# CORRESPONDENCE/MEMORANDUM

State of Wisconsin

DATE: September 14, 2018 FILE REF: 02-16-297977

TO:
John Hunt — Remediation and Redevelopment (Project Manager)
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Steve Galarneau — Office of Great Waters (Director)

FROM: Scott Inman — Remediation and Redevelopment (Sediment Engineer)

SUBJECT: Review Comments regarding Former Amoco Oil Barge Dock Issue Response Report

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|---|---|
| **Site Name** | Former Amoco Terminal – Oil Barge Dock |
| **BRRTs Site No.** | 02-16-297977 |
| **Upland Location** | 2904 Winter Street<br>Superior, Wisconsin |
| **Waterbody** | Superior Bay, Lake Superior (WBIC 2751220) |
| **Responsible Party** | BP Products North America, Inc.<br>201 Helios Way<br>Houston, TX 77079 |
| **Responsible Party Contact** | unknown |
| **Consultant** | Antea Group<br>5910 Rice Creek<br>Parkway, Suite 100<br>Shoreview, MN 55126 |
| **Consultant Contact** | Wayne Hutchinson |
| **Document Reviewed** | Issue Response Report<br>Superior Harbor Sediment<br>Former Amoco Oil Barge Dock |
| **Date Submitted** | November 17, 2017 |

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**Introduction**

In a July 28, 2017 Closure Not Recommended Letter, we [the Department of Natural Resources (DNR)] requested that BP Products North America (BP) assess the potential for the Amoco Oil Barge Dock (Dock) to have contributed to the sediment contamination found in samples collected in the St. Louis Area of Concern by the *Mud Puppy II* in 2015. Although several core samples were collected, one sediment core [SW15-SLB03 (6-samples)] is pertinent because it was collected in the slip adjacent to the Dock, the others were not.

The Antea Group (Antea) responded to the request for BP by providing their 2017 *Issue Response Report.* For the Report, Antea performed various types of analysis to try to ascertain the source of sediment contamination. Antea performed the following:

- forensic analysis of the parent and alkylated polycyclic aromatic hydrocarbons (pPAH and aPAH) at SW15-SLB03
    - Enlisted Pace Analyatical Laboratory (Pace) to perform forensic analysis
- reviewed other BRRTs cases in the vicinity
- reviewed other properties in the vicinity
- reviewed concentrations of metals in coal data provided by USGS
- provided chemical composition of fuels that were distributed through the terminal
- reviewed historical Sanborn maps
- reviewed concentrations of metals, semivolatile organic compound (SVOC) and volatile organic compounds (VOC) chemistry to attempt to ascertain the source of the contamination

Based on their analysis, Antea concluded that the Dock was not a source and that there were several other sources to the sediment contamination. Antea therefore, requested a letter from us "confirming this harbor sediment issue is closed as it pertains to the Amoco Terminal Barge Dock."

I have reviewed the *Issue Response Report* and also performed analysis of the PAH results. I found Antea's conclusions and recommendations to be in direct contradiction to the information provided in the Report and my own conclusions. In particular*, section 4.2.1 PAH Assemblage Source Allocation* of the Report states that "definitive conclusions for whether or not coal or petroleum was the source could not be determined due to the limited hydrocarbon suite analysis."

My conclusion is that there may be multiple sources and pathways (surface and subsurface) to the sediment contamination in the slip, but we cannot dismiss the Dock based on the current information and analysis. Moreover, while it may not be "definitive" as to the exact percentage that the Dock contributed, the PAH forensic analysis is convincing that the Dock contributed to PAH contamination in the slip sediments. In addition, multiple lines of evidence, including the products that were transferred at the Dock (petroleum: gasoline, diesel, jet fuel, or crude oil) and the long operational history (1890-1993, 103 years), most of which was before environmental law, suggest that the products transferred at the Dock are the most likely sources. The plausible pathways include:

- From a tanker to the surface water
- A spill off the barge dock
- A break or leak in the above-ground pipeline, surface runoff to sediment

- A leak in the underground storage tank and a subsurface pathway to the sediment

Antea makes a good case that coal is the source of the arsenic (and plausible other metals) found in the sediments.

I, therefore, recommend the following:

1. Bureau of Remediation and Redevelopment (R&R):
    a. Create a new Bureau for Remediation and Redevelopment Tracking Systems (BRRTS) case for the sediment in the slip.
    b. Send Responsible Party letters to BP and the C. Reiss Coal Dock (for petroleum and coal, respectively).
    c. Require BP to investigate adjacent (west and south of SW15-SLB03) to identify if a subsurface pathway exists at depth on their property associated with the gravel layer described on the core log for SW15-SLBO3
    d. Request Murphy Oil (BRRTS NO. 03-16-000721) delineate the horizontal and vertical extent of their groundwater plume.
2. Office of Great Waters
    a. Concurrent with the R&R actions listed above, if possible, attempt to further the allocation discussion by collecting additional sediment cores and expanding the parameter list, as suggested by Pace, to include:
        i. A detailed full scan GC/MS analysis
            1. Aliphatic hydrocarbons
        ii. Microscopic analysis to detect any coal particles

**PAH Forensic Analysis**

I performed several analyses of the PAHs analytical results based on the methodology described in Stogiannidis and Laane's 2015 "*Source Characterization of Polycyclic Aromatic Hydrocarbons by Using Their Molecular Indices: An Overview of Possibilities" (*Stogiannidis and Laane, 2015). These analyses aid in the interpretation of the source of the PAHs. After performing said analysis, I agree with Antea's and Alan Jeffrey's (Pace) conclusions that SLB01, SLB02, SLB04, SLB05, and SLB06 of the SW15 series (which are not located in the slip adjacent to the Dock) are from a pyrogenic sources that are different from SLB03's source. Said locations are not discussed further. The results of my analyses of the six intervals for sediment core SLB03, the core location in the slip, are below:

*SW15-SLB03 PAH results*

1. aPAHs
    a. aPAH dominate the matrix in all six samples
    b. aPAHs range from 81-88% of the total PAH concentration based on 38 compounds (TPAH38)[1]
2. Low molecular weight (LMW) PAHs
    a. LMW PAHs dominate the matrix in all six samples
    b. LMW PAHs range from 73-91% of TPAH38, the percentage increases with depth
3. Naphthalene Homologue Group
    a. Naphthalenes are the most dominate PAH homologue group
    b. Nathalenes (N0+N1+N2+N3+N4) account for 41-69% of the TPAH38; the percentage increases with depth
    c. alkyl naphthalenes (N1+N2+N3+N4) account for 40-68% of the TPAH38; the percentage increases with depth.
4. Pattern
    a. samples results exhibit a bell-shaped distribution pattern, an indication of a petrogenic source
5. Ring type
    a. 2-ring PAHs dominate the matrix in all six samples
    b. 2-ring PAHs range from 46-79% of TPAH38, the percentage increases with depth
    c. 6-ring PAHs account for only 1% of the TPAH38
6. Perylene content: Concentrations of perylene range from 0.6 to 1.4 ppm and are less than 0.7% of TPAH38
7. Samples contained ppm levels of benzene and xylene
8. TPAHs with MW > 202
    a. Concentrations ranged from 21-61 ppm which is 13% to 33% of TPAH38, respectively; the percentage decreases with depth

**PAH Forensic Interpretation**

*Relative to Bullets 1-8*

The bullets above cannot rule out the Dock as a source. Moreover, these results suggest that products transferred at the Dock are the main source of PAH contamination at SLB03 because:

- Crude oils contain primarily the alkyl homologs of aromatic compounds and relatively small quantities of the unsubstituted "parent" aromatic structures. (NPS, 1997)
    - Consistent with Bullet 1, aPAHs dominated the matrix, ranging from 81-88% of the TPAH38
- Petroleum products contain mainly two- three-ringed PAHs (Stogiannidis and Laane, 2015);
    - Consistent with Bullet 2, LMW (two- three-ringed PAHs) account for 73 -91% of the TPAH38[2]

[1] Assuming ND = 1 RL. Analysis of ND treatment shows that NDs are 4% of the total or less, the exception being the 6-8 ft sample, that was 6%. Less than 15% is acceptable and will not affect the conclusions in this memorandum.
[2] Unless otherwise indicated, all results are from SW15-SLB03.

- The higher the coal rank, the more dominant the LMW compounds are over the HMW compounds (petrogenic characteristic). In higher coal ranks, the bell-shaped profile shifts to a pyrogenic-like skewed pattern that is dominated by parent PAHs. (Stogiannidis and Laane, 2015).
    - Although SW15-SLB03 is dominated by LMW PAHs (Bullet 2), the samples are also dominated by aPAHs (Bullet 1) not pPAHs. Suggesting that high coal ranks do not fit the data.
- Many crude oils are dominated by alkyl naphthalenes (Stogiannidis and Laane, 2015)
    - Consistent with Bullet 3, alkyl naphthalenes are the dominating PAHs, accounting for 40 – 68% of TPAH38
- Consistent with Bullet 4 and the attached graphs, the PAHs exhibit a bell-shaped pattern consistent with a Petrogenic source.
- Diesel PAHs are largely comprised of 2-3-ring PAHs and their alkylated homologues (Stogiannidis and Laane, 2015)
    - Consistent with Bullet 5, 2-3 ring alkylated homologous account for 63 – 79% of TPAH38.
- The PAH distribution patterns in coals are a function of coal rank. Lower rank coals such as lignite and sub-bituminous coal may contain significant amounts of perylene (Stogiannidis and Laane, 2015).
    - Consistent with Bullet 6, SW15-SLB03 contains low perylene concentrations, suggesting that if coal were present, it would be a higher rank, not low rank.
- Neither high nor low rank coal PAH distribution patterns are exhibited by the data, supported by Bullets 1, 5, and 6.
- Of the five target alkylated PAH series of diesel, the most abundant (>55%) is alkylated naphthalene and the least abundant (<0.02%) is chrysene; thus, the absence of chrysene can be used to identify diesel or diesel soot (Wang et al. 1999a, 2001)
    - Consistent with Bullet 3, alkyl naphthalenes account for 40 – 68% of TPAH38.
    - Alkylated chrysene accounts for 3-9% of TPAH38, higher than 0.02%. However, alkylated chrysene (C1+C2+C3+C4) ranged from 4.2-11.9 ppm, averaging 7 ppm, compared to a range of 0.4-5.4 ppm and averaged 1.9 ppm for SLB02 and SLB05. Thus, the ranges for chrysene overlapped, even though the TPAH38 concentration was up to 25x higher in LB03.
- LMW, 2-ringed PAHs and VOCs (benzenes) are generally not found in sediments. These compounds generally volatilize or dissolve in water. Consistent with Bullet 7, their presence in the solid phase suggests that an oil or another compound is trapping and altering their behavior, preventing these compounds from behaving as they normally would.
- PAHs having a MW greater than that of pyrene (202) are hardly present in light distillates such as jet B fuel or gasoline (Stogiannidis and Laane, 2015);
    - Consistent with bullet 8, PAHs with MWs weights greater than 202 are 13% to 33% of TPAH38; the percentage decreases with depth.

*Addition Interpretation*

- Weathering: The increase in naphthalene and LMW PAHs with depth is an indication of weathering at the surface and less with depth
- Diagnostic Ratios: There is a difference in the Phenanthrene / Anthracene (P/A) ratio of the samples at depth (6-8 ft and 8–10 ft) and the other four sampls. The P/A drops from 10.8 to 1.9 in proximity to the gravel layer. This could suggest multiple pathways of contamination (surface and subsurface).
- Petrogenic source:
    a. The fraction of pyrogenic PAHs ((Fl0 + PY0) / (PA2 + PA3 + PA4)) and the Pyrogenic Index (Σ(3-6 ring EPAPP)/(Σ5 alkylated PAHS) 7-22% and indicate a petrogenic source.
    b. "The distributions of the PAHs in the SW15-SLB03 sediment indicated unequivocally that their source is a thermogenic product, rather than the pyrogenic products in SW15-SLB02 and SW15-SLB05" Allan Jeffrey, Pace, Appendix F.

