Overview

- HDHHS BPCP conducted a comprehensive survey project of emissions from a combined petroleum refinery and chemical plant complex in the Houston Ship Channel area.
- Source of emissions of benzene and other volatile organic compounds.
- Used Differential Absorption Light Detection and Ranging (DIAL)

Method

- 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.

Talk Objectives

1. Explore the comparability of DIAL with MAAML and FTIR and use of plume composition
2. Present measured emissions by process area
3. Compare measured and emission factor emissions

Scope of Talk

- Assume DIAL measurements are accurate (i.e., this study does not test DIAL but uses DIAL results to understand emissions)
- For detailed questions regarding field activities contact, Co-author and project manager, Dan Hoyt Hoyt.Daniel@epamail.epa.gov
- Don Richner, CIH will discuss the DIAL methodology following this presentation

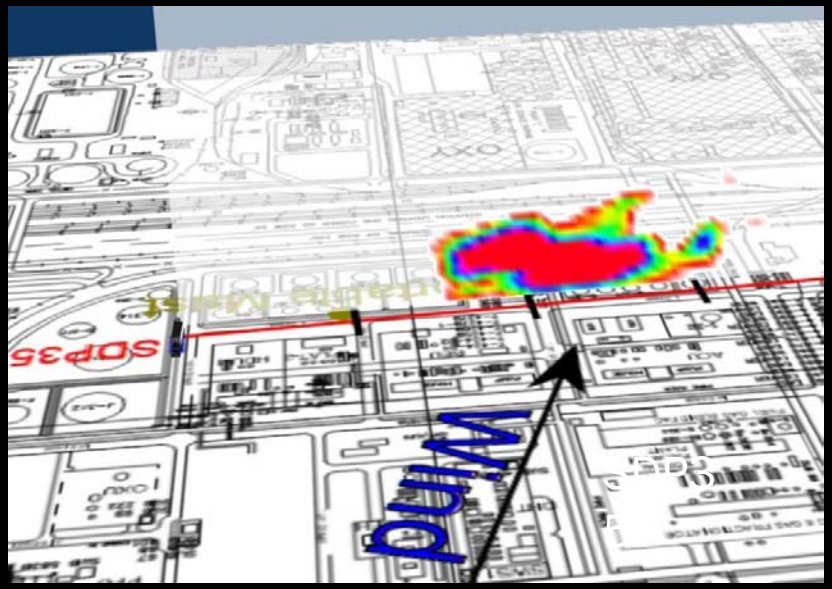
Differential Absorption Light Detection and Ranging (DIAL)

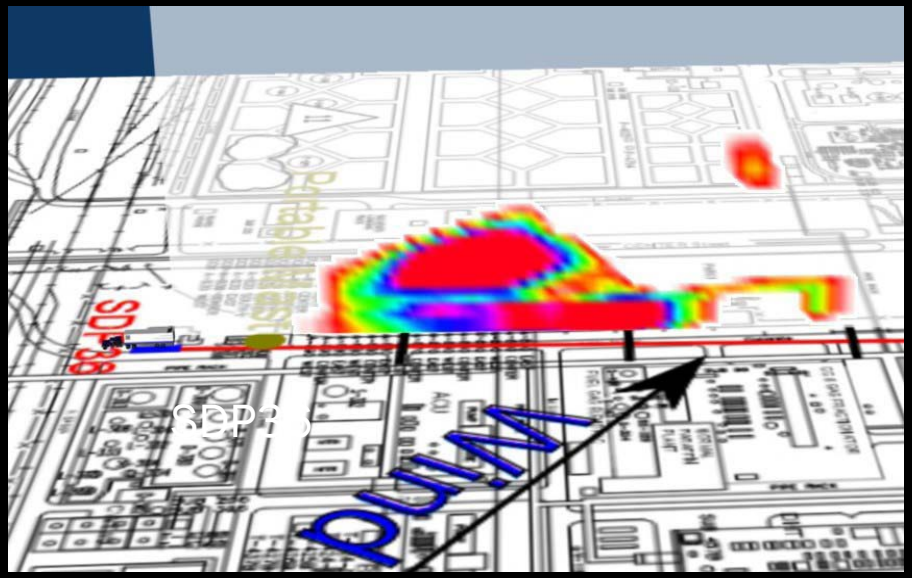
- DIAL was located so that measurements occurred along a vertical plane, perpendicular to the predominant wind direction and downwind from any sources of interest.
- DIAL provided plume locations and estimated concentrations of either alkane VOC or benzene.
- Benzene and VOC emissions rates were estimated by integrating DIAL measured concentrations along the vertical plane with the wind data.

Contractor was NPL:

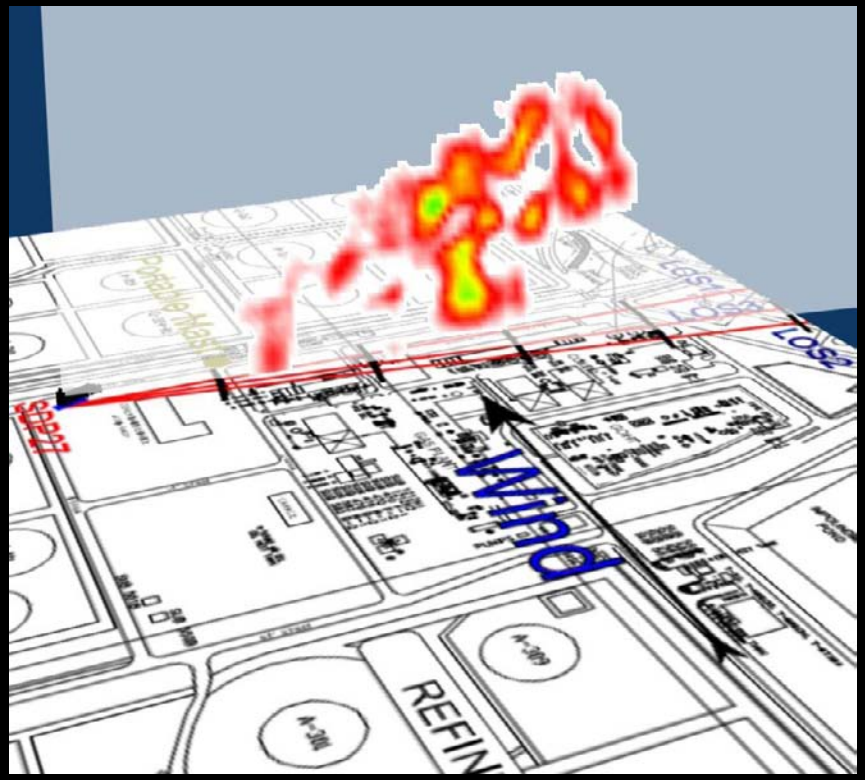
"Differential Absorption Lidar (DIAL) Measurements of VOC and Benzene Emissions from a Refinery Site in Houston, TX, US, January/February/March 2010"

