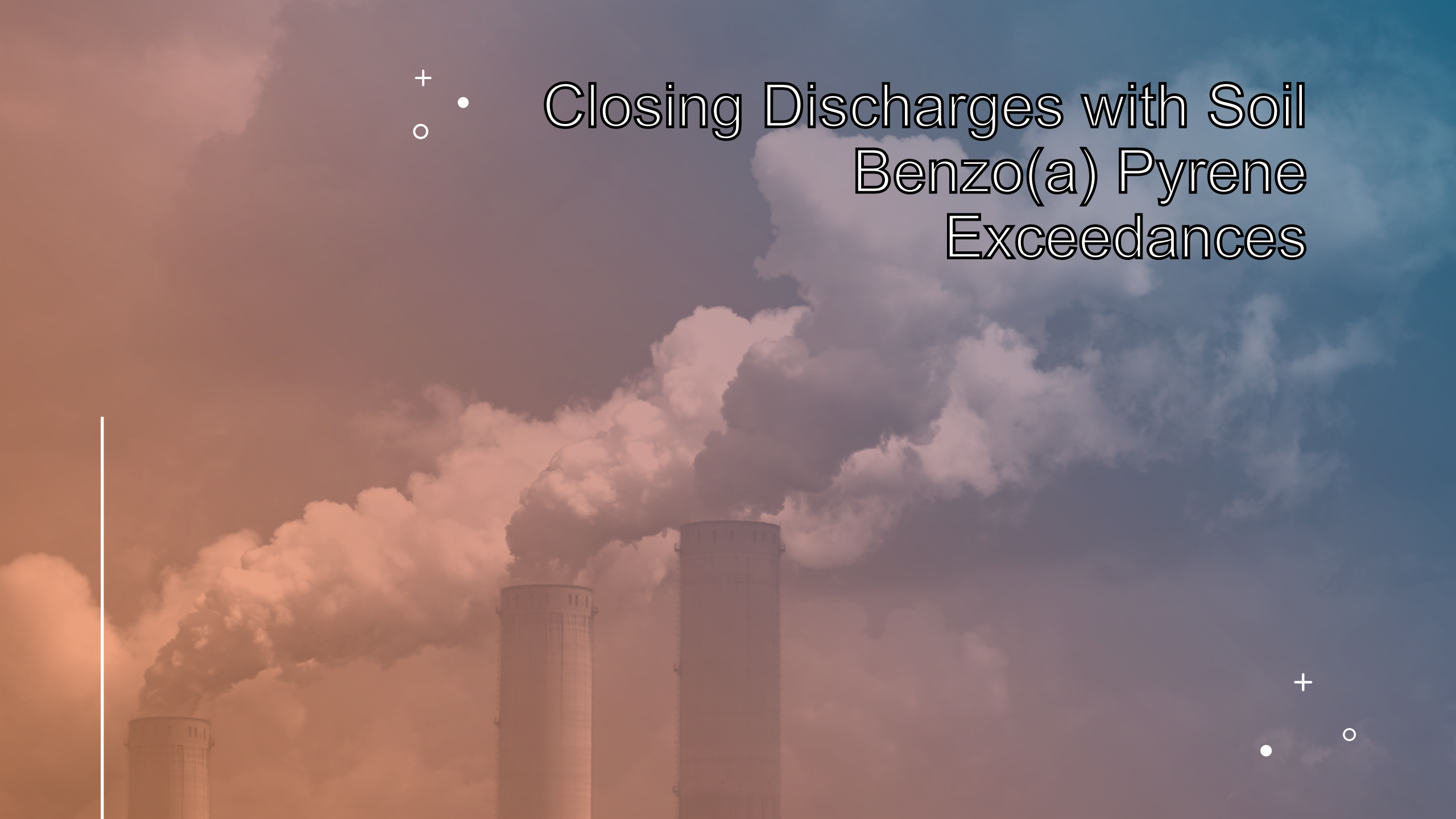


Closing Discharges with Soil Benzo(a) Pyrene Exceedances

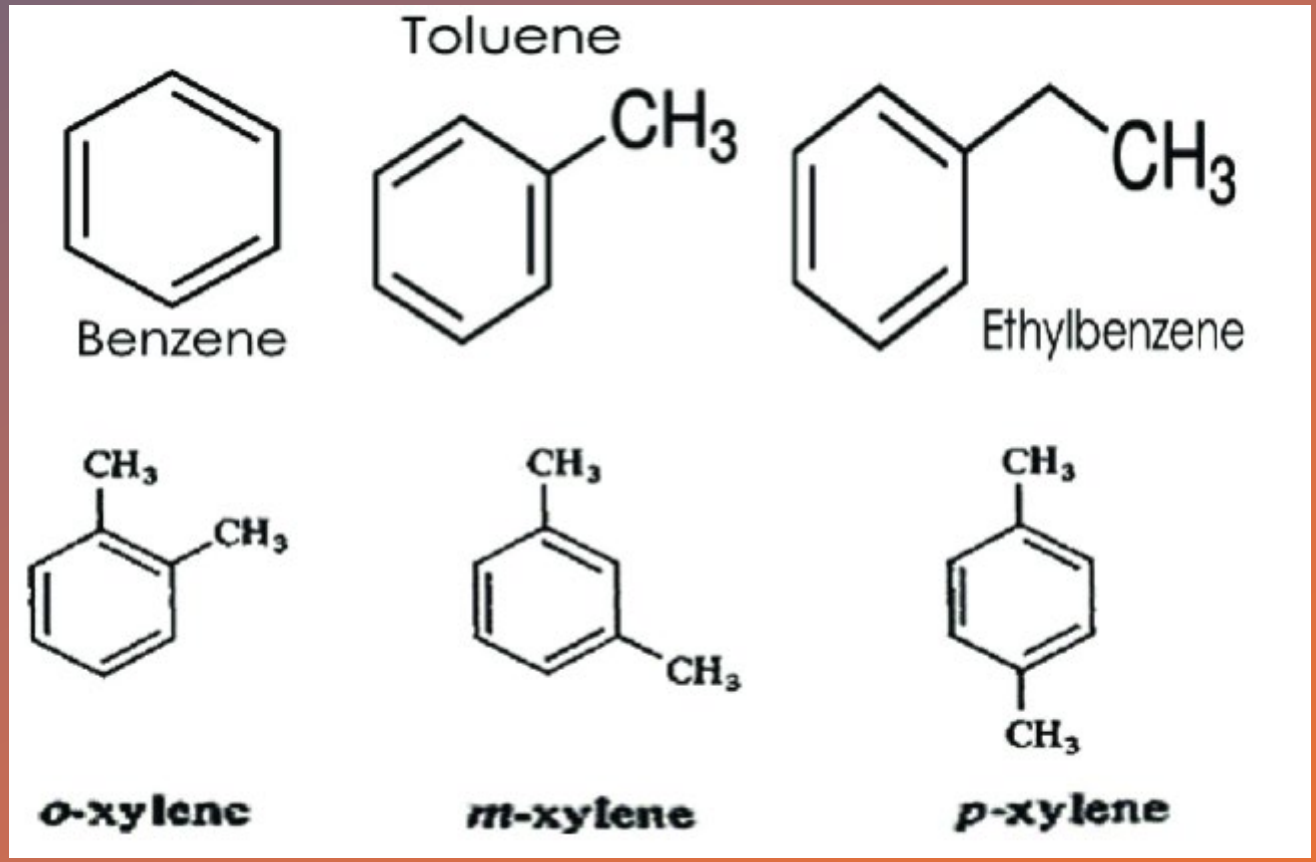
Studies

- Forensic Site Investigation Report Comprehensive, GHD, October 9, 2020
- Benzo(a)Pyrene: What It Is, Occurrences, Paths to Site Closure and Draft Sampling Methodology, Jerry Cook, P.G., Paul Angelillo, R.G., Ken Busen, P.G.
- Forensic Study Tools to Evaluate PAH Source Origins: A Case Study, David Sheehan, P.E., Nicholas Maksimoski,
- Groundwater Monitoring Parameters and Pollution Sources, Third Edition, May 1989, Geoffery Watts, DEP, BWC

