FORENSIC STUDY TOOLS TO EVALUATE POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) SOURCE ORIGINS: A CASE STUDY

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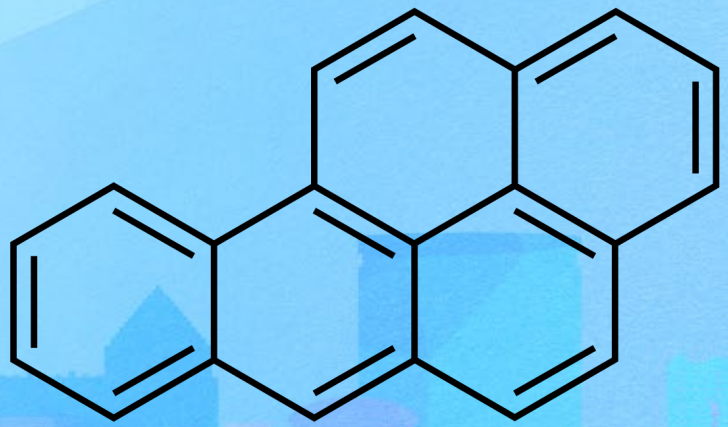
Overview

Goals of Presentation

- Brief Discussion on Pyrogenic vs. Petrogenic PAHs.
- Brief Discussion on Department of Environmental Protection (DEP) Forensic Study.
- Study Evaluation Methods.
- Evaluation Methods Applied to Case Study.
- Conclusion.

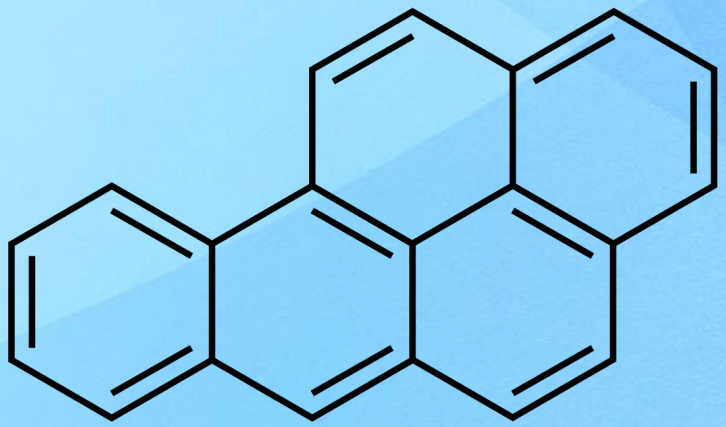
Petrogenic Vs Pyrogenic

- Petrogenic
  - From petroleum products asphalt, diesel, gasoline, home heating oil, motor oil, lubricants, unprocessed coal and crude oil.



- Pietara J, O'Reilly K, Boehm P. 2010. *A Review of PAHs*. Stormwater.
- Mahler BJ, Van Metre PC, Bashara JT, Wilson JT, Johns DA. 2005. *An Unrecognized source of urban polycyclic aromatic hydrocarbons*. Environmental Science and Technology.
- Neff JM, Stout SA, Gunster DG. 2005, *Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments*. Integrated Environmental Assessment and Management.

Petrogenic Vs Pyrogenic



- Pyrogenic
  - Anthropogenic sources include residential wood burning, diesel and gasoline engine exhaust, emissions from coal-fired power plants, creosote, and coal tar from pavement sealants.

- Pietara J, O'Reilly K, Boehm P. 2010. *A Review of PAHs*. Stormwater.
- Mahler BJ, Van Metre PC, Bashara JT, Wilson JT, Johns DA. 2005. *An Unrecognized source of urban polycyclic aromatic hydrocarbons*. Environmental Science and Technology.
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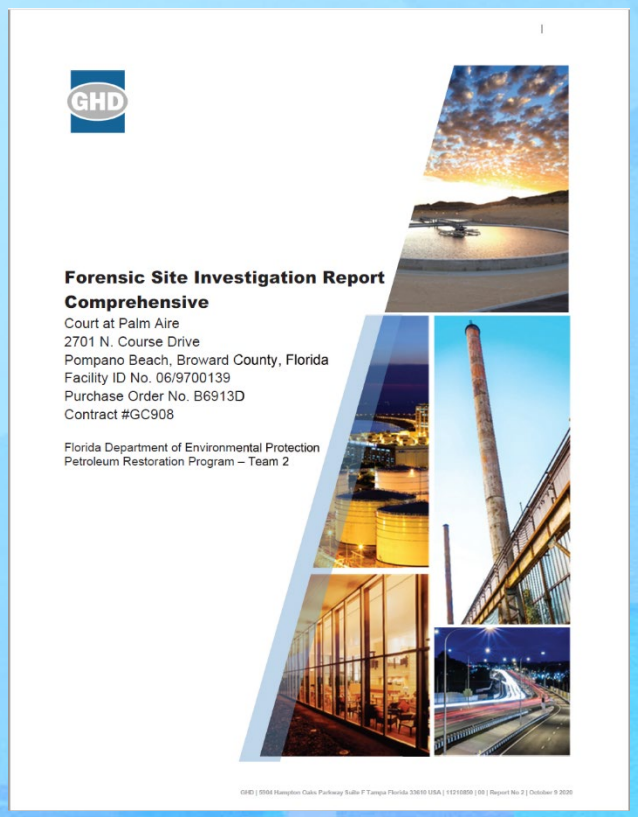
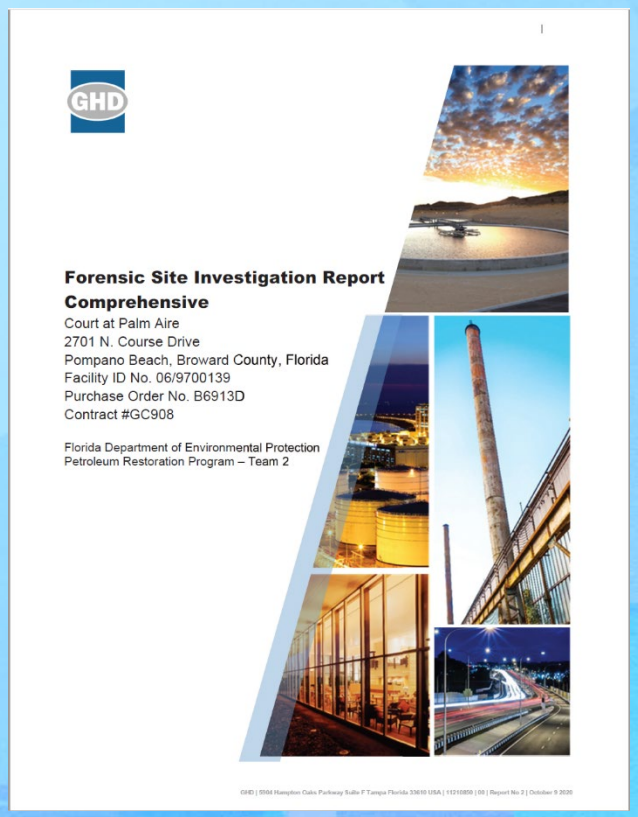
DEP Forensic Study



- October 2020.
- Seven Petroleum Restoration Program Sites – Two located in Broward.
- One Agency Term Contractor (ATC) (GHD Services) worked on all seven sites to get soil and groundwater data.

DEP Forensic Study



- Sites with known PAH impacts (particularly Benzo (a) Pyrene (BaP) and BaP equivalents) were chosen for evaluation.
- Goal: Can we develop a method of determining if PAH impacts at a site are related to a release or more likely related to combustion/pavement PAHs.