ACU/BEU Area Emissions

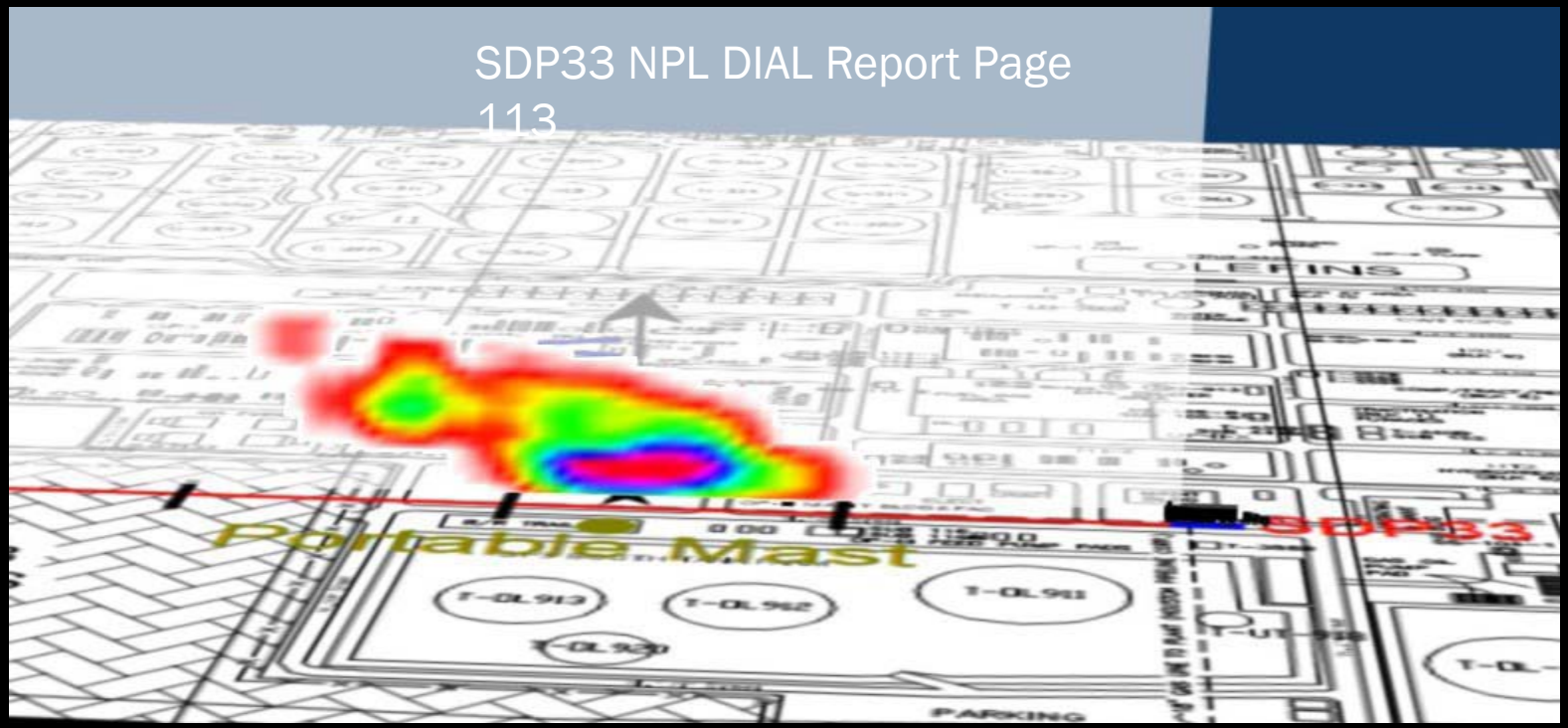




General Coker Area



Tanks T0L-913/T0L-920



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,
- Location was at times within 50 meters of the DIAL unit, referred to as the "DIAL dead zone."
- Plan was to place the MAAML in the location where the plume was detected/expected, but site constraints prevented this approach

Open-Path Fourier Transform Infrared (FTIR)

- FTIR placed outside of the "DIAL dead zone," 2 m above ground level, 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.
- 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

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.

MAAML Data

Collected simultaneously with DIAL to:

1. validate extreme events detected by DIAL and
2. to provide chemically speciated plume descriptions.

Rationale for MAAML and FTIR

Overlapping objectives but, the MAAML and the FTIR have different strengths.

MAAML :

- Larger list of speciation constituents at lower detection limits than the FTIR
- Drawbacks- point monitor and hourly sample duration.

FTIR:

- Can be more closely aligned with the DIAL path since it measures along a linear path as DIAL does.
- FTIR results are reported in minutes.
- Drawbacks -smaller list of speciation constituents and higher detection limit.

Process Areas Studied

- 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.

