributed from the lower part of the coker, the concentration profiles measured on the top of the coker should be viewed as a mix of speciation profiles for the top and the bottom of the coker.

Using this method, for the bottom of the coker, 20 periods were selected for inclusion in the analysis. These 20 periods ranged in duration from approximately 2 hours to 5.5 hours. For the top of the coker, 15 periods ranging in duration from approximately 3 to 8 hours were selected for analysis.

Step 2. The single-beam spectra were averaged for each beam separately over the duration of the analysis period and analyzed for the 18 compounds analyzed. The number of measurement cycles for each period analyzed ranged from 8 to 29 cycles. The longer the period and the more measurement cycles included in the analysis, the lower the minimum detection limit ("MDL") for the compound and period of interest. As more spectra are averaged, the noise in the spectrum is reduced, and thus the signal-to-noise is improved and the MDL lowered.

Step 3. Measured concentration values were compared with the MQL of 9 times the standard deviation, or 9σ. Values greater than the MDL were used in the analysis. Values less than the MQL were considered to be "non-detectable" and were set equal to zero. This is consistent with the approach used for estimating average VOC emissions. Due to the difficulty in measuring p-xylene with an open-path FTIR ("OP-FTIR") instrument, for this compound the MQL is set equal to 12σ. Concentrations of p-xylene below this value were considered to be non-detectable and were set equal to zero.

Step 4. The concentration of each compound of interest was averaged across the configuration – four beams for the bottom of the coker and three beams for the top of the coker – for each period analyzed.

Step 5. The average mass fraction for each pollutant during each period analyzed was determined, and the total for each period summed to 1.0 (or 100%).

Results

Average Total VOC Emission Rates

Presented in Table 3 are the average calculated VOC emission rates and the standard deviation for Methods 1 and 2 as discussed above.[1]

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[1] The standard deviation is a measure of the variability of the data relative to the mean or average. A low standard deviation indicates that the data points tend to be very close to the mean, whereas a high standard deviation indicates that the data are spread out over a large range of values.

Table 3. Average VOC Emission Rates

Bottom of Coker Emission Estimation Method	Average VOC Emission Rate (lb/hr)			Standard Deviation (lb/hr)	
	Bottom	Top	Total	Bottom	Top
1	24.5 ±7.7	8.5	33.0	80.8	27.1
2	16.8	8.5	25.3	77.8	27.1

Figures 11 through 13 present statistics for the data set. As shown:

- A relatively few high emission periods have a significant impact on the average mass flux values. For the bottom of the coker, the mean is approximately 3.3 times higher than the median for the entire data set when using Method 1 to estimate the emission rate. When using Method 2 to estimate emissions from the bottom of the coker, the median is zero. For the top of the coker, the mean is nearly four times the median. This shows the impact that these high emission periods have on the averages.

- With respect to maximum hourly emissions, the relatively few extreme rates may not be representative of normal routine operations but result in increased mean and standard deviation values.

- Assuming a "normal" distribution, the data would be evenly distributed around the mean. As shown, the data is not distributed evenly around the mean and the distribution is not normal.

- When the standard deviation exceeds the mean, it can imply that: the data set is either too small to accurately determine the true mean value (unlikely for a year-long study); and/or the emission data is, by nature, highly variable.