**Other Evidence**:

1. The Dock was used to transport petroleum products that are most likely to have contaminated the sediment consistent with the forensic analysis. Appendix I includes analytical results of Gasoline Grades - Produce Product Code 9, 10 , 11. The product results indicate naphthalene concentrations of 2,690-5,080 ppm and 2-Methylnaphthalene concentrations of 963 to 4,105 ppm, sufficient concentrations to contaminate the sediments with found levels of LMW PAHs. Stated differently, the products transported at the Dock are consistent with the contamination found in the sediments at SW15-SLB03.
2. Appendix G – Indicates a product "Jet Naptha" which is consistent with naphthlenes being the dominant homologue group.
3. Appendix F – Figure 6, shows the distribution of coal and crude oil. Concentrations in SW15-SLB03 are higher for naphthalenes (N0-N4, up to 85 ppm) than the concentration in coal in Figure 6, which is up to 75 ppm. One would expect a higher concentration in the source material than found in the environment after dilution and dispersion.

**Conclusions & Responses:**

Antea's conclusions are restated, and then responses are offered.

**Antea Conclusion 1:**

*Any residual soil or groundwater contamination related to the Amoco Barge Dock near sediment sample SW15-SLB03 has been identified and/or removed during the October 2002 delineation and excavation. Sidewall soil samples collected around the excavation area performed in October 2002 indicated no PVOC contaminant levels that exceeded NR 720 RCL or NR 746 Soil Screening Levels. Two rounds of groundwater sampling performed in the area of the excavation in November 2002 and April 2003 indicated no contaminant levels that exceeded NR 140 ES Standards.*

**Response 1:**

The soil sample results after tank removal (Figure 5) support this conclusion. However, without containment, is like likely that there would be a subsurface pathway from the Dock to the sediments. The core log for SW15-SLB03 (attached) found a thin gravel layer on top of a clay confining layer at 9.2 ft. The core log called out "potential coal/coke" and a very strong chemical odor in the description for the gravel layer. Also, the presence of the contamination in the slip confirms that the site was not fully investigated.

**Antea Conclusion 2:**

*The Murphy Oil Marine Terminal Tank #2 open LUST investigation (BRRTS #03-16-000721) is located upgradient of sediment sample site SW15-SLB03. The concentrations of PVOCs at the site greatly exceed the NR 720 RCL, and are a potential source for the results found in the sediment sample*.

**Response 2:**

Antea also asserts that the Murphy Oil Marine Terminal Tank #2 (BRRTS NO. 03-16-000721) groundwater plume (MW-1 through MW-6) "is not delineated vertically or horizontally…..and this source may have been a contributor to the PVOCs found in the sediment sample in SW15-SLB03."

The concentrations of naphthalene in groundwater were indicated as 113, and 191 ppb in MW2, and MW-4, respectively. Although the referenced concentrations are in groundwater, the soil concentrations did not exceed NR 720 soil to groundwater pathway residual contaminate level of 658 ppb in either MW-2 or MW-4. The maximum concentration Antea indicated in the *Issue Response Report* was 398 ppb. It is unlikley to me that a low concentration dissolved phase plume would be the source of high solid phase concentrations in the sediment some distance away.

**Conclusion 3:**

*After analysis of PAH ratios and concentration distributions, including independent expert analysis, it can be concluded that the sediment contamination found in SW15-SLB03 originates from a thermogenic (petrogenic) source, suggestive of coal. Sediment samples SW15-SLB01, SW15-SLB02, SW15-SLB04, SW15-SLB05, and SW15-SLB06 have PAH ratios that suggest pyrogenic sources.*

**Response 3:**

The conclusion contradicts the text that "definitive conclusions for whether or not coal or petroleum was the source could not be determined due to the limited hydrocarbon suite analysis." I disagree that it is definitively coal, most of the evidence in this memorandum suggests that petroleum from the Barge Dock could have contributed and is likely the main source.

**Conclusion 3:**

*Heavy metals contained in SW15-SLB03 are representative of coal compounds and do not resemble the contents of any gasoline, diesel, or other distillates that were historically shipped to the Amoco Barge Dock slip. Docks across the bay from the sediment sample location have been shipping iron ore or taconite pellets from 1893 up to the present day. These industrial shipping areas are a suspected source for the high levels of iron found in the sediment.*

**Response 3:**

No disagreement.

**Conclusion 4**

*The SVOC dibenzofuran detected in the sediment samples has been identified by the US EPA as relating to coal/coke sources.*

**Response:**
Dibenzofuran is not a primary contaminant of concern, four of the six samples at SW15-SLB03 were non-detect. This is an insignificant contaminant compared to the metals, PAHs, and VOCs.

**References**

Eirwin et. all. National Park Service. 1997 (NPS, 1997). Environmental Contaminants Encyclopedia Entry on Alkyl PAHS (Alkyl Homogos of PAHS).

Efstahios Stogiannidis and Remi Laane. 2015. (Stogiannidis and Laane, 2015). Source Characterization of Polycyclic Aromatic Hydrocarbons by Using Their Molecular Indices: An Overview of Possibilities. University Amerstam, The Netherlands.

Wang Z, Fingas M, (Wang et al, 1999) Page DS (1999a) Oil Spill identification. J. Chromatogr A. 846:369-411.

**Attachments**
SW15-SLB03 Core Log
SW15-SLB03 PAH Calculations
SW15-SB03 Graphs

# SEDIMENT BORING SW15-SLB03

EA Engineering, Science, and Technology, Inc., PBC

**PROJECT NAME** Superior Waterfront
**DATE COLLECTED** 7/9/2015
**DATE LOGGED** 7/9/2015 3:35:00 PM
**DRILLING CONTRACTOR** Cetacean Marine
**DRILLING METHOD** Vibracore
**LOGGED BY** H. Williams

**RECOVERY** 100%
**LOCATION** Superior, WI
**NORTHING*** 5176498.19
**EASTING*** 567208.87
**ELEVATION (Sediment Surface)** 592.3 ft (NAVD 88)
**WATER DEPTH** 10.5 ft