Results for Objective 1: Evaluate and verify the DIAL system benzene and VOC measurements using MAAML and the FTIR

- Conclusion: correlation coefficient did not fully reflect the degree of agreement or inappropriate
- Reason: location constraints, comparing emissions to concentration under fluctuating wind speed, varying detection limits, sample time durations, and measurement techniques

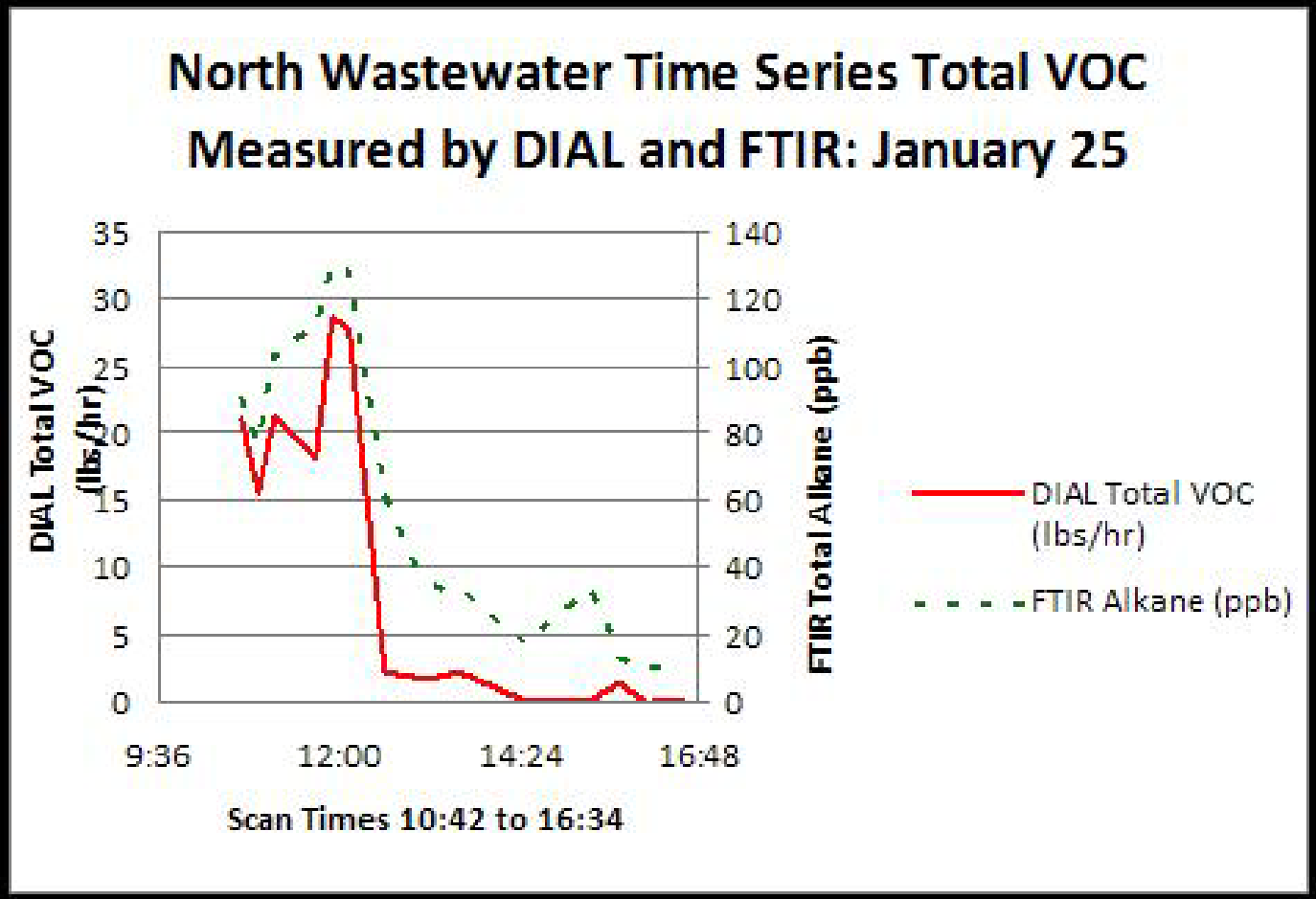
Results for Objective 1: Evaluate and verify the DIAL system benzene and VOC measurements using MAAML and the FTIR

- Alternative approach:

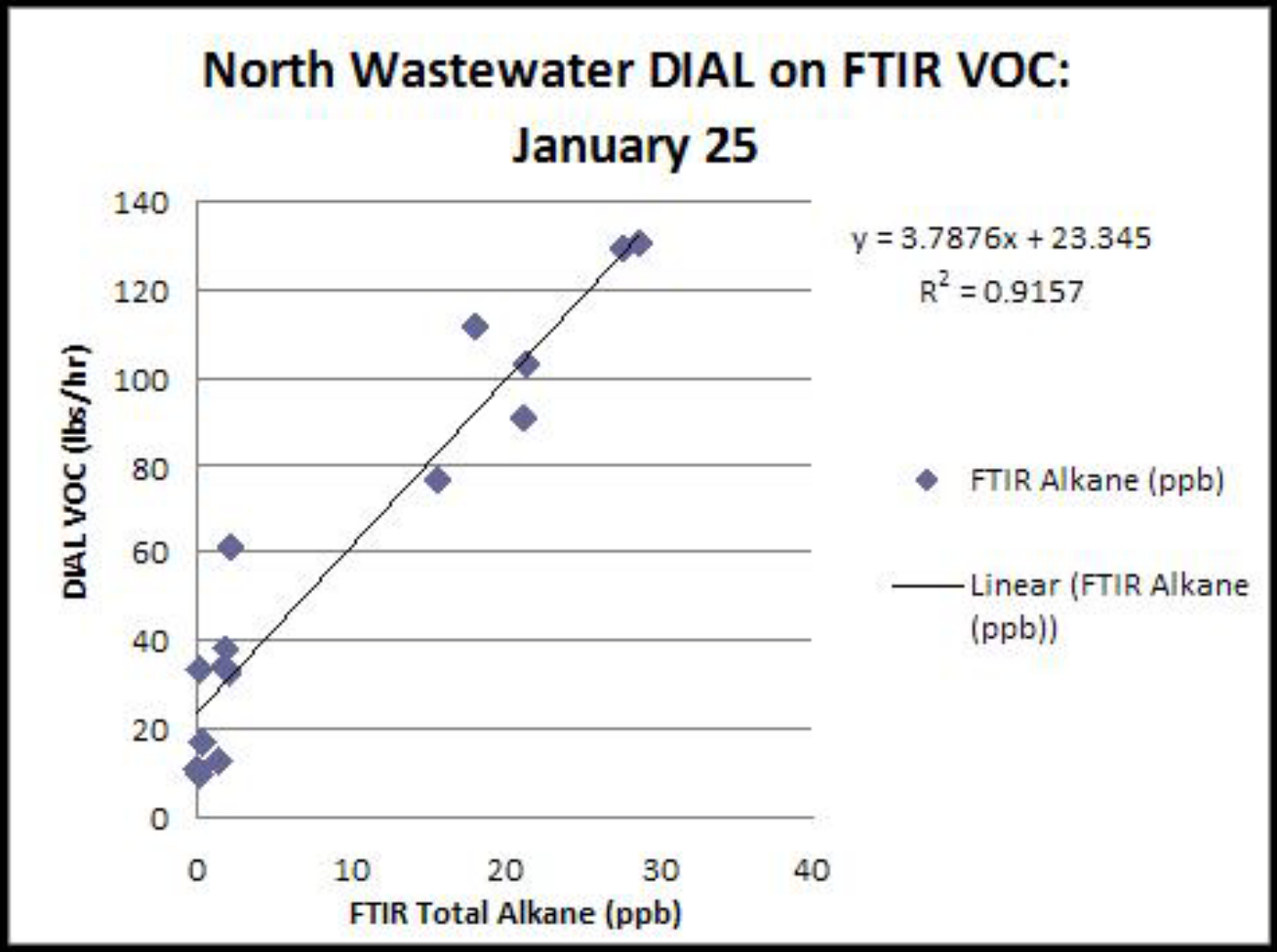
"How well do the techniques compare?"

