Measurement and Analysis of Benzene and VOC Emissions in the Houston Ship Channel Area and Selected Surrounding Major Stationary Sources Using DIAL (Differential Absorption Light Detection and Ranging) Technology to Support Ambient HAP Concentrations Reductions in the Community (DIAL Project)

Final Report

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Executive Summary

The Houston Department of Health and Human Services through its Bureau of Pollution Control and Prevention (Houston) conducted a comprehensive survey project regarding emissions from a combined petroleum refinery and chemical plant complex in the Houston Ship Channel area. The complex is a source of emissions of benzene and other volatile organic compounds (VOCs). The project used Differential Absorption Light Detection and Ranging (DIAL), a remote sensing methodology for measuring air pollutants. The survey indicates that measured emissions from process areas and tanks exceed the emission factor estimates for benzene and VOCs. Of the 17 areas where DIAL emissions measurements were conducted, six were compared to VOC emission factor estimates and four were compared to benzene emission factor estimates. In only one process area did emission factors produce a VOC emissions estimate comparable to the DIAL measured results, which was the Catalytic Reformer-3 Unit. Emission factors used to estimate emissions from the Southwest Tanks VOCs produced the most potential underestimated emissions compared to the DIAL measured emissions, off by a factor of 132. The comparison of benzene emission factor estimates to the DIAL measured emissions produced potential underestimated emissions ranging from a factor of 5 at the Aromatics Concentration Unit/Benzene Extraction Unit area, to a factor of 93 for the tanks located south of the ACU/BEU area.

DIAL was shown to be an effective technology for the measurement of mass flux from fugitive, non-point emission sources. DIAL is limited, however, in that it can only measure the mass flux of a single compound or a class of compounds that absorb energy at a defined wavelength during a scan. DIAL cannot directly provide information on the chemical composition of a plume of pollutants, and therefore, additional analysis is necessary to fully characterize the plume's actual composition.

Additional challenges are revealed in this survey. The time period of compositional measurements may prevent characterization of temporal variations of the plume. The compositional measurement techniques are typically limited to fixed locations, usually close to ground level. Moving these analytical platforms above ground level for elevated plumes such as those anticipated for delayed coker emissions, combined with routine changes in wind direction, represents a significant challenge.

The survey also uses two other measurement techniques to explore the efficacy of using them to validate or augment DIAL measurements. The two techniques, open path Fourier transform infrared (FTIR) and a fixed point monitor on a mobile ambient air monitoring laboratory (MAAML), were routinely and simultaneously deployed with DIAL. The pairing of DIAL with these techniques takes advantage of their complementary strengths to allow for improved plume characterization with respect to mass flux and chemical composition. In this survey project, measurements from the FTIR compared better with DIAL emissions than measurements from MAAML. This project identified key factors which should be controlled, if possible, in future investigations to improve the coordinated use of these technologies as well as integration of the collected data. As a result, verification of the data using these techniques in this study is inconclusive in many cases. Most of these factors were anticipated a priori, but remained obstacles. The significance of other factors was not apparent in advance. The main factors to control for improved comparability and usability include: degree of equipment overlap with the DIAL plume, equal MAAML sample collection duration, FTIR detection limits, availability of

scan images, availability of spatially segmented DIAL concentration measurement data, availability of spatially segmented DIAL emissions measurement data, refinement of temporal molecular weight, and ability to sample at plume height. A full discussion is provided in the report.

For surveys focused on a single aromatic compound such as benzene, measurements from Ultraviolet Differential Absorption Spectroscopy (UV DOAS) can be used in a role similar to FTIR. UV DOAS measurements, also deployed during the survey for a limited time, compare well to DIAL measurements.

1. Introduction

The Houston Department of Health and Human Services through its Bureau of Pollution Control and Prevention (Houston) conducted a comprehensive survey project of emissions from a combined petroleum refinery and chemical plant complex in the Houston Ship Channel area. The complex is a source of emissions of benzene and other volatile organic compounds. The project used Differential Absorption Light Detection and Ranging (DIAL), a remote sensing methodology for measuring air pollutants. Feasible emissions reductions strategies were identified with the goal of improving ambient air quality in the community.

The objectives of the project were to:

1) Develop, improve and demonstrate DIAL System emissions measurement methods for estimating the mass flux of benzene and volatile organic compounds (VOC) from individual emissions sources at a Houston area refinery facility with significant benzene emissions.

2) Evaluate and verify the DIAL system benzene and VOC measurements using the City of Houston’s Mobile Ambient Air Monitoring Laboratory (MAAML), canister sampling, and other monitoring/open path measurement techniques.

3) Identify unanticipated/underestimated sources of benzene and VOC.

4) Evaluate emission estimation techniques currently utilized to determine VOC and benzene emission rates by comparing DIAL measurements with estimated emissions.

5) Assess the feasibility of emissions reduction strategies based on the measured impact from the most significant individual benzene emissions sources identified at the selected Houston area sites.

6) Assess the cost effectiveness of the DIAL system based on project costs, estimated emissions reduction strategies costs and the estimated cost savings to be realized through preventing the loss of valuable products, intermediates and/or raw materials via the proposed emissions reduction strategies.

2. Methodology

This section details the methods used to measure the emissions during this study. General screening measurements with DIAL, MAAML, and Open-Path Fourier Transform Infrared (FTIR) were conducted initially to ascertain those areas having the most significant emissions. Following screening, the most important areas were re-measured on more than one day, over 6 to 8 hour periods.

2.1 Differential Absorption Light Detection and Ranging (DIAL)

DIAL was located so that measurements occurred along a vertical plane, perpendicular to the predominant wind direction and downwind from any sources of interest. Wind direction and speed attributes for wind field characterization were measured with a mast on the DIAL unit at 12 m above ground level, a portable mast at 2 m above ground level placed in a location downwind from the expected emissions sources, and a mast located outside the site fence line, away from obstructions, at 11 m and 3 m above ground level. A mast on the MAAML at 10 m above ground level was also utilized to collect wind data. Appendix A: NPL DIAL Report, describes how the wind fields were interpreted during the study and how the wind measurements were utilized.

DIAL provided plume locations and estimated concentrations of either alkane VOC or benzene. Where DIAL measured alkane VOC, actually the carbon-hydrogen (C-H) bond associated with alkane hydrocarbons were measured, for hydrocarbon molecules containing three or more carbon atoms. The alkane C-H bond measurements were then used to estimate a mass concentration based on an assumed molecular mass and assumed optical absorption coefficient of the measured species. The molecular mass and optical absorption coefficient for this project were assumed to be that of gasoline, 73.3 and 1.47 (ppm.km)-1 respectively. Therefore, where VOC emissions rates are reported, the mass associated with non-aliphatic hydrocarbon species (such as aromatic and alkene VOC species) are either not included or biased low. Each day of DIAL VOC measurements also included pumped Perkin Elmer Automatic Thermal Desorption (ATD) tubes samples, collected where DIAL and photoionization detector (PID) monitoring indicated the plume was located. The ATD samples were analyzed by gas chromatography (GC) and mass spectrometric (MS) or flame ionization detector (FID) methods. Benzene and VOC emissions rates were estimated by integrating DIAL measured concentrations along the vertical plane with the wind data. DIAL measurements were conducted in accordance with the QAPP as delineated in appendix H.

2.2 City of Houston's Mobile Ambient Air Monitoring Laboratory (MAAML)

MAAML provided metrological and GC/MS/FID (EPA Method TO-14A/15) measurements of 51 hydrocarbon compounds including alkane VOC and benzene at point locations, 4.27 m above ground level. The MAAML location was at times within 50 meters of the DIAL unit, referred to as the "DIAL dead zone." The original plan was to place the MAAML in the location where the plume was detected/expected, but site constraints prevented this approach. However, the data gathered by placing of the MAAML outside of the DIAL measurement range did provide some useful information in certain instances. In those instances, MAAML provided data regarding whether or not the DIAL measured plume extended near ground level into the dead zone. MAAML also provided useful data regarding relative concentration levels of hydrocarbons throughout the site, informing where and when those levels were abnormally elevated. MAAML measurements conformed to the QAPP, appendix I.

2.3 Open-Path Fourier Transform Infrared (FTIR)

The FTIR was typically placed outside of the “DIAL dead zone,” at a height of around 2 m above ground level, directly downwind from the selected emissions source (perpendicular to the predominant wind direction). FTIR provided measurements of around 20 compounds including alkane VOC and benzene along a linear path of around 80 m to 150 m. FTIR therefore provided path-length concentrations of compounds in the DIAL measured plume (when the plume was located at or near ground level along the FTIR path). FTIR data can be used to estimate plume composition based on the relative concentrations of the compounds measured by DIAL, as compared to concentration measurements of other compounds not measured by DIAL (when the DIAL measured plume was located at or near ground level and along the FTIR path). The FTIR data could also be used to evaluate whether the molecular weight assumptions utilized for DIAL emissions rates calculations were appropriate and to verify alkane VOC or benzene emissions measured by DIAL when plumes were at or near ground level along the FTIR path.

The DIAL measurements were validated for alkane VOC using an inline gas calibration cell audit, where the calibration cell was filled with a specific concentration of propane, unknown to the DIAL team. The DIAL team then estimated the propane concentration using the DIAL equipment.

Emissions measurements that appeared anomalous were differentiated from routine emissions via interpretation of the DIAL emission results in comparison to process and management details supplied by site representatives. Important process and management details provided by the site representatives that correlated with elevated emissions rates included tank filling, equipment malfunctions and maintenance activities. Both the routine and anomalous emissions provide important information.

2.4 Ultraviolet Differential Absorption Spectroscopy (UV DOAS)

DIAL measurements of benzene were validated using simultaneous UV DOAS measurements. The DIAL – UV DOAS comparison, described in section 5 of the NPL report, was carried out downwind of Tanks T-OL913 and T-OL914, and also the North Wastewater Area. A 51-minute integrated Summa sample (No. 1350) was collected in the plume of T-OL913 and T-OL920 during the comparison and the results indicated that the plume composition was primarily alkanes, alkenes, and toluene. Sorbent tube samples collected by NPL at the wastewater area indicated that the majority of the compounds were alkanes. The DIAL results compared well with the UV DOAS, and spectral or other interferences were not evident. The minor differences in the results could be due to the fact that the DIAL and UV DOAS did not measure exactly the same parcel of air, the DIAL having a vertical scan resolution of 1 meter, and the UV DOAS optical path having a vertical dimension of 0.11 meter. Also, the DIAL scan height was approximately 3 to 4 meters for most of the UV DOAS path, whereas the UV DOAS beam was at a height of 2 m.

3. Results

This section presents an overview of the study results by individual process area: Southwest Tanks, West Tanks, Delayed Coker, Gas Oil Hydrotreater (GOHT), and West Dock Area, Olefins Process Area, Olefins Tanks and Flares Area, Catalytic Reformer-3 (CR-3), East Property Flare, East Tanks, North Wastewater Area, East Wastewater and Flares Area, Tank Farm B, Tanks T-OL913 and T-OL920, North Property Flare, Aromatics Concentration Unit (ACU) and Benzene Extraction Unit (BEU), Tanks South of ACU and BEU, Tanks South of North Wastewater, and Refinery West Tanks. A discussion of the results is presented in the next section.

The overview of the results consists of the summarized DIAL results, as well as the summarized results of the two other measurement techniques routinely employed simultaneously: MAAML and FTIR. Data from an additional two other measurement techniques used less consistently, UV DOAS and SUMMA canisters, are presented in the appendices D and F respectively. The UV DOAS measurements show agreement with DIAL emissions. Also, refer to the appendices for the individual measurements for any specific method.

FTIR data was collected simultaneously with DIAL for three reasons: 1) to provide a percent composition weighted molecular weight for use in comparing emission rate estimates; 2) to validate extreme events detected by DIAL; and 3) to provide chemically speciated plume descriptions.

MAMML data was collected simultaneously with DIAL to validate extreme events detected by DIAL and to provide chemically speciated plume descriptions.

Although the two methods have overlapping objectives, the MAAML and the FTIR have different strengths. The MAAML provides a larger list of speciation constituents at lower detection limits than the FTIR. The major drawbacks of using the MAAML data to compare with DIAL are the differences in measurement method, MAAML is a point monitor, and the difference in sample duration, MAAML reports results in hourly intervals. While the FTIR has a smaller list of speciation constituents and a higher detection limit, it can be more closely aligned with the DIAL path since it measures along a linear path as DIAL does. In addition, the FTIR results are reported in minutes. The collection of both types of data provides insight into their relative merit in assisting and complementing DIAL in characterizing the emissions.

The overview of the results also contains information about where the DIAL plume was located in relation to the MAAML and the FTIR during the scan image of the area that was provided. Based on scans where the image was available, in the majority of instances the plume was low enough that MAAML and the FTIR were sampling air at the same level as DIAL. There are many scans, however, where an image was not provided. Therefore, the MAAML and the FTIR speciation data was not applied: 1) to DIAL scans without an image when DIAL emissions were not correlated with the MAAML and the FTIR data or 2) to DIAL emissions with an image when the emissions were not correlated with the MAAML or the FTIR data.

Within the individual process area section is a table listing a summary of the results followed by a figure of the area where the measurements were taken.

The results table lists the following information:

1) Date of measurements.
2) DIAL location and line of sight (LOS).
3) Time of DIAL measurements.
4) Type of DIAL measurements taken on that day. DIAL measures either benzene or total alkanes detected, which is expressed here more generally as total VOC.
5) Average DIAL measured emission rate for that day (lbs/hr).
6) Time of MAAML measurements.
7) Location of the MAAML vehicle with respect to the plume. The location was based on individual DIAL scan plume images, purported to be representative of the scans along a particular DIAL line of sight (LOS) on that day. This assessment indicated whether the concentrations measured by the MAAML were expected to be related to DIAL data. Unfortunately due to constraints, the MAAML was usually located out of the plume between the plume and the DIAL trailer (out), but in a few DIAL scan plume images it was located in the plume (in). There were many scans where an image was not available. The location noted in the table is based on the times when scan images were available. The plume may have shifted during other scans where images are not available.
8) MAAML concentration correlation with DIAL plume emissions. This column contains the degree of linear correlation of benzene when DIAL was measuring benzene or of the total alkanes when DIAL was measuring total VOCs between the MAAML and DIAL measurements. The total of the alkanes was estimated from the MAAML sum total concentration of: propane, n-pentane and hexane. The MAAML concentration data was reported hourly. In order to relate the MAAML hourly concentrations to the DIAL emission rates, DIAL emissions were averaged over the hour. The statistical correlation was calculated when there were a minimum of four comparable hours. Depending upon the location of the MAAML with respect to the plume, we expected that it would be more likely that MAAML data would be correlated with the DIAL data when the MAAML was in the plume (“in” as described above) than if it was between the trailer and the plume (“out” as described above). In both scenarios, “in” or “out”, because we are relating an emission rate measured on a plane to a concentration measured using a fixed point, correlations would only be found if the wind speed remained relatively constant with low variability over the sampling period. While we did not expect to find a correlation between DIAL emissions and MAAML concentration data when the scan showed that the MAAML was “out” of the plume, we assessed the correlation hypothesizing that if we did find correlations, this suggested that the plume shifted from “out” to “in” over time in scans where images were not available or DIAL did not pick up the entire plume. Some datasets included one high value which could be an influential outlier. These outliers are real extreme points because they were picked up by both techniques, however, the correlation coefficient has limited use when it is heavily influenced by one point. When the slope of a linear regression with and without the suspected influential outlier point changed by more than 10%, the point was considered influential. The correlations with and without the point are presented. The estimated correlation is listed in the table.
9) MAAML outliers (the measured VOC concentrations found to be statistical outliers within the MAAML data during the time DIAL was running on the day of measurement) are listed. Outliers were defined as those measurements that appear at magnitudes above

this limit: Outlier limit = upper quartile of measured concentrations + 1.5 x the inter quartile range. When the MAAML benzene or total VOCs were correlated with DIAL emissions, the outliers provided additional information about the constituents in the plume.

10) Time of FTIR measurements.
11) Percent of FTIR measurements aligned with DIAL plume. This column indicates the percentage of the overall FTIR path that aligned with the DIAL plume, based on individual DIAL scan plume images, purported to be representative of the scans along a particular DIAL LOS on that day.
12) FTIR correlation with DIAL plume. The degree of correlation of benzene when DIAL was measuring benzene or total alkanes when DIAL was measuring total VOCs between the FTIR and DIAL measurements. DIAL measurements showed differences in concentration throughout the spatial extent of the measured plumes. These spatial differences coupled with the differing length of the linear path of the two measurements (DIAL had a longer path than FTIR), indicate that the best comparisons between FTIR and DIAL would be between the FTIR and only those DIAL measurements along the FTIR path. Unfortunately, these segmented DIAL measurements were not available. If there was no alignment as described in 11 above, we did not expect correlation, while if there was overlap based on the representative DIAL scan image we did expect correlation. In order to relate the FTIR concentrations to the DIAL emission rates, the FTIR emissions were averaged over the DIAL scan time. If we did find correlation when the FTIR was not aligned with the plume, we hypothesized that the plume shifted for scans where images were not available or DIAL did not pick up the entire plume. As with the MAAML data, some datasets included one high value which could be an influential outlier. When the slope of a linear regression with and without the suspected influential outlier point changed by more than 10%, the point was considered influential. The correlations with and without the point are presented. The estimated correlation, as well as a measure of direction and strength of association, is listed in the table.

The figure in each process area section shows only the DIAL LOS that measured significant plume emission rates. In addition to the DIAL LOS, the figure depicts the location of the MAAML and FTIR, the horizontal location of the plume or plumes based on individual DIAL scan plume images, purported to be representative of the scans along that particular DIAL LOS on that day, as well as the process area structures. There may be additional lines of sight that measured no or insignificant emissions rates but those were not included in the figures. Figures depicting every DIAL LOS can be found in appendix A: NPL DIAL Report.

3.1 Southwest Tanks

Table 3.1 Southwest Tanks

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/13/2010	SDP01/ LOS1, LOS2†, LOS3†	12:26-17:36	VOC	16-19 (possible emission sources: A-333, A-331, A-330, A-329, A-332)	10:00-16:00	In (Scan 12)	r = 0.62, not significant p-value =0.26	Propylene, trichloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane, 1, 3 butadiene	12:20-16:53	No, 0% (Scan 12)	Not linear
1/15/2010	SPD03/LOS1	11:35-13:21	VOC	11 (possible emission sources: A-325, A-326)	11:00-16:00	Out (Scan 65)	NA, too few data points	Toluene, ethylbenzene, m,p,o xylene, 1,2,4-Trimethylbenzene, 1,3-Dichlorobenzene, 1,2-Dichlorobenzene, 1,2,4-Trichlorobenzene, Hexachloro-1,3-Butadiene	12:30-16:54	No, 0% (Scan 65)	NA, too few data points
1/15/2010	SPD03/LOS2, LOS3	13:42-16:50	VOC	61 (possible emission sources: AP-17, AP-16, with possible contributions from another tanks)	11:00-16:00	Out (Scan 73, Scan 77)	NA, too few data points, plot below is combined data for LOS1, 2 and 3		12:30-16:54	No, 0% (Scan 73, Scan 77)	NA, too few data points
1/19/2010	SPD06/LOS3	12:43-13:17	VOC	43 (possible emission source: AP-17)	9:00-16:00	Out (Scan 157)	NA, too few data points	trichloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane,	10:44-16:47	No, 0% (Scan 157)	NA, too few data points
2/8/2010	SPD23/LOS1, LOS2†	10:55-12:07	Benzene	2-3 (possible emission sources: AP-18, AP-19)	10:00-11:00	In (Scan 545)	NA, too few data points	n-butane, n-pentane	11:09-12:00	Yes, 50% (Scan 545)	NA, too few data points

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

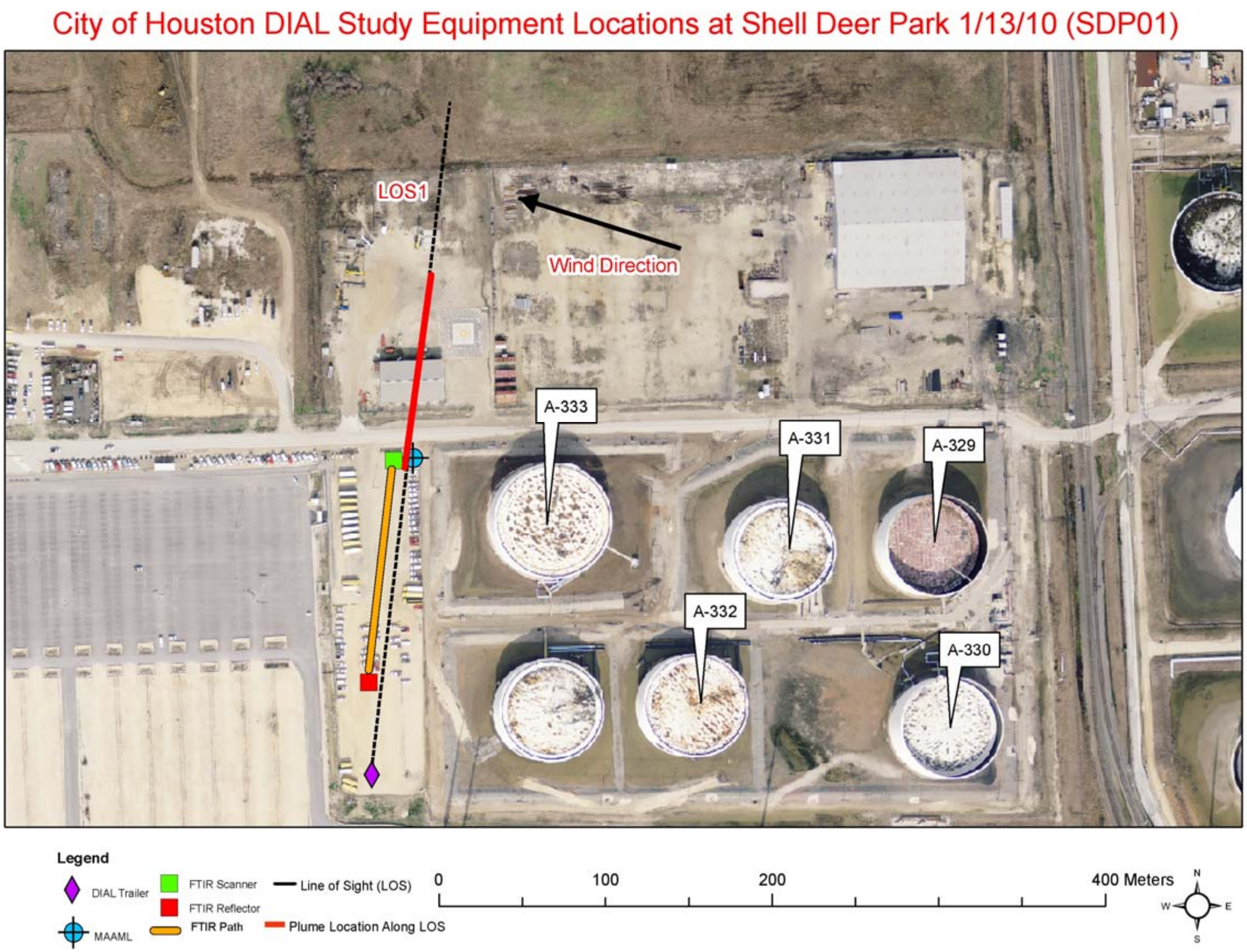

Figure 3.1a Southwest Tanks 1/13/2010

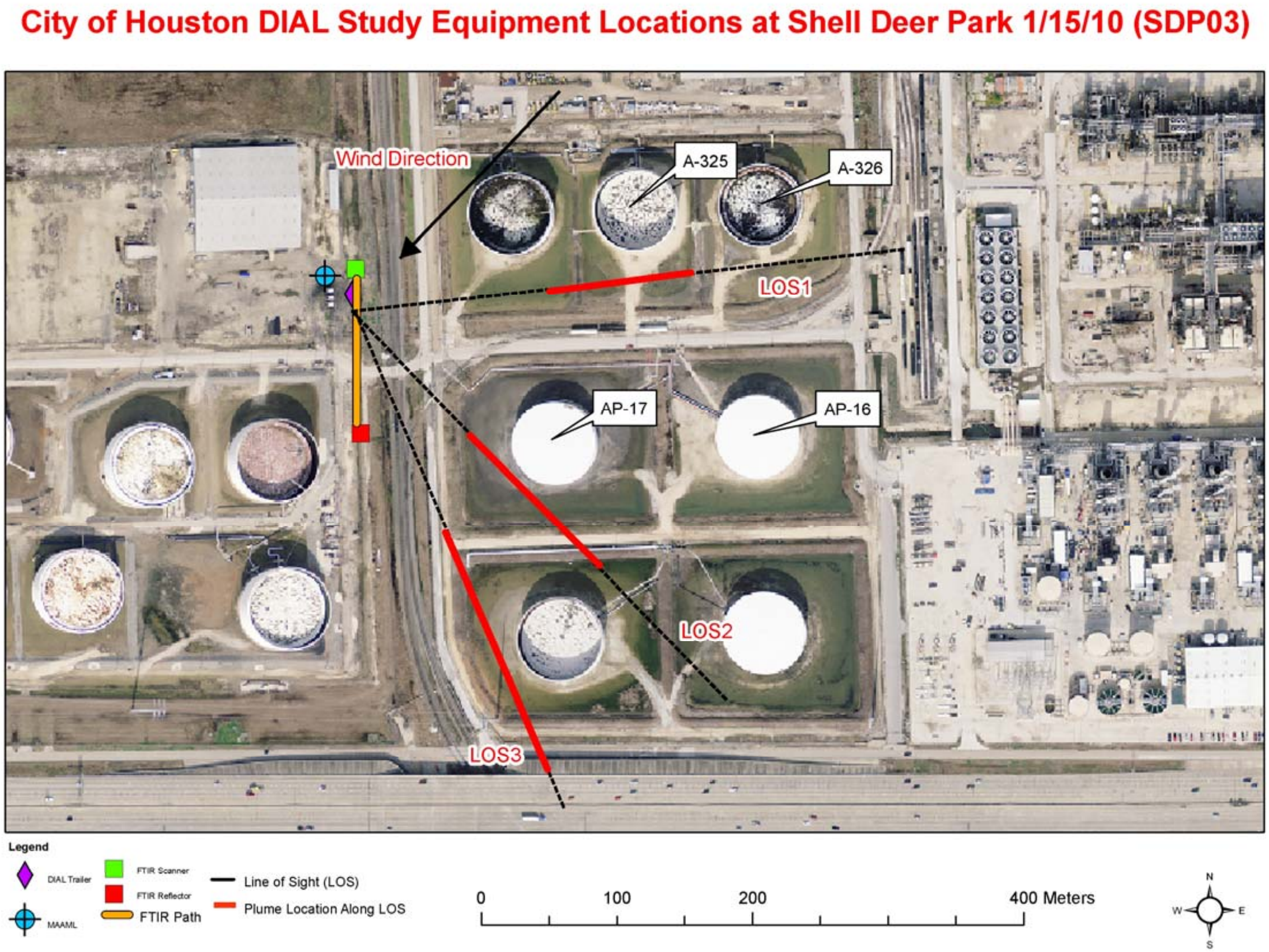

Figure 3.1b Southwest Tanks 1/15/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/19/10 (SDP06)

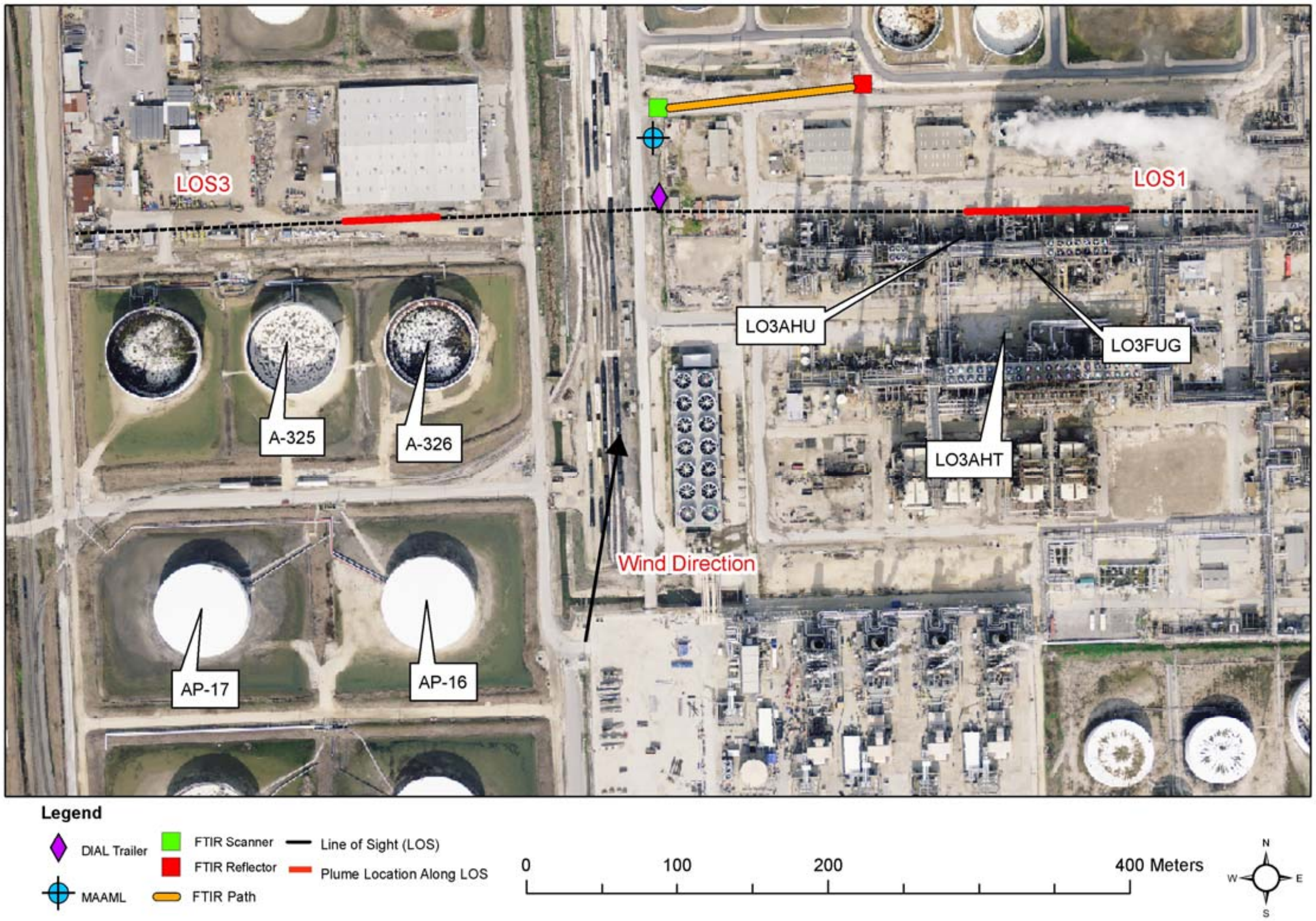

Figure 3.1c Southwest Tanks 1/19/2010

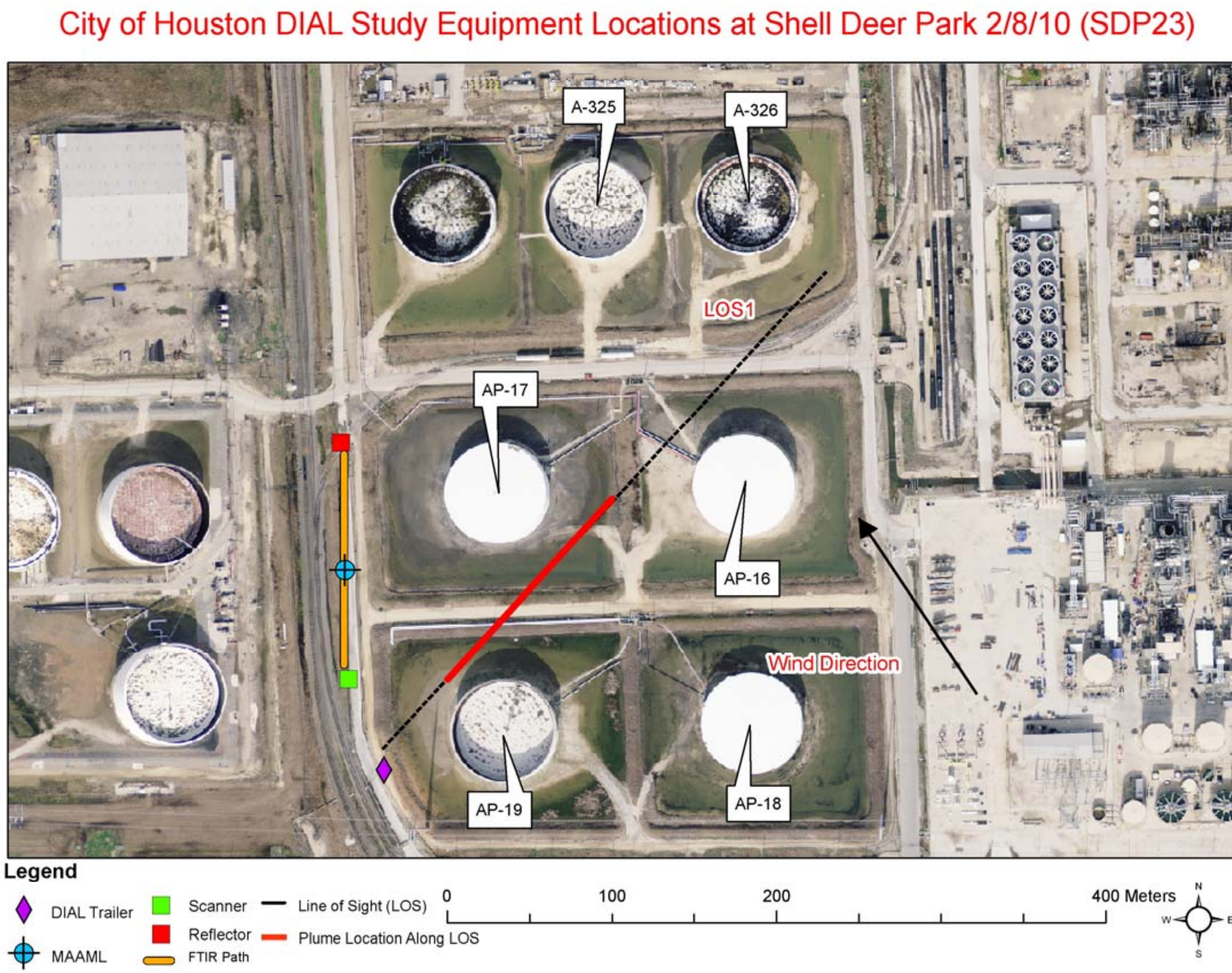

Figure 3.1d Southwest Tanks 2/8/2010

3.2 West Tanks

Table 3.2 West Tanks

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/14/2010	SPD02/LOS1	12:32-14:18, 16:36-17:12	VOC	16 (possible emission sources: A-310, A-319, G-324-R1)	12:00-16:00	Out (Scan 39)	R=-0.53, not significant p-value =0.44	ethylene, propylene, acetylene, vinyl chloride, 1,3-butadiene, methylene chloride, 1-hexene, trichloroethylene, chloroform, 1,2-dichloroethane, chlorobenzene, ethylbenzene, 1,1,2,2-tetrachloroethane, xylene, 1,2,4-trimethylbenzene , 1,2-dichlorobenzene , 1,3-dichlorobenzene , 1,4-dichlorobenzene , hexachloro-1,3-butadiene,	15:28-17:01	No, 0% (Scan 39)	NA, too few data points
1/14/2010	SPD02/LOS2	14:25-15:37, 16:08-16:32	VOC	17 (possible emission sources: AP-1, AP-2, AP-3, AP-4, AP-5, AP-6)	12:00-16:00	Out (Scan 44)	NA, too few data points		15:28-17:01	No, 0% (Scan 44)	NA, too few data points
1/14/2010	SPD02/LOS2	15:56-16:08	VOC	4000 (possible emission source: A-318)	12:00-16:00	Out (Scan 52)	NA, too few data points		15:28-17:01	No, 0% (Scan 52)	FTIR did not pick up the spike found by DIAL
1/16/2010	SPD04/LOS3[†]	12:39-13:48	VOC	0.4 (possible emission source: A-319)	10:00-16:00	Visual Representation of LOS3 not available	NA, too few data points	cumene	15:18-16:13	Visual Representation of LOS3 not available	NA, too few data points