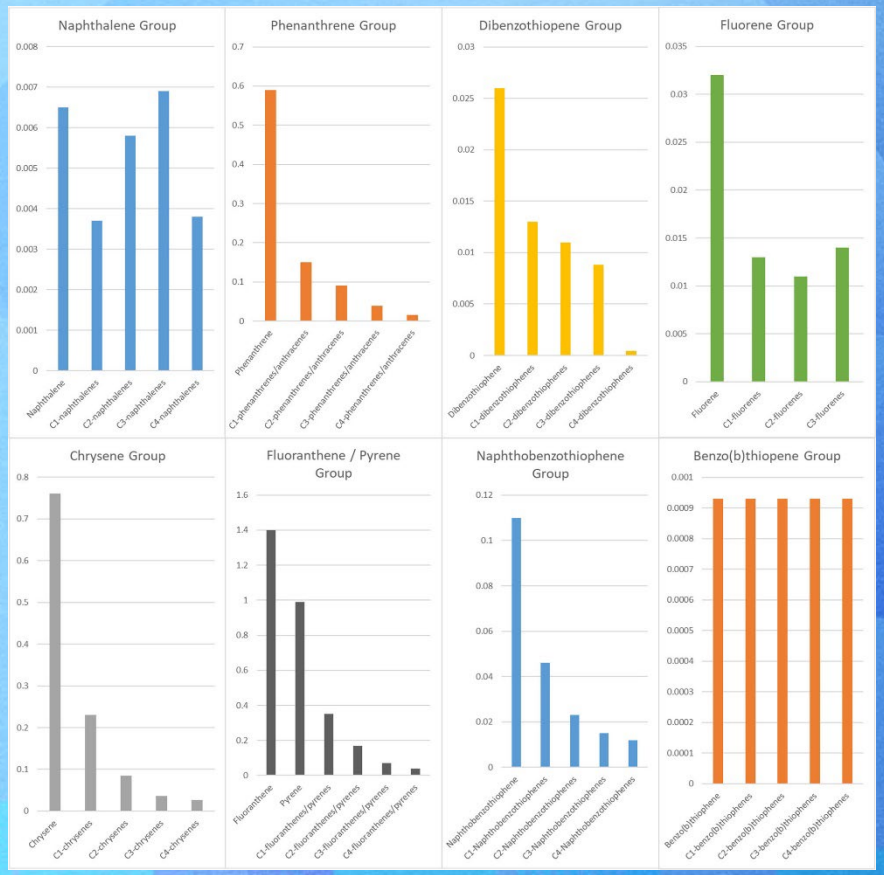
FDEP Forensic Study Goals

Why Do the Study?

- PAH lab results showed BaP/BaP Equivalents exceedances.
- Shallow soils, in many cases in the top two feet.
- If not related to release, let's not waste time and money addressing impacts through the Petroleum Restoration Program (PRP).
- Try to determine if those PAH exceedances are related to the release.
- If they are not, let's issue a Site Rehabilitation Completion Order (SRCO).

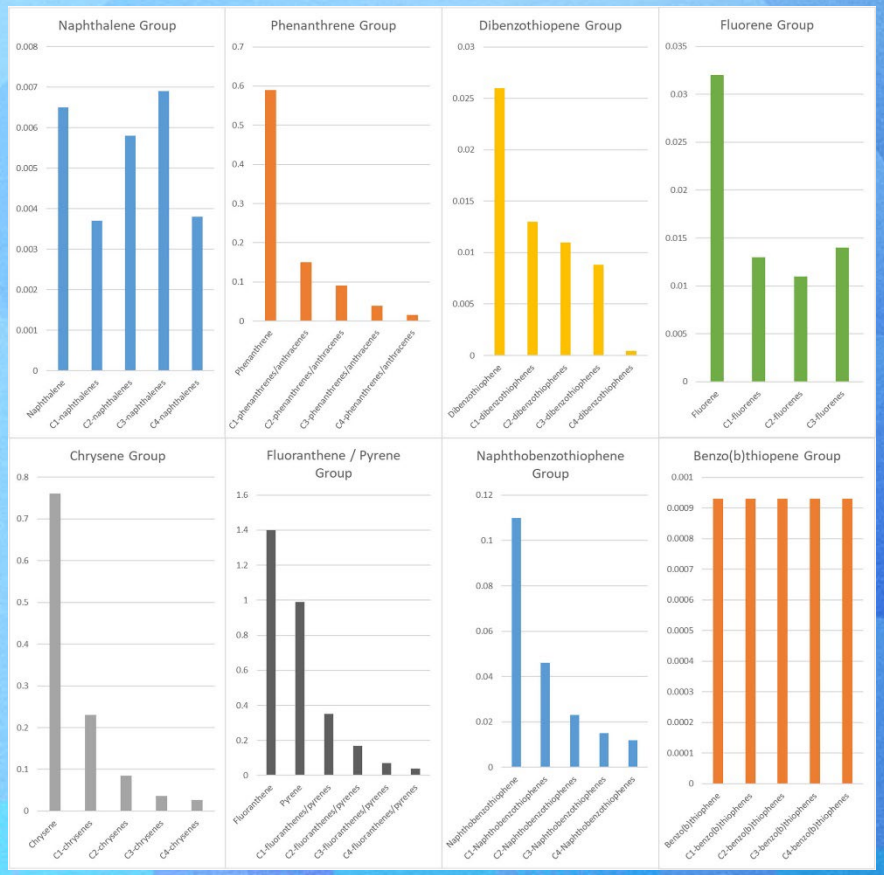
Forensic Study Method

- Look at BaP data and Organic Vapor Analyzer (OVA).
  - OVA can indicate petroleum impacts.
  - High BaP and low OVA suggest pyrogenic.
  - Low BaP and high OVA suggest petrogenic.



Forensic Study Method

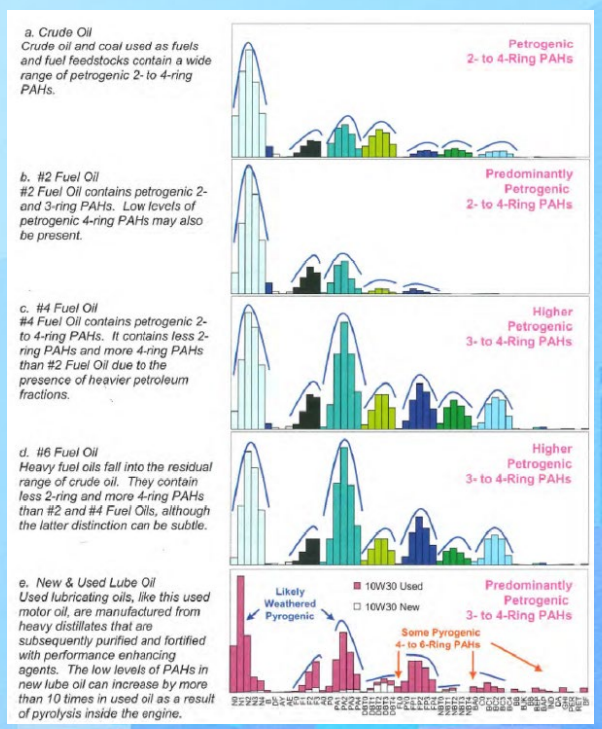
- Parent vs. Alkylated
  - Left-skewed suggest pyrogenic.
  - Uniform or bell shaped suggest petrogenic.
  - Right-skewed suggest weathered or biodegraded petroleum product.

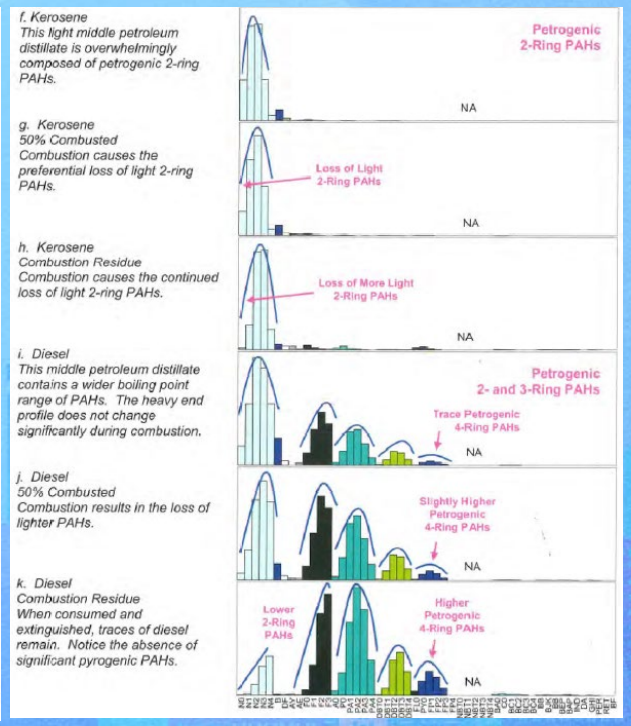


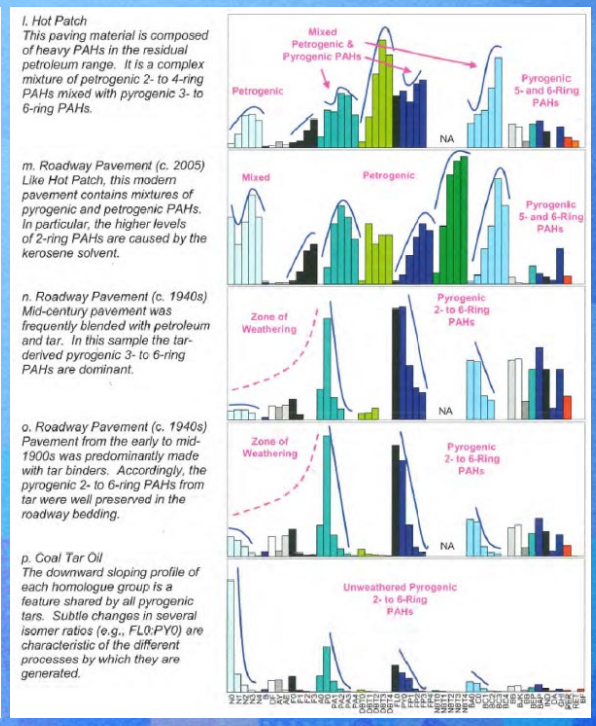
Forensic Study Method

Compare PAH Distribution to established PAH Reference Histograms.