"In the future, how can we better design the study so that these techniques can be used to estimate emissions?"

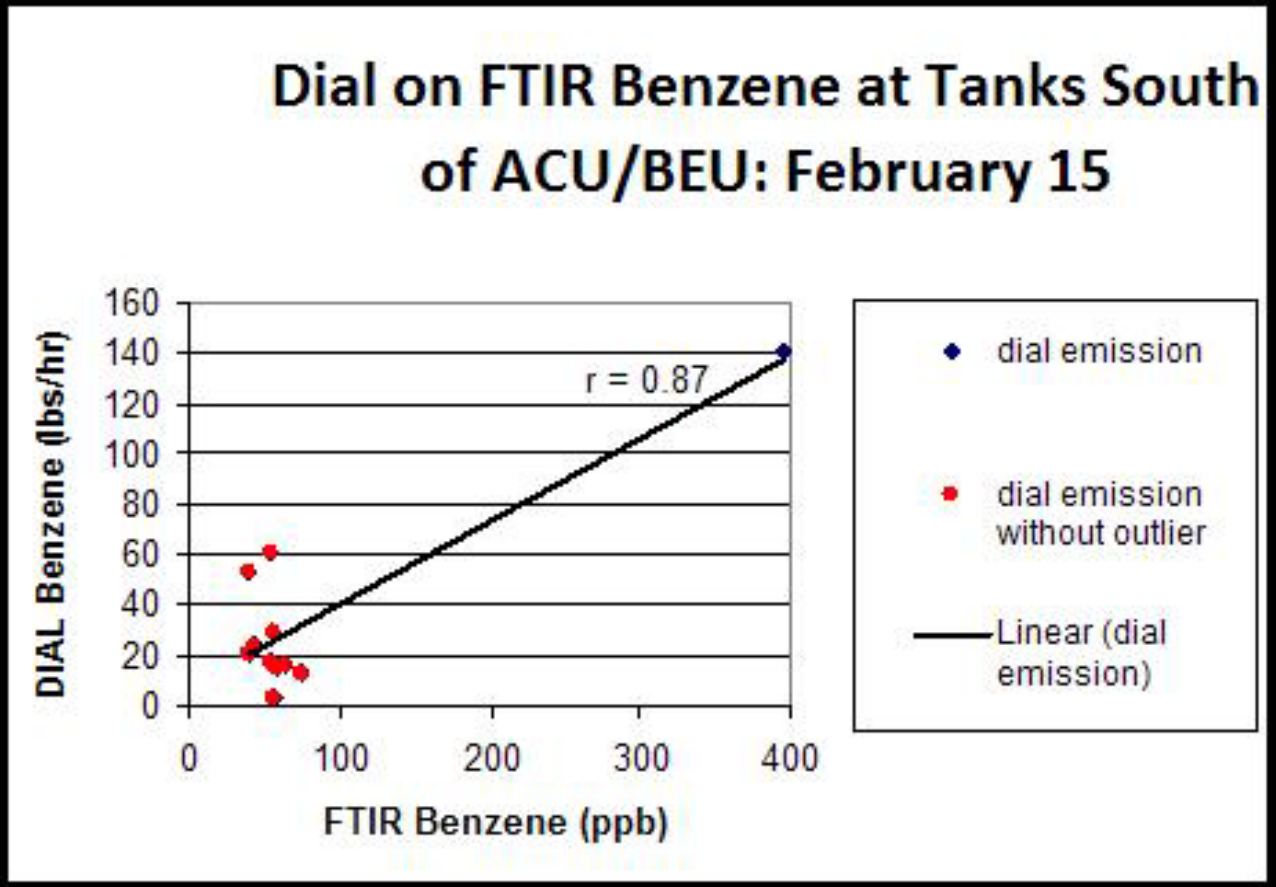
Results for Objective 1:
Best Example of Match was DIAL VOC emission rate (lbs/hr) and FTIR total alkane (ppb)