[†]This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

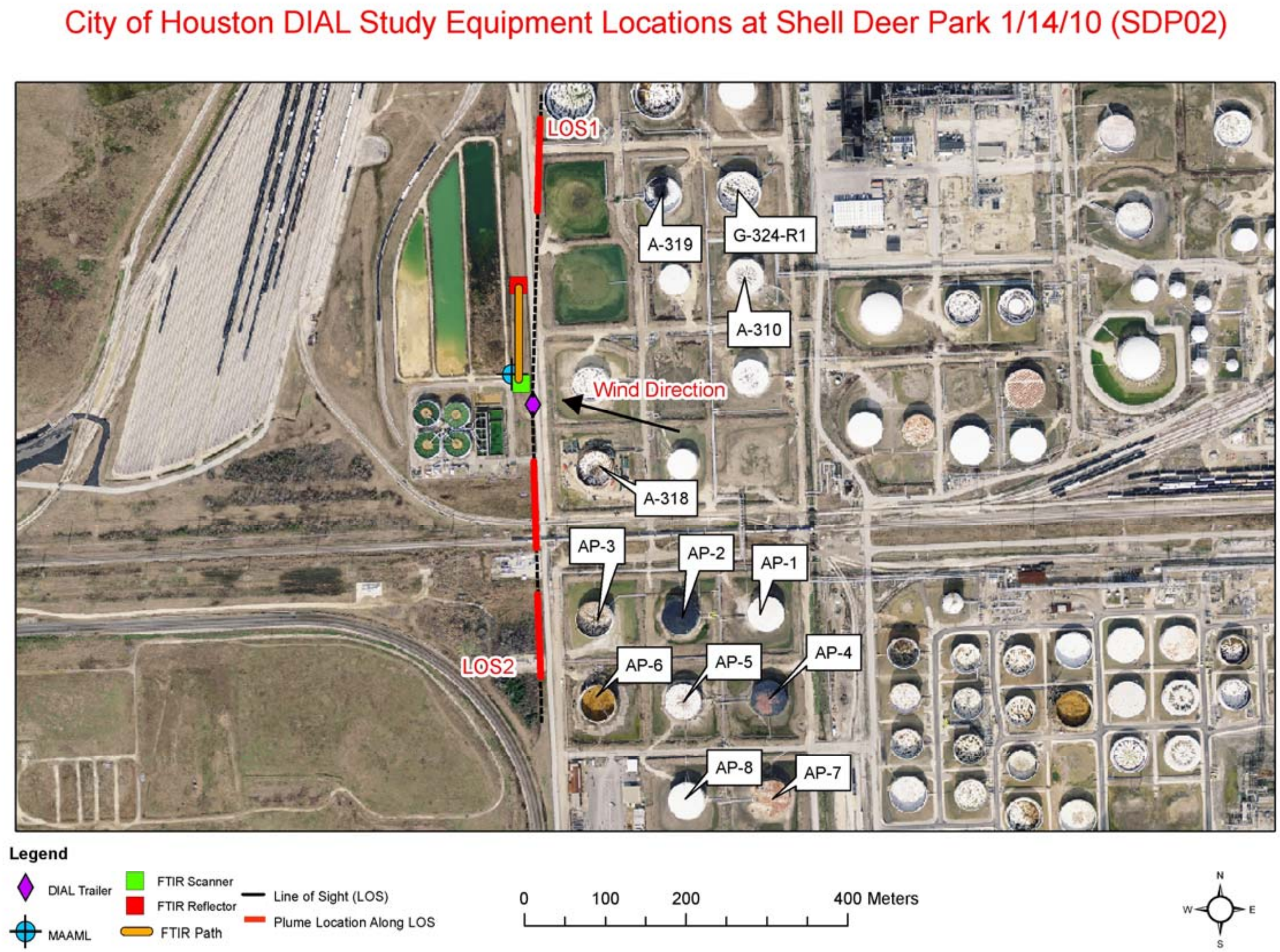

Figure 3.2a West Tanks 1/14/2010

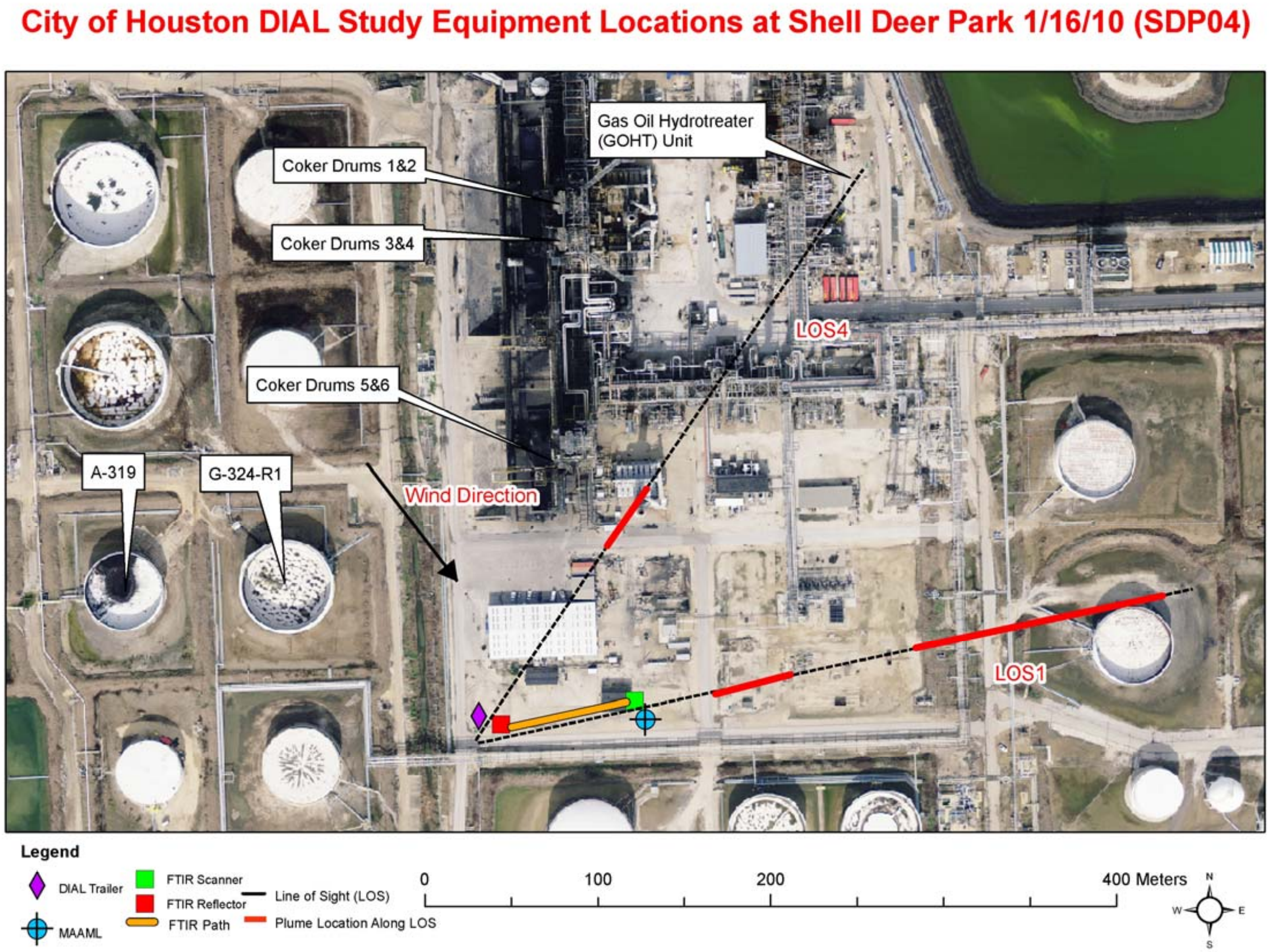

Figure 3.2b West Tanks 1/16/2010

3.3 Coker, GOHT, and West Dock Area

Table 3.3 Coker, GOHT, and West Dock Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/16/2010	SPD04/LOS1, LOS2[†], LOS4, LOS5[†]	10:58-12:34, 14:21-17:13	VOC-Coker and flare	2-3 (possible emission source: Coker)	10:00-16:00	Out (Scan 84, Scan 108)	r =-0.95, regression significant p-value=0.01	Trichloro-fluoromethane 1,1,2-Trichloro-trifluoroethane cumene, 1,3-Dichloro-benzene	15:18-16:13	No, 0% (Scan 84, Scan 108)	NA, Too many nondetects in FTIR
1/27/2010	SPD14/ LOS2[†], LOS3[†]	12:53-14:42, 16:53-17:09	VOC-Coker	1-2 (possible emission sources: Coker, GOHT)	10:00-16:00	Visual representation of LOS2 and LOS3 not available	NA, too few data points	Methyl chloride, vinyl chloride, 1,2-Dichloro-ethane, trichloro-ethylene	11:58-16:47	Visual representation of LOS2 and LOS3 not available	NA, Too many nondetects in FTIR
1/27/2010	SPD14/LOS1, LOS4[†]	12:15-12:40, 14:48-15:49	VOC-Dock	9 (possible emission sources: West Dock area and tanks D-363, F-347, F-349)	10:00-16:00	Out (Scan 332)	NA, too few data points		11:58-16:47	No, 0% (Scan 332)	NA, Too many nondetects in FTIR

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/4/2010	SPD20 /LOS1†, LOS2	10:17-14:25, 15:01-16:50	VOC	3-4 (possible emission source: Coker)	9:00-16:00	Out (Scan 513)	Not linearly related	1 hexene, methylene chloride, 1,3 butadiene, propylene, ethylene, 1,2 dichloro-ethane, trichloro-ethylene, chloro-benzene, cumene	10:45-16:47	Yes, 100% (Scan 513)	Not statistically linearly correlated, but they do have the same pattern
2/11/2010	SPD27/LOS1, LOS2, LOS3†	11:22-16:47	Benzene	5-27 (possible emission source: Coker)	10:00-16:00	Out (Scan 620, Scan 633)	r = -0.49, but regression not statistically significant p-value = 0.32	1 hexene, methylene chloride, 1,3 butadiene, propylene, 1,2 dichloro-ethane, trichloro-ethylene, chloro-benzene, chloroform	11:24-13:53	Yes, 5% (Scan 620) No, 0% (Scan 633)	All nondetect in FTIR
2/17/2010	SPD31/ LOS1†, LOS3	10:06-11:24, 12:19-15:38, 16:14-16:54	Benzene	22-31 (possible emission sources: Coker, GOHT, West Dock area, tanks D-363, F-347, F-349)	09:00-16:00	Out (Scan 745)	r =-0.59 with all of the data, but regression not statistically significant, and one influential outlier p-value = 0.16, r =0.25 when outlier removed and regression not significant p-value = 0.62, when looking only from 12-16 hrs, r =0.74, no influential outlier and regression not significant p-value= 0.15	Trichlorofluoromethane, methylene chloride, cumene	*10:48-16:46	Yes, 100% (Scan 745)	NA, too few data points, FTIR reports a benzene spike at scan 737 which is not reported by DIAL

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
3/27/2010	SPD37/ LOS1, LOS3	9:58-11:28, 12:16-16:51	VOC	3-4 (possible emission source: Coker)	09:00-16:00	Out (Scan 844, Scan 868)	r =0.56, regression not statistically significant p-value= 0.18	Cumene, 1,3,5 trimethylbenzene and 1,2,4 trimethylbenzene	9:46-16:47	Yes, 10% (Scan 844) No, 0% (Scan 868)	Analyzed segment with fewest nondetects not linearly related but similar

* FTIR by Time averaging method (TAM)

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

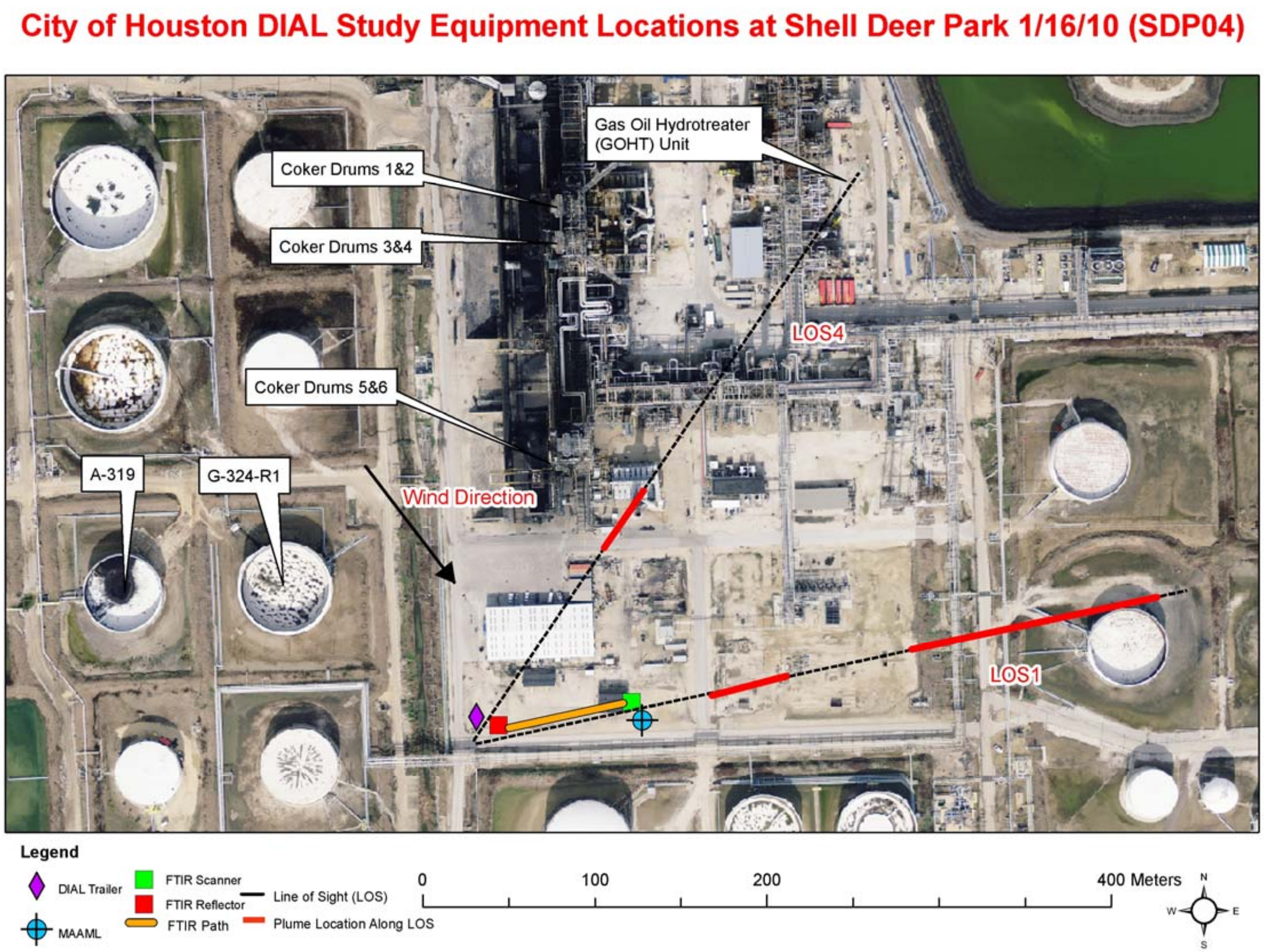

Figure 3.3a Coker, GOHT, and West Dock Area 1/16/2010

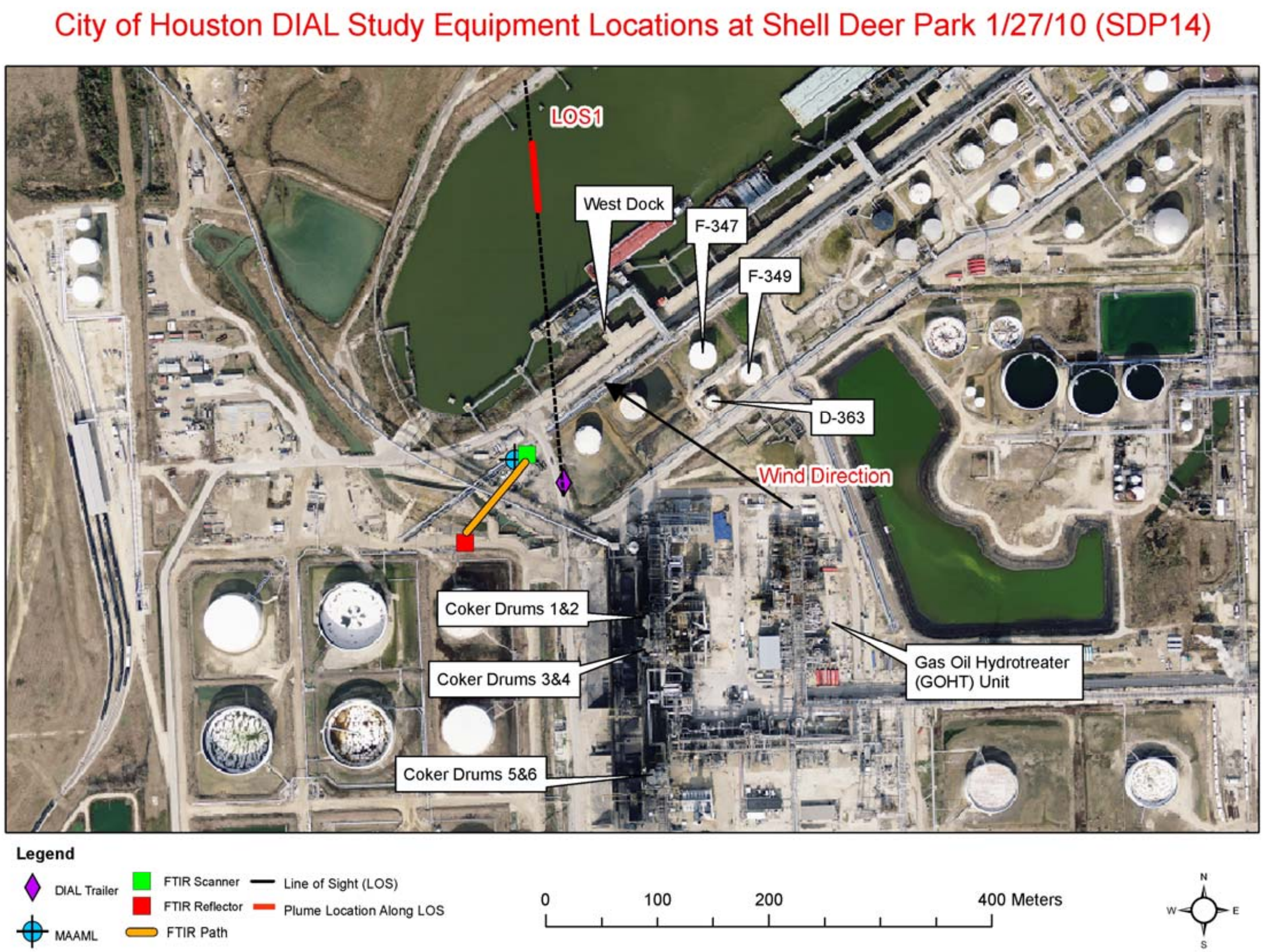

Figure 3.3b Coker, GOHT, and West Dock Area 1/27/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/4/10 (SDP20)

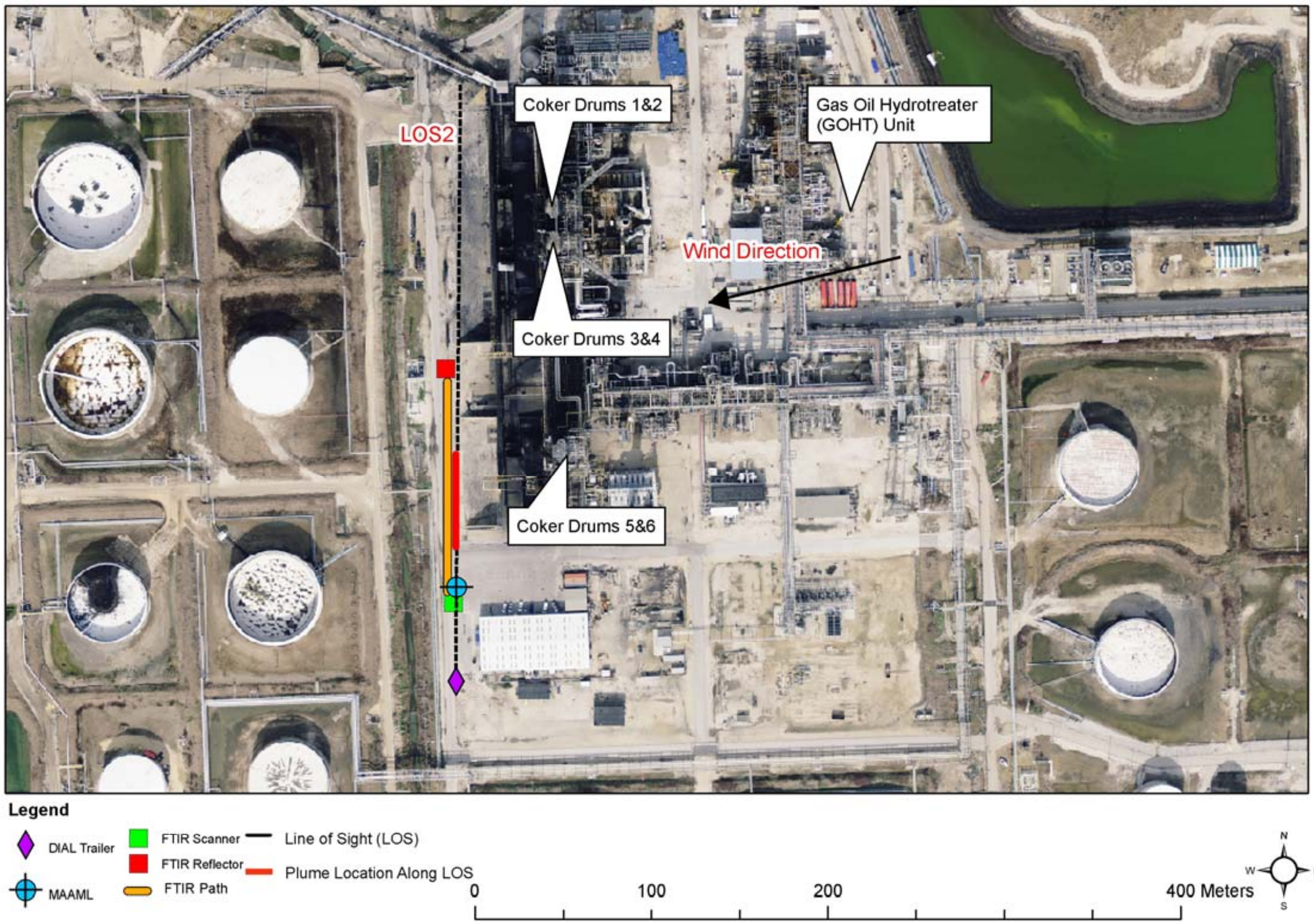

Figure 3.3c Coker, GOHT, and West Dock Area 2/4/2010

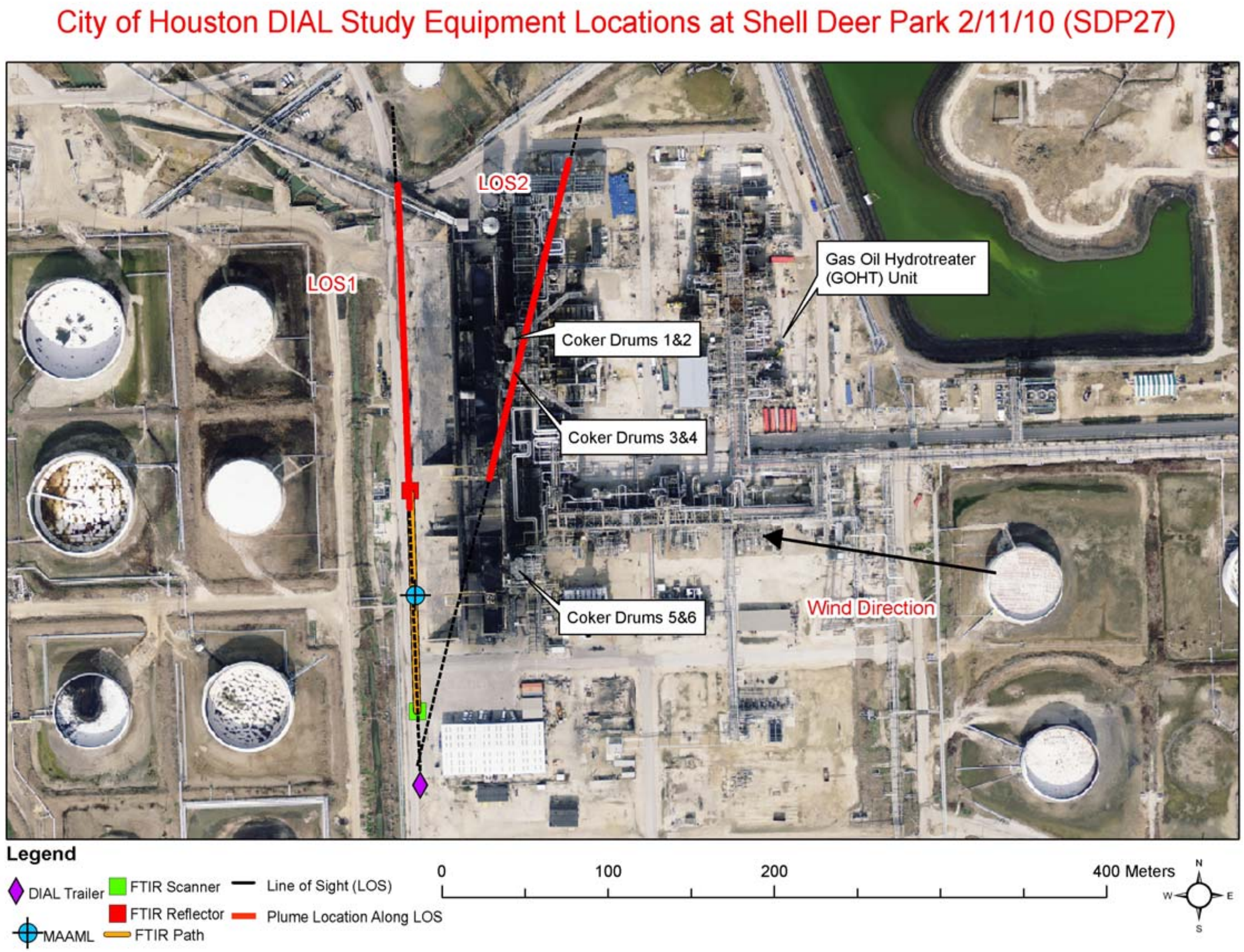

Figure 3.3d Coker, GOHT, and West Dock Area 2/11/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/17/10 (SDP31)

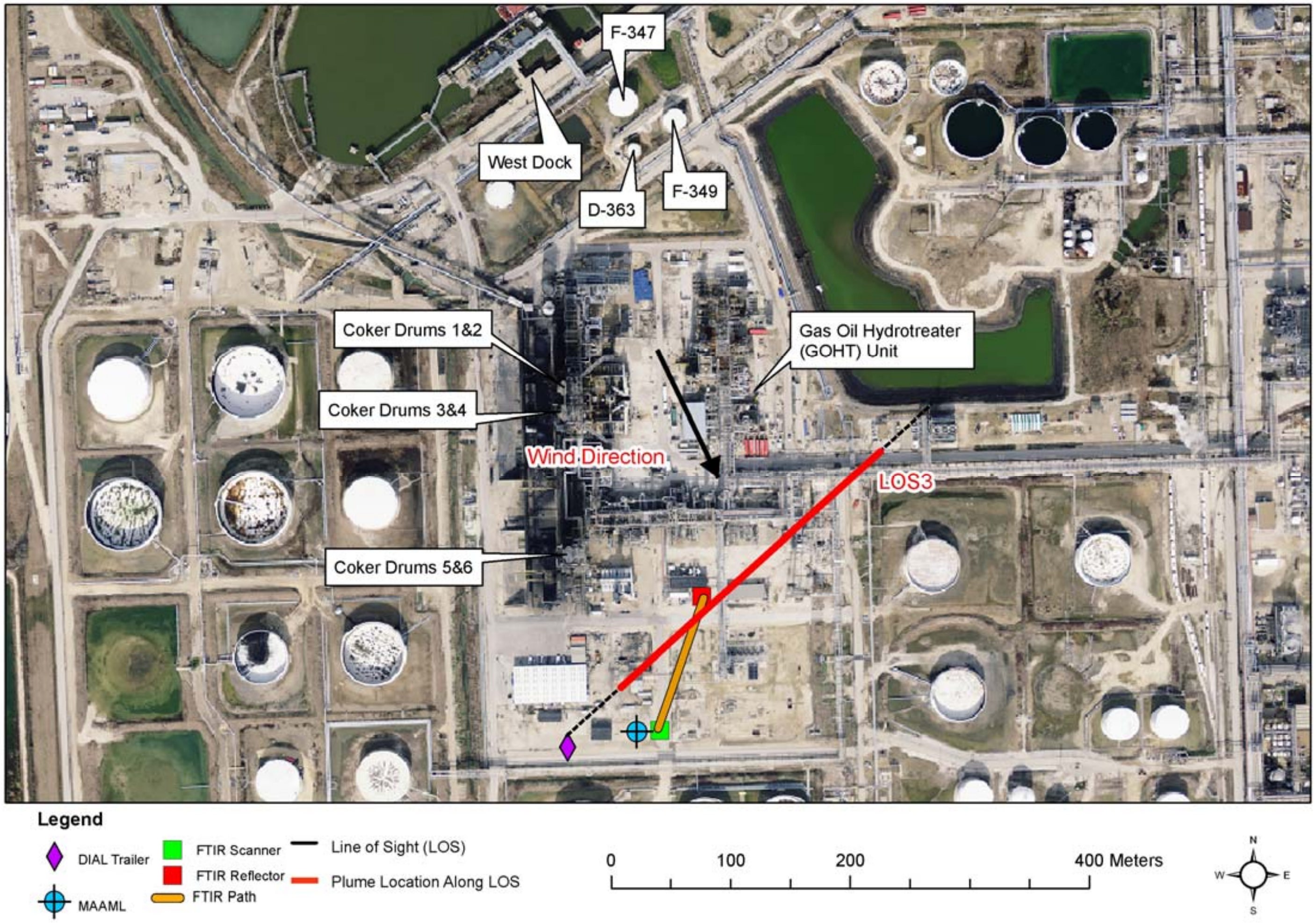

Figure 3.3e Coker, GOHT, and West Dock Area 2/17/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 3/27/10 (SDP37)

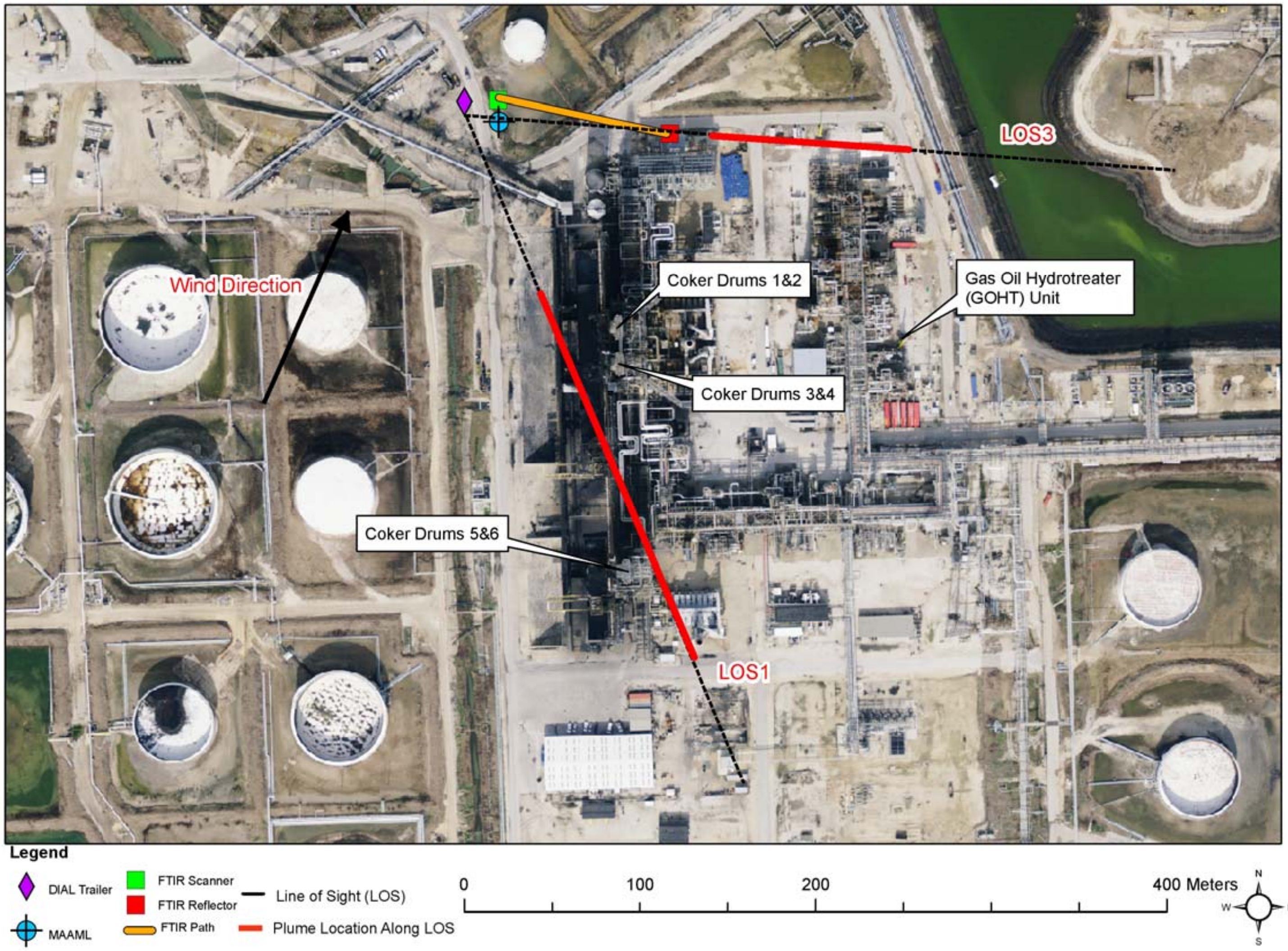

Figure 3.3f Coker, GOHT, and West Dock Area 3/27/2010

3.4 Olefins Process Area

Table 3.4 Olefins Process Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/18/2010	SPD05/LOS1, LOS2[†], LOS3[†]	10:46-15:19	VOC	4-5 (possible emission sources: Analyzer House U Vent (LO3AHU), Analyzer House T Vent (LO3AHT), LO3 Unit (LO3FUG))	10:00-16:00	Out (Scan 115)	With all of the data not linearly related. r=0.092 not statistically significant p-value=0.88, removing data with windshift, relationship is log linear, r=.80 for hours 12 on but not statistically significant p-value=0.19	Ethane, ethylene, propylene, 1,3 butadiene	10:46-16:48	No, 0% (Scan 115)	Not linearly related, however, FTIR and Wind Direction are highly correlated at r=0.76
1/19/2010	SPD06/LOS1	10:27-11:51, 13:18-14:18	VOC	4 (possible emission sources: Analyzer House U Vent (LO3AHU), Analyzer House T Vent (LO3AHT), LO3 Unit (LO3FUG))	9:00-16:00	Out (Scan 145)	NA, too few data points	trichloroethylene, tetrachloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane	10:44-16:47	No, 0% (Scan 145)	Not linearly related