- Petrogenic = skewed to the left.
- Pyrogenic = skewed to the right.







Murphy, BL, Morrison RD. 2006. *Introduction to Environmental Forensics*

Forensic Study Method

Examine Single Ratio Histograms

- Low Molecular Weight/High Molecular Weight.
- Combustion/Total.
- Fluoranthene (FLA)/(FLA + pyrene (PYR)).
- Benzo[a]anthracene (BaA)/(BaA + Chrysene).
- Indeno[c,d]pyrene (IcdP)/(IcdP + Benzo[g,h,i]pyrene (BghiP)).

Forensic Study Method

Likely Pyrogenic:

- If the Low Molecular Weight (LMW)/High Molecular Weight (HMW) ratio is < 1.
- If the Combustion/Total ratio is close to 1.0.
- If the FLA/(FLA + PYR) > 0.4.
- If the BaA/(BaA + Chrysene) > 0.2.
- If the (IcdP)/(IcdP + BghiP) > 0.2.

Forensic Study Method

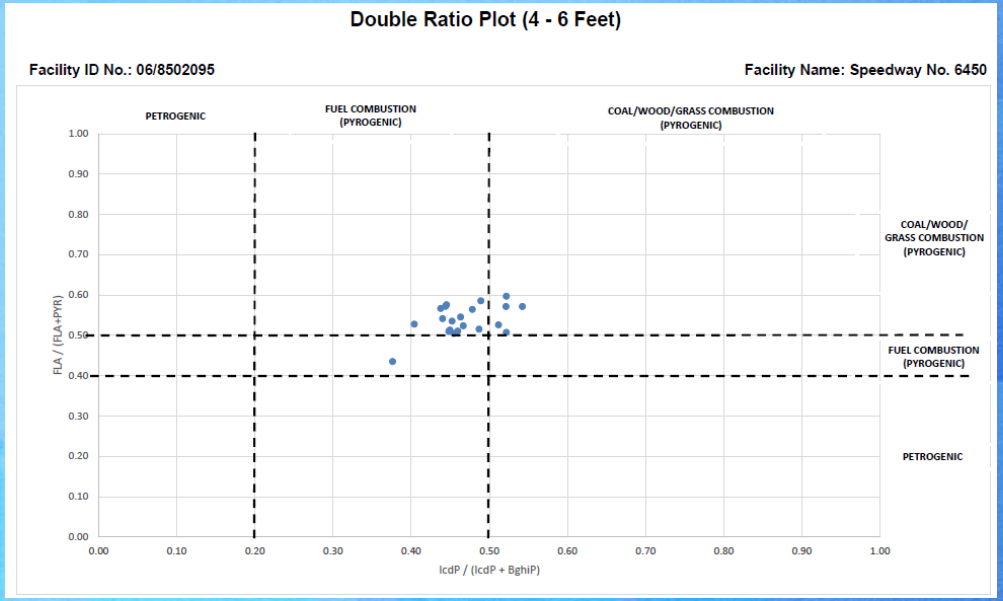
Likely Petrogenic:

- If the LMW/HMW ratio is > 1.
- If the Combustion/Total ratio is < 0.8.
- If the FLA/(FLA + PYR) < 0.4.
- If the BaA/(BaA + Chrysene) < 0.2.
- If the (IcdP)/(IcdP + BghiP) < 0.2.

Forensic Study Method

Create a Double Ratio Plot using the concentrations of four PAHs:

- Fluoranthene (FLA).
- Pyrene (PYR).
- Indeno(1,2,3-c,d)pyrene (IcdP).
- Benzo(g,h,i)perylene (BghiP).

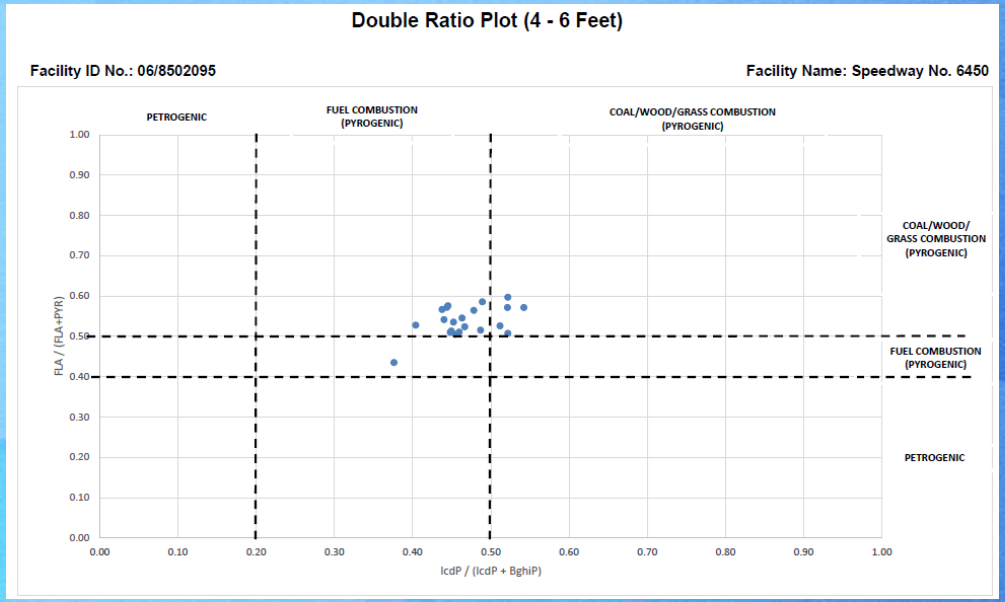


Forensic Study Method

Plotted with the axes representing these ratios:

$$\frac{FLA}{FLA + PYR} \quad \& \quad \frac{IcdP}{IcdP + BghiP}$$

See if the results are clustered, and where on the chart they cluster.



The Case Study

Speedway #6450

FDEP Facility No. 06/8502095

Address:

6395 Taft Street

Hollywood, Broward County

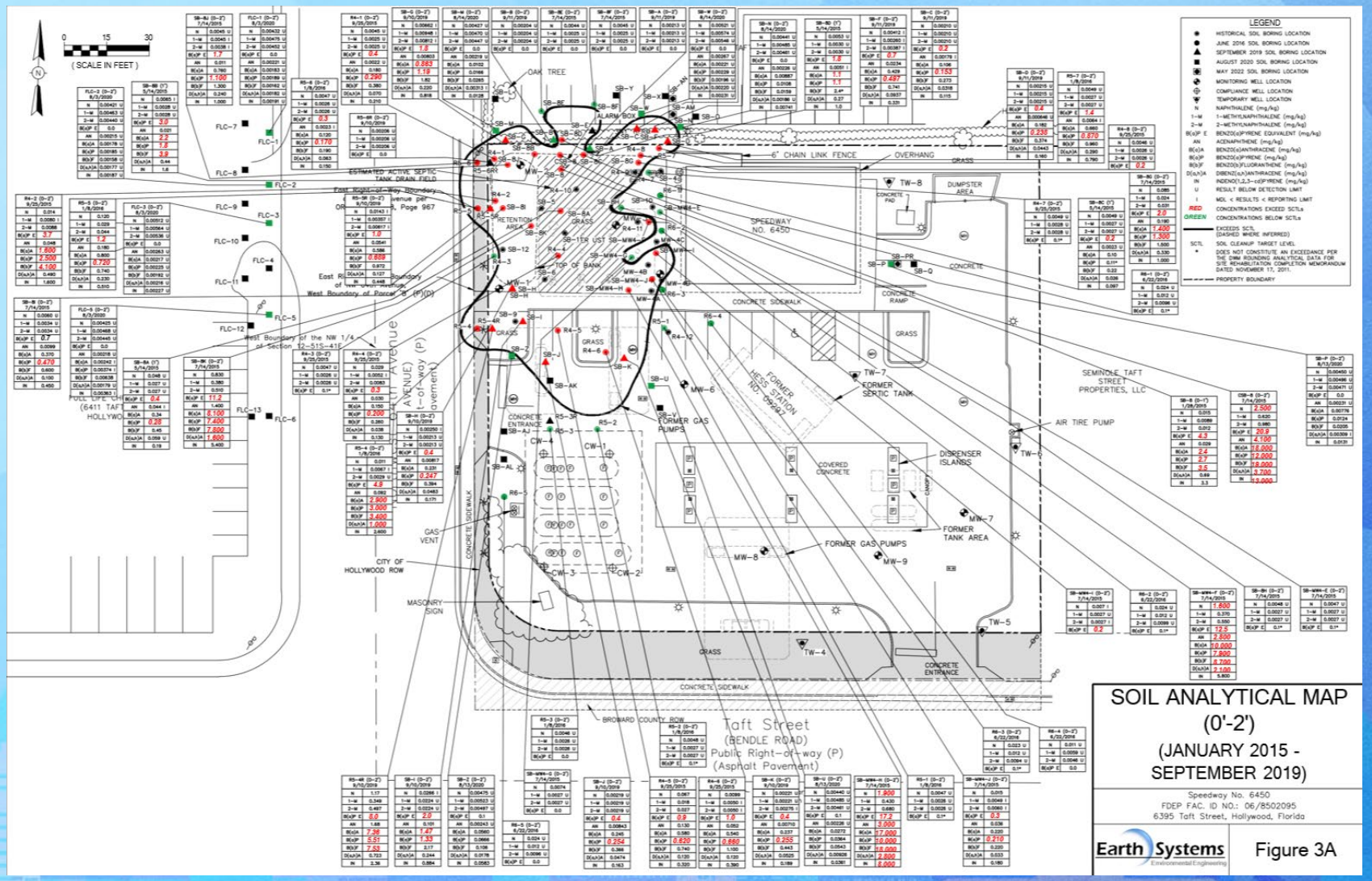
The Case Study

Speedway #6450

An active Speedway retail petroleum facility with a convenience store.

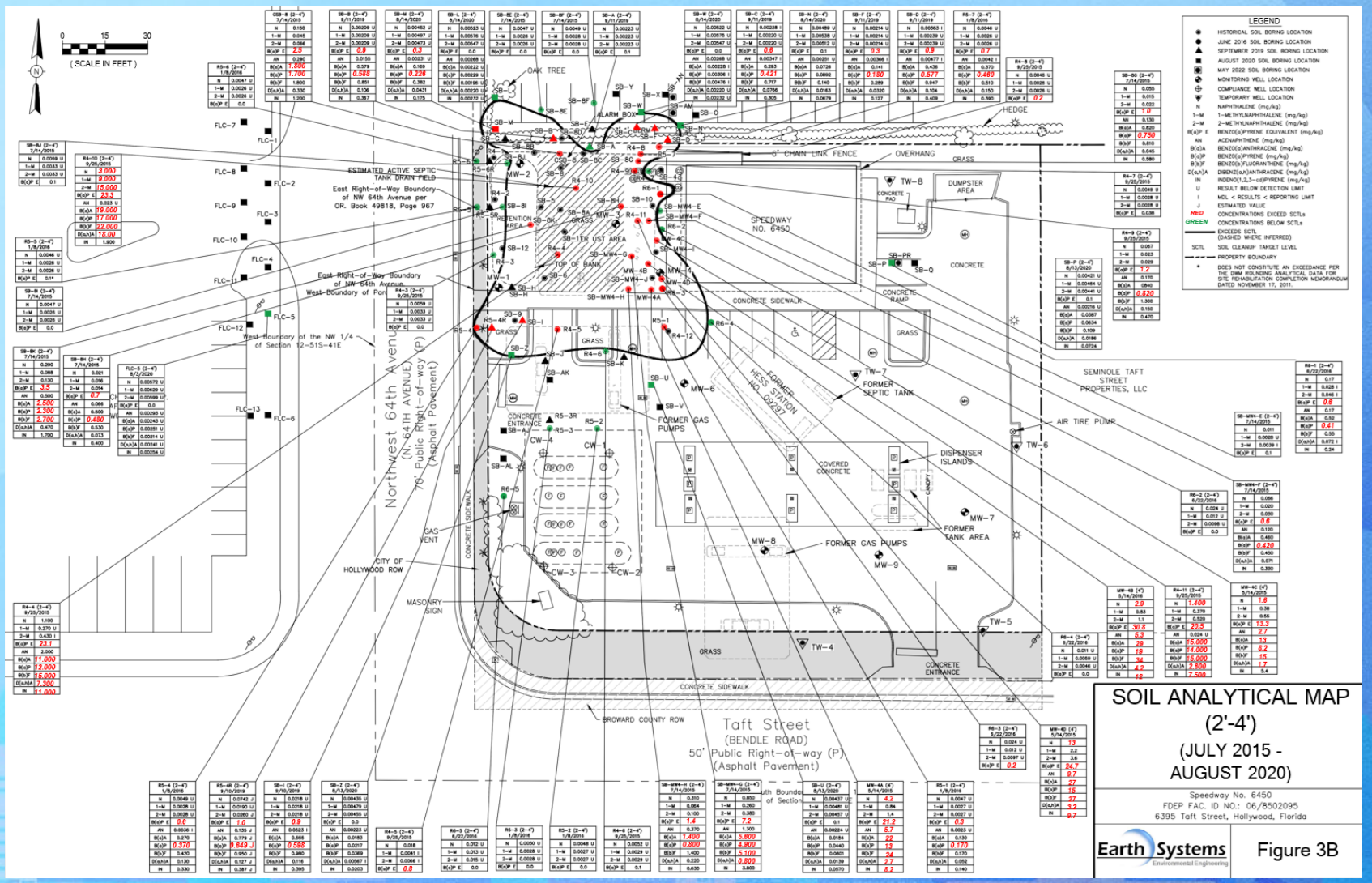
BROWARD COUNTY FLORIDA

The Case Study



BROWARD COUNTY FLORIDA

The Case Study



The Case Study

SOIL ANALYTICAL MAP (4'-6') (JANUARY 2015 - MAY 2022)

Speedway No. 6450
FDEP FAC. ID NO.: 06/8502095
6395 Taft Street, Hollywood, Florida

Earth Systems
Environmental Engineering

Figure 3C

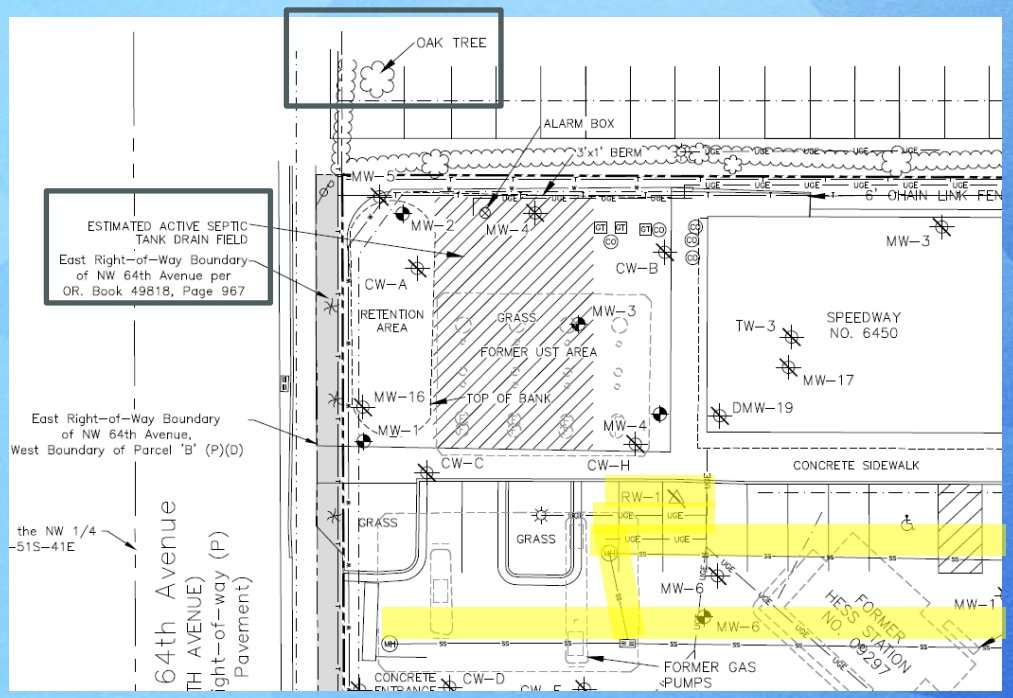
LEGEND
- HISTORICAL SOIL BORING LOCATION
- JUNE 2016 SOIL BORING LOCATION
- SEPTEMBER 2019 SOIL BORING LOCATION
- AUGUST 2020 SOIL BORING LOCATION
- MAY 2022 SOIL BORING LOCATION
- MONITORING WELL LOCATION
- COMPLIANCE WELL LOCATION
- TEMPORARY WELL LOCATION
- N — NAPHTHALENE (mg/kg)
- 1-M — 1-METHYLNAPHTHALENE (mg/kg)
- 2-M — 2-METHYLNAPHTHALENE (mg/kg)
- B(a)P E — BENZO(a)PYRENE EQUIVALENT (mg/kg)
- AN — ACENAPHTHENE (mg/kg)
- B(a)A — BENZO(a)ANTHRACENE (mg/kg)
- B(a)P — BENZO(a)PYRENE (mg/kg)
- B(b)F — BENZO(b)FLUORANTHENE (mg/kg)
- D(a,h)A — DIBENZ(a,h)ANTHRACENE (mg/kg)
- IN — INDENO(1,2,3-cd)PYRENE (mg/kg)
- NA — NOT ANALYZED
- U — RESULT BELOW DETECTION LIMIT
- I — MDL < RESULTS < REPORTING LIMIT
- J — ESTIMATED VALUE
- RED — CONCENTRATIONS EXCEED SCTLs
- GREEN — CONCENTRATIONS BELOW SCTLs
- EXCEEDS SCTL (DASHED WHERE INFERRED)
- SCTL — SOIL CLEANUP TARGET LEVEL
- PROPERTY BOUNDARY
- * — DOES NOT CONSTITUTE AN EXCEEDANCE PER THE DWM ROUNDING ANALYTICAL DATA FOR SITE REHABILITATION COMPLETION MEMORANDUM DATED NOVEMBER 17, 2011.

