BENZO[A]PYRENE: WHAT IT IS, OCCURRENCES, PATHS TO SITE CLOSURE AND DRAFT SAMPLING METHODOLOGY

Jerry Cook PG; Paul Angelillo, RG; Ken Busen, PG
Petroleum Restoration Program/Division of Waste Management
Florida Department of Environmental Protection

Tallahassee, FL | Feb. 22, 2024

POLYCYCLIC AROMATIC HYDROCARBONS (PAH) - PAUL ANGELILLO, RG

What They Are.

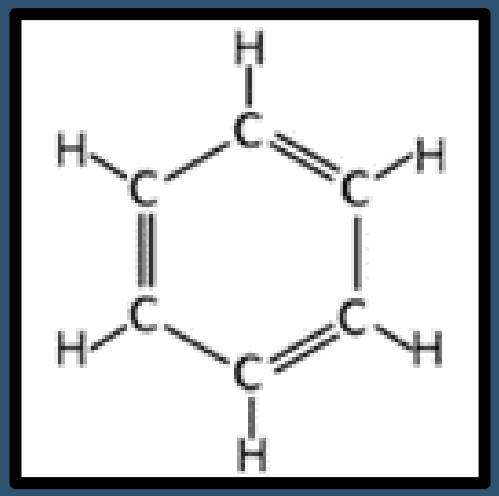
Forensic Analysis.

Lines of Evidence.

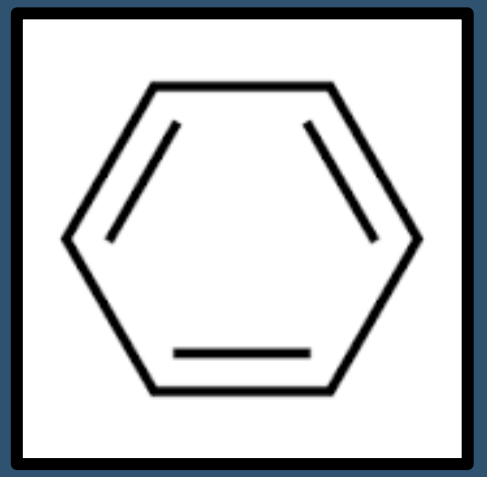
Case Histories.

PAHS ARE FORMED OF AROMATIC RINGS

- Benzene is an organic chemical compound with the molecular formula C_6H_6. The benzene molecule is composed of six carbon atoms joined in a planar hexagonal ring with one hydrogen atom attached to each, forming an **aromatic** ring.



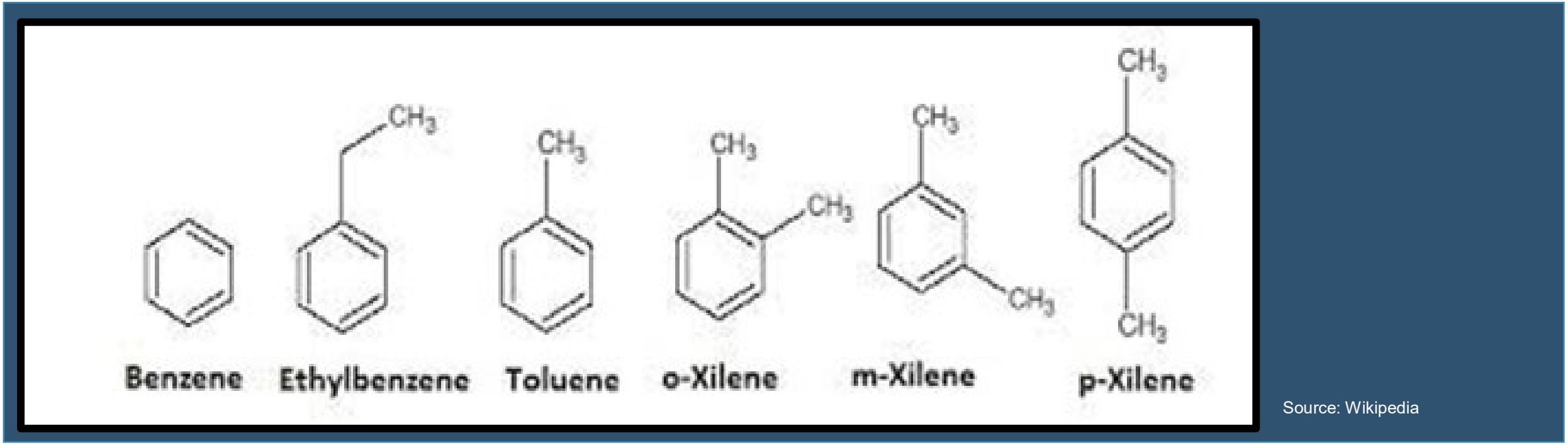
Source: Wikipedia



Source: Wikipedia

ONE RING: BENZENE, TOLUENE, ETHYLBENZENE, XYLENE (BTEX)

- Many of the earliest-known examples of aromatic compounds, such as benzene and toluene, have distinctive, pleasant aromas.
- This property led to the term "aromatic" for this class of compounds and the term "aromaticity."

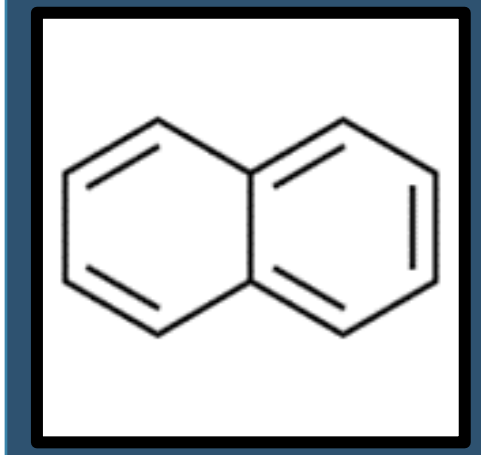


Source: Wikipedia

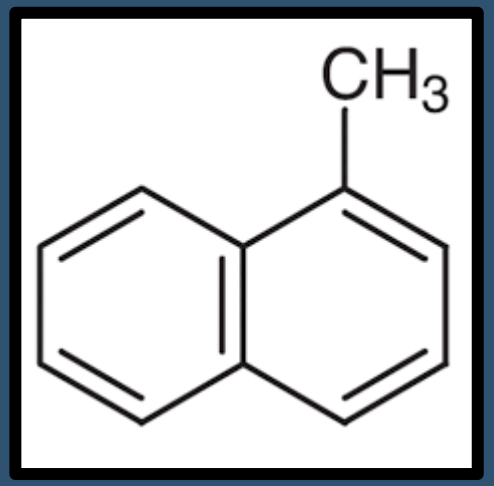
TWO RINGS

- A PAH is a class of organic compounds that is composed of multiple aromatic rings. The simplest PAH is naphthalene, having two aromatic rings:

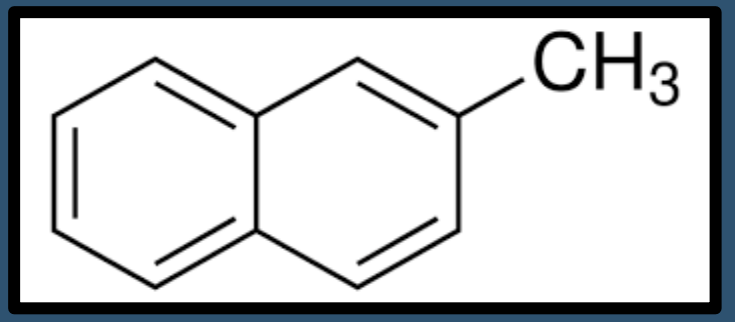
naphthalene



1-methylnaphthalene



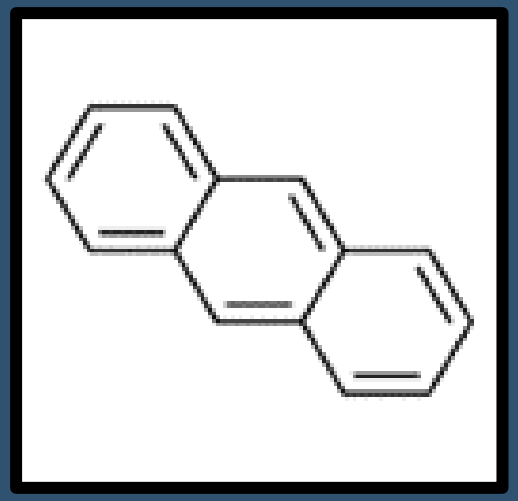
2-methylnaphthalene



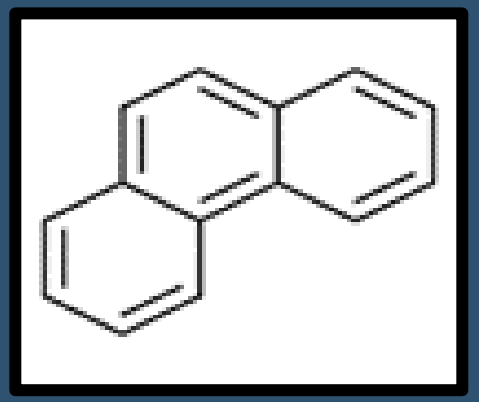
Source: Wikipedia

THREE RINGS

- The three-ring compounds, anthracene and phenanthrene:



Anthracene

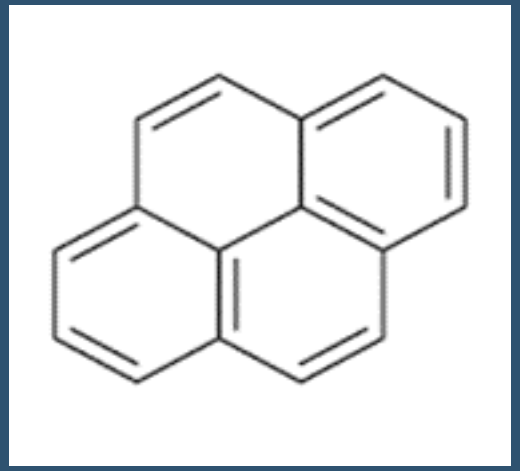


Phenanthrene

Source: Wikipedia

FOUR RINGS

- Pyrene is a polycyclic aromatic hydrocarbon consisting of four fused benzene rings with the chemical formula $C_{16}H_{10}$:

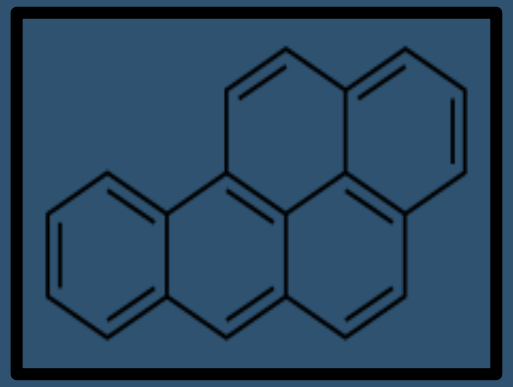


Source: Wikipedia

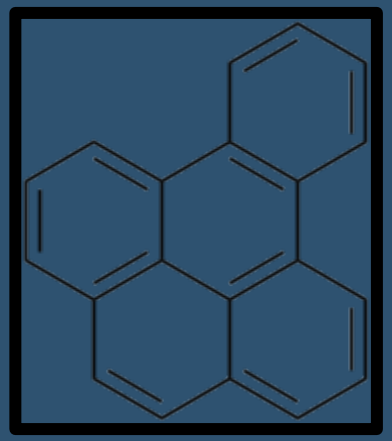
FIVE RINGS: BENZO[A]PYRENE (BAP)

- BaP is a five-ring PAH with the formula $C_{20}H_{12}$. The compound is one of the benzopyrenes, formed by a benzene ring fused to pyrene, usually as the result of incomplete combustion at temperatures between 300 °C (572 °F) and 600 °C (1,112 °F):

BaP



BeP



Source: Wikipedia

BAP OCCURRENCE

- Common among the hundreds of PAH compounds, including BaP, is they are uncharged, non-polar and planar. Many are colorless.
- Many of them are found in coal and in oil deposits and are also produced by the incomplete combustion of organic matter. For example, in engines and incinerators or when biomass burns in forest fires. PAHs – Contaminated Site Cleanup Information.
- Complete combustion occurs in an unlimited supply of oxygen. Hydrocarbons will leave only two byproducts – water and carbon dioxide (CO_2).

BAP OCCURRENCE

- BaP is naturally emitted by volcanic eruptions and can also be found in asphalt, coal, crude oil, gasoline and diesel fuels, coal tar, cigarette smoke, wood smoke and roasted foods, such as coffee. Fumes that develop from fat dripping on hot charcoal are rich in benzopyrene, which can condense on grilled foods.

Source: Wikipedia

- It has been estimated that more than 20% of the carbon in the universe may be associated with PAHs.

Source: Wikipedia

BAP OCCURRENCE

- Benzopyrene often occurs together with other related aromatic species such as benzofluoranthenes, benzoanthracenes, dibenzoanthracenes and indenopyrenes, which appear on the DEP BaP Conversion Table.