BTEX

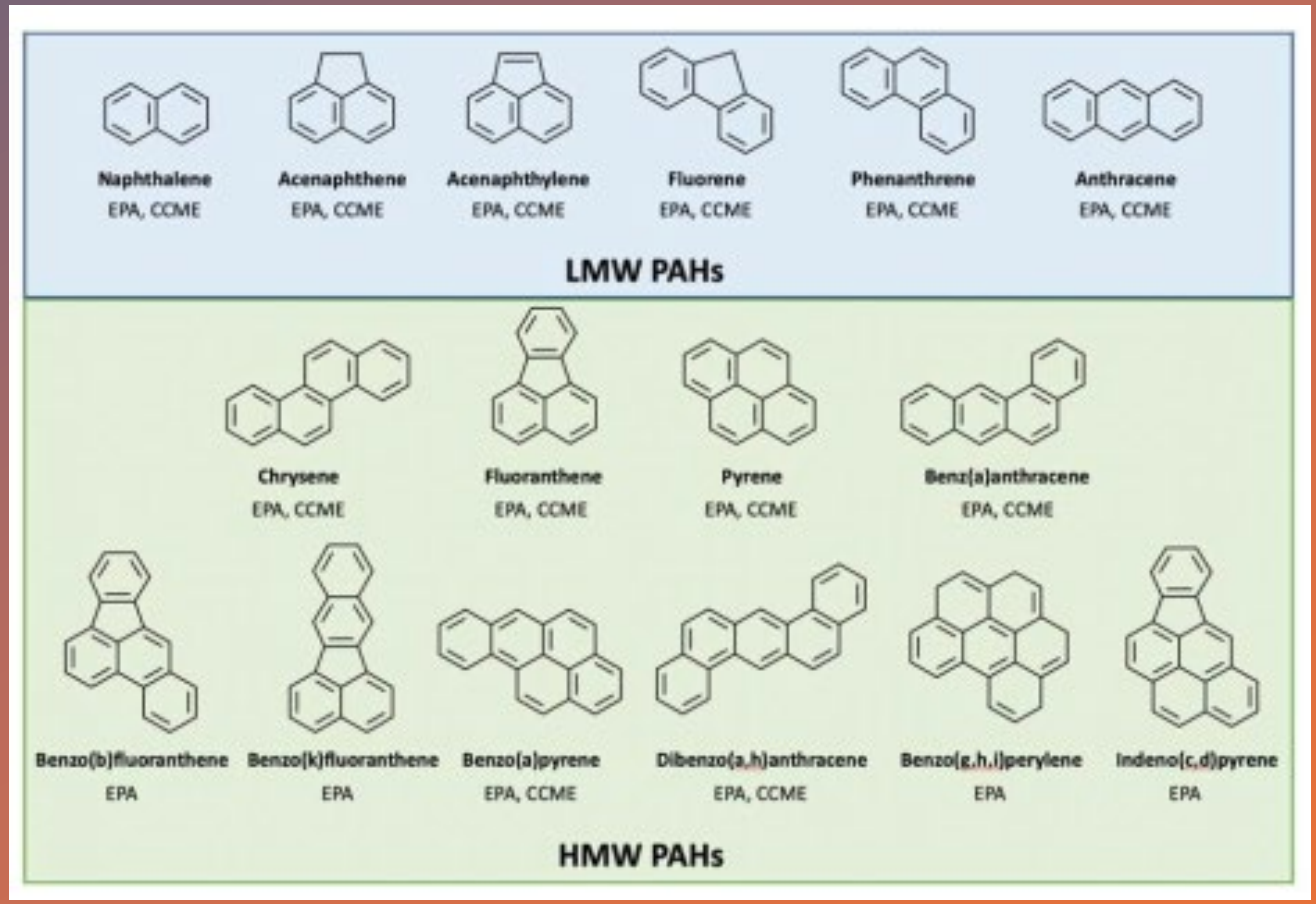
Benzene, toluene, ethylbenzene, and xylenes are commonly referred to as BTEX. They are volatile organic compounds that are found in petroleum and petroleum products, such as gasoline, coal, and wood tars. BTEX compounds are clear, colorless, highly flammable liquids at room temperature.

They have a sweet smell and evaporate quickly. BTEX are used in the manufacture of a variety of consumer goods, including chemicals, rubber, leather, plastics, cleaners and paints, and paint thinners. BTEX are toxic.