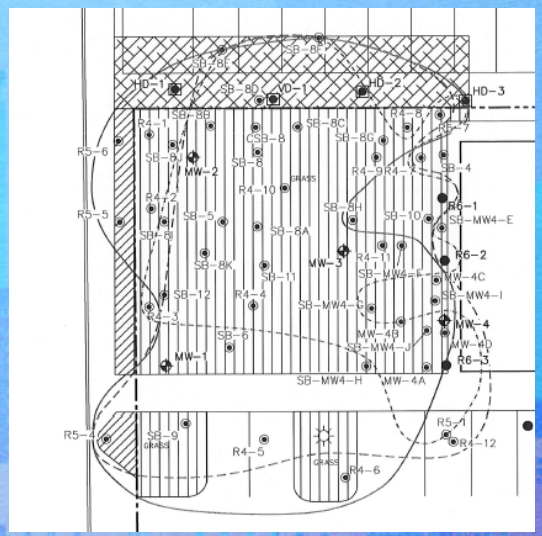
SPEEDWAY NO. 6450
Northwest 64th Avenue (N. 64TH AVENUE) 70' Public Right-of-way (P) (Asphalt Pavement)
Taft Street (BENDLE ROAD) 50' Public Right-of-way (P) (Asphalt Pavement)
FULL LIFE CHURCH CORP. (6411 TAFT STREET, HOLLYWOOD, FL)
FORMER HESS STATION NO. 09297
FORMER GAS PUMPS
FORMER SEPTIC TANK
FORMER TANK AREA
DISPENSER ISLANDS
COVERED CONCRETE
CONCRETE SIDEWALK
BROWARD COUNTY ROW
CITY OF HOLLYWOOD ROW
SEMINOLE TAFT STREET PROPERTIES
(SCALE IN FEET)

The Case Study - Complications

Speedway #6450

- Potential Source Removal.
  - Over 500 yd^3
- Several complicating factors for implementation.

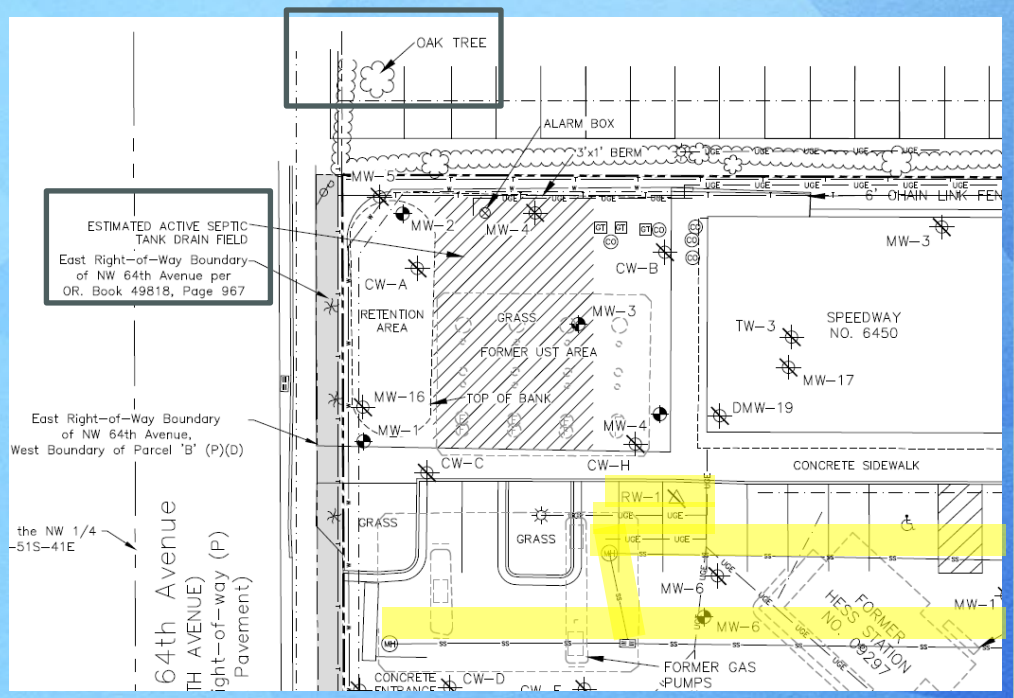


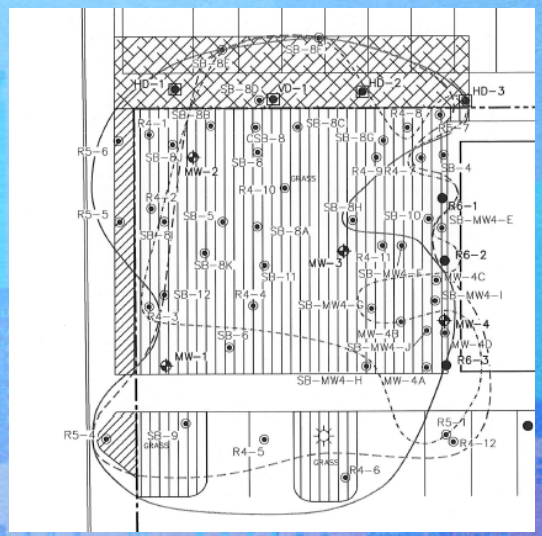


The Case Study - Complications

Speedway #6450

- Complications with excavation area.
  - Parcel to North owned by Seminole Tribe/Historic Oak Tree.
  - Septic drain field.