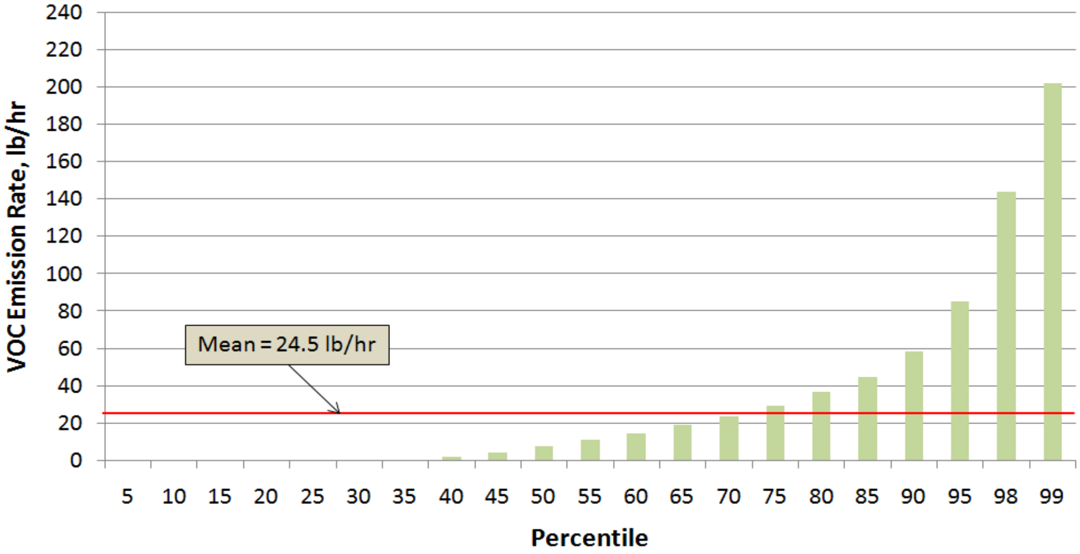

Figure 11. VOC Emission Rate Distribution, Bottom of the Coker, Method 1

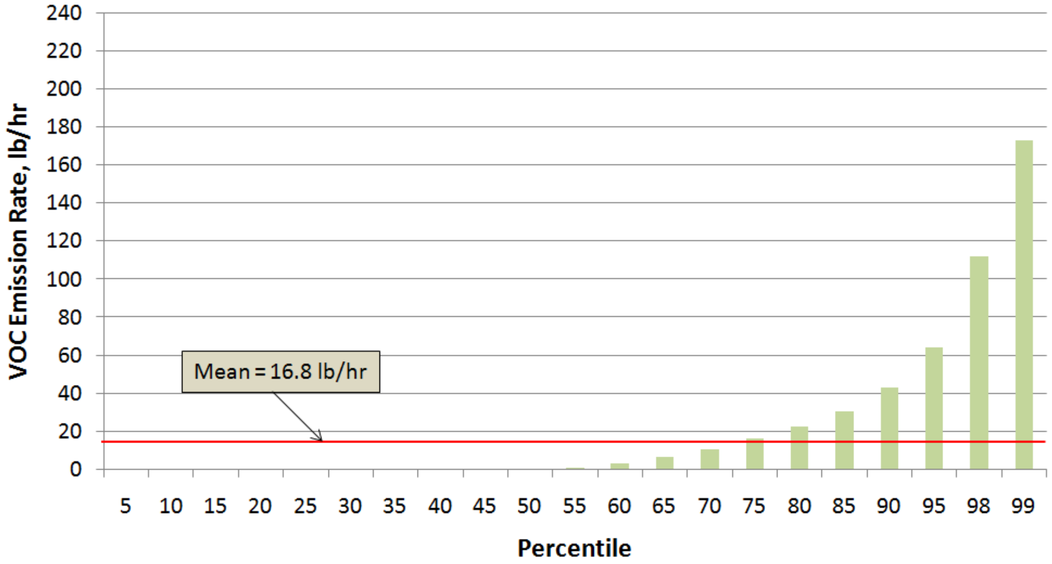

Figure 12. VOC Emission Rate Distribution, Bottom of the Coker, Method 2

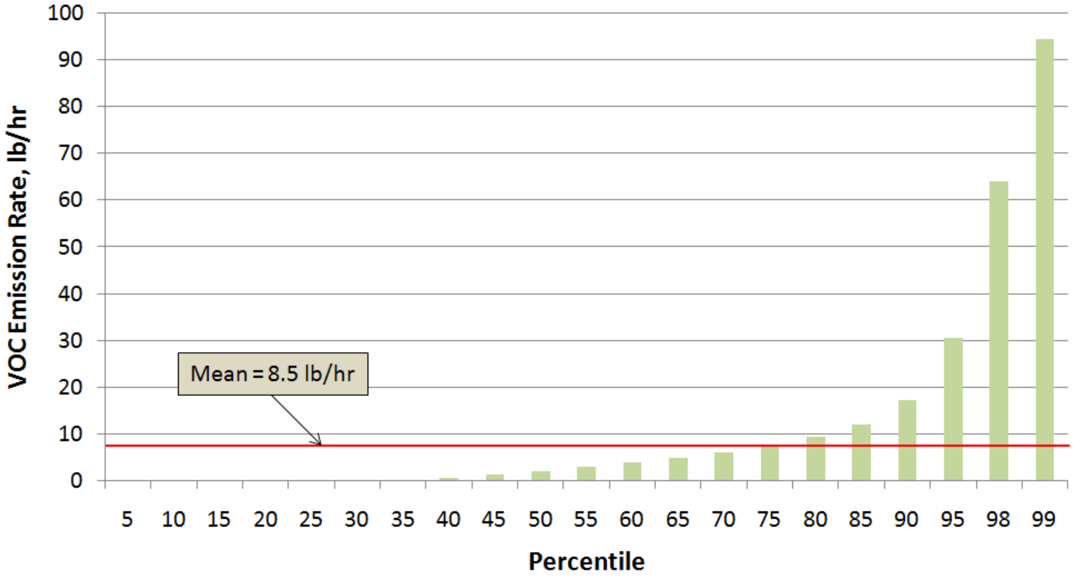

Figure 13. VOC Emission Rate Distribution, Top of the Coker

Average Speciated VOC Emission Rates

Figure 14 graphically depicts the time-weighted average percentage of the total measured mass for each of the 18 compounds analyzed. The time-weighted average concentration takes into consideration the duration of each period:

$$C_T = \frac{1}{T} \times \sum_{i=1}^{n} (Ci \times Ti)$$

Where:

C_T = Time-weighted average mass concentration, µg/m^3;

Ci = Mass concentration of compound during period i, µg/m^3;

Ti = Duration of period i, minutes;

T = Sum of the durations of periods i through n, minutes.

Note that OP-FTIR is not capable of speciating individual alkanes at low levels. Therefore, concentrations presented for n-butane are a mixture of light alkanes in the general range of C3 (propane) through C6 (hexanes). The concentrations presented for n-octane are for a mixture of heavier alkanes in the general range of C7 (heptanes) through C10 (decanes).