PAHs,
Polycyclic aromatic hydrocarbons (PAHs) are a class of chemicals that occur naturally in coal, crude oil, and gasoline. They also are produced when coal, oil, gas, wood, garbage, and tobacco are burned. PAHs generated from these sources can bind to or form small particles in the air. High-temperature cooking will form PAHs in meat and in other foods.

Naphthalene is a PAH that is produced commercially in the United States to make other chemicals and mothballs. Cigarette smoke contains many PAHs.



Cleanup Target Levels

Soil Cleanup Target Levels
for Petroleum Products' Contaminants of Concern
[from Table II of Chapter 62-777, F.A.C. (effective April 17, 2005)]

Contaminants of Concern	Direct Exposure Residential (mg/kg)	Direct Exposure Commercial/ Industrial (mg/kg)	Leachability Based on Groundwater Criteria (mg/kg)	Leachability Based on Freshwater / Marine Surface Water Criteria (mg/kg)	Leachability Based on Groundwater of Low Yield/Poor Quality Criteria (mg/kg)
PAHs:					
Acenaphthene	2,400	20,000	2.1	0.3 / 0.3	21
Acenaphthylene	1,800	20,000	27	NA / NA	270
Anthracene	21,000	300,000	2,500	0.4 / 0.4	25,000
Benzo(a)anthracene	#	#	0.8	NA / NA	8
Benzo(a)pyrene	0.1	0.7	8	NA / NA	80
Benzo(b)fluoranthene	#	#	2.4	NA / NA	24
Benzo(g,h,i)perylene	2,500	52,000	32,000	NA / NA	320,000
Benzo(k)fluoranthene	#	#	24	NA / NA	240
Chrysene	#	#	77	NA / NA	770
Dibenz(a,h)anthracene	#	#	0.7	NA / NA	7
Fluoranthene	3,200	59,000	1,200	1.3 / 1.3	12,000
Fluorene	2,600	33,000	160	17 / 17	1,600
Indeno(1,2,3-cd)pyrene	#	#	6.6	NA / NA	66
Methylnaphthalene, 1-	200	1800	3.1	10 / 10	31
Methylnaphthalene, 2-	210	2100	8.5	9.1 / 9.1	85
Naphthalene	55	300	1.2	2.2 / 2.2	12
Phenanthrene	2,200	36,000	250	NA / NA	2,500
Pyrene	2,400	45,000	880	1.3 / 1.3	8,800

Each concentration must be converted to Benzo(a)pyrene equivalent (see pp. 61-62 of the February 2005 Technical Report). In the "BaP Conversion Table" select the "Residential" tab for 62-780.680(1) closure or the "Commercial- Industrial" tab for 62-780.680(2) closure, and enter the appropriate analytical result for each carcinogenic PAH using the instructions provided; the spreadsheet calculates the equivalent concentrations, adds them up, compares the total to the applicable Benzo(a)pyrene Direct Exposure CTL and indicates whether it is exceeded or not.

BaP Equivalency

12/12/2025

Benzo(a)pyrene Conversion Table

For Direct Exposure Soil Cleanup Target Levels

Facility/Site Name: _____

Location: _____

Facility/Site ID No.: _____

Soil Sample No. _____

Sample Date _____

Location: _____

Depth (ft): _____

INSTRUCTIONS: Calculate Total Benzo(a)pyrene Equivalents if at least one of the carcinogenic PAHs is detected in the sample at a concentration equal to or higher than the Method Detection Limit (MDL), whether quantified with certainty (the concentration reported has no qualifier) or estimated (the concentration reported has a "J", "T" or "I" qualifier). Enter the contaminant concentrations (in mg/kg) for all seven carcinogenic PAHs in the yellow boxes using the following criteria (and see table below):

1. If quantified with certainty, or estimated and has the "J" qualifier, enter the reported value;
2. If not detected at the MDL (the concentration reported is the MDL followed by the "U" qualifier) enter 1/2 of the reported value;
3. If detected at a concentration lower than the MDL and the concentration is estimated (has the "T" qualifier) enter the estimated value;
4. If detected at a concentration equal to or higher than the MDL but lower than the Practical Quantitation Limit (PQL) and the concentration is estimated (has the "I" qualifier) enter the estimated value;
5. If detected at a concentration equal to or higher than the MDL but lower than the PQL and it is not estimated (the concentration reported is the PQL followed by the "M" qualifier) enter 1/2 of the reported value.