- The US Environmental Protection Agency (EPA) designates 16 PAHs as priority pollutant contaminants, ranging from naphthalene (two ring) to benzo[ghi]perylene (BghiP six ring). Source: US EPA

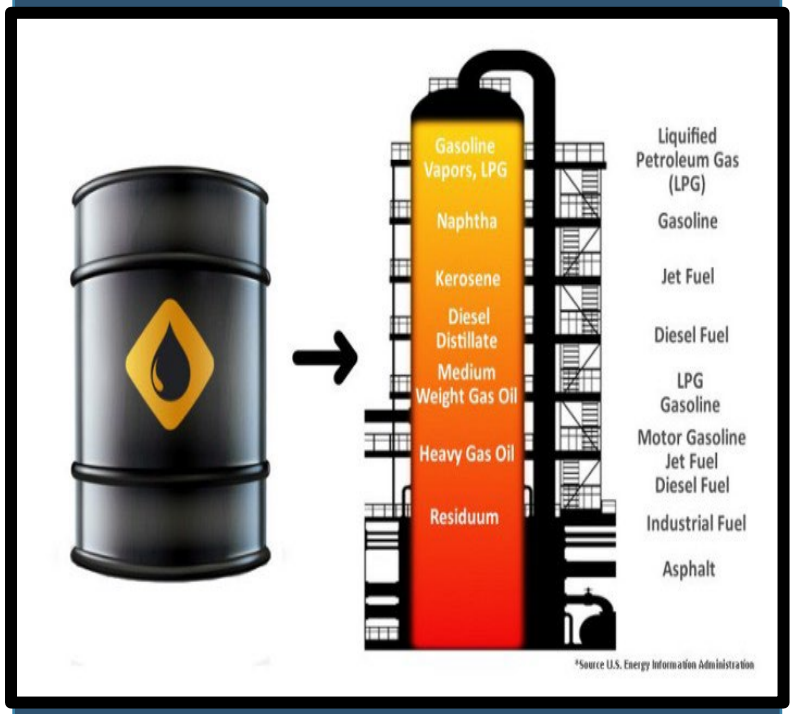
ENVIRONMENTAL FATE AND TRANSPORT

- Most PAHs are insoluble in water, which limits their mobility in the environment, although PAHs absorb to fine-grained organic-rich sediments. Aqueous solubility of PAHs decreases as molecular mass (i.e., number of rings) increases. Source: Wikipedia
- Two-ringed PAHs, and to a lesser extent three-ringed PAHs, dissolve in water, making them more available for biological uptake and degradation. In contrast, compounds with five or more rings have low solubility in water and low volatility. They are therefore predominantly in a solid state, bound to particulate air pollution, soils or sediments. In a solid state, these compounds are less accessible for biological uptake or degradation, increasing their persistence in the environment. Source: Wikipedia

PETROGENIC AND PYROGENIC PAHS

Although there are many different individual sources, PAH source materials are generally classified as either petrogenic (derived from petroleum) or pyrogenic (derived from combustion).

National Institute of Water and Atmospheric Research, Hamilton



Source: OneStepPower
https://www.onesteppower.com/post/what-is-in-a-barrel-of-oil

Source: Mike McMillan/USFS - https://inciweb.nwcg.gov/incident/photographs/6748

PETROGENIC PAHS

- Petrogenic sources tend to be dominated by weight PAHs: two-ring naphthalenes and three-ring phenanthrenes (but not three-ring anthracenes). The term 'naphthalenes' and 'phenanthrenes' includes the parent PAH compound (i.e. naphthalene and phenanthrene) and all related compounds that have methyl (and other alkyl groups – ethyl, propyl, isopropyl, etc.) groups attached to the parent PAH compound. In petrogenic sources, the amount of alkylated PAHs exceed the amount of parent PAHs.

Source: National Institute of Water and Atmospheric Research, Hamilton

- Alkylation is an important reaction at the refinery for the production of fuels from petroleum.

Source: Mettler Toledo - Alkylation Reactions

WHAT IS ALKYLATION?

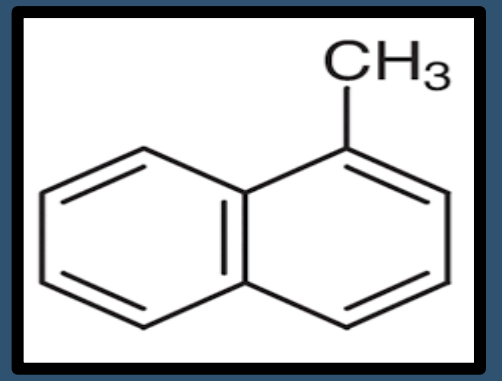
- Alkylation is a chemical process by which an alkyl group is attached to an organic substrate molecule. An alkyl group is an alkane molecule that is missing a hydrogen atom. For example, methyl groups are the simplest alkyls and result from the removal of a hydrogen atom from methane. Mettler

Source: Toledo - Alkylation Reactions

methane

Source: Adobe Stock

1-methylnaphthalene



Source: Wikidata
https://www.wikidata.org/wiki/Q2813819

PYROGENIC PAHS

- Pyrogenic PAHs are dominated by phenanthrene and the mid-to-large sized PAHs (i.e. four-six rings). Because these materials were formed via combustion processes, the PAH composition is dominated by parent compounds (only very small amounts of alkylated PAHs are present).

Source: National Institute of Water and Atmospheric Research, Hamilton

PETROGENIC VS PYROGENIC PAHS

- Because of key differences between pyrogenic and petrogenic PAHs, information regarding potential sources can be determined by forensic study of PAH composition profiles (or ‘fingerprints’) or by using established key diagnostic ratios of certain PAHs. Initial source identification, based on these kinds of parameters, can provide a significant amount of preliminary information regarding petrogenic/pyrogenic source differentiation.

Source: National Institute of Water and Atmospheric Research, Hamilton

PETROGENIC VS PYROGENIC PAHS

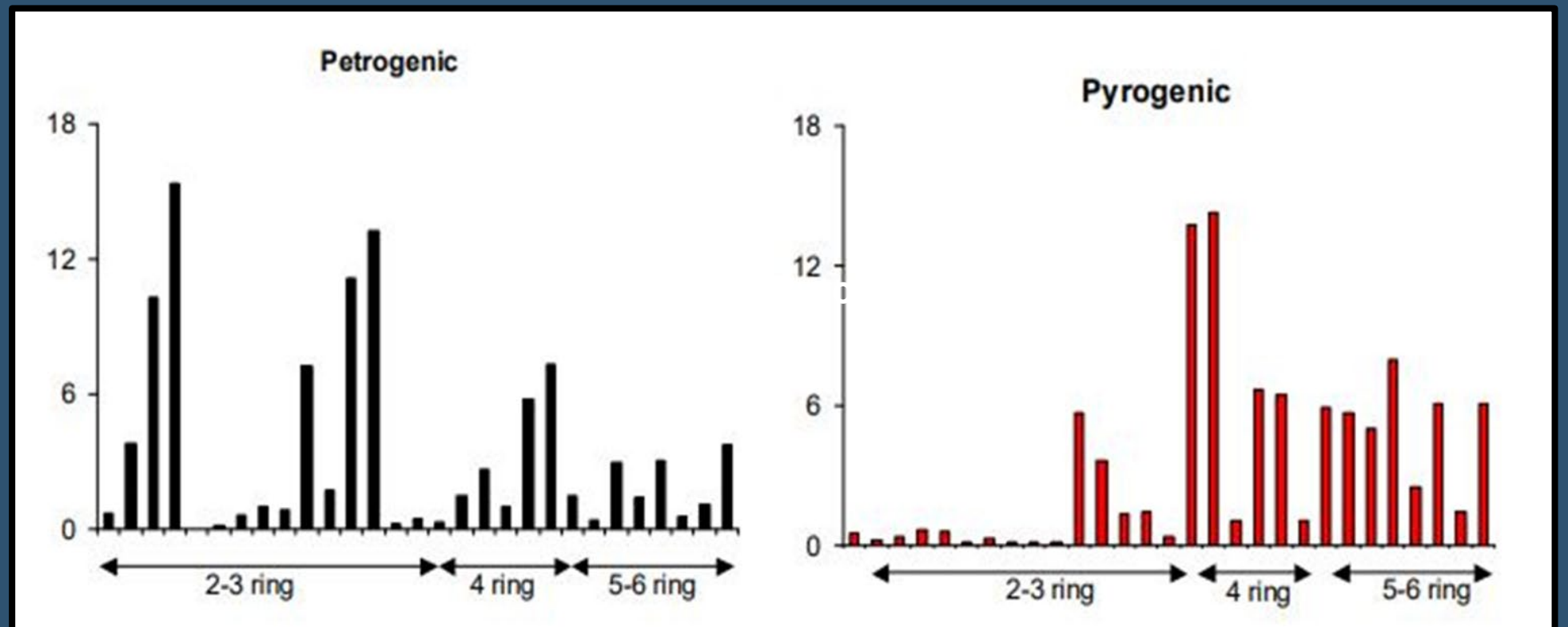


Figure 1: Characteristic PAH profiles of petrogenic versus pyrogenic source (y-axis is percentage of individual PAHs)

Source: National Institute of Water and Atmospheric Research, Hamilton

DEP FORENSIC REPORT

Dated Oct. 9, 2020.

FORENSIC METHODS

Overall Distribution:

- The overall distribution of PAHs gives an indication of source material based on the mass contributions of the individual PAHs.

Parent vs. Alkylated PAH Distributions:

- Another useful tool utilizes a comparison between each group of parent PAHs with their respective alkylated homologs.

FORENSIC METHODS

Single Ratio Histogram:

- Several PAH diagnostic ratios can be used to differentiate between pyrogenic and petrogenic sources. Some ratios give a more detailed analysis of the types of combustion (*e.g.,* coal, grass, wood, tar, diesel and petrol), types of emissions (traffic vs. non-traffic) and biodegradability (fresh particles vs. weathered).
- There are specific numerical thresholds that are used to determine the PAH pollution sources. Five ratios have been considered for this line of evidence due to their applicability in distinguishing petrogenic vs. pyrogenic PAH origins.

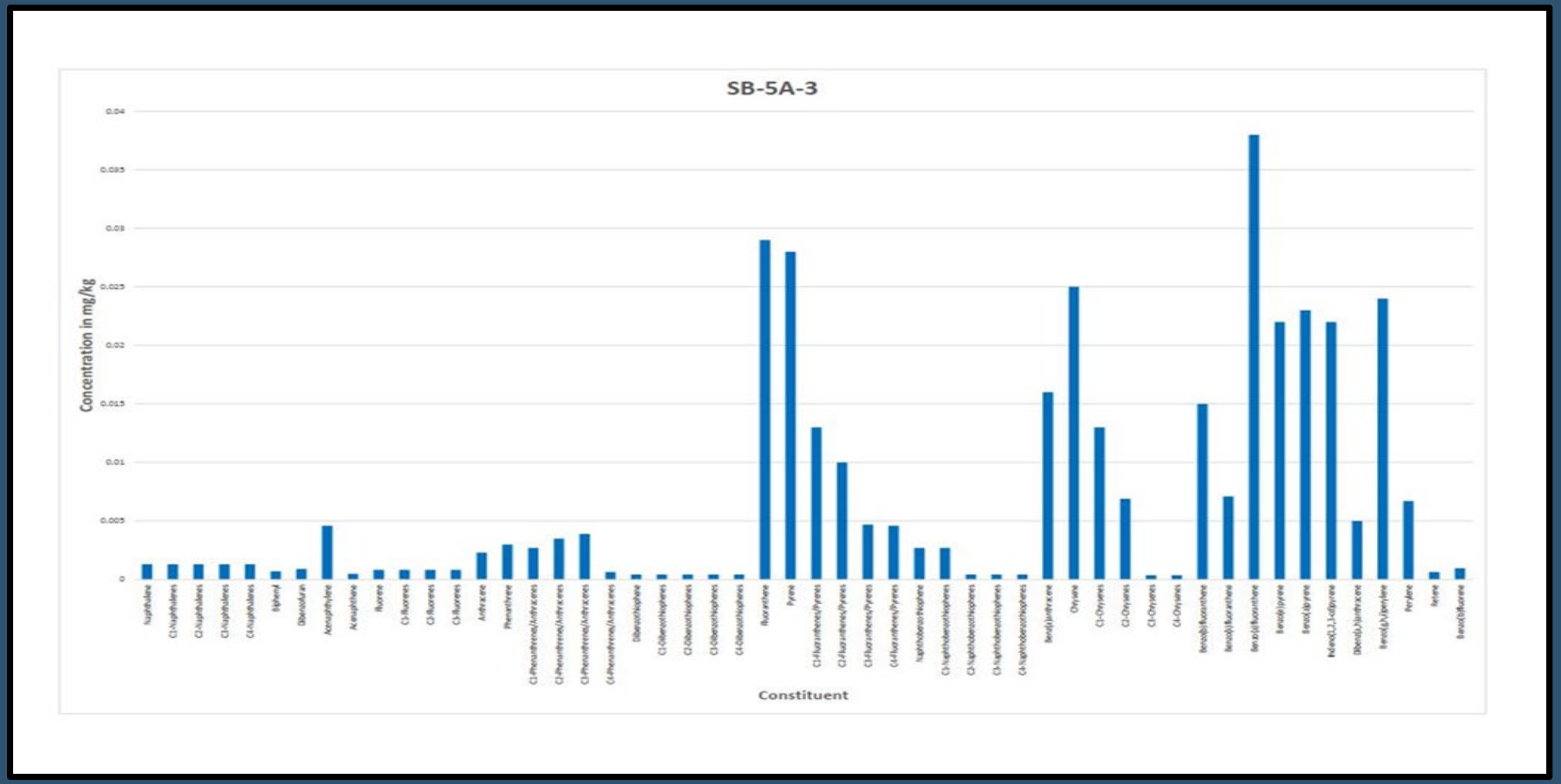
FORENSIC METHODS

- Low Molecular Weight/High Molecular Weight (LMW/HMW):
  - This ratio is the sum of two and three-ring PAHs (LMW) divided by the sum of the four and five-ring PAHs (HMW). If the ratio is smaller than 1.0, the source is considered pyrogenic. If the ratio is greater than 1.0, the source is considered petrogenic.
- Combustion PAHs/total PAHs:
  - If the ratio is very close to 1.0, it is an indication that almost all of the PAHs detected are from a pyrogenic source. If the ratio is 0.8 or lower, it is an indication that at least 20% of the PAHs are petrogenic.

