Study of the Accuracy of Emission Factors and Emission Estimating Methods Using the DIAL System

What does DIAL tell us about benzene and VOC emissions from refineries?

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City of Houston

Don Richner, CIH
City of Houston

DIAL Project Team

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Cary Secrest, EPA
Shell Deer Park, Deer Park, TX

DIAL Report

http://www.greenhoustontx.gov/benzenereports.html

Additional questions: Hoyt.Daniel@epamail.epa.gov

Background

Why is this important?

- Estimates of emissions are used to:
  - Support permit decisions
  - Evaluate the efficacy of a control (MACT), residual risk
  - Support SIP models of criteria pollutants
- We **ALL** agree there are errors in the inventory

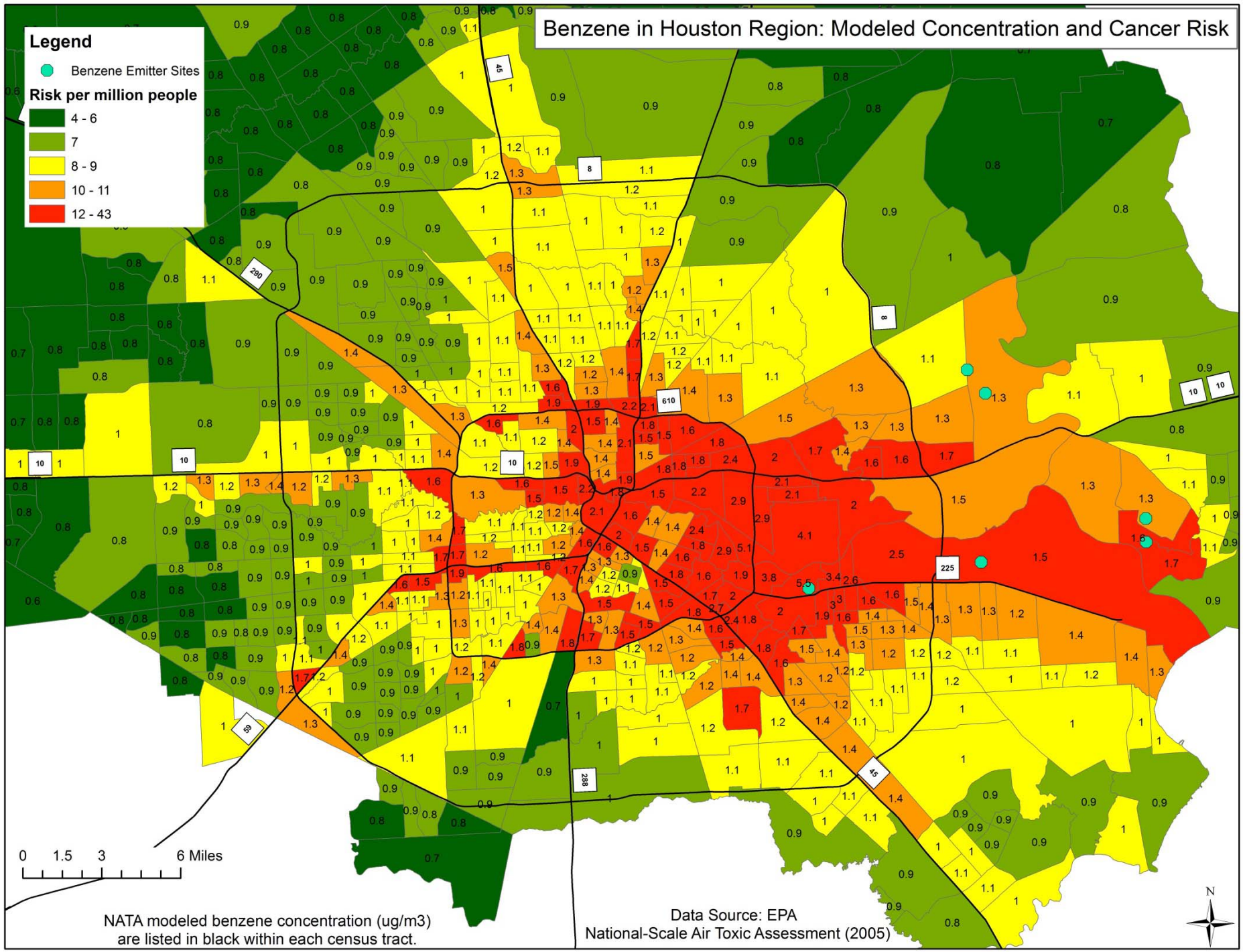
Why is this important?
(continued)

POLLUTION
BIG ISSUES

- More than 400 chemical manufacturing facilities.
- 2 of the 4 largest refineries in the U.S.
- No zoning.
- Non attainment for ozone.

HOUSTON FACTS

- 4th largest US city;
  2010 pop: 2,099,451.
- Largest US port for international tonnage.
- 2nd largest US port in total cargo
- 10th largest port in the world
- Home to 2 of the largest 4 refineries in the U.S.


Benzene in Houston Region: Modeled Concentration and Cancer Risk
Legend
Benzene Emitter Sites
Risk per million people
4 - 6
7
8 - 9
10 - 11
12 - 43
0 1.5 3 6 Miles
NATA modeled benzene concentration (ug/m3)
are listed in black within each census tract.
Data Source: EPA
National-Scale Air Toxic Assessment (2005)
N

Summary of Background

Problem

- MACT isn't working for Houston
- Emissions are under represented
- People are at risk

Solutions…many

- Regulate via a city ordinance
- Voluntary benzene reduction plan
- Data quality petition to EPA

  The DIAL study….

Purpose of DIAL Study

- **Generally**: Obtain more information regarding the accuracy of emission factors and emission estimating methods authorized by law and widely used in industry.

- **Specifically**: Assess emission rates of VOC and benzene from different areas of the site and to identify potential emission sources within these areas.

DIAL

(1) $$P_x(r) = E_x \frac{D_x}{r^2} B_x(r) \exp\{-2 \int_0^r [A_x(r') + \alpha_x C(r')] d'r\}$$

(2) $$CL(r) = \frac{1}{2\Delta\alpha} \frac{1}{N} \sum_{i=1}^{N} \log \frac{S_{ON,i}(r)}{S_{OFF,i}(r)}$$

(3) $$C(r) = \frac{dCL(r)}{dr}$$

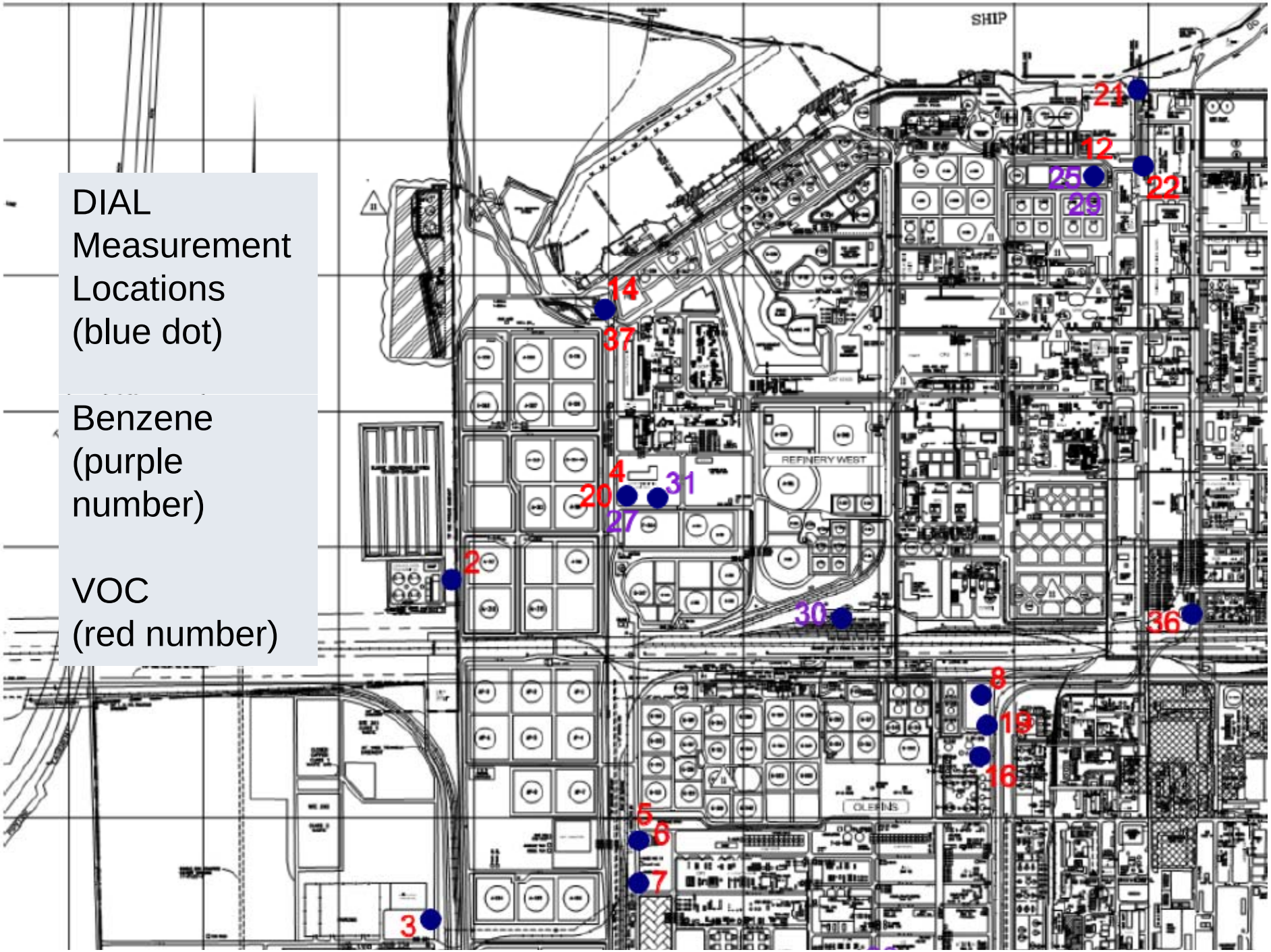
Measuring VOC and Benzene Emissions with DIAL

- **DIAL**: Differential absorption LIDAR, a form of laser radar.
- Uses an IR laser to measure VOC and a UV laser to measure benzene.
- Lasers measure the absorption profile across an elevated path to obtain concentration profile
- Wind speed sensors are used to measure the wind profile.
- VOC and benzene emission rates are calculated from the product of gas concentrations and the wind velocity component perpendicular to the DIAL measurement plane.