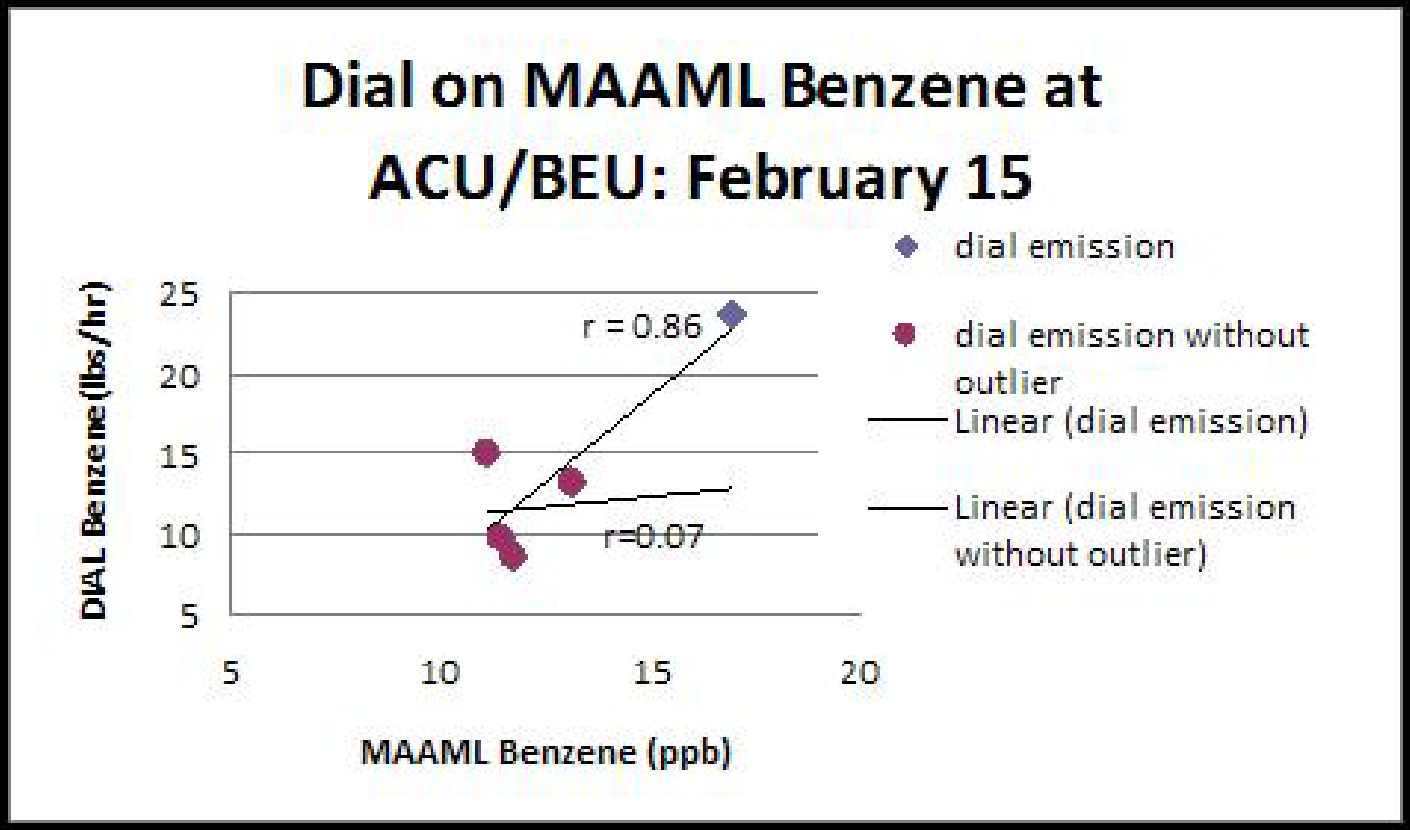
Results for Objective 1:
Best Example of Match was DIAL VOC emission rate (lbs/hr) and FTIR total alkane (ppb)



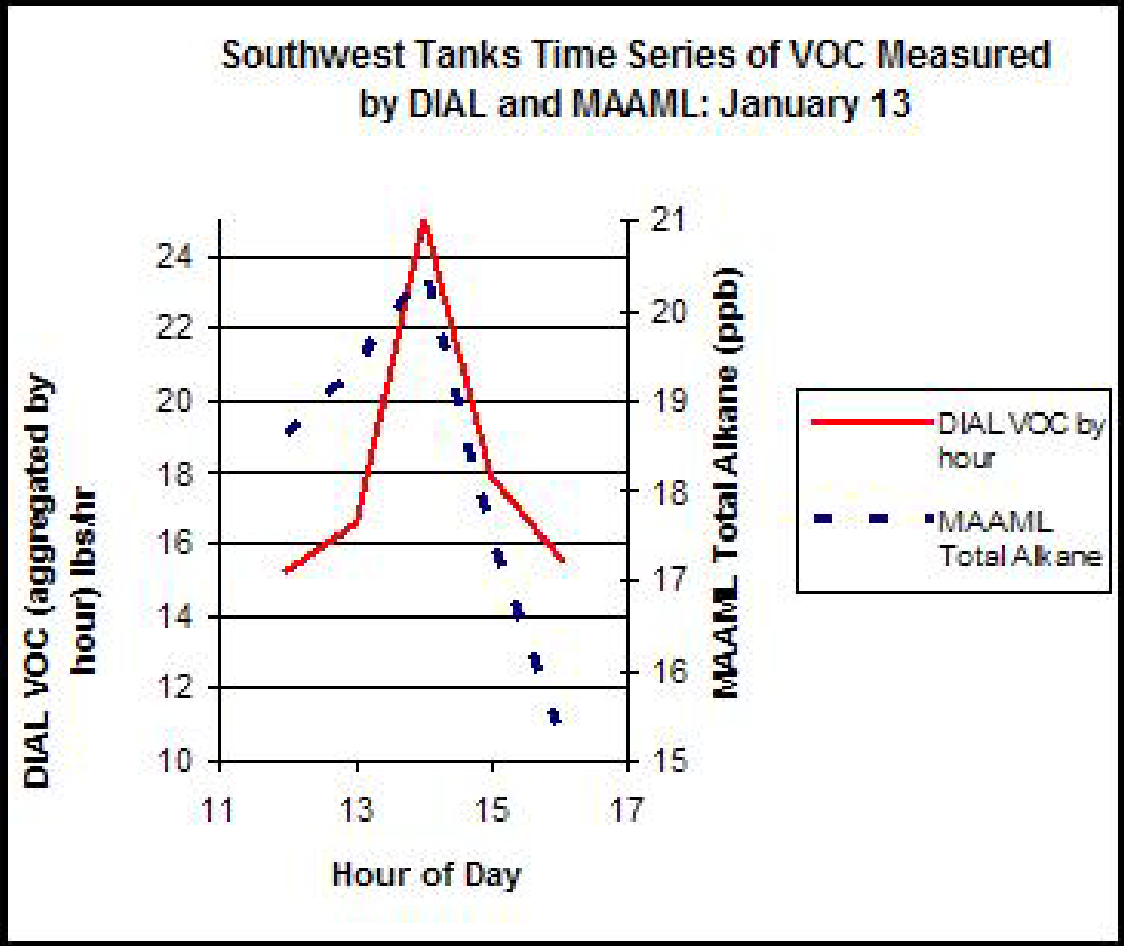
Results for Objective 1: Inappropriate use of DIAL VOC emission rate (lbs/hr) and FTIR total alkane (ppb)



