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**FINAL REPORT**  
**PRESQUE ISLE BAY SEDIMENT STUDY — DATA REVIEW**

**EPA Contract No. 68-C2-0134**  
**Work Assignment 4-456**

to

**Environmental Protection Agency, Region III**  
**Water Protection Division**  
**Philadelphia, PA**

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### 1.0 INTRODUCTION

#### 1.1 BACKGROUND

Presque Isle Bay is located in the northwestern corner of Pennsylvania on the southern shore of Lake Erie. Most of its watershed comprises urban and industrial areas within the City of Erie and Millcreek Township, PA. The primary tributaries are Mill Creek (including Garrison Run) and Cascade Creek, which together account for about two-thirds of the water flowing into the bay. Additional inflows include direct precipitation, combined sewer overflows (CSOs), permitted wastewater discharges, and nonpoint urban runoff. The land use within the Presque Isle Bay watershed is 80% urban. Being a relatively closed system with flushing time of almost 2.5 years, the Bay has suffered from the accumulation and degradation of wastes discharged by point and nonpoint sources.

In January 1991, Presque Isle Bay was designated as the 43rd Great Lakes Area of Concern (AOC) by the U.S. Department of State. As an Area of Concern, the Bay received priority attention from the Pennsylvania Department of Environmental Resources (PADER), now Pennsylvania Department of Environmental Protection (PADEP), in the form of an Ecosystem Study/Background Report issued in June 1991 (1). This report was updated to a Remedial Action Plan (RAP) in December 1992 (2). The RAP summarized currently identified impaired uses of the Bay, along with pollutants of concern. It also listed recommendations for further data collection.

In May 1994, grab samples of sediment were collected by the U.S. Environmental Protection Agency (EPA) and PADER from 21 stations throughout Presque Isle Bay for bulk chemistry analysis; 12 stations for toxicity testing; and eight stations for macro invertebrate community analysis. In addition, net tows were deployed at four stations for the analysis of the zooplankton community and 12 discrete whole-water samples (four stations at three depths each) were collected for phytoplankton enumeration. These samples were analyzed by Battelle and other institutions [EPA Work Assignment 107 (WA107)]. The results of this study were compiled into the Battelle Report *Presque Isle Bay Sediment Quality Evaluation Report for May 1994 Study*, September 29, 1994 (3).

Simultaneously, in May 1994, sediment core samples were collected by EPA and PADER at the same locations and submitted to Battelle under Amendment 1 to WA107 for polycyclic aromatic hydrocarbon (PAH) analysis and under Amendment 2 to WA107 for Lead-210 dating. The PAH analyses were performed on cores from 20 of the 21 stations and the dating was conducted on eight cores. The results of these two additional tasks were presented in the data reports *Evaluation of Polycyclic Aromatic Hydrocarbons (PAH) in Presque Isle Bay Sediment Cores for May 1994 Study*, September 29, 1994 (4) and *Evaluation of Lead-210 in Presque Isle Bay Sediment Cores for May 1994 Study*, August 31, 1995 (5), respectively.

#### 1.2 OBJECTIVES AND SCOPE

EPA and PADER have reviewed the reports from these and other earlier studies, and have concluded that the PAH probably are the primary contaminants of concern in the sediments of Presque Isle Bay. Battelle was under Work Assignment 456 contracted to review and comment on selected documents and data sets, with a focus on the PAH data.

The primary objective of this Work Assignment was to attempt to answer the following questions using the data that were previously generated under WA107 and in two fish tumor studies performed by PADER:



- Why are PAH levels highest at the top of the cores (stratigraphically speaking)? Do PAH levels break down over a period of time or are the most recent sediments truly more contaminated; one would think that conditions today are greatly improved over those a half a century ago but the results do not seem to show this to be true.
- The lead-210 dating report indicates a deposition rate of almost 1 cm/yr. Does this seem unusually high considering that the Presque Isle Bay watershed is extremely small (25 square miles), and that land use is approximately 80% urban and 20% rural? Assuming this number is fairly accurate, and that the PAH data show the most recent sediments being the most highly contaminated, what can we expect conditions to be in the future and is this typical of other shallow estuaries in the Great Lakes?
- Are there any obvious explanations for the fish tumor data that can be made based on the available chemistry data? Are the PAH metabolite concentrations alone sufficiently high to cause the observed fish tumors, and how do the PAH metabolite levels in Presque Isle Bay compare to such data from other locations?
- What are the options for remediation? The most favorable course of action is no action; simply allow natural recovery to occur whereby newer, cleaner sediments would be deposited at sufficient depths to protect the bottom-dwelling aquatic life. The lead-210 dating report would support this option due to the high volume of sediments entering the Bay each year. The PAH data, however, would rule out this option because of the high concentrations of PAH in the recent sediments.
- Should natural recovery be ruled out as an option? Are air deposition, urban run-off, and other non-point sources so prolific as to account for the high levels of contaminants found in the sediments? If air deposition is the major source, would any remediation effort be prudent until regional, national, and global air pollution sources are eliminated?

### 1.3 APPROACH

The primary approach for preparing this report was to review a set of documents and analytical data previously produced by Battelle and other investigators and to interpret those data with respect to the PAH contamination of Presque Isle Bay sediment. The discussions in this report are based on those earlier studies — no new data have been generated.

The following seven documents, and the data contained therein, were the primary sources of information for the preparation of this report:

- Presque Isle Bay Ecosystem Study; Background Report, June, 1991 (1).
- Presque Isle Bay Remedial Action Plan, December, 1992 (2).
- WA107 Reports (3 Battelle reports)
  - Presque Isle Bay Sediment Quality Evaluation Report for May 1994 Study — Final Report, September 29, 1994 (3).
  - Evaluation of Polycyclic Aromatic Hydrocarbons in Presque Isle Bay Sediment Cores for May 1994 Study — Data Report, September 29, 1994 (4).
  - Evaluation of Lead-210 in Presque Isle Bay Sediment Cores for May 1994 Study — Data Report, August 31, 1995 (5).

- Presque Isle Bay Brown Bullhead Tumor Study; March, 1992 to October, 1993 (6).
- A Study of Tumors in Fish of Presque Isle Bay 1995 (7). PAH metabolite data for bile collected from the fish used in this study were also submitted to Battelle for review.

The reports were reviewed with the intent to answer the questions that have been raised using the information and data available in these reports. The three WA107 reports were the primary documents used to obtain analytical data, while the information in the two Presque Isle Bay background study documents were used mainly to obtain general background and supporting information.

The two fish tumor study reports were also reviewed and, where possible, attempts were made to look at relationships between the Presque Isle Bay sediment contamination and the biological data reported in these two reports. Fish bile PAH metabolite data were also supplied by PADEP for this report. Attempts were made to assess the significance of the chemistry data in light of the tumor results. For instance, the tumor and PAH metabolite data were reviewed for general relationships such as species, age, and location. However, these data were not used for statistical analysis in an attempt to correlate chemical measurements with biological data. A rigorous quantitative analysis of the biological data, and the associated chemistry data, was beyond the scope of this Work Assignment. Additionally, it is unlikely that credible quantitative statistical relationships can be obtained between the quantitative chemistry data and the descriptive biology data from these studies because the sampling was not based on statistical design. The data sets used in this study were small, and sediment and biota samples were collected at different times from different sampling locations. Brown bullheads make regular movements throughout Presque Isle Bay, so direct correlations between fish health and sediment contamination at a particular location may be confounded by uncertainty about recent movements of the fish.

The scientists working on this report used their technical knowledge, professional judgement, and experience to interpret the available data and best answer the questions at hand. Limited amounts of readily available scientific literature were also be used as supporting information, but an extensive literature review was beyond the scope of this Work Assignment.



### 2.0 SEDIMENT CORE DATING

Figure 2-1 shows the locations of the 21 sediment sampling stations that were used in Battelle's Presque Isle Bay sediment quality evaluation that was performed under Work Assignment 107 (3). Surface sediment was collected at all 21 stations. Sediment cores were collected at all stations except PIB02 (4). Eight cores were submitted for analysis to determine the approximate sedimentation rate and "age" of the sediment at various depths using the lead-210 ( $^{210}\text{Pb}$ ) activity technique (lead-210 dating). Sedimentation rate information proved to be valuable for interpretation of the sediment core PAH data.

Reliable and usable lead-210 data were obtained for the sediment cores collected at stations PIB07, PIB10, PIB14, and PIB18 (5). The estimated sedimentation rate for these four cores ranged from 0.87 cm/yr to 1.01 cm/yr, and averaged 0.92 cm/yr. The mixing zone (the layer of surface sediment that is mixed as a result of human activities, physical environmental conditions, and bioturbation) was estimated to be 10 cm for all cores. The assumption in reviewing sediment core dating information is that the mixing is confined to the surface mixed layer.

Although there probably is more variation in the sedimentation rate within the Bay than the four dated cores reveal, the average sedimentation rate of 0.92 cm/yr is useful for generating approximate dates of the sediment at various depths. Additionally, three of the four cores that were successfully dated (PIB07, PIB10, and PIB14) were collected from a general area of the Bay that is the most important from a chemical contamination perspective.

The sedimentation rate of 0.92 cm/yr may appear high for most bay systems. However, this is not really surprising when considering that this sedimentation rate was derived with sediment cores that were collected fairly close to the shore on the city side of the Bay and three of the four cores were collected within 1,000 m of where Cascade Creek discharges to the Bay. The fourth core was collected near the mouth of Mill Creek. A fifth core that was collected farther away (at PIB12, on the Presque Isle side of the Bay) had an estimated sedimentation rate of 0.54 cm/yr, suggesting that the sedimentation rate decreases away from the city side of the Bay, but there are not sufficient amounts of core dating data available to confirm this.



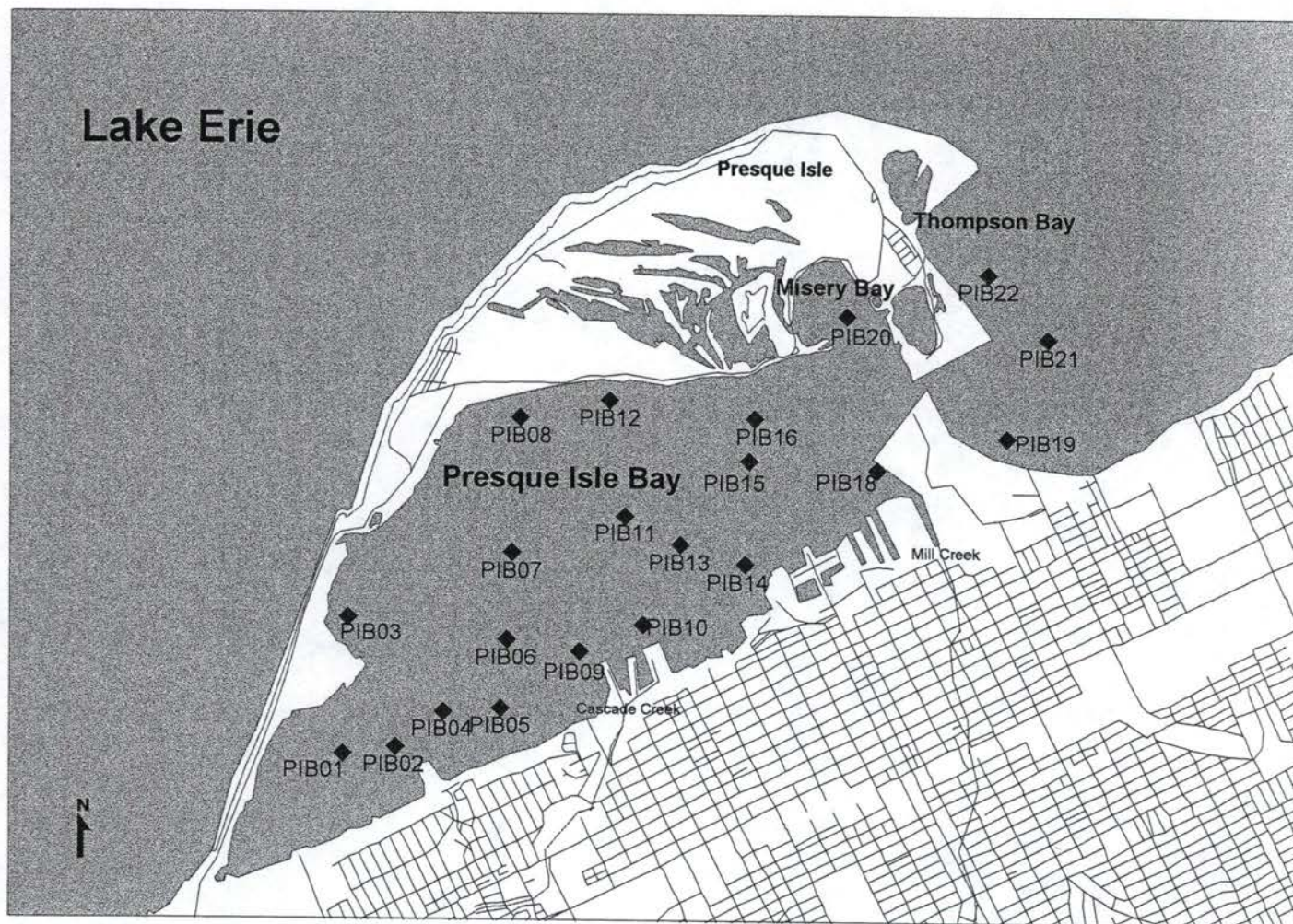


Figure 2-1. Presque Isle Bay and the WA107 Sediment Sampling Stations



### 3.0 CHEMICAL CHARACTERIZATION STUDIES

Most of the early studies of chemical contamination in Presque Isle Bay focused on the parameters described in the document *Guidelines for the Pollutational Classification of Great Lakes Harbor Sediments*, which was prepared by USEPA Region V in 1977 to guide dredging activities in the Great Lakes. Contaminants measured in these early studies conducted in the 1980's included a series of metals, PCB, nutrients, and basic water quality parameters. The Presque Isle Bay Ecosystem Study Background Report (1), and the related Remedial Action Plan (2), identified 16 pollutants of concern based on the EPA evaluation criteria, but also added PAH as a pollutant of concern. Studies performed by EPA and PADEP in the 1990's have identified PAH as the likely primary class of pollutants of concern.

#### 3.1 PAH CHARACTERIZATION

Previous studies of Presque Isle Bay have implicated PAH as a class of potential contaminants of particular concern. For this report EPA has requested Battelle to review the previously referenced reports and data with a primary focus on the PAH contamination of Presque Isle Bay. The WA107 reports prepared by Battelle in 1994 (3, 4) are the primary sources of PAH data used for this report.