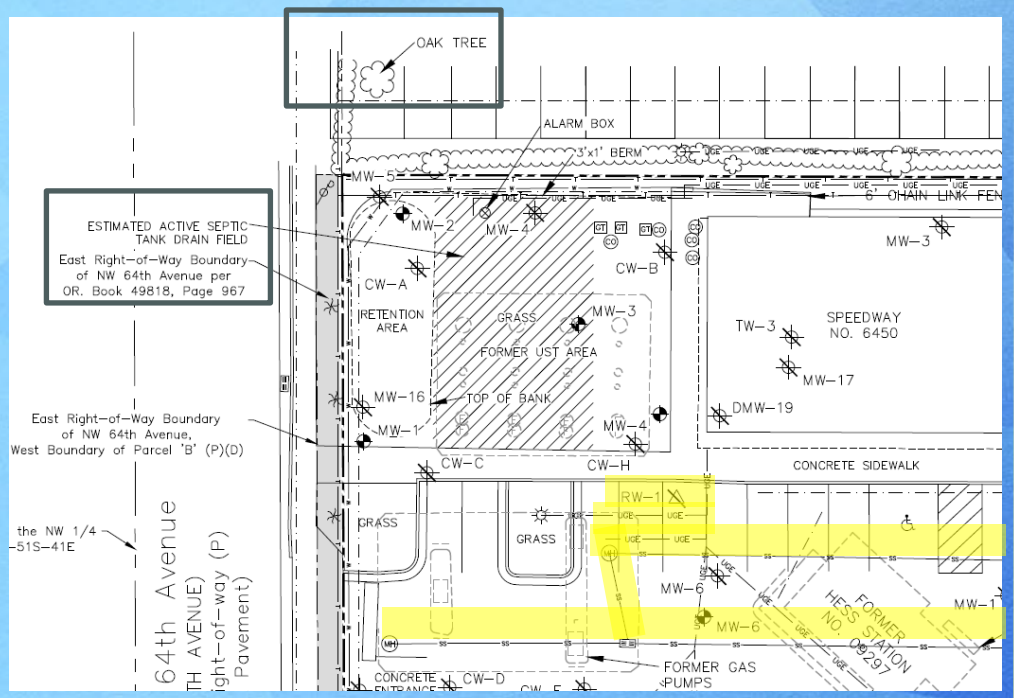


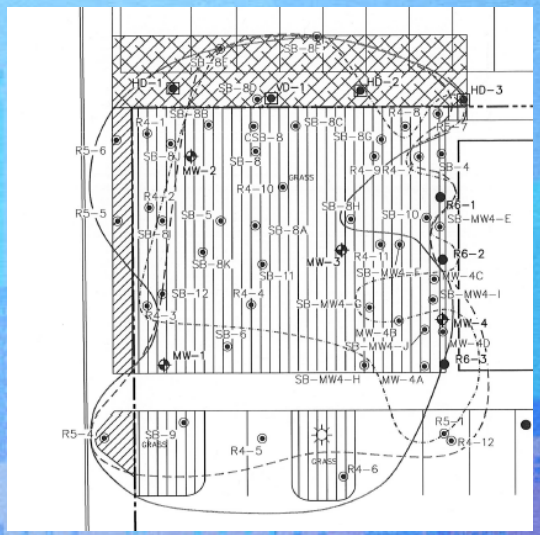


The Case Study - Complications

Speedway #6450

- Complications with excavation area.
  - Active station/utilities.
  - Narrow parcel to west owned by City with Department of Transportation Right of Way (ROW) further west.





The Case Study – OVA and Lab

Speedway #6450

- Low OVAs but multiple exceedances of PAHs (mainly BaP and BaP equivalents).

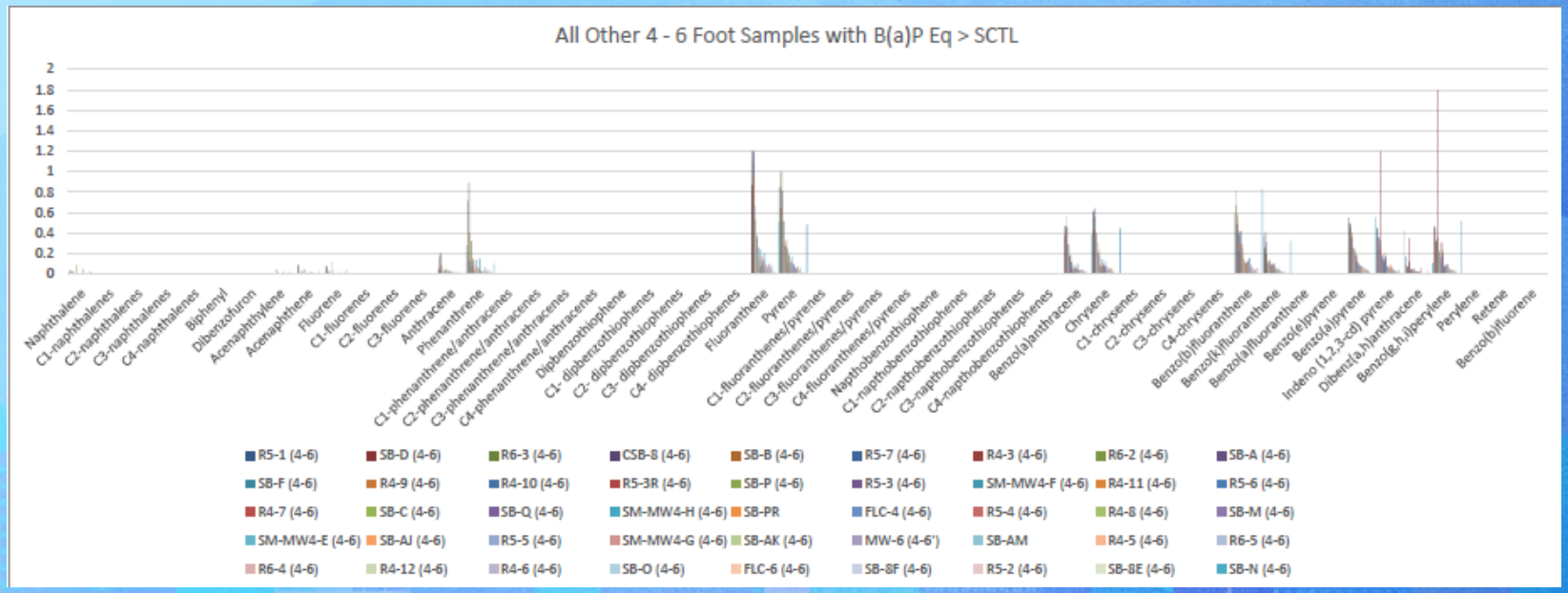
BORING NO.	DATE COLLECTED	DEPTH TO WATER	SAMPLE INTERVAL (FBLS)	OVA READING (ppm)	COMMENTS
SB-L	8/14/2020	NE	0-2	<1	Sample collected for lab analysis/Not analyzed
			2-4	<1	Sample collected for lab analysis
			4-6	<1	Sample collected for lab analysis/Not analyzed
SB-M	8/14/2020	NE	0-2	<1	Sample collected for lab analysis
			2-4	<1	Sample collected for lab analysis
			4-6	<1	Sample collected for lab analysis
SB-N	8/14/2020	NE	0-2	<1	Sample collected for lab analysis
			2-4	<1	Sample collected for lab analysis
			4-6	<1	Sample collected for lab analysis
SB-O	8/14/2020	NE	0-2	<1	Sample collected for lab analysis/Not analyzed
			2-4	<1	Sample collected for lab analysis/Not analyzed
			4-6	<1	Sample collected for lab analysis
SB-P	8/13/2020	NE	0-2	<1	Sample collected for lab analysis
			2-4	<1	Sample collected for lab analysis
			4-6	<1	Sample collected for lab analysis
SB-Q	8/13/2020	NE	0-2	<1	Sample collected for lab analysis/Not analyzed
			2-4	<1	Sample collected for lab analysis/Not analyzed
			4-6	<1	Sample collected for lab analysis
SB-U	8/13/2020	NE	0-2	<1	Sample collected for lab analysis
			2-4	<1	Sample collected for lab analysis
SB-V	8/13/2020	NE	0-2	<1	Sample collected for lab analysis/Not analyzed
			2-4	<1	Sample collected for lab analysis/Not analyzed
SB-W	8/14/2020	NE	0-2	<1	Sample collected for lab analysis
			2-4	<1	Sample collected for lab analysis
SB-X	8/14/2020	NE	0-2	<1	Sample collected for lab analysis/Not analyzed
			2-4	<1	Sample collected for lab analysis/Not analyzed
SB-Y	8/14/2020	NE	0-2	<1	Sample collected for lab analysis/Not analyzed
			2-4	<1	Sample collected for lab analysis/Not analyzed
SB-Z	8/13/2020	NE	0-2	<1	Sample collected for lab analysis
			2-4	<1	Sample collected for lab analysis
SB-AJ	8/13/2020	NE	0-2	<1	
			2-4	<1	
			4-6	<1	Sample collected for lab analysis
SB-AK	8/13/2020	NE	0-2	<1	
			2-4	<1	
			4-6	<1	Sample collected for lab analysis
SB-AL	8/13/2020	NE	0-2	<1	
			2-4	<1	
			4-6	<1	Sample collected for lab analysis/Not analyzed