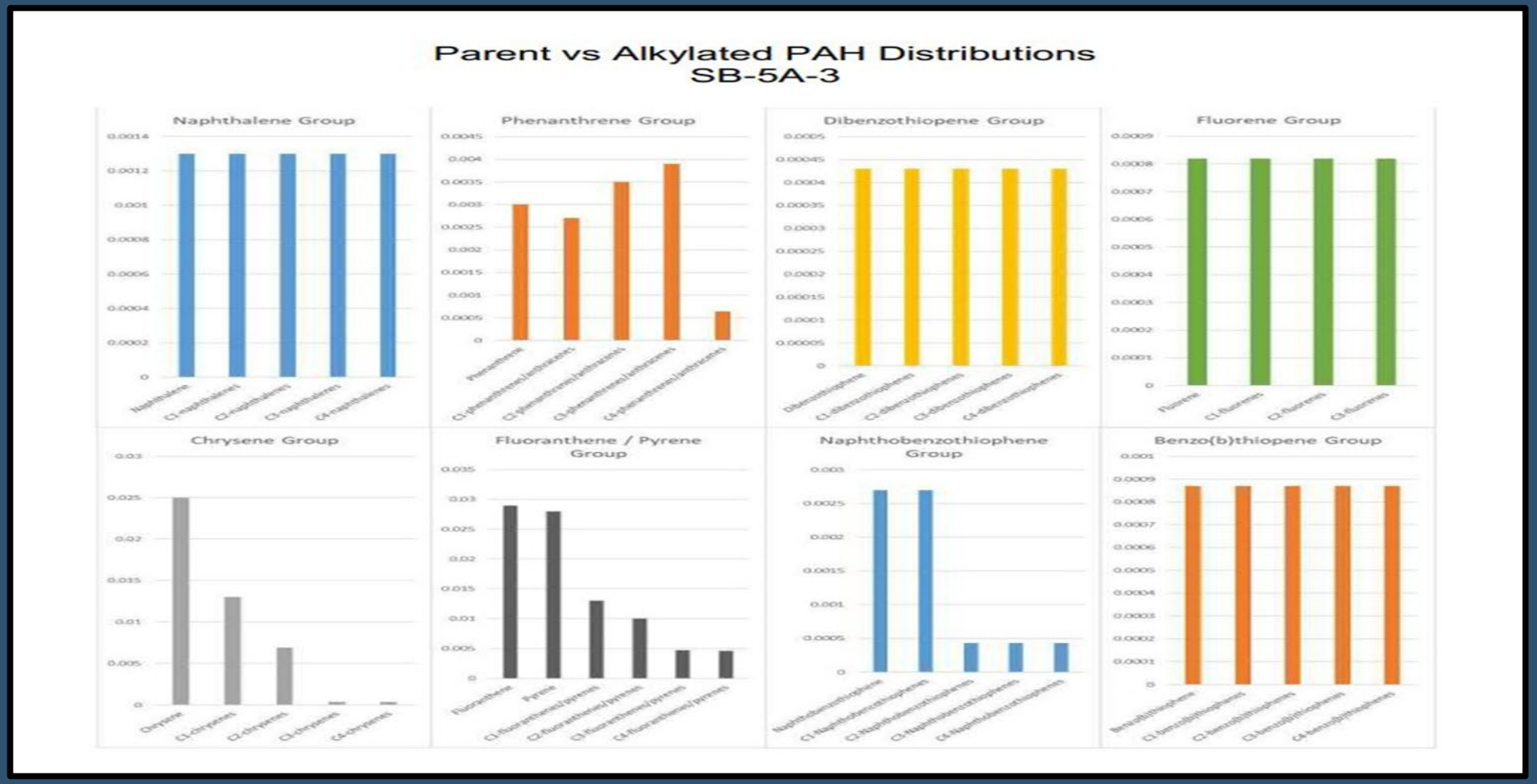
FORENSIC METHODS

- Fluoranthene(FLA)/(FLA + pyrene(PYR)):
  - If this ratio is below 0.4, it is implied that there is an abundance of petrogenic PAHs in the sample. A ratio higher than 0.4 implies the presence of pyrogenic PAHs with 0.4 – 0.5 indicating fossil fuel combustion, while higher than 0.5 implies grass, wood or coal combustion.
- Benzo[a]anthracene(BaA))/(BaA + chrysene(CHR)):
  - A resulting ratio below 0.2 indicates the PAHs are from a petrogenic source. If the ratio is above 0.2, it indicates coal or petroleum combustion, thus unrelated to a petroleum release.
- Indeno[c,d]pyrene(IcdP)/(IcdP+Benzo[g,h,i]pyrene(BghiP)):
  - A resulting ratio of 0.2 or lower indicates the presence of petrogenic PAHs. If the ratio is between 0.2 and 0.5, it indicates petroleum combustion, and a result greater than 0.5 indicates grass or wood combustion.

OVERALL DISTRIBUTION



PARENT VS ALKYLATED



SINGLE RATIO TABLE

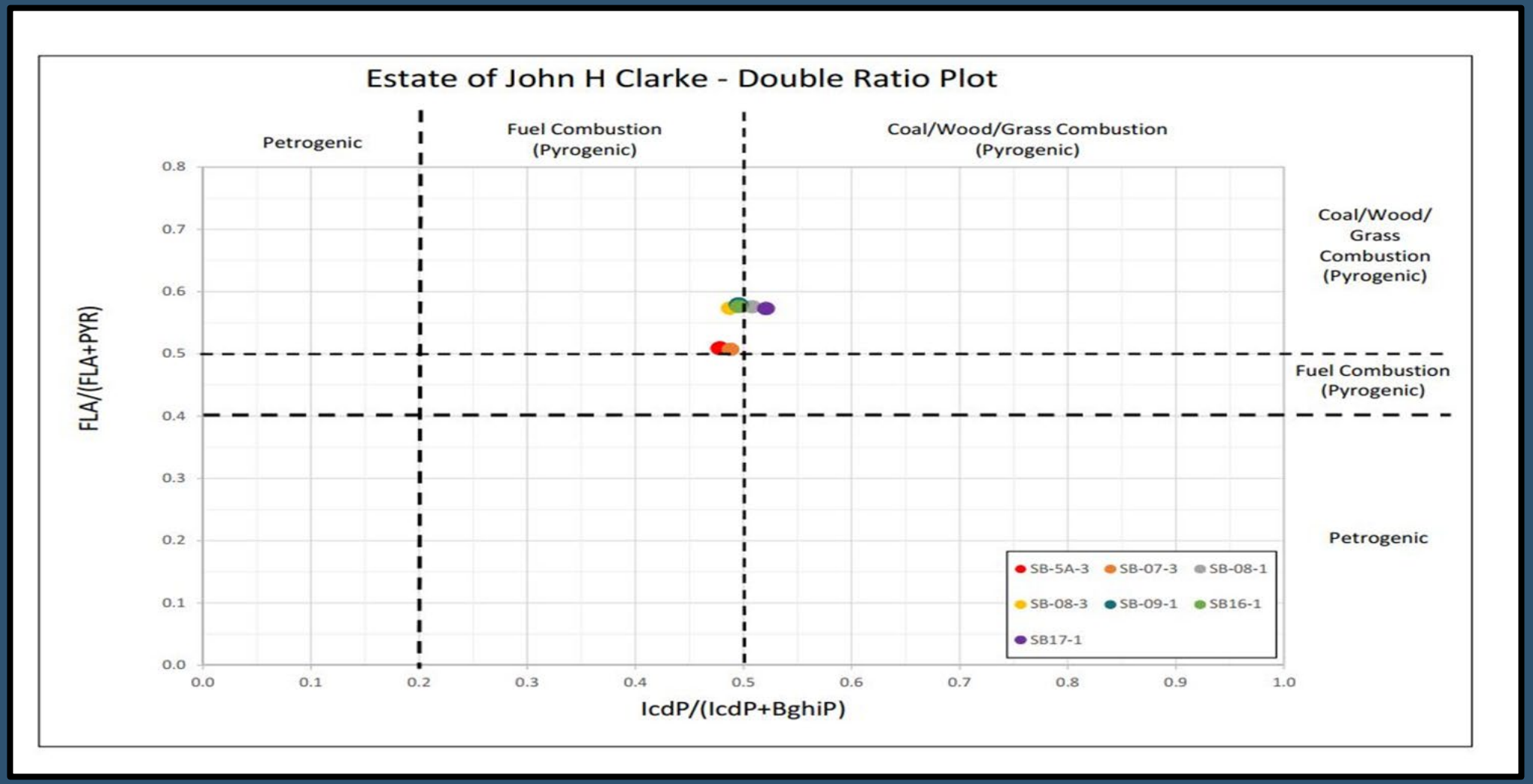
Estate of John H Clarke - Single Ratios					
Sample Location	ΣLMW/ ΣHMW	ΣCOMB/ ΣTOTAL	Fla/ Fla+Pyr	B(a)A/ (B(a)A+Chr)	I(123)P/ (I(123)P+B(ghi)P)
SB-5A-3	0.03	0.82	0.51	0.39	0.48
SB-07-3	0.03	0.82	0.51	0.38	0.49
SB-08-1	0.05	0.84	0.58	0.39	0.51
SB-08-3	0.05	0.84	0.57	0.38	0.49
SB-09-1	0.06	0.83	0.58	0.38	0.50
SB16-1	0.12	0.81	0.58	0.48	0.50
SB17-1	0.04	0.84	0.57	0.38	0.52
Petrogenic	>1	<0.8	<0.4	<0.2	<0.2
Pyrogenic	<1	~1	>0.4	>0.2	>0.2

DOUBLE RATIO PLOT

A two-dimensional plot can be used to determine if a certain sample indicates characteristics of the presence of a pyrogenic or petrogenic source of PAHs. The data is plotted using the IcdP/(IcdP+BghiP) ratio on the x-axis and the FLA/(FLA+PYR) ratio on the y-axis.

The double ratio plot is used to determine the position of data points with respect to established values for petrogenic and pyrogenic sources and evaluate the potential for single or multiple sources. Tightly clustered data points would indicate a higher confidence level of a single source, whereas more dispersed data points or multiple clusters would appear to indicate multiple PAH sources.

DOUBLE RATIO PLOT



CONCLUSION

- Since the majority of the analytical-based lines of evidence indicate the PAH impacts identified at this facility are pyrogenic in nature, the identified BaP concentrations do not appear to be attributed to the discharge of petroleum products including the documented March 23,1990, release.

- The forensic site investigation report for the estate of John H. Clarke facility was submitted to the DEP on July 16, 2020.

BACKGROUND CONCENTRATIONS

- Guidance for Comparing Background and Site Chemical Concentrations in Soil.
- DEP March 2019.
- Guidance explains where to collect background samples, number of background samples required, and non-statistical and statistical approaches for comparing site and background data.

NON-STATISTICAL APPROACHES

- Direct comparison of site concentrations with background.
- Comparison of 95% Upper Confidence Level (UCL) between site and background.
- Weight of evidence demonstration that contaminants are not related.

WEIGHT OF EVIDENCE DEMONSTRATION

- Contaminants found, during the course of site assessment, can be excluded from cleanup if the weight of evidence clearly demonstrates that the contaminant is not related to the discharge.

- The guidance lists seven lines of evidence that can be considered. Other lines of evidence are possible, such as chemical fingerprinting, performed as part of an environmental forensics evaluation.

- In general, no single line of evidence will provide sufficient justification to determine a contaminant is not related to the discharge.

WHAT WE ARE SHOWN:

WHAT WE ARE TOLD:

- These relatively low PAH exceedances, which are strictly limited to the 0-0.5 ft. below land survey (BLS) interval, are not characteristic of a petroleum release from the underground storage tank (UST) system and appears more likely to be associated with asphalt paving or anthropogenic conditions in the area.

- Soil borings, GSB-3 and GSB-5, are located in asphalt paved areas at the Site (if the Agency Term Contractor [ATC] only had a DEP procedure for collecting BaP shallow soil sample).

WHAT WE ARE TOLD:

- Soil borings GSB-6, GSB-6R and GSB-7 were advanced in an unpaved, curbed swale northwest of the UST tank farm at the site. The shallow soil in this area appeared to be filled and not in-place native soil.

- Note that based on the PAH testing results for collected groundwater samples for this site reported later in this Site Assessment Report (SAR) no Groundwater Cleanup Target Level (GCTL) exceedances, PAHs are not considered to be Contaminants of Concern (COCs) in groundwater for this site.

RESPONSE:

- Otherwise, these exceedances must be fully delineated and either included in any proposed engineering controls or remediated.

- ERM notes that these soil borings are immediately adjacent to the petroleum release source area and soil boring, GSB-6, also had the most elevated site Organic Vapor Analyzer (OVA) readings.

RESPONSE:

- PAH contamination in the vicinity of GSB-6, GSB-6R and GSB-7 has not been fully delineated to applicable Soil Cleanup Target Level (SCTLs).

- Environmental Risk Management LLC observed that in their 2022 SAR, ATC states that “PAH exceedances at these soil boring locations are not characteristic of a petroleum release and appear more likely to be associated with asphalt paving or anthropogenic conditions in the area.” While that statement may be true, ATC will have to demonstrate that the exceedances are not due to petroleum releases from their property by utilizing a background data study and a weight of evidence demonstration.

BAP SOILS CLOSURE SOLUTIONS – JERRY COOK, PG

- Otherwise known as “What can I do now with these BaP soil exceedances?”

SO, YOU HAVE A PROBLEM WITH ONLY BAP SOILS- WHAT NOW?

- Explanation that allows for anthropogenic designation.
- Source Removal.
- Conditional Closure.
- Forensic evaluation with lines of evidence.

SO, YOU HAVE A PROBLEM WITH ONLY BAP SOILS - WHAT NOW? ANTHROPOGENIC

- Questions to ask – assessment details.

- Distance from source areas (e.g. USTs, dispensers):
  - Closer hits likely to be petrogenic.

- Background soil data:
  - 62-780 F.A.C. specific procedures.

- Soil depth intervals:
  - Shallow soils may indicate anthropogenic.
  - Deeper soils can be related to soils that have been reworked or from petrogenic discharge.

ESTABLISHING PLAUSIBLE BAP ANTHROPOGENIC ORIGINS

- Aerial photo reviews:
  - Agricultural practices, soils reworked, near railroads and industrial area.

- Phase I Environmental Site Assessment (ESA) history:
  - Past site usage may indicate.

SOURCES RELATED TO LOCATION ASPECTS

- On-site possibilities – asphalt:
  - Reworked surface paving.
  - Drainage paths into swales or grassy receiving areas (especially no curbs).