| DEPTH BELOW MUDLINE (ft) | SAMPLE INTERVAL (inches) | SAMPLE TYPE | SAMPLE SUBMITTED FOR ANALYSIS (Sample ID at sample depth) | GRAPHIC LOG | USCS CLASS | MATERIAL DESCRIPTION | Depth (ft) |
|---|---|---|---|---|---|---|---|
| 0 | | | | | | | |
| -1 | 18 | Composite | SW15-SLB03-0520 | | | | |
| -2 | | | | | | | |
| -3 | 24 | Composite | SW15-SLB03-2040 | | SM | SILT & SAND: black/ dark grey, f grained sand, trace m grained sand, low plasticity, cohesive, moist, trace rootlets and small wood pieces throughout, strong hydrocarbon/ chemical odor, large branch (@6.75-7'), slight sheen | |
| -4 | | | | | | | |
| -5 | 24 | Composite | SW15-SLB03-4060 | | | | |
| -6 | | | | | | | |
| -7 | 24 | Composite | SW15-SLB03-6080 | | | | 7.0 |
| -8 | | | | | SC-SM | SILT & SAND: black/ dark grey, f grained sand, trace m grained sand, trace clay, medium plasticity, very cohesive, moist, trace rootlets and small wood pieces throughout, strong hydrocarbon/ chemical odor, large branch (@6.75-7'), slight sheen | |
| -9 | 24 | Composite | SW15-SLB03-8010 | | GP | GRAVEL: black, f-c grained, very strong chemical odor, potentiall coal/coke, slight sheen | 9.2 |
| | | | | | CL-ML | SILTY CLAY: black/ dark brown, some vf grained | 9.3 |
| -10 | | | | | | | 10.0 |

NOTES:
* Coordinates in NAD83 UTM 15N (meters)

SEDIMENT LOG SUPERIOR WATERFRONT.GPJ 11/12/15

# SEDIMENT BORING SW15-SLB03

EA Engineering, Science, and Technology, Inc., PBC

**PROJECT NAME** Superior Waterfront
**DATE COLLECTED** 7/9/2015
**DATE LOGGED** 7/9/2015 3:35:00 PM
**DRILLING CONTRACTOR** Cetacean Marine
**DRILLING METHOD** Vibracore
**LOGGED BY** H. Williams

**RECOVERY** 100%
**LOCATION** Superior, WI
**NORTHING*** 5176498.19
**EASTING*** 567208.87
**ELEVATION (Sediment Surface)** 592.3 ft (NAVD 88)
**WATER DEPTH** 10.5 ft

| DEPTH BELOW MUDLINE (ft) | SAMPLE INTERVAL (inches) | SAMPLE TYPE | SAMPLE SUBMITTED FOR ANALYSIS (Sample ID at sample depth) | GRAPHIC LOG | USCS CLASS | MATERIAL DESCRIPTION | Depth (ft) |
|---|---|---|---|---|---|---|---|
| -10 | | | | | | sand, medium plasticity, cohesive, moist, trace rootlers, strong chemical odor, slight sheen | |
| -11 | | | | | | End of Boring at 1.75 ft. | |
| -12 | | | | | | | |
| -13 | | | | | | | |
| -14 | | | | | | | |
| -15 | | | | | | | |
| -16 | | | | | | | |
| -17 | | | | | | | |
| -18 | | | | | | | |
| -19 | | | | | | | |
| -20 | | | | | | | |

NOTES:
* Coordinates in NAD83 UTM 15N (meters)

**Table 1 - SW15-SLB03 PAH Analysis**

| PAH | | | | SW15-SLB03 Depth Interval (ft) and Concentration (µg/kg) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Full Name | Shorthand | # rings | MW | 0-0.5 | 0.5-2.0 | 2.0-4.0 | 4.0-6.0 | 6.0-8.0 | 8.0-10.0 | average |
| 1-Methylnapthalene | 1M | 2 | 142 | 1,500 | 9,400 | 13,000 | 16,000 | 7,500 | 12,000 | 9,900 |
| 2-Methylnapthalene | 2M | 2 | 142 | 1,700 | 4,700 | 7,300 | 7,900 | 4,700 | 9,500 | 5,967 |
| Napthalene | N0 | 2 | 128 | 620 | 1,800 | 3,100 | 2,600 | 1,400 | 1,700 | 1,870 |
| C1-Napthalenes | N1 | 2 | 142 | 2,200 | 9,100 | 13,000 | 15,000 | 8,000 | 14,000 | 10,217 |
| C2-Napthalenes | N2 | 2 | 156 | 9,200 | 65,000 | 61,000 | 85,000 | 44,000 | 58,000 | 53,700 |
| C3-Napthalenes | N3 | 2 | 170 | 9,700 | 79,000 | 67,000 | 80,000 | 39,000 | 41,000 | 52,617 |
| C4-Napthalenes | N4 | 2 | 184 | 4,200 | 36,000 | 29,000 | 30,000 | 14,000 | 12,000 | 20,867 |
| Flourene | F0 | 3 | 166 | **290** | 1,200 | 1,100 | 1,100 | **510** | 670 | 812 |
| C1-Flourenes | F1 | 3 | 180 | 650 | 3,100 | 2,200 | 1,700 | 1,100 | 1,000 | 1,625 |
| C2-Flourenes | F2 | 3 | 194 | 1,500 | 4,700 | 3,800 | 2,600 | 1,700 | 1,100 | 2,567 |
| C3-Flourenes | F3 | 3 | 208 | 1,100 | 4,100 | 3,600 | 2,700 | 1,800 | 1,100 | 2,400 |
| Acenapthylene | AY | 3 | 152 | **37** | 210 | 1300 | 420 | 440 | 270 | 446 |
| Acenaphthlene | AE | 3 | 154 | 130 | 740 | 750 | 810 | 330 | 710 | 578 |
| Anthracene | A0 | 3 | 178 | **130** | **700** | **760** | **360** | 1,100 | 1,000 | 675 |
| Phenanthrene | P0 | 3 | 178 | **1,000** | 5,500 | 5,500 | 3,900 | 2,100 | 1,500 | 3,250 |
| C1-Phenanthrenes/Anthracenes | PA1 | 3 | 192 | 2,900 | 12,000 | 10,000 | 6,700 | 4,100 | 2,700 | 6,400 |
| C2-Phenanthrenes/Anthracenes | PA2 | 3 | 206 | 3,000 | 13,000 | 11,000 | 7,300 | 4,600 | 3,300 | 7,033 |
| C3-Phenanthrenes/Anthracenes | PA3 | 3 | 220 | 2,800 | 12,000 | 10,000 | 8,100 | 5,300 | 4,600 | 7,133 |
| C4-Phenanthrenes/Anthracenes | PA4 | 3 | 234 | 2,300 | 5,300 | 5,400 | 4,600 | 3,000 | 3,000 | 3,933 |
| Flouranthene | FL0 | 3 | 166 | **840** | **1,600** | 2,600 | **1,700** | **760** | **1,000** | 1,417 |
| Pyrene | PY0 | 4 | 202 | **840** | 2,700 | 3,100 | 1,900 | **940** | **1,100** | 1,763 |
| C1-Flouranthrenes/Pyrenes | FP1 | 4 | 180 | 2,200 | 5,300 | 6,100 | 3,900 | 2,000 | 2,200 | 3,617 |
| C2-Flouranthrenes/Pyrenes | FP2 | 4 | 194 | 2,300 | 5,400 | 5,800 | 3,700 | 1,900 | 2,100 | 3,533 |
| C3-Flouranthrenes/Pyrenes | FP3 | 4 | 208 | 1,700 | 4,200 | 4,400 | 2,900 | 1,500 | 1,700 | 2,733 |
| Benzo(a)anthracene | BaA | 4 | 228 | **560** | 1,300 | 1,600 | **1,000** | **480** | **590** | 922 |
| Chrysene | C0 | 4 | 228 | **640** | 1,700 | 2,000 | **1,200** | **640** | **730** | 1,152 |
| C1-Chrysenes | C1 | 4 | 242 | 1,100 | 3,000 | 2,800 | 1,600 | 1,100 | 1,000 | 1,767 |
| C2-Chrysenes | C2 | 4 | 256 | 2,000 | 4,700 | 3,900 | 2,200 | 1,100 | 1,200 | 2,517 |
| C3-Chrysenes | C3 | 4 | 270 | 1,300 | 2,700 | 1,900 | 1,400 | 1,100 | 1,000 | 1,567 |
| C4-Chrysenes | C4 | 4 | 284 | 730 | 1,500 | 1,700 | 1,400 | 1,100 | 1,000 | 1,238 |
| Perylene | PER | 5 | 252 | 270 | 600 | 1,300 | 1,400 | 1,100 | 1,000 | 945 |
| Benzo(b)fluoranthene | BbF | 5 | 252 | **570** | **1300** | **1600** | **1100** | **500** | **730** | 967 |
| Benzo(a)pyrene | BaP | 5 | 252 | **610** | **1200** | **1100** | **650** | **310** | **500** | 728 |
| Benzo(e)pyrene | BeP | 5 | 252 | **670** | 1,700 | 1,800 | **1,400** | 1,100 | 1,000 | 1,278 |
| Benzo(k)flouranthene | BkF | 5 | 252 | **420** | **300** | **420** | **320** | 160 | **250** | 312 |
| Dibenzo(a,h)anthracene | DA | 5 | 278 | 170 | 230 | 260 | 1,400 | 1,100 | 1,000 | 693 |
| Indeno(1,2,3-cd)pyrene | IP | 6 | 276 | **310** | **480** | **700** | **410** | 1,100 | **270** | 545 |
| Benzo(g,h,i)perylene | ghi | 6 | 276 | **500** | **1200** | **1500** | **810** | **360** | **410** | 797 |