Contaminant	Concentration (mg/kg)	Toxic Equivalency Factor	Benzo(a)pyrene Equivalents
Benzo(a)pyrene		1.0	0.0000
Benzo(a)anthracene		0.1	0.0000
Benzo(b)fluoranthene		0.1	0.0000
Benzo(k)fluoranthene		0.01	0.0000
Chrysene		0.001	0.0000
Dibenz(a,h)anthracene		1.0	0.0000
Indeno(1,2,3-cd)pyrene		0.1	0.0000

DE Residential = 0.1 mg/kg; DE Industrial = 0.7 mg/kg

Total Benzo(a)pyrene Equivalents = **0.0**

The concentration shown does not exceed the Residential Direct Exposure SCTL of 0.1 mg/kg.

The concentration shown does not exceed the Industrial Direct Exposure SCTL of 0.7 mg/kg.

Summary Criteria for Table Entries			
Detection	**Concentration Reported**	**Data Qualifier**	**Enter**
Various	Quantified with certainty	None	reported value
Various	Estimated	J	reported (estimated) value
ND at MDL	MDL	U	1/2 reported value
< MDL	Estimated	T	reported (estimated) value
≥ MDL but < PQL	Estimated	I	reported (estimated) value
≥ MDL but < PQL	PQL	M	1/2 reported value

Petrogenic: Pyrogenic?

- “Whether caused by natural processes or through anthropogenic means, any PAH source involving combustion is considered pyrogenic, which is the predominant mechanism for the presence of carcinogenic PAHs in the environment.

- The majority of pyrogenic sources can be attributed to atmospheric emission from the combustion process and the resulting deposition from rainfall. As such, heavily populated and industrial areas would typically be more prone to the occurrence of PAHs from pyrogenic sources.

- Petrogenic PAH impacts are typically the result of fuel handling, storage, and distribution systems. The actual composition of the PAH fingerprint is dependent upon the type of source”

- Forensic Site Investigation Report Comprehensive, GHD
- October 9, 2020

Conceptual Site Model, CSM

- Is the occurrence of PAHs related to the petroleum storage system?

- The evaluation of the PAH impacts encountered at an individual site begins with a detailed file review to serve as the basis of a Conceptual Site Model (CSM).
- The CSM represents the physical, chemical, and biological processes that affect the potential transport, migration, and actual or potential exposure to contamination in all affected media to human and ecological receptors. The first key component to take into consideration is the facility's physical location, emissions and deposition.

Conceptual Site Model, (CSM)

- People are exposed to PAHs through eating foods that are grilled, roasted, smoked, or barbecued (4). Additionally, foods that are roasted or toasted like cereals, grains, nuts and coffee contain PAHs (3; 6). Any method that can char or burn food will produce PAHs.
- When cooking meat, PAHs are formed when the meat itself burns or chars, and when fat from the meat drips down and burns in the flames (4; 5). This is commonly seen with chargrilled and barbecued meats including fish (4). Additionally, foods that are commercially roasted, liked roasted cereals and coffee, can contain PAHs (3; 6) . Smoked foods may also contain PAHs as a result of the smoking process.
- Asphalt, asphalt impurities in soil, non-native fill, rubber mulch

Questions to ask:

Is your site a gasoline only site/discharge?
Where is the PAH contamination in relation to discharge points?
Do soil logs include possible asphalt grains?
Samples taken below facility backfill? at least > 1'.
Historic fires?

- Perform a background study on site.

- LMW PAHs are key indicators of diesel fuel contamination.
- Napthalenes, Anthracene, Fluorene, Phenanthrene

Single Ratio Histograms

- 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, petrol), types of emissions (traffic versus non-traffic), and biodegradability (fresh particles versus weathered).
- There are specific numerical thresholds that are used to determine the PAH pollution sources.
- Five (5) ratios have been considered for this line of evidence due to their applicability in distinguishing petrogenic versus pyrogenic PAH origins.