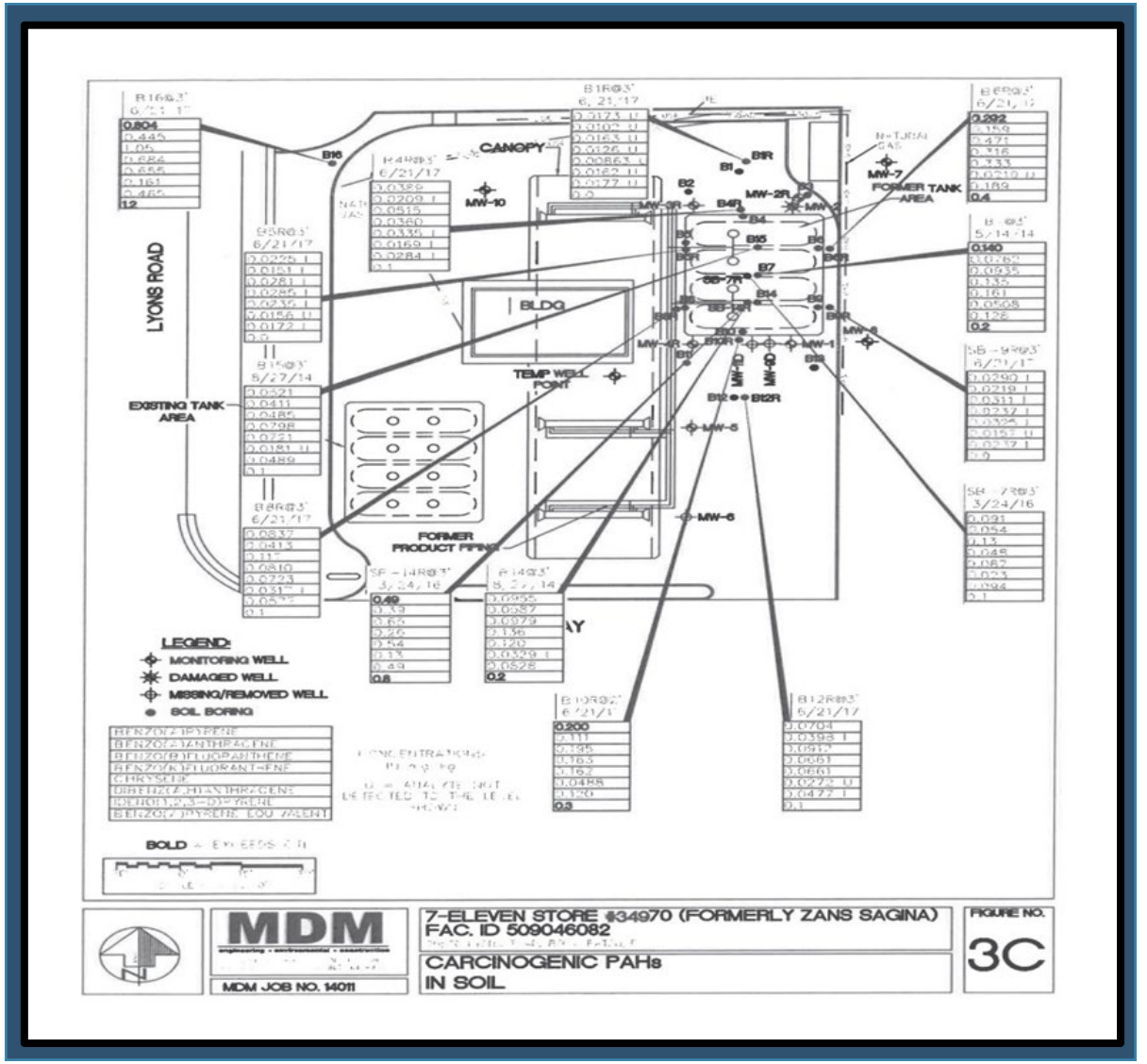
- Off-site location issues:
  - Nearby railroad tracks.
  - Significant exhaust sources either from stationary emissions stacks or moving vehicles.

A REVIEW OF SITES WITH NO FURTHER ACTION

- Facility ID 509046082 – Soil history.
- Facility ID 508944606 – Site with industrial sources.
- Facility ID 50894434 – Site with asphalt sealant and reworked surfacing.

509046082

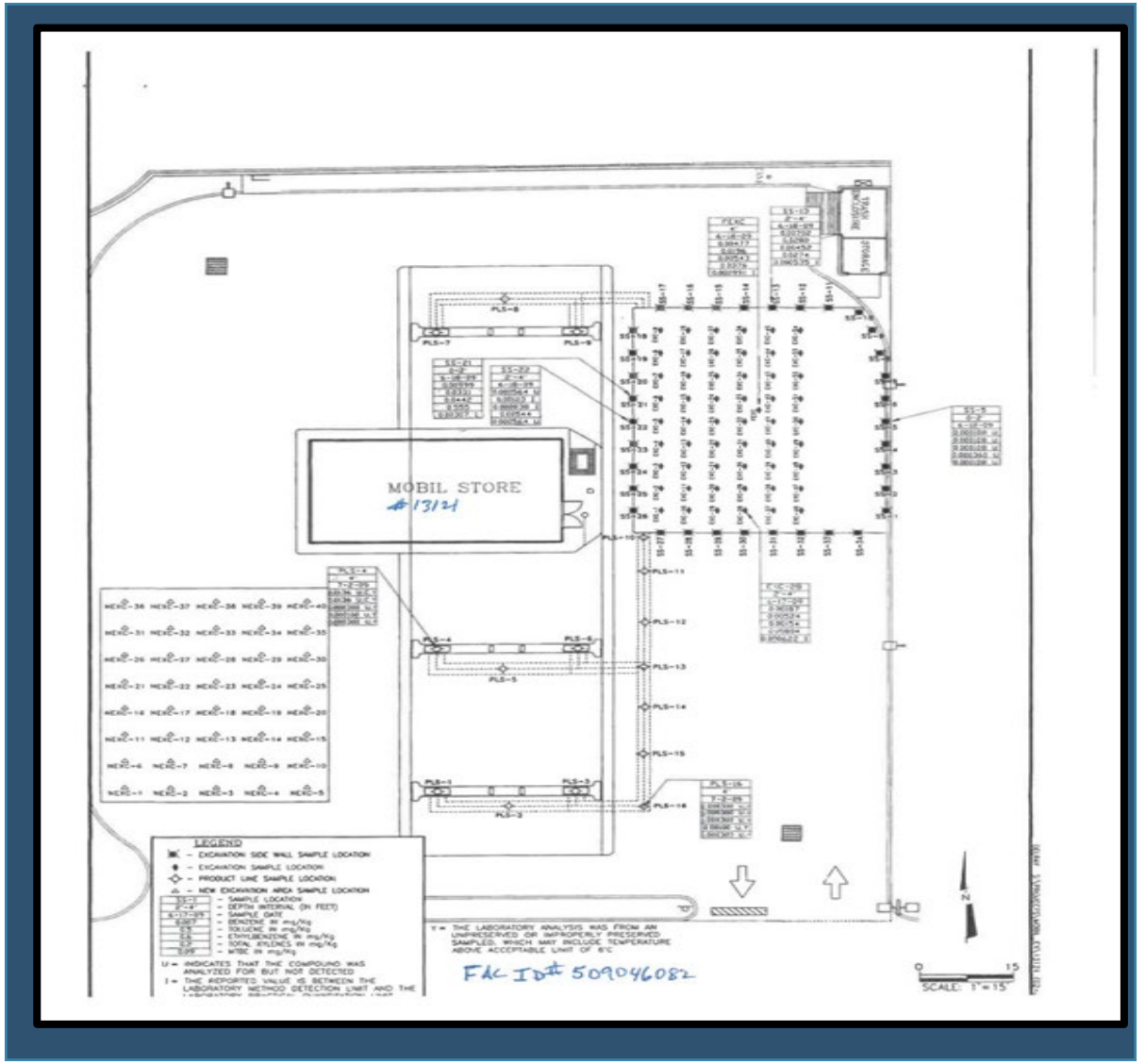
Old reports may include relevant info such as the Tank Closure Assessment Report (TCAR) detailing re-use of “dirty” soils.



Source: OCULUS

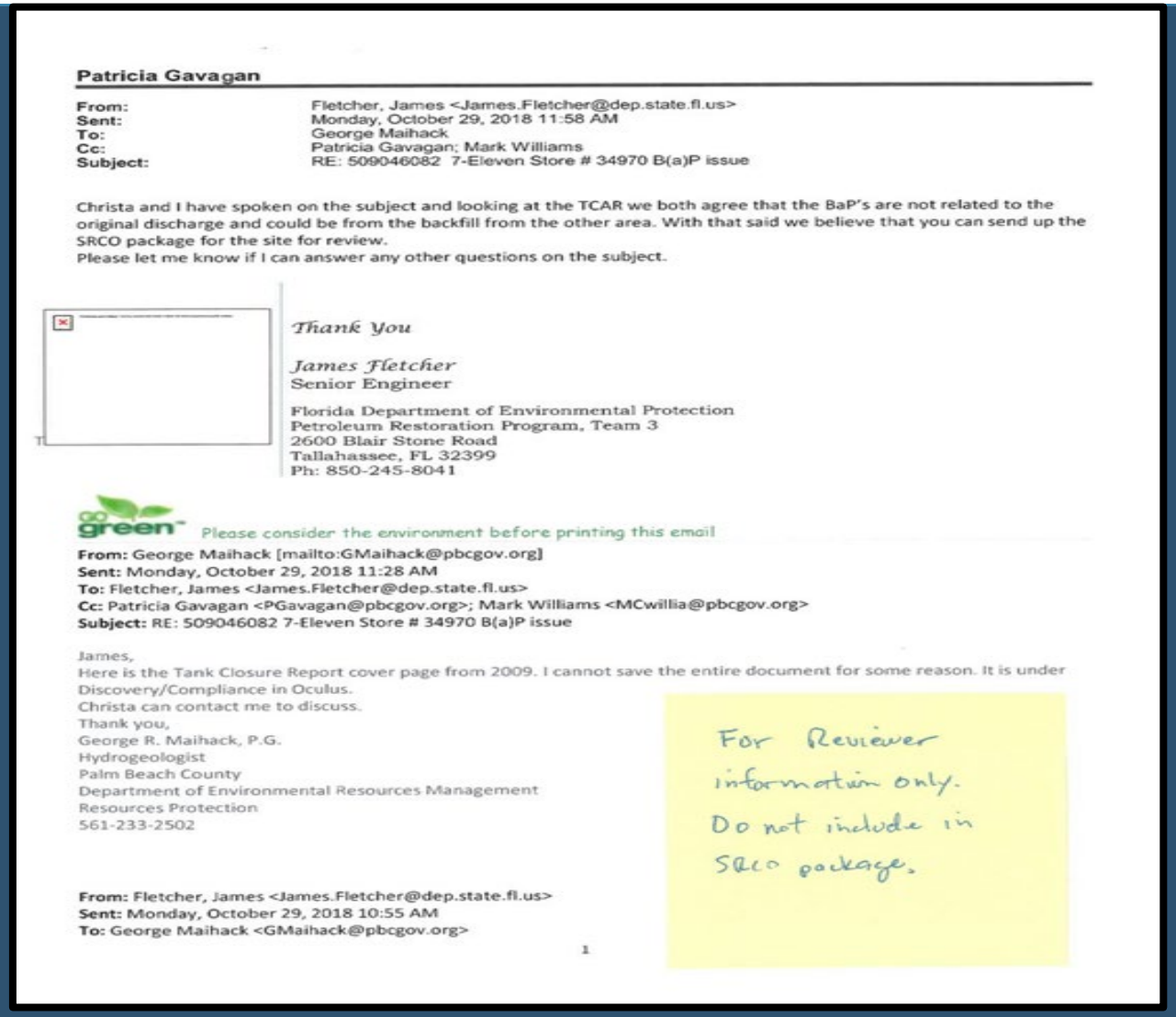
59046082

TCAR details tell the story.



Source: OCULUS

ENGAGING DEP REVIEW PROCESS



Patricia Gavagan

From: Fletcher, James <James.Fletcher@dep.state.fl.us>
Sent: Monday, October 29, 2018 11:58 AM
To: George Maihack
Cc: Patricia Gavagan; Mark Williams
Subject: RE: 509046082 7-Eleven Store # 34970 B(a)P issue

Christa and I have spoken on the subject and looking at the TCAR we both agree that the BaP's are not related to the original discharge and could be from the backfill from the other area. With that said we believe that you can send up the SRCO package for the site for review.
Please let me know if I can answer any other questions on the subject.

Thank You

James Fletcher
Senior Engineer

Florida Department of Environmental Protection
Petroleum Restoration Program, Team 3
2600 Blair Stone Road
Tallahassee, FL 32399
Ph: 850-245-8041

Please consider the environment before printing this email

From: George Maihack [mailto:GMaihack@pbcgov.org]
Sent: Monday, October 29, 2018 11:28 AM
To: Fletcher, James <James.Fletcher@dep.state.fl.us>
Cc: Patricia Gavagan <PGavagan@pbcgov.org>; Mark Williams <MCwillia@pbcgov.org>
Subject: RE: 509046082 7-Eleven Store # 34970 B(a)P issue

James,
Here is the Tank Closure Report cover page from 2009. I cannot save the entire document for some reason. It is under Discovery/Compliance in Oculus.
Christa can contact me to discuss.
Thank you,
George R. Maihack, P.G.
Hydrogeologist
Palm Beach County
Department of Environmental Resources Management
Resources Protection
561-233-2502

For Reviewer information only. Do not include in SRCO package.