DIAL Study

The National Physical Laboratory (NPL) under contract to the City used differential absorption lidar (DIAL) technology to assess concentrations of

- Benzene
- Aliphatic hydrocarbons (C3-C15) at a refinery and chemical plant (we refer to this range as VOCs)


DIAL Measurement Locations (blue dot)
Benzene (purple number)
VOC (red number)
SHIP
REFINERY WEST
OLEFINS
21
12
25
29
22
14
37
4
20
31
27
2
30
36
8
19
16
5
6
7
3

Emission Factor Calculations for Process Area Emissions

- Includes the sum of all sources in the area when the DIAL study measurements were made.
- Calculations were based on approved EPA methodology.
- The temperature used was the monthly average during the month that the DIAL measurements were made.

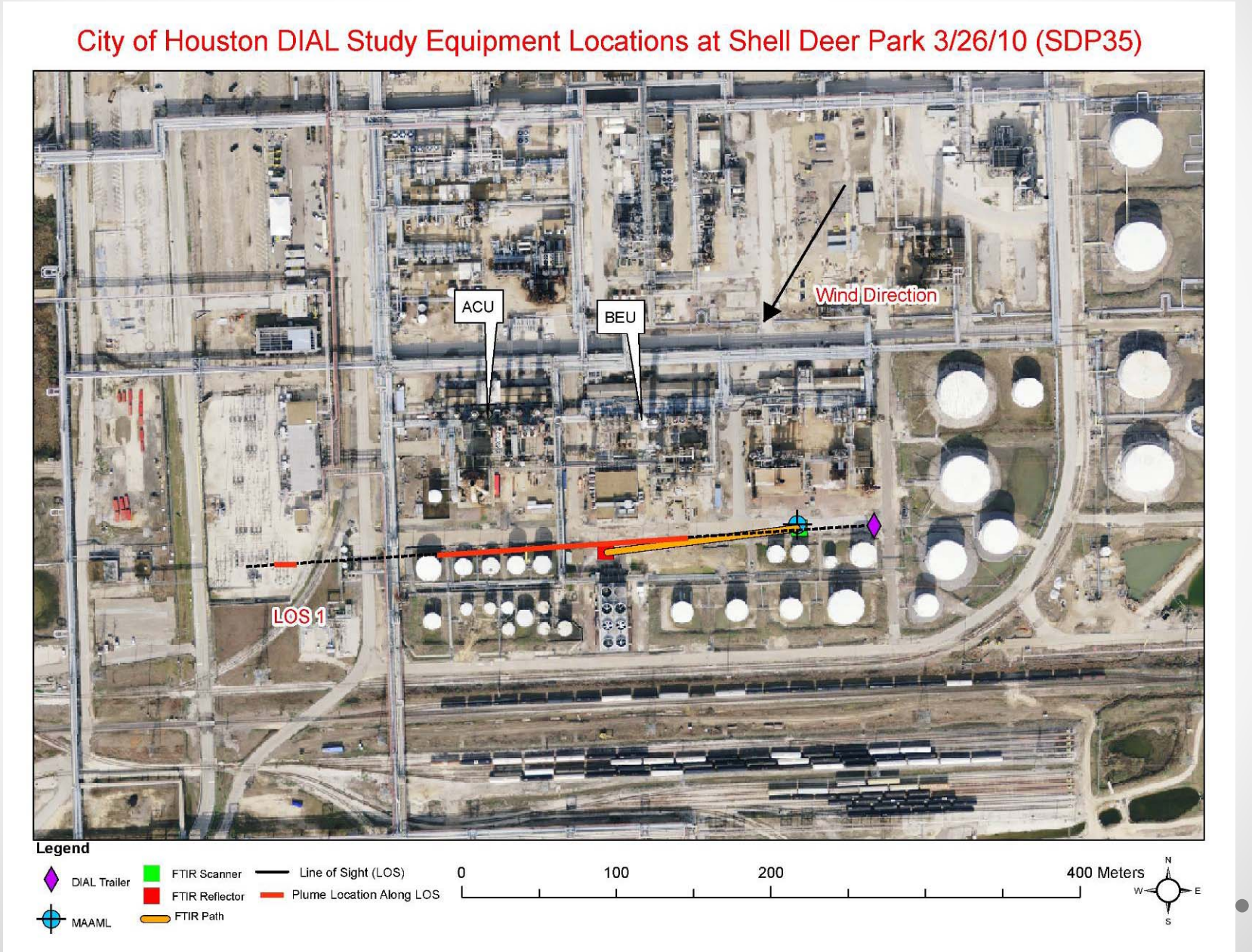
Emission Factor Calculations for Process Area Emissions *(continued)*

Methods used to calculate emissions for each source type were as follows:

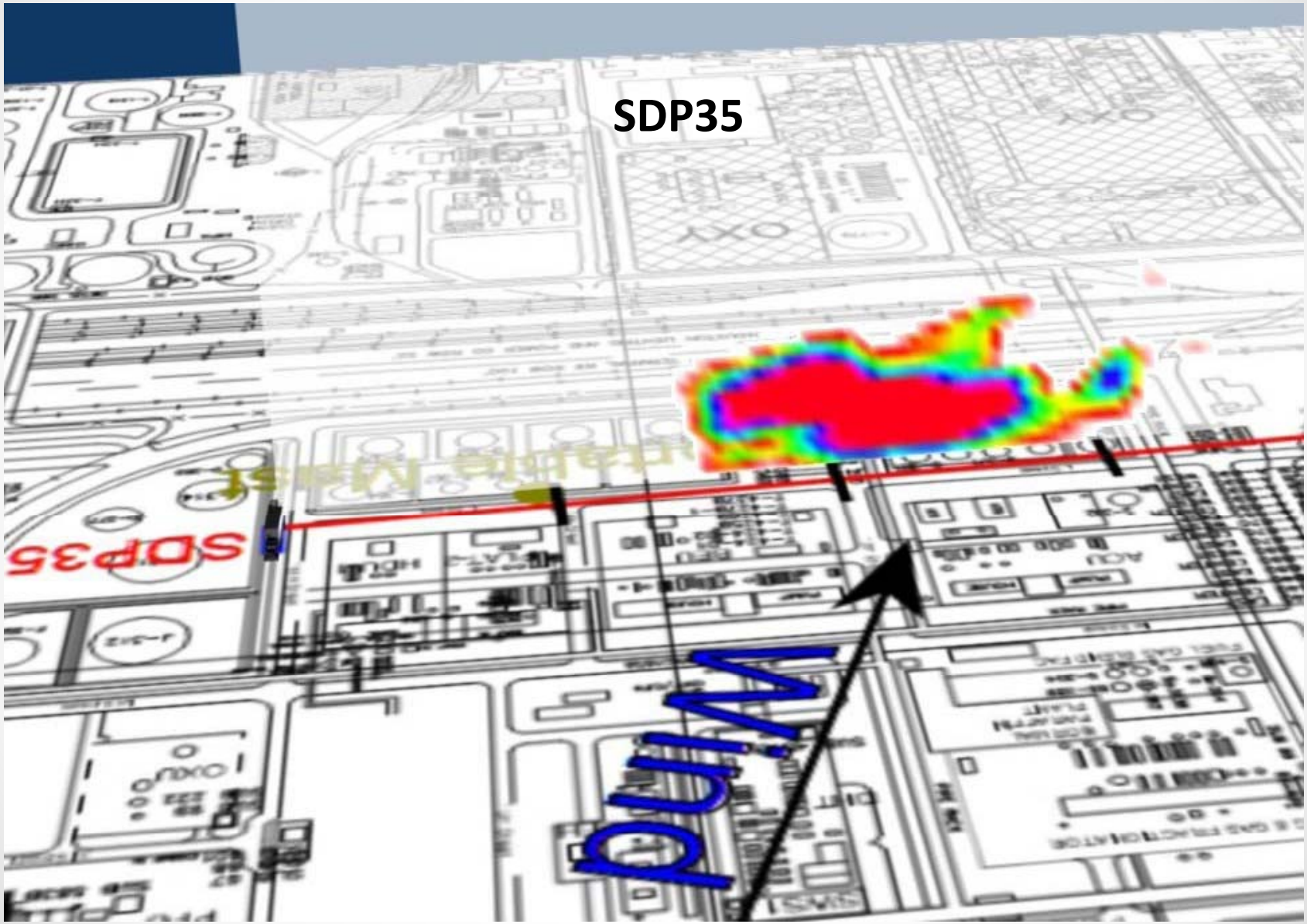
- Tanks – EPA's Tanks 4.0
- Fugitive emissions – Emissions were calculating using the LEAKDAS© software.