| Color Coding | | | |
|---|---|---|---|
| **> TEC** | **> MEC** | >PEC | Sample max |

| Reported Totals with ND = 1/2 RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| TPAH17 | **9,367** | 26,860 | 34,040 | 26,880 | **15,280** | **20,930** | 22,226 |
| TPAH | 63,000 | 290,000 | 270,000 | 280,000 | 150,000 | 160,000 | 202,167 |

| Count of ND | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| TPAH16 | 0 | 0 | 1 | 1 | 3 | 2 | 1.2 |
| TPAH17 | 0 | 0 | 1 | 1 | 3 | 2 | 1.2 |
| TPAH18 | 0 | 0 | 1 | 2 | 4 | 3 | 1.7 |
| TPAH34 | 0 | 0 | 1 | 3 | 7 | 6 | 2.8 |
| TPAH35 | 0 | 0 | 1 | 4 | 8 | 7 | 3.3 |
| TPAH38 | 0 | 1 | 2 | 5 | 9 | 8 | 4.2 |

| Sum ND concentration with ND = RL | Average |
|---|---|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| TPAH16 | 0 | 0 | 1,300 | 1,400 | 3,300 | 2,000 | 1,333 |
| TPAH17 | 0 | 0 | 1,300 | 1,400 | 3,300 | 2,000 | 1,333 |
| TPAH18 | 0 | 0 | 1,300 | 2,800 | 4,400 | 3,000 | 1,917 |
| TPAH34 | 0 | 0 | 1,300 | 4,200 | 7,700 | 6,000 | 3,200 |
| TPAH35 | 0 | 0 | 1,300 | 5,600 | 8,800 | 7,000 | 3,783 |
| TPAH38 | 0 | 600 | 2,600 | 7,000 | 9,900 | 8,000 | 4,683 |

| Calculated Totals with ND = RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| TPAH16 | 7,667 | 22,160 | 27,390 | 19,680 | 12,230 | 12,430 | 16,926 |
| TPAH17 | 9,367 | 26,860 | 34,690 | 27,580 | 16,930 | 21,930 | 22,893 |
| TPAH18 | 10,037 | 28,560 | 36,490 | 28,980 | 18,030 | 22,930 | 24,171 |
| TPAH34 | 58,547 | 292,260 | 269,990 | 280,480 | 148,630 | 164,430 | 202,390 |
| TPAH35 | 59,217 | 293,960 | 271,790 | 281,880 | 149,730 | 165,430 | 203,668 |
| TPAH38 | 62,687 | 308,660 | 293,390 | 307,180 | 163,030 | 187,930 | 220,480 |

| Calculated Totals with ND = 1/2 RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| TPAH16 | 7,667 | 22,160 | 26,740 | 18,980 | 10,580 | 11,430 | 16,260 |
| TPAH17 | 9,367 | 26,860 | 34,040 | 26,880 | 15,280 | 20,930 | 22,226 |
| TPAH18 | 10,037 | 28,560 | 35,840 | 27,580 | 15,830 | 21,430 | 23,213 |
| TPAH34 | 58,547 | 292,260 | 269,340 | 278,380 | 144,780 | 161,430 | 200,790 |
| TPAH35 | 59,217 | 293,960 | 271,140 | 279,080 | 145,330 | 161,930 | 201,776 |
| TPAH38 | 62,687 | 308,360 | 292,090 | 303,680 | 158,080 | 183,930 | 218,138 |