Property Sample Collected From	Sample ID	Date	Collection Interval (ft bls)	OVA Response (ppm)	Naphthalene	1-Methyl naphthalene	2-Methyl naphthalene	Acenaphthene	Acenaphthylene	Anthracene	Benz(a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(g,h,i)perylene	Benzo(k)fluoranthene	Chrysene	Dibenz(a,h)anthracene	Fluoranthene	Fluorene	Indeno (1,2,3-cd) pyrene	Phenanthrene	Pyrene	BAP Equivalents
Source	RS-3 (4-6)	01/08/16	4-6	>15,000	0.0051 U	0.0029 U	0.0029 U	0.0024 U	0.0043 I	0.012	0.037	0.120*	0.140	0.200	0.110	0.074	0.056	0.074	0.0025 U	0.170	0.013	0.071	0.2
Off-site (ROW)	RS-4 (4-6)	01/08/16	4-6	38.3	0.050 U	0.028 U	0.028 U	0.024 U	0.023 U	0.021 I	0.042 I	0.059 I	0.069	0.059 I	0.054 I	0.074 I	0.062 U	0.090	0.024 U	0.051 I	0.034 I	0.062 I	0.1*
Off-site (ROW)	RS-5 (4-6)	01/08/16	4-6	16.0	0.0049 U	0.0028 U	0.0028 U	0.0068 I	0.0022 U	0.018	0.042	0.039	0.031	0.029	0.016	0.046	0.012	0.100	0.0076	0.028	0.070	0.071	0.1*
Off-site (ROW)	RS-6 (4-6)	01/08/16	4-6	7.2	0.0049 U	0.0027 U	0.0027 U	0.0023 U	0.023	0.033	0.056	0.082	0.091	0.078	0.100	0.083	0.027	0.100	0.0024 U	0.073	0.019	0.094	0.1*
Source	RS-7 (4-6)	01/08/16	4-6	88.7	0.0048 U	0.0027 U	0.0027 U	0.0032 I	0.0057 I	0.030	0.290	0.360	0.400	0.360	0.310	0.400	0.120	0.660	0.0044 I	0.330	0.130	0.510	0.6
Source	R6-1 (4-6)	06/22/16	4-6	0	0.16	0.033 I	0.052 I	0.21	0.0075 U	0.30	0.88	0.71	1.1	0.51	0.36	0.83	0.14	1.8	0.18	0.44	1.6	1.5	1.1
Source	R6-2 (4-6)	06/22/16	4-6	0	0.024 U	0.012 U	0.0097 U	0.037 I	0.0077 U	0.074	0.28	0.25	0.37	0.18	0.13	0.30	0.042 I	0.53	0.029 I	0.15	0.32	0.52	0.4
Source	R6-3 (4-6)	06/22/16	4-6	0	0.032 I	0.012 U	0.017 I	0.084	0.0076 U	0.17	0.56	0.49	0.67	0.32	0.26	0.56	0.075	1.1	0.072 I	0.28	0.72	1.0	0.7
Source	R6-4 (4-6)	06/22/16	4-6	0	0.023 U	0.012 U	0.0095 U	0.011 U	0.0075 U	0.0099 U	0.0087 U	0.0084 U	0.054 U	0.0083 U	0.016 U	0.0086 U	0.011 U	0.0097 U	0.0093 U	0.013 U	0.027 U	0.0076 U	0.0
Source	R6-5 (4-6)	06/22/16	4-6	0	0.026 U	0.028 U	0.032 U	0.029 U	0.025 U	0.024 U	0.023 U	0.0094 I	0.060 U	0.029 U	0.017 U	0.028 U	0.040 U	0.026 U	0.036 U	0.040 U	0.030 U	0.040 U	0.0
SUPPLEMENTAL SOIL ASSESSMENT - SEPTEMBER 2019 / AUGUST 2020																							
Source	SB-A (4-6)	09/11/19	4-6	0	0.00216 U	0.00216 U	0.00216 U	0.00211 I	0.000647 U	0.0126	0.178	0.249	0.418	0.233	0.111	0.206	0.0485	0.377	0.00271 I	0.187	0.0730	0.278	0.4
Source	SB-B (4-6)	09/11/19	4-6	0	0.00253 U	0.00253 U	0.00253 U	0.0218	0.000759 U	0.0821	0.455	0.406	0.579	0.309	0.194	0.438	0.0726	0.958	0.0235	0.243	0.402	0.812	0.6
Source	SB-C (4-6)	09/11/19	4-6	0	0.00212 U	0.00212 U	0.00212 U	0.000636 U	0.000636 U	0.00263 I	0.0461	0.0773	0.120	0.0770	0.0431	0.0667	0.0154	0.0809	0.000636 U	0.0597	0.0170	0.0706	0.1
Source	SB-D (4-6)	09/11/19	4-6	0	0.00391 I	0.00257U	0.00257U	0.00460 I	0.000772 U	0.0341	0.378	0.494	0.813	0.451	0.235	0.424	0.0924	0.866	0.00957	0.360	0.194	0.648	0.7
Source	SB-E (4-6)	09/11/19	4-6	0	0.00312 I	0.00223 U	0.00223 U	0.00491 I	0.00904	0.0521	0.544	0.673	1.03	0.666	0.325	0.700	0.138	0.956	0.00901	0.550	0.226	0.830	1.0
Source	SB-F (4-6)	09/11/19	4-6	0	0.00242 U	0.00242 U	0.00242 U	0.00183 I	0.000727 U	0.0131	0.168	0.241	0.420	0.212	0.115	0.193	0.0414	0.350	0.00299 I	0.165	0.0718	0.268	0.4
Source	RS-3R (4-6)	09/11/19	4-6	1000	0.00363 I	0.00229 U	0.00229 U	0.000769 I	0.000686 U	0.0104	0.0629	0.180	0.288	0.307	0.0852	0.0883	0.0452	0.124	0.00120 I	0.208	0.0172	0.111	0.3
Full Life Church	FLC-4 (4-6)	08/03/20	4-6	<1	0.00473 U	0.00521 U	0.00496 U	0.00243 U	0.00251 U	0.00624 I	0.0451	0.0673	0.158	0.0908	0.0483	0.0721	0.0219	0.117	0.00238 U	0.0758	0.0220	0.0950	0.1

The Case Study – Parent vs Alkylated

Speedway #6450

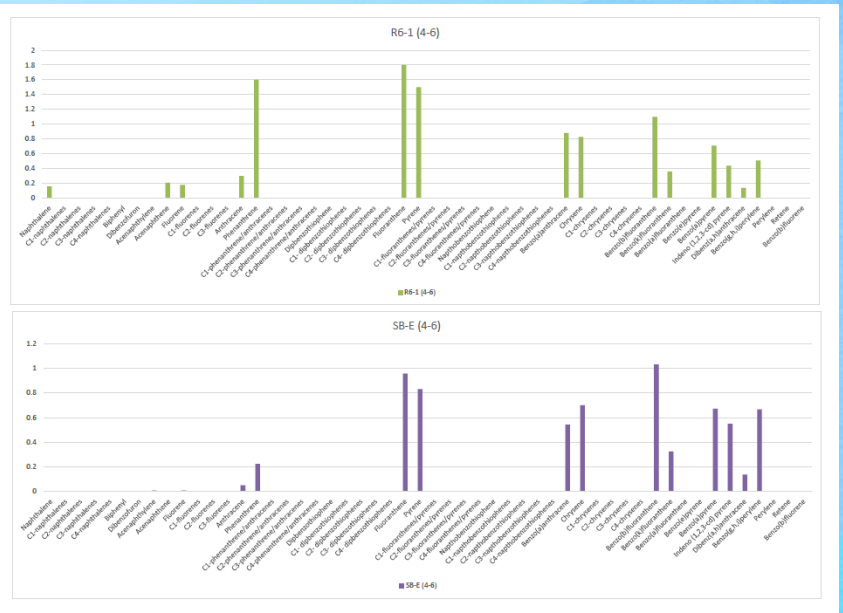
- Looking at the Parent vs. Alkylated we see a bell curve that is skewed to the left.

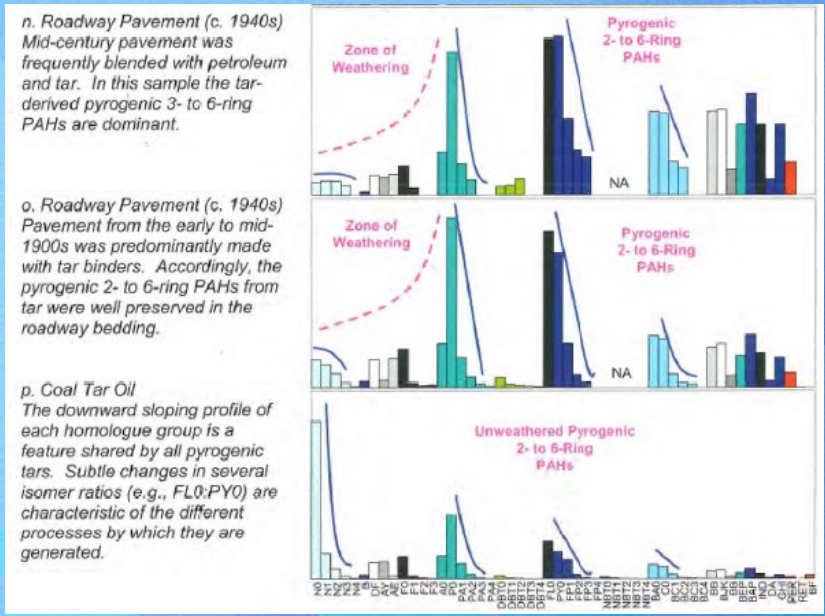


The Case Study – Parent vs Alkylated

Speedway #6450

- Looking at the Parent vs. Alkylated we see a bell curve that is skewed to the left.





The Case Study – Single Ratios

Speedway #6450

- The LMW/HMW ratio is < 1.
  - Likely Pyrogenic.
- The Combustion/Total ratio is close to 1.0.
  - Likely Pyrogenic.