RESULTS

ACU/BEU Area Emissions

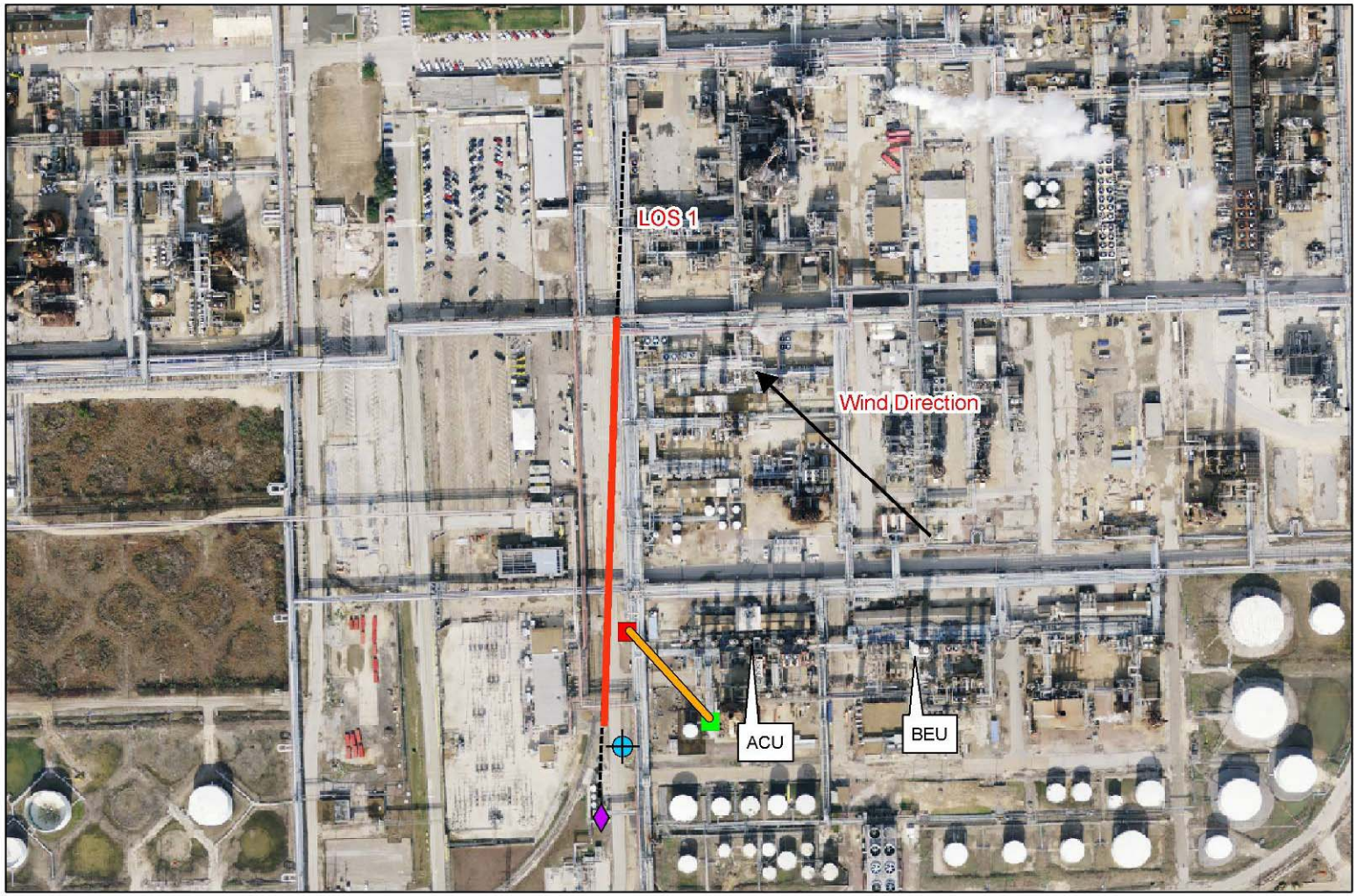


ACU/BEU Area Emissions

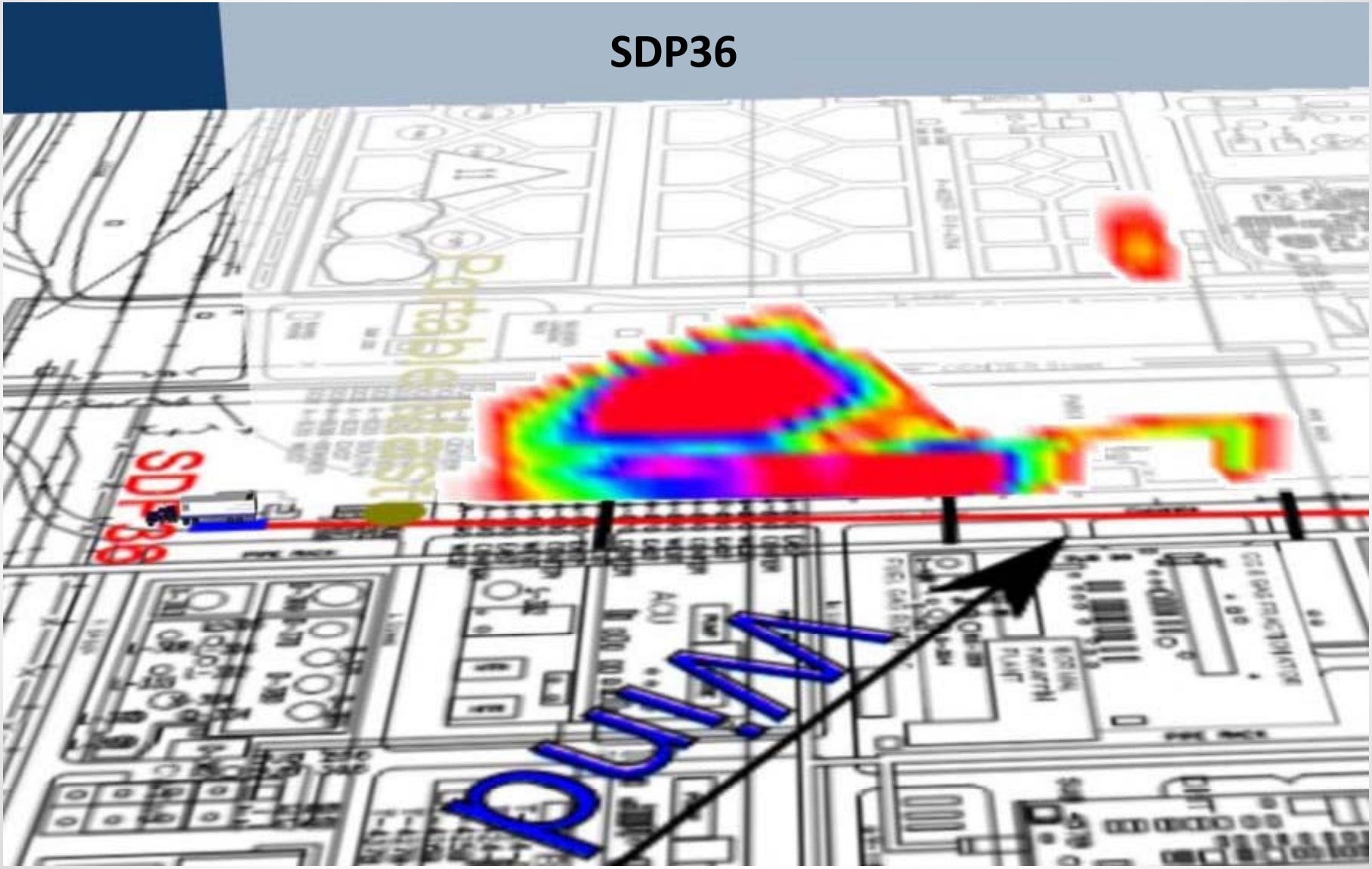


ACU/BEU Area Emissions

City of Houston DIAL Study Equipment Locations at Shell Deer Park 3/26/10 (SDP36)



ACU/BEU Area Emissions



ACU/BEU Area Emissions

Date/Time	DIAL Result (lbs/hour)	Emissions Factor Based Calculations (lbs/hour)
2/12/2010 10:40 -16:40	**27 lbs/hour Benzene**	3.41 lbs/hour Benzene
2/15/2010 10:18 -15:09	13 lbs/hour Benzene	3.41 lbs/hour Benzene
3/26/2010 10:53 - 17:05	**64 - 65 lbs/hour VOC**	2.49 lbs/hour VOC

DIAL results found in the NPL DIAL Report Page 136. For scans SDP35, NPL DIAL Report Page 65 & SDP36, NPL DIAL Report Page 67.

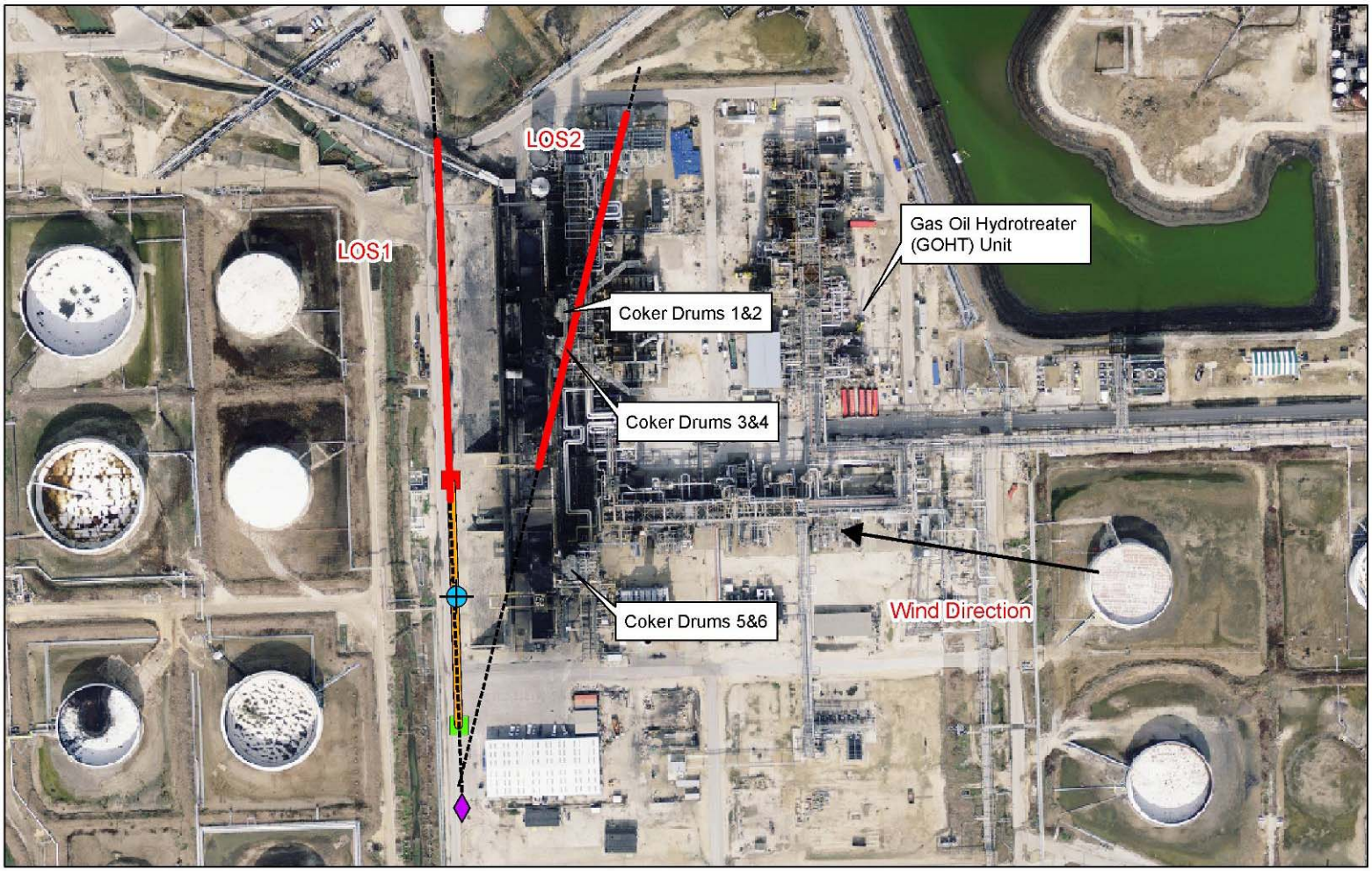
CR3 Area Data

Date/Time	Report Reference	DIAL Result (lbs/hour) VOC	Emissions Factor Based Calculations (lbs/hour)
1/21/2010 13:10 - 15:23	NPL DIAL Report Pages 29, 72 and 79	8 – 12 lbs/hour	20.67 lbs/hour
3/25/2010 10:53 - 16:54	NPL DIAL Report Pages 62, 73 and 80	30 lbs/hour	20.67 lbs/hour