[†]This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

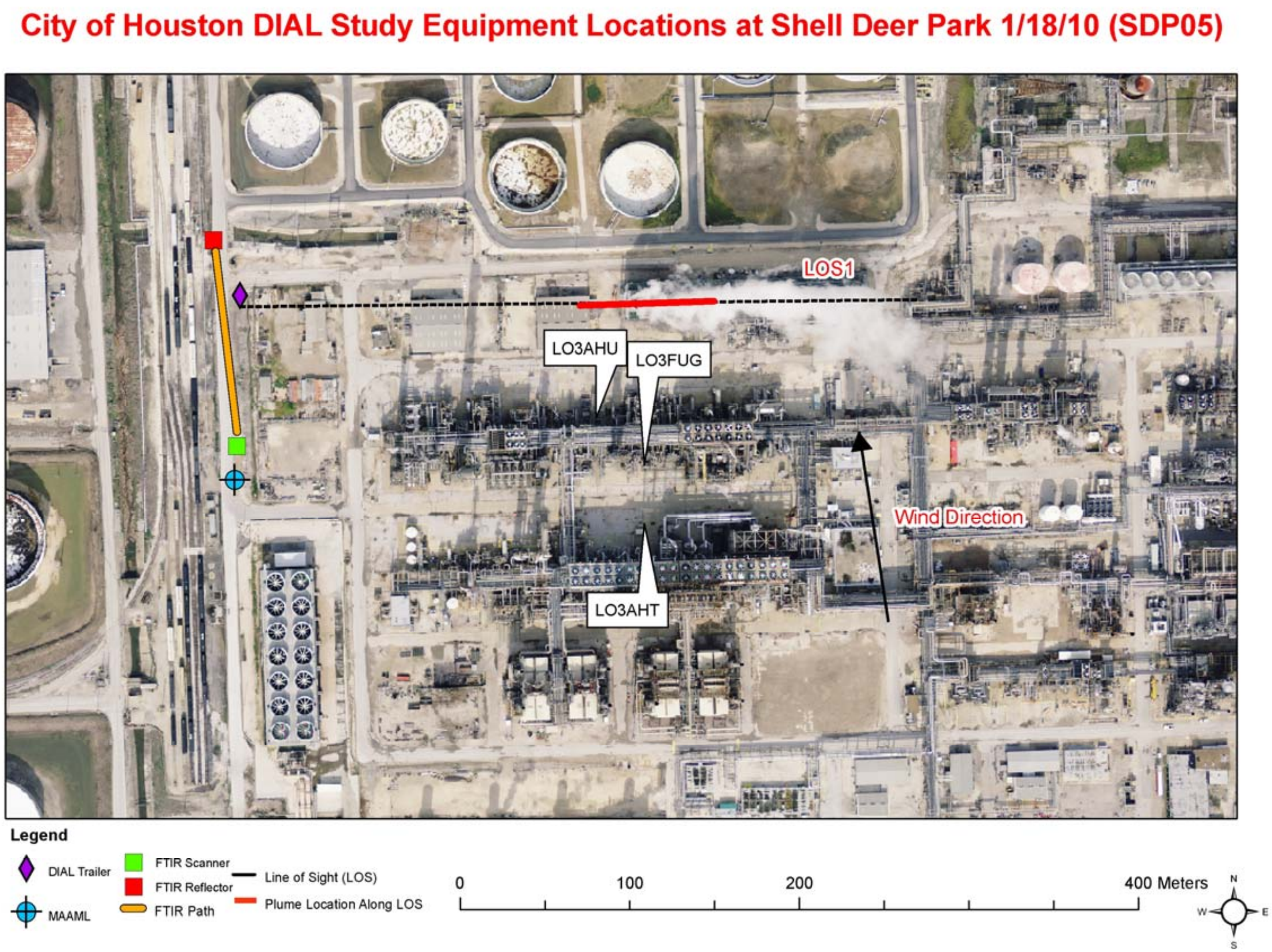

Figure 3.4a Olefins Process Area 1/18/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/19/10 (SDP06)

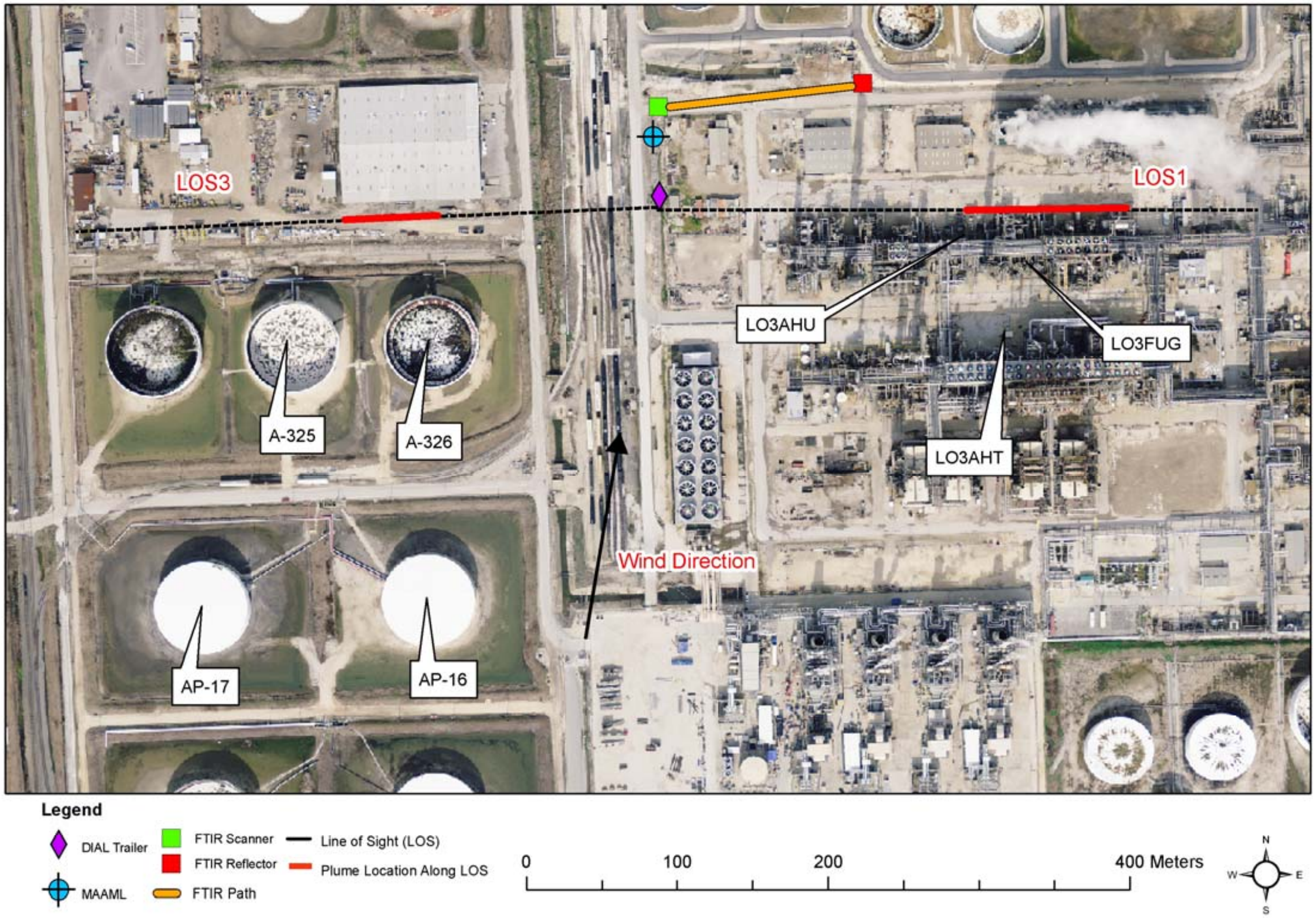

Figure 3.4b Olefins Process Area 1/19/2010

3.5 Olefins Tanks and Flares Area

Table 3.5 Olefins Tanks and Flares Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/20/2010	SPD08/ LOS1	11:57-13:06, 14:06-14:42	VOC	5 (possible emission sources: tanks R-311, R-312, G-332, G-361, ground flare OP3GRFLA, elevated flares OP3ELFLA, OP2ELFLA)	10:00-16:00	Out (Scan 176)	NA, too few data points	Chloro-benzene, hexachloro 1,3 butadiene, 1,1,1 trichloro-ethane, trichloro-ethylene,	11:24-16:32	No, 0% (Scan 176)	Too many nondetects to assess
1/20/2010	SPD08/ LOS3†, LOS4	15:00-16:19	VOC	2-3 (possible emission sources: tanks G-332, G-361, ground flare OP3GRFLA, elevated flares OP3ELFLA, OP2ELFLA)	10:00-16:00	Out (Scan 193)	NA, too few data points	none	11:24-16:32	No, 0% (Scan 193)	Too many nondetects to assess
1/29/2010	SPD16/ LOS1†, LOS2†, LOS3†	14:01-16:56	VOC	0 (target emission sources: ground flare OP3GRFLA, elevated flares OP3ELFLA, OP2ELFLA)	9:00-16:00	Visual representation of LOS1, LOS2, and LOS3 not available	NA, too few data points	none	10:47-16:48	Visual representation of LOS1, LOS2, and LOS3 not available	Too many nondetects to assess

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

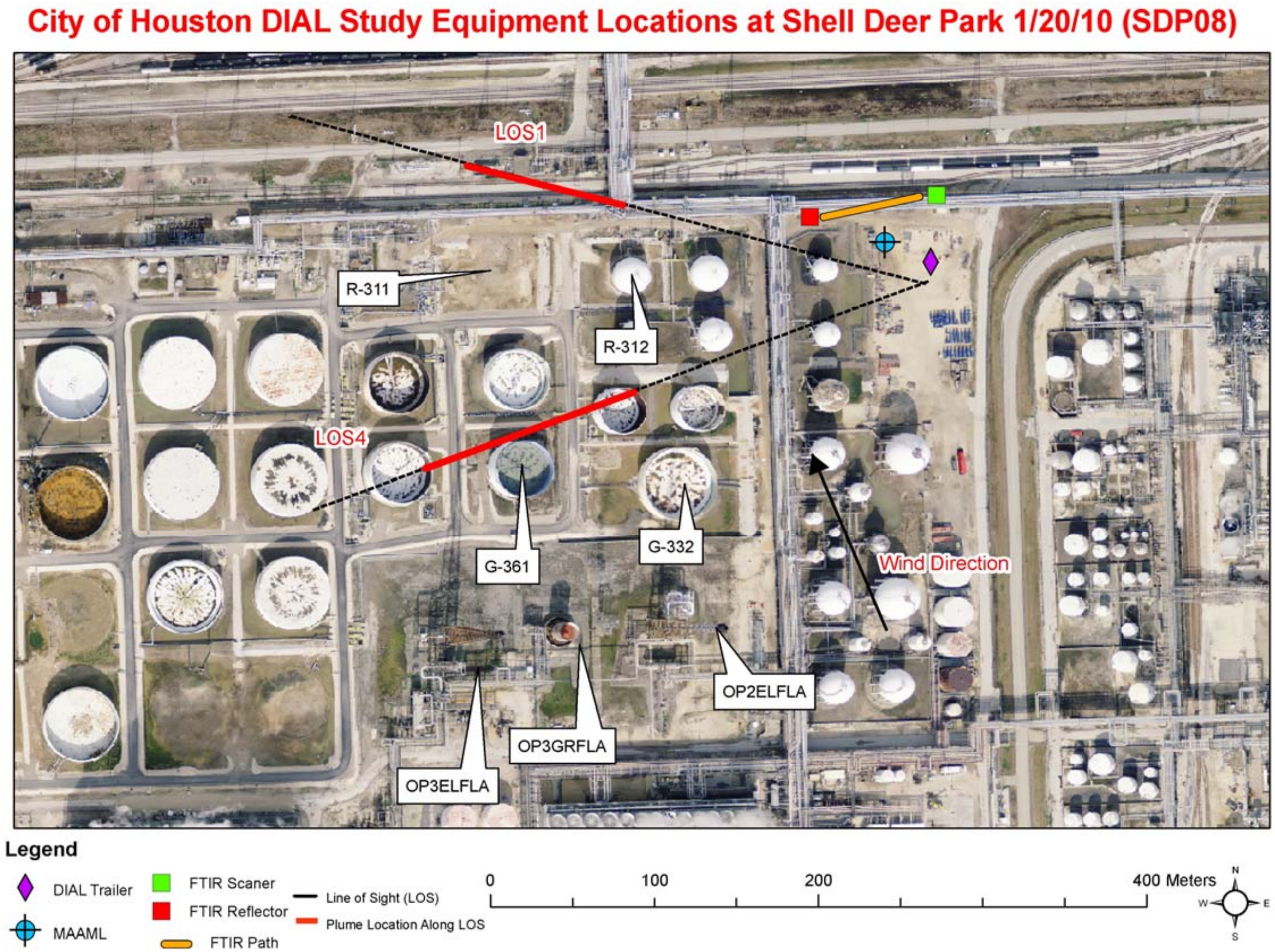

Figure 3.5a Olefins Tanks and Flares Area 1/20/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/29/10 (SDP16)

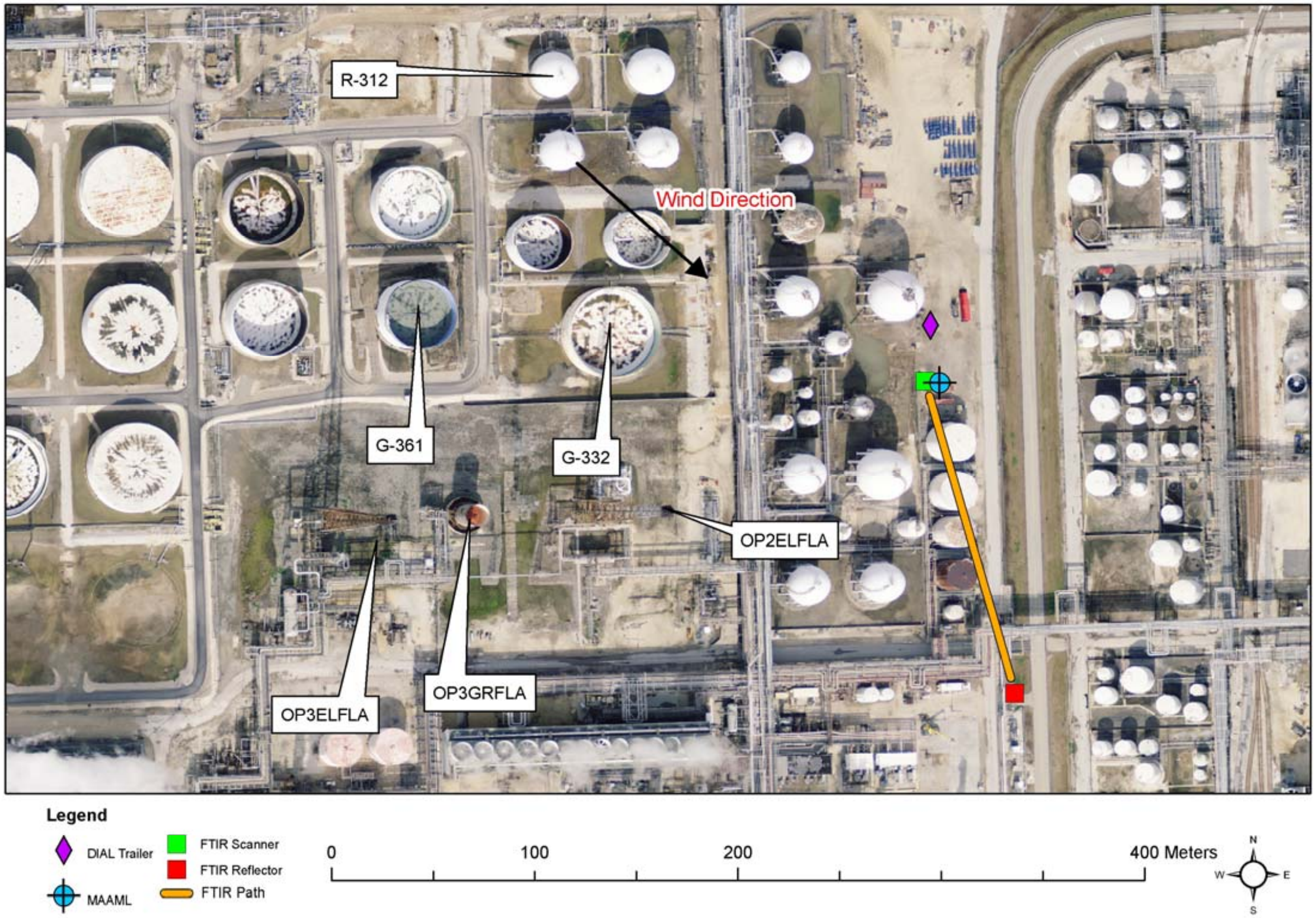

Figure 3.5b Olefins Tanks and Flares Area 1/29/2010

3.6 CR-3

Table 3.6 CR-3

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/21/2010	SPD09/LOS2, LOS3†	13:10-15:23	VOC	8-12	10:00-16:00	Out (Scan 209)	NA, too few data points	1 hexene, tetrachloroethylene, trichloroethylene,	11:08-16:48	No, 0% (Scan 209)	NA, too many nondetects in FTIR
3/25/2010	SPD34/LOS1	10:53-12:56, 14:05-15:00, 15:59-16:54	VOC	30	9:00-16:00	Out (Scan 809)	Not linearly related. r=0.41 not statistically significant p-value=0.59	Ethane, propane, n-pentane, n-butane, chloroform, toluene, tetrachloroethylene, ethylbenzene, m/p-xylene, styrene, cumene, 1,2,4 trimethylbenzene, 1,3 dichlorobenzene, hexachloro 1, 3 butadiene	10:27-16:48	Yes, 90% (Scan 809)	Not statistically linearly related, similar pattern in center of time series

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/21/10 (SDP09)

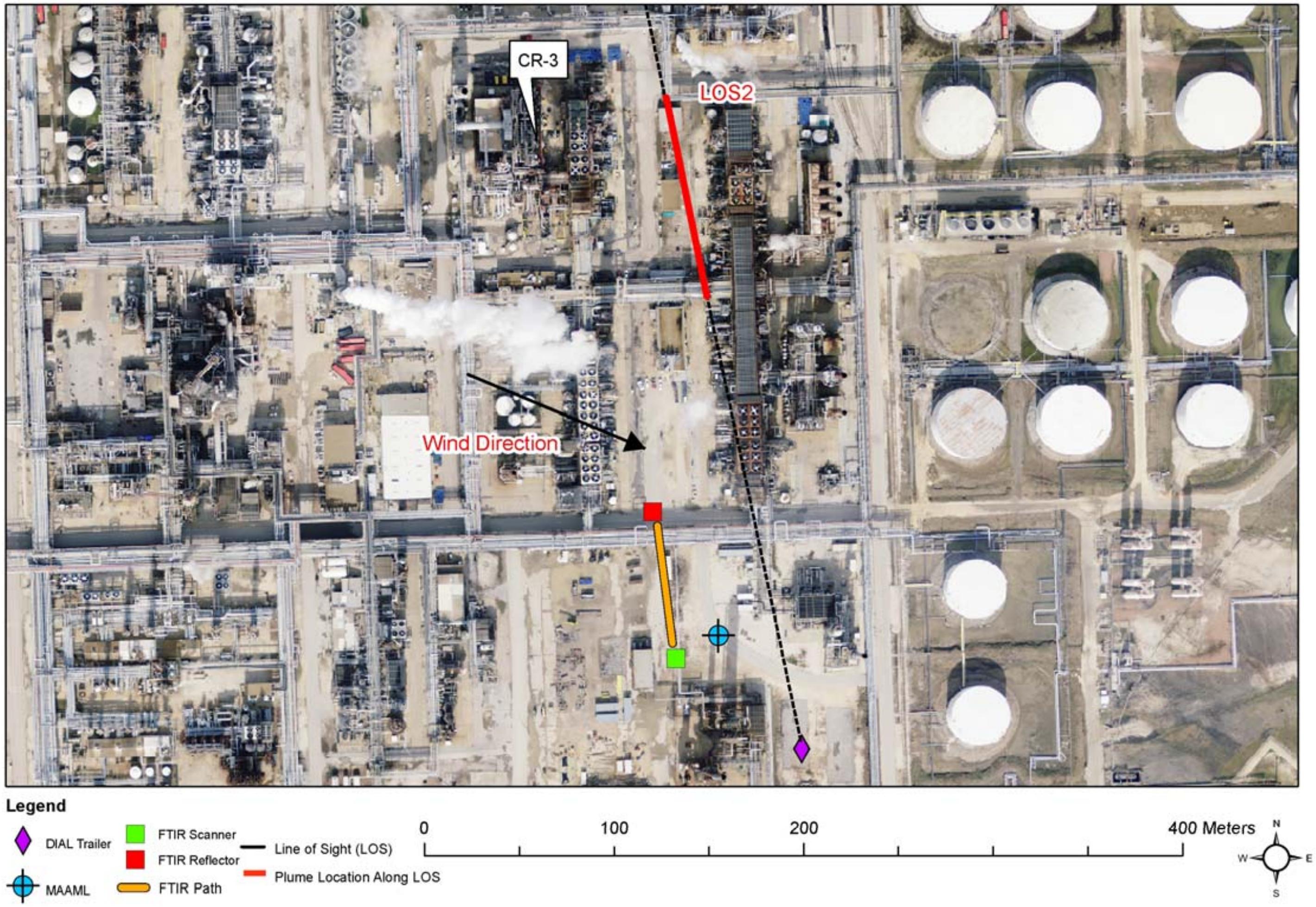

Figure 3.6a CR-3 1/21/2010

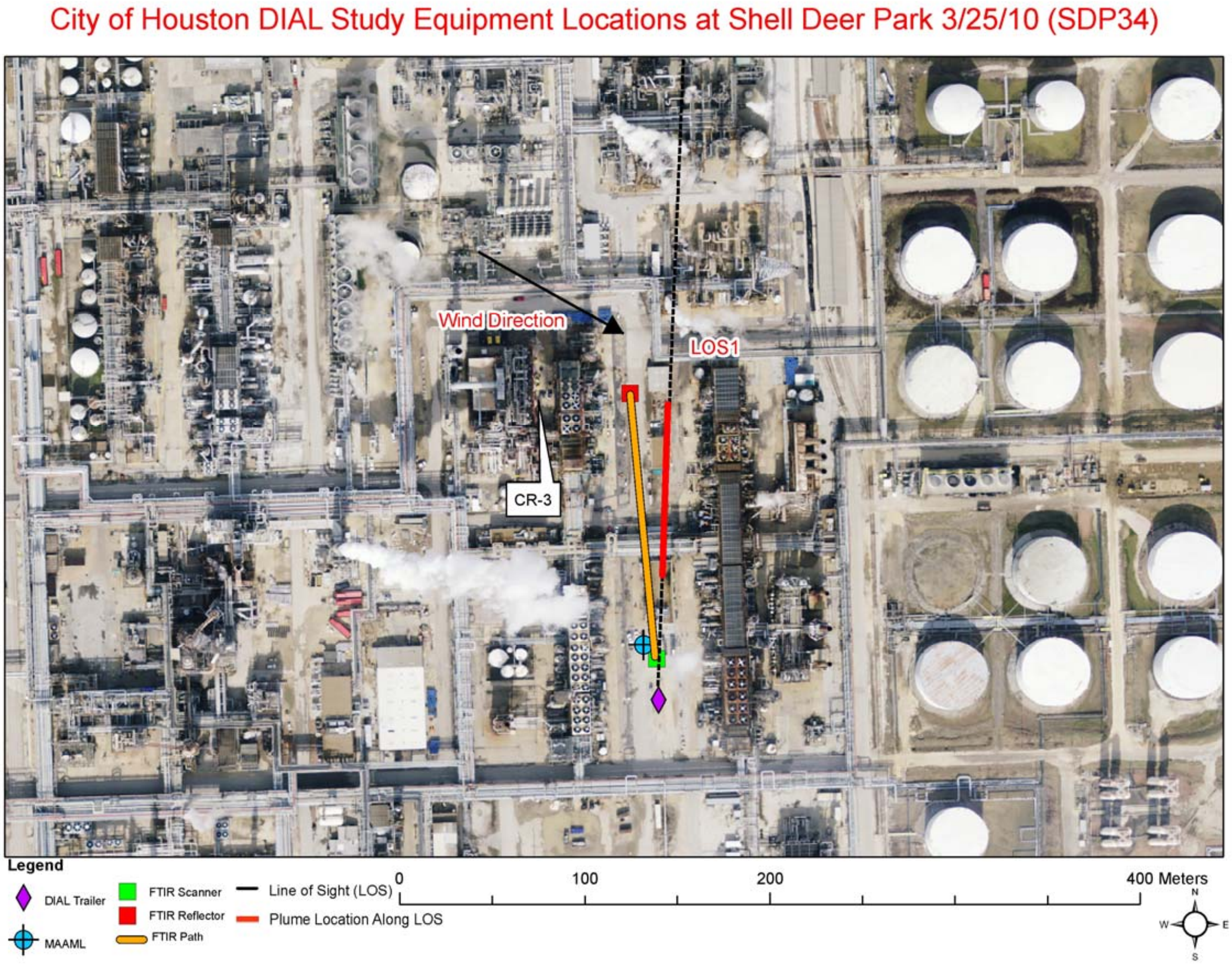

Figure 3.6b CR-3 3/25/2010

3.7 East Property Flare

Table 3.7 East Property Flare (EP Flare)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/22/2010	SDP10/LOS1†	12:07-12:58, 14:03-14:38	VOC	0	10:00-16:00	Visual representation of LOS1 not available	NA, too few data points	none	*11:22-16:47	Visual representation of LOS1 not available	Not linearly related
2/2/2010	SDP18/ LOS1†, LOS2†	10:54-17:05	VOC	0-1	10:00-16:00	Visual representation of LOS1 and LOS2 not available	Not linearly related. r=-0.59 not statistically significant p-value=0.21	Ethane, propane, 1,3 butadiene, n butane, n pentane, 1 hexene, 1,2 dichloroethane, trichloroethylene, tetrachloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane	10:56-16:47	Visual representation of LOS1 and LOS2 not available	Not linearly related

* FTIR by Time averaging method (TAM)
†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/22/10 (SDP10)

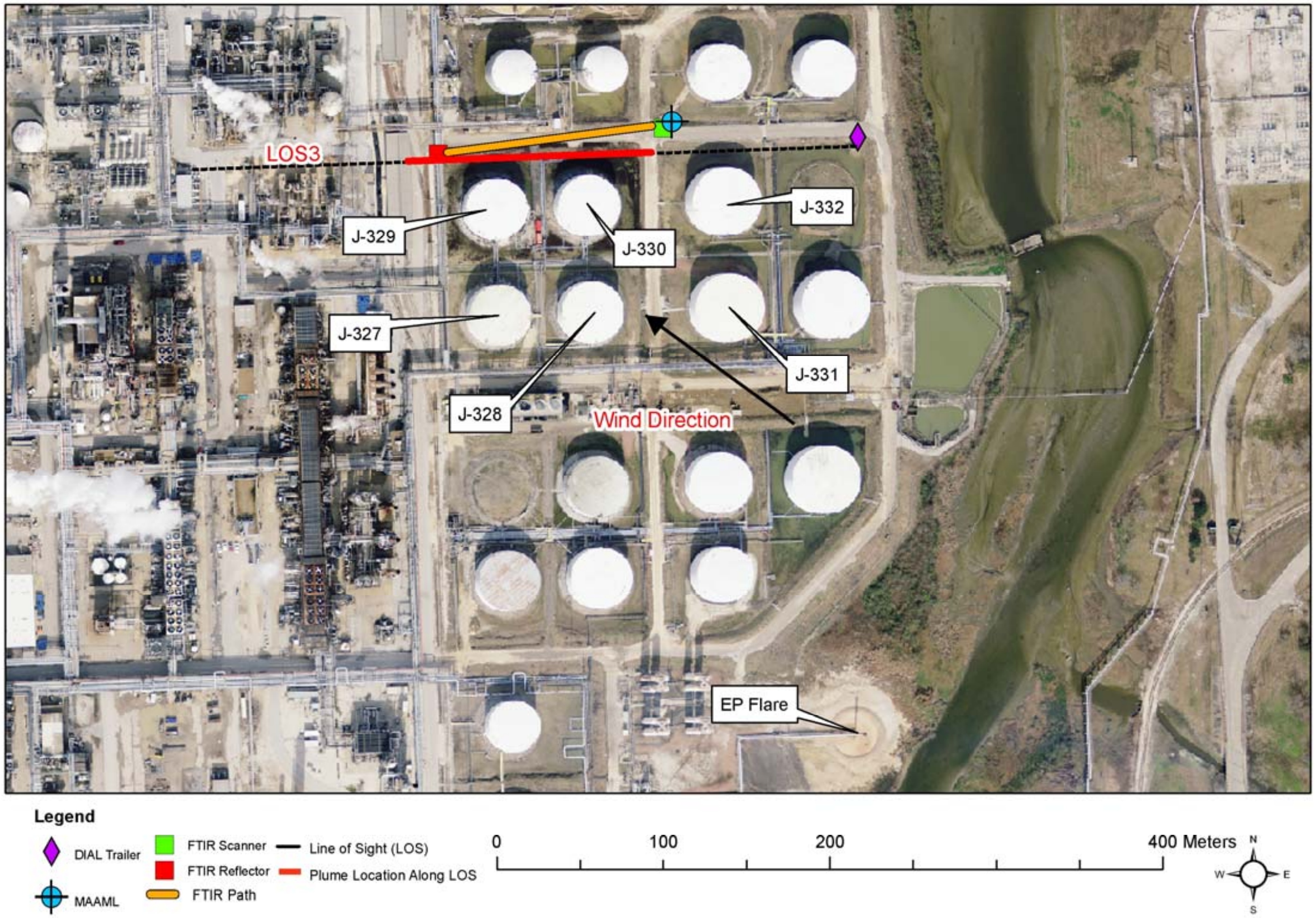

Figure 3.7a East Property Flare 1/22/2010

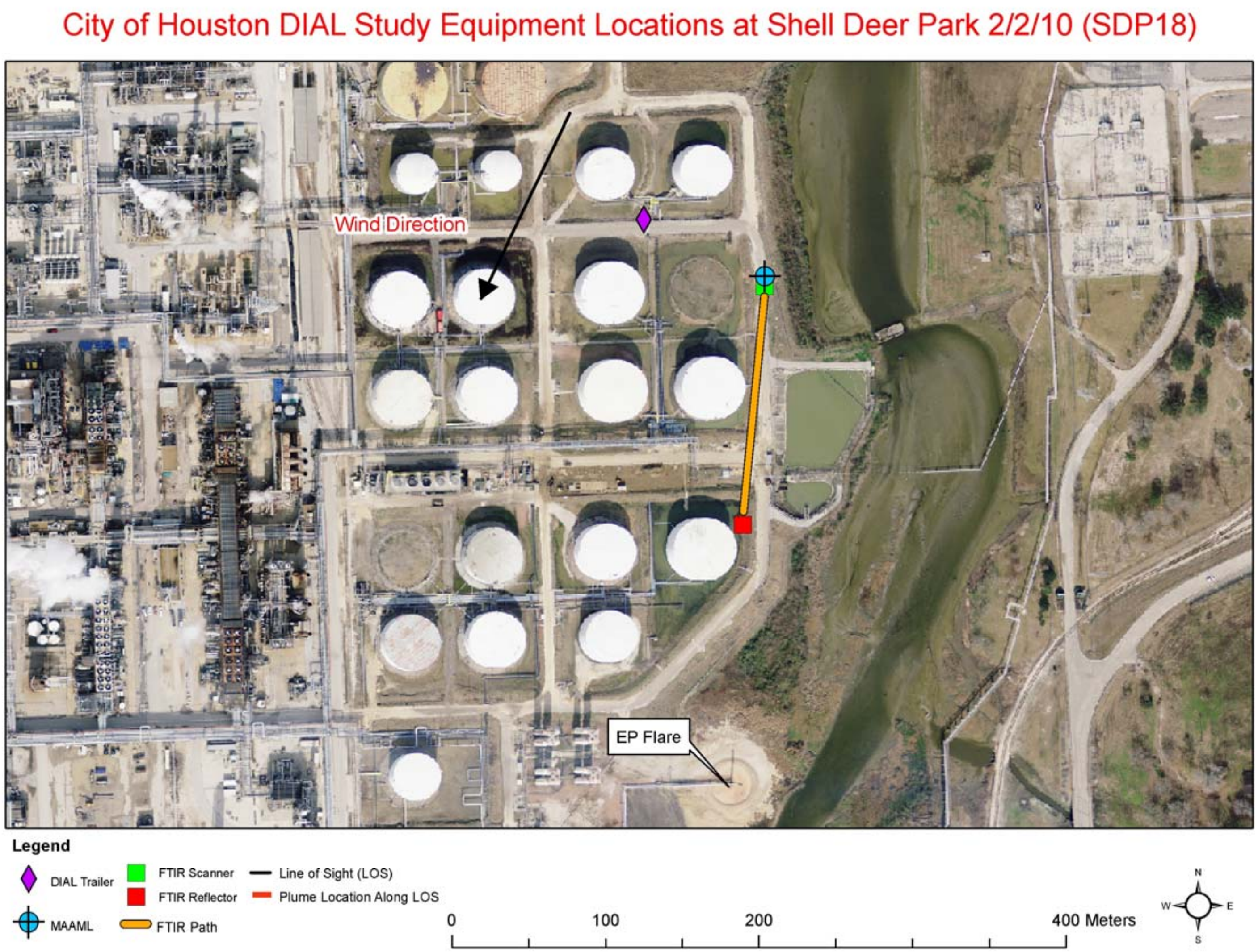

Figure 3.7b East Property Flare 2/2/2010

3.8 East Tanks

Table 3.8 East Tanks (J-327, J-328, J-329, J-330, J-331, and J-332)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/22/2010	SPD10/ LOS3	15:53-17:03	VOC	31	10:00-16:00	Out (Scan 247)	NA, too few data points	none	*11:22-16:47	Yes, 100% (Scan 247)	Not linearly related, similar pattern
1/23/2010	SPD11/ LOS1†, LOS2	10:57-13:37, 15:50-17:06	VOC	5-19	10:00-16:00	Out (Scan 263)	linearly related r=0.72 not statistically significant p-value=0.16	Ethylene, propylene,n butane, n pentane, 2 methylpentane, hexane, toluene, ethylbenzene, m/p xylene, o xylene, cumene, 1,2 4 trimethylbenzene	10:25-16:47	No, 0% (Scan 263)	Not linearly related
1/28/2010	SPD15/ LOS1†, LOS2	11:23-14:59, 16:17-16:41	VOC	32-33	10:00-16:00	Out (Scan 365)	With all data points (hour 11 through 14 and hour 16) linearly related inversely with r=-0.11 not statistically significant p-value=0.86, there is a wind shift at hour 11 when removed still no relationship with r=0.31 not statistically significant p- value=0.69	Ethylene, dichlorodifluormethane, acetylene, 1,2 dichlorotetrafluormethane, vinyl chloride, methylene chloride, 1 hexene, trichloroethylene, toluene, tetrachloro-ethylene, chlorobenzene	11:09-16:51	No, 0% (Scan 365)	Linearly related, inverse relationship, r=-0.55, regression is significant p-value =0.02, Dial is positively correlated with wind direction and FTIR is negative correlated with wind direction. Multiple linear regression predicting emission rate from FTIR and wind direction has coefficients not significant