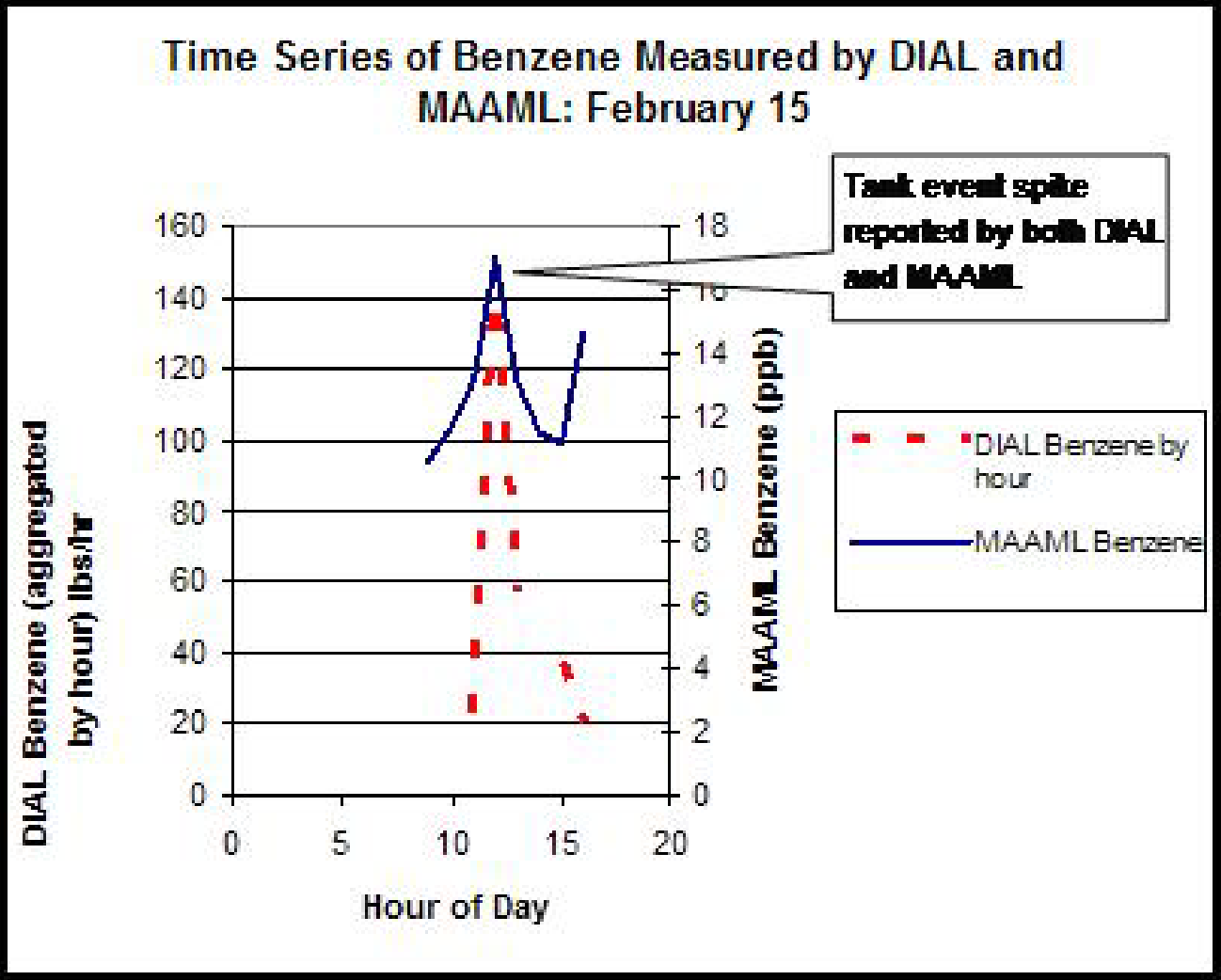
Results for Objective 1: Inappropriate use of correlation for DIAL Benzene emission rate (lbs/hr) and MAAML (ppb)