No abnormal conditions were identified for either 1/21/2010 or 3/25/2010

General Coker Area

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/11/10 (SDP27)



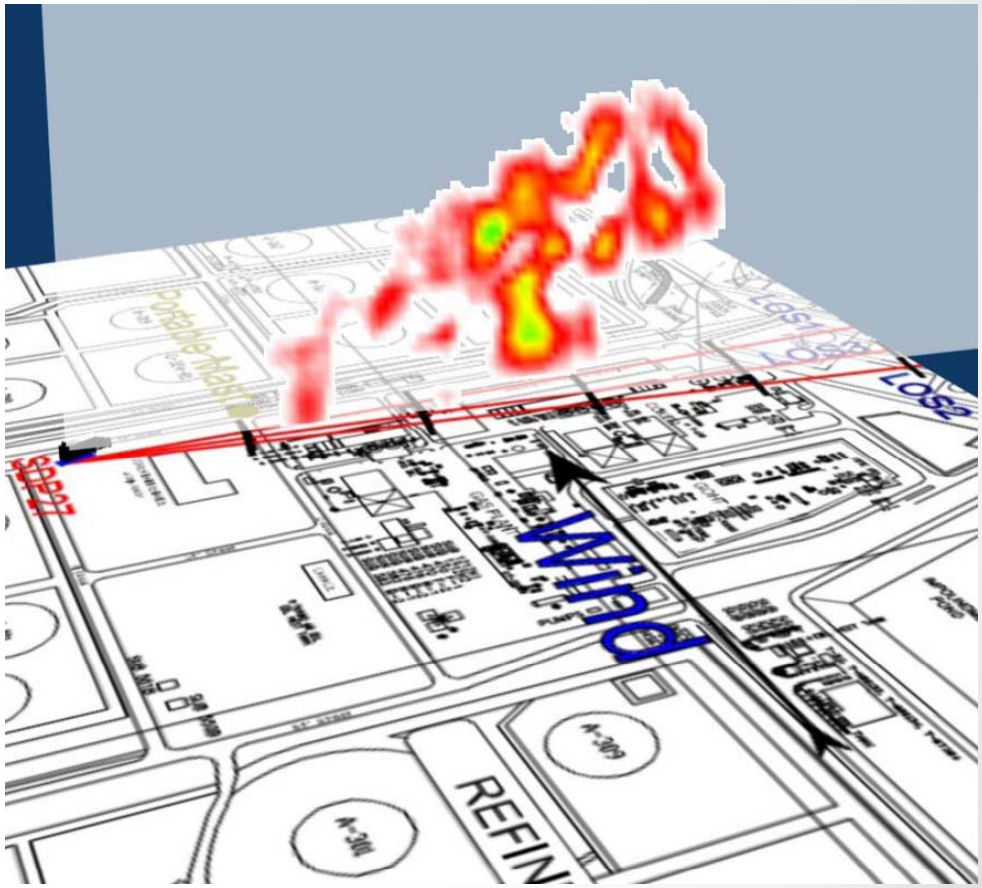
General Coker Area

2/11/2010 15:42-15:58
(27 lbs/hr benzene)

Scan 633, LOS2, Benzene from Coker Drums 5 &6

Single Scan, NPL DIAL Report Pages 94, 114 and 117

Note the location and elevation of the plume for potential monitoring applications



Coker Area Data

Date/Time	DIAL Result (lbs/hour)	Emissions Factor Based Calculations (lbs/hour)
1/16/2010, 10:58 -17:13 – NPL DIAL Report Pages 16, 72, 75	2 - 3 lbs/hour VOC	0.64 lbs/hour VOC
1/27/2010, 14:27 - 17:09 – NPL DIAL Report Pages 39, 73, 75	2 lbs/hour VOC	0.64 lbs/hour VOC
2/4/2010, 10:17 -16:50 – NPL DIAL Report Pages 54, 73, 75-76	3 -4 lbs/hour VOC	0.66 lbs/hour VOC
2/11/2010, 11:22 - 16:47 – NPL DIAL Report Pages 94, 114, 116-117	**5 - 27 lbs/hour Benzene**	0.0 lbs/hour Benzene
2/17/2010, 10:06 - 16:54 – NPL DIAL Report Pages 108, 114, 117; Reference in NPL report to **possible contributions from tanks and the dock**	22- 31 lbs/hour Benzene	0.01 lbs/hour Benzene
3/27/2010, 9:58- 16:51 – NPL DIAL Report pages 108, 114, 117	3 - 4 lbs/hour VOC	0.01 lbs/hour VOC

Emission Factor Calculations
Delayed Coker Drum De-heading Emissions

- Used factors from the Emission Estimation Protocol for Petroleum Refineries, Version 1.0, December 2009,Submitted to: OAQPS, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

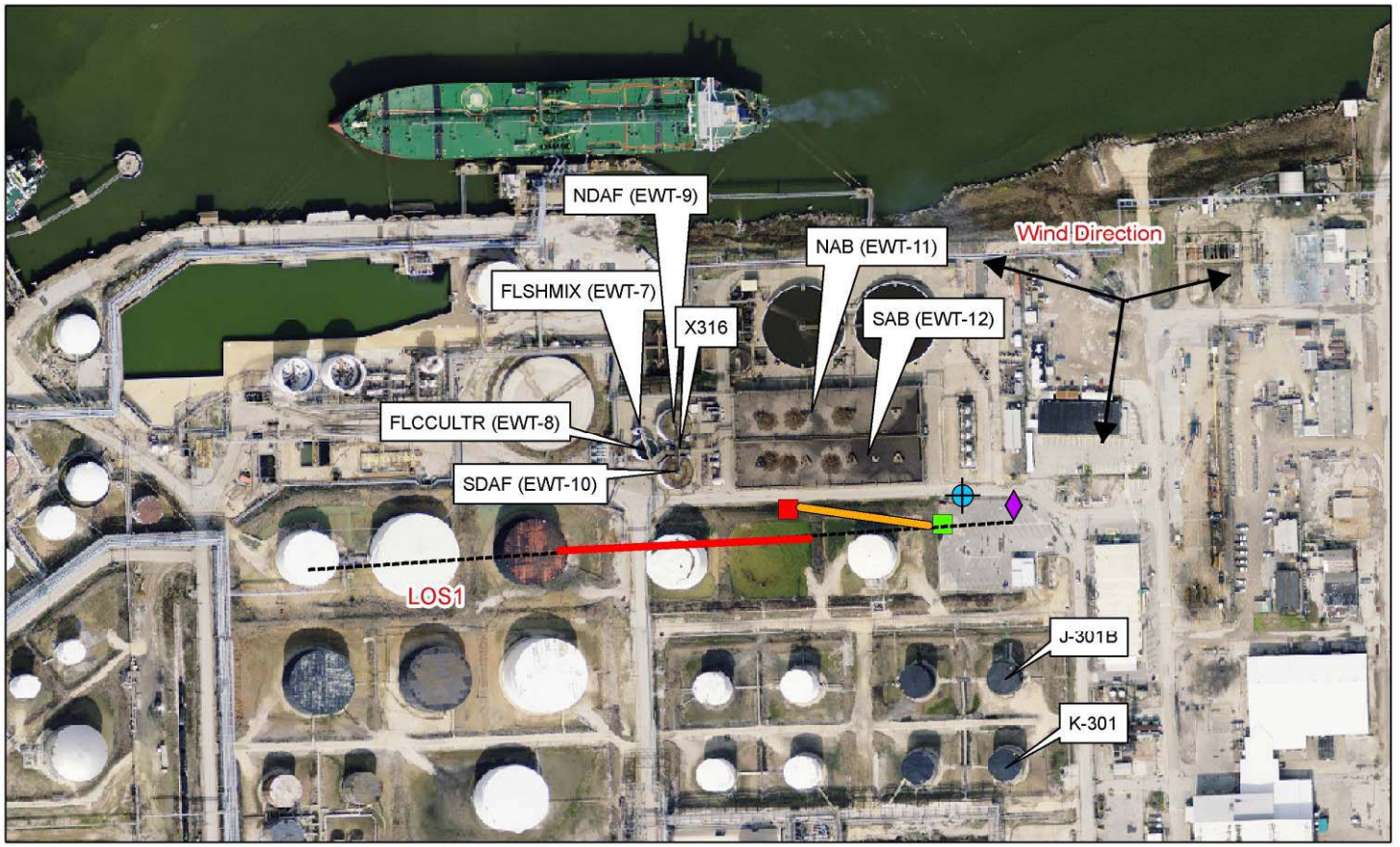
- There is only one set of emission factors available; inputs due to varying coke types (e.g. size) are currently not available.

Coker Area Data

DIAL measured benzene was not consistent with the measured VOC based on the feed composition to the Coker process.