* FTIR by Time averaging method (TAM)
†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

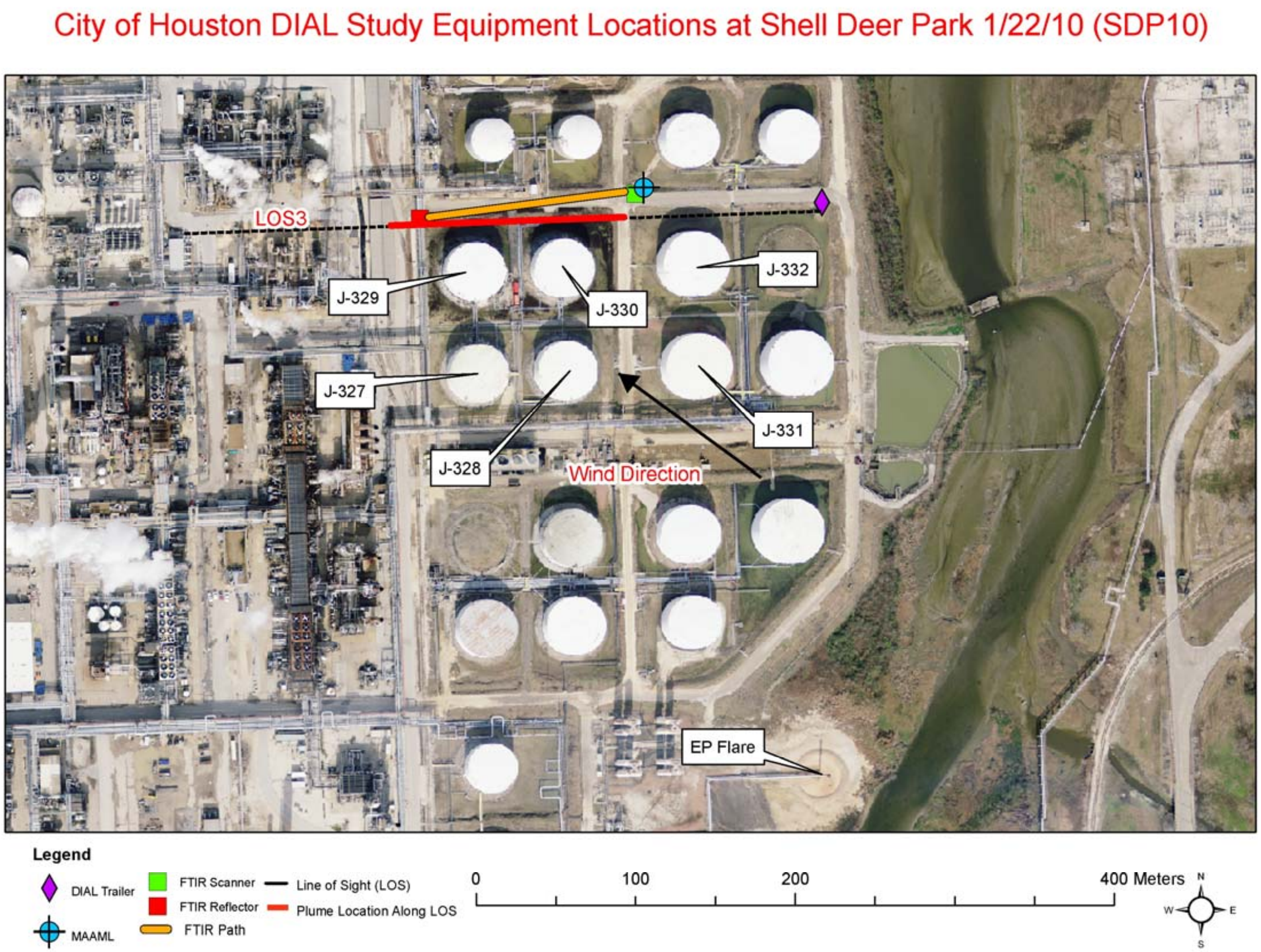

Figure 3.8a East Tanks 1/22/2010

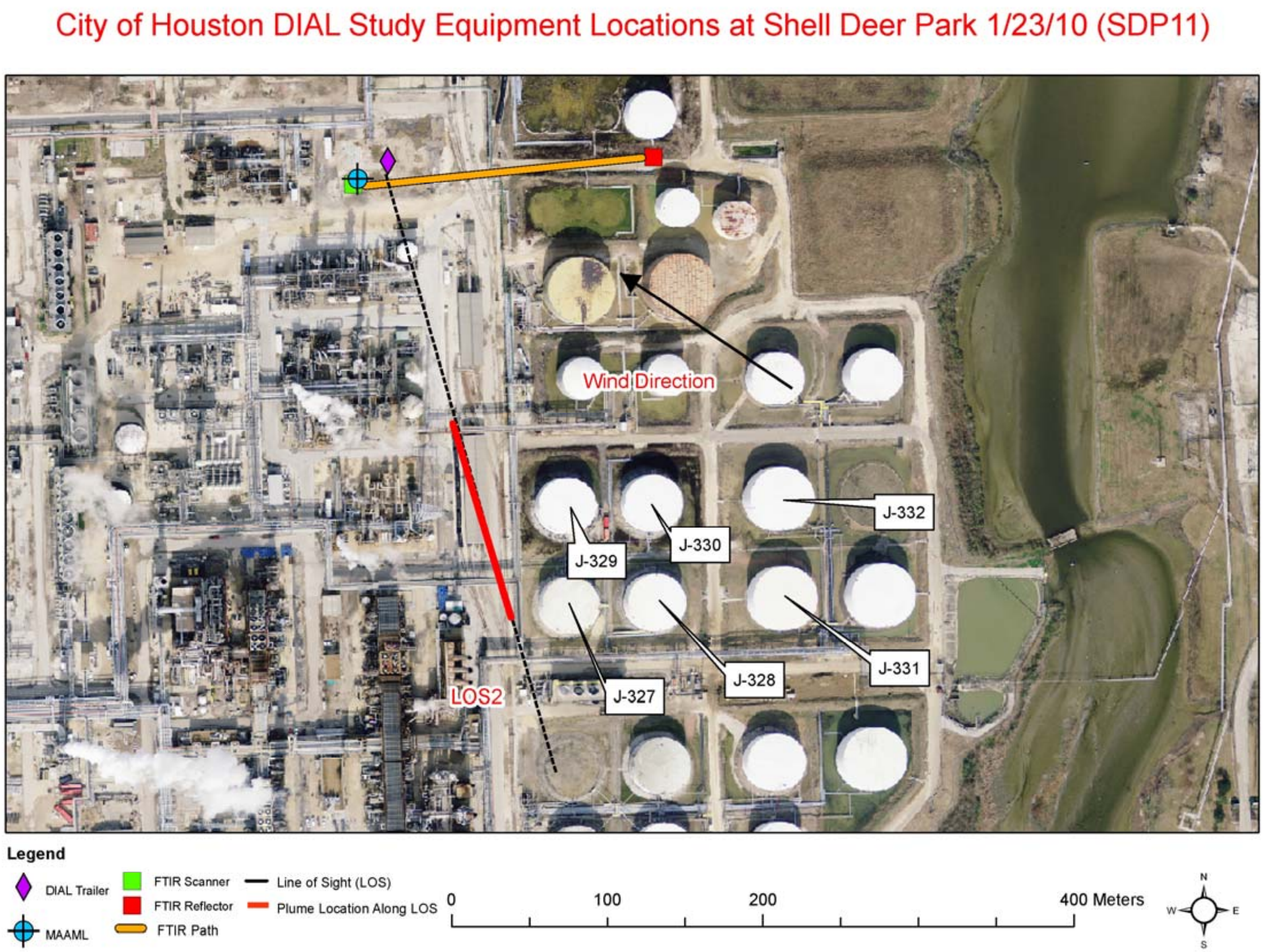

Figure 3.8b East Tanks 1/23/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/28/10 (SDP15)

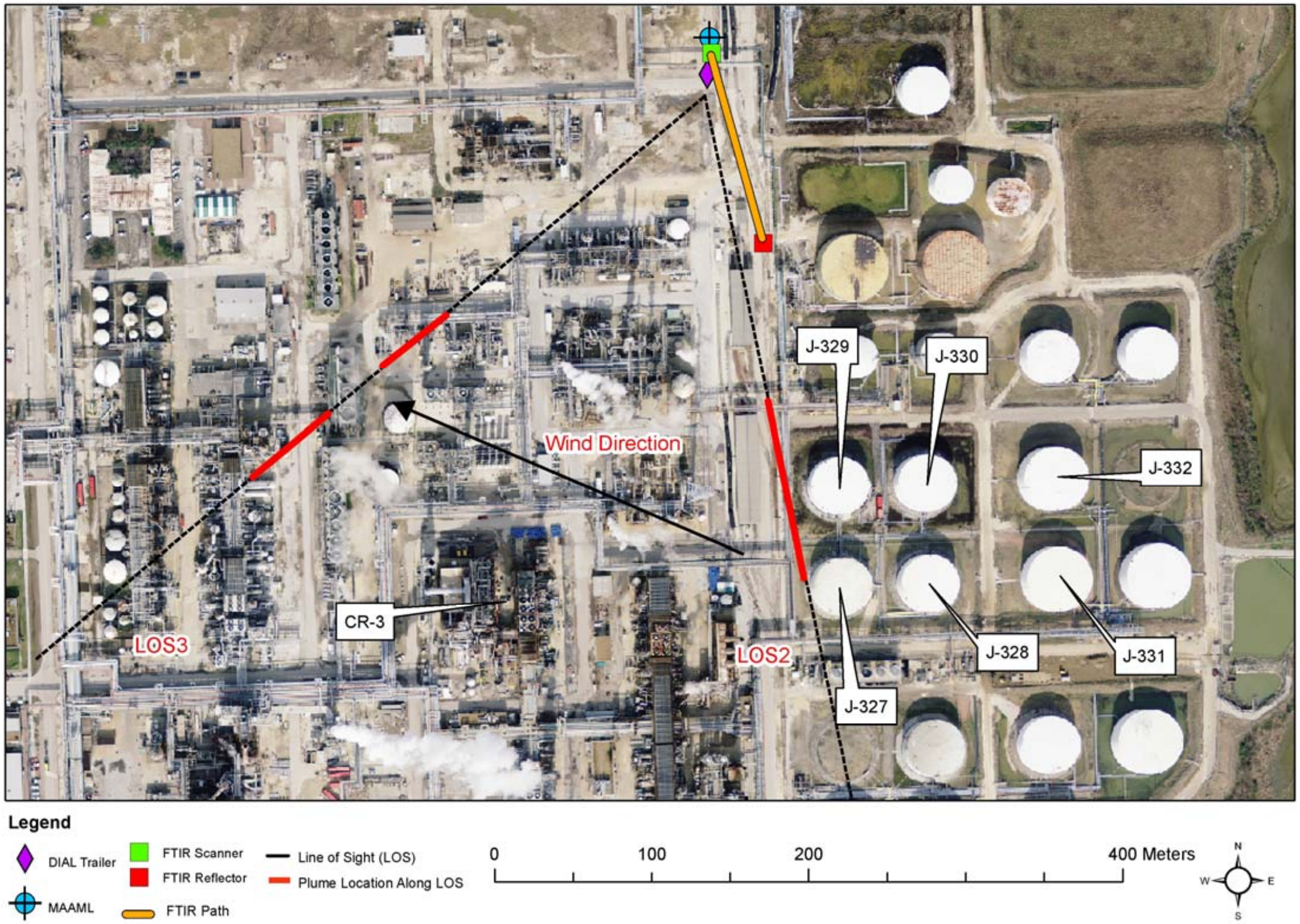

Figure 3.8c East Tanks 1/28/2010

3.9 North Wastewater Area

Table 3.9 North Wastewater Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/25/2010	SPD12/LOS1, LOS2†	10:42-13:54	VOC	2-22 (possible emission sources: west area of aeration basin SAB (EWT-12) and NAB (EWT-11), and aeration tanks west of aeration basin NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7) and FLCCULTR (EWT-8))	10:00-16:00	Out (Scan 280)	NA, too few data points, not linearly related and wind change	Ethane, ethylene, propane, acetylene, vinyl chloride, n butane, methylene chloride, 1,1,2 trichlorotrifluorethane, 1 hexene, trichloroethylene, toluene, tetrachloroethylene, m/p xylene, o xylene, 1,2,4 trimethylbenzene, 1,3 dichlorobenzene, 1,2 dichlorobenzene, hexachloro 1,3 butadiene	10:41-16:47	Yes, 5% (Scan 280)	Linearly related, r=0.95, regression significant p-value<0.001
1/30/2010	SPD12/LOS1, LOS2, LOS5, LOS6†	12:26-14:47, 15:48-17:01	VOC	800-1200 (possible emission sources: aeration tanks west of aeration basin NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7) and FLCCULTR (EWT-8))	10:00-16:00	Out (Scan 401, Scan 405, Scan 415)	Hour 12-14 (all downwind of wastewater) are correlated, r=0.31, regression is not significant p-value =0.61	1-hexene	11:05-16:50	Yes, 40% (Scan 401) No, 0% (Scan 405) Yes, 10% (Scan 415)	Linearly related, r=0.56, regression significant p-value=<0.04

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/5/2010	SPD21/LOS1, LOS2, SPD22/LOS1	10:50-14:11, 14:47-16:56	VOC	400-600 (possible emission sources: aeration basin SAB (EWT-12) and NAB (EWT-11), and aeration tanks west of aeration basin NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7) and FLCCULTR (EWT-8))	10:00-16:00	In (Scan 529, Scan 532) Out (Scan 537)	Not linearly related as a group or by SDP	N-pentane	*14:02-16:48	Yes, 100% (Scan 529, Scan 532) Yes, 30% (Scan 537)	Linearly related, correlated, r=0.66, regression is not significant p-value =0.15
2/9/2010	SPD25/LOS1	10:42-11:59, 13:10-16:57	Benzene	6 (possible emission sources: trickling filter (TKRFIL), NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7), FLCCULTR (EWT-8), X-330, X330SM, T-301, and T-302)	9:00-16:00	Out (Scan 571)	Not linearly related, MAAML reported a spike of benzene at hour 15 that DIAL did not report	Ethane, propane, n-butane, 1,1,2 trichlorotrifluoroethane, n pentane, 2 methyl pentane, 1 hexene, hexane, 1,2 dichloroethane, benzene, toluene, chlorobenzene, m/p xylene, o xylene, 1,2,4 trimethylbenzene	*10:46-16:46	No, 0% (Scan 571)	Not linearly related, FTIR reported a spike of benzene at hour 15 that DIAL did not report

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/13/2010	SPD29/LOS3	12:53-14:40, 16:27-16:42	Benzene	4 (possible emission sources: SAB (EWT-12), NAB (EWT-11), EWT-13, EWT-14, trickling filter (TKRFIL), NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7), FLCCULTR (EWT-8), X-330, X330SM, T-301, and T-302)	10:00-16:00	Out (Scan 672)	Not linearly related	none	11:22-16:43	No, 0% (Scan 672)	NA,all but one nondetect

* FTIR by Time averaging method (TAM)
†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

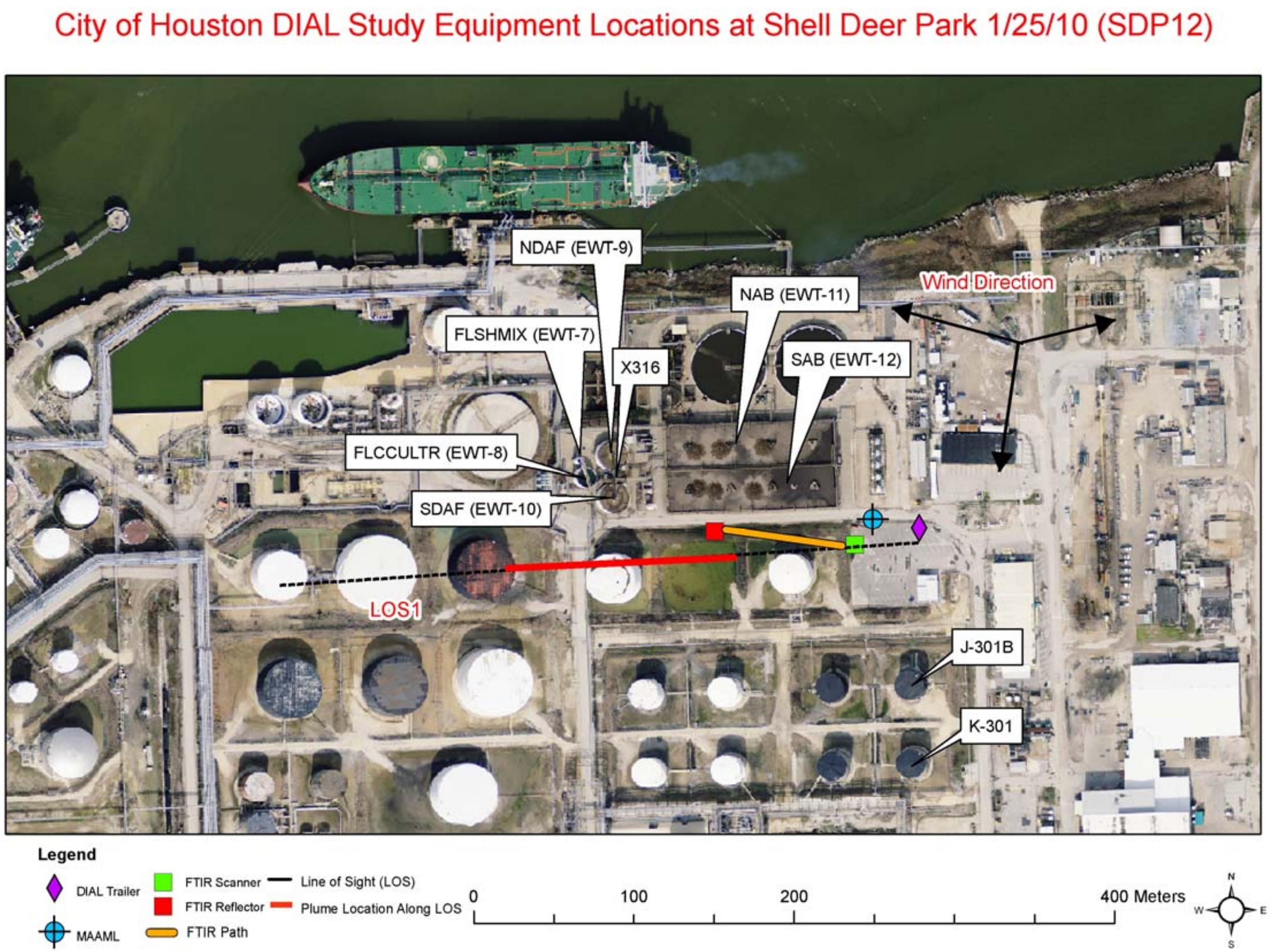

Figure 3.9a North Wastewater Area 1/25/2010

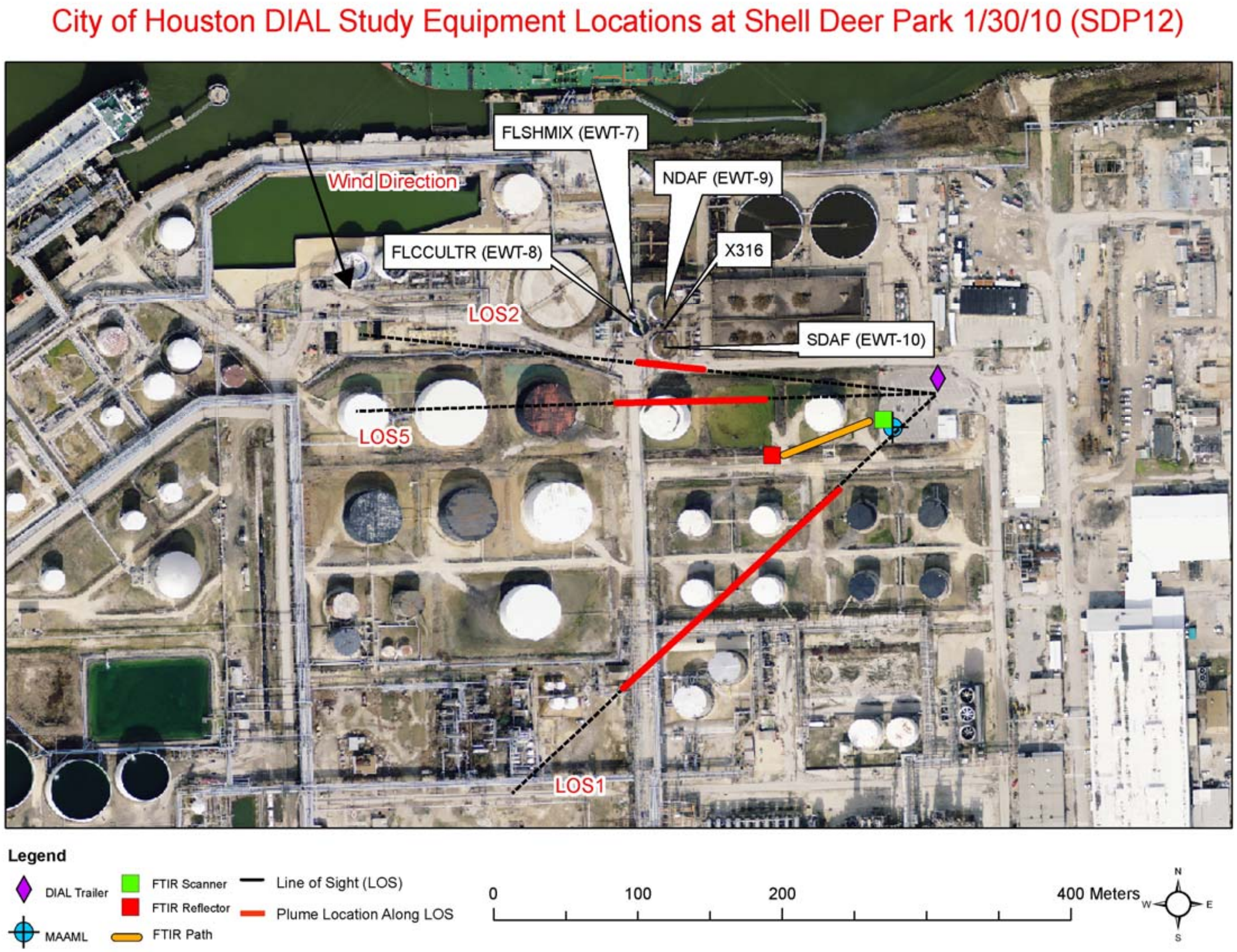

Figure 3.9b North Wastewater Area 1/30/2010

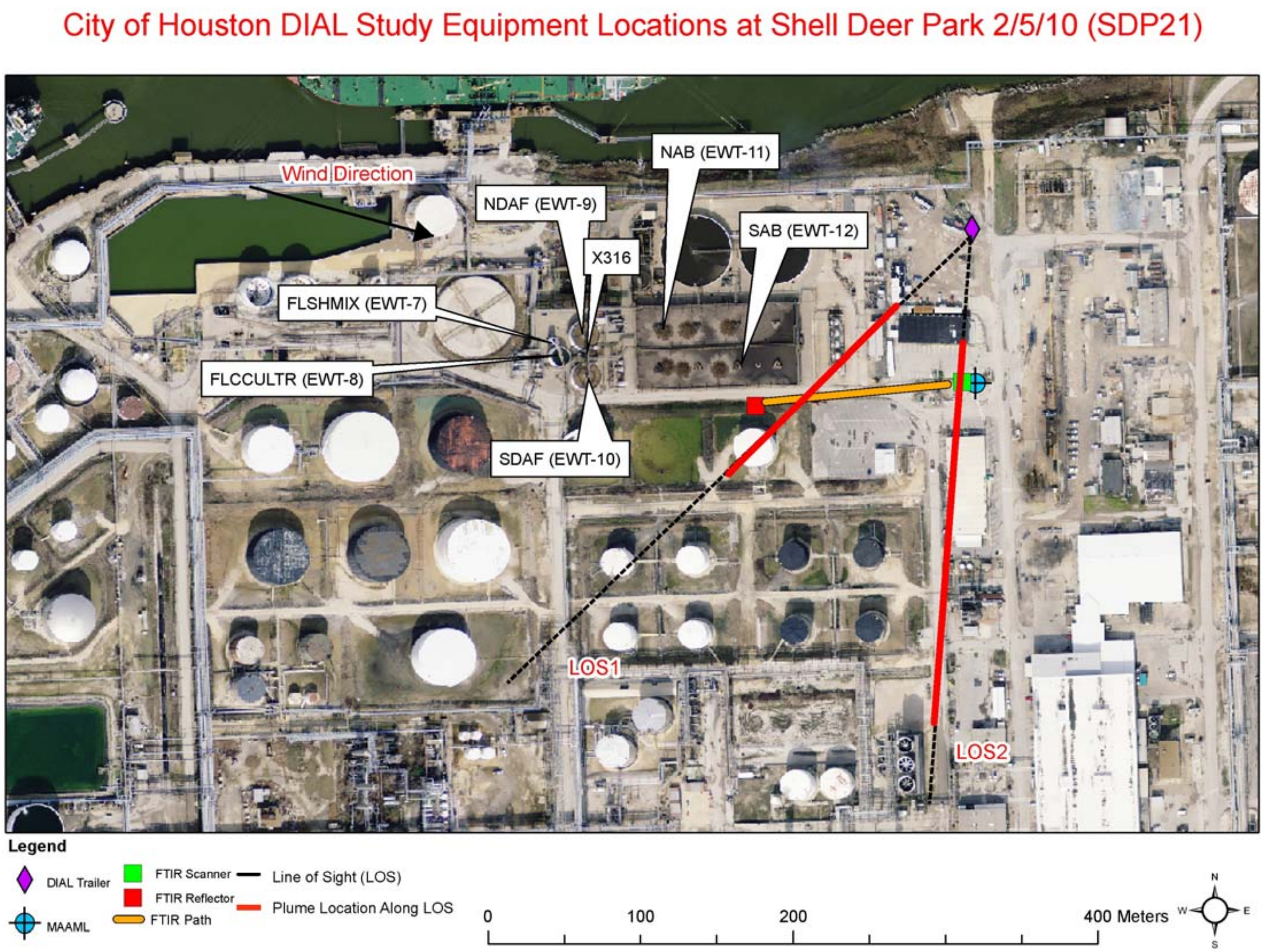

Figure 3.9c North Wastewater Area 2/5/2010

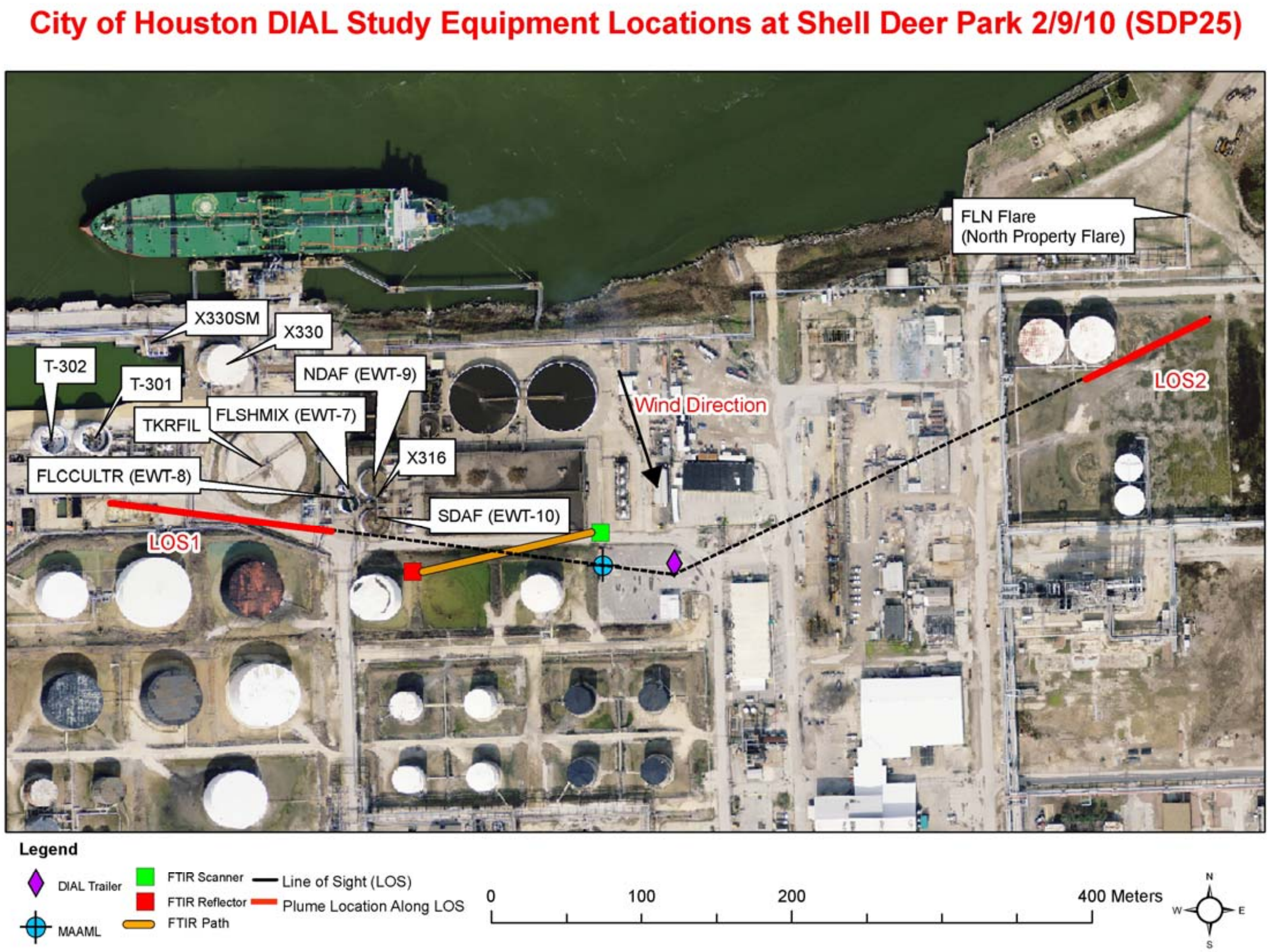

Figure 3.9d North Wastewater Area 2/9/2010

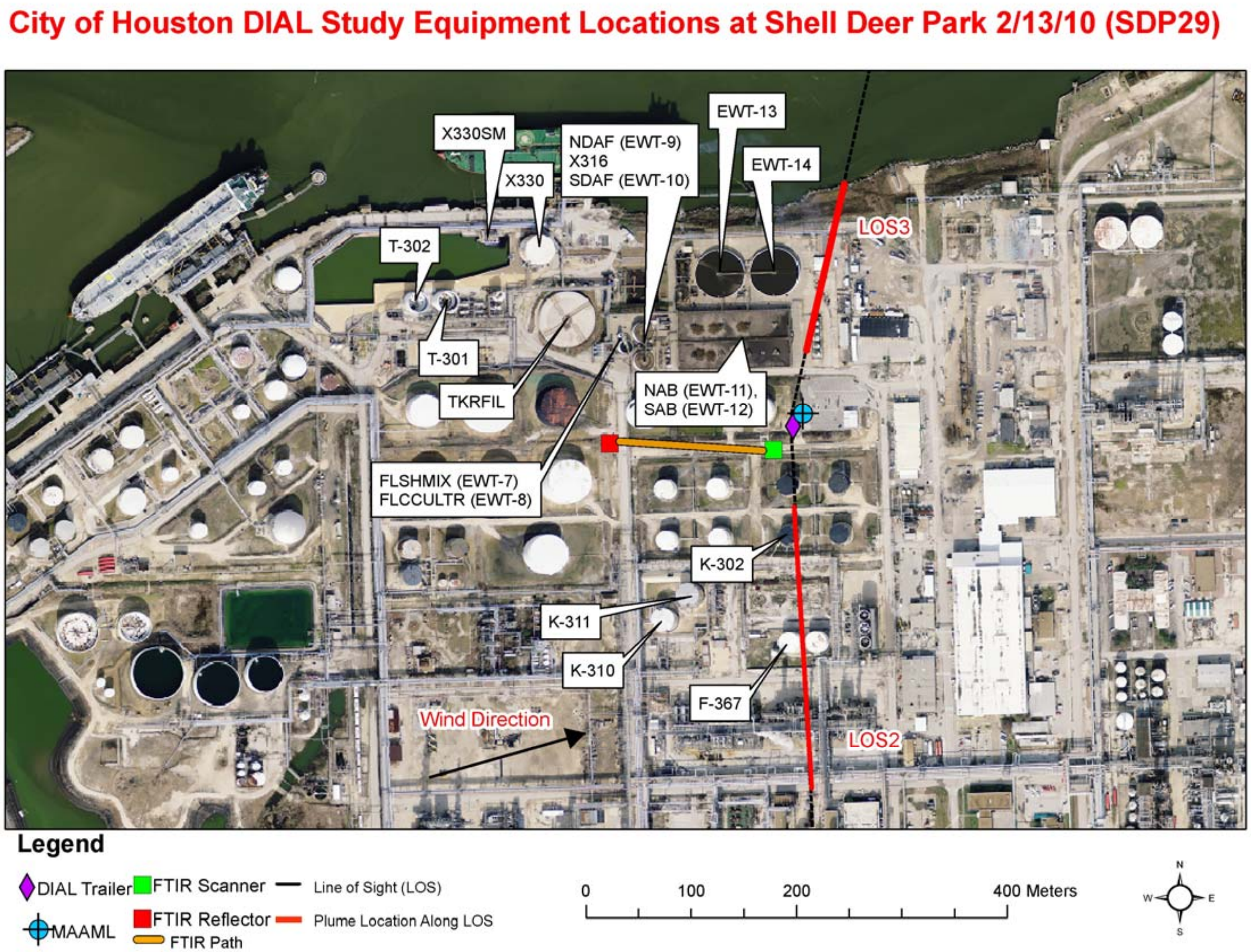

Figure 3.9e North Wastewater Area 2/13/2010

3.10 East Wastewater and Flares Area

Table 3.10 East Wastewater and Flares Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/26/2010	SPD13/ LOS2	14:53-15:21	VOC	1 (possible emission source: A1313 (HIPA Flare))	10:00-16:00	Out (Scan 309)	NA, too few data points	toluene	11:18-16:45	No, 0% (Scan 309)	NA, too few data points
2/1/2010	SPD17/ LOS1, LOS2†, LOS5†	12:16-14:13, 15:46-17:05	VOC	23-27 (possible emission sources: WAERAT, MAERAT, EAERAT, A-13113, A-1304, T-1372, T-1331, T-1332, T-1333, T-1334, T-1310, T-320, NAPI, and SAPI)	10:00-16:00	Out (Scan 422)	NA, too few data points	Ethane, ethylene, propane, propylene, acetylene, vinyl chloride, 1,3 butadiene, tri chlorofluoro-methane, 1 hexene, toluene, 1,2,4 trimethyl-benzene, 1,2 dichloroethane	11:52-16:47	Yes, 10% (Scan 422)	No linear relationship for overall time series, however there is a similar pattern in DIAL and FTIR over time when the wind direction is greater than 100 degrees for time period 12:16-14:13
2/1/2010	SPD17/ LOS3†, LOS4†	14:20-15:10	VOC	0 (possible emission source: A1301 (A&S Flare)	10:00-16:00	Visual representation of LOS3 and LOS4 not available	NA, too few data points	Ethylene, 1,3 butadiene, methylene chloride, chloroform, toluene,	11:52-16:47	Visual representation of LOS3 and LOS4 not available	Few data points, Linearly related, correlated, r=0.56, regression is not significant p-value =0.32