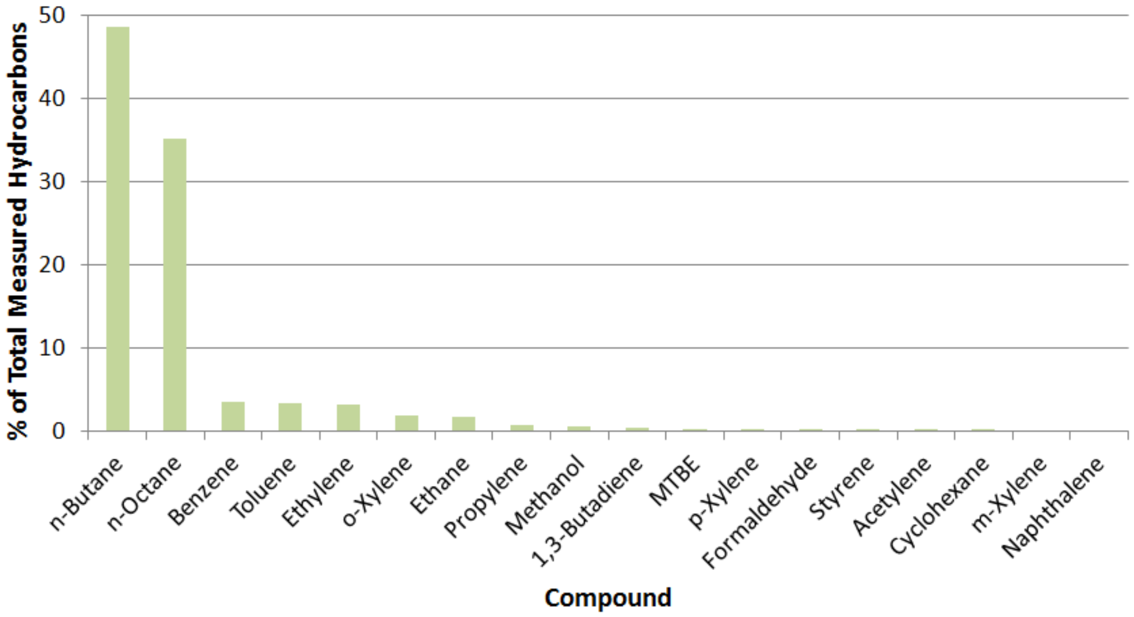

Figure 14. Time-Weighted Average Percentage of Total Measured Hydrocarbon Mass

As shown, on average, emissions from the coker are dominated by alkanes.

Lessons Learned

Significant effort went into planning the configuration, duration, and execution of the remote sensing study. As in any major effort, lessons are learned in the process of executing the plan that were not anticipated going into the project. This is especially true when completing a test using a method on a scale and in a setting that was never attempted before. The following section summarizes some key lessons learned in implementing the study and interpreting the results.

Implementation of the Test

The design configuration for the OP-FTIR instruments and retroreflector mirror arrays was necessarily constrained by the physical layout of the unit. The final configuration was believed to have been the best compromise given the physical constraints. In hindsight, one additional parameter that should have been considered was the potential for interference from steam plumes – particularly with predominant meteorological conditions. Significant time periods were discarded for certain paths due to signal loss caused by steam interference that was not an apparent problem during initial site surveys.

The project team identified the need to try to mitigate condensation, dust, and caking on the retroreflector assemblies through the use of powered fans, filters, and heating strips. While the implemented engineering solutions may have helped in practice, the most-effective means of maintaining adequate signal strength was to implement a periodic cleaning program. Initially this was scheduled based on actual decay in signal strength, but ultimately the procedures were changed to require weekly cleaning regardless of actual signal decay. Additionally, the manufacturer recommended use of strong organic solvents for cleaning the gold surfaces. When this proved ineffective, bench-scale testing in our lab demonstrated that a household, multi-purpose surface cleaner was more effective and did not damage the substrate.

The study was implemented in phases, with the initial efforts focused on setting up the equipment and software necessary to begin collecting data. Since this was a long-term study, this was the critical path. The tools used to complete quality assurance, quality control, and analysis of the collected data were developed while data was collected. This created the limitation that throughout the study, results were not available to the project team in real-time or near real-time. In retrospect, although it would have delayed the test, having results near real-time would have allowed for additional analysis and investigative work to validate and determine causes of data spikes – either from within the Coker study area or as caused by interference from on-property or off-property upwind sources.

With a location in a highly-industrialized area, the project team recognized the potential for upwind interference, which was one of the reasons for the length of time included in the study. In practice, the qualifying results came primarily from the wind vectors with the least potential for nearby interference. A shorter duration study focused on the season with the most-favorable historical wind-patterns may have been sufficient.

Limitations on the Use of the Data

Because of the time involved to complete each series of measurements (more than 60 minutes), highly transient and/or highly variable emissions are not expected to be accurately represented by a single 15 minute average. However, as more and more measurements are taken and averaged, the measured average converges on the actual average.

Caution must be exercised when trying to use any measurement technique, including VRPM, with a relatively long measurement period (as discussed, in the case of this VRPM study, 15 minutes) to profile short-term emission periods. For example, it is not appropriate to use the results of this VRPM study to try and estimate emissions from a single coker operation. However, it is appropriate to use the VRPM findings to estimate emissions from repetitive operations occurring over an extended period of time.

The method selected to determine the mass flux was a source of significant uncertainty in the results. Ultimately both methods were presented for the final report.

Patterns in Results

It was anticipated that the results would show a correlation with the cyclical pattern of the Coker operational cycle. In reviewing the results, no clear correlation to the batch Coker cycle was observed. Furthermore, there does not appear to be any obvious diurnal or seasonal dependency like might be expected from evaporative losses such as tanks and transfer operations. Instead, the results varied widely and did not follow a distinct pattern. If any trend was observable, it was that for about half of the qualified study results, the emissions from this Coker did not appear to add significantly to background concentrations such that the emissions were detectable by the method.

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