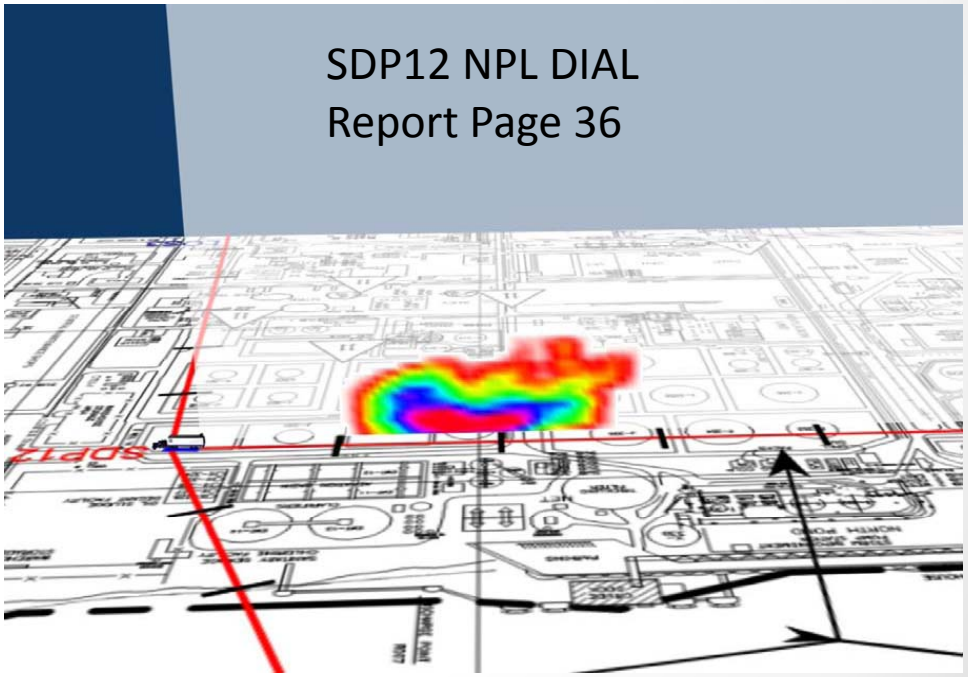
Waste Water Treatment-North Effluent Treater Area Data

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/25/10 (SDP12)



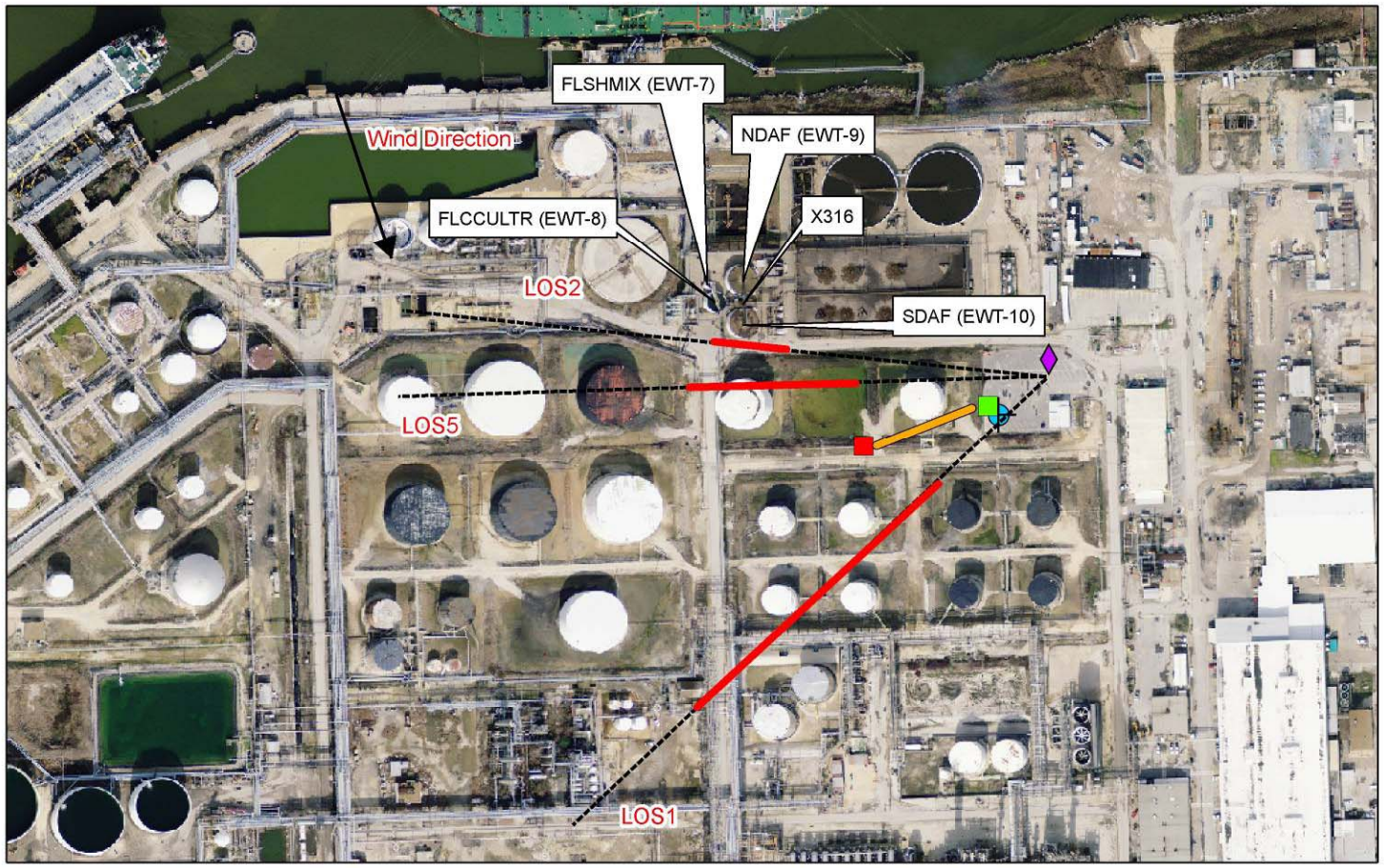
Waste Water Treatment-North Effluent Treater Area Data

- 22 lbs/hr VOC Alkane.
- 32.8 lbs/hr Total VOC based on composition data (NPL DIAL Report Page 135).
- 1/25/2010, 10:42-12:34 .(NPL DIAL Report Pages 35, 72 and 80) DAF skimmer was not functioning normally during this test.



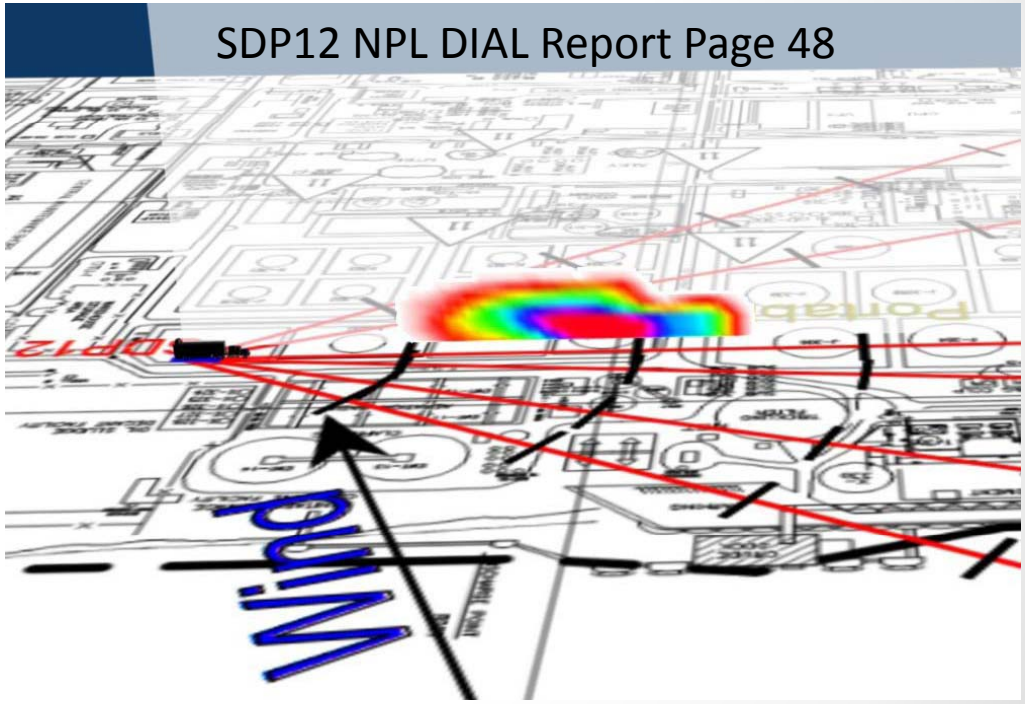
Waste Water Treatment-North Effluent Treater Area Data

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/30/10 (SDP12)



Waste Water Treatment-North Effluent Treater Area Data (continued)

- 1/30/2010, 10:42-12:56 (NPL DIAL Report Pages 35, 72 and 80)
- 800-1200 lbs/hr VOC Alkane
- Plume was 99% Alkane based on composition data (NPL DIAL Report Page 136)



Waste Water Treatment-North Effluent Treater Area Data

Date/Time	Report Reference	DIAL Result (lbs/hour)	Emissions Factor Based Calculations (lbs/hour)
1/25/2010, 10:42 - 12:34	NPL DIAL Report Pages 35, 72 and 80	22 lbs/hour VOC	6.5 lbs/hour VOC
1/30/2010, 12:26 - 17:01	NPL DIAL Report Pages 45, 73 and 80-81	**800 - 1200 lbs/hour** VOC	15 lbs/hour VOC
2/5/2010, 10:50 - 16:56	NPL DIAL Report Pages 57, 73 and 81	400 - 600 lbs/hour VOC	11.5 lbs/hour VOC
2/9/2010, 10:42 - 16:57	NPL DIAL Report Pages 88, 114 and 115-116	6 lbs/hour Benzene	0.019 lbs/hour Benzene
2/13/2010 ,12:53 - 16:42	NPL DIAL Report Pages 100, 114 and 116	4 lbs/hour Benzene	0.20 lbs/hour Benzene