| Calculated Totals with ND = 0 | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| TPAH16 | 7,667 | 22,160 | 26,090 | 18,280 | 8,930 | 10,430 | 15,593 |
| TPAH17 | 9,367 | 26,860 | 33,390 | 26,180 | 13,630 | 19,930 | 21,560 |
| TPAH18 | 10,037 | 28,560 | 35,190 | 26,180 | 13,630 | 19,930 | 22,255 |
| TPAH34 | 58,547 | 292,260 | 268,690 | 276,280 | 140,930 | 158,430 | 199,190 |
| TPAH35 | 59,217 | 293,960 | 270,490 | 276,280 | 140,930 | 158,430 | 199,885 |
| TPAH38 | 62,687 | 308,060 | 290,790 | 300,180 | 153,130 | 179,930 | 215,796 |

| ND % of Total with ND = RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| TPAH16 | 0% | 0% | 5% | 7% | 27% | 16% | 9% |
| TPAH17 | 0% | 0% | 4% | 5% | 19% | 9% | 6% |
| TPAH18 | 0% | 0% | 4% | 10% | 24% | 13% | 8% |
| TPAH34 | 0% | 0% | 0% | 1% | 5% | 4% | 2% |
| TPAH35 | 0% | 0% | 0% | 2% | 6% | 4% | 2% |
| TPAH38 | 0% | 0% | 1% | 2% | 6% | 4% | 2% |

| ND % of Total with ND = 1/2 RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| TPAH16 | 0% | 0% | 2% | 4% | 16% | 9% | 5% |
| TPAH17 | 0% | 0% | 2% | 3% | 11% | 5% | 3% |
| TPAH18 | 0% | 0% | 2% | 5% | 14% | 7% | 5% |
| TPAH34 | 0% | 0% | 0% | 1% | 3% | 2% | 1% |
| TPAH35 | 0% | 0% | 0% | 1% | 3% | 2% | 1% |
| TPAH38 | 0% | 0% | 0% | 1% | 3% | 2% | 1% |

| Concentration Breakdown by # of Rings with ND = 1 RL including all 38 PAHs Reported | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| 2 | 29,120 | 205,000 | 193,400 | 236,500 | 118,600 | 148,200 | 155,137 |
| 3 | 16,677 | 64,150 | 58,010 | 41,990 | 26,840 | 21,950 | 38,270 |
| 4 | 13,370 | 32,500 | 33,300 | 21,200 | 11,860 | 12,620 | 20,808 |
| 5 | 2,710 | 5,330 | 6,480 | 6,270 | 4,270 | 4,480 | 4,923 |
| 6 | 810 | 1,680 | 2,200 | 1,220 | 1,460 | 680 | 1,342 |

| % Breakdown by # of Rings with ND = 1 RL including all 38 PAHs Reported | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| 2 | 46% | 66% | 66% | 77% | 73% | 79% | 68% |
| 3 | 27% | 21% | 20% | 14% | 16% | 12% | 18% |
| 4 | 21% | 11% | 11% | 7% | 7% | 7% | 11% |
| 5 | 4% | 2% | 2% | 2% | 3% | 2% | 3% |
| 6 | 1% | 1% | 1% | 0% | 1% | 0% | 1% |

| Concentration Breakdown by MW with ND= 1 RL including all 38 PAHs Reported | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| Low Molecular Weight PAHs (3 or less rings) | 45,797 | 269,150 | 251,410 | 278,490 | 145,440 | 170,150 | 193,406 |
| High Molecular Weight PAHs (4 or more rings) | 16,890 | 39,510 | 41,980 | 28,690 | 17,590 | 17,780 | 27,073 |
| LMW | 73% | 87% | 86% | 91% | 89% | 91% | 86% |
| HMW | 27% | 13% | 14% | 9% | 11% | 9% | 14% |

| Concentration by PAH Homologue Group with ND = 1 RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| Nathalenes (N0+N1+N2+N3+N4) | 25,920 | 190,900 | 173,100 | 212,600 | 106,400 | 126,700 | 139,270 |
| Flourenes (F0+F1+F2+F3) | 3,540 | 13,100 | 10,700 | 8,100 | 5,110 | 3,870 | 7,403 |
| Phenanthrenes/Anthracenes (A0+P0+PA1+PA2+PA3+PA4) | 12,130 | 48,500 | 42,660 | 30,960 | 20,200 | 16,100 | 28,425 |
| Flouranthrenes/Pyrenes (FL0+PY0+FP1+FP2+FP3) | 7,880 | 19,200 | 22,000 | 14,100 | 7,100 | 8,100 | 13,063 |
| Chrysenes (C0+C1+C2+C3+C4) | 5,770 | 13,600 | 12,300 | 7,800 | 5,040 | 4,930 | 8,240 |