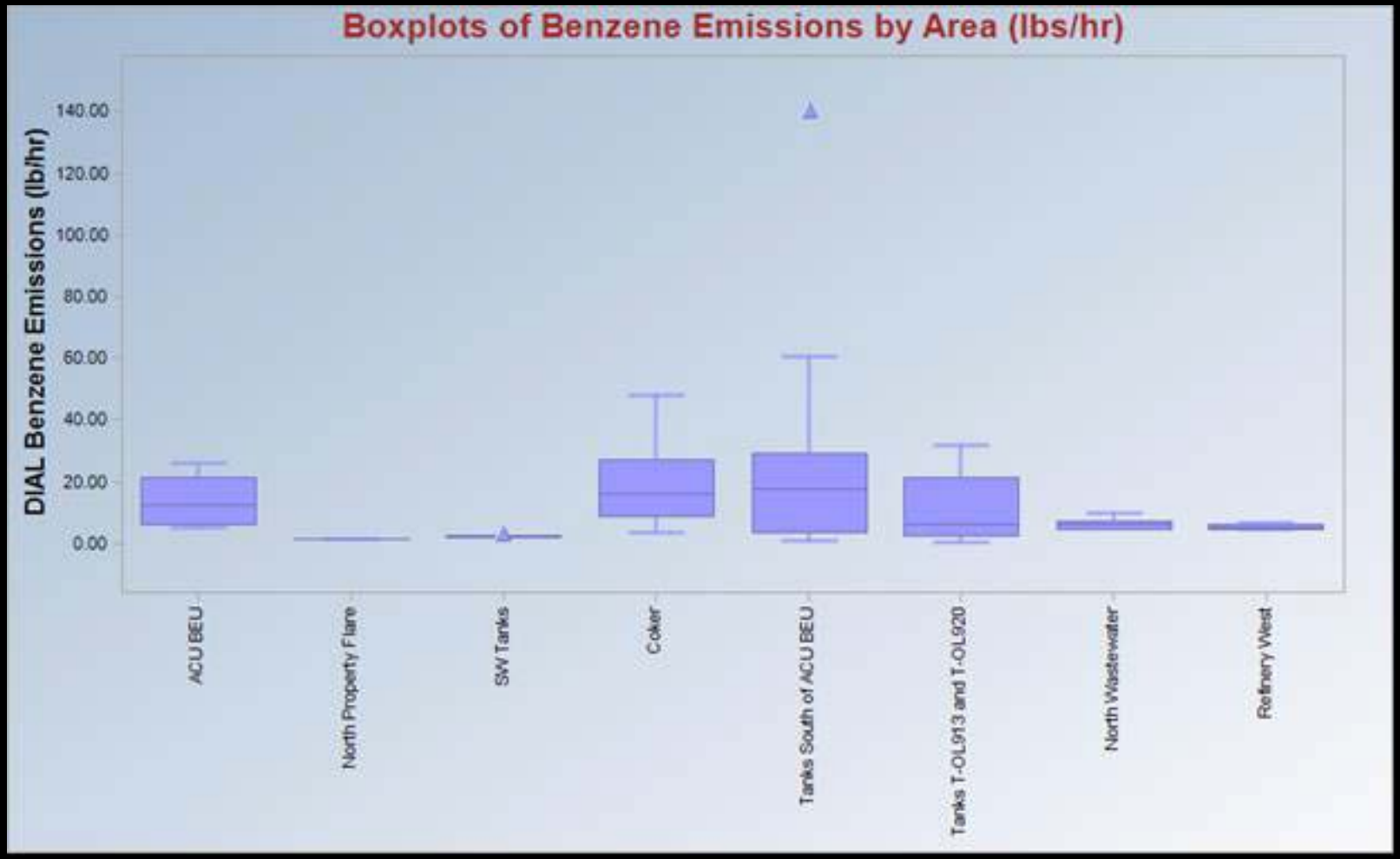
Results for Objective 1: Similar Pattern of DIAL VOC emission rate (lbs/hr) and MAAML (ppb)



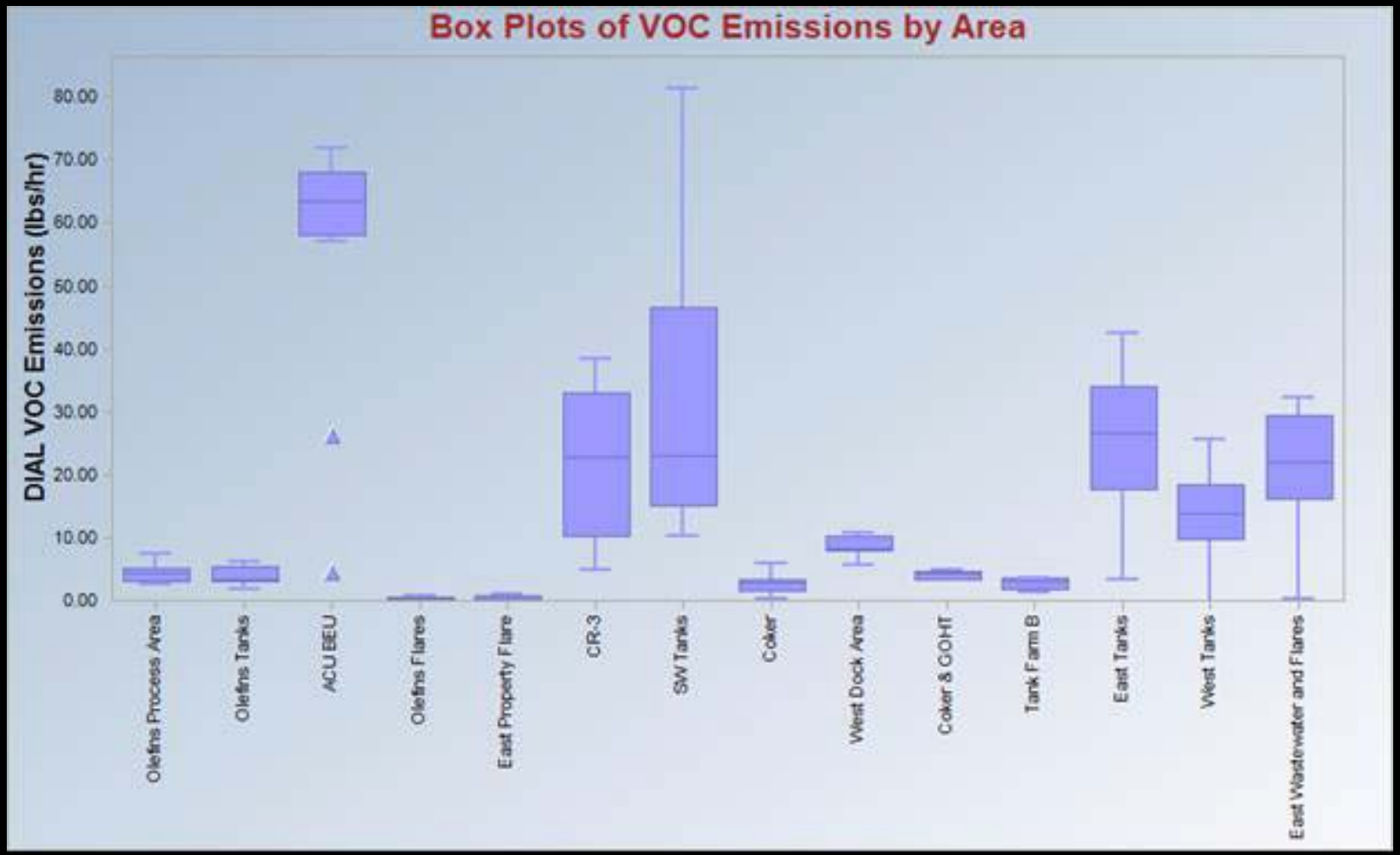
Results for Objective 1: Spike of DIAL Benzene emission rate (lbs/hr) and MAAML (ppb)