Waste Water Treatment-South Effluent Treater Area Data

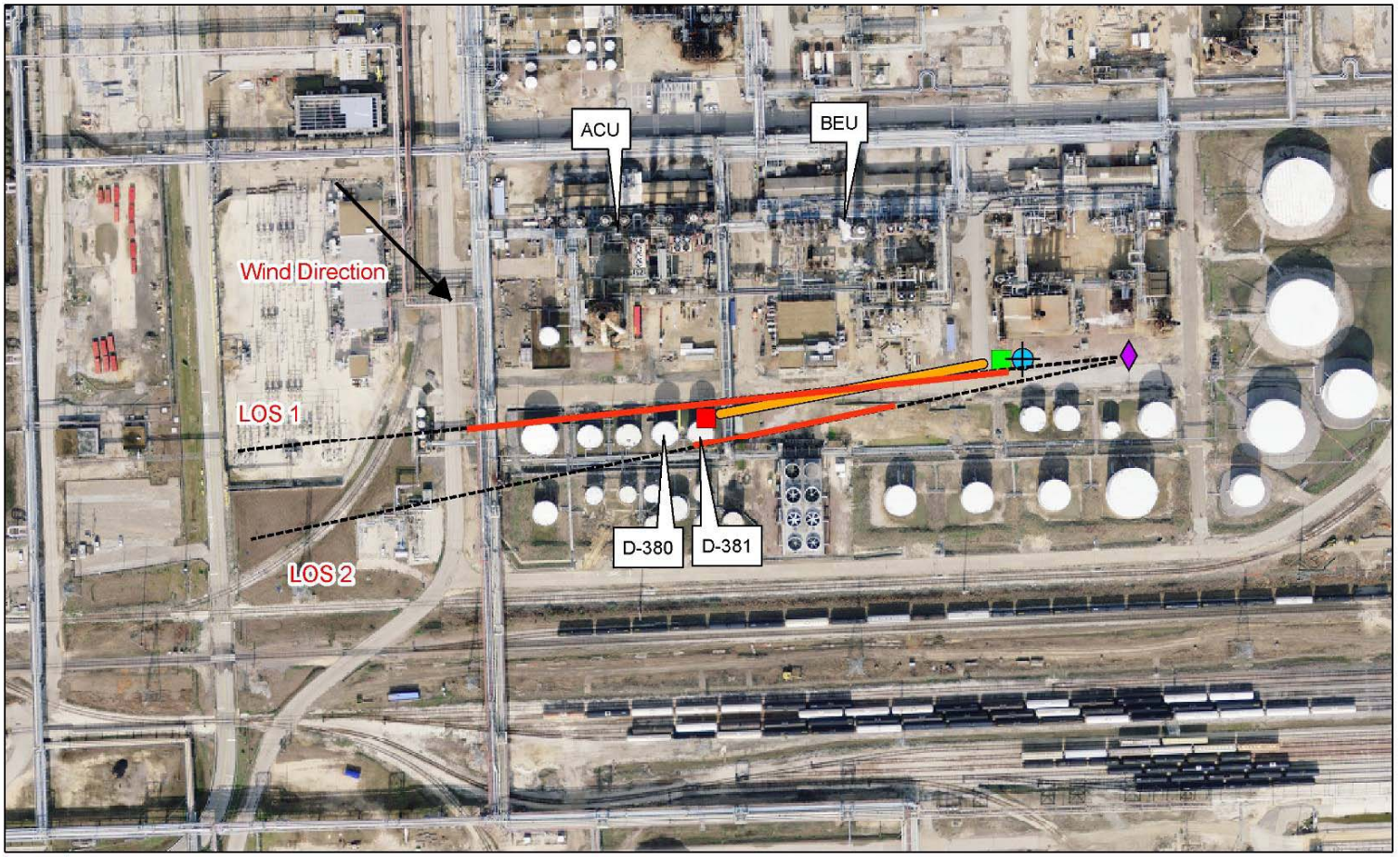
Date/Time	Report Reference	DIAL Result (lbs/hour)	Emissions Factor Based Calculations (lbs/hour)
2/1/2010, 12:16 - 17:05	NPL DIAL Report Pages 49, 73 and 82	23 - 27 lbs/hour VOC	5.88 lbs/hour VOC

Wastewater Treatment

- Emissions data were calculated with factors from EPA approved wastewater protocols.
- Flow rates, temperatures and composition data are inputs to the model.

Tank Emissions – D-380 and D-381

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



Tank Emissions – D-380 and D-381

February 15, 2010: Tank just south of ACU/BEU complex

Tank D-381: Internal floating roof, Temp 86 deg F, VOC Vapor Pressure 2.4 psia, Filling at 1.09 ft/hr from 11:47 to 17:00 (No process data for Tank D-380)