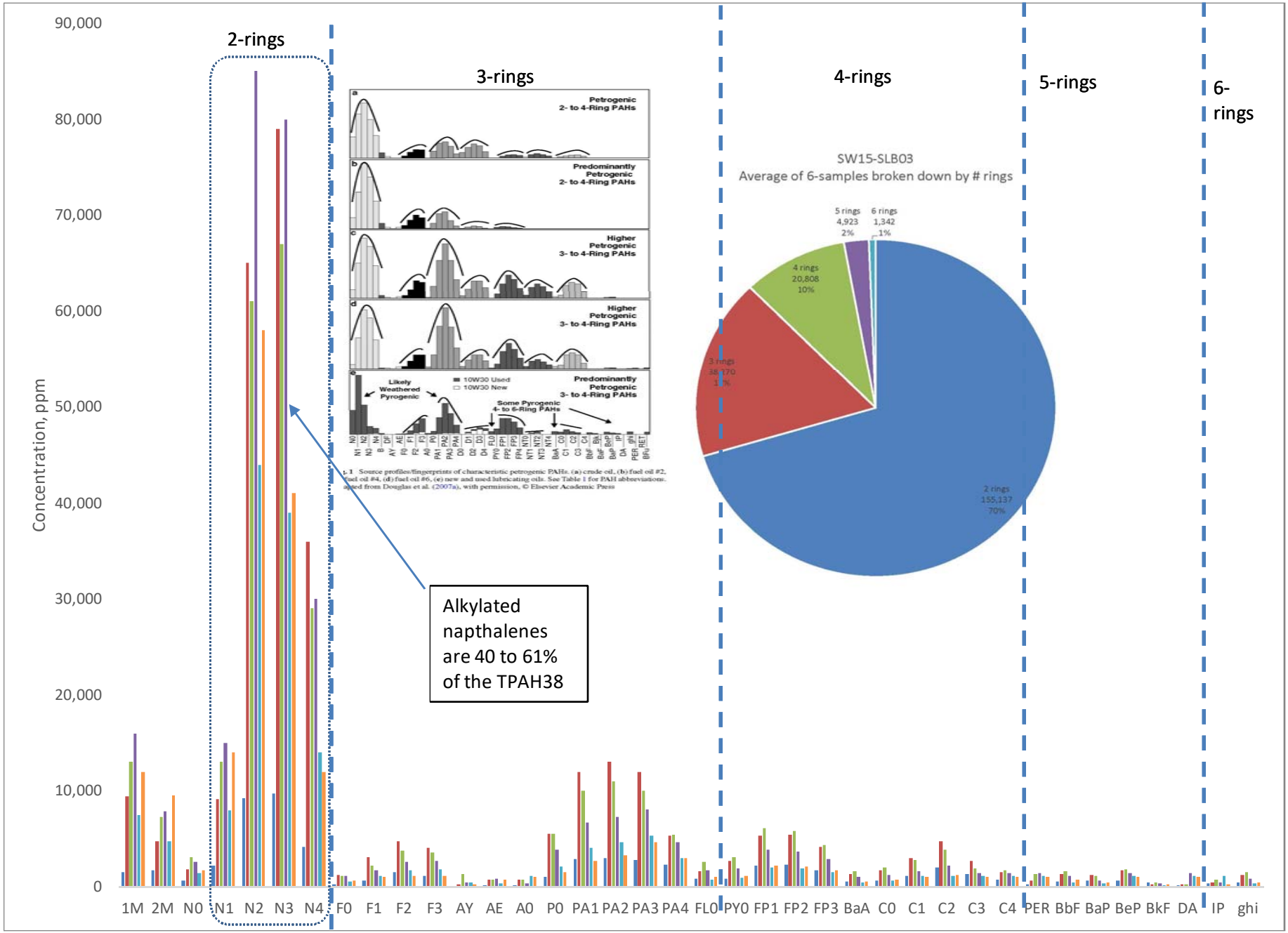
| % of PAH Homologue Group to TPAH38 with ND = 1 RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| Nathalenes (N0+N1+N2+N3+N4) | 41% | 62% | 59% | 69% | 65% | 67% | 61% |
| Flourenes (F0+F1+F2+F3) | 6% | 4% | 4% | 3% | 3% | 2% | 4% |
| Phenanthrenes/Anthracenes (A0+P0+PA1+PA2+PA3+PA4) | 19% | 16% | 15% | 10% | 12% | 9% | 13% |
| Flouranthrenes/Pyrenes (FL0+PY0+FP1+FP2+FP3) | 13% | 6% | 7% | 5% | 4% | 4% | 7% |
| Chrysenes (C0+C1+C2+C3+C4) | 9% | 4% | 4% | 3% | 3% | 3% | 4% |

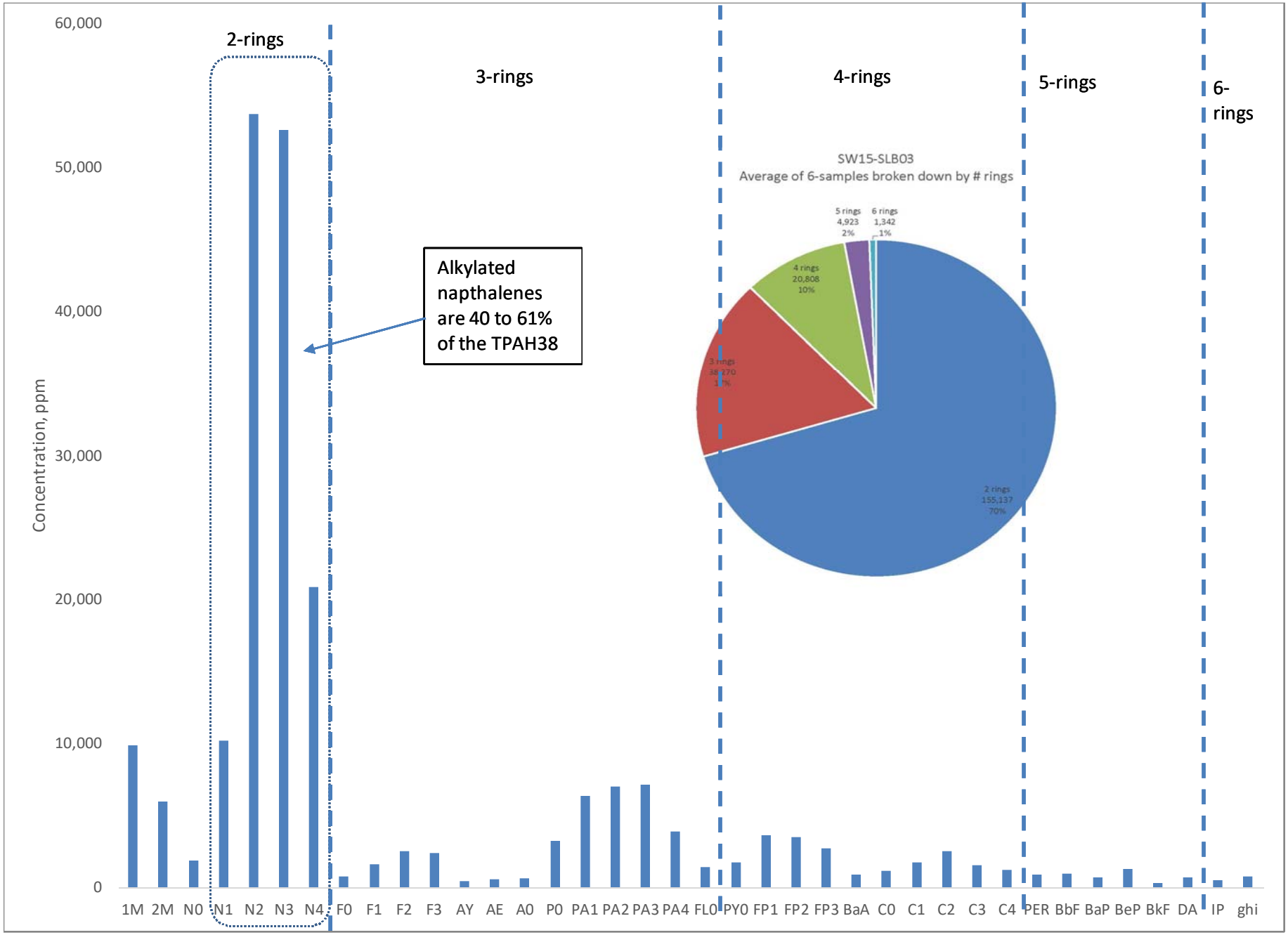
| aPAH by Homologue Group with ND = 1 RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| Nathalenes (N1+N2+N3+N4) | 25,300 | 189,100 | 170,000 | 210,000 | 105,000 | 125,000 | 137,400 |
| Flourenes (F1+F2+F3) | 3,250 | 11,900 | 9,600 | 7,000 | 4,600 | 3,200 | 6,592 |
| Phenanthrenes/Anthracenes (PA1+PA2+PA3+PA4) | 11,000 | 42,300 | 36,400 | 26,700 | 17,000 | 13,600 | 24,500 |
| Flouranthrenes/Pyrenes (FP1+FP2+FP3) | 6,200 | 14,900 | 16,300 | 10,500 | 5,400 | 6,000 | 9,883 |
| Chrysenes (C1+C2+C3+C4) | 5,130 | 11,900 | 10,300 | 6,600 | 4,400 | 4,200 | 7,088 |
| aPAH38 | 50,880 | 270,100 | 242,600 | 260,800 | 136,400 | 152,000 | 185,463 |
| %aPAH | 81% | 88% | 83% | 85% | 84% | 81% | 83% |