##### *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*

Polycyclic aromatic hydrocarbons (PAH), also commonly called polynuclear aromatic hydrocarbons, are ubiquitous trace components of terrestrial, aquatic, and marine environments. PAH are composed of two or more fused benzene (aromatic) rings (8). Naphthalene ( $C_{10}H_8$ ), which consists of two fused aromatic rings, is the lowest molecular weight PAH. PAH with up to nine rings have been identified in the heavy residual fractions of crude oil and in coal tars.

PAH may be formed by four different mechanisms (8):

- Very rapid, high temperature (e.g., 700°C) incomplete combustion (pyrolysis) of organic matter (e.g., combustion of fossil fuels)
- Very slow (e.g., millions of years) rearrangement and transformation of organic matter at moderate temperatures of 100–300°C to form fossil fuels (coal and petroleum)
- Relatively rapid (days to years) transformation of certain pigments and sterols in soils and sediments
- Direct biosynthesis by organisms

The last two processes appear not to be quantitatively important sources of PAH in the environment and result in the production of very simple assemblages of PAH. Examples of these assemblages include perylene and certain  $C_2$  and  $C_3$  alkyl phenanthrenes (retene).

Coal and petroleum are rich sources of PAH. Coal generally is considered an aromatic material. Most of the PAH in coal is tightly bound in the coal structure and is not readily leached out. Nevertheless, a substantial fraction of the total PAH in sediments from industrial bays and estuaries may be derived from coal dust (9).



A typical crude petroleum may contain from 0.2 to more than 7 percent PAH. The abundance of aromatic hydrocarbons in petroleum decreases markedly with increasing molecular weight. In most cases, the 1-ring (benzenes) through 3-ring (phenanthrenes) aromatics account for at least 90 percent of the aromatic hydrocarbons that can be resolved in crude petroleum (8).

The aromatic hydrocarbons in coal and petroleum usually contain one or more alkyl hydrocarbon chains containing one or more carbon atoms. As a general rule, these alkyl aromatics are more abundant than the parent compounds in petroleum. Homologues with two to five alkyl carbons usually are more abundant than less or more highly alkylated homologues.

A major source of PAH containing three or more aromatic rings in the environment is combustion of organic matter (8). Combustion of any organic material, including fossil fuels, will generate a wide variety of PAH. The PAH assemblages produced by pyrolysis of organic matter are complex, and, unlike the assemblages in petroleum, are dominated by 4-, 5-, and 6-ring PAH. In pyrogenic PAH assemblages, the dominant compound in each homologous series is the unalkylated parent compound or a homologue with only one or two alkyl carbons. In contrast, as mentioned above, in petrogenic PAH assemblages, the relative abundance of compounds in each homologous series increases to a maximum for the homologues containing three to four, and occasionally five, alkyl carbons. However, the relative distribution for the different alkyl homologues varies significantly for different crude and refined petroleum products.

Another important, though localized, source of PAH in the aquatic environment is creosote, coal tars, and related materials derived from the high-temperature carbonization of coal and petroleum. These materials are derived from high-temperature processing of fossil fuels, and so the PAH contained in them have some of the properties of both pyrogenic and petrogenic PAH assemblages. Asphalt and tar, used to pave roads and parking lots and to waterproof the roofs of houses, also are byproducts of petroleum and contain abundant PAH. Paved road surfaces often contain high concentrations of PAHs, derived from a combination of deposition of exhaust soot from vehicles, wear of tires releasing carbon black, rich in pyrogenic PAHs, and wear of the asphalt pavement. PAH washed by rain from road surfaces often reaches the aquatic environment in runoff from land, particularly through storm drains and combined sewer overflows (8). Coal and coke tars produced during coal gasification to produce manufactured gas, and coking to produce coke for the iron and steel industry usually contain at least 50 percent PAHs (8); if the tars were not used commercially, they often were disposed in land fills at the manufactured gas plants or coking facilities. PAH-contaminated soils may still exist at former manufactured gas and coal coking facilities in the Erie, PA, area, such as the Pennsylvania Fuel Gas site that also house the Erie Coke Plant (formerly Kopper's Coke, which before that was Interlake Steel Corporation), at the foot of Wayne St. Additionally, Erie Coke still has an active coking operation. Discharge of ground water and surface storm water from such sites could contribute PAHs to Presque Isle Bay and the outer harbor.

It has been proposed that PAH of pyrogenic and petrogenic origin have a different behavior in the aquatic environment (10). PAH of pyrogenic origin are mostly tightly bound to soot particles owing to the high-temperature formation process and are not readily desorbed and bioaccumulated by aquatic organisms. Crude and refined petroleum products enter the aquatic environment in soluble, colloidal, bulk, or more loosely bound form and, therefore, are more mobile and available for uptake and bioaccumulation. PAH from creosote and other solid tar-derived products seem to have a behavior intermediate between those of pyrogenic and petrogenic PAH (11). Solid creosote, asphalt, and tar are not very mobile, but small amounts of PAH can dissolve into the water phase; these PAH in solution are mobile and bioavailable.



### 3.1.1 PAH in Sediment

#### *PAH Concentrations in Presque Isle Bay Sediment*

Most of the early Presque Isle Bay contaminant data are for metals, PCBs, nutrients, and basic water quality parameters (1, 2). There is only a limited amount of PAH data for Presque Isle Bay.

The Fish & Wildlife Service conducted a study in 1990 in which 16 Presque Isle Bay sites were ranked by severity of contamination (1). The highest PAH concentrations were found to be at eight nearshore sites along the city side of the Bay — the area from the Erie Yacht Club to, and including, the Harbor Basin (from sites PIB02 to PIB18 in Figure 2-1). In a study sponsored by USEPA in 1993, PAH were detected at every site sampled in the Bay, and significantly elevated levels of PAH were measured in the sediment near the mouths of Mill Creek and Cascade Creek, and the boat docks (6). Total PAH concentrations as high as 29.8 mg/kg were measured at a station near the mouth of Mill Creek (near Station PIB18).

In May 1994 EPA and PADEP collected surface sediments and sediment cores at 18 stations inside Presque Isle Bay and 3 stations just outside the Bay (Figure 2-1). These samples were sent to Battelle for the analysis of a suite of 40 PAH, including the 16 EPA priority pollutant PAH (3, 4). The results of these PAH analyses are summarized in Table 3-1; the PAH data are summarized as the sum of all 40 parameters (Total PAH) and as the sum of the priority pollutant PAH (Total PAH<sub>16</sub>). The data for the individual PAH compounds can be found in Appendix A and B. The data for one of the sediment core samples (a duplicate for the top core segment for PIB16) from the WA107 work has been excluded from this review because it was clearly an outlier, as was also indicated in the original report (4).

The 40 PAH compounds provide valuable source characterization and additional interpretive information that cannot be obtained with only the priority pollutant PAH, and gives a more complete picture of the PAH loading. The sum of the 16 priority pollutant PAH was typically 55 to 65% of the sum of the 40 PAH in the surface sediment samples from Presque Isle Bay, and 40 to 60% in the sediment cores. For sediment core samples with very low PAH concentrations, where perylene was the dominant PAH, the sum of the 16 priority pollutant PAH was typically below 40% (and for some samples even below 10%) of the sum of the 40 PAH. Perylene is not derived primarily from petrogenic or pyrogenic sources; most is formed through the natural decay of aquatic plant material in anoxic layers of freshwater and marine sediments (8).

Surface sediment total PAH concentrations ranged from 1.7 to 40.7 mg/kg for the 18 stations inside the Bay (0.9 to 26.3 mg/kg total PAH<sub>16</sub>), and from 0.2 to 12.3 mg/kg for the three stations outside the Bay. The PAH concentrations in the sediment cores varied greatly with location and depth and ranged from 0.03 to 58 mg/kg total PAH.

The data generated by Battelle revealed elevated surface sediment PAH levels in the same general locations as had been determined in the earlier EPA and Fish & Wildlife studies, with the exception that the PAH concentrations at PIB18 were lower than expected based on the 1993 EPA study. The areas of highest PAH concentration in the 1994 study (WA107) were the city side of the Bay, adjacent to docks and in proximity to where streams that flow through the city of Erie discharge to the Bay (Figure 3-1). Samples collected at PIB09 and PIB10 were found to have the highest surface sediment PAH concentrations (40.7 and 39.9 mg/kg, respectively), with the concentrations generally decreasing away from these stations and the docks on the city side of the Bay. The sediment core PAH concentrations for the most recently deposited sediment (i.e., last 50 years) were highest at PIB09, PIB10, PIB11, and PIB14, indicating that the area between Cascade Creek and Mill Creek not only receives more direct input of PAH than other parts of the Bay today but has seen the greatest input of PAH for quite some time.



Table 3-1. Presque Isle Bay Sediment Total PAH Concentrations — From WA107

Station ID	Sediment Depth (cm)	Median Depth (cm)	Median Year <sup>a</sup> (date)	Years Represented <sup>a</sup> (19xx - 19yy)	Total PAH <sup>b</sup> (mg/kg)	Total PAH <sub>16</sub> <sup>c</sup> (mg/kg)
PIB01-S	0 - 13	7	1987	1980 - 1994	15.01	8.96
PIB01-C1	0 - 53	27	1965	1936 - 1994	3.81	1.54
PIB01-C2	53 - 101	77	1910	1885 - 1936	1.10	0.08
PIB02-S <sup>d</sup>	0 - 13	7	1987	1980 - 1994	20.66	12.84
PIB03-S <sup>d</sup>	0 - 13	7	1987	1980 - 1994	1.96	0.93
PIB03-C1	0 - 58	29	1963	1931 - 1994	11.84	6.75
PIB03-C2	58 - 122	90	1896	1862 - 1931	0.31	0.04
PIB04-S	0 - 13	7	1987	1980 - 1994	25.66	15.53
PIB04-C1	0 - 61	30	1961	1928 - 1994	2.40	0.69
PIB04-C2	61 - 110	85	1901	1875 - 1928	1.20	0.09
PIB05-S	0 - 13	7	1987	1980 - 1994	29.15	16.77
PIB05-C1	0 - 61	30	1961	1928 - 1994	6.16	2.74
PIB05-C2	61 - 122	91	1895	1862 - 1928	1.93	0.09
PIB06-S	0 - 13	7	1987	1980 - 1994	27.23	16.19
PIB06-C1	0 - 61	30	1961	1928 - 1994	4.43	1.69
PIB06-C2	61 - 122	91	1895	1862 - 1928	1.49	0.07
PIB07-S	0 - 13	7	1987	1980 - 1994	26.86	16.69
PIB07-C1	0 - 15	8	1986	1978 - 1994	16.57	8.02
PIB07-C2	61 - 128	94	1891	1855 - 1928	1.46	0.07
PIB08-S	0 - 13	7	1987	1980 - 1994	22.68	13.17
PIB08-C1	0 - 53	27	1965	1936 - 1994	3.63	2.00
PIB08-C2	53 - 94	74	1914	1891 - 1936	1.88	0.12
PIB09-S	0 - 13	7	1987	1980 - 1994	40.65	26.28
PIB09-C1	0 - 52	26	1966	1938 - 1994	33.25	16.58
PIB09-C2	52 - 101	76	1911	1885 - 1938	2.17	0.46



Table 3-1 (continued). Presque Isle Bay Sediment Total PAH Concentrations — From WA107

Station ID	Sediment Depth (cm)	Median Depth (cm)	Median Year <sup>a</sup> (date)	Years Represented <sup>a</sup> (19xx - 19yy)	Total PAH <sup>b</sup> (mg/kg)	Total PAH <sub>16</sub> <sup>c</sup> (mg/kg)
PIB10-S	0 - 13	7	1987	1980 - 1994	39.90	25.30
PIB10-C1	0 - 15	8	1986	1977 - 1994	28.04	16.35
PIB10-C2	15 - 61	38	1953	1928 - 1977	57.99	35.91
PIB10-C3	61 - 91	76	1911	1895 - 1928	5.83	2.50
PIB11-S	0 - 13	7	1987	1980 - 1994	29.19	16.89
PIB11-C1	0 - 15	8	1986	1977 - 1994	29.45	17.11
PIB11-C2	15 - 53	34	1957	1936 - 1977	14.99	6.31
PIB11-C3	53 - 125	89	1897	1858 - 1936	2.26	0.47
PIB12-S	0 - 13	7	1987	1980 - 1994	18.28	10.97
PIB12-C1	0 - 49	24	1967	1941 - 1994	9.41	4.62
PIB12-C2	49 - 91	70	1918	1895 - 1941	0.06	0.02
PIB13-S	0 - 13	7	1987	1980 - 1994	23.30	14.10
PIB13-C1 <sup>d</sup>	0 - 58	29	1963	1931 - 1994	15.27	7.72
PIB13-C2 <sup>d</sup>	58 - 122	90	1896	1861 - 1931	4.63	1.83
PIB14-S	0 - 13	7	1987	1980 - 1994	27.49	16.73
PIB14-C1	0 - 30	15	1977	1961 - 1994	53.37	15.92
PIB14-C2	38 - 61	50	1940	1928 - 1953	18.08	7.64
PIB14-C3	61 - 130	95	1890	1853 - 1928	2.27	0.39
PIB15-S	0 - 13	7	1987	1980 - 1994	22.49	13.69
PIB15-C1	0 - 56	28	1964	1933 - 1994	16.23	7.55
PIB15-C2	56 - 122	89	1897	1861 - 1933	1.43	0.15
PIB15-C3	183 - 206	194	1783	1770 - 1795	1.52	0.08
PIB16-S	0 - 13	7	1987	1980 - 1994	18.16	9.88
PIB16-C1	0 - 15	8	1986	1977 - 1994	7.43	3.92
PIB16-C2	15 - 61	38	1953	1928 - 1977	1.40	0.11
PIB16-C3	61 - 107	84	1903	1878 - 1928	0.82	0.04
PIB16-C4	107 - 152	130	1853	1828 - 1878	0.37	0.02

Table 3-1 (continued). Presque Isle Bay Sediment Total PAH Concentrations — From WA107

Station ID	Sediment Depth (cm)	Median Depth (cm)	Median Year <sup>a</sup> (date)	Years Represented <sup>a</sup> (19xx - 19yy)	Total PAH <sup>b</sup> (mg/kg)	Total PAH <sub>16</sub> <sup>c</sup> (mg/kg)
PIB18-S	0 - 13	7	1987	1980 - 1994	1.69	1.14
PIB18-C1	0 - 61	30	1961	1928 - 1994	6.99	3.44
PIB18-C2	61 - 107	84	1903	1878 - 1928	0.03	0.01
PIB19-S	0 - 13	7	1987	1980 - 1994	12.27	8.07
PIB19-C1	0 - 61	30	1961	1928 - 1994	6.54	3.98
PIB19-C2	61 - 91	76	1911	1895 - 1928	5.59	2.49
PIB19-C3	91 - 130	110	1874	1853 - 1895	0.76	0.25
PIB20-S	0 - 13	7	1987	1980 - 1994	9.97	5.48
PIB20-C1	0 - 76	38	1953	1911 - 1994	12.98	7.08
PIB20-C2	76 - 152	114	1870	1828 - 1911	1.54	0.11
PIB21-S	0 - 13	7	1987	1980 - 1994	0.18	0.07
PIB21-C1	0 - 61	30	1961	1928 - 1994	0.43	0.11
PIB21-C2	61 - 76	69	1919	1911 - 1928	0.19	0.05
PIB22-S	0 - 13	7	1987	1980 - 1994	0.76	0.24
PIB22-C1	0 - 27	14	1979	1964 - 1994	1.45	0.29
PIB22-C2	27 - 107	67	1921	1878 - 1964	1.25	0.14

<sup>a</sup> Median age and year, and years represented, are based on a sedimentation rate of 0.92 cm/year.