3.2.6.1 Low Molecular Weight/High Molecular Weight (LMW/HMW) $NP + FLU + PHE$ / $BaA + FLA + PYR + CHR + BaP + BeP + DahA + PER$

3.2.6.2 Combustion (COMB)/TOTAL

FLA + PYR + BaA + CHR + BkF + BbF +BaP + IcdP + BghiP /
FLA+PYR+BaA+CHR+BkF+BbF+BaP+IcdP+BghiP+NP+PHE+DO+FLU+BaF+BeP+PER+DahA+BF

3.2.6.3 FLA/(FLA + PYR)

3.2.6.4 BaA/(BaA + CHR)

3.2.6.5 IcdP/(IcdP+BghiP)

BeP = Benzo(e)pyrene, PER = Perylene, DO = Dibenzothiophene, not in standard PAH analysis. Although these compounds are missing from standard PAH analysis, LMW/HMW and COMB/TOTAL can be used as additional lines of evidence without these compounds. Realize that exclusion of these compounds results in an increase in the denomination and skews the ratios.

Table 5 - PAH Source by Forensics Methods - Island Estates Mobil

Facility Id. #: 52/8515334

Summary of Determination of Source of BaP Equivalent Exceedances as per *Forensic Site Investigation Report Comprehensive*

Sources

Petrogenic = any PAH impacts resulting from fuel handling, storage, and distribution systems

Gasoline and diesel fuel are distilled and hence have a petrogenic fingerprint. At no point in refining are these products burned. Production of gasolines results in exclusion of PAH constituents therefore; unleaded and leaded gasolines are not a source.

Pyrogenic = any PAH source involving exposure to heat - combustion

atmospheric combustion emissions sources, production facilities, heavily trafficked roadways
recycled oil
waste oil
asphalt and tar coatings
fires

Documented petroleum products on site; Leaded and unleaded gasoline

	SB-3RR
Benzo(a)pyrene (BaP)	0.3
Benzo(b)Flouranthene (BbF)	0.52
Benzo(k)flouranthene (BkF)	0.19
Dibenzo(a,h)anthracene (DahA)	0.0086
Fluorene(FLU)	0.013
Naphthalene (NP)	0.013
Phenanthrene(PHE)	0.16
Flourananthene (FLA)	0.58
Pyrene (PYR)	0.47
Benzo(a)anthracene (BaA)	0.23
Chrysene (CHR)	0.4
Indeno(1,2,3-c,d)pyrene (IcdP)	0.24
Benzo(g,h,i)perylene (BghiP)	0.3
Total BaP Equivalent	0.41

Soil Boring No.		Total BaP Equivalent	Report Subsection **3.2.6.3** Ratio FLA/(FLA+PYR) <0.4=Petrogenic >0.4=Pyrogenic 0.4-0.5 = fossil fuel combustion >0.5=grass, wood, coal combustion	Report Subsection **3.2.6.4** Ratio BaA/(BaA+CHR) <0.2 = Petrogenic >0.2 = Pyrogenic coal/petro combustion	Report Subsection **3.2.6.5** Ratio IcdP/(IcdP+BghiP) <0.2 =Petrogenic 0.2-0.5 = Pyrogenic Petro combustion >0.5 = Pyrogenic grass or wood combustion	Report Subsection **3.2.6.1** Ratio LMW/HMW >1.0 =Petrogenic <1.0 = Pyrogenic	Report Subsection **3.2.6.2** Ratio COMB/TOTAL close to 1.0 =Pyrogenic <0.8=at least 20% Petrogenic
	Industrial	**0.7**					
	Residential	**0.1**					

			Results	Results	Results	Results	Results
SB-3RR		**0.41**	0.55 combustion grass, wood, coal	0.37 combustion pyrogenic	0.44 combustion pyrogenic	0.09 Pyrogenic	0.94 Pyrogenic

LMW= NP+FLU+PHE
HMW=BaA+FLA+PYR+CHR+BaP+DahA
COMB=FLA+PYR+BaA+CHR+BkF+BbF+BaP+IcdP+BghiP
TOTAL=FLA+PYR+CHR+BkF+BbF+BaP+IcdP+BghiP+NP+PHE+BaF+DahA+BF

Table 5 - PAH Source by Forensics Methods - Island Estates Mobil

Facility Id. #: 52/8515334

Summary of Determination of Source of BaP Equivalent Exceedances as per *Forensic Site Investigation Report Comprehensive*

Sources

Petrogenic = any PAH impacts resulting from fuel handling, storage, and distribution systems

Gasoline and diesel fuel are distilled and hence have a petrogenic fingerprint. At no point in refining are these products burned. Production of gasolines results in exclusion of PAH constituents therefore; unleaded and leaded gasolines are not a source.