| aPAH by Homologue Group with ND = 1 RL | | | | | | | Average |
|---|---|---|---|---|---|---|---|
| Nathalenes (N1+N2+N3+N4) | 40% | 61% | 58% | 68% | 64% | 67% | 60% |
| Flourenes (F1+F2+F3) | 5% | 4% | 3% | 2% | 3% | 2% | 3% |
| Phenanthrenes/Anthracenes (PA1+PA2+PA3+PA4) | 18% | 14% | 12% | 9% | 10% | 7% | 12% |
| Flouranthrenes/Pyrenes (FP1+FP2+FP3) | 10% | 5% | 6% | 3% | 3% | 3% | 5% |
| Chrysenes (C1+C2+C3+C4) | 8% | 4% | 4% | 2% | 3% | 2% | 4% |

| Calculated Diagnostic Ratios | | | | | | |
|---|---|---|---|---|---|---|
| P0 / A0 | 7.7 | 7.9 | 7.2 | 10.8 | 1.9 | 1.5 |
| Fl0 / PY0 | 1.0 | 0.6 | 0.8 | 0.9 | 0.8 | 0.9 |
| BaA / C0 | 0.88 | 0.76 | 0.80 | 0.83 | 0.75 | 0.81 |
| (Fl0 + PY0) / ($PA_2$ + $PA_3$ + $PA_4$) | 21% | 14% | 22% | 18% | 13% | 19% |
| Σ(3-6 ring EPAPP)/(Σ5 alkylated PAHS) | 14% | 8% | 10% | 7% | 8% | 7% |

| LMW PAH Ratios | | | | | | |
|---|---|---|---|---|---|---|
| N0/N1 | 28% | 20% | 24% | 17% | 18% | 12% |
| 2M/1M | 1.13 | 0.50 | 0.56 | 0.49 | 0.63 | 0.79 |
| N0/F0 | 2.14 | 1.50 | 2.82 | 2.36 | 2.75 | 2.54 |
| N0+N1/N2 | 620 | 1,800 | 3,100 | 2,600 | 1,400 | 1,700 |
| ΣN1-N4/ΣC1-C3 | 5.8 | 18.2 | 19.8 | 40.4 | 31.8 | 39.1 |
| ΣN1-N4/TPAH38 | 40% | 61% | 58% | 68% | 64% | 67% |
| Perylene % | 0.4% | 0.2% | 0.4% | 0.5% | 0.7% | 0.5% |


90,000
80,000
70,000
60,000
50,000
40,000
30,000
20,000
10,000
0
Concentration, ppm
2-rings
3-rings
4-rings
5-rings
6-rings
Petrogenic
2- to 4-Ring PAHs
Predominantly
Petrogenic
2- to 4-Ring PAHs
Higher
Petrogenic
3- to 4-Ring PAHs
Higher
Petrogenic
3- to 4-Ring PAHs
Likely
Weathered
Pyrogenic
10W30 Used
10W30 New
Some Pyrogenic
4- to 6-Ring PAHs
Predominantly
Petrogenic
3- to 4-Ring PAHs
N0 N1 N2 N3 N4 B DF AY AE F0 F1 F2 F3 A0 P0 PA1 PA2 PA3 PA4 D0 D1 D2 D3 D4 FL0 PY0 FP1 FP2 FP3 FP4 N1D N1T N2T N3T N4T BaA C0 C1 C2 C3 C4 BbF BkF BaP IP DA ghi PER BP1 RET
SW15-SLB03
Average of 6-samples broken down by # rings
5 rings
4,923
2%
6 rings
1,342
1%
4 rings
20,808
10%
3 rings
38,770
18%
2 rings
155,137
70%
Alkylated
napthalenes
are 40 to 61%
of the TPAH38
1M 2M N0 N1 N2 N3 N4 F0 F1 F2 F3 AY AE A0 P0 PA1 PA2 PA3 PA4 FL0 PY0 FP1 FP2 FP3 BaA C0 C1 C2 C3 C4 PER BbF BaP BeP BkF DA IP ghi


60,000
50,000
40,000
30,000
20,000
10,000
0
Concentration, ppm
2-rings
3-rings
4-rings
5-rings
6-rings
Alkylated napthalenes are 40 to 61% of the TPAH38
SW15-SLB03
Average of 6-samples broken down by # rings
5 rings 4,923 2%
6 rings 1,342 1%
4 rings 20,808 10%
3 rings 38,270 17%
2 rings 155,137 70%
1M 2M N0 N1 N2 N3 N4 F0 F1 F2 F3 AY AE A0 P0 PA1 PA2 PA3 PA4 FL0 PY0 FP1 FP2 FP3 BaA C0 C1 C2 C3 C4 PER BbF BaP BeP BkF DA IP ghi