<sup>b</sup> The Total PAH concentration is the sum of all 40 PAH parameters/compounds determined in WA107.

<sup>c</sup> The Total PAH<sub>16</sub> concentration is the sum of the 16 EPA priority pollutant PAH.

<sup>d</sup> The total PAH concentration for this sample is the average of duplicate sample analyses.

The lower than expected surface sediment concentration at PIB18 is clearly a function of the coarse grain size (it was 100% sand) and low organic content of this sample. The total organic carbon (TOC) normalized PAH concentration for PIB18 was actually higher than at any other station, followed by PIB09 and PIB10 (Figures 3-1 and 3-2). The TOC normalized data for PIB18 suggests that there is a greater input of PAH to the area around this station than the non-normalized data suggest. The apparently elevated TOC normalized data for PIB21 should be considered unreliable because the TOC content was so low for this sediment (0.01%, which is at or below the detection limit for most conventional TOC analyses).

The results observed for station PIB18 are consistent with information reported by PADEP. This is an area with great variability in the physical characteristics of the sediment, and a deviation of only several feet from the channel created by Mill Creek will determine the sand and organic content of the sample (6). The sample collected at PIB18 in the 1994 WA107 study was collected at a water depth of only 3 ft, while the samples at the other 20 stations were collected at a depth of between 11 and 23 ft of water. It is likely that if the PIB18 sample had been collected only a short distance further away from the shore, it would have been in slightly deeper water where the sediment has a higher TOC content and the surface sediment PAH concentration would probably have been higher than what were measured in the WA107 study.



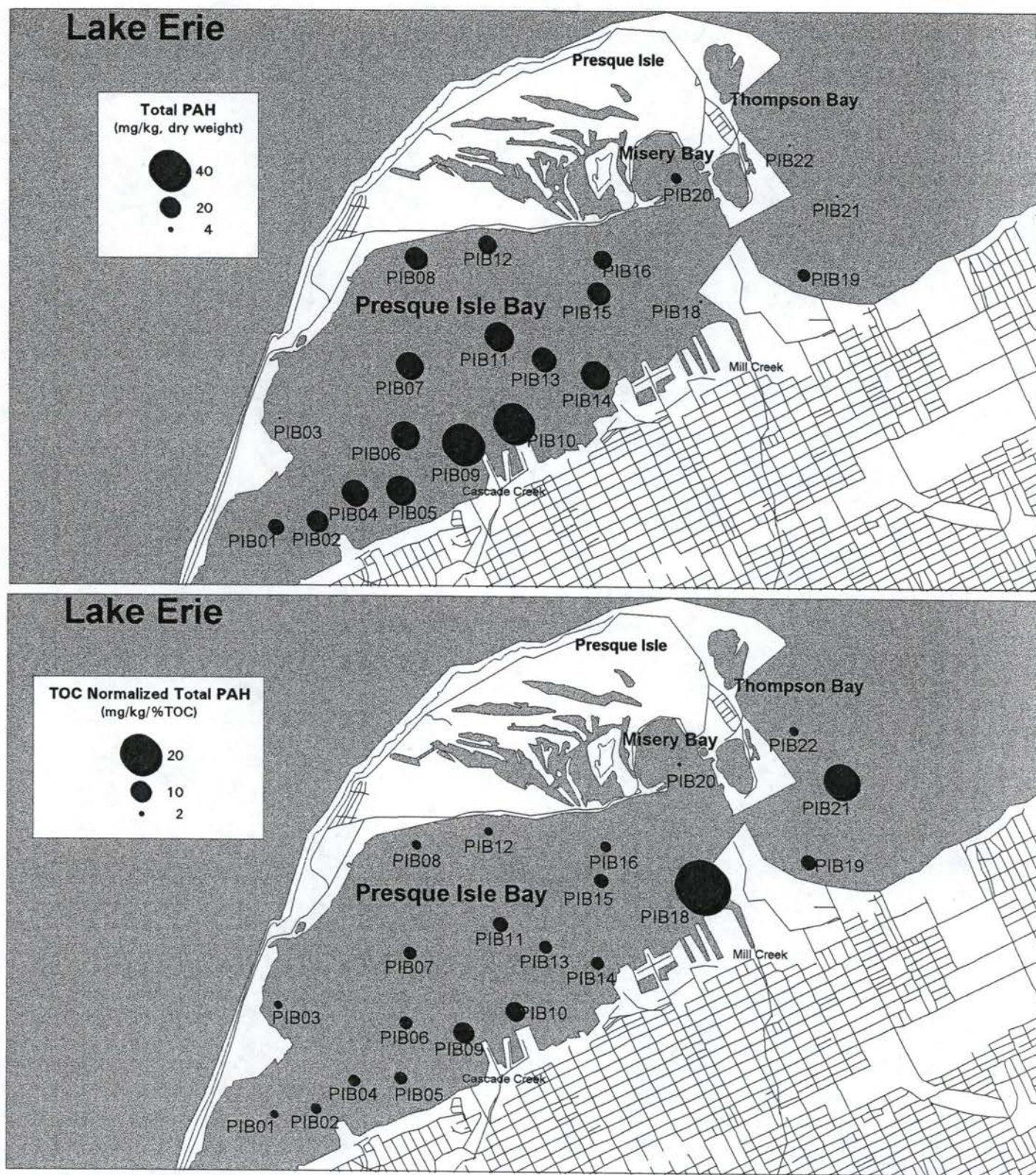


Figure 3-1. Presque Isle Bay with WA107 Surface Sediment PAH Concentrations — Non-Normalized (upper) and Normalized to TOC Content (lower)



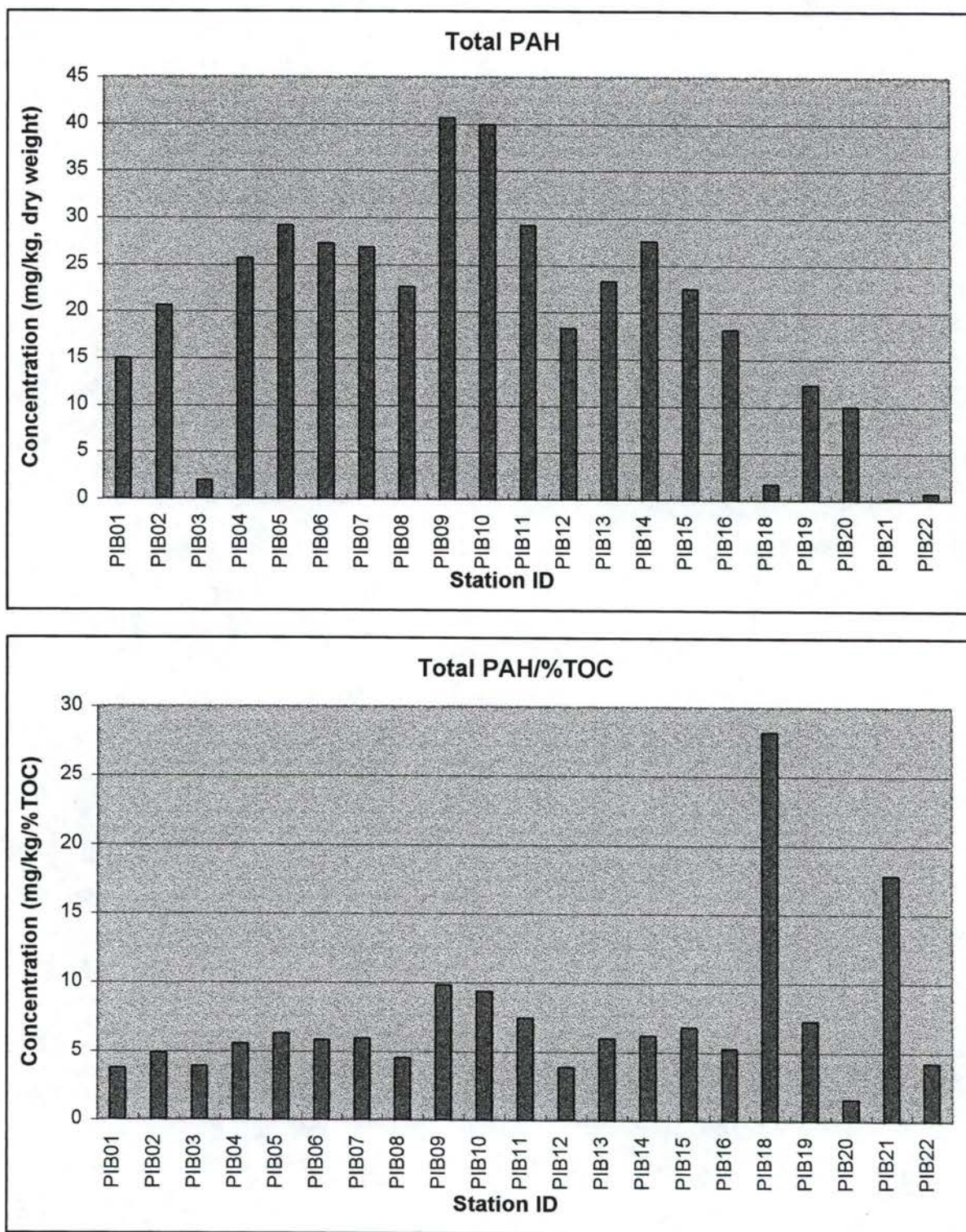


Figure 3-2. Bar Chart of WA107 Surface Sediment PAH Concentrations — Non-Normalized (upper) and Normalized to TOC Content (lower)



The analytical results from WA107 in 1994 and the EPA study one year earlier clearly indicate that the areas adjacent to the discharge points of Cascade Creek, Mill Creek, and the docks and on city-side of the Bay have the highest level of PAH in Presque Isle Bay. The sediment PAH concentration within the Bay is also higher than immediately outside the Bay, suggesting that the sources of PAH to the Bay are different than what can be explained by regional "background" PAH inputs (e.g., atmospheric deposition or chronic low-level petrogenic inputs from general activities on Lake Erie). The TOC normalized sediment concentrations are surprisingly uniform throughout the Bay, with the exception of PIB18 and to a lesser degree PIB09 and PIB10. These data suggest that most of the PAH enter the Bay near PIB09, PIB10, and PIB18, are transported throughout the water column of the Bay, and deposit and concentrate in the sediment as a function of the organic content of the sediment.

#### *PAH Concentrations in Other Coastal Sediments*

The PAH concentrations that have been measured for Presque Isle Bay sediment are comparable to levels measured in other urban coastal sediments. Concentrations of total PAHs (sum of only 8 parent PAH compounds) in surficial sediments from western Lake Erie near the mouth of the River Raisin, Michigan, ranged from 0.53 to 3.75 mg/kg (12). Concentrations of total PAH in surficial sediments from offshore lake Michigan range from 0.2 to 12 mg/kg dry wt (13, 14). PAH concentrations in sediments tend to decrease with distance from shore. PAH concentrations in sediment cores tend to increase with depth to maxima at depths corresponding to the 1960s and mid 1980s.

In 1990, total PAH concentrations equivalent to a range of approximately 1 to 90 mg/kg were measured in Dorchester Bay sediment (0.6 to 66 mg/kg for 24 PAH that typically comprise about 75% of the 40 PAHs in urban sediment and were determined in WA107). Dorchester Bay is within Massachusetts Bay, and about 5-7 miles south of central Boston. In 1994 the same Dorchester Bay stations were resampled, and sediment was also collected at several other Boston Harbor locations (15). This time the total PAH concentrations in the surface sediment ranged from 0.5 to 128 mg/kg, and for 12 of the 14 stations the levels were between 7 and 40 mg/kg. The highest sediment PAH concentrations were measured near combined sewer overflow (CSO) discharge locations in both the 1990 and 1994 studies. Concentrations of total PAHs (naphthalene through benzo(a)pyrene) in sediments from Boston Harbor, Massachusetts, were measured in the mid 1980s and found to be in the range of 0.48 to 718.4 mg/kg (16). The authors suggested that the PAHs in the hot spots in Boston inner harbor are derived from combined sewer overflows containing road runoff and domestic sewage.

A total of 60 sites were sampled in a 1990 survey of sediment contamination of Long Island Sound (17). The Long Island Sound samples were mostly collected from less urban locations than the Presque Isle Bay samples, and total PAH concentrations ranged from about 1 to 30 mg/kg (0.7 to 22 mg/kg for the set of 24 PAH), and averaged about 8 mg/kg. At remote reference locations in Long Island Sound the total PAH concentrations ranged from 3.1 to 3.7 mg/kg.

A large number of surface sediment and sediment core samples were collected at various locations in lower Narragansett Bay in 1993 (18). The total PAH concentration in the surface sediment ranged from less than 1 mg/kg at the reference locations to approximately 30 mg/kg for locations with no identified impact from PAH point source contamination; 58 mg/kg was measured at a location near a known source of PAH input.

Concentrations of total PAH between phenanthrene and benzo(g,h,i)perylene in surficial sediments of the Elizabeth River, Virginia ranged from 1.4 to 326 mg/kg in a study conducted in the mid 1980s (11). These PAHs were derived primarily from creosote plants along the river. Subsurface sediments near a creosote treatment plant contain up to 13,000 mg/kg total aromatic hydrocarbons (11). Concentrations of total PAHs in sediments from Havana Bay, Cuba, are as high as 2,800 mg/kg (19). These PAHs are primarily



pyrogenic, derived from runoff from land and effluents from gas manufacture and electric power plants on the shores of the bay. PAHs derived from effluents from an aluminum smelter on the Swedish Baltic coast are present in nearby marine sediments at concentrations of 14 to 211 mg/kg (20). Highest concentrations of PAHs in sediments usually are derived from specific industrial sources (gas manufacture, coke ovens, aluminum smelting), treated domestic/industrial sewage, and urban road runoff (21).