DIAL Benzene (lbs/hr) per Scan, LOS2, NPL DIAL Report Page 103

11:23-11:38: **29**

11:40-11:58: **18**

11:59-12:17: 141

13:35-13:53: **61**

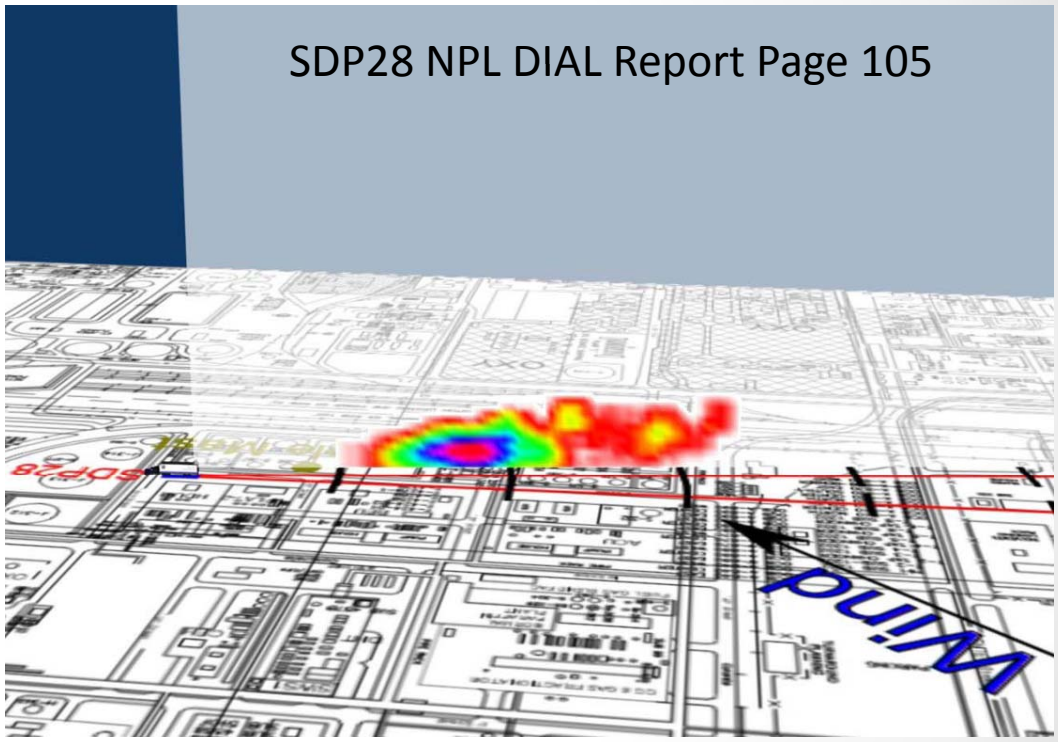
13:54-14:12: **53**

15:17-15:38: **43**

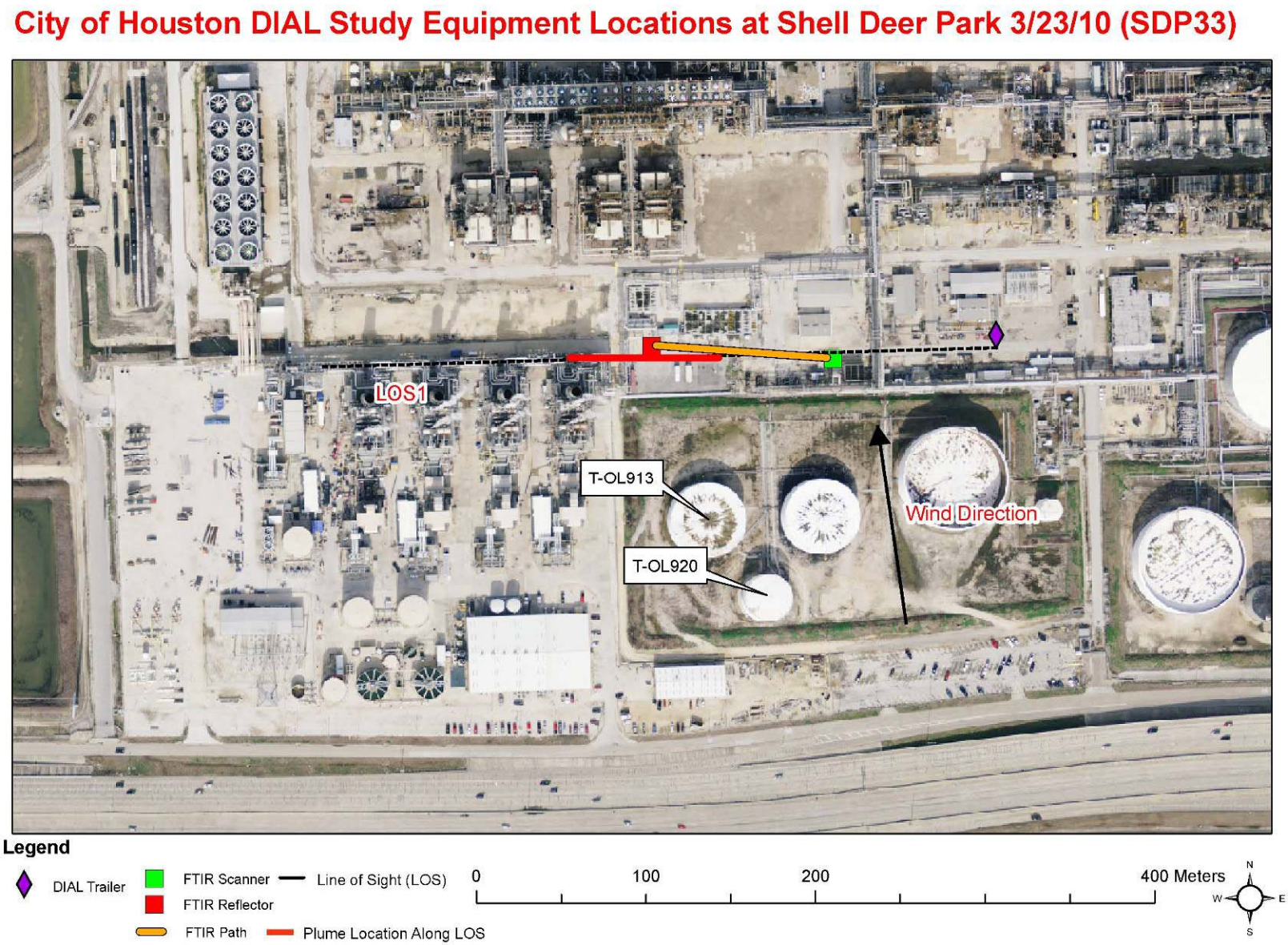
15:46-16:11: **32**

16:19-16:37: **21**

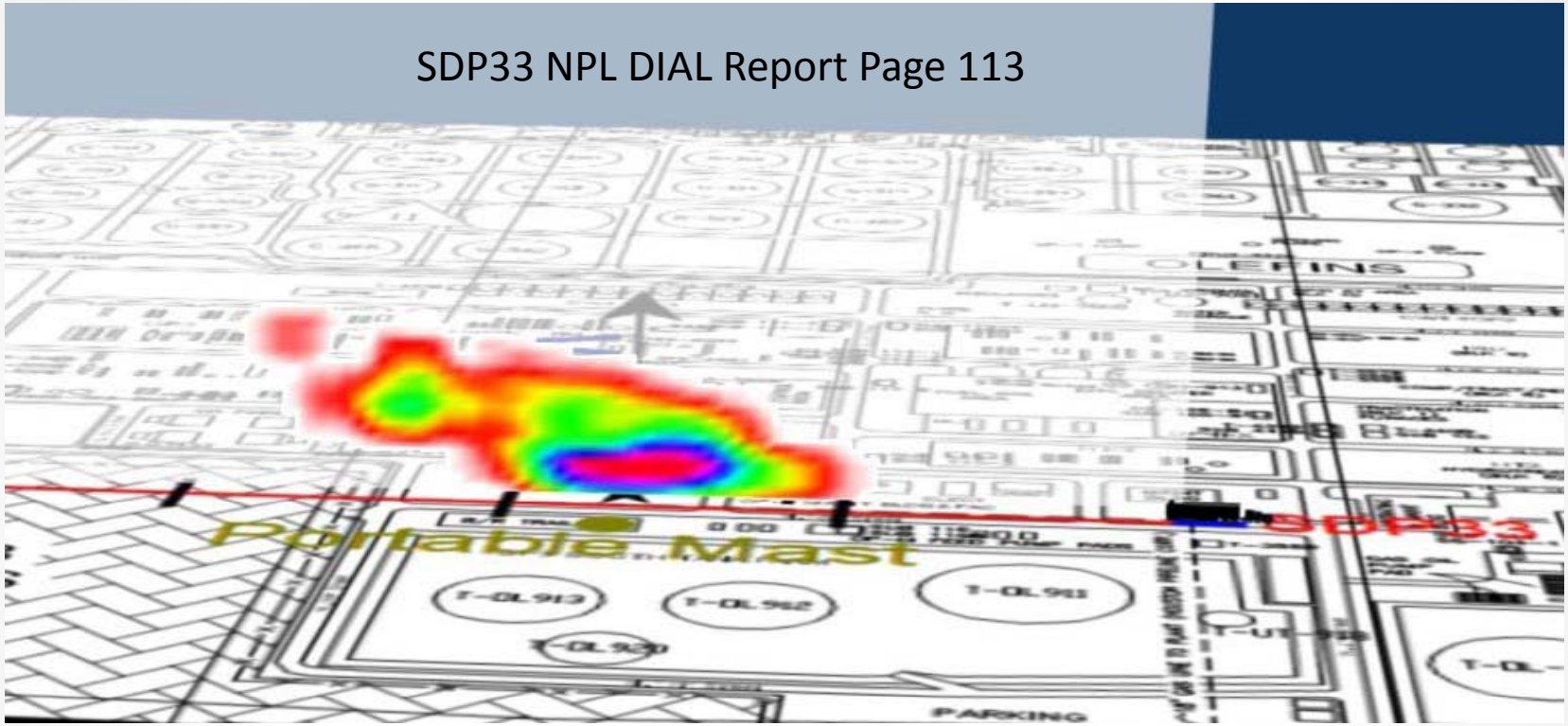
17:03-17:13: **12**



Tanks TOL-913/TOL-920



Tanks TOL-913/TOL-920



3/23/2010, 10:18-17:05 **(Benzene, 25 lbs/hr) NPL DIAL Report Pages 112, 114 and 115**

Tank Emissions

Floating Roof Tanks
D-350, D352, D-371, D-370, D-380 and D-381

Tank	Date/Time	Report Reference	Tank DIAL Result (lbs/hour)	Emission Factor Based Calculations (lbs/hour)
D-350	02/12/10 16:49-17:46	NPL DIAL Report Pages 97, 114 &117-118	**25 lbs/hour** Benzene	0.03 lbs/hour Benzene
D-352	03/22/10 12:29-16:45	NPL DIAL Report Pages 110, 114 & 118	5 lbs/hour Benzene	0.02 lbs/hour Benzene
D-351	02/12/10 16:49-17:46	NPL DIAL Report Pages 97, 114 & 117-118	**25 lbs/hour** Benzene	0.09 lbs/hour Benzene
D-371	02/15/10 11:00-17:00	NPL DIAL Report Page 103	Not Available	0.02 lbs/hour Benzene
D-370	02/15/10 11:00-17:00	NPL DIAL Report Page 103	Not Available	0.02 lbs/hour Benzene
D-380	02/15/10 11:23-17:13	NPL DIAL Report Page 103	13 lbs/hour Benzene	0.25 lbs/hour Benzene
D-381	02/15/10 11:23-17:13	NPL DIAL Report Page 103	13 lbs/hour Benzene	0.30 lbs/hour Benzene

Tank Emissions

Tanks AP 16 &17 and G-324

Type	Tank	Date/Time	Report Reference	Tank DIAL Result (lbs/hour)	Emission Factor Based Calculations (lbs/hour)
Fixed	AP-16	01/15/10 13:42-16:50	NPL DIAL Report Pages 12, 72 & 74	**51 lbs/hour VOC**	0.14 lbs/hour VOC
Fixed	AP-17	01/15/10 13:42-16:50	NPL DIAL Report Pages 22, 72 and 74	**51 lbs/hour VOC**	0.25 lbs/hour VOC
Fixed	AP-17	01/19/10 12:00-14:00	NPL DIAL Report Page 74	43 lbs/hour VOC	0.46 lbs/hour VOC
Floating	G-324	01/14/10 12:32-17:12	NPL DIAL Report Pages 8, 72 and 74-75	16 lbs/hour VOC	0.26 lbs/hour VOC

Tank Emissions

Distilling Kerosene Tanks J-327 and J-328

Type	Tank	Date/Time	Report Reference	Tank DIAL Result (lbs/hour)	Emission Factor Based Calculations (lbs/hour)
Fixed	J-327	01/22/10 15:53-17:03	NPL DIAL Report Pages 31, 72 & 78	**31 lbs/hour VOC**	0.14 lbs/hour VOC
Fixed	J-327	01/23/10 10:57-17:06	NPL DIAL Report Pages 33, 72 & 78	5-19 lbs/hour VOC	0.15 lbs/hour VOC
Fixed	J-327	01/28/10 11:23-16:41	NPL DIAL Report Pages 41, 73 & 78	**32-33 lbs/hour VOC**	0.11 lbs/hour VOC
Fixed	J-328	01/22/10 15:53-17:03	NPL DIAL Report Pages 31, 72 & 78	**31 lbs/hour VOC**	0.12 lbs/hour VOC
Fixed	J-328	01/23/10 10:57-17:06	NPL DIAL Report Pages 33, 72 & 78	5-19 lbs/hour VOC	0.12 lbs/hour VOC
Fixed	J-328	01/28/10 11:23-16:41	NPL DIAL Report Pages 41, 73 & 78	**32-33 lbs/hour VOC**	0.16 lbs/hour VOC

Tank Emissions

Hydrocracker Feed Tanks J-331 and J-332

Type	Tank	Date/Time	Report Reference	Tank DIAL Result (lbs/hour)	Emission Factor Based Calculations (lbs/hour)
Fixed	J-331	01/22/10 15:53-17:03	NPL DIAL Report Pages 31, 72 & 78	31 lbs/hour VOC	0.54 lbs/hour VOC
Fixed	J-331	01/23/10 10:57-17:06	NPL DIAL Report Pages 33, 72 & 78	5-19 lbs/hour VOC	0.43 lbs/hour VOC
Fixed	J-331	01/28/10 11:23-16:41	NPL DIAL Report Pages 41, 73 & 78	32-33 lbs/hour VOC	0.06 lbs/hour VOC
Fixed	J-332	01/23/10 10:57-17:06	NPL DIAL Report Pages 41, 73 & 78	5-19 lbs/hour VOC	0.31 lbs/hour VOC
Fixed	J-332	01/28/10 11:23-16:41	NPL DIAL Report Pages 33, 72 & 78	32-33 lbs/hour VOC	0.06 lbs/hour VOC

Tank Emissions

Floating Roof Tanks TOL-913 and TOL-920

Tank	Date/Time	Report Reference	Tank DIAL Result (lbs/hour)	Emission Factor Based Calculations (lbs/hour)
TOL-913	02/08/10 14:15-17:23	NPL DIAL Report Pages 86, 114 & 115	6 lbs/hour benzene	1.15 lbs/hour benzene
TOL-913	02/10/10 9:55-17:05	NPL DIAL Report Pages 91, 114 &115	5 lbs/hour benzene	1.17lbs/hour benzene
TOL-913	03/23/10 10:18-17:05	NPL DIAL Report Pages 112, 114 & 115	**25 lbs/hour benzene**	1.18lbs/hour benzene
TOL-920	02/08/10 14:15-17:23	NPL DIAL Report Pages 86, 114 & 115	6 lbs/hour benzene	0.83 lbs/hour benzene
TOL-920	02/10/10 9:55-17:05	NPL DIAL Report Pages 91, 114 & 115	5 lbs/hour benzene	0.83lbs/hour benzene
TOL-920	03/23/10 10:18-17:05	NPL DIAL Report Pages 112, 114 & 115	**25 lbs/hour benzene**	0.83lbs/hour benzene

The measurements on 2/8/2010 and 2/10/2010 may be biased low because lower Elevation scan angles may have been partially blocked by structures.
NPL DIAL Report Page 115

Tank Emissions

Floating Roof Tanks A-310, A-326, A-330, A-332, A333 and A-325

Tank	Date/Time	Report Reference	Tank DIAL Result (lbs/hour)	Emission Factor Based Calculations (lbs/hour)
A-310	01/14/10 12:32-17:12	NPL DIAL Report Pages 8, 72 & 74-75	16 lbs/hour VOC	0.17 lbs/hour VOC
A-326	01/15/10 11:35-13:21	NPL DIAL Report Pages 12, 72 & 74	lbs/hour VOC	0.34 lbs/hour VOC
A-330	01/13/10 12:26-17:36	NPL DIAL Report Pages 6, 72 & 73-74	16-19 lbs/hour VOC	0.45 lbs/hour VOC
A-332	01/13/10 12:26-17:36	NPL DIAL Report Pages 6, 72 &73-74	16-19 lbs/hour VOC	1.27 lbs/hour VOC
A-333	01/13/10 12:26-17:36	NPL DIAL Report Pages 6, 72 & 73-74	16-19 lbs/hour VOC	0.43 lbs/hour VOC
A-325	01/15/10 11:35-13:21	NPL DIAL Report Pages 12, 72 & 74	11 lbs/hour VOC	0.22 lbs/hour VOC

Tank Emissions *(continued)*

Date	Method	Tank	Result (ppm = parts per million)
2/9/2010	FLIR IR Camera	A-318	No emissions detected
2/10/2010	FLIR IR Camera	TOL-913	No emissions detected
2/16/2010	FLIR IR Camera	D-380	No emissions detected
2/16/2010	FLIR IR Camera	D-381	No emissions detected
2/16/2010	Gas Chromatograph	D-380	2.05 ppm Air sample collected at the tank vents while tank was in the running gauge mode
2/16/2010	Gas Chromatograph	D-381	36.8 ppm Air sample collected at the tank vents while filling, 0.712 ppm in static mode

Inspection records were checked on all tanks and no abnormal conditions were noted.