From: Fletcher, James <James.Fletcher@dep.state.fl.us>
Sent: Monday, October 29, 2018 10:55 AM
To: George Maihack <GMaihack@pbcgov.org>

1

Source: OCULUS

THE DETAILS HELP EXPLAIN THE SITUATION

TABLE 2
SUMMARY OF SOIL ANALYSES
PAHs by EPA Method 8310 and TRPH by FL-PRO

Mobil # 13121 (02-JH1)
20570 LYONS ROAD
BOCA RATON, FL 33434
FDEP Facility ID: 509046082

Sample Location	Date	Acenaphthene	Acenaphthylene	Anthracene	Benzo(a) Anthracene	Benzo(a) Pyrene	Benzo(b) Fluoranthene	Benzo(g,h,i) Perylene	Benzo(k) Fluoranthene	Chrysene	Dibenzo(a,h) Anthracene	Fluoranthene	Fluorene	Indeno(1,2,3-c,d) Pyrene	1-Methyl-naphthalene	2-Methyl-naphthalene	Naphthalene	Phenanthrene	Pyrene	TRPH
Direct Exposure Residential		2,400	1,800	21,000	#	0.1	#	(2,800	#	#	#	3,200	2,600	#	200	210	55	2,200	2,200	340
Direct Exposure Commercial/Industrial		20,000	20,000	300,000	#	0.7	#	52,000	#	#	#	59,000	33,000	#	1800	2100	300	36,000	45,000	2,700
Leachability based on Groundwater Criteria		2.1	27	2,500	0.8	6	2.4	32,000	24	77	0.7	1,200	160	8.6	3.1	8.5	1.2	250	360	340
SB-2 (4')	03/19/09	0.00656 U	0.0682 I	0.00438 U	0.00345 U	0.689 R1	0.833	0.00288 U	1.52 R1	0.00368 U	8.50 R1	0.00380 U	0.00449 U	0.545	0.00291 U	0.00687 U	0.0100 U	0.0134 J4,U	0.00158 U	45.9 V
SB-2 (4')	03/19/2009*	NA	NA	NA	0.000808 U	0.000924 U	0.000808 U	NA	0.000693 U	0.000808 U	0.0417	NA	NA	0.0316	NA	NA	NA	NA	NA	NA
** SB-3 (4')	03/19/09	1.24	0.272	0.0589 R10	0.176	0.262	0.326	0.204	0.160 R1	0.484 R1	0.210 R1	2.51 R1	0.00482 U	0.273	0.373	0.00919 U	0.618 R10	1.04	0.929	25.2 V
SB-4 (4')	03/19/09	0.0133 U	0.152 I	0.00424 U	0.00335 U	0.00301 U	0.00301 U	0.00279 U	0.00323 U	0.00323 U	0.00491 U	0.00524 U	0.00435 U	0.00379 U	0.00892 U	0.00859 U	0.0151 U	0.0129 U	0.00502 U	11.4 V

NOTE: All results reported in milligrams per kilogram (mg/kg).
"PAHs" denotes Polynuclear Aromatic Hydrocarbons. "TRPH" denotes Total Recoverable Petroleum Hydrocarbons.
"Direct Exposure Residential" refers to Chapter 62-777 F.A.C. Table II Soil Cleanup Target Levels (SCTLs), Direct Exposure Residential Target Levels.
"Direct Exposure Commercial/Industrial" refers to Chapter 62-777 F.A.C. Table II Soil Cleanup Target Levels, Direct Exposure Commercial Target Levels.
"Leachability Based on Groundwater Criteria" refers to Chapter 62-777 F.A.C. Table II Soil Cleanup Target Levels, Leachability Based on Groundwater Criteria Target Levels.
" # " indicates that each concentration must be converted to Benzo(a) pyrene (BaP) equivalent using the "BaP Conversion Table".
"All SCTLs are from Chapter 62-777, FAC effective April 17, 2005"
"I" denotes the reported value is between the laboratory method detection limit and method reporting limit
"R1" denotes the RPD between the primary and confirmatory analysis exceeded 40%. Per method 8000B, the higher value was reported.
"R10" denotes the RPD between the primary and confirmatory analysis exceeded 40%. Per method 8000B, the lower value was reported.
"J4" denotes the sample matrix interfered with the ability to make an accurate determination
"U" denotes the compound was analyzed but not detected
"V" denotes the analyte was detected in both the sample and the associated method blank
* = Soil sample re-analyzed by Method EPA 8270C for Benzo(a)pyrene equivalents
NA = Sample not analyzed

** contamination was not from an area that could have been impacted by fuel and thus had to have come from the previous agricultural use of the site. The soil from SB-3 was excavated as it was deemed to be pre-construction and that area was excavated in June 2009 to put the new tanks in place.

Source: OCULUS

ENGAGING DEP REVIEW PROCESS

Cc: Mark Williams <MCwillia@pbcgov.org>
Subject: 509046082 7-Eleven Store # 34970 B(a)P issue

Good morning George,
I just had a request from Crista regarding the site we talked about involving BaP's. I guess the ATC contacted Haz-Waste down stairs and it has gone through Susan and Brian then back to Crista and then me. So, they want to know what information you had on previous hits that you emailed me. I recall you saying it was in a past report. Can you provide me with that report so I can send it to all concerned.
Let me know if I can clarify anything above.

Thank You

James Fletcher
Senior Engineer

Florida Department of Environmental Protection
Petroleum Restoration Program, Team 3
2600 Blair Stone Road
Tallahassee, FL 32399
Ph: 850-245-8041

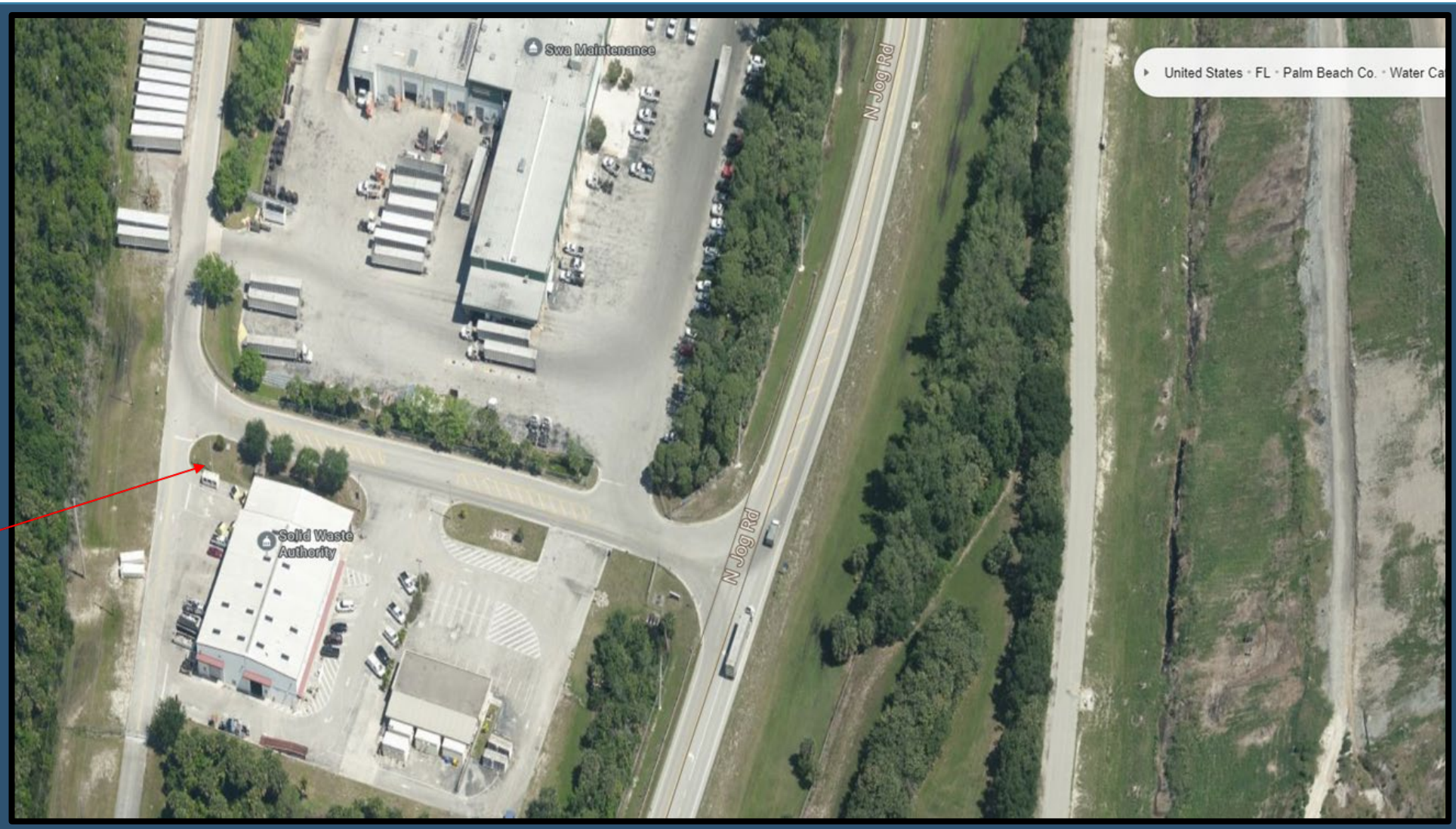
go green Please consider the environment before printing this email

Under Florida law, e-mail addresses are public records. If you do not want your e-mail address released in response to a public records request, do not send electronic mail to this entity. Instead, contact this office by phone or in writing.

2

Source: OCULUS

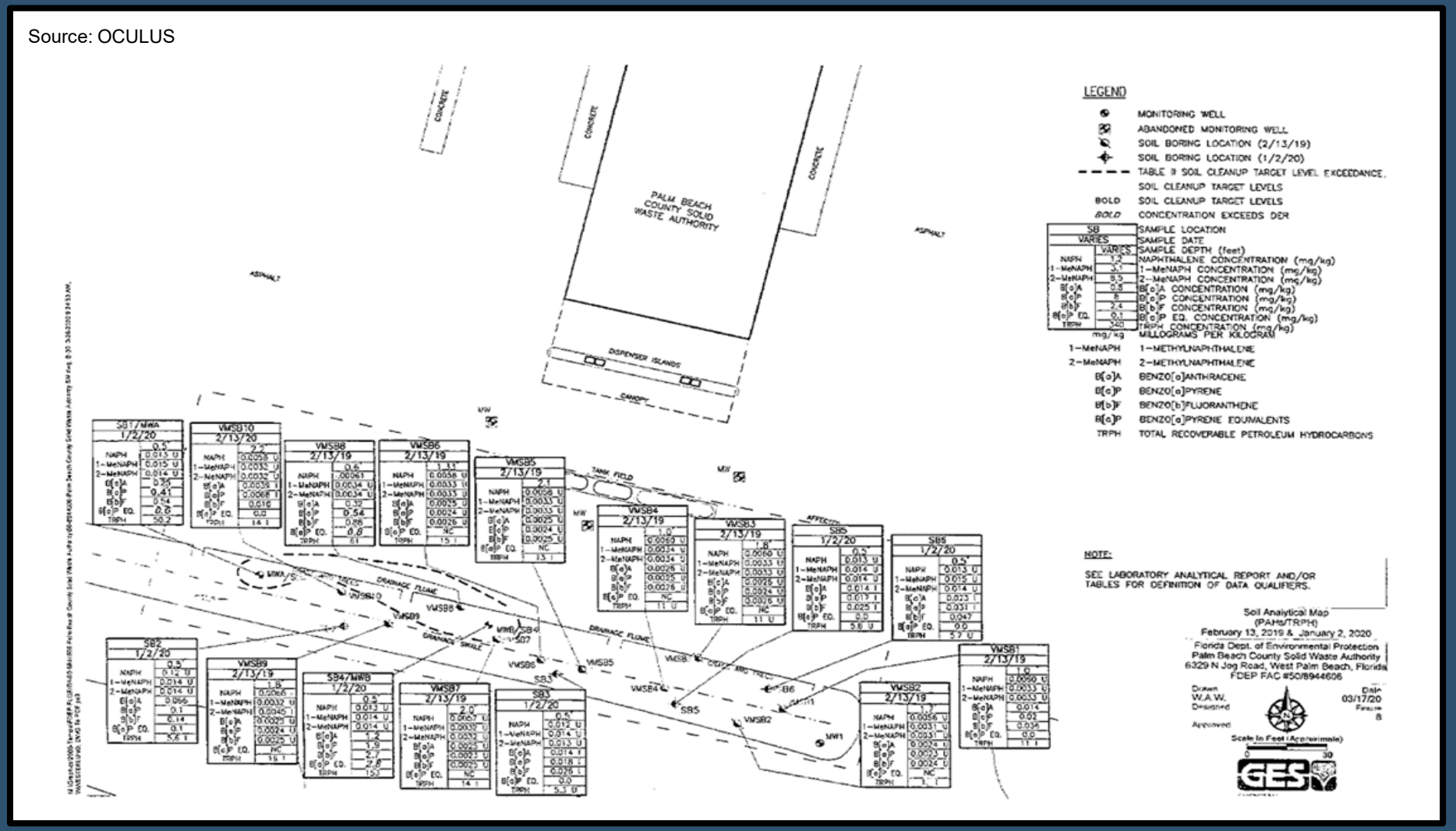
508944606 – INDUSTRIAL ACTIVITY



Source: OCULUS

INDUSTRIAL ACTIVITY

Source: OCULUS



508944606 – INDUSTRIAL ACTIVITY

Facility Name: Palm Beach County - Solid Waste Authority
Facility Address: 6329 N Jog Road, West Palm Beach, Palm Beach County, Florida
Facility Number: 508944606