The "high" concentration (geometric mean plus one standard deviation of National Status and Trends Program site means) of total PAHs in sediments from U.S. National Status and Trends monitoring sites, including the Great lakes, is 2.18 mg/kg dry wt (22) based on 24 PAH compounds (which is typically equivalent to about 3 mg/kg for the 40 PAH measured in the WA107 study). High concentrations for low molecular weight PAHs (2- and 3-ring PAHs) and high molecular weight PAHs (4- through 6-ring PAHs) are 0.45 mg/kg and 1.73 mg/kg, respectively, reflecting the greater abundance and persistence of pyrogenic (mostly high molecular weight PAHs) than petrogenic (mostly lower molecular weight PAHs) PAHs. Between 22 and 23 percent of coastal sediments monitored in various U.S monitoring programs, including some in the Great Lakes, contain concentrations of total low and high molecular weight PAHs equal to or greater than the corresponding National Status and Trends high values. Thus, some of the sediments in Presque Isle Bay contain PAH concentrations comparable to concentrations in coastal, mostly urban, sediments throughout the country. However, most of the surface sediments from Presque Isle Bay contain concentrations of mostly pyrogenic PAHs that are substantially higher than concentrations in uncontaminated or slightly contaminated non-urban, coastal sediments.

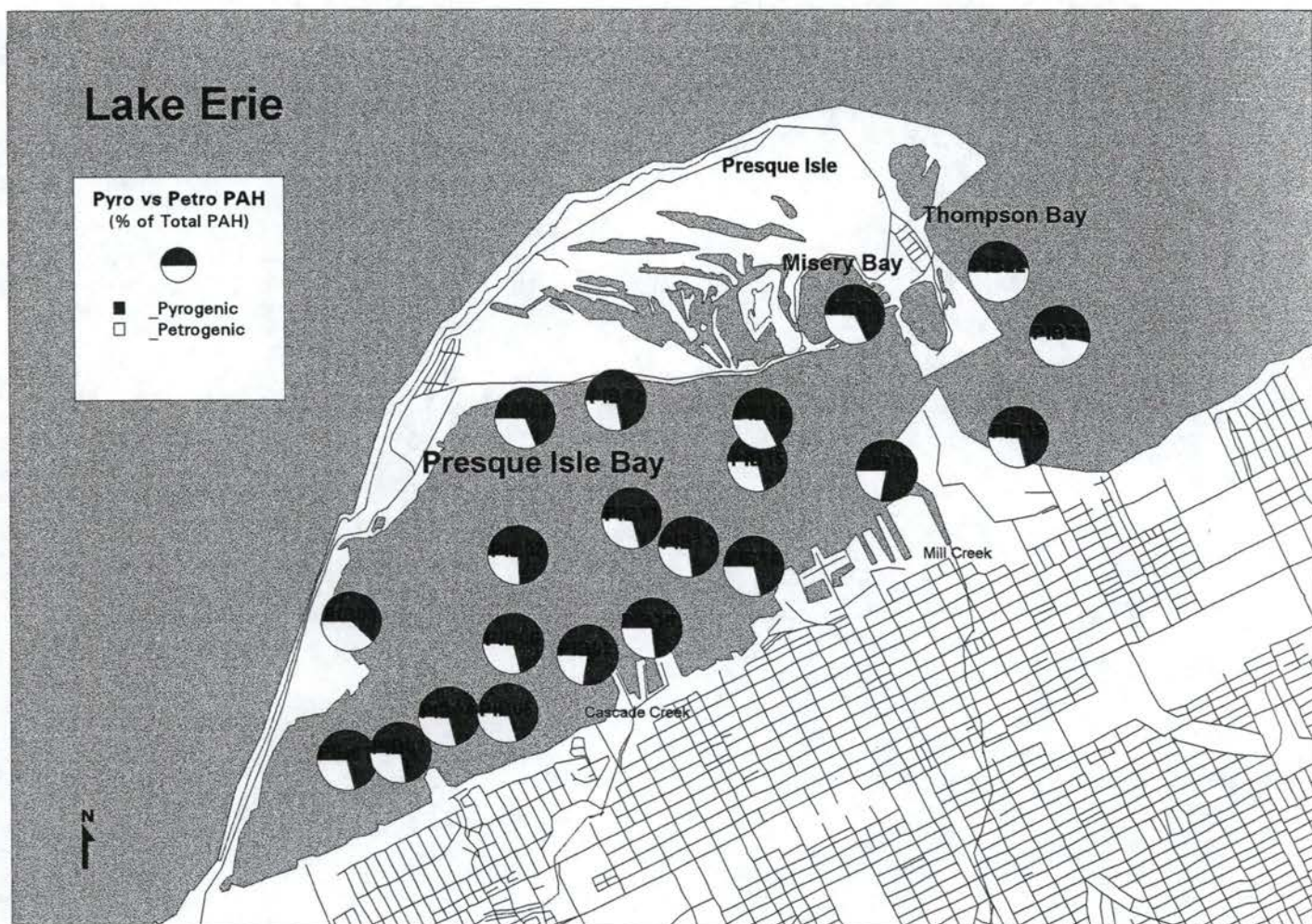
#### *Presque Isle Bay Sediment PAH Compound Distribution and Characteristics*

The dominant PAH in the surface sediment of Presque Isle Bay, and in most subsurface sediment deposited in the past 50 years, are the four- and five-ring PAH (Appendix A and B). These PAH are mostly identified with pyrogenic sources, although lower molecular weight PAH, with likely petrogenic origin, are present at lower concentrations. The pyrogenic PAH constitute between 70 and 80% of the total PAH in most of the surface sediments from within the Bay (Figure 3-3). The surface sediment collected outside the Bay (PIB21 and PIB22) have equal amounts of pyrogenic and petrogenic PAH, indicating a relatively greater exposure to sources of petroleum PAH (although the total PAH input is clearly lower at these locations). For this approximation, the pyrogenic PAH are defined as the sum of the PAH starting with fluoranthene, pyrene, benz[a]anthracene and going up in molecular weight from there, plus the parent PAH phenanthrene and anthracene. The petrogenic PAH are the rest of the 40 PAH that were determined (naphthalene through C3-dibenzothiophene, except phenanthrene and anthracene, plus C1-fluoranthenes and pyrenes).

The relative proportion of pyrogenic PAH was typically lower in the sediment core samples than in the surface sediment. Perylene was the predominant PAH in a number of sediment core samples, particularly the ones that represented "old" sediment and those that had very low overall concentrations of PAH. Perylene is formed primarily from decaying organic material (e.g., aquatic plant material), and most is not from petrogenic and pyrogenic sources (23). The relatively consistent and low ratio of petrogenic to pyrogenic PAH in the surface sediment within the Bay indicate a similarity in the source of the contamination and that there have been no recent major inputs of common petroleum products that significantly contribute to the PAH (Figure 3-4).

Figure 3-5 shows the PAH distribution patterns for typical Bay surface sediment (PIB09 and PIB20), and for sediment collected outside the Bay at PIB22. Figure 3-6 shows the PAH composition in selected reference products and materials. The PAH composition of all surface sediment samples and additional petroleum and other products are given in Appendix C and D, and the plots in the appendices include the identification of each of the PAH compounds along the x-axis of these plots.





**Figure 3-3. Presque Isle Bay with Petrogenic vs Pyrogenic PAH Distribution in WA107  
Surface Sediment Samples**



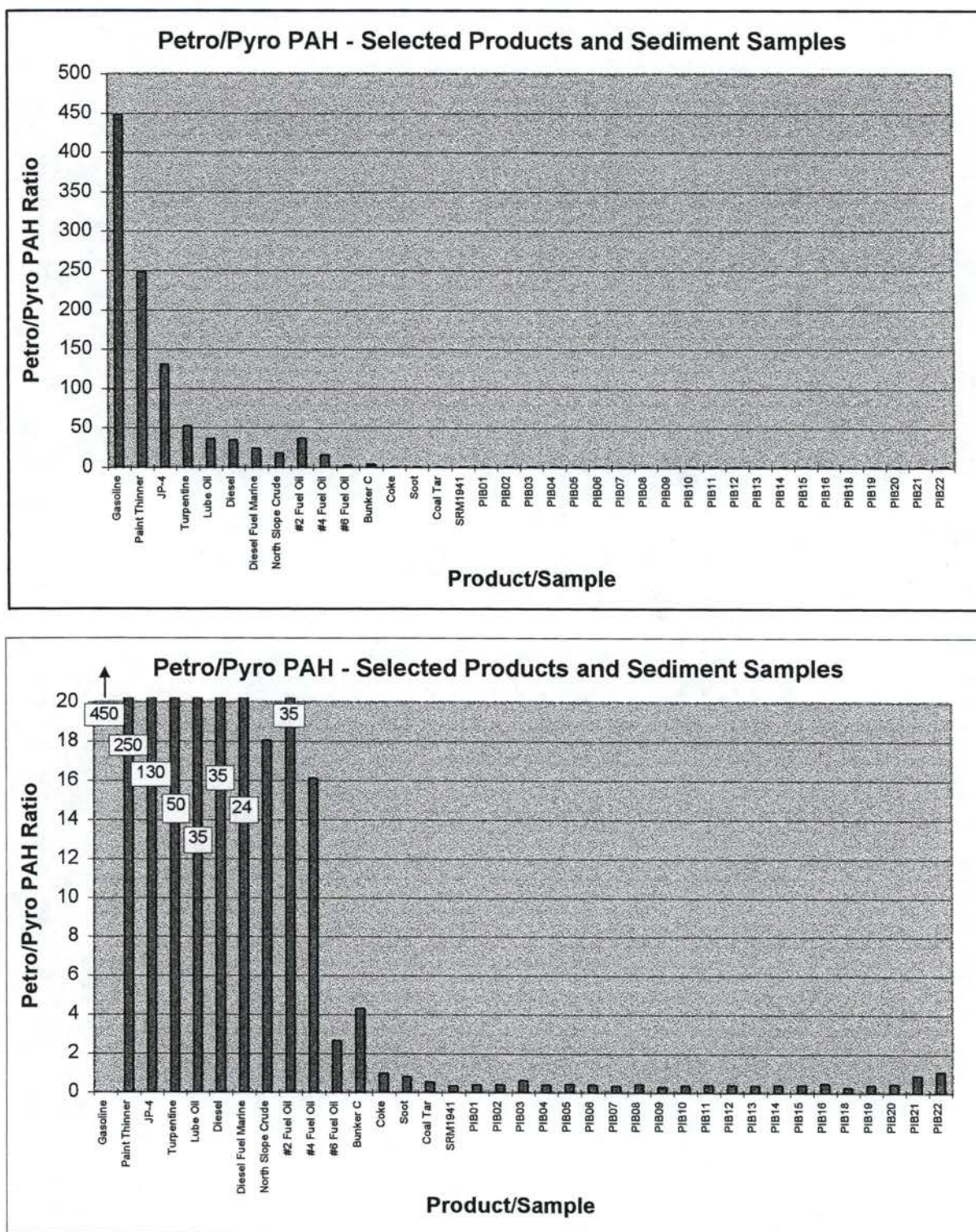


Figure 3-4. Bar Chart with Petrogenic/Pyrogenic PAH Ratio for Selected Petroleum Products and the WA107 Surface Sediment Samples