The FLIR infrared camera utilizing an optical imagining technology provides a quick and accurate measurement of hydrocarbon emission leaks.

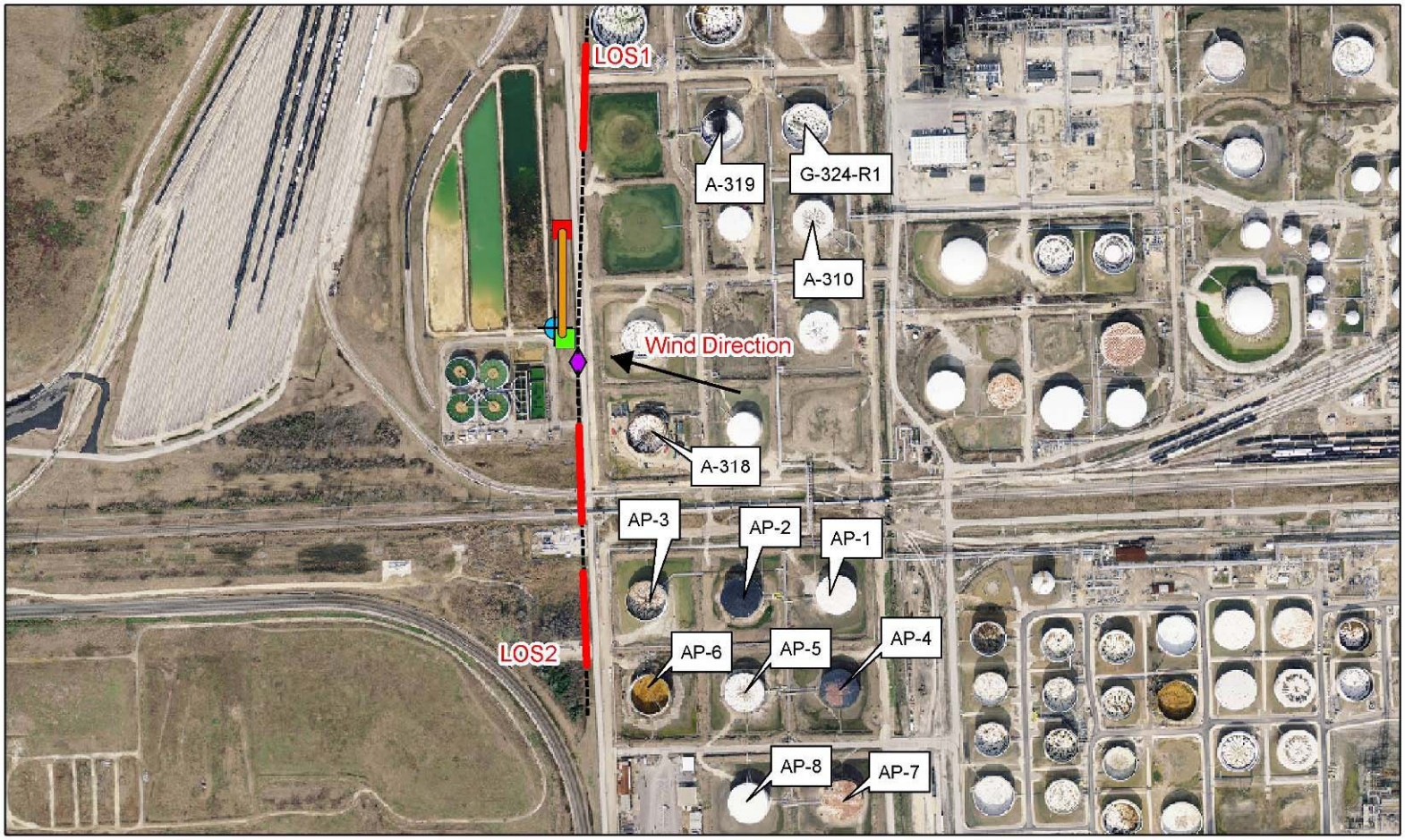
Tank Emission Factor Based Calculations

- Used EPA's Tanks 4.0 method to determine tank emission factors.

- Tank operating parameters used in Tanks 4.0 to calculate tank emissions.
  - Maximum tank throughput and temperature of contents.
  - Vapor pressure based on maximum temperature.
  - External factors such as solar absorption factors were obtained from EPA's Tanks 4.0.

Tank A-318 Maintenance *(continued)*

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/14/10 (SDP02)



Legend

DIAL Trailer
MAAML
FTIR Scanner
FTIR Reflector
FTIR Path
Line of Sight (LOS)
Plume Location Along LOS

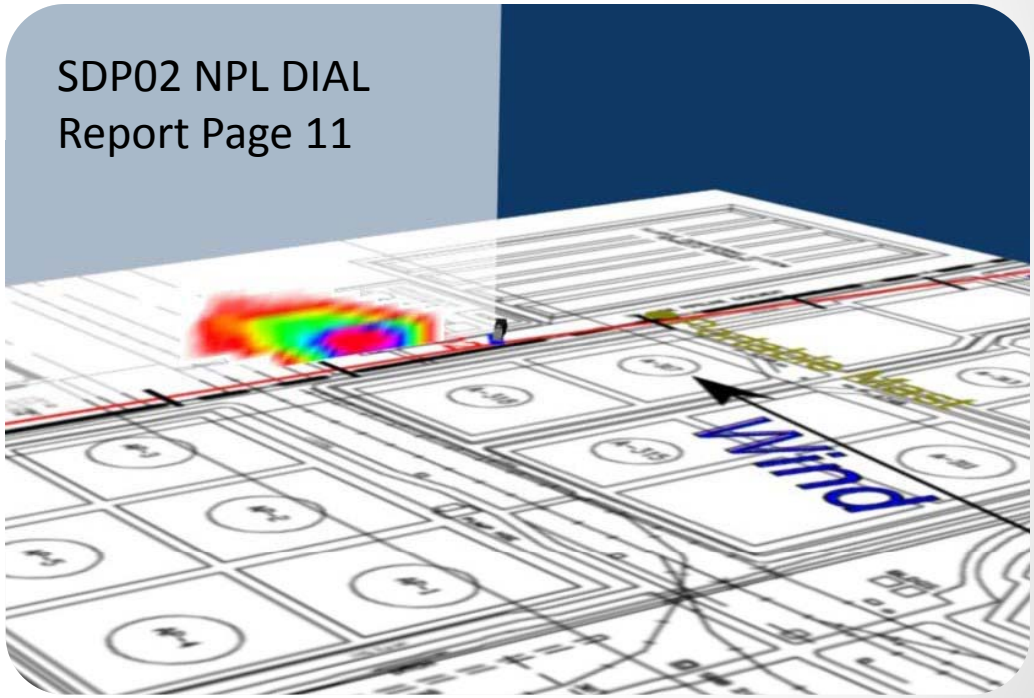
0 100 200 400 Meters

N W E S

Tank A-318 Maintenance *(continued)*

1/14/2010, 15:56-16:08 (**4000 lbs/hr VOC Alkane**) Single Scan, NPL DIAL Report Pages 8, 72, 74-75.

A single scan found the noted emission rate, but scans before and after may have missed this source as the winds shifted and the plume may have been too close to the DIAL.



Tank A-318 Maintenance *(continued)*

Type	Tank	Date	Time	Tank	Emission Factor Based
				DIAL Result (lbs/hour)	Calculations (lbs/hour)
Floating	A-318	1/14/2010	15:56-16:08	**4,000 lbs/hour VOC**	Maintenance activity

Single Scan NPL DIAL Report Pages 8, 72, 74-75.

Shifting winds and the closeness of the plume to the DIAL may have affected the results (i.e., we didn't pick up the plume until the wind shifted)

Tank A-318 Maintenance

- This tank had been out of service several months before NPL took the DIAL measurement.
- Approximately two inches of heavy low vapor pressure asphalt like material was in the bottom of the tank at the time of the test.
- Cutter stock had previously been used as part of the cleaning process, but was not in use at the time of the testing.

Uncertainties Associated with DIAL Measurements

Factors Contributing to Uncertainties

- Measurement uncertainties: instrumental variability in measuring IR and UV absorptions.
- Concentration uncertainties: uncertainties associated in using absorption data measured at a single wavelength to determine concentrations of VOC and benzene.
- **Wind field uncertainties: associated with applying wind speed data measured at one or two locations to a different elevated location where DIAL absorption is measured.**
- Emissions uncertainties: questions regarding impact of "wake effects" from nearby structure and roadways on calculated emissions rates or emissions from nearby units.

Summary of Results

- The DIAL method has uncertainty in measurement and uncertainty in converting from concentrations to mass rates.
- During the time period studied, the mass emissions calculated using recognized and widely used emission factors were lower than the DIAL results.
- Further study is warranted given the size of the difference in emissions determined by the two methods.

Questions?

We will spend a minute reviewing questions and then respond…