	Sample		Naphth-alene	1-Methyl Naphthalene	2-Methyl Naphthalene	Acenaph-thene	Acenaph-thylene	Anthracene	Benzo(a) Anthracene	Benzo(a)-Pyrene	Benzo(b)-Fluoranthene	Benzo(g,h,i)-Perylene	Benzo(k)-Fluoranthene	Chrysene	Dibenz(a,h)-Anthracene	Fluor-anthene	Fluorene	Indeno(1,2,3-c,d) Pyrene	Phen-anthrene	Pyrene	Benzo(a) Pyrene Equivalent	TRPH
Location	Date	Depth																				
Direct Exposure Residential SCTLs (mg/kg)			65	200	210	2400	1800	21000	#	0.1	#	2500	#	#	#	3200	2500	#	2200	2400	0.1	460
Direct Exposure Commercial/Industrial SCTLs (mg/kg)			300	1800	2100	20000	20000	300000	#	0.7	#	52000	#	#	#	50000	33000	#	36000	45000	0.7	2700
Leachability Based on Groundwater Criteria (mg/kg)			1.2	3.1	8.5	2.1	27	2500	0.8	8	2.4	32000	24	77	0.7	1200	160	6.8	250	880	---	340
VMSB-1	02/13/19	1.0	0.0060 U	0.0033 U	0.0033 U	0.0028 U	0.0027 U	0.0024 U	0.014	0.02	0.035	0.020	0.013	0.025	0.0073 U	0.030	0.0029 U	0.021	0.0076 I	0.025	0.0	11 I
VMSB-2	02/13/19	1.7	0.0056 U	0.0031 U	0.0031 U	0.0027 U	0.0025 U	0.0022 U	0.0024 U	0.0023 U	0.0024 U	0.0060 U	0.0021 U	0.0024 U	0.0069 U	0.0021 U	0.0027 U	0.0039 U	0.0022 U	0.0020 U	NC	12 I
VMSB-3	02/13/19	1.8	0.0060 U	0.0033 U	0.0033 U	0.0029 U	0.0027 U	0.0024 U	0.0026 U	0.0024 U	0.0026 U	0.0064 U	0.0022 U	0.0026 U	0.0073 U	0.0023 U	0.0029 U	0.0042 U	0.0023 U	0.0022 U	NC	11 U
VMSB-4	02/13/19	1.9	0.0060 U	0.0034 U	0.0034 U	0.0029 U	0.0027 U	0.0024 U	0.0026 U	0.0025 U	0.0026 U	0.0065 U	0.0023 U	0.0026 U	0.0074 U	0.0023 U	0.0029 U	0.0043 U	0.0024 U	0.0022 U	NC	11 U
VMSB-5	02/13/19	2.1	0.0058 U	0.0033 U	0.0033 U	0.0028 U	0.0026 U	0.0023 U	0.0025 U	0.0024 U	0.0025 U	0.0063 U	0.0022 U	0.0025 U	0.0072 U	0.0022 U	0.0028 U	0.0041 U	0.0023 U	0.0021 U	NC	13 I
VMSB-6	02/13/19	1.3	0.0058 U	0.0033 U	0.0033 U	0.0029 U	0.0027 U	0.0023 U	0.0025 U	0.0024 U	0.0026 U	0.0063 U	0.0022 U	0.0025 U	0.0072 U	0.0022 U	0.0028 U	0.0041 U	0.0023 U	0.0021 U	NC	13 I
VMSB-7	02/13/19	2.0	0.0057 U	0.0032 U	0.0032 U	0.0027 U	0.0026 U	0.0023 U	0.0025 U	0.0023 U	0.0025 U	0.0061 U	0.0021 U	0.0025 U	0.0070 U	0.0022 U	0.0028 U	0.0040 U	0.0022 U	0.0021 U	NC	14 I
* VMSB-8	02/13/19	0.6	0.00091 U	0.0034 U	0.0034 U	0.0029 U	0.0032 I	0.017	0.32	0.54	0.88	0.57	0.31	0.63	0.11	0.60	0.0030 U	0.60	0.094	0.48	0.8	61
VMSB-9	02/13/19	1.8	0.0058 I	0.0032 U	0.0045 I	0.0028 U	0.0026 U	0.0023 U	0.0025 U	0.0024 U	0.0025 U	0.0062 U	0.0022 U	0.0025 U	0.0071 U	0.0022 U	0.0028 U	0.0041 U	0.0023 U	0.0021 U	NC	16 I
VMSB-10	02/13/19	2.2	0.0058 U	0.0032 U	0.0032 U	0.0027 U	0.0026 U	0.0023 U	0.0039 I	0.0068 I	0.010	0.0070 I	0.0064 I	0.0065 I	0.0071 U	0.00661	0.0028 U	0.0071 I	0.0023 U	0.0069 I	0.0	14 I
* SB-1 @ 0.5'	01/02/20	0.5	0.013 U	0.015 U	0.014 U	0.013 U	0.012 U	0.013 U	0.25	0.41	0.54	0.36	0.23	0.38	0.063	0.51	0.013 U	0.29	0.12	0.43	0.6	50.2
SB-2 @ 0.5'	01/02/20	0.5	0.12 U	0.014 U	0.014 U	0.012 U	0.011 U	0.013 U	0.066	0.1	0.14	0.095	0.061	0.11	0.0083 U	0.14	0.013 U	0.071	0.053 I	0.12	0.1	5.6 I
SB-3 @ 0.5'	01/02/20	0.5	0.012 U	0.014 U	0.013 U	0.012 U	0.011 U	0.012 U	0.014 I	0.018 I	0.026 I	0.0089 U	0.011 I	0.016 I	0.0081 U	0.024 I	0.013 U	0.0080 U	0.012 U	0.020 I	0.0	5.3 U
* SB-4 @ 0.5'	01/02/20	0.5	0.013 U	0.014 U	0.014 U	0.032 I	0.012 I	0.079	1.2	1.9	2.7	1.6	1.2	2.1	0.37	3.4	0.033 I	1.2	1.1	2.5	2.8	153
SB-5 @ 0.5'	01/02/20	0.5	0.013 U	0.014 U	0.014 U	0.013 U	0.011 U	0.013 U	0.014 I	0.017 I	0.025 I	0.0082 U	0.011 I	0.020 I	0.0084 U	0.024 I	0.013 U	0.0084 U	0.012 U	0.020 I	0.0	5.5 U
SB-6 @ 0.5'	01/02/20	0.5	0.013 U	0.015 U	0.014 U	0.013 U	0.012 U	0.013 U	0.023 I	0.031 I	0.047	0.0094 U	0.015 I	0.04	0.0087 U	0.047	0.013 U	0.0086 U	0.012 U	0.039	0.0	5.7 U

Notes:

All results reported in milligrams per kilogram (mg/kg)

Direct Exposure Residential Soil Cleanup Target Level (SCTLs), Table II, FDEP Chapter 62-777 Florida Administrative Code (FAC)

Commercial/Industrial SCTLs, Table II, FDEP Chapter 62-777 F.A.C.

Leachability Based on Groundwater Criteria SCTLs, Table II, FDEP Chapter 62-777 F.A.C.

PAHs - Polycyclic Aromatic Hydrocarbons

ft b/s - feet below land surface

NS - Not sampled

- Site concentrations for carcinogenic PAHs must be converted to benzo(a)pyrene equivalents before comparisons with the direct exposure SCTL for benzo(a)pyrene as described in the February 2005 "Final Technical Report: Development of SCTLs for Chapter

--- - Contaminant is not a health concern for this exposure scenario

Bolded values indicate concentrations exceed applicable SCTLs

Data Qualifiers and Definitions:

I - The reported value is between the laboratory method detection limit and method reporting limit

U - The compound was analyzed for but not detected

*BaP sources pyrogenic- high diesel truck traffic and on-site incinerator in the area

Source: OCULUS

SITE RENOVATIONS WITH REWORKED ASPHALT 508944434

TABLE 4C: SOIL ANALYTICAL SUMMARY - Carcinogenic PAHs

Facility ID#: 508944434 **Facility Name:** Texaco Station

	Sample				OVA	Laboratory Analyses							
	Boring/ Well No.	Date Collected	Depth to Water (ft)	Sample Interval (fbls)	Net OVA Reading (ppm)	Benzo (a) pyrene (mg/kg)	Benzo (a) anthra-cene (mg/kg)	Benzo (b) fluoran-thene (mg/kg)	Benzo (k) fluoran-thene (mg/kg)	Chry-sene (mg/kg)	Dibenz (a,h) anthra-cene (mg/kg)	Indeno (1,2,3-cd) pyrene (mg/kg)	Benzo (a) pyrene equivalent (mg/kg)
	Leachability Based on Groundwater Criteria (mg/kg)					8	0.8	2.4	24	77	0.7	6.6	**
	Direct Exposure Residential (mg/kg)					0.1	#	#	#	#	#	#	0.1
	SB-3 @ 3'	10/04/2016	4	2-3	17.3	0.011 U	0.027 U	0.082 I	0.020 U	0.033 U	0.046 U	0.046 U	0.040
*	MW-17 @ 1'/B-1	8/7/2019	1.5	1	21.6	**0.178**	0.229	0.357	0.121	0.17	0.00475 U	0.137	**0.3**
*	B-2R @ 1'	6/16/2020	2	1	0.0	**0.36**	0.30	0.57	0.20	0.42	0.097	0.43	**0.6**
	MW-9RR @ 1'	6/16/2020	2	1	0.0	0.061	0.049	0.091	0.035	0.067	0.016	0.075	0.1
	MW-1R	10/25/2021	3.5	2.5	0.0	0.0	0.025	0.050	0.018	0.036	0.0076 I	0.032	0.1
	MW-2R	10/25/2021	3	2	0.0	0.011	0.0074 I	0.019	0.0073 I	0.017	0.0019 I	0.011	0.0
*	MW-3R	10/25/2021	4.5	3.5	3.8	**0.26**	0.24	0.35	0.14	0.27	0.053 I	0.22	**0.4**
	MW-8R	10/26/2021	4	3	0.0	0.020 U	0.024 U	0.025 I	0.028 U	0.035 U	0.020 U	0.029 U	0.0
	WP-1R	10/26/2021	4	2.5	0.8	0.035	0.030	0.052	0.019	0.037	0.0067 I	0.028	0.1

Notes:

NA = Not Analyzed NC = Not Calculated

O - see following pages for BaP conversion tables

Bold = Constituent detected at concentration shown.

I = The reported value is between the laboratory limit of detection (MDL) and the laboratory limit of quantitation (PQL).

U = Indicates that a specific compound was analyzed for but not detected. The reported value shall be the MDL.

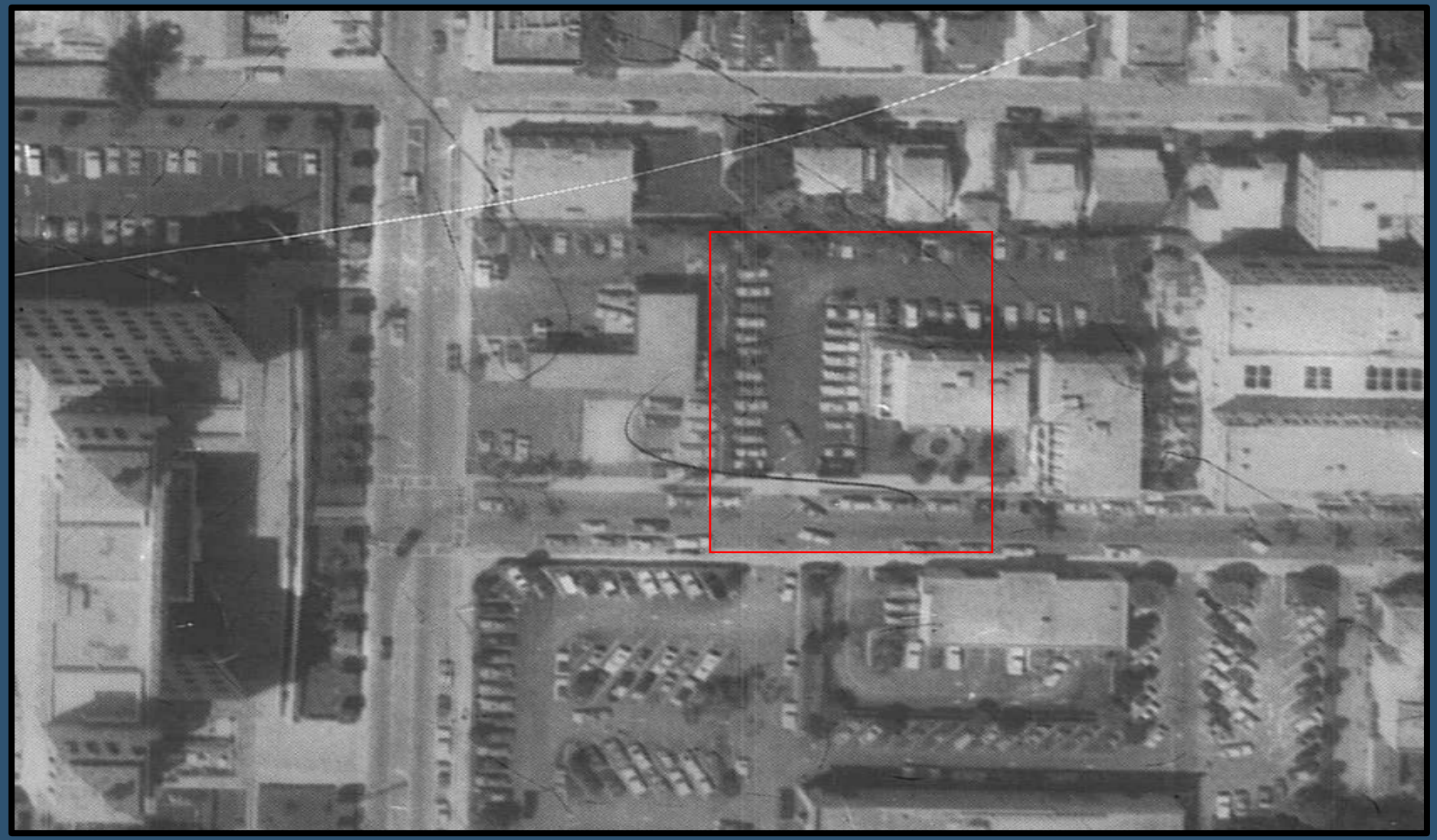
** = Leachability value not applicable.

= Direct Exposure value not applicable except as part of the Benzo(a)pyrene equivalent.