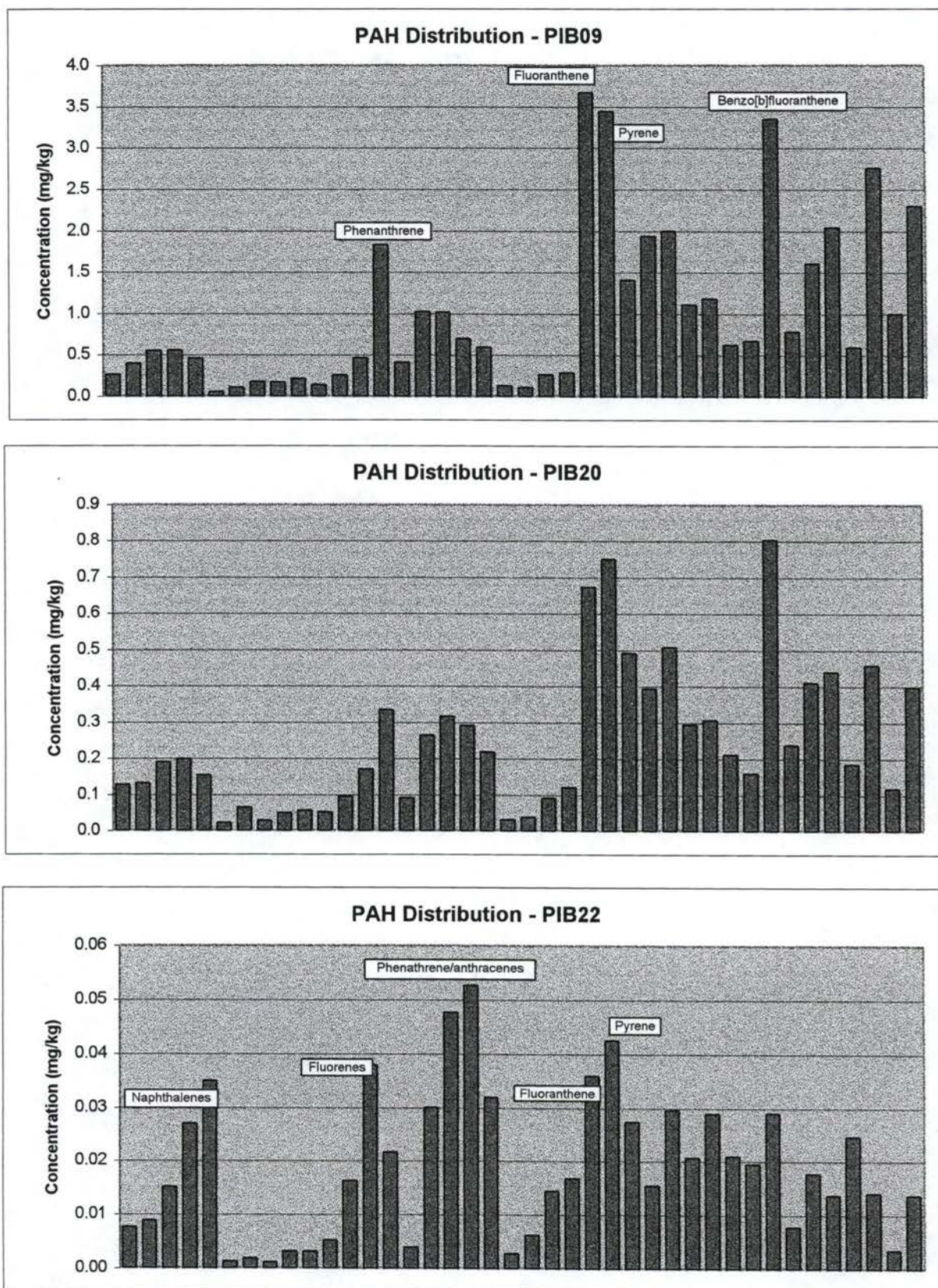


Figure 3-5. PAH Distribution Plots for Selected WA107 Surface Sediment Samples



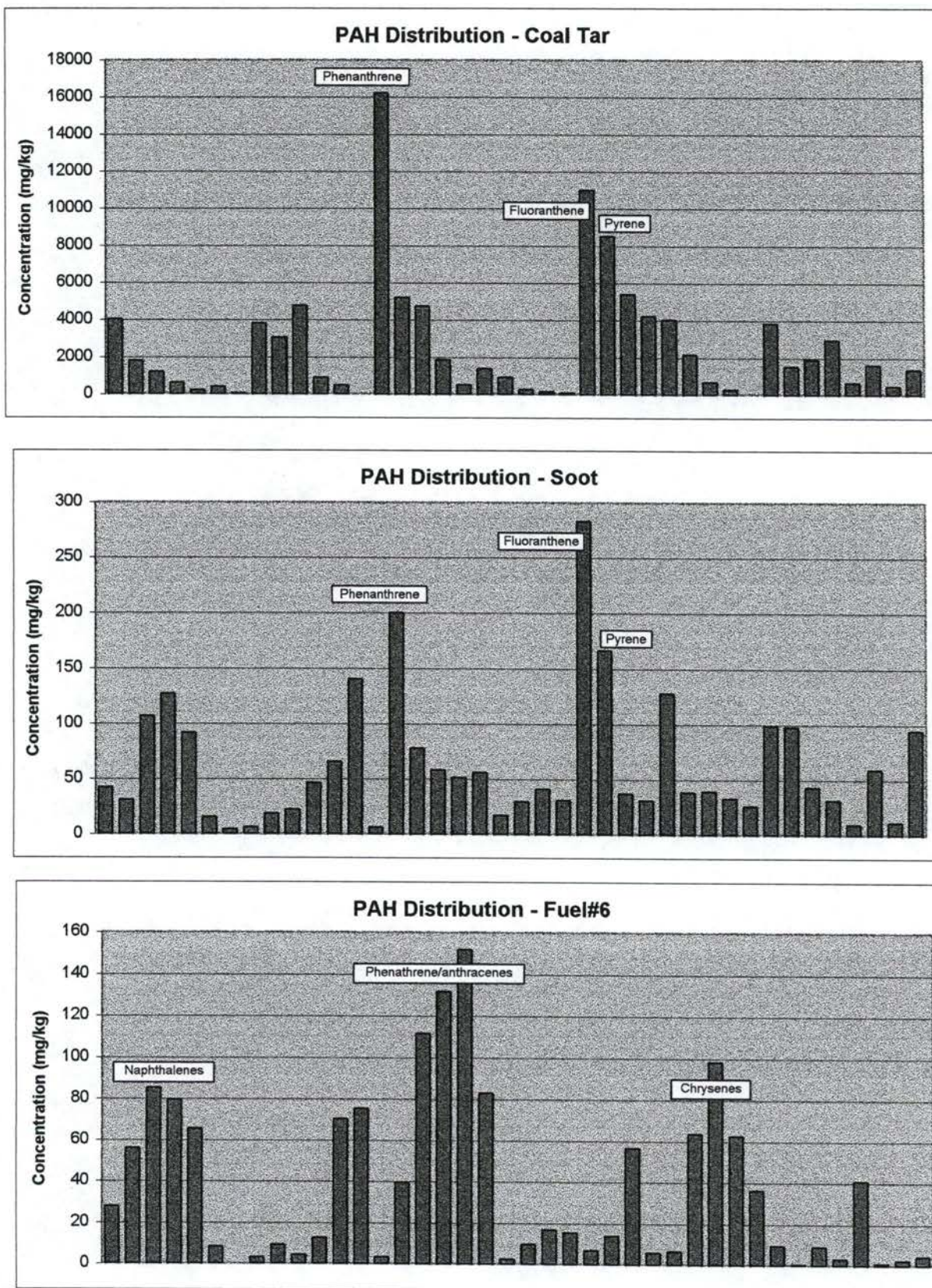


Figure 3-6. PAH Distribution Plots for Selected Hydrocarbon Products



The high molecular weight PAH distribution in the surface sediment is characteristic of PAH inputs from primarily combustion sources, or hydrocarbon materials containing a mixture of pyrogenic and petrogenic high molecular weight PAHs (e.g., coal and coke tar, coal gasification tars, carbon black, creosote, and, to some degree, asphalt). Low levels of petrogenic PAH (e.g., alkylated naphthalenes, phenanthrenes, and dibenzothiophenes) are also present in the samples from within the Bay, suggesting some contribution from weathered petroleum product, such as a middle distillate or heavy residual fuel oil (e.g., diesel fuel and No. 6 fuel oil) or lubricating oil. The samples from outside the Bay (e.g., PIB22) are, relatively, more enriched in the petrogenic PAH, with increased relative concentrations of alkylated naphthalenes, fluorenes, phenanthrenes, and dibenzothiophenes, suggesting a greater relative input from a mid to heavy weight petroleum product, or mixed sources of petroleum.

Figure 3-7 shows a diagnostic double ratio plot prepared for the purpose of displaying the PAH composition characteristics of the surface sediment samples and a series of petroleum and other materials. The sediment samples clearly have a PAH composition that has little in common with standard sources of petroleum contamination, and more closely resembles the pyrogenic-type materials (e.g., coal and coke tars and soot). The location of a standard reference material (SRM) is also indicated in Figure 3-7, and clearly has a similar PAH composition as the Presque Isle Bay samples. This SRM is a sediment collected in an east coast estuarine environment and is considered to be a good representation of typical background PAH derived primarily from pyrogenic sources.

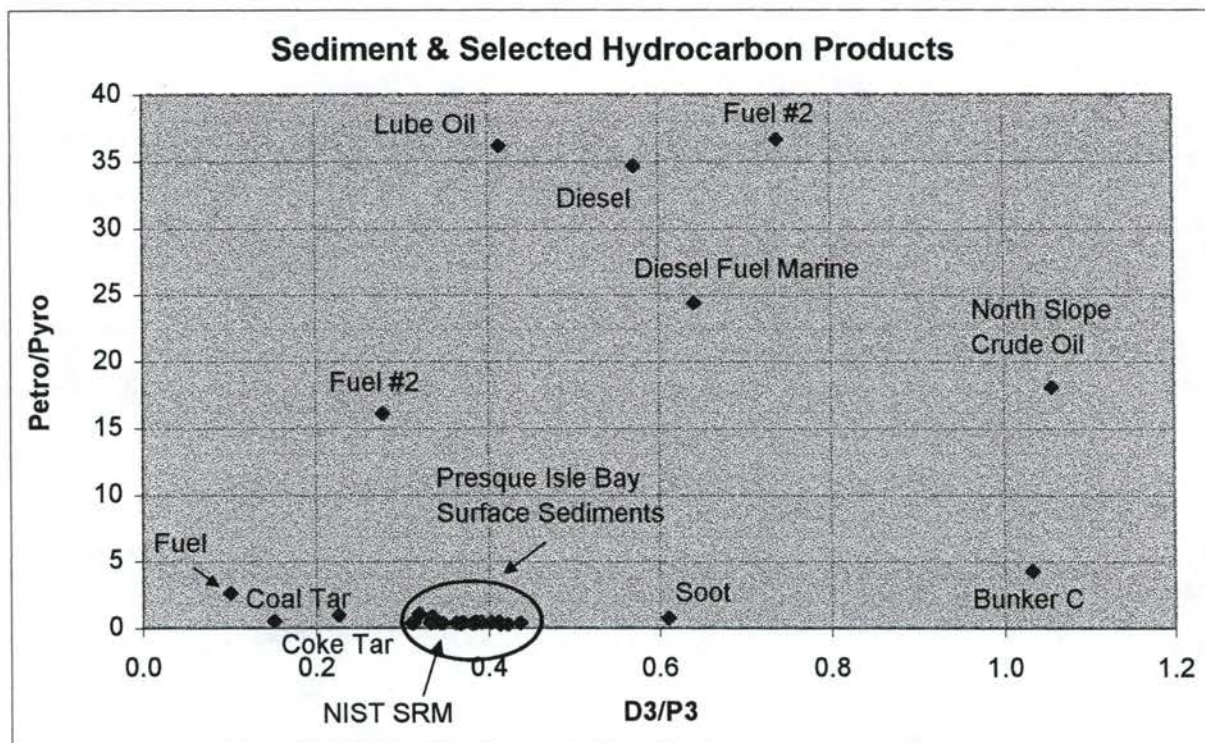
The PAH distributions observed for Presque Isle Bay are similar to those commonly observed in most urban aquatic systems in the US that do not have significant petroleum point source pollution. The PAH in the surface sediment of Dorchester Bay and Boston Harbor are 60-70% pyrogenic PAH, with an even higher pyrogenic component near CSO discharges. The PAH composition is also quite similar to what is observed in most remote locations, except that the low molecular weight petrogenic PAH are typically even less prevalent. For instance, pyrene, fluoranthene, and benzo[b]fluoranthene were the predominant PAH in sediment traps that were deployed in a rural lake in England over a one year period to measure deposition from new deposits and bottom sediment resuspension (24). These are also the major PAH in the Presque Isle Bay surface sediment. Sediment cores collected throughout Lake Michigan displayed a similar distribution of PAH (25).

#### *Presque Isle Bay Sediment PAH Concentrations as a Function of Time*

PAH remain stable in the sediment for long periods of time after having been deposited, and sediment core analysis can therefore be used to obtain information on historical PAH loadings; some PAH compound degradation may occur if the sediment remains oxygenated at depth. During the 1994 sediment survey of Presque Isle Bay, sediment cores were collected at 20 of the 21 stations. The cores were sliced and submitted to Battelle for PAH analysis, and a few cores were submitted for lead-210 dating, as described in Section 2. Table 3-1 summarizes the total PAH data for all sediment core (and surface sediment) samples, and the individual PAH compound data for the core samples can be found in Appendix B.

The age (year of deposition) of the sediment samples has been *estimated* using the previously discussed depositional rate of 0.92 cm/yr, and this assumption has been used for the age data in Table 3-1. It should also be pointed out that the "surface" sediment samples that have been discussed were collected to a depth of about 5" (12.7 cm), per information provided by EPA. This means that surface sediment included the sediment deposited in the past 10-25 years (assuming a sedimentation rate of about 0.5 to 1 cm/yr for different parts of the Bay), and goes deeper than the mixing zone, so sediment truly deposited 10 to 25 years ago is part of the surface sample — *the surface sediment PAH data do not provide a picture of the PAH concentration of sediment deposited only in 1994.*





**Figure 3-7. Diagnostic Double Ratio Plot for the WA107 Surface Sediment Samples and Selected Hydrocarbon Products**

Similarly, the core slices represent the average PAH concentration over many years, and the core data for most samples integrate the PAH input over more than 50 years. This lack of resolution clearly inhibits any detailed assessment of the PAH input patterns over time. Figure 3-8 displays the total PAH concentration in the surface sediment and sediment core samples for PIB09 and PIB10. The PAH concentration data are plotted versus the median date (year) of the sediment core sample, with the "error bars" indicating the actual start and end years of sediment in the sample (assuming a sedimentation rate of 0.92 cm/yr). PIB09 and PIB10 were plotted together because they are located near each other, had PAH concentrations that were quite similar to each other at the various depths and therefore provided more data points for plotting. The two stations are also from one of the most important general locations within Presque Isle Bay, from a PAH contamination perspective. Similar plots are given for each station in Appendix E.

It is clear from these sediment core plots that PAH levels (i.e., PAH inputs) were lower 75-200 years ago than today, but it is not perfectly clear when the PAH input reached a maximum, and if the PAH inputs are now declining. Figure 3-8 suggests that PAH input to the locations where these cores were taken reached a maximum some time between 1940 and 1970. The peak concentration plotted in Figure 3-8 (58 mg/kg) is the average concentration between 1928 and 1977 for this sample, and was probably not at all the concentration in 1953, as the plot may seem to indicate. The concentration could, for instance, have been 20-30 mg/kg in the 1920's, 30's, 40's, and then shot up to 100 mg/kg for the 50's, 60's and 70's, and then declined sharply. Although such a scenario is unlikely, it is an illustration of the uncertainty that is inherent in these sediment core data because the samples were not prepared and analyzed as smaller segments, representing shorter periods in time.