Sample ID	B(a)P Equiv Conentration (mg/kg)	FLA/ (FLA+PYR)	BaA/ (BaA+CHR)	IcdP/ (IcdP+BghiP)
MW-4 (4-6')	18.6	0.57	0.48	0.54
R4-4 (4-6)	5.8	0.53	0.54	0.51
R6-1 (4-6)	1.1	0.55	0.51	0.46
SB-E (4-6)	1.0	0.54	0.44	0.45
R5-1 (4-6)	0.88	0.59	0.44	0.49
SB-N (4-6)	0.80	0.51	0.46	0.45
R4-3 (4-6)	0.77	NA	NA	0.40
R6-3 (4-6)	0.70	0.52	0.50	0.47
SB-D (4-6)	0.70	0.57	0.47	0.44
CSB-8 (4-6)	0.65	0.60	0.42	0.52
SB-B (4-6)	0.60	0.54	0.51	0.44
R5-7 (4-6)	0.59	0.56	0.42	0.48
R6-2 (4-6)	0.40	0.50	0.48	0.45
SB-A (4-6)	0.40	0.58	0.46	0.45
SB-F (4-6)	0.40	0.57	0.47	0.44
R4-9 (4-6)	0.32	0.51	0.45	0.52
R5-3R (4-6)	0.30	0.53	0.42	0.40
R4-10 (4-6)	0.28	0.51	0.41	0.45
R5-3 (4-6)	0.21	0.51	0.33	0.46
SB-P (4-6)	0.20	0.44	0.48	0.38
SM-MW4-F (4-6)	0.15	0.57	0.42	0.52
R4-11 (4-6)	0.15	0.52	0.41	0.49
Petrogenic	--	<0.4	<0.2	<0.2
Pyrogenic	--	>0.4	>0.2	>0.2

FLA - Fluoranthene
PYR - Pyrene
BaA - Benzo(a)anthracene
CHR - Chrysene
IcdP - Indeno(1,2,3-c,d)pyrene,
BghiP - Benzo(g,h,i)perylene

- Only samples exhibiting B(a)P Equivalent concentrations in excess of SCTLs included in table.
- Data arranged in the order of highest B(a)P Equivalent concentration to lowest concentration.
- NA - Ratios for compounds below the MDL were not calculated

The Case Study – Single Ratios

Speedway #6450

- The FLA/(FLA + PYR) > 0.4.
  - Likely Pyrogenic.
- The BaA/(BaA + Chrysene) > 0.2.
  - Likely Pyrogenic.
- The (IcdP)/(IcdP + BghiP) > 0.2.
  - Likely Pyrogenic.

Sample ID	B(a)P Equiv Conentration (mg/kg)	FLA/ (FLA+PYR)	BaA/ (BaA+CHR)	IcdP/ (IcdP+BghiP)
MW-4 (4-6')	18.6	0.57	0.48	0.54
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SB-E (4-6)	1.0	0.54	0.44	0.45
R5-1 (4-6)	0.88	0.59	0.44	0.49
SB-N (4-6)	0.80	0.51	0.46	0.45
R4-3 (4-6)	0.77	NA	NA	0.40
R6-3 (4-6)	0.70	0.52	0.50	0.47
SB-D (4-6)	0.70	0.57	0.47	0.44
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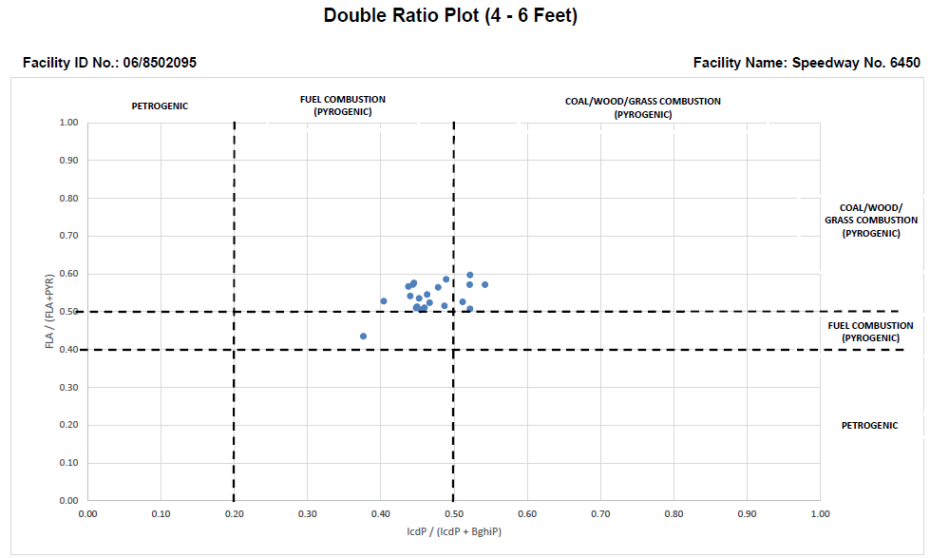
The Case Study – Double Ratio

Speedway #6450

- The Double Ratio plots showed us good clustering all on the Pyrogenic side of the chart.
- Conclusion: The impacts are the result of Pyrogenic sources and not related to the release.



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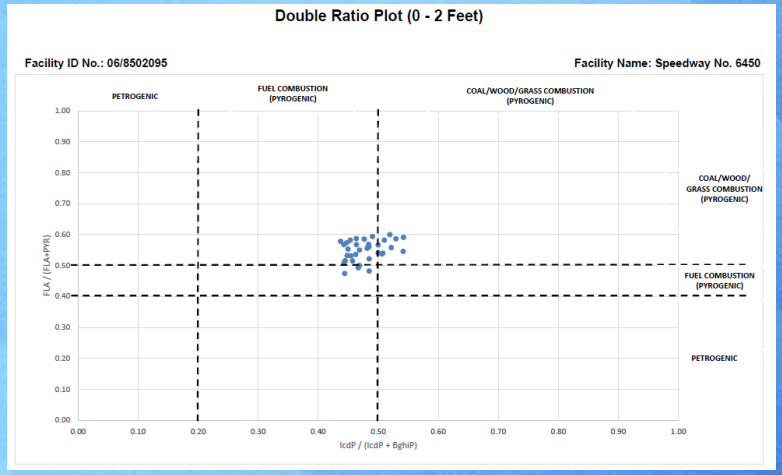

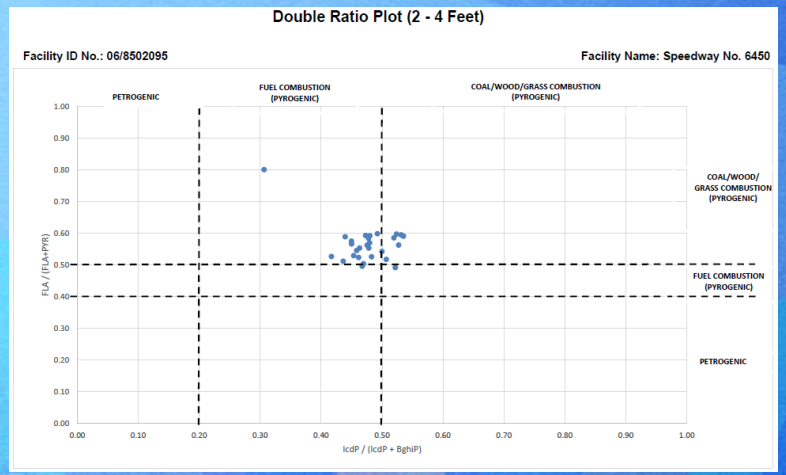

Closure

- The ATC completed the evaluation of data.
- The ATC has stated that in their professional opinion the PAHs are not related to the release.
- The ATC recommends No Further Action (NFA).

Closure

- The Local Program agrees with the ATC's conclusions.
- The Local Program creates a memo to PRP with their agreement attaching necessary backup data such as tables and maps.

Closure

- PRP reviews the memo from the Local Program and the supporting information and if they concur, issues a response to the Local Program.
- The Local Program reviews the response from the PRP.
- SRCO Order is prepared by Local Program for issue by PRP.

Closure

What Did We Learn?

- Basics of differences between Petrogenic and Pyrogenic PAHs.
- What tools the 2020 Forensic Study used to determine the origin of PAH impacts.
- How to use those tools.

Closure

What Did We Learn?

- The example of the Speedway #6450 Case Study showing how the tools were used.
- How to obtain a SRCO when the conclusion is the impacts are not related to the release.

Acknowledgement

The FDEP Forensic Study Document, with the data on all 7 study sites:

Forensic Site Investigation Report Comprehensive

Court at Palm Aire, 2701 N. Course Drive

Pompano Beach, Broward County, Florida

Facility ID No. 06/9700139

Purchase Order No. B6913D, Contract #GC908

Prepared by GHD Services, Inc.

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