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

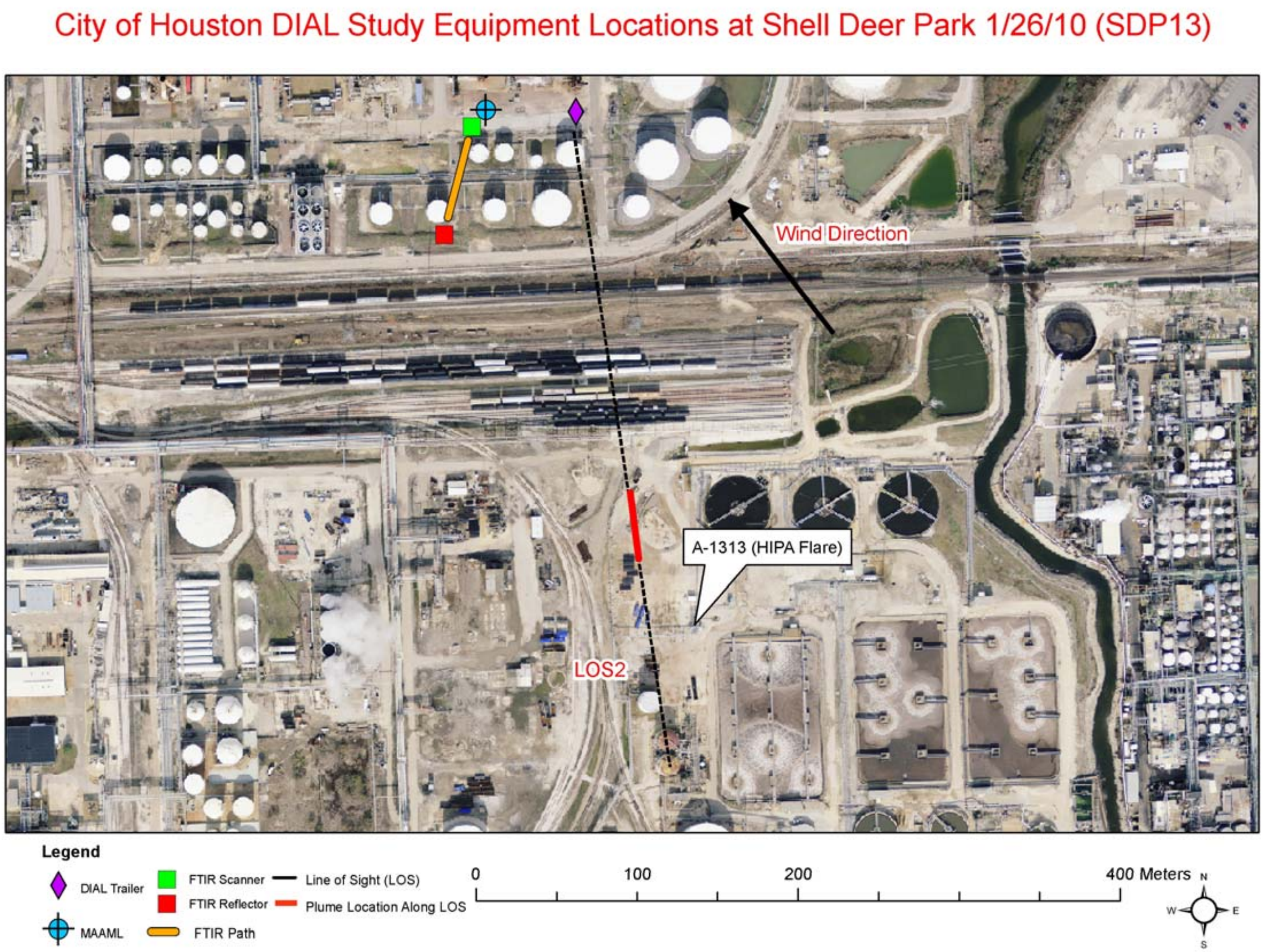

Figure 3.10a East Wastewater and Flares Area 1/26/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/1/10 (SDP17)

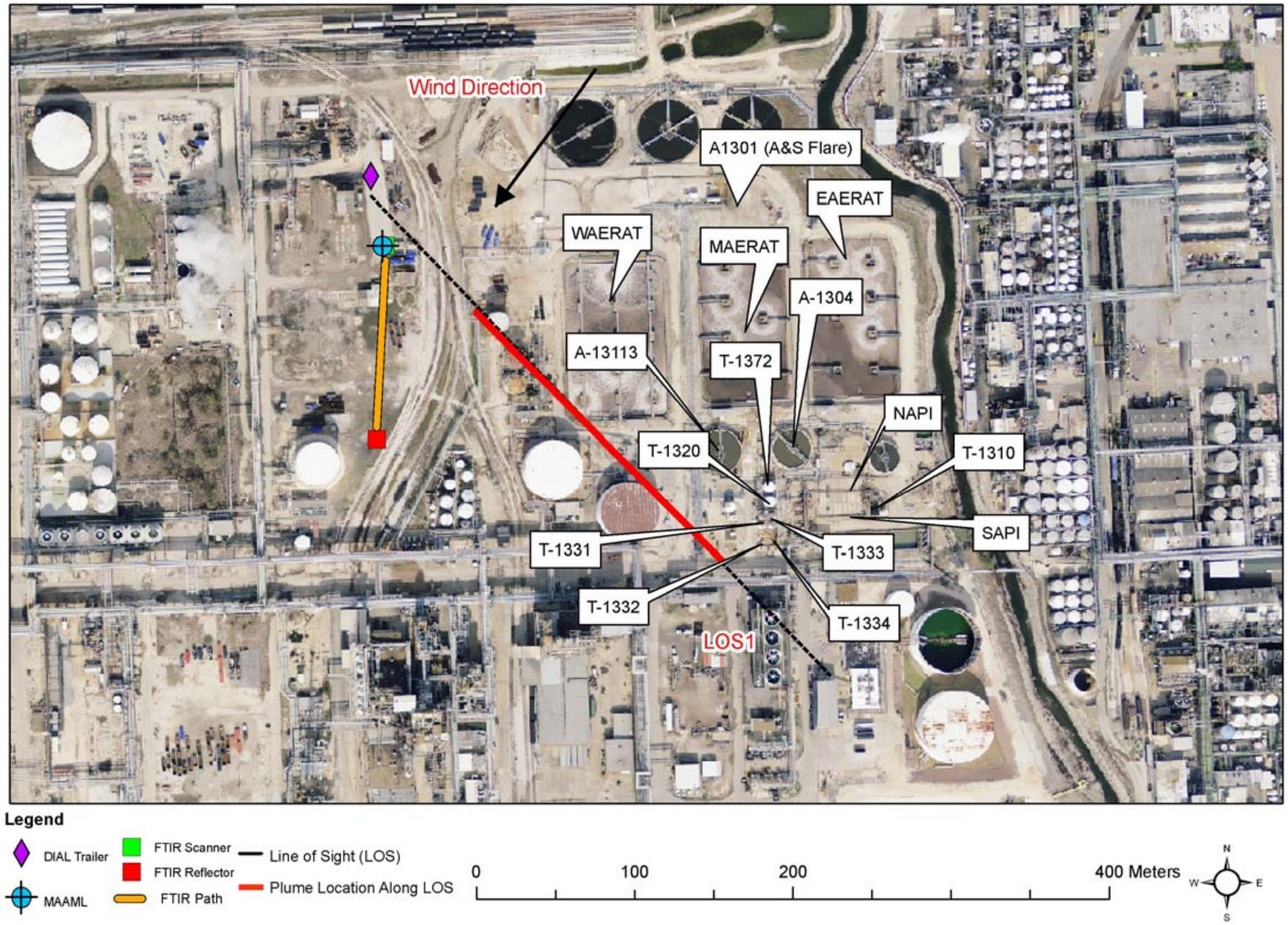

Figure 3.10b East Wastewater and Flares Area 2/1/2010

3.11 Tank Farm B

Table 3.11 Tank Farm B

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/3/2010	SPD19/LOS1	10:30-16:54	VOC	3 (possible emission sources: tanks T3, T4, T216, T89, T181, T185B, T73C, T69C, T3150, T77B, T198, T189, T188, T344, T8B with possible up wind contributions)	9:00-16:00	Out (Scan 487)	Not linearly related	Ethylene, vinyl chloride, 1,3 butadiene, ethyl chloride, methylene chloride, 1,1 dichloroethane, 1 hexene, cis 1,2 dichloroethylene, chloroform, 1,2 dichloroethane, trichloroethylene, 1,1,2 trichloroethane, chlorobenzene	10:22-16:47	Yes, 5% (Scan 487)	Not linearly related, has similar pattern

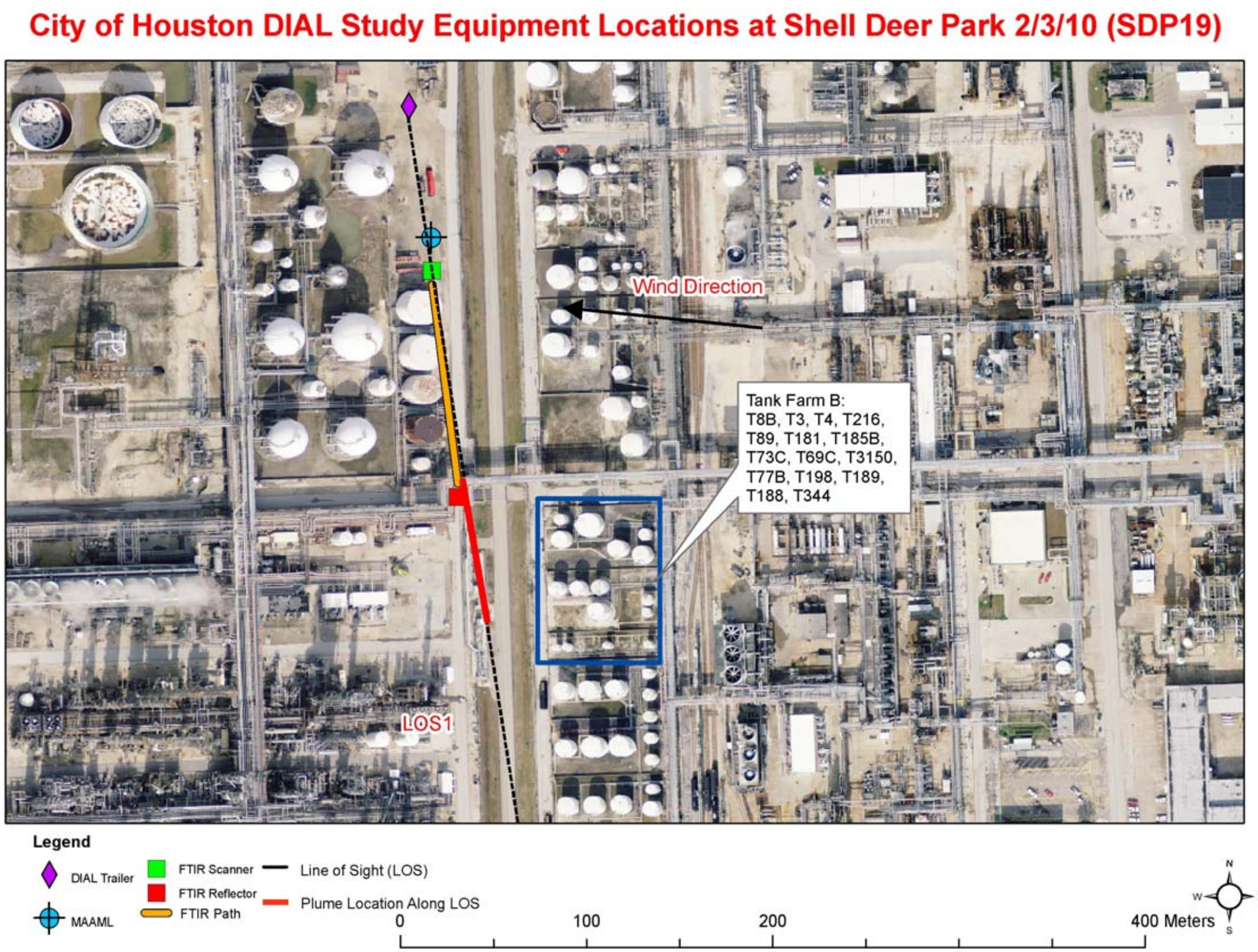

Figure 3.11a Tank Farm B 2/3/2010

3.12 Tanks T-OL913 and T-OL920

Table 3.12 Tanks T-OL913 and T-OL920

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/8/2010	SPD24/LOS1	14:15-17:23	Benzene	6	13:00-16:00	In (Scan 555)	NA, too few data points	1,3 butadiene, n pentane	14:20-16:47	Yes, 80% (Scan 555)	FTIR all nondetect
2/10/2010	SPD26/LOS1	9:55-17:05	Benzene	5	9:00-16:00	Out (Scan 614)	Not linearly related, MAAML detects high benzene in hour 15-16 that isn't well reflected in DIAL	Ethane, ethylene, propylene, acetylene, 1,3 butadiene, trichlorofluormethane, methylene chloride, 1 hexene, hexane, chloroform, 1,2 dichloroethane, benzene, trichlorotheylene	10:45-16:45	Yes, 50% (Scan 614)	FTIR all nondetect except at 12:43 when benzene detected at 64 ppb, nothing in hour 15-16
3/23/2010	SPD33/LOS1	10:18-17:05	Benzene	25	MAAML not deployed	MAAML not deployed	NA	NA	*10:14-16:47	Yes, 100% (Scan 778)	Not linearly related, but similar pattern in time series

* FTIR by Time averaging method (TAM)

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/8/10 (SDP24)

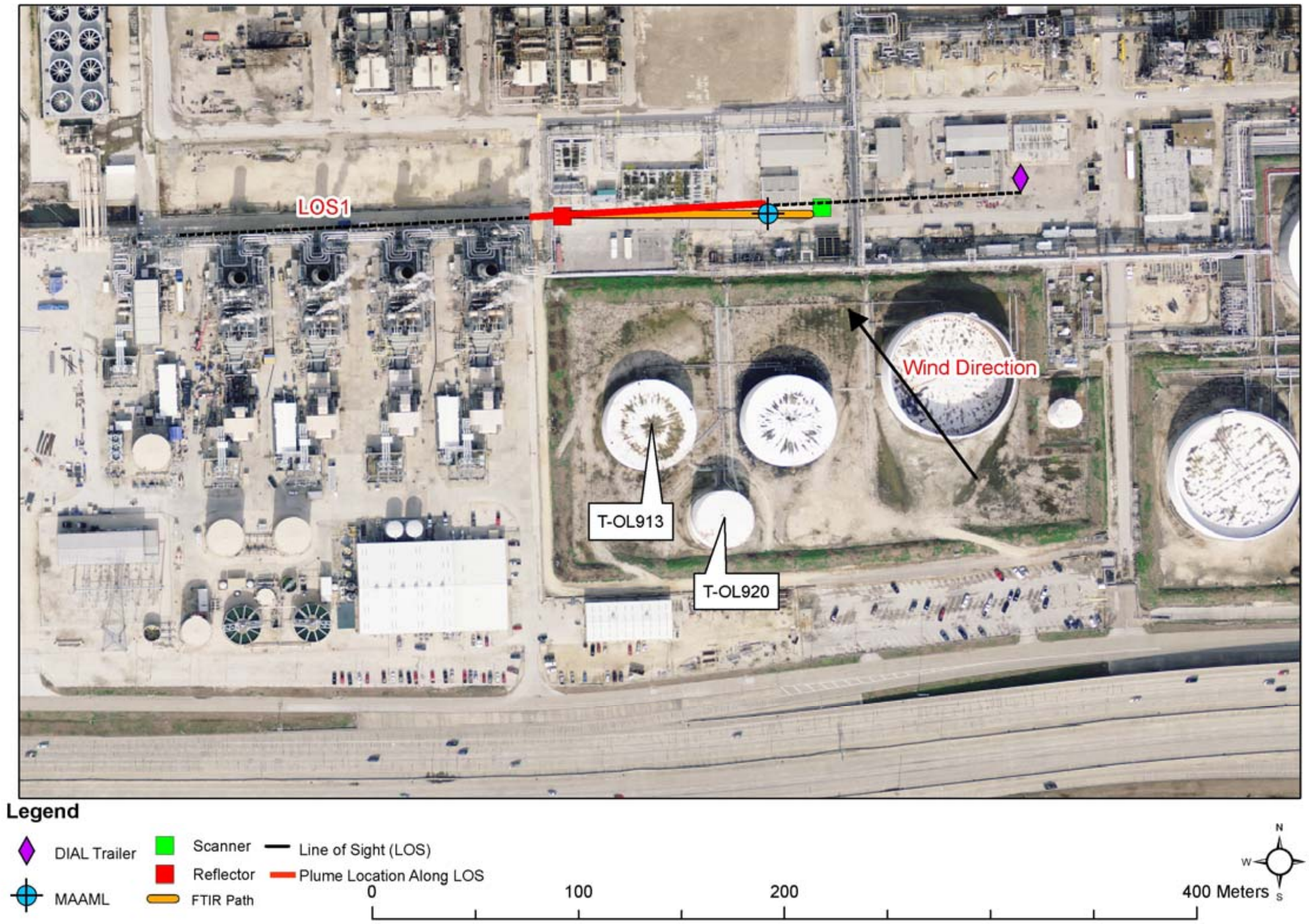

Figure 3.12a Tanks T-OL913 and T-OL920 2/8/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/10/10 (SDP26)

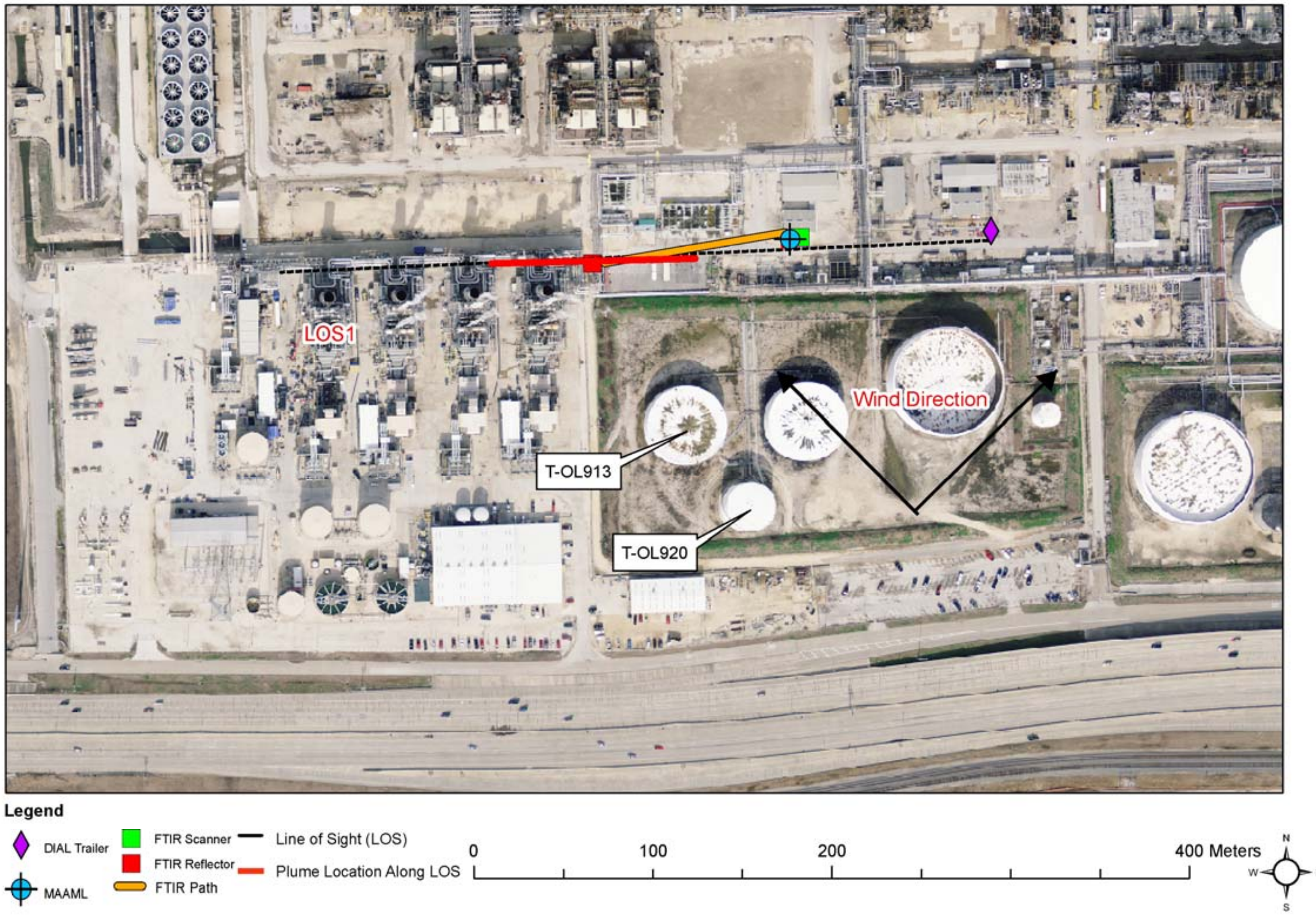

Figure 3.12b Tanks T-OL913 and T-OL920 2/10/2010

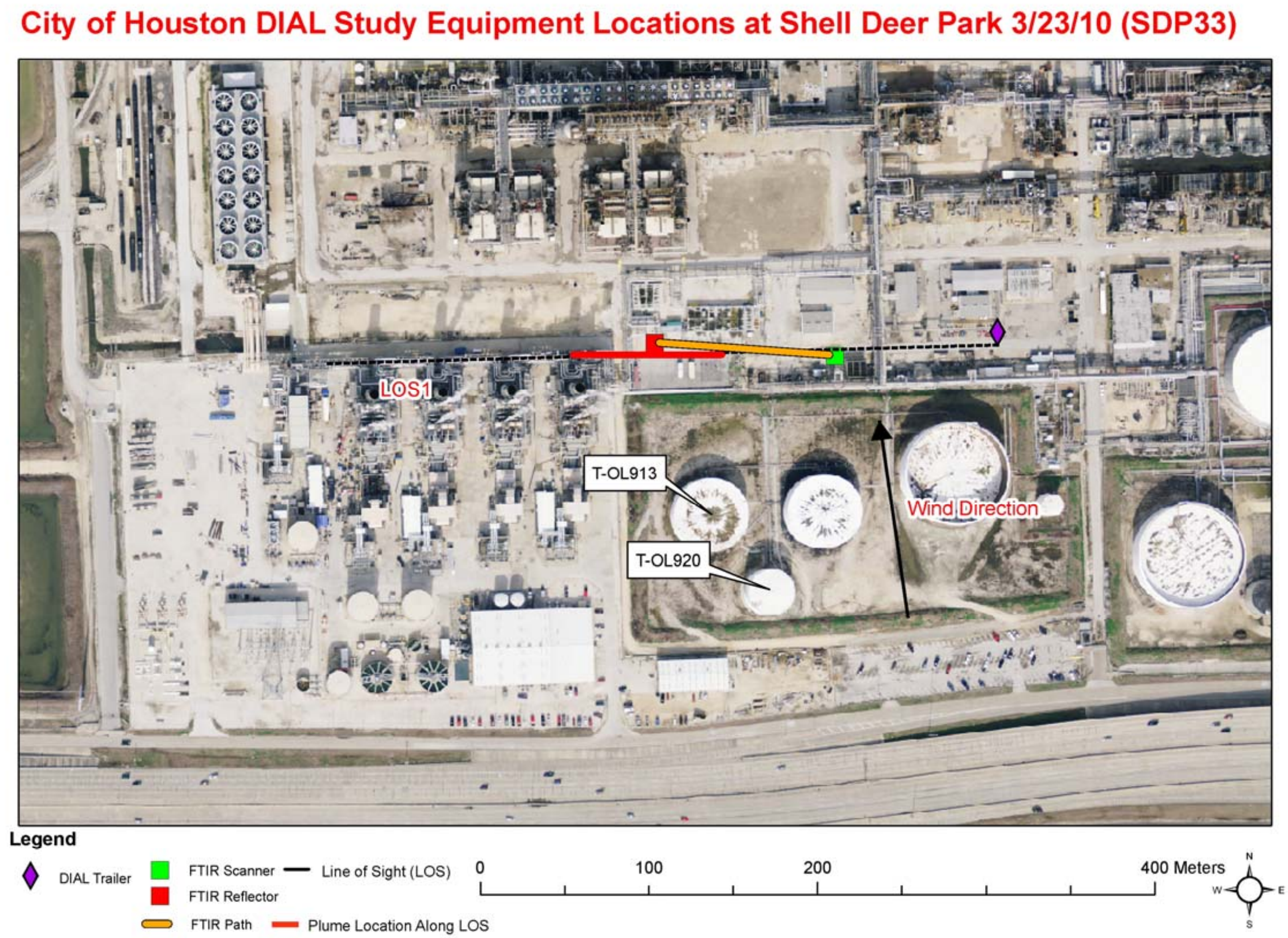

Figure 3.12c Tanks T-OL913 and T-OL920 3/23/2010

3.13 North Property Flare

Table 3.13 North Property Flare (FLN Flare)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/9/2010	SPD25/LOS2	12:04-12:50	Benzene	2	9:00-16:00	Out (Scan 574)	NA, too few data points	none	*10:46-16:46	No, 0% (Scan 574)	NA, too few data points

* FTIR by Time averaging method (TAM)

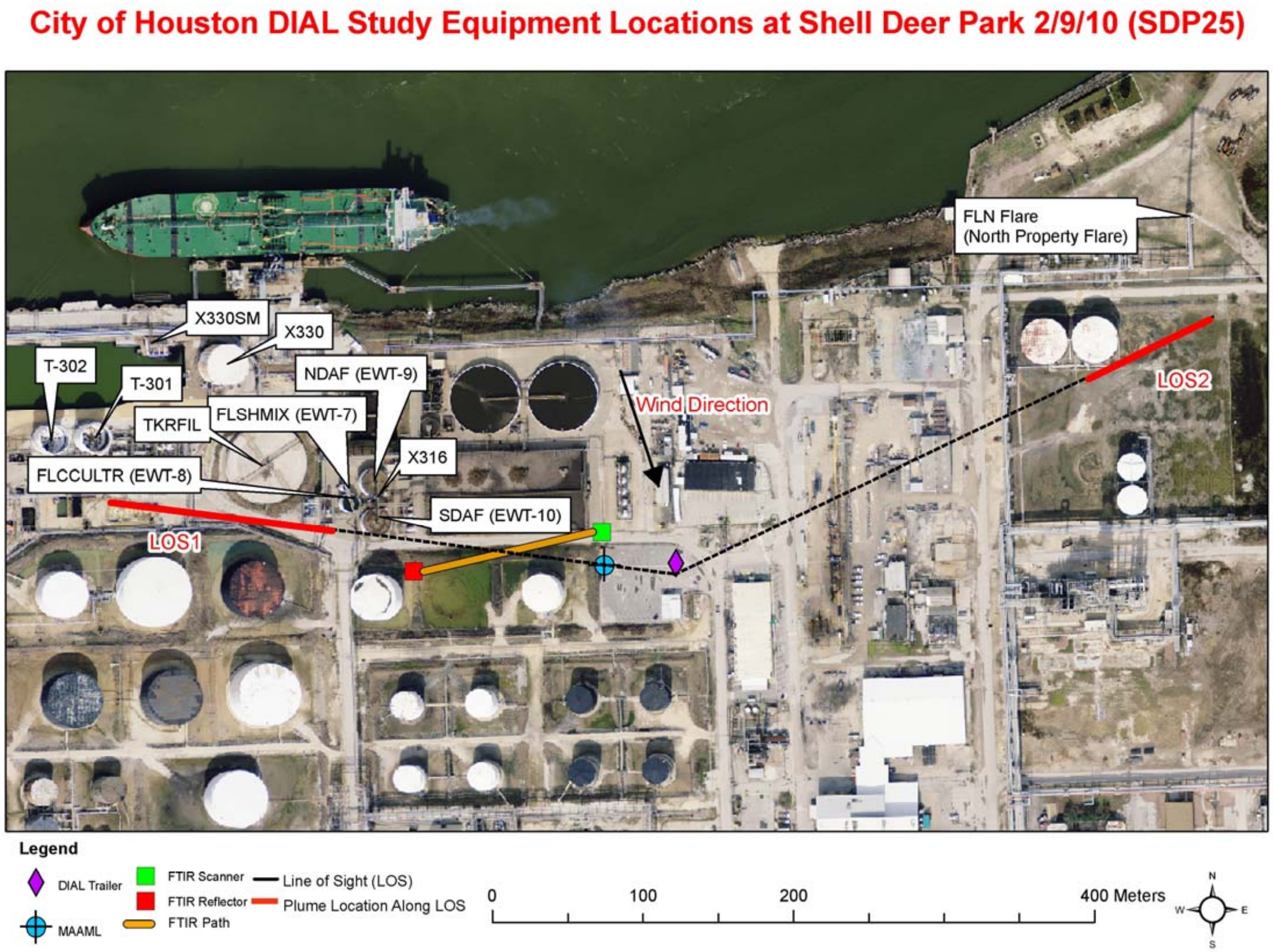

Figure 3.13a North Property Flare 2/9/2010

3.14 ACU and BEU

Table 3.14 ACU and BEU

<table>
<tr><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th>7</th><th>8</th><th>9</th><th>10</th><th>11</th><th>12</th></tr>
<tr><th>Date</th><th>DIAL Location / LOS</th><th>DIAL hours</th><th>DIAL</th><th>Average DIAL emission rate (lbs/hour)</th><th>MAAML hours</th><th>Location of MAAML</th><th>MAAML correlation with DIAL plume</th><th>MAAML outliers</th><th>FTIR hours</th><th>FTIR aligned with DIAL plume</th><th>FTIR correlation with DIAL plume</th></tr>
<tr><td>2/12/2010</td><td>SDP28/LOS1</td><td>10:40-16:40</td><td>Benzene</td><td>27</td><td>10:00-16:00</td><td>Out (Scan 647)</td><td>r =-0.57, p-value =0.18</td><td>Ethane, propane, dichlorodifluoromethane, 1-hexene, benzene, toluene, tetrachloroethylene, cumene</td><td>11:13-15:57</td><td>Yes, 80% (Scan 647)</td><td>Benzene nondetect</td></tr>
<tr><td>2/15/2010</td><td>SPD28/LOS1</td><td>10:18-11:15,
12:21-13:13,
14:18-15:09</td><td>Benzene</td><td>13</td><td>9:00-16:00</td><td>Out (Scan 693)</td><td>r =0.86 with outlier value p-value = 0.06, and r=0.07 without p-value = 0.93</td><td>Benzene, tetrachlorethane</td><td>*10:38-16:45</td><td>Yes, 100% (Scan 693)</td><td>r=0.92 with outlier, p-value=0.0014, r = 0.014 without outlier p-value = 0.98</td></tr>
<tr><td>3/26/2010</td><td>SPD35/LOS1</td><td>10:53-13:33</td><td>VOC</td><td>64-65</td><td>10:00-13:00</td><td>Out (Scan 824)</td><td rowspan="2">r =0.44 after excluding one hour when wind changed direction, not significant p-value = 0.38</td><td>1,3 butadiene, 1-hexene, benzene</td><td>*10:28-12:58</td><td>Yes, 40% (Scan 824)</td><td rowspan="2">No alkanes detected</td></tr>
<tr><td>3/26/2010</td><td>SPD36/LOS1</td><td>14:38-17:05</td><td>VOC</td><td>64-65</td><td>14:00-16:00</td><td>Out (Scan 836)</td><td>Ethylene, propylene, vinyl chloride, methylene chloride, benzene, toluene, 2-methyl pentane, o xylene, m/p xylene, ethylbenzene</td><td>*13:02-16:47</td><td>Yes, 100% (Scan 836)</td></tr>
</table>

* FTIR by Time averaging method (TAM)

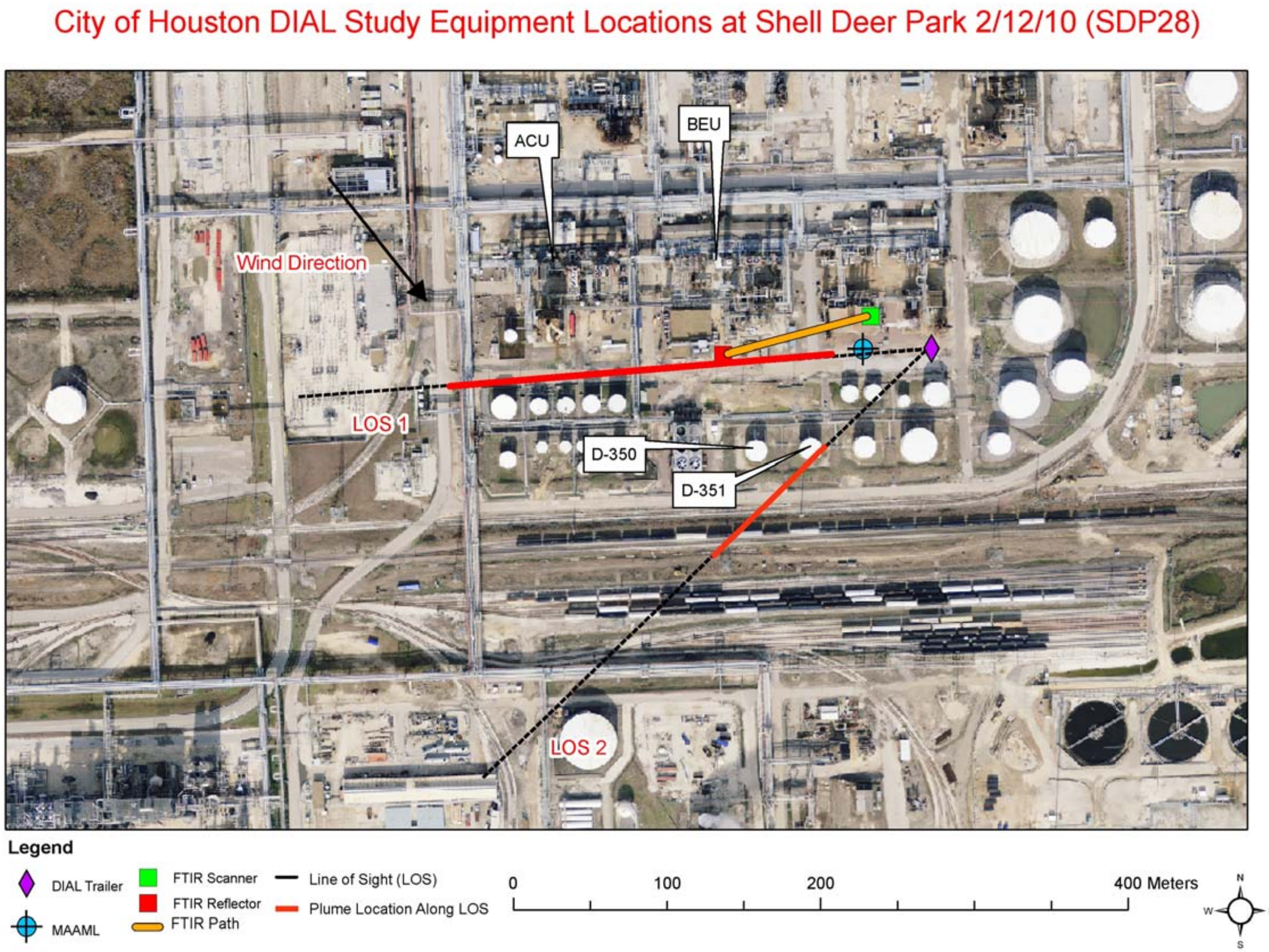

Figure 3.14a ACU and BEU 2/12/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/15/10 (SDP28)