*Site was fully redeveloped from a gas station to Chase Bank; fully leveled and re-graded for the new Chase Bank building and parking areas, wherein the parking areas have been resurfaced over the years with an applicable asphalt coating and newer landscaping installed. No petroleum chemicals of concern were detected in the vadose zone soil samples with the exception of Benzo(a)pyrene and Benzo(a)pyrene equivalent in boring MW-3R at 3.5 feet which was part of the 1988 soil excavation and, since being back-filled with clean soils, would not be attributable to the historical release. B-1 and B-2R @ 1 foot samples are also attributed to the site redevelopment and not the historical discharge. *(PO C03BC5, Task 2, Annual Natural Attenuation Monitoring Report, Conclusions and Recommendations, MDM Services, Inc.)*

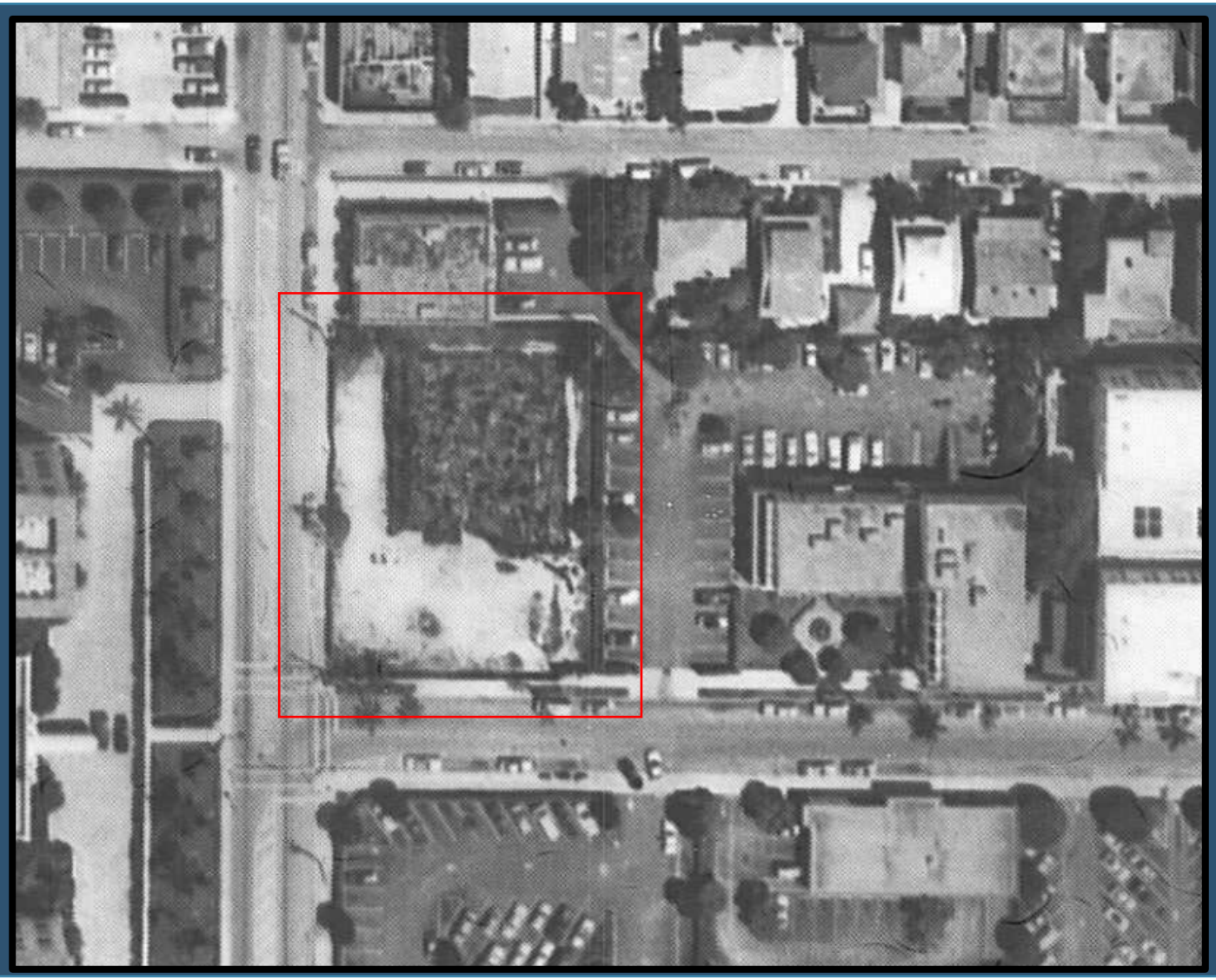
Source: OCULUS

GAS STATION LAYOUT – 1984
508944434



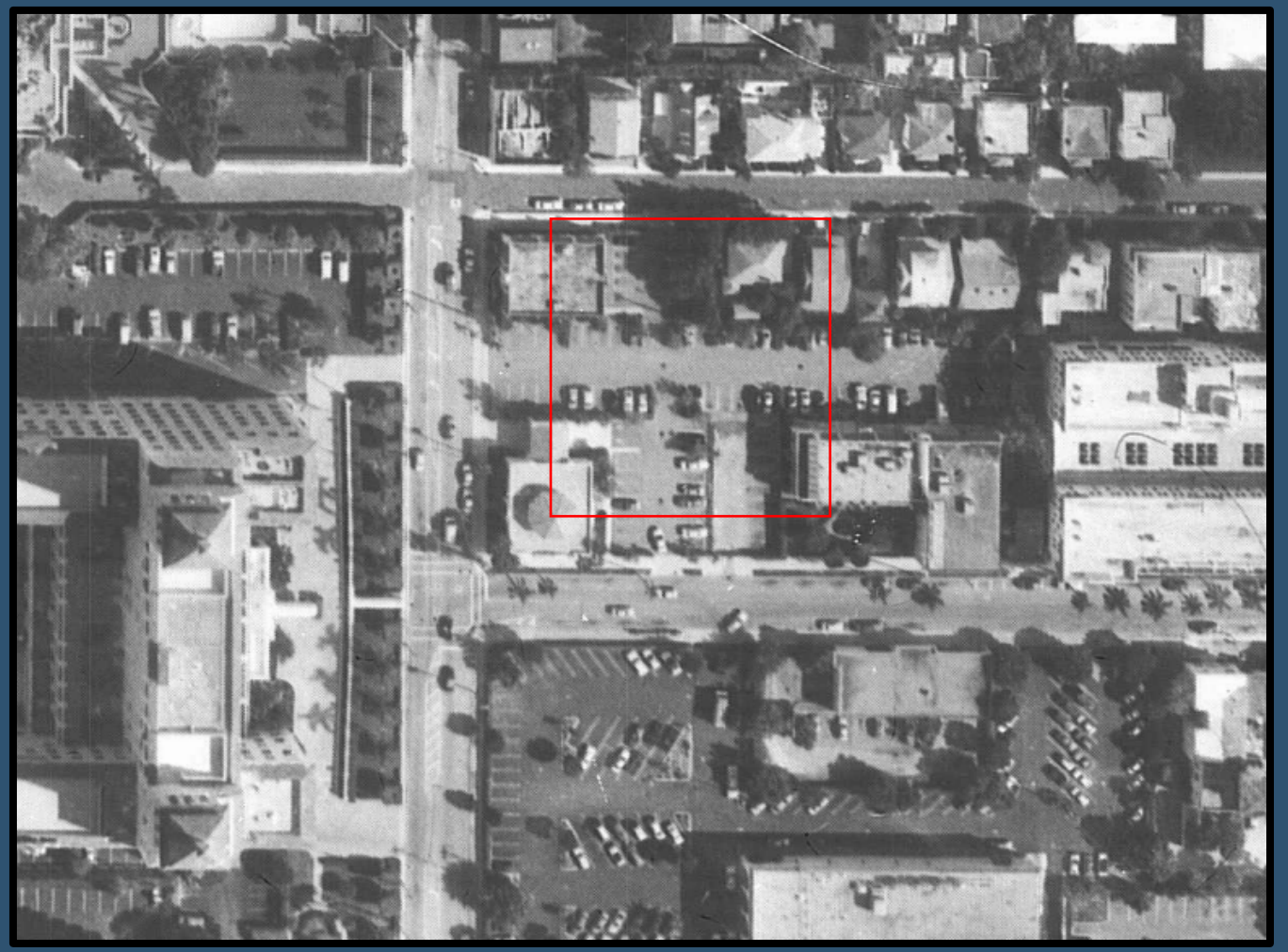
Source: OCULUS

1989 AERIAL
508944434



Source: OCULUS

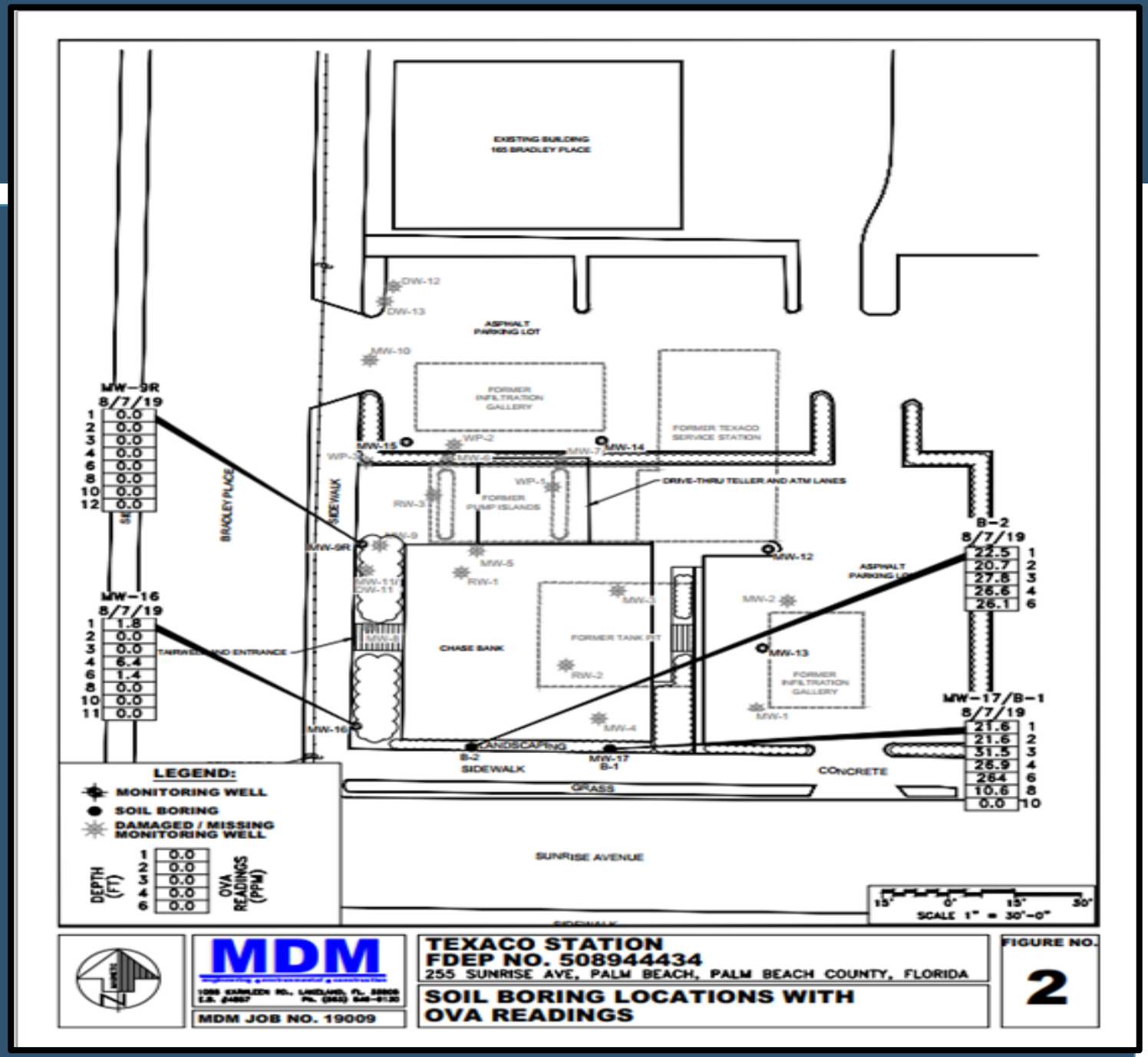
RE-DEVELOPED BANK SITE – 1993



Source: OCULUS

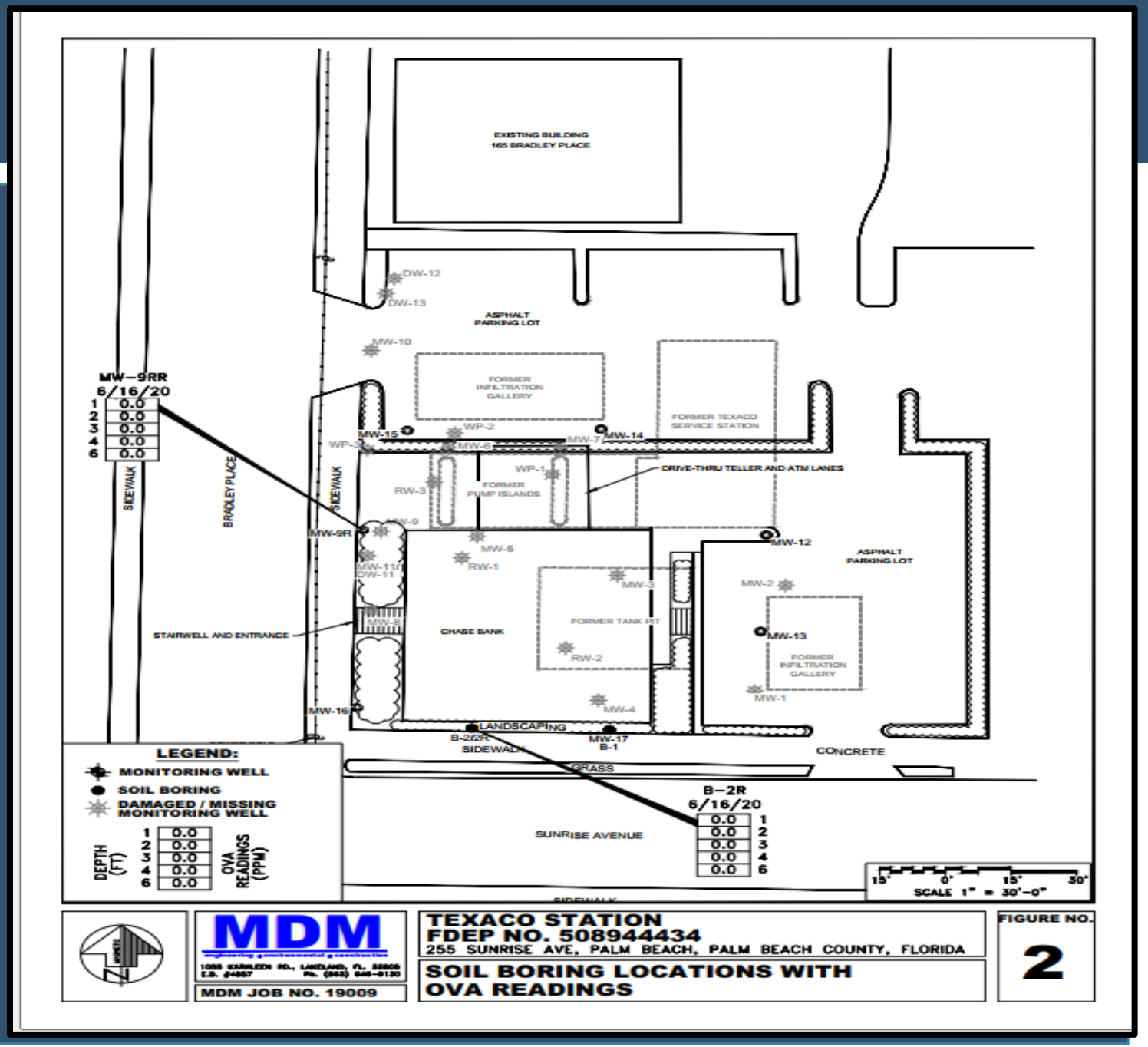
Soil Boring Locations

508944434



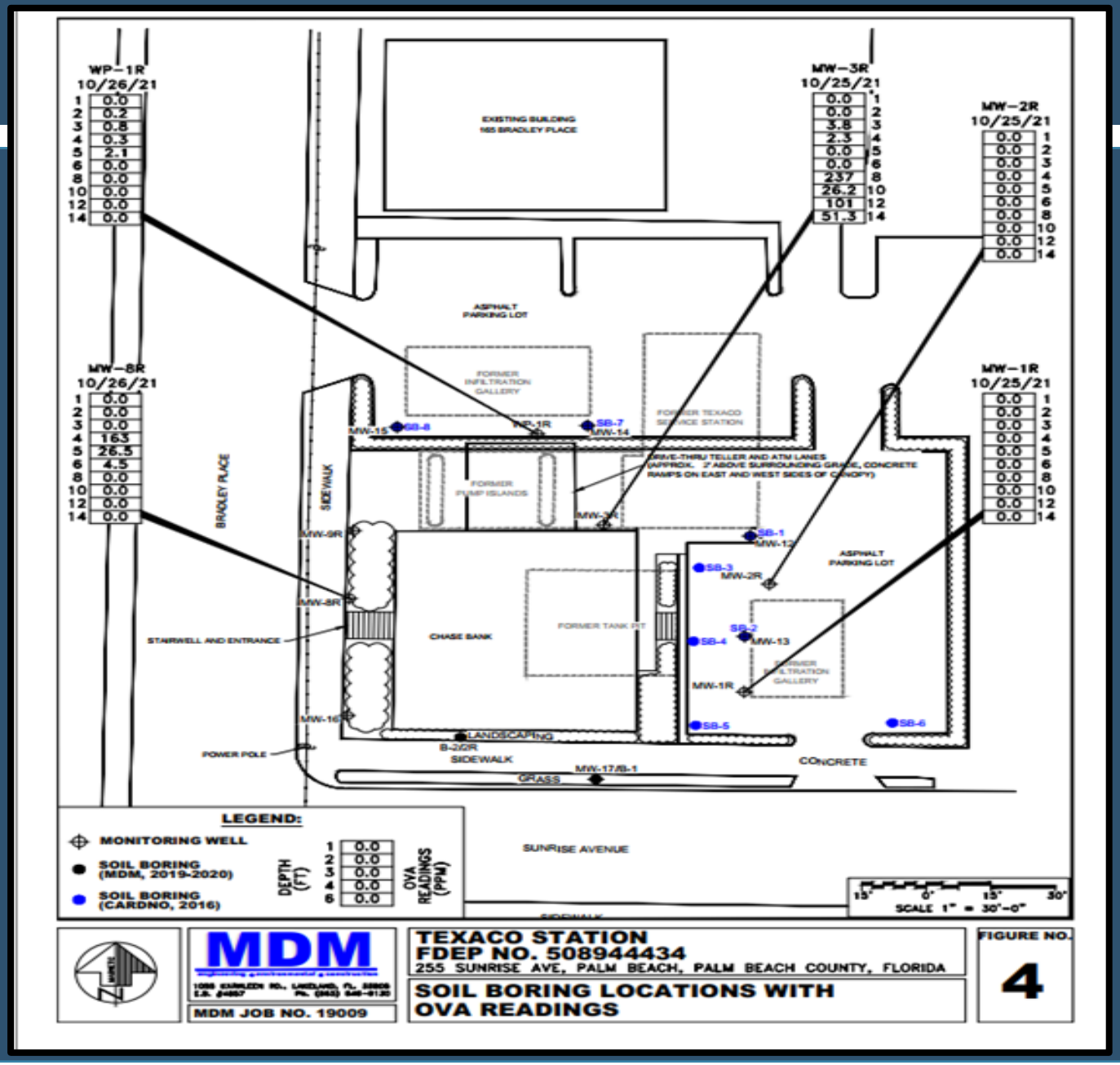
Source: OCULUS

SB LOCATIONS 508944434



Source: OCULUS

SB LOCATIONS 508944434



Source: OCULUS

508944434

Soil Boring-Monitoring Well-17/B-1

Source: OCULUS


508944434
Soil Boring-Monitoring Well-3R
Source: OCULUS

SOIL SAMPLING METHODOLOGY CAN MINIMIZE BAP – KEN BUSEN, PG

DRAFT

Guidelines and Procedures for Collecting Benzo(a)Pyrene (BaP) Shallow Soil Samples

Background:

What is Benzo(a)Pyrene? Pyrene is a parent class of polycyclic aromatic hydrocarbon (PAH) consisting of four fused benzene rings, resulting in a slat aromatic system with a chemical formula of $C_{16}H_{10}$. Benzo(a)pyrene is also a PAH that is the result of incomplete combustion of organic matter at temperatures between 300 °C and 600 °C. The chemical formula is $C_{20}H_{12}$ and is one of the benzopyrenes, formed by a benzene ring fused to pyrene. BaP belongs to a group of PAH carcinogens known to have disproportionate effects during development of children and therefore have a greater potential for risk of cancer in children than in adults. In accordance with Chapter 62-777, F.A.C. the carcinogenic PAHs are weighted and summed to determine BaP equivalents. Therefore, all references to BaP in this guideline will consist of BaP equivalents.

DRAFT

Guidelines and Procedures for Collecting Benzo(a)Pyrene (BaP) Shallow Soil Samples

The University of Florida (UF) Center for Environment and Human Toxicology evaluated BaP and its equivalents for age-dependent adjustment factors in relation to Chapter 62-777, F.A.C., Contaminant Cleanup Target Levels (UF, July 25, 2018). Under Chapter 62-777, F.A.C., soil cleanup target levels (SCTLs) for residential sites is 0.1 miligrams per kilogram (mg/kg) while SCTLs for commercial sites are 0.7 mg/kg. Alternative SCTLs were proposed with concentrations of 1.0 mg/kg for residential and 3.1 mg/kg for commercial. The UF study indicated that the alternative SCTL of 1.0 mg/kg for residential is not sufficiently protective of children in a residential setting. However, the commercial alternative SCTL of 3.1 mg/kg could still be applied where no children are expected to be present. To obtain the leachability to groundwater SCTL for BaP, individual leachability CTLs for each carcinogenic PAH must be considered. A carcinogen is any substance, radionuclide, or radiation that promotes carcinogenesis, the formation of cancer. This may be due to the ability to damage the genome or disrupt cellular metabolic processes.

DRAFT

Guidelines and Procedures for Collecting Benzo(a)Pyrene (BaP) Shallow Soil Samples

October 2020 Forensic Investigation Report by GHD Services Inc:

GHD was issued a Purchase Order under the Forensic Contact No. GC908 by the Petroleum Restoration Program to conduct a study of seven sites with reported lingering BaP contamination to assist in the development of a methodology for evaluating encountered BaP impacts. The report issued in October 2020 provides fingerprinted soil analysis for assessing the origin and potential mechanisms for the presence of BaP at the sites.

The study reports that PAH compounds found at the seven studied sites were either petrogenic (petroleum refined based) or pyrogenic (the result of burning) in origin and could either be natural or anthropogenic. Natural sources of PAHs include wildfires, volcanic activity or the presence of fossil fuels such as coal or oil. Decomposing plant material has been proposed as another potential natural source. Anthropogenic sources are created by petroleum releases either by leakage or spills and degradation of PAH containing materials, such as asphalt or roof shingles that are brought to the site by man.

Petrogenic products, such as gasoline and diesel fuel, are distilled fractions of crude oil in the refining process, at no point are these products burned or taken to temperatures sufficient to isolate high molecular weight PAHs, leaving only lower molecular weight compounds in these products. Gasoline has hydrocarbon compounds ranging from four to 12 carbons in their hydrocarbon chains. Diesel fuel refinement results in eight to 26 hydrocarbon chained compounds. Typically, PAHs from pyrogenic sources tend to exhibit a higher molecular mass (i.e., four-six ring PAHs). PAHs from petrogenic sources tend to exhibit a lower molecular weight (Wang and Fingas, 2003). As such, carcinogenic PAHs are not present in gasolines but are present in diesel fuels, fuel oils, motor oil, etc. Higher molecular weight PAHs, due to heat exposure and higher molecular weight compounds, are present in recycled oil, waste oil, asphalt and tar coatings, and could also include weathered fuels.

In summary, because of the exclusion of higher weight PAHs, unleaded and leaded gasolines cannot be a source of BaPs. Whereas higher weighted fuels such as diesel fuels, fuel oils, motor oil and higher molecular weighted oils that have been exposed to heat such as recycled oil, waste oil, asphalt, tar coatings and possibly weathered fuels.