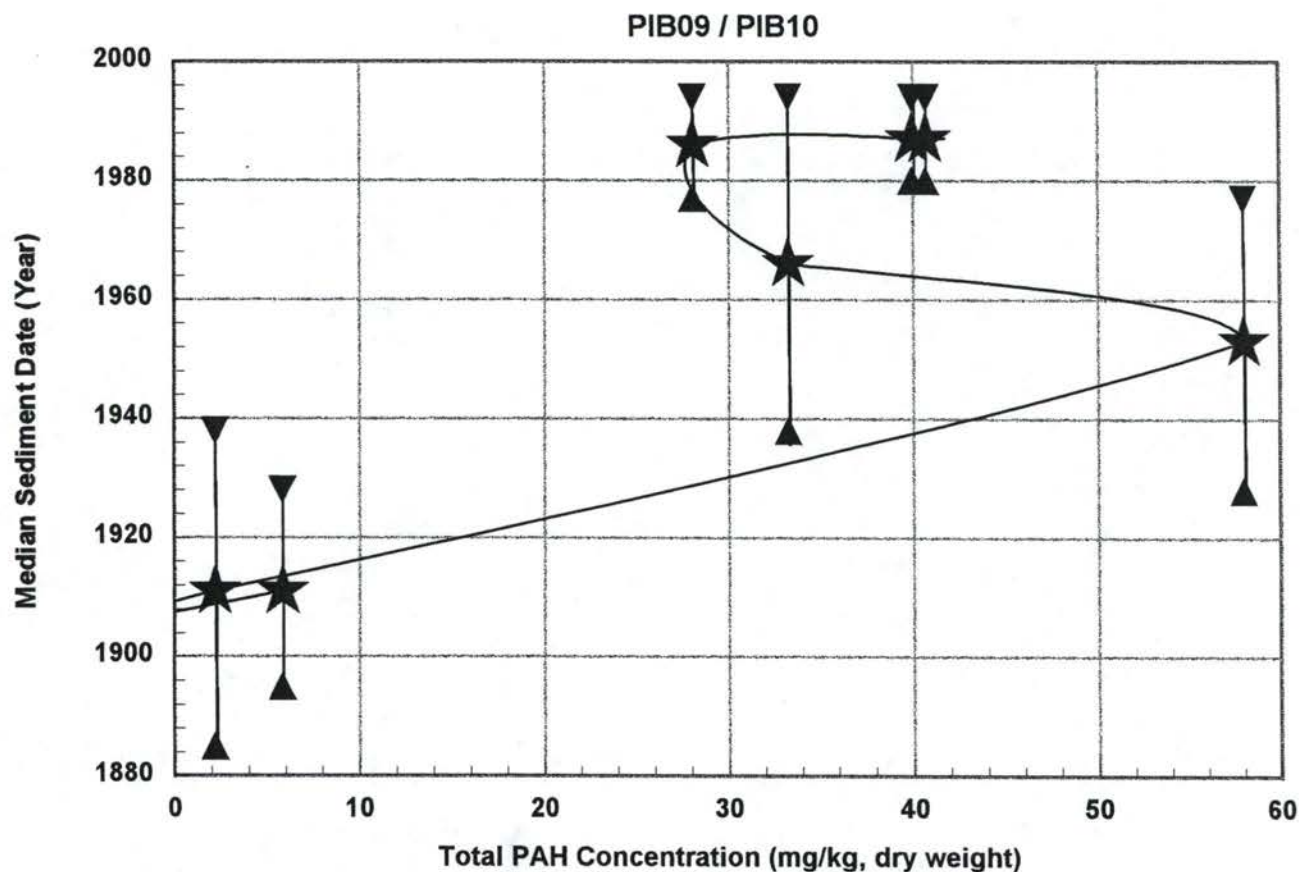


Figure 3-8. Total PAH Concentration of WA107 Sediment Samples Collected at Stations PIB09 and PIB10 and the Approximate Median Date (Year) Represented by the Samples

However, it is widely accepted that the dramatic increase in PAH fluxes observed in sediment in the North American aquatic environment from the early to mid 1900's is a direct result of the acceleration of industrial activities and other increases in the use of fossil fuels. Several studies have shown that anthropogenic inputs of PAH in urban areas of North America generally peaked some time between 1950 and 1975 (25, 26), although there are clearly regional differences. The dramatic increase in PAH is generally attributed to the onset of coal combustion and later use of other fossil fuels, while a slight decline in recent years is thought to have resulted from a shift from coal to oil and gas use, and to implementation of various pollution control measures, particularly removal of particulate matter (soot) from stack gases.

In a detailed study of the characteristics of PAH deposition in Lake Michigan sediment, cores were collected from the northern part of the lake to the south (25). The data show that the accumulation of PAH increased sharply starting around 1900, reached a maximum and a plateau between 1940 and 1970, and has since begun a gradual decline. However, the decline in PAH input is not dramatic, and is still undetectable in many systems. In a similar study of sediment cores from the Upper Mystic Lake (a small lake near Boston, MA), inputs of pyrogenic PAH were determined to have peaked around 1960, leveled off, and began a slow decline around 1970 (27).



The sediment data generated in WA107 do not contradict this widely observed scenario of a rapid increase in PAH from 1900, a peak PAH input sometime between 1950 and 1975, and a leveling off or slight decline in the past 20 years. The data, and the plots generated with those data, can accommodate such a picture, but there are not enough historical data points to confirm it.

### 3.1.2 PAH Metabolites in Fish Bile

PAH are typically not accumulated to high concentrations in the tissue of fish because fish have the ability to metabolize and actively excrete these compounds. However, fish from PAH-contaminated environments usually contain measurable concentrations of PAHs in muscle and liver tissues; the tissue residues usually correlate well with PAH concentrations in the ambient water (28). Because of the limited retention of PAHs in fish tissues, data on PAH metabolite levels in the bile of the fish can be used instead to provide a measure of recent exposure to PAHs (29). An analytical method developed by Krahn and coworkers (30, 31, 32) frequently is used to measure approximate concentrations of metabolites produced from congener groups with different numbers of aromatic rings (i.e., a total 2-aromatic ring PAH metabolite concentration is typically reported as naphthalene equivalents, 3-ring metabolites as phenanthrene equivalents, and 5-ring PAH metabolites as benzo[a]pyrene equivalents).

Metabolic oxidation of PAHs in the tissues of most animals, including fish, effectively detoxifies the PAHs. However, some of the PAH metabolites, if they are not rapidly conjugated with sulfate or glucuronide, may be more toxic than the parent, unmetabolized, PAH. Some PAH metabolites of certain 4- through 6-ring PAHs, such as benzo(a)pyrene, are known carcinogens (8). The PAH themselves are not carcinogenic: rather, the carcinogenic PAH are metabolized by the cytochrome P450 mixed function oxygenase system to produce reactive metabolites that may covalently bind to nuclear DNA, causing mutations and, in some cases cancer. However, most PAHs and their metabolites, particularly the 2- and 3-ring PAHs typical of petrogenic PAH assemblages, are not carcinogenic. The PAH metabolites in bile, even the benzo(a)pyrene equivalent metabolites, are primarily conjugated and detoxified; they can not be converted to carcinogens. Thus, the presence of PAH metabolites in fish bile only indicates that the fish has been exposed to bioavailable forms of the different PAH classes in the ambient water, food, or sediments, and has bioaccumulated some. It is not possible to attribute benign and cancerous tumors in fish to the presence of PAH metabolites in the bile. The presence of benzo(a)pyrene equivalent metabolites in a tumored fish is suggestive that exposure to high molecular weight, potentially carcinogenic PAHs could have contributed to the development of the tumors. There is growing evidence that PAHs in sediments are causing or contributing to neoplastic diseases, including cancers, in freshwater and marine fish populations throughout the country, including eastern Lake Erie (32).

It is important to realize that the PAH metabolite analytical methods used in the investigations reported here provide only a rough estimate of the total metabolite concentration for a given aromatic class of compounds. There typically are dozens or hundreds of individual PAH metabolite compounds, particularly for the higher molecular weight PAHs, that comprise the reported single PAH metabolite value, and each metabolite has a unique analytical response that is sometimes dramatically different from that of the parent PAH calibrant (i.e., the accuracy of the determined concentration is highly dependant on the relative composition of the individual metabolites, which are not individually identified or determined).

Additionally, the PAH metabolite composition and concentration depend on the PAH composition in the ambient environment and other environmental factors, and is highly species dependant. The mixed function oxygenase enzyme system responsible for PAH metabolism is highly inducible in fish (activity increases following exposure); induction ability varies from one species to another (33, 34). The metabolites produced from a particular PAH vary from one species to another (35). Therefore, it is difficult to compare PAH metabolite data from different locations, studies, and fish species in a meaningful way. However,



PAH metabolite concentrations can be used to obtain relative contaminant exposure estimations for fish of the same species if they were collected in similar environments.

PAH metabolite levels were determined in the bile of brown bullheads (*Ameiurus nebulosus*, formerly *Ictalurus*) from Presque Isle Bay as part of a study that was performed by PADEP in 1992 and 1993 (6). Clean fish were collected from Misery Bay with the intent to use them as reference fish (tumored fish from Misery Bay were thrown back into the water). The PAH metabolite data that were generated in this study (Study 1) and a follow up study (Study 2) are presented in Table 3-2.

Based on the results of the first study (Study 1 in Table 3-2), PADEP concluded that the bullheads with external tumors had higher levels of PAH metabolites in their bile than those with no tumors (6). The data seem to support this conclusion; un-tumored fish collected from Misery Bay contained naphthalene equivalent metabolite concentrations in bile ranging from 34 to 52  $\mu\text{g/g}$ , while the levels in the tumored fish from the Point area and Lagoon system ranged from 59 to 190  $\mu\text{g/g}$  (Table 3-2). The benzo(a)pyrene equivalent fraction is the most likely fraction to be correlated with tumor incidence, because the PAH carcinogens are high molecular weight PAHs, such as benzo(a)pyrene (8). The benzo(a)pyrene equivalent metabolite levels in un-tumored brown bullhead from Misery Bay ranged from less than 0.10 to 0.14  $\mu\text{g/g}$ , compared to a range of less than 0.10 to 0.55  $\mu\text{g/g}$  in bile of fish from the lagoons and Point areas (Table 3-2). Concentrations of phenanthrene equivalent metabolites in bile of tumored brown bullheads from Lagoons and Point areas also were higher than those in un-tumored fish from Misery Bay.

In 1995, PADER sponsored a second Presque Isle Bay fish tumor study in which the PAH metabolite concentrations in both bowfin (*Amia calva*) and brown bullhead were determined (study 2 in Table 3-2). The PAH metabolite data were not included in the referenced tumor study report (7), but were delivered separately to Battelle for review. Many more fish were collected in this second study, allowing for a more thorough assessment of the data. Fish were collected at four locations inside the Bay system and from Thompson Bay just outside the Bay. Additionally, brown bullheads were collected from Eaton Reservoir as reference fish for this study, and a second species of fish (bowfin) was collected from the Presque Isle Bay locations.

A total of nine brown bullhead and 12 bowfin were collected at Point-Sara's Cove in the 1995 study. The average naphthalene and phenanthrene equivalent PAH metabolite concentrations in bowfin bile were much lower than those in brown bullhead bile (Figure 3-9 and Table 3-2), as was the tumor rate, even though the benzo(a)pyrene equivalent levels were similar. Benzo(a)pyrene equivalent metabolites in bile of brown bullheads ranged from 0.27 to 6.37  $\mu\text{g/g}$ , compared to a concentration range of 0.20 to 4.07  $\mu\text{g/g}$  in bile of bowfin. None of the bowfin from Point Sara's Cove (and only one of the bowfin collected in the whole study) had tumors. Eight of the nine brown bullheads collected at Point Sara's Cove had visible body tumors, mouth tumors, and/or abnormal body pigmentation.

The higher rate of tumors in brown bullhead, compared to bowfin, probably is a function of the closer contact of brown bullheads with the sediment, differences in food organisms, differences in feeding habits in general, and differences in the ability of the two species of fish to produce carcinogenic metabolites from chemicals in sediments and food. A major cause of the higher incidence of tumors in brown bullheads than in other fish from the same habitat may be the greater ability of the brown bullhead cytochrome P450 mixed function oxygenase system to produce carcinogenic metabolites from carcinogenic PAHs, such as benzo(a)pyrene (34). Brown bullhead detoxification enzymes produce a high proportion of 7,8- and 9,10-diol metabolites of benzo(a)pyrene, the proximate carcinogens for this PAH.



Table 3-2. Presque Isle Bay and Eaton Reservoir Bile PAH Metabolite Data

Species	Naphthalene Equivalent (µg/g)	Phenanthrene Equivalent (µg/g)	Benzo[a]pyrene Equivalent (µg/g)	Tumors	Location	Age (Years)
<b>Study 1<sup>a</sup></b>						
Brown Bullhead	120	37	0.23	Severe Tumors	Lagoons	
Brown Bullhead	130	78	0.42	Tumored	Lagoons	
Brown Bullhead	86	37	0.22	Tumored	Lagoons	
Brown Bullhead	130	38	0.27	Tumored	Lagoons	
Brown Bullhead	83	24	<0.10	Tumored	Lagoons	
Brown Bullhead	39	10	<0.10	Clean	Misery Bay	
Brown Bullhead	52	15	0.14	Clean	Misery Bay	
Brown Bullhead	34	9.7	<0.10	Clean	Misery Bay	
Brown Bullhead	110	33	0.26	Tumored	Point	
Brown Bullhead	94	27	0.19	Tumored	Point	
Brown Bullhead	88	23	0.22	Tumored	Point	
Brown Bullhead	190	57	0.55	Tumored	Point	
Brown Bullhead	84	40	0.21	Tumored	Point	
Brown Bullhead	59	18	0.21	Tumored	Point	
Brown Bullhead	69	23	0.19	Tumored	Point	
Brown Bullhead	74	27	0.2	Tumored	Point	
Brown Bullhead	70	22	0.14	Tumored	Point	
<b>Study 2<sup>b</sup></b>						
Brown Bullhead	164	61.8	0.011	C <sup>c</sup>	Cascade Creek	4
Brown Bullhead	283	180	0.915	BT <sup>c</sup>	Cascade Creek	7
Brown Bullhead	127	58	0.034	BP, BT, MT <sup>c</sup>	Cascade Creek	16
Brown Bullhead	184	95.5	0.323	BT, MT	Cascade Creek	17
Brown Bullhead	256	20.7	0.498	C	Eaton Reservoir	5
Brown Bullhead	168	18.6	0.72	BP, BT	Eaton Reservoir	5
Brown Bullhead	97.6	10.4	0.373	C	Eaton Reservoir	6
Brown Bullhead	139	12.9	0.371	C	Eaton Reservoir	7
Brown Bullhead	230	17.2	0.591	BT	Eaton Reservoir	9
Brown Bullhead	126	12.1	0.426	BT	Eaton Reservoir	11
Brown Bullhead	165	14.4	0.546	BP	Eaton Reservoir	15
Brown Bullhead	121	9.85	0.391	BT	Eaton Reservoir	15
Brown Bullhead	126	12.7	0.435	MT	Eaton Reservoir	16
Brown Bullhead	120	13	0.513	C	Eaton Reservoir	17
Brown Bullhead	134	28	0.359	C	Lagoon	3
Brown Bullhead	225	73.8	0.002	C	Lagoon	3
Brown Bullhead	164	82.1	0.032	C	Lagoon	3
Brown Bullhead	280	48.2	0.52	BP	Lagoon	4
Brown Bullhead	32.8	25.7	0.792	C	Lagoon	4
Brown Bullhead	356	50.7	0.821	C	Lagoon	4



Table 3-2 (continued). Presque Isle Bay and Eaton Reservoir Bile PAH Metabolite Data