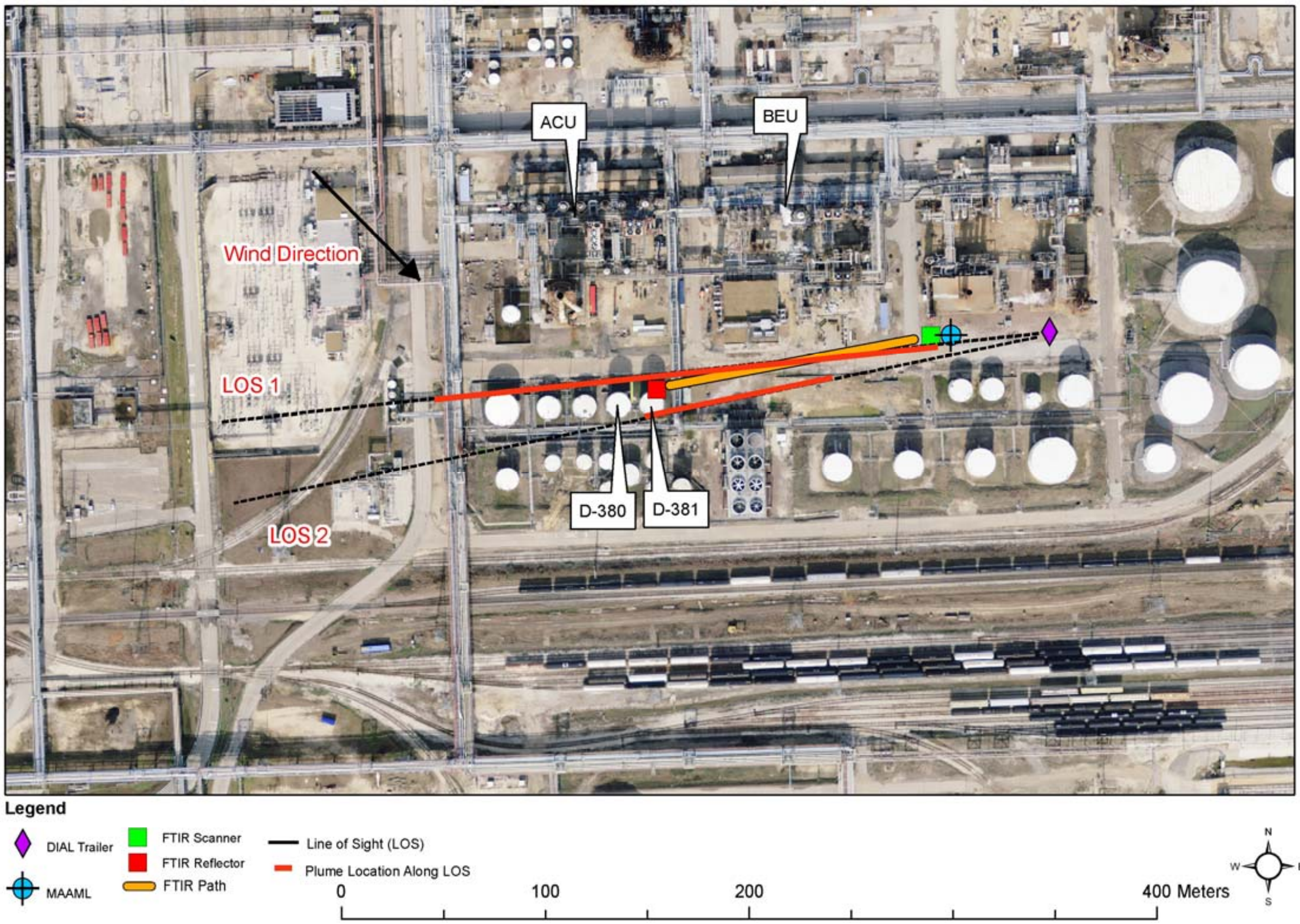

Figure 3.14b ACU and BEU 2/15/2010

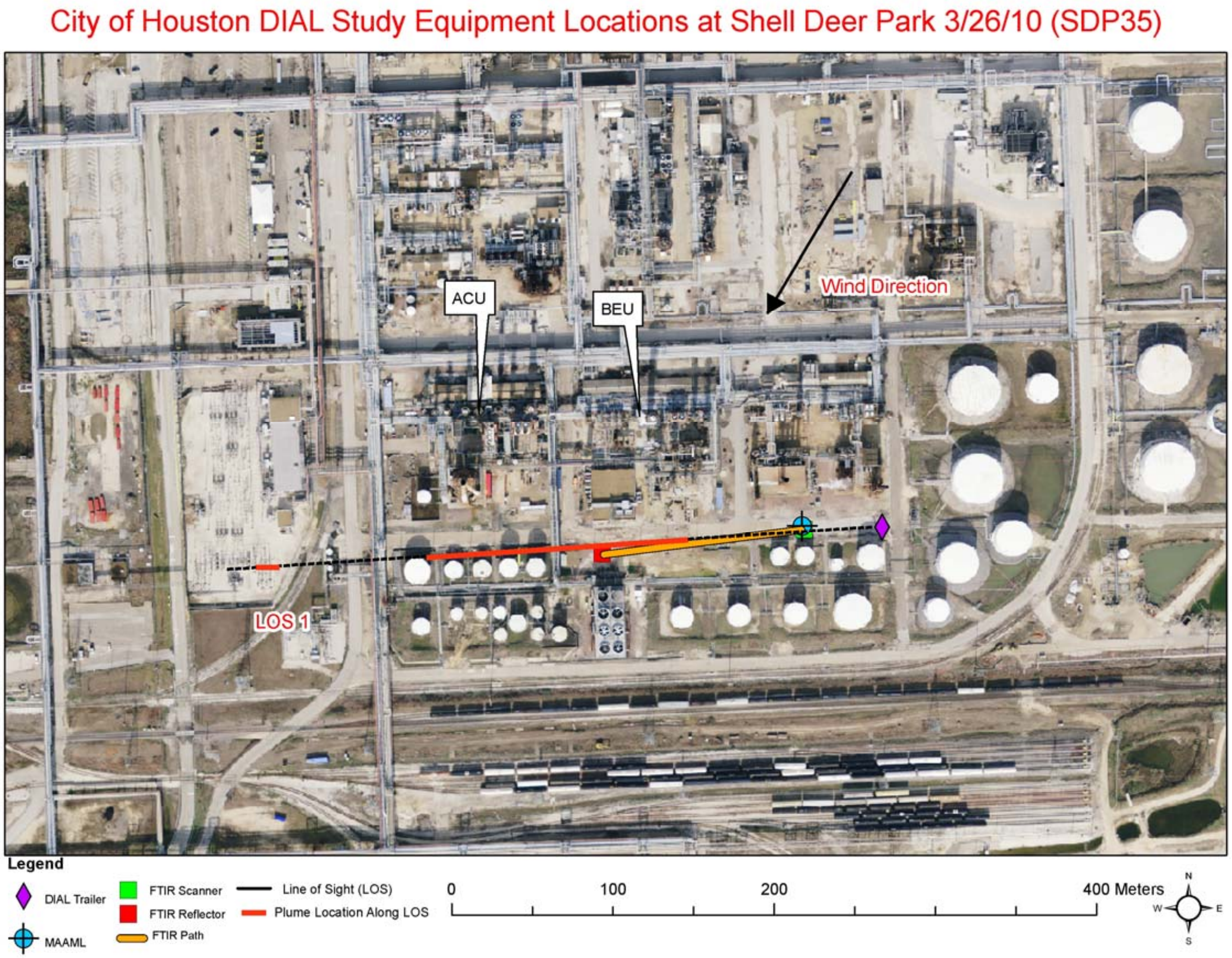

Figure 3.14c ACU and BEU 3/26/2010

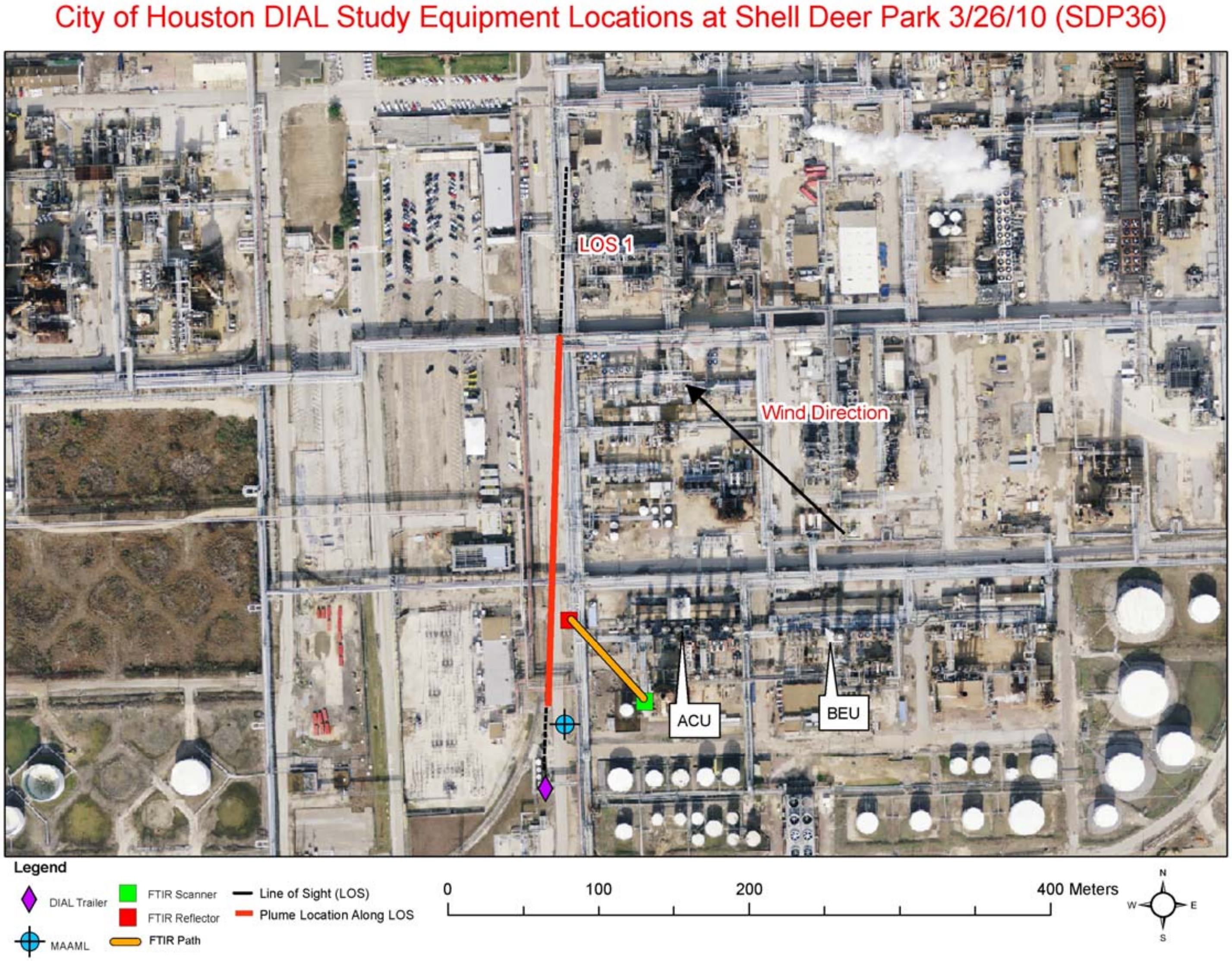

Figure 3.14d ACU and BEU 3/26/2010

3.15 Tanks South of ACU and BEU

Table 3.15 Tanks South of ACU and BEU

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/12/2010	SDP28/LOS2	16:49-17:26	Benzene	25 (possible emission source: D-350 and D-351)	10:00-16:00	Out (Scan 658)	NA, too few data points	Benzene, dichlorodifluoromethane	11:13-15:57	Yes, 10% (Scan 658)	NA, too few data points
2/15/2010	SPD28/LOS2	11:23-12:17, 13:35-14:12, 15:17-17:13	Benzene	29-141 (possible emission source: D-381)	9:00-16:00	Out (Scan 697)	Tank event at hour 12 reported by both MAAML and DIAL is a statistically influential outlier, r = 0.72, p-value = 0.16	Benzene, tetrachloroethylene	*10:38-16:45	Yes, 60% (Scan 697)	Tank event at scan 697 reported by both FTIR and DIAL is a statistically influential outlier, r=0.87 and regression significant p-value <0.0001, after outlier removed, r=-0.41, regression not significant p-value=0.24
3/22/2010	SDP32/LOS1	12:29-13:33, 14:53-15:50	Benzene	5 (possible emission source: D-352)	MAAML not deployed	MAAML not deployed	NA, too few data points	NA	13:52-16:47	No, 0% (Scan 768)	FTIR nondetect

* FTIR by Time averaging method (TAM)

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/12/10 (SDP28)

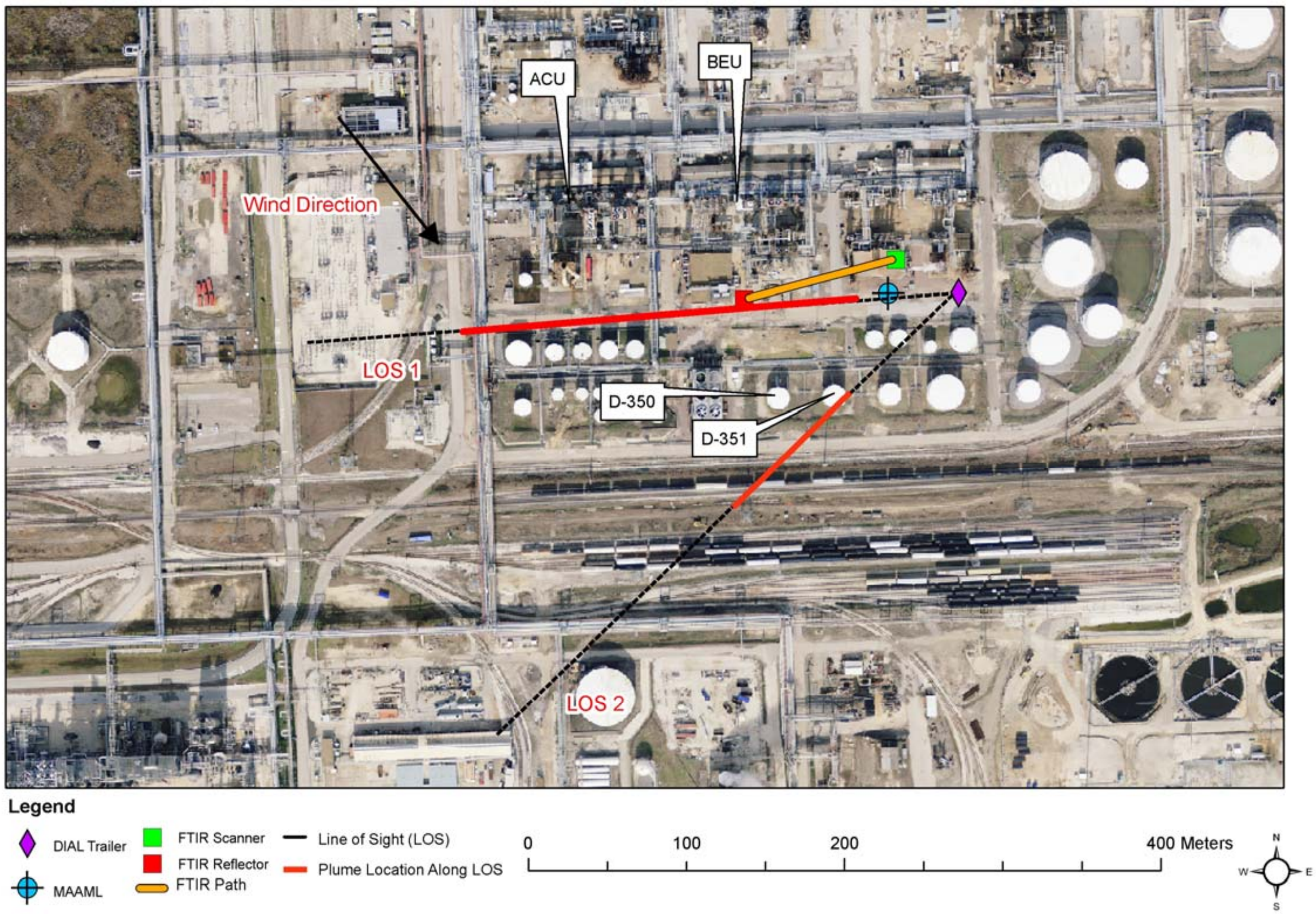

Figure 3.15a Tanks South of ACU and BEU 2/12/2010

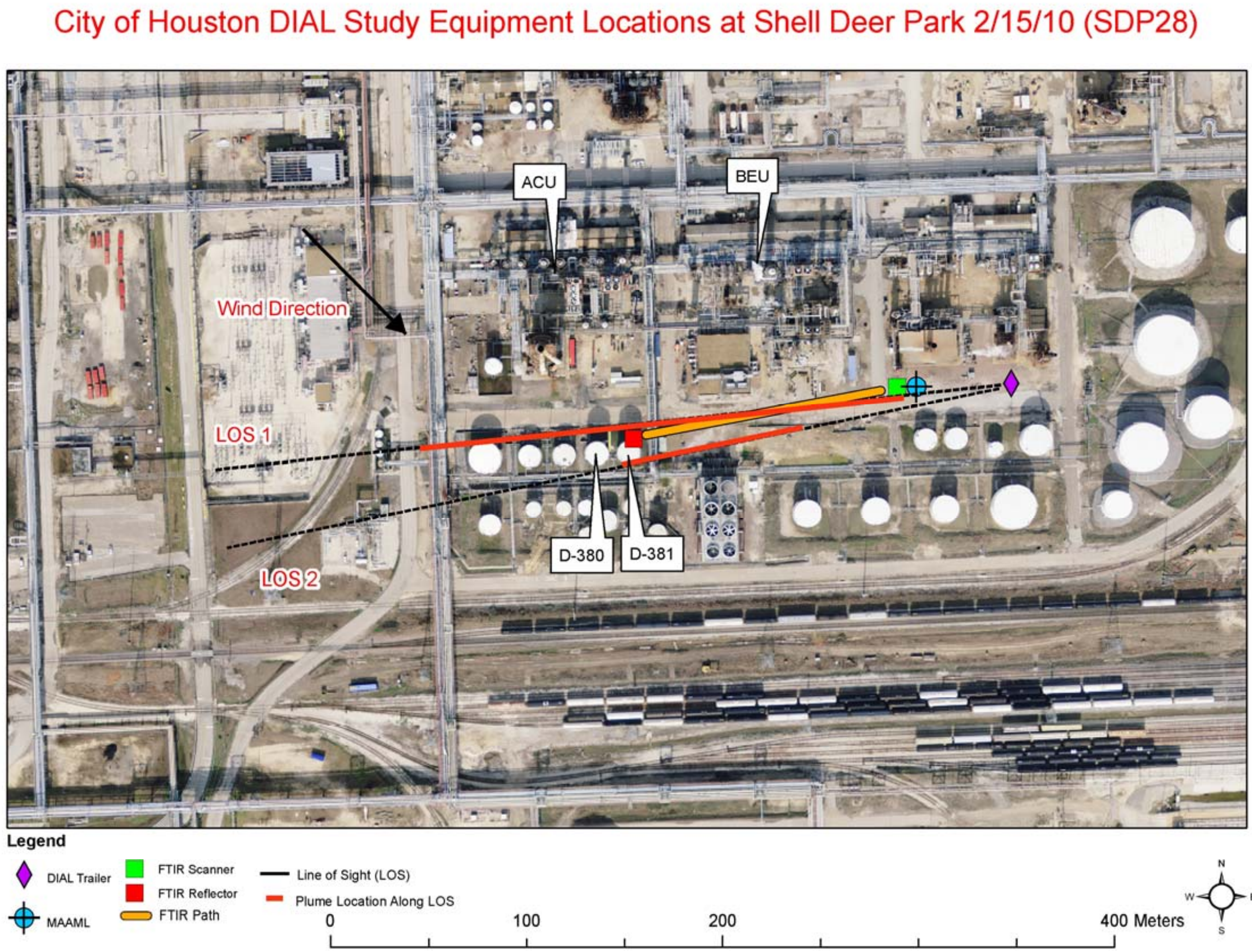

Figure 3.15b Tanks South of ACU and BEU 2/15/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 3/22/10 (SDP32)

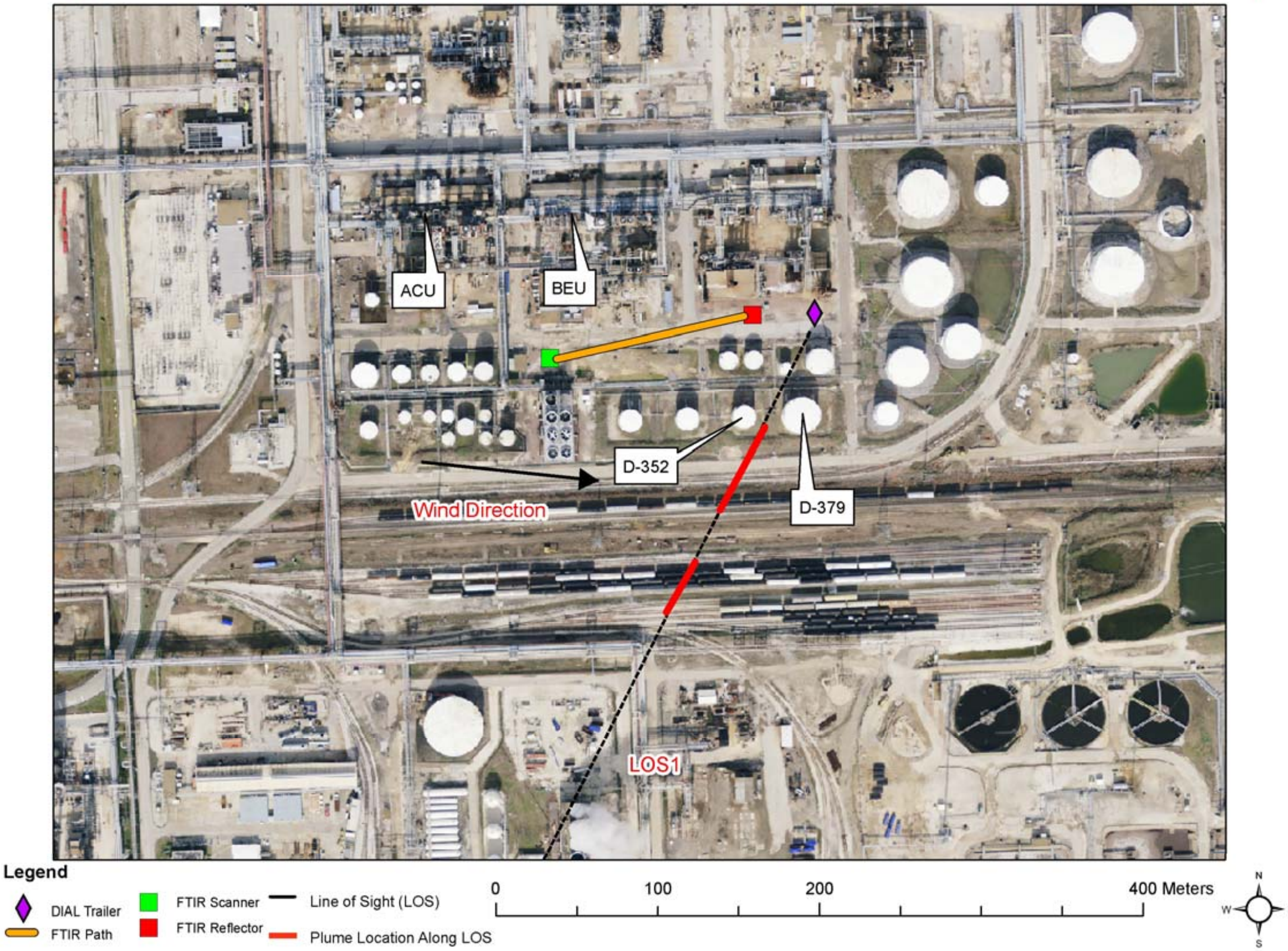

Figure 3.15c Tanks South of ACU and BEU 3/22/2010

3.16 Tanks South of North Wastewater

Table 3.16 Tanks South of North Wastewater (K-302, K-310, K-311, and F-367)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/13/2010	SPD29/ LOS2	11:14-11:27, 11:44-12:19	Benzene	6	10:00-16:00	Out (Scan 669)	NA, too few data points, benzene ND at hour 15 when FTIR picked up spike	none	11:22-16:43	No, 0% (Scan 669)	All nondetect except 116 ppb benzene at 15:55

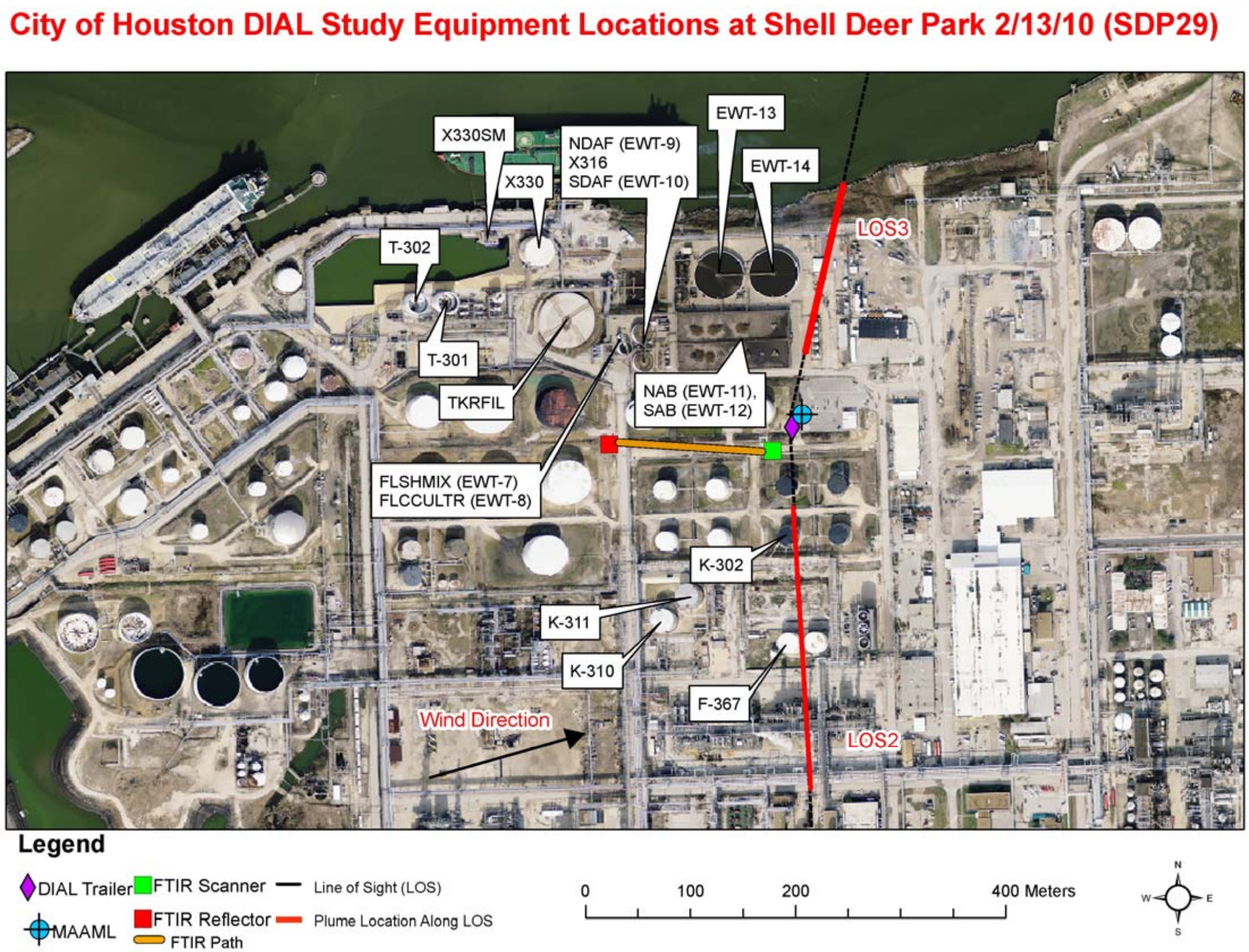

Figure 3.16a Tanks South of North Wastewater 2/13/2010

3.17 Refinery West Tanks

Table 3.17 Refinery West Tanks (A-301, A-309, A-308, F-361, and F-357)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/16/2010	SPD30/ LOS1, LOS2†	10:06-12:47, 16:33-16:43	Benzene	5-6	9:00-16:00	Out (Scan 714)	NA, too few data points	Hexane, tetrachloroethylene	10:33-16:46	Yes, 100% (Scan 714)	Too many nondetects in FTIR data

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/16/10 (SDP30)

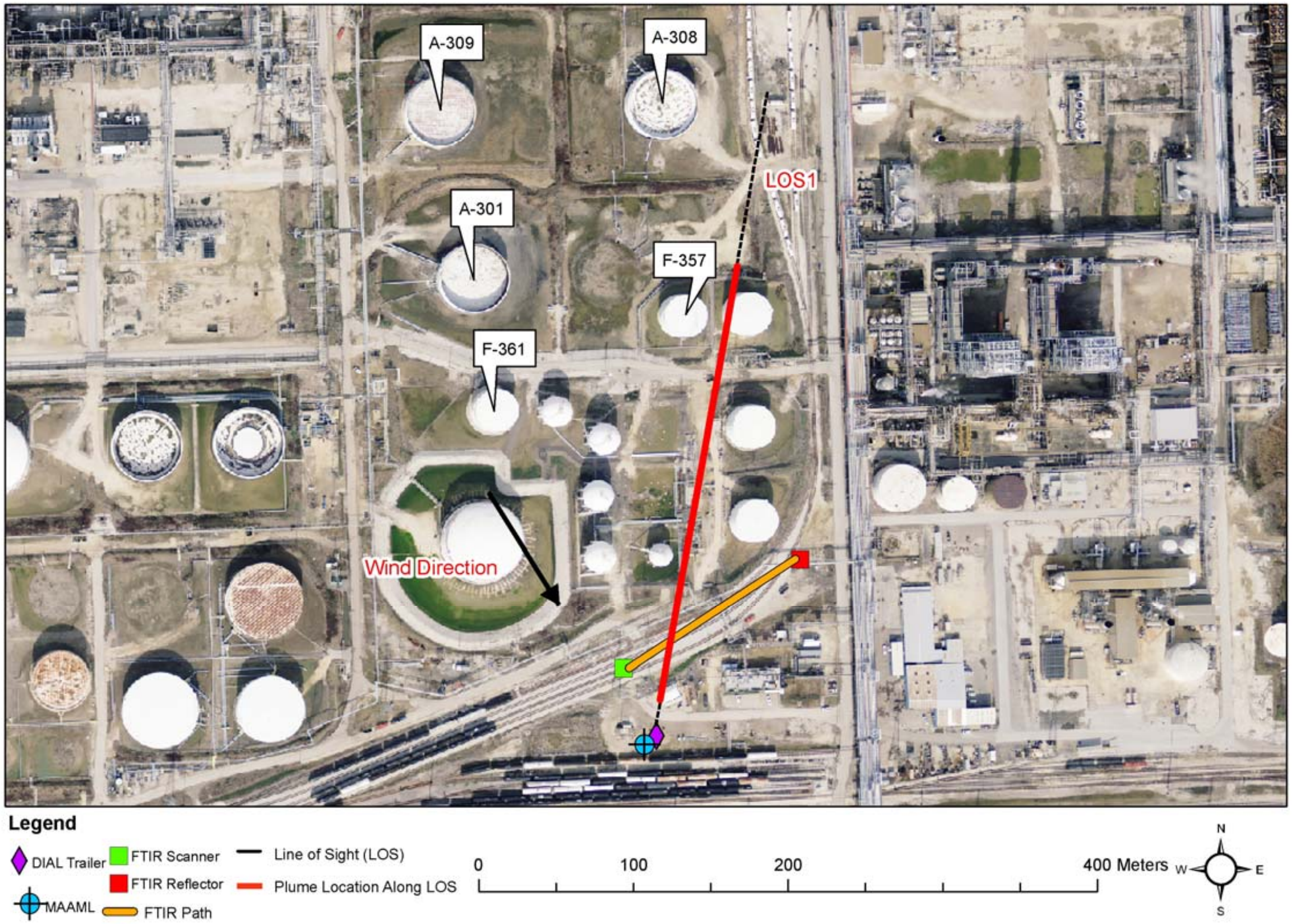

Figure 3.17a Refinery West Tanks 2/16/2010

4. Discussion

This section reports an interpretation of the results with respect to the project objectives.

4.1 Discussion Regarding Report Objective: Evaluate and verify the DIAL system benzene and VOC measurements using the City of Houston's Mobile Ambient Air Monitoring Laboratory (MAAML), canister sampling, and other monitoring/open path measurement techniques.

The analysis discussed in this report that is used to verify DIAL measurements focus on the two techniques used most often simultaneously with DIAL: MAAML and the FTIR (open path). Data from two other measurement techniques used less consistently, UV DOAS and SUMMA canisters, are presented in the appendices D and F respectively.

In order to evaluate and verify the DIAL system emissions measurements with these two techniques, we chose to systematically compare all of the emissions data collected against the concentrations, where there were enough data available to make the comparison while noting the location of the instruments in relation to the DIAL LOS for the scan images provided. As noted previously, although we recognized that relationships would more likely exist when the MAAML was "in" the plume versus "out" and FTIR had good overlap with the DIAL LOS, we chose to systematically examine all comparisons so as not to overlook any information that could be gleaned from this extensive body of data.

Throughout our analysis it became apparent that for various reasons (e.g., location constraints, comparing emissions to concentration under fluctuating wind speed, varying detection limits, sample time durations, and measurement techniques) a simple correlation coefficient did not fully reflect the degree of agreement between the measurements and in some cases correlation coefficients weren't appropriate. Therefore, we further examined the data to more completely answer the question, "How well do the techniques compare?" and "In the future, how can we better design the study so that these techniques can be used to estimate emissions?" The paragraphs below present the correlations found for each technique when the location was in the plume or aligned with the DIAL LOS and the statistically significant correlations when the location was "out" or not aligned. In addition, we highlight some examples of other verification of DIAL via similar pattern (in the face of wind speed changes) and simultaneous identification of spikes. In summary, verification of the DIAL measurements with the MAAML and FTIR measurements was evaluated using: statistical correlation (4.1.1), similar patterns in a time series (4.1.2) and identification of spikes (4.1.3).

4.1.1 Statistical Correlation

While a linear relationship between the DIAL emissions rate and ambient concentration is important to analyze in order to complete this report objective, evaluate and verify DIAL measurements, due to study constraints there were limited times when the MAAML or FTIR were measuring inside the plume or aligned with the DIAL LOS, respectively, and the wind speed was constant with low variability. We present the data from situations where MAAML was in the plume/FTIR aligned and the statistically significant correlations when MAAML was out of the plume/FTIR not aligned.

4.1.1.1 DIAL Emissions Correlation with MAAML

There were two locations and dates where MAAML was measuring concentration "in" the plume based on the scan image and there were enough data to calculate a correlation:

1. Southwest Tanks 1/13/2010, r=0.62, regression not significant, p-value=0.26.

2. North Wastewater 2/5/2010, not linear.

There were two locations and dates where MAAML was "out" of the plume based on the scan image, there were enough data to calculate a correlation, and the correlation was statistically significant (α=0.10):

1. Coker, GOHT, and West Dock Area 1/16/2010, r=-0.95, regression significant, p-value=0.01. The emission rates in this area were low and the wind speed variable.