DRAFT

Guidelines and Procedures for Collecting Benzo(a)Pyrene (BaP) Shallow Soil Samples

2008 Study of PAHs in Urban Soil by Christopher Teaf.

The study found that soil with BaP levels from 1 to 5 parts per million, although exceeding Florida Soil Cleanup Target Levels (SCTLs) for both residential and commercial/industrial concentrations, are consistently reported in many urban settings which may call for a default urban background level for PAHs. Worldwide sources of PAHs can include vehicle exhaust from internal combustion engines, road asphalt, cigarette smoke, exposure to petroleum material or coal, volcanic eruptions, forest fires, oil-based heating, indoor and outdoor grilling, jet exhaust, road paving, fireplaces, agricultural burnings, public sewage treatment plants and compost-based fertilizers.

Urban air quality can contain PAH concentrations three to five times higher than in rural air. Additionally, PAH concentrations can be five to 10 times higher in winter as opposed to summer. Most PAHs entering into the air are transported to other media. Surface water receives its share from airborne deposition. Urban runoff effluents from industrial plants, petroleum processing and oil spills can also be major contributors.

In studies, the lowest observed levels of PAHs in rural soil were located far from major highways. Soil in a remote Wyoming woods contained 210 ug/kg of total PAHs (probable cause is forest fires) while soil measured in New York City's Fountain Avenue Landfill contained concentrations between 400 and 10,000 ug/kg.

Stationary and mobile anthropogenic sources account for as much as 80% of PAHs, with great variability regionally and locally. Due to the ubiquity of BaP and associated PAHs, remediation should not commence without establishing a site-specific background, if possible.

DRAFT

Guidelines and Procedures for Collecting Benzo(a)Pyrene (BaP) Shallow Soil Samples

Evaluating possible BaP presence at sites:

The Petroleum Restoration Program (PRP) is predicated on assessment and remediation of petroleum products that are released to the environment from spills, and releases from leaking petroleum storage systems and pipelines. The presence of BaP could be the result of several sources and may not be related to the documented petroleum release or spill. The presence of BaP that is a result of pyrogenic or anthropogenic activities should not be the focus or responsibility of the PRP. The PRP should focus its efforts solely on BaP from petrogenic sources and how they relate to BaP from non-petrogenic sources.

Questions to ask when evaluating BaP at a site:

1. Is the site in an industrial or urban area?
    a) Heavily populated and industrial areas would typically be more prone to the occurrence of PAHs from pyrogenic sources.
2. What is the history of the site (previous petroleum storage, pavement, land use)?
3. Discharges reported at the site (gasoline, diesel, kerosene, waste oil)?
    a) 4. These are the areas that should be focused on.
5. Surface cover at the site – asphalt pavement, areas with non-native fill?
    a) Is the pavement old or degraded? Could fill material be source of BaPs?
    b) Does underlying soil contain high organic content?
    c) PAHs have relatively low solubility and high partitioning coefficients, causing them to readily adsorb to organic materials in soils. Thus, PAHs have an affinity toward organic soils.
6. Heavy traffic area such as major streets or industrial traffic (heavy emissions and deposition)?
7. Topography to determine if stormwater runoff from an upgradient source could be a contributor?
8. Are or were roads in the vicinity historically ever non-paved and were oiled for dust control?
9. Does the site or site area have a history of fire(s) or industrial usage
10. Similar history and uses of surrounding properties?

	Petroleum Restoration Program Guidance **Procedures for Collecting Benzo(a)Pyrene Shallow Soil Samples**	**Author:** Ken Busen **Updated:** 8/12/2023

BaP is part of a parent class of PAHs that have a known cancer risk for children and adults. The sources of BAP can be either natural or anthropogenic and can be either petrogenic (petroleum refined based) or pyrogenic (the result of burning organic material). BaP from PRP sites can be the result of a petroleum discharge or man-placed materials located on the property such as asphalt pavement or asphalt shingles. Care must be taken when collecting shallow soil samples to ensure that non-petroleum discharge materials, such as degraded asphalt, are not incorporated into the soil samples that could result in erroneous BaP values. The following is a sampling procedure to avoid near surface degraded asphalt from affecting soil sample analyses from a shallow soil boring collected at 1- to 2-ft. below land surface.

Equipment:

Hand auger with a 3- to 3.5-in. outside diameter.
3- to 4- ft. of 4-in. inside diameter PVC casing marked with 1-foot increments on the outside.

Note: The hand auger should fit inside the PVC casing.

Procedure:

1. Remove vegetation and debris at the surface.
2. Begin hand augering for one to two bucket fulls.
3. Place the PVC casing in the boring and push to refusal.
4. Continue augering and pushing casing down for each cycle to desired depth.
5. Collect soil sample and place in proper containers.
6. Continue augering and pushing casing down to next sampling depth; or
7. Remove PVC casing and fill in the borehole.
8. Decontaminate PVC casing between each borehole and auger between each sampling point.

QUESTIONS

- Comments?
- Other successful strategies?

THANK YOU

Ken Busen | Paul Angelillo | Jerry Cook
Petroleum Restoration Program/Division Waste Management
Florida Department of Environmental Protection

Contact Information:
Phone 850-245-8882; 561-233-2507; 561-681-3834
Ken.Busen@floridadep.gov; jmcook@pbcgov.org; pangelillo@pbcgov.org


FLORIDA DEPARTMENT OF
ENVIRONMENTAL PROTECTION