Species	Naphthalene Equivalent (µg/g)	Phenanthrene Equivalent (µg/g)	Benzo[a]pyrene Equivalent (µg/g)	Tumors	Location	Age (Years)
Brown Bullhead	62.9	11.1	0.23	C	Lagoon	4
Brown Bullhead	98.3	21.7	0.006	C	Lagoon	4
Brown Bullhead	134	58.6	0.001	C	Lagoon	4
Brown Bullhead	438	65.5	0.067	BP, MT	Lagoon	9
Brown Bullhead	425	77.1	0.924	BP, BT	Lagoon	12
Brown Bullhead	106	337	0.146	BP, BT	Lagoon	12
Brown Bullhead	89.3	14.2	0.327	BP, BT, MT	Lagoon	13
Brown Bullhead	156	63.1	0.228	MT	Lagoon	14
Brown Bullhead	207	40.6	0.385	BP, BT, MT	Lagoon	15
Brown Bullhead	314	42.9	0.576	BT	Lagoon	15
Brown Bullhead	214	78.1	0.157	BP, BT, MT	Lagoon	15
Brown Bullhead	96.9	23.2	1.93	BT	Point - Sara's Cove	4
Brown Bullhead	273	57.2	6.37	BT	Point - Sara's Cove	4
Brown Bullhead	100	19.2	0.351	BP, BT	Point - Sara's Cove	10
Brown Bullhead	126	28.7	0.669	BT	Point - Sara's Cove	11
Brown Bullhead	159	23	0.627	BP, BT	Point - Sara's Cove	11
Brown Bullhead	82.3	12.4	0.269	BP, BT, MT	Point - Sara's Cove	12
Brown Bullhead	95	15.1	0.362	BP, BT	Point - Sara's Cove	14
Brown Bullhead	130	41.8	2.08	C	Point - Sara's Cove	15
Brown Bullhead	174	29.5	0.935	BT, MT	Point - Sara's Cove	16
Brown Bullhead	300	52.7	5.98	BT, MT	Sara's Cove	
Brown Bullhead	131	69.8	0.089	C	Sara's Cove	4
Brown Bullhead	106	24.8	0.474	C	Sara's Cove	4
Brown Bullhead	116	28.3	0.919	MT	Sara's Cove	4
Brown Bullhead	0	0	0	C	Sara's Cove	4
Brown Bullhead	124	32.2	1.25	C	Sara's Cove	5
Brown Bullhead	150	31.8	1.59	BP, BT	Sara's Cove	5
Brown Bullhead	0	0	0	C	Sara's Cove	5
Brown Bullhead	122	30.1	0.973	C	Sara's Cove	5
Brown Bullhead	91	26.1	0.559	BT	Sara's Cove	7
Brown Bullhead	115	36.8	2.13	BT, MT	Sara's Cove	10
Brown Bullhead	166	47.8	1.61	BT	Sara's Cove	12
Brown Bullhead	36.7	9.64	0.085	BP, MT	Sara's Cove	13
Brown Bullhead	149	68.1	0.159	BP, MT	Sara's Cove	16
Brown Bullhead	168	82	0.144	BP, BT	Sara's Cove	16
Brown Bullhead	122	25.8	1.11	BT, MT	Sara's Cove	16
Brown Bullhead	221	45.6	1.03	BP	Thompson Bay	4
Brown Bullhead	101	19.5	0.412	C	Thompson Bay	4
Brown Bullhead	237	31	0.346	C	Thompson Bay	4
Brown Bullhead	119	18.1	0.394	C	Thompson Bay	4



Table 3-2 (continued). Presque Isle Bay and Eaton Reservoir Bile PAH Metabolite Data

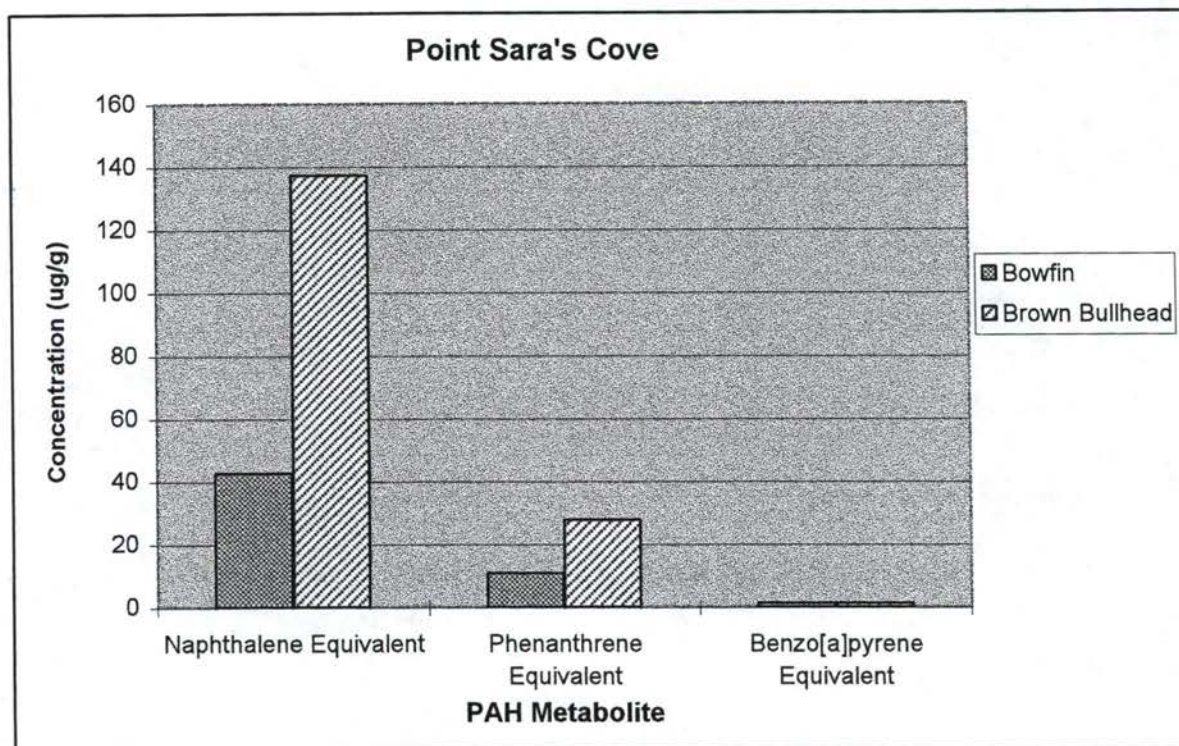
Species	Naphthalene Equivalent ( $\mu\text{g/g}$ )	Phenanthrene Equivalent ( $\mu\text{g/g}$ )	Benzo[a]pyrene Equivalent ( $\mu\text{g/g}$ )	Tumors	Location	Age (Years)
Brown Bullhead	300	45.2	0.597	BT	Thompson Bay	6
Brown Bullhead	134	35.7	0.852	BP	Thompson Bay	7
Brown Bullhead	221	48	0.575	BT	Thompson Bay	7
Brown Bullhead	192	26.4	0.404	BP, BT	Thompson Bay	7
Brown Bullhead	214	49.3	0.707	BT	Thompson Bay	7
Brown Bullhead	127	33.5	0.583	BT	Thompson Bay	7
Brown Bullhead	137	26.6	0.059	BP, BT	Thompson Bay	8
Brown Bullhead	171	70.1	0.145	MT	Thompson Bay	10
Brown Bullhead	146	23.9	0.359	BT, MT	Thompson Bay	11
Brown Bullhead	135	45.2	0.009	C	Thompson Bay	11
Brown Bullhead	200	47.7	0.718	BT, MT	Thompson Bay	12
Brown Bullhead	312	123	0.329	BP, BT	Thompson Bay	12
Brown Bullhead	181	23.7	0.276	BP, MT	Thompson Bay	13
Brown Bullhead	210	36.3	0.624	BT, MT	Thompson Bay	14
Brown Bullhead	273	25.5	0.008	BP, MT	Thompson Bay	14
Bowfin	138	42.7	0.5	C	Cascade Creek	4
Bowfin	95.6	12.2	0.221	C	Cascade Creek	7
Bowfin	32	5.73	0.186	C	Lagoon	
Bowfin	69.4	14	1.34	C	Misery Bay	6
Bowfin	49.5	8.82	0.47	C	Misery Bay	7
Bowfin	25.2	8.4	0.568	C	Point - Sara's Cove	
Bowfin	46	8.65	0.195	C	Point - Sara's Cove	3
Bowfin	37.9	9.68	0.699	C	Point - Sara's Cove	4
Bowfin	76.4	23.3	2.73	C	Point - Sara's Cove	4
Bowfin	43.4	18.2	0.707	C	Point - Sara's Cove	4
Bowfin	36.7	4.46	0.681	C	Point - Sara's Cove	4
Bowfin	38.6	5.77	0.42	C	Point - Sara's Cove	4
Bowfin	32.4	7.96	4.07	C	Point - Sara's Cove	8
Bowfin	42.4	16	1.16	C	Point - Sara's Cove	8
Bowfin	49.3	11.8	4.05	C	Point - Sara's Cove	9
Bowfin	44.4	8.67	0.605	C	Point - Sara's Cove	10
Bowfin	39.1	8.49	0.987	C	Point - Sara's Cove	10
Bowfin	50	14.6	2.09	BP	Sara's Cove	3
Bowfin	48.7	13.8	1.15	C	Sara's Cove	9
Bowfin	200	56.6	0.959	C	Thompson Bay	8
Bowfin	74.5	7.72	0.212	C	Thompson Bay	10

<sup>a</sup> PADEP. 1993. Presque Isle Bay Brown Bullhead Tumor Study; Conducted from March 29, 1992 to October 7, 1993 (6).

<sup>b</sup> PADER. 1996. A Study of Tumors in Fish of Presque Isle Bay, 1995 (7).

<sup>c</sup> Study 2 tumor codes: Clean (C), body tumor (BT), body pigment (BP), and mouth tumor (MT).





**Figure 3-9. Average PAH Metabolite Concentrations in the Bile of Fish Collected at Point Sara's Cove — Bowfin versus Brown Bullhead**

Demersal fish often have a higher incidence of tumors than pelagic species, probably because of the closer contact with carcinogen-containing sediments. For instance, brown bullheads, freshwater drum (*Aplodinotus grunniens*) and white suckers (*Catostomus commersoni*) from the Buffalo River, NY, the Black River, OH, and other industrialized tributaries of Lake Erie contained high incidences of oral and epidermal tumors and liver cancers (36). The catfish in most locations had the highest incidences of tumors and also contained elevated concentrations of PAHs in their tissues. Brown bullheads collected on the Black River below a coke plant had a high incidence of gross neoplastic disease, compared to fish from a clean reference area, and tumor incidence increased with age of the fish (37). These observations agree well with the observations made for brown bullheads from Presque Isle Bay and lend support to the hypothesis that elevated concentrations of PAHs in sediments of the bay are contributing to the high incidence of tumors in the fish residing there.

Figure 3-10 shows the average PAH metabolite concentrations in brown bullheads from the six locations that were sampled. The naphthalene equivalent PAH metabolite concentrations did not vary greatly between the different locations, and the fish from the reference location (Eaton Reservoir) had concentrations that were about mid-range (higher than two Presque Isle Bay locations and lower than two other Presque Isle Bay locations and Thompson Bay). There was greater variability in the phenanthrene and benzo[a]pyrene equivalent metabolite concentrations, and no clear pattern emerged. The phenanthrene equivalent metabolite concentrations were highest for the fish collected at Cascade Creek and lowest for Eaton Reservoir, while the benzo[a]pyrene equivalent metabolite concentrations were lowest for the fish



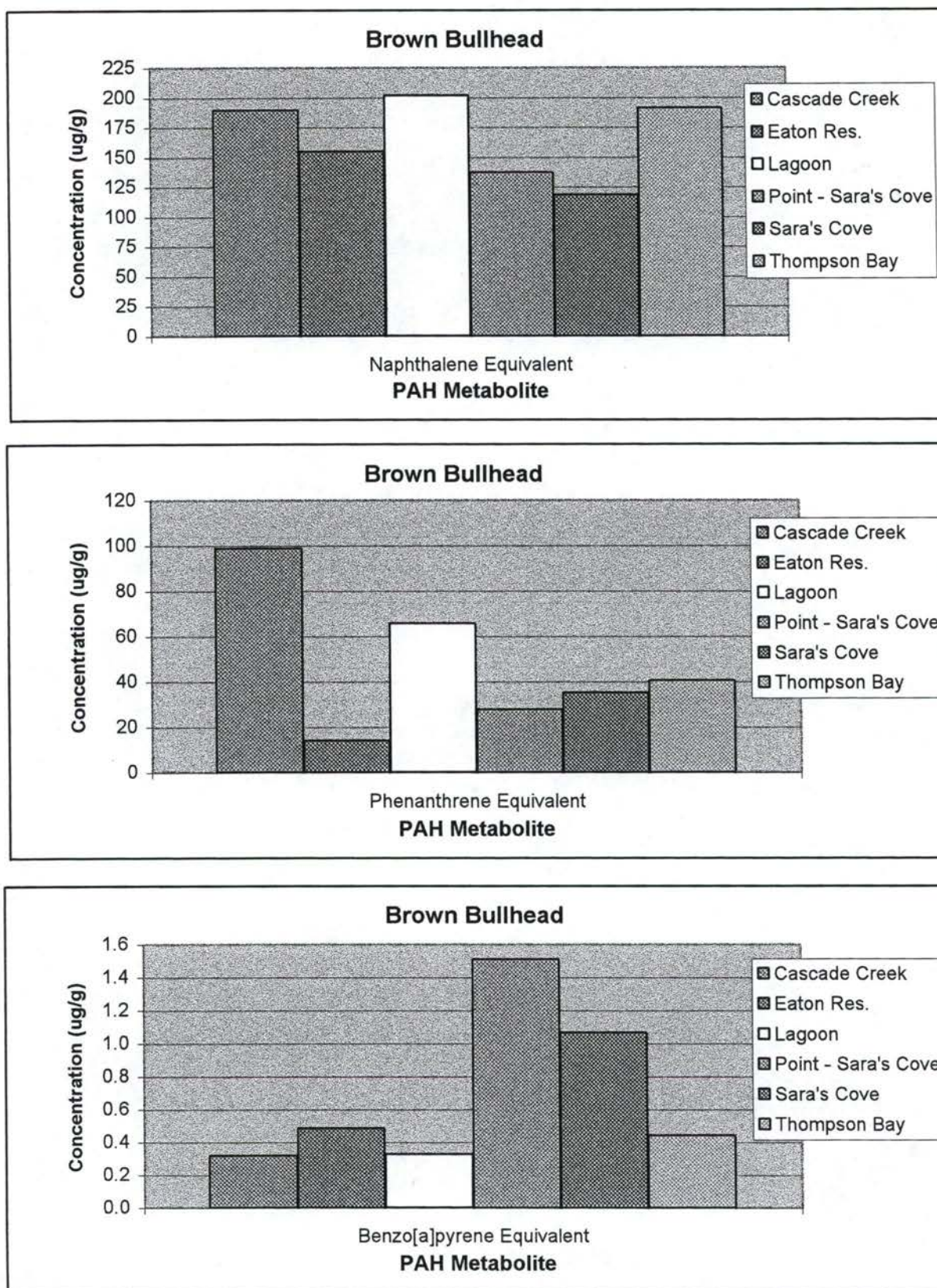


Figure 3-10. Average PAH Metabolite Concentrations in the Bile of Brown Bullhead Collected at Four Presque Isle Bay Locations, Thompson Bay, and Eaton Reservoir



collected near Cascade Creek and again about mid-range for the Eaton Reservoir fish. The PAH concentrations in sediments from the different sampling sites do not explain the variability in PAH metabolite composition between sampling locations because, as discussed earlier, the PAH composition of the surface sediment is quite similar throughout the Bay.