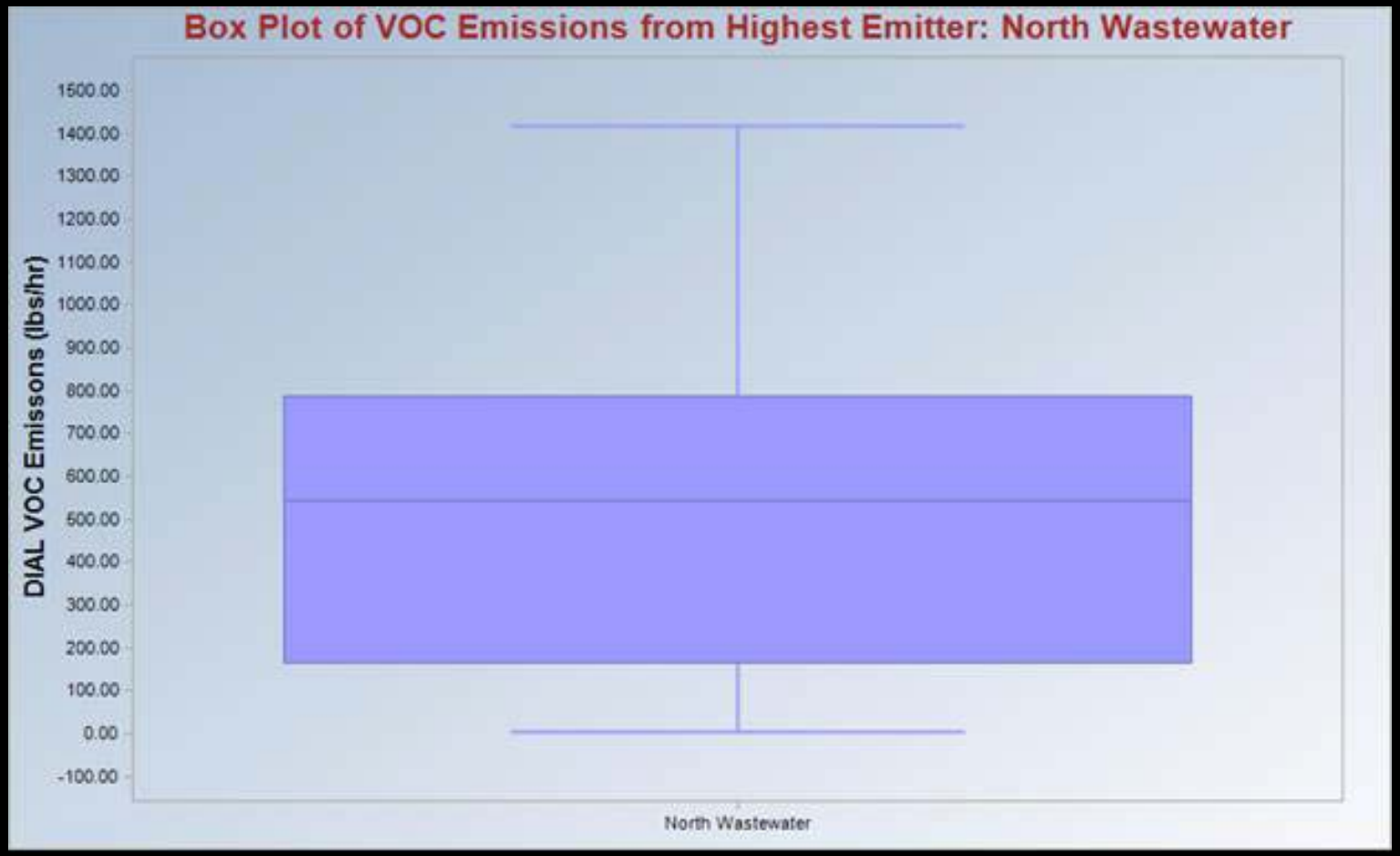
Results for Objective 2:
Boxplots of Benzene Emissions by Area (lbs/hr)



Results for Objective 2:
Boxplots of VOC Emissions by Area (lbs/hr)



Results for Objective 2:
Boxplots of VOC Emissions by Area (lbs/hr)



Results for Objective 3: Compare measured and emission factor 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
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

Results for Objective 3: Compare measured and emission factor 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
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

Results for Objective 3: Compare measured and emission factor 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
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

Results for Objective 3: Compare measured and emission factor 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

Thanks to

- Arturo Blanco, Francis Agostini, James Rhubottom, Youjun Qin, Peter Chen, Isaac Desouza and Don Richner
- Shell Deer Park Richard Bourns and Barb Bessette-Henderson
- Alex Cuclis, Ram A. Hashmonay, Steve Ramsey, and Cary Secrest.