2. ACU and BEU 2/15/2010, r=0.86, regression significant, p-value=0.06. The MAAML concentration and DIAL emission at hour twelve is an outlier.

In general, these limited cases where MAAML is in the plume indicate that the fixed site point monitor as used here is not a useful technique to validate DIAL emissions. We believe that a better correlation may result if we were to compare DIAL concentration to MAAML concentration, and the heights, measuring times and molecular weights were the same.

The statistically significant strong inverse correlation when the MAAML was outside the plume in example 1 suggests that the plume moved in and out of the DIAL measurement range and when DIAL missed the plume, MAAML picked it up. This scenario could result in DIAL emissions estimates that are biased low.

Statistically significant strong correlations when MAAML was outside of the plume suggest that turbulence caused by structures resulted in plume dispersion beyond the DIAL measurement range and the dispersed plume was detected by MAAML with its lower detection levels. Alternatively, the provided scan image was not representative of the days DIAL measurements for that LOS. In either case the plume may have therefore extended beyond the DIAL measurement capability.

MAAML concentration data may be representative of the relative plume composition and used for potential speciation purposes when: 1. Statistically significant strong inverse correlations were detected between MAAML and DIAL for the DIAL measured species, during time periods that elevated concentrations of the DIAL measured species were measured by MAAML, and 2. statistically significant strong correlations were detected between MAAML and DIAL for the DIAL measured species, for other compounds measured by MAAML that also have statistically significant strong correlations with the DIAL measured species.

4.1.1.2 DIAL Emissions Correlation with FTIR

There were eleven locations and dates where FTIR was measuring concentrations on a line overlapping to some extent with the DIAL LOS based on the plume scan image and there were enough data to calculate a correlation:

1. Coker, GOHT and West Dock Area 2/4/2010, 100% overlap, not linearly related.
2. Coker, GOHT and West Dock Area 3/27/2010, 10% overlap, not linearly related.
3. CR-3 Area 3/25/2010, 90% overlap, not linearly related.
4. North Wastewater 1/25/2010, 5% overlap, r=0.95 and p-value<0.001.
5. North Wastewater 1/30/2010, overlap moves from 40% to 0% to 10%, r=0.56, p-value=0.04.
6. North Wastewater 2/5/2010, overlap moves from 100% to 30%, r=0.66, p-value=0.15.
7. East Wastewater and Flares Area 2/1/2010, overlap 10%, not linearly related.
8. Tank Farm B 2/3/2010, 5% overlap, not linearly related.
9. Tanks T-OL913 and T-OL920 3/23/2010, overlap 100%, not linearly related.
10. ACU and BEU 2/15/2010, 100% overlap, r=0.92, p-value=0.0014, influential outlier, correlation without outlier r=0.014, p-value=0.98.
11. Tanks South of ACU and BEU 2/15/2010, 60% overlap, r=0.87, p-value=0.0001, influential outlier, correlation without outlier r=-0.41, p-value=0.24.

There was one location and date where FTIR was measuring concentrations on a line not overlapping with the DIAL LOS based on the plume scan image and there were enough data to calculate a correlation that was significant. This occurred at the East Tanks Area on January 28. There was a linear relationship that was inverse, r=-.55 with a p-value of 0.02. DIAL was positively correlated with wind direction and FTIR was negatively correlated with wind direction. This suggests that the plume moved in and out of the DIAL measurement range and when the plume moved completely or partially outside of the DIAL range, it moved into the FTIR path. This scenario could result in DIAL emissions estimates that are biased low. The FTIR technique has advantages over MAAML in many ways. It is a similar method of measurement (linear) and the sample duration is shorter and better matches the sample duration of DIAL scans. Beyond better overlap of FTIR and DIAL LOS, the key problem with the use of FTIR for comparison with DIAL in this study was the detection limit. There were many instances when there was good overlap but the FTIR could not detect at low enough concentrations to compare with the DIAL emissions.

The best example of a strong linear relationship between DIAL emission rate and ambient concentration was found at the North Wastewater Area on January 25 (figures 4.1a and 4.1b). The relationship was between DIAL VOC emission rate in lbs/hr and FTIR total alkane (ppb). The time series and the regression lines are presented below. The correlation coefficient r=0.96, the coefficient of determination r^2=0.91 and the regression was significant at p-value <0.001. This indicates that 91% of the variability in emission rates of VOC can be explained from the FTIR total alkane data. This exemplifies the strength of FTIR in verification of DIAL. Because there was strong correlation despite limited overlap, we hypothesize that the DIAL emissions were homogeneous enough that sampling 10% of the plume was adequate to characterize it.

A possible explanation for the strong DIAL emission rate and ambient concentration relationship at this location is that the source of emissions from the North Wastewater Area, was closer to the surface than the other sources measured during this project. Downwind of the North Wastewater Treatment aeration basins and along the FTIR measurement path, on-site personnel noted the presence of some wind turbulence that may have been induced by the basin structure. Emissions from the waste water treatment area may have been well-mixed at the elevation of the FTIR path. In the future, one could consider using an FTIR, and a backwards-Lagrangian Stochastic (bLS) measurement approach to compare FTIR and DIAL measurements on a pounds per hour basis. bLS has been extensively described in the literature, and has been shown to provide reasonable emission rate measurements for near-surface sources. bLS requires the use of 3 dimensional ultrasonic wind measurements, which was not in the scope of the project.

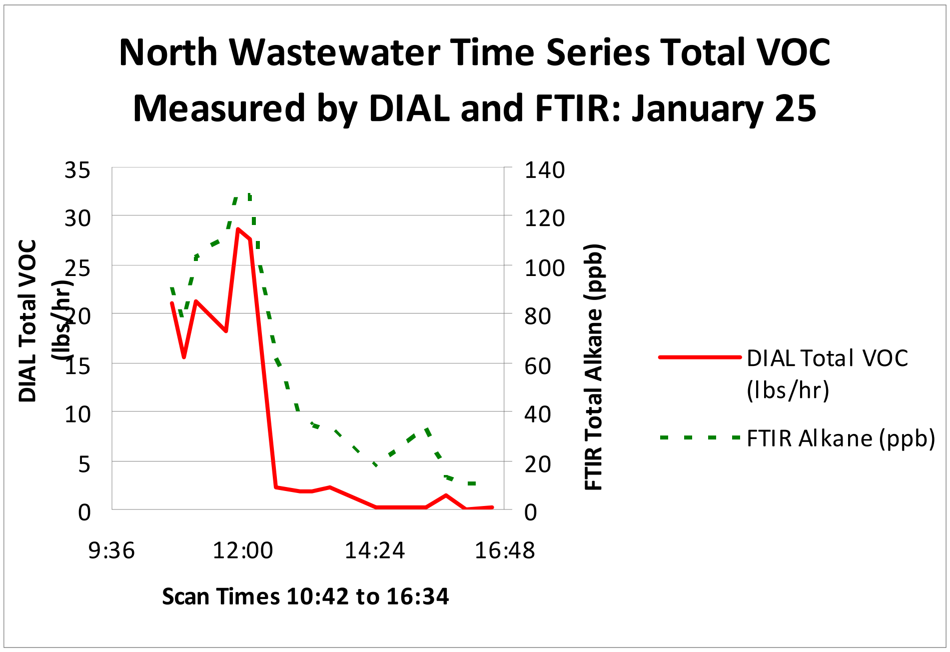

Figure 4.1a North Wastewater Time Series Total VOC Measured by DIAL and FTIR: January 25

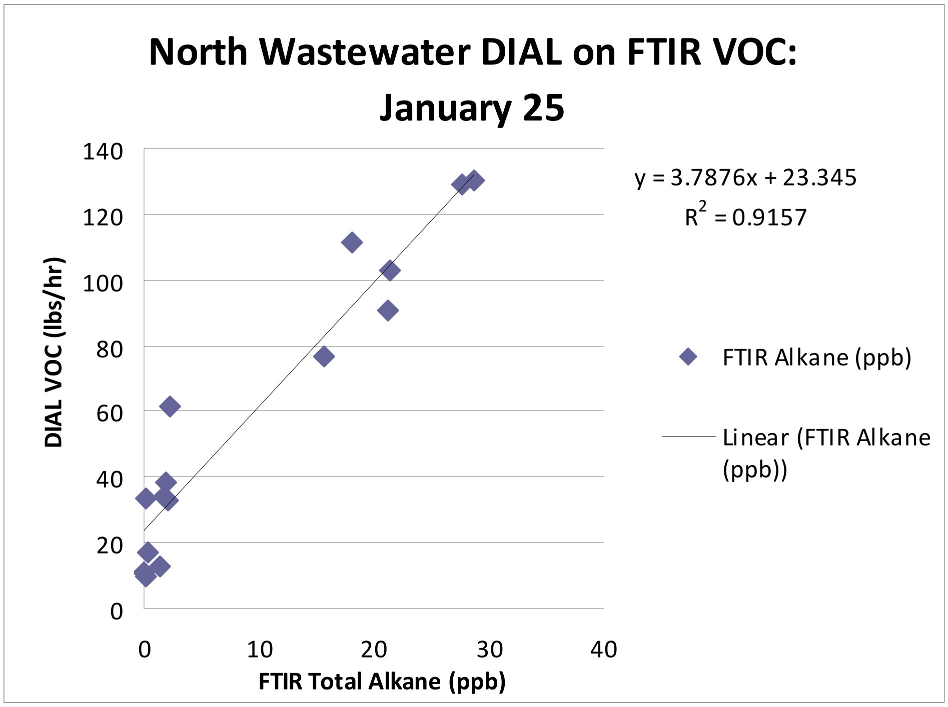

Figure 4.1b North Wastewater DIAL on FTIR VOC: January 25

4.1.1.3 Influential Outliers in Correlations

There are instances noted in the results where there is an influential outlier that pulls the line toward itself. From a statistical perspective the relationship it creates is not sound because the one point provides too much influence. The influential outlier is identified when the slope of the line moves by 10% or more when the relationship is reassessed without the point. When that point is removed, the linear relationship is insignificant and there appears to be no relationship between the DIAL emission rate and the concentration. This is exemplified with the figures 4.1c and 4.1d depicting benzene on February 15 at the ACU/BEU using the MAAML and at the Tanks south of the ACU/BEU using the FTIR.

While the statistical relationship from the overall data needs fortifying, we are optimistic from a practical technical standpoint that at higher emission rates we could develop a statistical model relating emission rate and concentration. The noise at lower emission rates needs to be addressed. If there had been more frequent data points around the peak or at the peak, the relationship would carry more weight. These examples indicate the DIAL emissions and the MAAML and FTIR measurements move in the same direction. In a basic sense, both the MAAML and the FTIR verified the spike that DIAL found on these days.

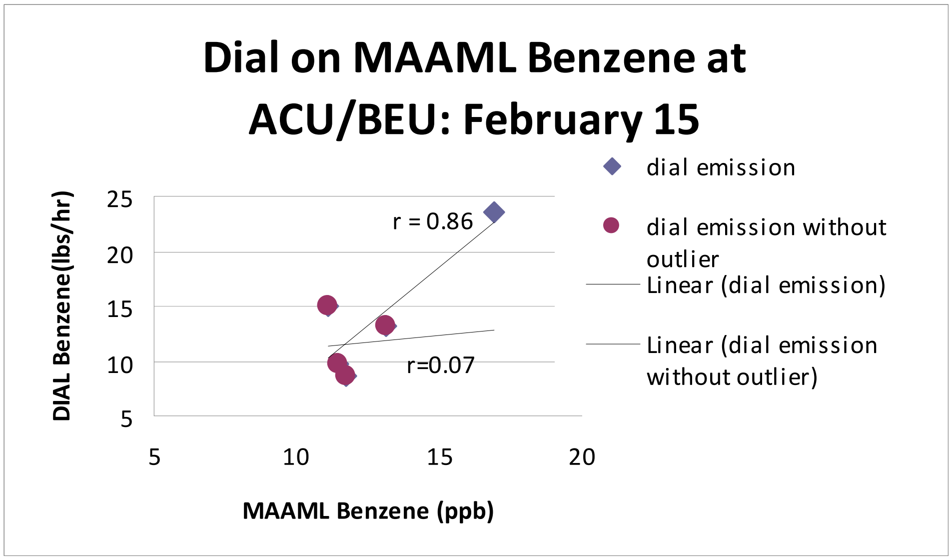

Figure 4.1c DIAL on MAAML Benzene at ACU/BEU: February 15

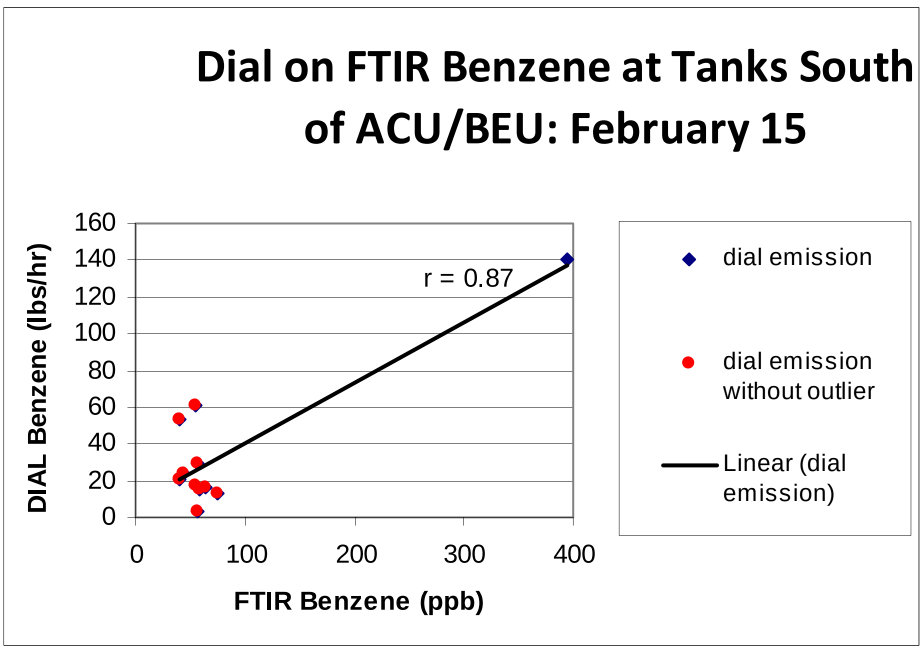

Figure 4.1d DIAL on FTIR Benzene at Tanks South of ACU/BEU: February 15

4.1.2 Similar Pattern

As discussed previously, there are many factors in play that can interfere with correlation (e.g., turbulent eddies, wind speed, varying detection limits, sample durations, shift in location). There were many instances in the time series of the results where although we did not have a strong correlation, we noted similar patterns in the rise and fall of concentration and emission rates. In other words, the patterns were very similar but the rate of change of the different methods was not stationary and therefore, the correlation coefficient (parametric or nonparametric) was low. One example of this occurred on January 13 at the Southwest Tanks (figure 4.1e) beginning at hour 13 and lasting until hour 17. Note that the difference in pattern at the first hour is not a valid starting point for comparison because DIAL did not begin measuring until 12:26.

However, beginning at the pattern at hour 13, we can see similarities in pattern in the two methods. The arrows show that the relationship between the concentration from the MAAML and the DIAL emission rate is not constant. While there were too many non-detects in the FTIR data to assess the DIAL and the FTIR data for this time frame, we look to the FTIR data to help explain the shifting DIAL emission rate and the MAAML concentration relationship over time. During hour 13, the FTIR started measuring many observations above the detection limit. The peak in the FTIR measurements occurred at 13:47. A closer look at this hour reveals a variable molecular weight as reported by the FTIR. The DIAL emissions were calculated assuming a constant molecular weight. Therefore, we note that the changing rate of emissions measured by DIAL and the concentrations measured by the MAAML is at least partially due to the use of a constant molecular weight. To a large extent, variability in the compound mix tended to keep the DIAL VOC mass estimate within an uncertainty range of 14% for this study, as evidenced by the NPL analysis of the many sorbent tube samples.

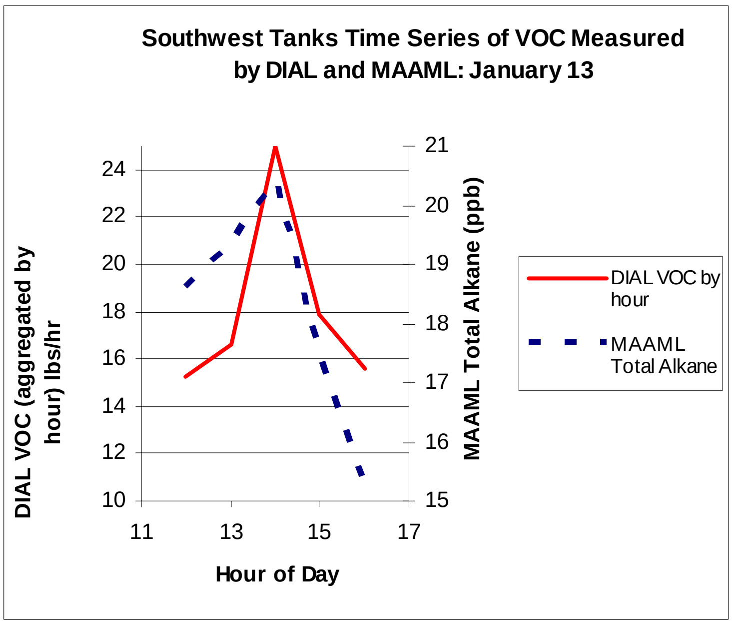

Figure 4.1e Southwest Tanks Time Series of VOC Measured by DIAL and MAAML: January 13

While there are many other examples of similar patterns, in comparison, on January 15 at the Southwest Tanks (figure 4.1f) the DIAL emissions and the MAAML concentration appear unrelated or at best inversely related. When the patterns were similar, the MAAML was found to be located inside the DIAL plume (see the summary table in the results section) and when the patterns appear unrelated, the MAAML was located outside the DIAL plume. This highlights the fact that the location of the MAAML to the DIAL plume is important in a valid verification of DIAL emissions using the MAAML data.

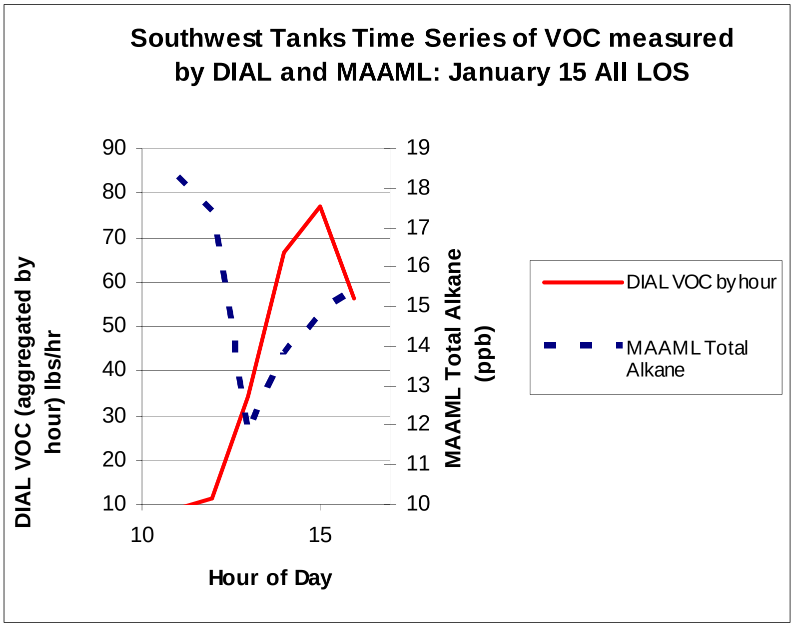

Figure 4.1f Southwest Tanks Time Series of VOC measured by DIAL and MAAML: January 15 All Lines of Sight

Other examples of similar patterns shown below are for East Tanks DIAL emissions compared with the FTIR concentration on January 22 (figure 4.1g), Tanks T-OL913 and T-OL920 DIAL emissions compared with the FTIR concentrations on March 23 (figure 4.1h), and Olefins Process Area DIAL emissions compared with the MAAML data on January 18 (figure 4.1i). The first hour, 10, in the time series of the Olefins Process Area cannot be compared with MAAML because the DIAL emission measurements were not initiated until 10:46. All three figures indicate a shifting relationship. Part of the changing relationship can be explained by a large number of non-detects in the FTIR data. The non-detects were replaced with the detection limit for analysis but this would introduce uncertainty.

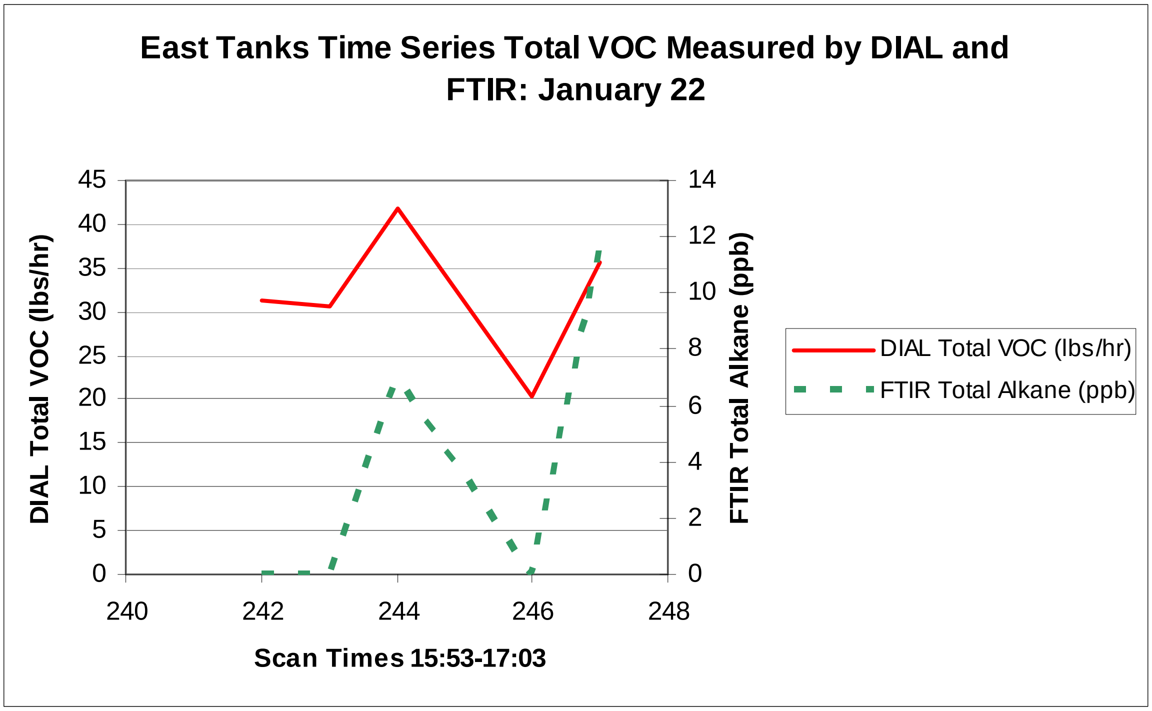

Figure 4.1g East Tanks Time Series Total VOC Measured by DIAL and FTIR: January 22

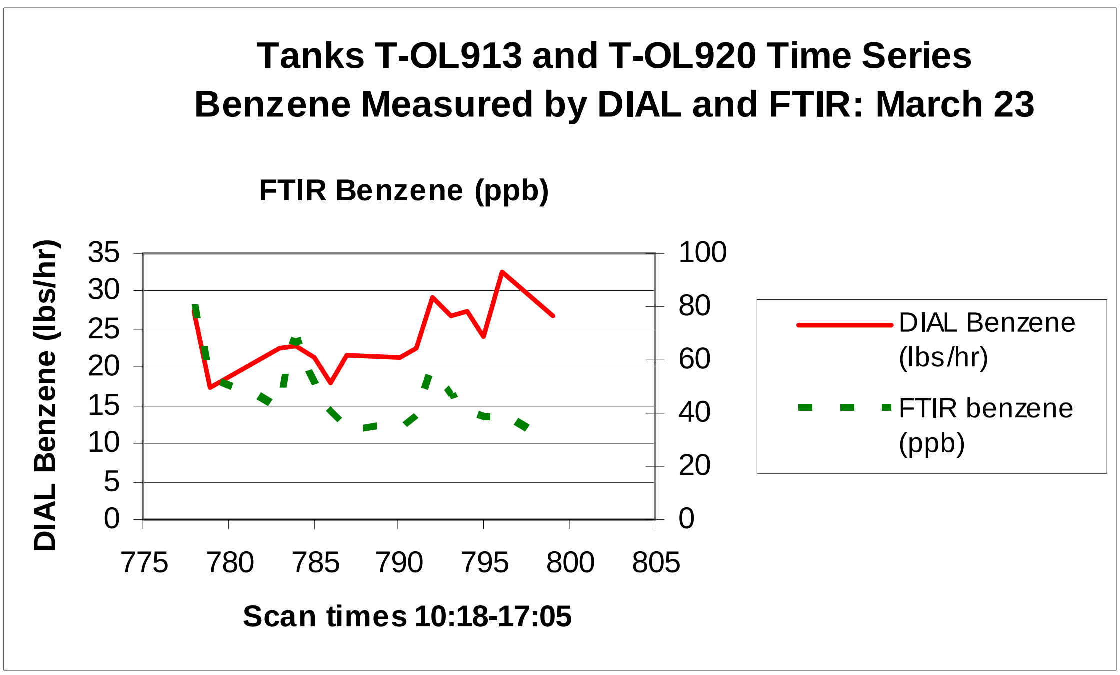

Figure 4.1h Tanks T-OL913 and T-OL920 Time Series Benzene Measured by DIAL and FTIR: March 23

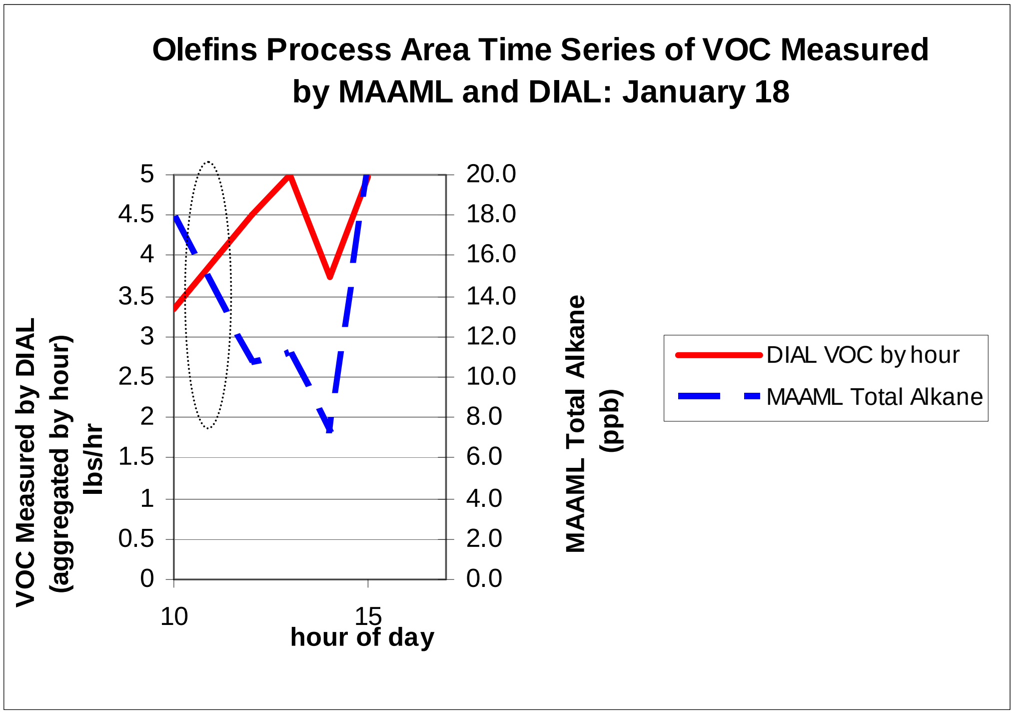

Figure 4.1i Olefins Process Area Time Series of VOC Measured by MAAML and DIAL: January 18

Measurements at the Olefins Process Area on January 18 (figure 4.1i) provide further information. Looking at the entire dataset that compares DIAL emissions to the MAAML concentrations, we find that the two methods are not linearly related. However, we discover that there is a wind shift. Looking at the data without the wind shift, the methods are more closely related. Recognizing that the relationship between DIAL and the FTIR would be less likely to be impacted by a wind shift, we move to analyze how well the FTIR data is related to the DIAL emissions during the wind change. Unfortunately, the FTIR is not in the DIAL plume and as expected it is not linearly related with DIAL. We did find that the FTIR measurements are highly *negatively* correlated with wind direction r=-0.76. This highlights an advantage that FTIR has over the MAAML. The FTIR concentration wind direction relationship can be used to identify sources.

We hypothesize that if the DIAL and the FTIR are aligned, the wind direction shift should impact them equally, if the source is not between them. The East Wastewater and Flares area on February 1 (figure 4.1j) is an example of a situation where both DIAL and FTIR have similar patterns. When the wind direction is plotted along with the time series, we find that DIAL either isn't impacted by wind or is similarly positively correlated with wind direction. Again, FTIR appears negatively correlated with wind direction. The difference here may be that FTIR is only 10% aligned with the DIAL plume.

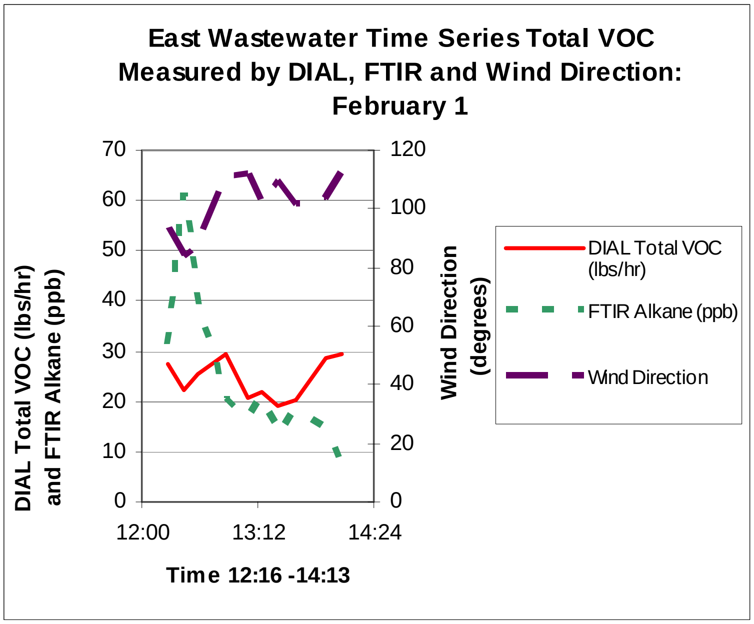

Figure 4.1j East Wastewater Time Series Total VOC Measured by DIAL, FTIR and Wind Direction: February 1

4.1.3 Identification of Spikes

DIAL identified important spikes in emissions as verified by the both the MAAML and the FTIR data. February 15 at the Tanks South of ACU and BEU (figures 4.1k and 4.1l) is a good example of the ability of both methods to find a spike in emission rates. While the linear regressions for this data are not statistically significant without the outlier, both methods were able to verify a spike. FTIR concentrations were much higher than the MAAML concentrations because the event was short term; MAAML reported 16.9 ppb benzene for the hour of peak while FTIR reported 394 ppb benzene at scan 697. MAAML concentrations were averaged over an hour while FTIR were averaged over the DIAL scan time.

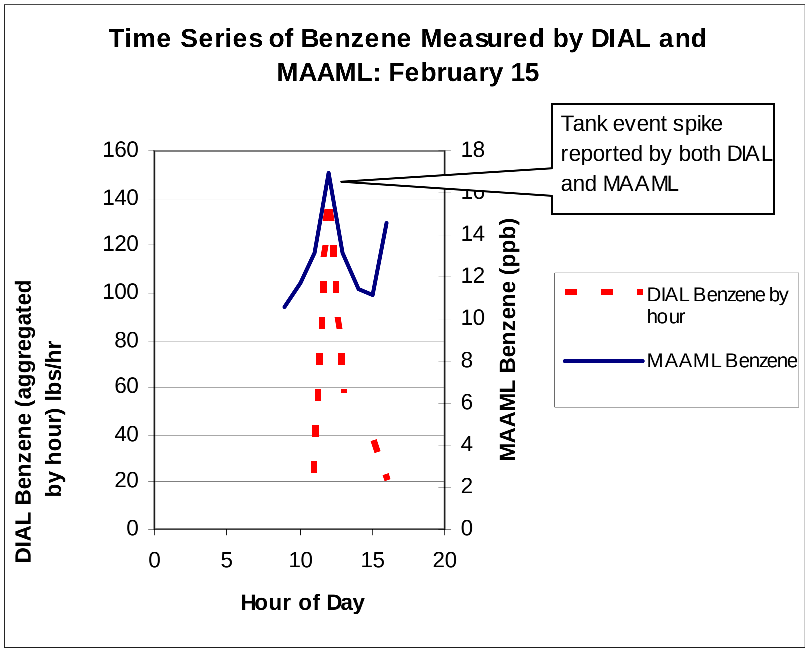

Figure 4.1k Time Series of Benzene Measured by DIAL and MAAML: February 15

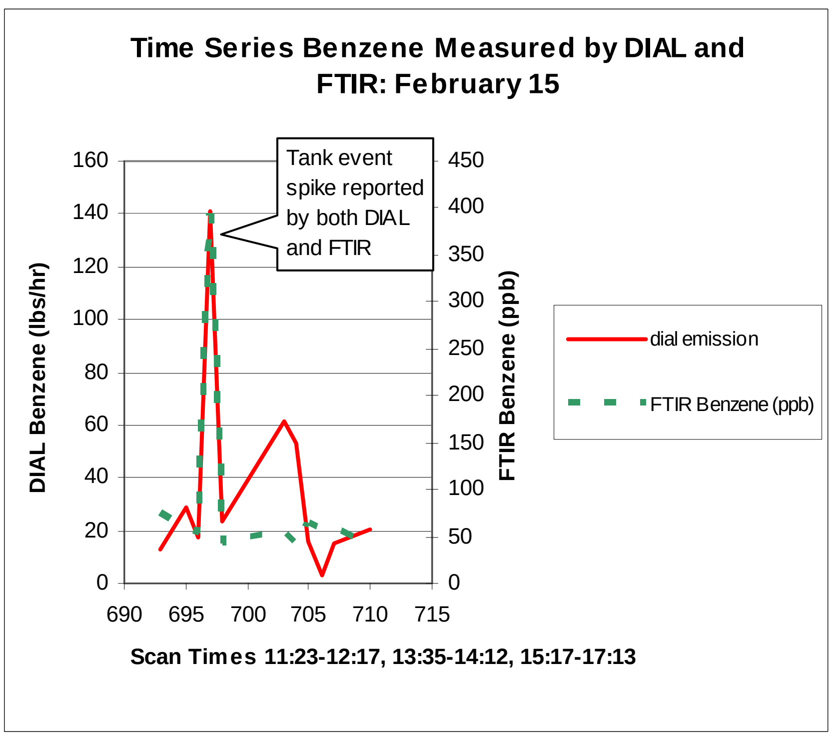

Figure 4.1l Time Series Benzene Measured by DIAL and FTIR: February 15

4.2 Discussion Regarding Report Objective: Develop, improve and demonstrate DIAL System emissions measurement methods for estimating the mass flux of benzene and volatile organic compounds (VOC) from individual emissions sources at a Houston area refinery facility with significant benzene emissions.