Pyrogenic = any PAH source involving exposure to heat - combustion

atmospheric combustion emissions sources, production facilities, heavily trafficked roadways
recycled oil
waste oil
asphalt and tar coatings
fires

Documented petroleum products on site; Leaded and unleaded gasoline

	SB-10RR
Benzo(a)pyrene (BaP)	1
Benzo(b)Flouranthene (BbF)	1.5
Benzo(k)flouranthene (BkF)	0.64
Dibenzo(a,h)anthracene (DahA)	0.0086
Fluorene(FLU)	0.019
Naphthalene (NP)	0.013
Phenanthrene(PHE)	1
Flourananthene (FLA)	2.3
Pyrene (PYR)	1.7
Benzo(a)anthracene (BaA)	0.85
Chrysene (CHR)	1.2
Indeno(1,2,3-c,d)pyrene (IcdP)	0.71
Benzo(g,h,i)perylene (BghiP)	0.83
Total BaP Equivalent	1.32

Soil Boring No.		Total BaP Equivalent	Report Subsection **3.2.6.3** Ratio FLA/(FLA+PYR) <0.4=Petrogenic >0.4=Pyrogenic 0.4-0.5 = fossil fuel combustion >0.5=grass, wood, coal combustion	Report Subsection **3.2.6.4** Ratio BaA/(BaA+CHR) <0.2 = Petrogenic >0.2 = Pyrogenic coal/petro combustion	Report Subsection **3.2.6.5** Ratio IcdP/(IcdP+BghiP) <0.2 =Petrogenic 0.2-0.5 = Pyrogenic Petro combustion >0.5 = Pyrogenic grass or wood combustion	Report Subsection **3.2.6.1** Ratio LMW/HMW >1.0 =Petrogenic <1.0 = Pyrogenic	Report Subsection **3.2.6.2** Ratio COMB/TOTAL close to 1.0 =Pyrogenic <0.8=at least 20% Petrogenic
	Industrial	**0.7**					
	Residential	**0.1**					

			Results	Results	Results	Results	Results
SB-10RR		**1.32**	0.58 combustion grass, wood, coal	0.41 combustion pyrogenic	0.46 combustion pyrogenic	0.15 Pyrogenic	0.91 Pyrogenic

LMW= NP+FLU+PHE
HMW=BaA+FLA+PYR+CHR+BaP+DahA
COMB=FLA+PYR+BaA+CHR+BkF+BbF+BaP+IcdP+BghiP
TOTAL=FLA+PYR+CHR+BkF+BbF+BaP+IcdP+BghiP+NP+PHE+BaF+DahA+BF

Memorandum

- **TO:** Florida Department of Environmental Protection, Appropriate District
- **THROUGH:** PRP Administrator, Environmental Administrator, Petroleum Restoration Program (PRP)
- **THROUGH:** Team Lead, PRP, Team Leader
- **FROM:** Site Manager and Technical Review, PRP DEP Petroleum Restoration Program Team

- SUBJECT: **Referral to Appropriate District, DEP**
  - Facility Contact
  - Site Name
  - Site Address
  - City, County
  - FDEP Facility ID#
  - Discharge Discovery Date: Discharge Date(s)

- The occurrence of Polycyclic Aromatic Hydrocarbons (PAH) contaminants of concern has been identified during the investigation of the petroleum discharge. Forensic Analyses of the suite of PAH compounds detected concluded that the contamination is associated with pyrogenic sources, the combustion of fossil fuel or coal. The contaminants are not associated with the petroleum discharge referenced above. This occurrence is being referred to your office for enforcement.
- The petroleum discharge occurred when brief description of discharge.
- Additional information for this site can be found in Oculus under the Storage Tanks catalog. If you have any questions regarding this matter, please contact the Site Manager at [*phone number*] or by *example@email.com*.

- EC: Exhibit A – Site Figures
- Exhibit B - Assessment Tables

These are the same as will be routed in the Site Rehabilitation Completion Order (SRCO).

Contact

Bill Newmyer, P.G.
WSP Team 6
Bill.Newmyer@wsp.com