4.2.1 Improve Verification Methodology

The process of verification of DIAL emissions with the FTIR and the MAAML measurements discussed in 4.1 has highlighted some important aspects of the DIAL measurement that should be included in methodology of use of DIAL to *improve* verification:

1) Use of a constant molecular weight incorporates bias and results in a shifting relationship between DIAL emissions and the FTIR and MAAML concentrations; therefore, molecular weight should adjust as dictated by the FTIR for best match.
2) Verification of DIAL can only occur when the FTIR is aligned with the DIAL plume.
3) Verification of DIAL emissions at lower emitting sources can only occur when the FTIR detection limit is low enough to avoid non-detects.
4) Verification of DIAL emissions at process units with plumes raised above ground level is not possible when the plume is beyond the reach of the FTIR. In future deployments the FTIR retro-reflector should be elevated to transect the DIAL plume when the plumes are above ground level.

The methodology section (2) presented the methods used and the results section presented the process area emissions (3) satisfying this objective. The following graphs provide a comparison between process areas.

4.2.2. Process Area Comparison

To summarize the range of emission rates of benzene and VOC total alkanes measured by DIAL in each process area during the course of the study we have graphed the emissions using side by side boxplots and calculated an upper 95 percent confidence limit of the mean of each area based on the data distributional shape.

Side by side boxplot figures 4.2a, 4.2b, and 4.2c are shown below. Boxplots indicate, from bottom to top, the low end of the range, the 25^{th} percentile, 50^{th} percentile, and the 75^{th} percentile and the high end of the range. Triangles indicate outliers. There was an extreme outlier in the data set (4,026 lbs/hr) taken when the West Tanks process area was measured that was not included in the statistical graphs and calculations because it was from a different source.

The boxplots indicate that relative to other areas, the lowest benzene emitting areas were the North Property Flare, the Southwest Tanks, the North Wastewater and the Refinery West area. The highest emitting area and the most variable emissions were found from the Tanks South of the ACU/BEU and this area also had an emission that was a statistical outlier. All of the remaining areas had a distribution of benzene emissions skewed high (to the right).

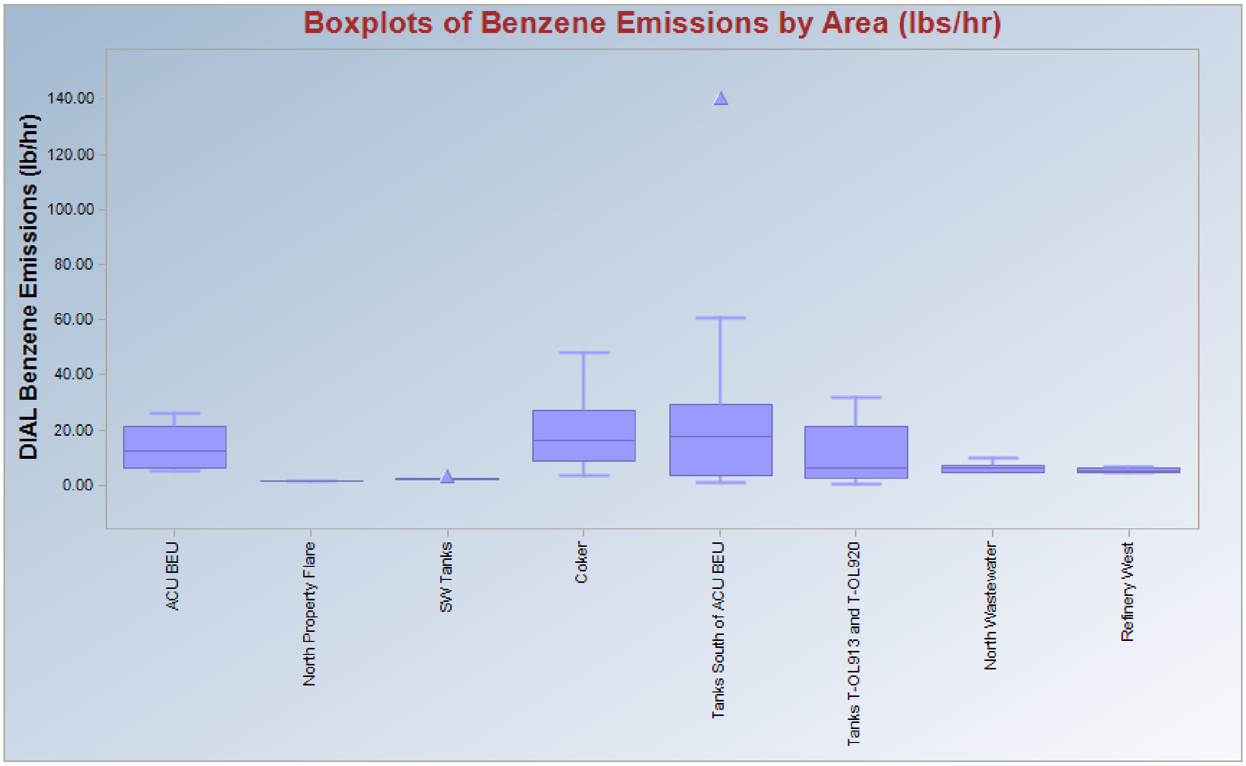

Figure 4.2a Boxplots of Benzene Emissions by Area (lbs/hr)

The range of emission rates of VOCs by area is shown in the side by side boxplots below. The boxplots indicate that relative to other areas, the lowest VOC emitting areas were the Olefins Process Areas, the Olefins Tanks, the Olefins Flares, the Coker, Coker and GOHT, and Tank Farm B followed by the West Dock Area. Emissions of VOC from these areas were all under 15 lbs/hr range of VOC. The highest and most variable area is the North Wastewater Area. These emissions are plotted separately because of the scale relative to the other areas. The next highest emitting area is the ACU/BEU. While this area has outliers on the low end, it is relatively less variable than the other areas which emit more than 15 lbs/hr. The Southwest tanks area emissions distribution is highly variable and skewed to the high end.

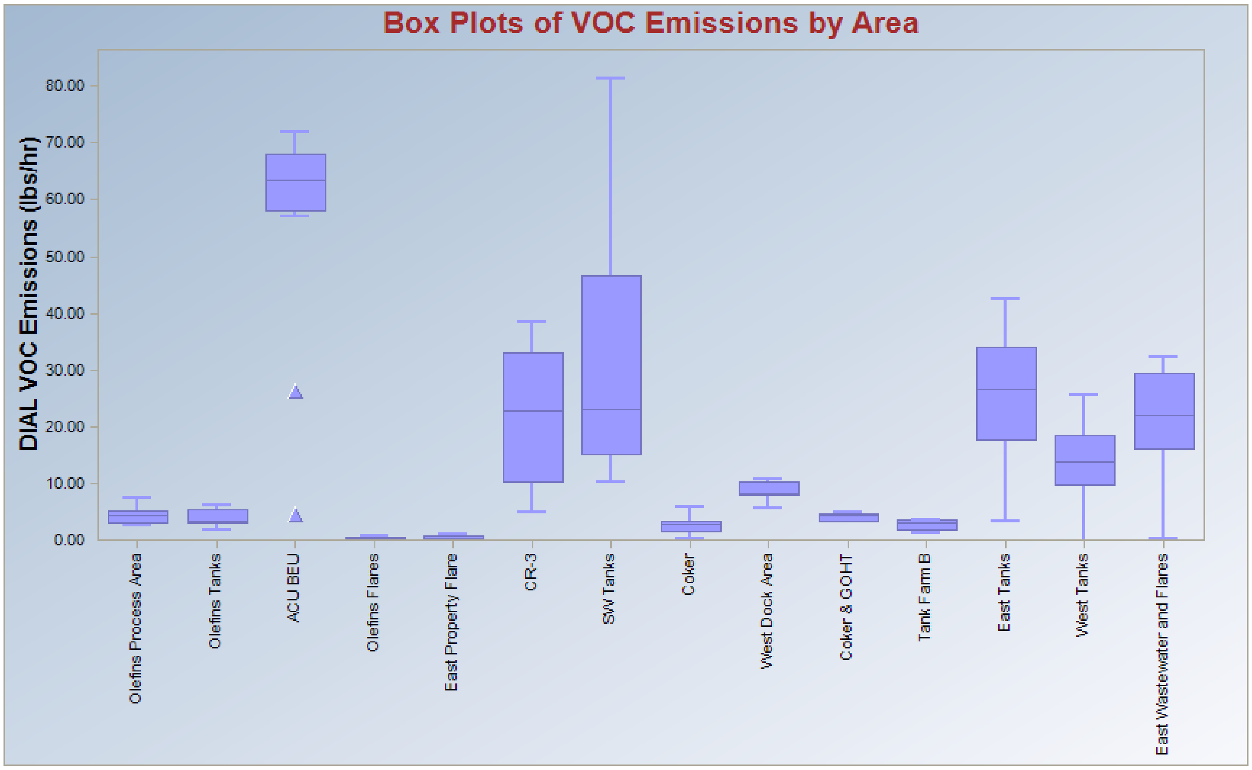

Figure 4.2b Boxplots of VOC Emissions by Area

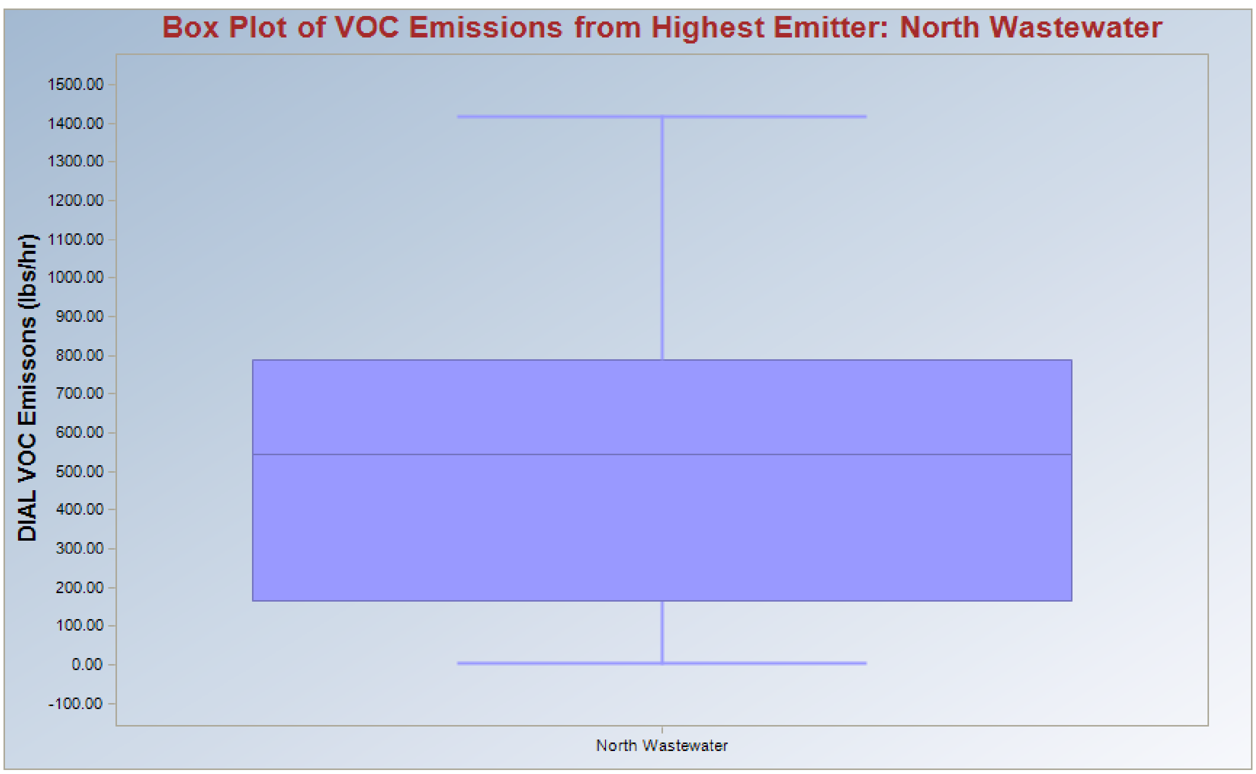

Figure 4.2c Boxplots of VOC Emissions by Area: Highest Emitter

Using the sample data by area, the number of samples, the variability of the samples and the sample distributional shape, the 95th upper confidence limit of the mean statistic was calculated using EPA's ProUCL. The 95th upper confidence limit of the mean is the estimate of the true emissions from the area. Tables 4.2a and 4.2b below list the process area, the distributional shape of the sample data and the 95th upper confidence limit of the mean in lbs/hr from each area. The highest benzene emissions are associated with the Tanks South of the ACU/BEU and the highest VOC emissions are associated with the North Wastewater.

PROUCL Recommended 95th Upper Confidence Limit of Emissions of Benzene by Process Area (lbs/hr)		
ACU BEU	Use 95% Student's-t UCL	16.77
North Property Flare	Too few observations	
SW Tanks	Use 95% Student's-t UCL	3.165
Coker	Use 95% Student's-t UCL	22.21
Tanks South of ACU BEU	Use 95% Approximate Gamma UCL	41.13
Tanks T-OL913 and T-OL920	Use 97.5% Chebyshev (Mean, Sd) UCL	19.76
North Wastewater	Use 95% Student's-t UCL	7.3
Refinery West	Use 95% Student's-t UCL	6.057

Table 4.2a PROUCL Recommended 95th Upper Confidence Limit of Emissions of Benzene by Process Area (lbs/hr)

PROUCL Recommended 95th Upper Confidence Limit of Emissions of VOC by Process Area (lbs/hr)		
Olefins Process Area	Use 95% Student's-t UCL	4.768
Olefins Tanks	Use 95% Student's-t UCL	4.49
ACU BEU	Use 95% Chebyshev (Mean, Sd) UCL	77.48
Olefins Flares	Use 95% Student's-t UCL	0.392
East Property Flare	Use 95% Student's-t UCL	0.474
CR-3	Use 95% Student's-t UCL	27.37
SW Tanks	Use 95% H-UCL	41
Coker	Use 95% Student's-t UCL	2.77
West Dock Area	Use 95% Student's-t UCL	9.568
Coker & GOHT	Use 95% Student's-t UCL	4.582
Tank Farm B	Use 95% Student's-t UCL	3.164
East Tanks	Use 95% Chebyshev (Mean, Sd) UCL	33.62
North Wastewater	Use 99% Chebyshev (Mean, Sd) UCL	1192
West Tanks	Use 95% Student's-t UCL	15.8
East Wastewater and I	Use 99% Chebyshev (Mean, Sd) UCL	43.35

Table 4.2b PROUCL Recommended 95th Upper Confidence Limit of Emissions of VOC by Process Area (lbs/hr)

4.2.3 Speciation of DIAL Plume

Use of the MAAML data to speciate the DIAL plume was explored in this study. We hypothesized that if the MAAML was in the DIAL plume and there was good correlation with MAAML benzene (or total VOC) and the DIAL benzene (or total VOC), respectively, then the other MAAML constituents correlated with the DIAL benzene (or total VOC) were present in the DIAL plume. Unfortunately, there were no instances during this study when MAAML was in the plume with good correlation with DIAL based on the scan image. There were days which can be used to demonstrate the speciation, when the MAAML was not recorded as inside the

DIAL plume based on the scan image but there was a positive correlation (r>0.74) and the p-value testing for 0 slope/significant regression was promising (p-value 0.16 or less, recognizing that typically evidence of significance is associated with a p-value of 0.10 or less). These days were:

- Coker, 2/17/2010, hours 12-16, r=0.74 p-value=0.15- Cumene is an outlier.
- East Tanks, 1/23/2010, r=0.73 p-value =0.16- (hour 11 to 13 and hour 15 to 16), ethylene, propylene,n butane, n pentane, 2 methylpentane, hexane, toluene, ethylbenzene, m/p xylene, o xylene, cumene, 1,2,4 trimethylbenzene were outliers.

Tables 4.2c and 4.2d below detail the speciation in terms of correlation with DIAL on these days. On February 17 at the Coker, when DIAL and MAAML have a correlation of benzene of 0.74, the DIAL benzene is relatively correlated with hexane, propylene and toluene and negatively correlated with o-xylene. On January 23 at the East Tanks, when DIAL and MAAML have a correlation of VOC of 0.73, the DIAL VOC is relatively correlated with benzene, hexane, 2-methylpentane, and propane and negatively correlated with 1,2,4-trichlorobenzene. The relatively well correlated constituents may be present in the DIAL plume at concentration ratios similar to what was measured by MAAML.

Correlation of MAAML Chemicals with DIAL Benzene by Hour: Coker on February 17	
Toluene	0.88
propylene	0.81
Hexane	0.76
Benzene	0.74
ethylene	0.63
m/p-xylene	0.60
n-Butane	0.58
2-methylpentane	0.57
ethane	0.57
propane	0.55
n-Pentane	0.27
Cumene	0.14
Methylene Chloride	0.07
acetylene	-0.11
Trichlorofluoromethane	-0.11
1,1,2-Trichlorotrifluoroethane	-0.56
o-Xylene	-0.77

Table 4.2c Correlation of MAAML Chemicals with DIAL Benzene by Hour: Coker on February 17

Correlation of MAAML Chemicals with DIAL VOC by Hour: East Tanks on January 23	
Hexane	0.79
Benzene	0.73
2-methylpentane	0.72
propane	0.72
1,2,4-Trimethylbenzene	0.63
Toluene	0.61
Ethylbenzene	0.60
n-Butane	0.55
n-Pentane	0.55
o-Xylene	0.50
Cumene	0.49
acetylene	0.46
m/p-xylene	0.45
ethane	0.44
1,3,5-Trimethylbenzene	0.43
ethylene	0.25
propylene	0.22
1,2-Dichlorobenzene	-0.15
Trichlorofluoromethane	-0.44
1,3-Dichlorobenzene	-0.90
1,1,2-Trichlorotrifluoroethane	-0.94
1,4-Dichlorobenzene	-0.94
1,2,4-Trichlorobenzene	-0.97

Table 4.2d Correlation of MAAML Chemicals with DIAL VOC by hour: East Tanks on January 23

4.3 Discussion Regarding Report Objective: Identify unanticipated/underestimated sources of benzene and VOC.

The boxplots and the statistics presented in the previous section suggest that in terms of benzene the largest sources come from the Tanks South of the ACU BEU, followed by the Coker, Tanks T-OL913 and T-OL920, and the ACU BEU.

The boxplots and the statistics presented in the previous section suggest that in terms of VOCs the largest sources come from the North Wastewater and West Tanks.

4.4 Discussion Regarding Report Objective: Evaluate emission estimation techniques currently utilized to determine VOC and benzene emission rates by comparing DIAL measurements with estimated emissions.

The 95th upper confidence limit of the mean emissions by process area estimated from the DIAL emission measurements using EPA PROUCL presented in Section 4.2 were compared to the emission rates estimated from emission factors. The 95th upper confidence limit of the mean values reflect the measured data. Based on the current data and associated statistics, the true emissions may be underestimated by a factor of as much as 132 for VOCs and 93 for benzene. See table 4.4a below.

Area		Date	Emission Factor Based Calculation (lbs/hr)	VOC (V) or Benzene (B)	Estimate of the 95th Upper Confidence Limit of the Mean (lbs/hr)**	Potential Underestimation Multiplier
Southwest Tanks	A-333	13-Jan	0.43	V		
	A-330	13-Jan	0.45	V		
	A-332	13-Jan	1.27	V		
		Total	2.15		20.18	9
	A-325	15-Jan	0.22	V		
	A-326	15-Jan	0.34	V		
	Total		0.56		13.15	23
	AP-17	19-Jan	0.46	V		
		Total	0.46		42.6	93
	AP-17	15-Jan	0.25	V		
	AP-16	15-Jan	0.14	V		
	Total		0.39		51.53	132
West Tanks	A-310	1/14	0.17	V		
	G-324-R1	1/14	0.26	V		
	Total		0.43		15.8	37
CR-3		21-Jan	20.67	V		
		25-Mar	20.67	V		
	Average		20.67		27.37	1
East Tanks	J-327	22-Jan	0.14	V		
	J-328	22-Jan	0.12	V		
	J-331*	22-Jan	4.63	V		
	J-332*	22-Jan	4.63	V		
	Total		9.52		37.05	4
	J-327	23-Jan	0.15	V		
	J-328	23-Jan	0.12	V		
	Total		0.27		18.07	67
	J-327	28-Jan	0.11	V		
	J-328	28-Jan	0.16	V		
	J-331*	28-Jan	4.63	V		
	J-332*	28-Jan	4.63	V		
	Total		9.53		35.98	4
Northwest Wastewater		25-Jan	6.5	V		
		30-Jan	15	V		
		5-Feb	11.5	V		
	Average		11		1192	108
		9-Feb	0.019	B		
		13-Feb	0.2	B		
	Average		0.11		7.3	67

* permit limits

** from ProUCL

Table 4.4a Comparison of DIAL measurements with estimated emissions

Area		Date	Emission Factor Based Calculation (lbs/hr)	VOC (V) or Benzene (B)	Estimate of the 95th Upper Confidence Limit of the Mean (lbs/hr)**	Potential Underestimation Multiplier
East Wastewater		1-Feb	5.88	V		
	Total		5.88		43.35	7
Tanks T-OL913 and T-OL920	T-OL913	8-Feb	1.15	B		
	T-OL913	10-Feb	1.17	B		
	T-OL913	23-Mar	1.18	B		
	T-OL920	8-Feb	0.83	B		
	T-OL920	10-Feb	0.83	B		
	T-OL920	23-Mar	0.83	B		
	Total of Tank Averages		2.00		19.76	10
ACU BEU		12-Feb	3.41	B		
		15-Feb	3.41	B		
	Average		3.41		16.77	5
		26-Mar	2.49	V		
	Total		2.49		77.48	31
Tanks South of ACU BEU	D-350	2-Feb	0.03	B		
	D-351	12-Feb	0.09	B		
	D-381	15-Feb	0.3	B		
	D-352	22-Mar	0.02	B		
	Total		0.44		41.13	93

** from ProUCL

Table 4.4a (continued) Comparison of DIAL measurements with estimated emissions

4.5 Discussion Regarding Report Objective: Assess the feasibility of emissions reduction strategies based on the measured impact from the most significant individual benzene emissions sources identified at the selected Houston area sites.

The February 2011 benzene contracts in the US were $4.35/gal, up 51 cents/gal from January and 93 cents/gal from November 2010 (http://www.icis.com/v2/chemicals/9075158/benzene/pricing.html). So a conservative estimate of the value of benzene emissions is $3.00/gal. The benzene emissions measured from Tank D381, a benzene concentrate tank on February 15, 2010 from 11:00 to 17:00 averaged around 40 lbs/hr, when the upwind process unit source emissions were subtracted. The timing of the emissions according to information from the site representatives corresponded with filling of the tank. Assuming a density of 7.365 lbs/gal (temperature of 68˚F and atmospheric pressure) and the conservative $3.00/gal value of benzene, indicates that each time Tank D381 is filled, approximately $80 of benzene is lost to air emissions. If the tank were filled once a week, annual loss from emissions would be $4,200, ignoring breathing losses. If the tank were filled daily, the annual loss from emissions would be $30,000, ignoring breathing losses. Based on the estimated capital and operations cost estimates of various vapor recovery systems, such as a Venturi Jet Ejector vapor recovery system, the feasibility and cost recovery period can be easily calculated.

4.6 Discussion Regarding Report Objective: Assess the cost effectiveness of the DIAL system based on project costs, estimated emissions reduction strategies costs and the estimated cost savings to be realized through preventing the loss of valuable products, intermediates and/or raw materials via the proposed emissions reduction strategies.

To estimate the value of emissions lost, it is assumed that the emitted gas could be used as fuel. Therefore, the value of natural gas is used. The March 2011 spot price for natural gas was $3.81/mmBTU and the spot price was higher in early 2010 during the project (http://www.eia.doe.gov/oog/info/ngw/ngupdate.asp). The net heating value of natural gas is assumed to be 20,432 BTU/lb (http://www.epa.gov/nvfel/methods/ngfe.pdf). Therefore the estimated value of the emissions is assumed to be approximately $0.0778/lb. The average total emissions rate measured during the project was 474 lbs/hr VOC (which excludes the high emissions rate wastewater day, 985 lbs/hr, due to a DAF skimmer problem and the high emissions rate tank event, 4,000 lbs/hr scan due to maintenance) and 105 lbs/hr benzene (which excludes the high emissions rate scan from tank D-381 during filling, 141 lbs/hr, and the high emissions rate, 27.1 lbs/hr scan during coker drain phase), for an average total emissions rate of 579 lbs/hr. At an estimated value of $0.0778/lb, that equates to emissions valued at $45/hr, $1,081 per day and $394,600 per year. If 25% of the measured emissions could be prevented or recovered, assuming the cost of a similar commercial DIAL study would be approximately $750,000, the payback period for the study, after emissions have been reduced, would be 7.6 years.

5. Conclusions

The data suggest the following conclusions:

Objective 1 Conclusions) Emissions of benzene and VOC from individual emissions sources at a large refinery/chemical plant were successfully measured using DIAL. The comprehensive emissions survey using DIAL was shown to be effective at a large, complex industrial site when combined with a variety of open-path and extractive technologies. There were limitations inherent to the conduct of the study that reduced the value of the data collected. These limitations were primarily related to not having flexible facility access or sufficient access to refinery operating data.

DIAL was shown to be an effective technology for the measurement of mass flux from fugitive, non-point emissions sources. DIAL is limited, however, in that it can only measure the mass flux of a single compound or a class of compounds that absorb energy at a defined wavelength during a scan, preventing DIAL from directly providing information on plume chemical composition. Therefore, additional analysis is necessary to fully characterize the actual plume composition. Additional challenges related to the compositional characterization of the DIAL measured plume include the time period of compositional measurements which may prevent characterization of temporal variations and the fact that the compositional measurement techniques are typically fixed measurement locations, close to ground level. Moving these analytical platforms above ground level for elevated plumes (such as delayed coker plumes) and with wind direction shifts represents a significant challenge.

When DIAL is scanning for total alkanes, emissions of non-alkane hydrocarbons that are important at petroleum refineries (e.g., aromatic compounds such as benzene, toluene and xylenes) can be under-accounted for in the total measured mass flux. The plume compositional analysis (estimated using extractive samples) can be used to estimate total VOC emissions from the total alkane mass flux measurements; however, the accuracy of this adjustment is limited by the accuracy of the extractive compositional analysis relative to the actual composition of the plume during the course of the scan. DIAL is expected to slightly underestimate VOC mass flux. DIAL validation studies conducted using a known mass release have confirmed this slight underestimation (by 3 – 12%), based on six separate studies conducted in Europe (http://www.epa.gov/ttnchie1/efpac/documents/wrkshop_fugvocemissions.pdf). A possible reason for this underestimation is that the DIAL technique assumes that there is no absorption of the pulsed reference laser beam operated at the "off-resonant wavelength" (refer to the description of the DIAL technique provided by NPL in the DIAL QAPP). There may be a relatively small amount of absorption at the "off-resonant wavelength," even though the "off-resonant wavelength" is selected at a wavelength that is not sensitive to the target species concentration.

Use of FTIR or UV-DOAS for surveys of benzene or other individual compounds of interest represents an improvement over the use of DIAL with only extractive techniques for plume compositional characterization for the following reasons:

1) The FTIR can be configured to provide accurate information on plume compositional analysis over the course of the entire DIAL scan. This, however, does require careful

coordination to ensure that the FTIR is aligned along the DIAL scan plane and that the FTIR retroreflector mirror is placed at a distance and height that allows the FTIR beam to be aimed through the plume of interest. Most likely, this requires having a scissor jack or other raised platform readily available for deployment and use, which was not incorporated into this study.

2) While not completely integrated into this study, the FTIR allows for more accurate determination of plume average molecular weight (used in the calculation of mass flux) and to account for the change in average molecular weight of the plume over the course of the scan.
3) Because it can detect a broader range of compounds during the course of a single scan, the FTIR may detect a release that the DIAL does not. While a single path FTIR instrument does not allow for direct measurement of mass flux, detection of a compound of interest, and knowing the time and location of where it was detected, may facilitate additional investigations into location and cause of the release.

The FTIR (operated in accordance with USEPA Method TO-16), could not be used in this study to consistently provide statistical validation of the DIAL measurements. The reasons for this include:

1) The FTIR and DIAL were often taking measurements along similar, but different paths.
2) The FTIR was limited to ground-level measurements (height of approximately 1.5 meters); whereas, the plumes being measured by the DIAL were often elevated.
3) The FTIR and DIAL have different detection limits, with DIAL typically having a lower detection limit for the compound of interest, such as benzene. Therefore, plumes with low concentrations of the target compound(s) may be below the detection limit of the FTIR, yet measured by the DIAL.

While the FTIR could not be used to statistically validate the DIAL measurements, in almost every instance when the DIAL detected emission events (used in the sense of a transient plume, not in the context of the regulatory definition of an event), the FTIR also detected the event in the same location and at the same time.

Use of the MAAML allowed for real-time analysis of plume composition. However, being an extractive point measurement system with limited operational mobility, operation inside of the refinery close to the emission sources proved problematic with respect to plume detection by the MAAML.

It is difficult, if not impossible, to understand whether measured emissions are representative of normal operation. It is similarly difficult to develop good quality emission factors without a complete exchange of information with the facility being surveyed. For example, emissions from a delayed coker are dependent upon many operating factors including residual throughput rates and drum cycle times. If a delayed coker is operating at reduced throughputs or longer batch cycle times at the time of the survey, emissions could be reduced relative to what they would be at higher throughputs or shorter cycle times. However, without adequate access to information on delayed coker operation at the time of the survey and how those operations compare with normal and/or maximum design conditions, it is very difficult to draw conclusions about how representative the measured emissions are.

Objective 2 Conclusions) DIAL emissions were verified by the FTIR concentrations, and less so by the MAAML concentrations, in several ways: linear least squares regression, simultaneous spikes and similar time series patterns. The strongest quantification of verification occurred through least squares linear regression of DIAL VOC emissions (dependent variable) upon concentration from the FTIR alkane concentrations (independent variable) at the North wastewater Area on January 25, r=0.96, regression significant at p-value 0.001. The reason that there were not many more successful least square regression results stems from two main issues:

1) During the statistical analysis, we uncovered multiple examples of influential statistical outliers in regressions. While these outliers may represent real points, a statistical relationship which includes these points would stand up to scrutiny better only if there had been more frequent points around the peak or at the peak. These outliers are real extreme points because they were picked up by both techniques. Their presence just highlights the need for shorter sample duration to obtain more matching points. On the other end of the spectrum, the regressions were often messy at the low concentration/emission areas where the relationship appears noisy. Lower FTIR detection limits may address this noise.

2) There were many instances in which DIAL and the FTIR or the MAAML exhibited similar patterns in the time series but the rise and a fall of concentration and the emission rate did not remain constant. We attributed this drift at least partially to the use of a constant molecular weight in the DIAL emission rate estimates, while the true molecular weight was shifting.

Other important notes on verification of DIAL emissions using either the FTIR or the MAAML are that:

1) The location of the verification measurement must be known with respect to the DIAL plume. The FTIR was by far better suited to verify the plume over the MAAML because of its similar open-path nature, which could be aligned with the DIAL. Note that sources with elevated plumes (e.g., the coker) were not amenable to verification using either method.
2) The change in concentration with wind direction highlights the fact that the FTIR could be used to provide a back trajectory of a source, while the MAAML could not.
3) The MAAML reported hourly concentrations. Therefore, the DIAL scan emissions had to be aggregated up to the hour for comparison and resulted in a loss of precision. Conversely, the FTIR measurements were aggregated up to duration of the scan for DIAL.
4) The MAAML was better than the FTIR at providing speciation data because the MAAML detection limits were lower and it measured a wider range of constituents. The best example of DIAL plume speciation using the MAAML data occurred at the East Tanks on January 23 where toluene accounted for 63% of the total ppb.

Objective 3 Conclusions) The areas with the lowest benzene emissions were the North Property Flare, the Southwest Tanks and the Refinery West. The areas with the lowest VOC emissions were the East Property Flare and the Olefins Flare. The fact that emissions from flares were consistently low in this study may indicate that either the emissions were lower than expected, this method is not suitable to measure emissions from flares, or we did not measure on days when flares were in normal use.

The boxplots and the statistics suggest that in terms of benzene the largest sources of emissions came from the Tanks South of the ACU/BEU area, followed by the Delayed Coker, Tanks T-OL913 and T-OL920, and the ACU/BEU area and in terms of VOCs the largest sources of emissions came from the North Wastewater and West Tanks.

Objective 4 Conclusions) Of the 17 areas where DIAL emissions measurements were conducted, six were compared to VOC emission factor estimates and four were compared to benzene emission factor estimates. In only one process area did emission factors produce a VOC emissions estimate comparable to the DIAL measured results, which was the Catalytic Reformer-3 (CR-3) Unit. Emission factors used to estimate emissions from the Southwest Tanks VOCs produced the most potential underestimated emissions compared to the DIAL measured emissions, off by a factor of 132. The comparison of benzene emission factor estimates to the DIAL measured emissions produced potential underestimated emissions ranging from a factor of 5 at the Aromatics Concentration Unit/Benzene Extraction Unit area, to a factor of 93 for the tanks located south of the ACU/BEU area. These limited comparisons indicate that the emissions factor estimations for process units are better than emissions factors estimations for tanks.

Objective 5 Conclusions) Although the evaluation of emissions reduction strategies did not include costs associated with environmental and public health impacts, the measured impacts from the most significant individual benzene emissions sources identified at the site, such as Tank D381, suggest that there are feasible strategies that could be employed. Emissions reduction alternatives should be evaluated and employed where feasible, for all of the most significant emissions sources identified, including the most significant VOC emissions sources. In some instances additional source information is necessary for reasonable feasibility evaluations (ACU/BEU and Coker). In other instances where the source is well defined and controls are readily available, such as the dissolved air flotation (DAF) unit, the feasibility of various control options could be easily evaluated.

Objective 6 Conclusions) Although the cost effectiveness evaluation of a comprehensive DIAL survey at a large refinery/chemical plant did not include costs associated with environmental and public health impacts, the evaluation based on project costs, estimated emissions reduction strategies costs and the estimated cost savings to be realized through preventing the loss of valuable products, intermediates and/or raw materials indicates that the current DIAL costs may be prohibitively high. If DIAL costs could be reduced, perhaps by having a unit built for dedicated North American service (reducing transportation and travel costs), the potential for significant savings from emissions reductions suggest that the feasibility of conducting comprehensive DIAL surveys at similar sites would significantly improve.

<u>Recommendations</u>

The following recommendations are offered with respect to the conduct of future surveys:

- The pairing of DIAL with FTIR takes advantage of the complementary strengths of these two technologies to allow for improved plume characterization with respect to mass flux and chemical composition. Future investigations should focus on improving the coordinated use of these technologies as well as integration of the collected data. For surveys focused on a single aromatic compound such as benzene, a UV-DOAS instrument can be used in a role similar to FTIR.

- Use of extractive point monitoring systems is of limited use in the context of supporting in-plant surveys of fugitive emission sources where those sources may be significantly elevated, plume dispersion is impacted by nearby facility structures, and access to critical monitoring areas is limited by plant operations or structures. Point monitoring systems are most effective when deployed for conduct of ambient air quality monitoring programs over longer time periods or when conducting mobile surveys, such as those that EPA has conducted in the past using the Trace Atmospheric Gas Analyzer (TAGA) mobile laboratory.

- Surveys at large, complex emission sources such as petroleum refineries need to be conducted with active participation by operations personnel. Ideally, this would include flexible access during the course of the survey to facilitate the free flow of information about activities, events and operating conditions. Perhaps the only way to effectively accomplish this is for the refinery to take lead in conducting the survey.

- To address industry's concerns that emissions data collected during the course of these types of short-duration surveys are not representative of long-term emissions, permanent open-path installations could be installed to monitor emissions on a long-term basis. While single-beam, open-path instruments do not directly measure mass emission rates, single-beam instruments can be used to estimate mass flux by correlating open-path concentrations with mass flux measured with instruments such as DIAL.

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Appendices