Figure 3-11 shows the metabolite concentrations for brown bullheads collected at the Lagoon location. The plot shows the average concentration for the fish with tumors versus those that were clean, and the data for the fish that were older than 10 years versus those that were less than 10 years old are also presented. Figure 3-12 presents the same type of data for brown bullhead collected at Sara's Cove. These data indicate that the PAH metabolite concentrations in brown bullheads at these locations are higher in the fish with tumors than in fish that do not have tumors, and also that the metabolite concentrations are higher in older fish than in younger fish.

Although there appears to be a correlation between the tumor incidence and bile metabolite concentrations in the bile of brown bullheads, the PAH metabolite levels measured in this study in brown bullhead bile were no higher than one might expect for this area, based on levels measured elsewhere. PAH metabolite levels are clearly species dependant, but the naphthalene equivalent PAH metabolite concentrations in fish populations in general have typically been reported to be significantly above 100  $\mu\text{g/g}$  in the bile of finfish from urban areas where the fish have a high incidence of tumors (e.g., Puget Sound), whereas fish from more remote areas generally have concentrations less than 100  $\mu\text{g/g}$  (31, 32, 38). In 1986, Krahn *et al.* (38) reported total PAH metabolite concentrations averaging about 200  $\mu\text{g/g}$  (as naphthalene equivalents) and about 210  $\mu\text{g/g}$  (as phenanthrene equivalents) in the bile of white sturgeon caught 57 miles downstream of an oil spill in the Columbia River 5 days after an oil spill. The bile of fish caught in a relatively remote area 13 miles upstream had naphthalene equivalent metabolite concentrations of 17 to 32  $\mu\text{g/g}$ , and 9.6 to 9.7  $\mu\text{g/g}$  as phenanthrene equivalents. In a separate study Krahn *et al.* (34) determined PAH metabolite levels of 1.3 to 21  $\mu\text{g/g}$  as benzo[a]pyrene equivalents in English sole collected from Puget Sound. There was a correlation between total PAH metabolite levels in the bile and incidence of hepatic tumors in the English sole (31).

In 1994, Battelle determined PAH metabolite concentrations in the bile of 18 unidentified finfish collected nearshore off the coast of Long Beach, California, near the site of domestic sewage discharges from the city and county of Los Angeles and found the concentrations to range from 58 to 655  $\mu\text{g/g}$ , 43 to 536  $\mu\text{g/g}$ , and 1.9 to 59  $\mu\text{g/g}$ , for naphthalene, phenanthrene, and benzo[a]pyrene equivalents, respectively. In another study, bile was collected from 20 unidentified finfish near a site with known hydrocarbon contamination, and the naphthalene equivalent metabolite concentrations were generally in the 200 to 1,200  $\mu\text{g/g}$  range (18 of the 20 samples had concentrations greater than 200  $\mu\text{g/g}$ ), and the phenanthrene equivalent concentrations were about half these levels (39). At a reference location that was known to be clean, the naphthalene equivalent metabolite concentrations ranged from 24 to 60  $\mu\text{g/g}$  in three fish.

The PAH metabolite data for Presque Isle Bay suggest that there may be a relationship between the presence of tumors in brown bullheads and the metabolite concentrations in the bile of the fish. The tumor and brown bullhead data for fish from Lagoon, Sara's Cove, and to a lesser degree Eaton Reservoir and Thompson Bay seem to suggest that there is also an increase in tumor frequency with the age of the fish, even when the PAH metabolite concentrations are not necessarily higher than in younger fish (Table 3-2). Similar observations were made for Black River brown bullheads by Bauman *et al.* (40). This implies that exposure to bioavailable forms of carcinogenic PAH or other chemical carcinogens above a certain level may induce tumors in a relatively short period of time, while a chronic exposure to lower levels over a longer period of time can have the same effect. However, tumors are not formed quickly even during exposure to very high levels of PAH, and the PAH metabolite concentrations measured in these studies



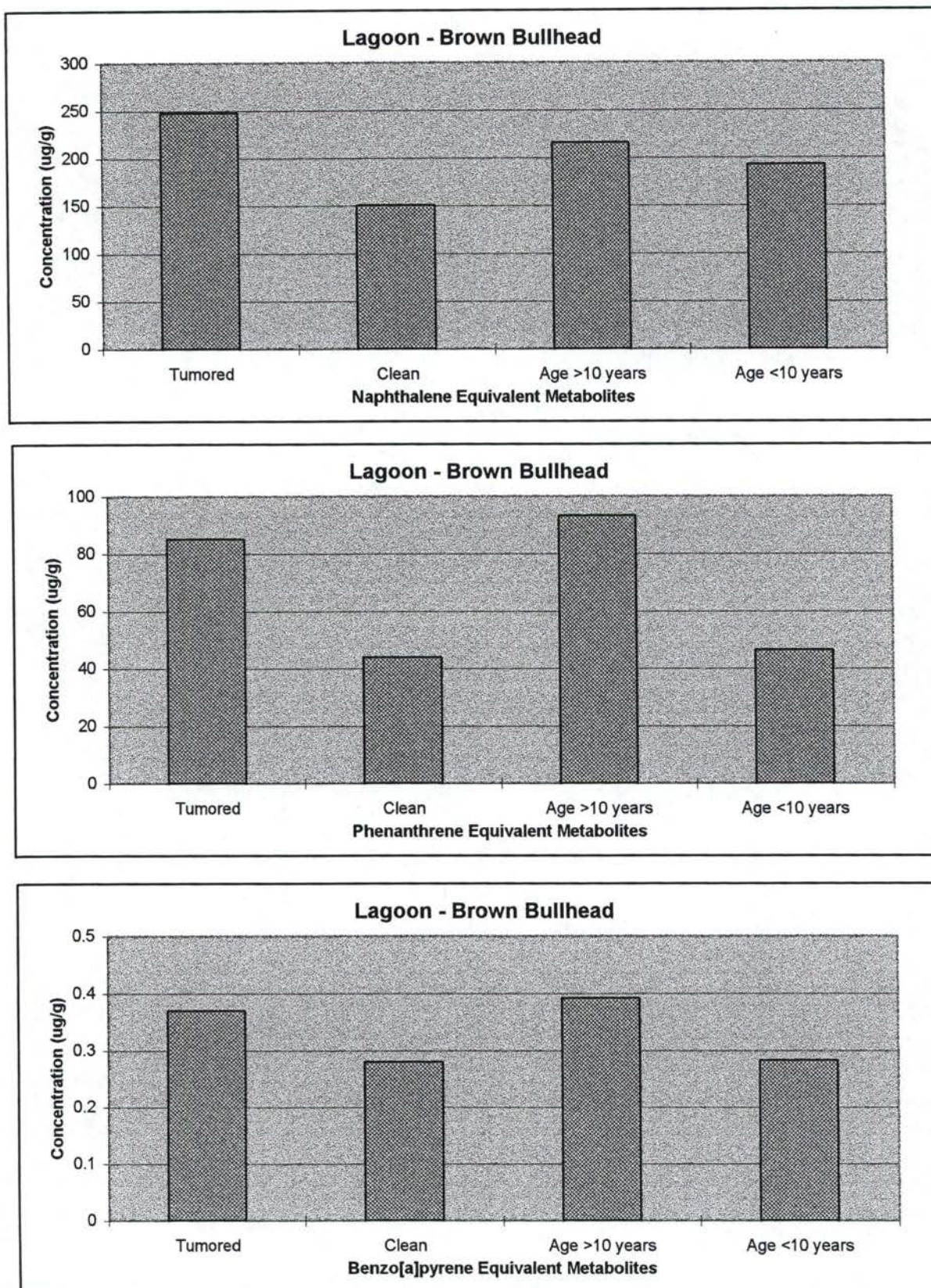


Figure 3-11. Average PAH Metabolite Concentrations in the Bile of Brown Bullhead Collected at Lagoon — Tumored versus Clean Fish and >10 Year Old versus <10 Year Old Fish



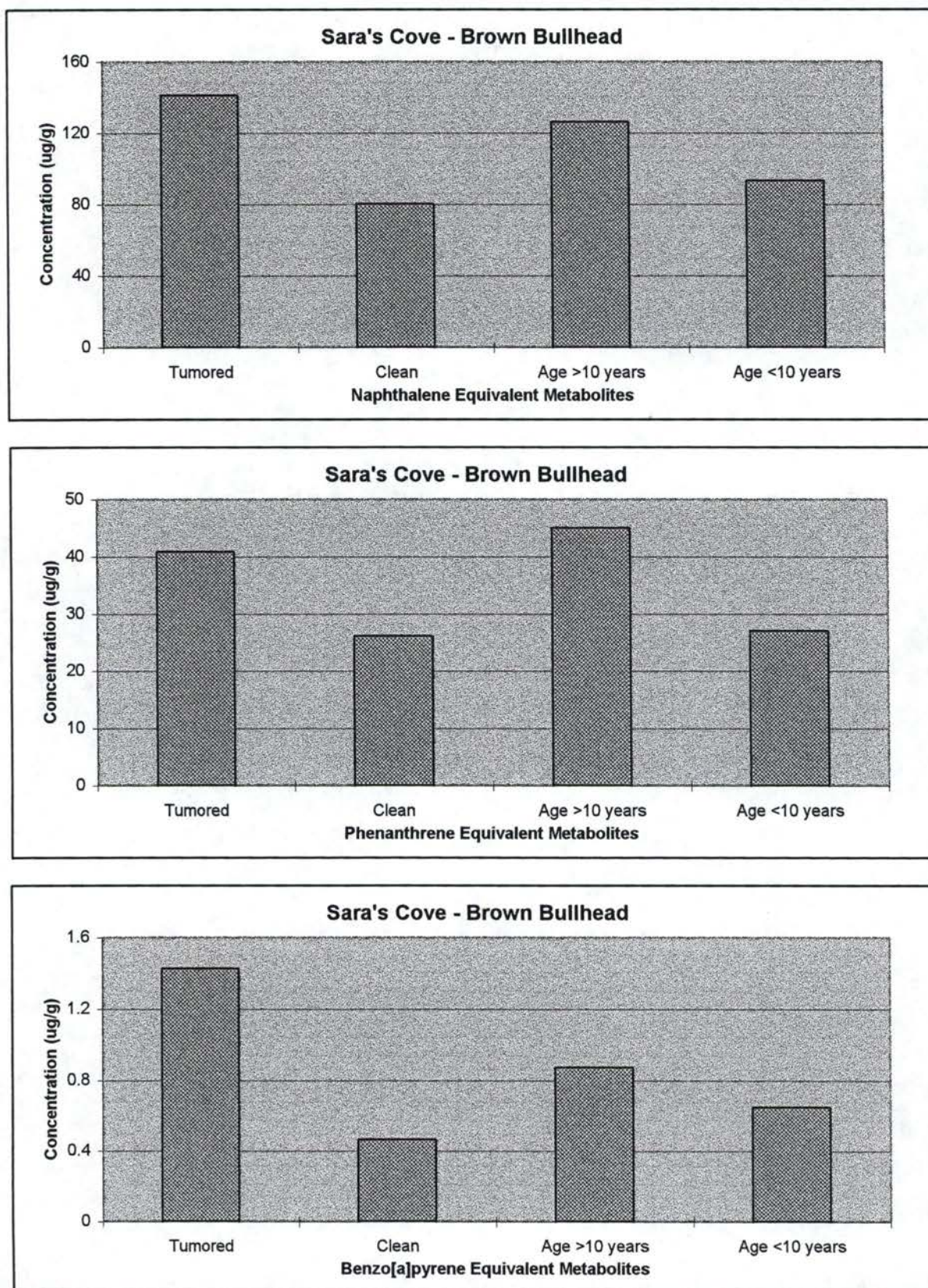


Figure 3-12. Average PAH Metabolite Concentrations in the Bile of Brown Bullhead Collected at Sara's Cove — Tumored versus Clean Fish and >10 Year Old versus <10 Year Old Fish



were the levels at the time the fish were collected, which may have been quite different from the levels in the same fish a year earlier or for most of the life of the fish. The rate of excretion of bile into the digestive tract, and therefore, the half-life of bile metabolites, is dependent on the feeding rate of the fish, but probably is less than one or two days. Thus, concentrations of bile metabolites remain elevated in the bile for only as long as the fish is exposed to elevated concentrations of bioavailable forms of PAHs in the ambient water, food, and sediments (41). Thus, concentrations of PAH metabolites in the bile of a fish reflects its recent (within a few days) exposure to bioavailable PAHs in its environment. Whole fish samples and bile were frozen immediately after collection, so holding time of the samples did not affect the PAH metabolite concentrations measured. This uncertainty in the historic levels and variability of PAH metabolites in individual fish makes it difficult to infer a cause and effect relationship between PAH metabolite levels and tumors. For instance, the data reveal some instances where there were young fish with low PAH metabolite concentrations and tumors collected from the same location where much older fish with high PAH metabolite concentrations and no tumors also were caught.

The PAH metabolite data for Eaton Reservoir, a presumably uncontaminated reference site, may also confound the results. Eaton Reservoir was chosen because it was considered to be in the same general geographical area, but expected to be free from the elevated PAH levels of Presque Isle Bay. There were no sediment PAH data reported with the metabolite data, so the actual PAH concentrations in Eaton Reservoir sediments are unknown. It is, however, clear that the PAH metabolite concentrations reported for the brown bullheads collected from Eaton Reservoir are about the same as those in the brown bullheads from Presque Isle Bay, and certainly not notably lower. The tumor incidence also appears to be about the same for Eaton Reservoir and Presque Isle Bay. Although the number of fish sampled are too few to draw any definitive conclusions, the data do raise the following questions:

1. Are the PAH metabolite concentration and tumor rates observed for brown bullheads from Eaton Reservoir and Presque Isle Bay what can be expected for this general area even after reduction of PAH contributions from local sources?
2. Are there other environmental contaminants/triggers, unrelated to PAH levels in sediments, that are causing or contributing to the high incidence of tumors in brown bullheads?

### 3.2 OTHER CONTAMINANT CHARACTERIZATION

Some of the early environmental assessment work that was performed in Presque Isle Bay in the 1980's generated highly variable and somewhat questionable data. For instance, sediment mercury concentrations were reported to have increased by a factor of more than 100 from 1982 to 1986, and the data suggested that arsenic levels increased by a factor of more than 10 in the same time period (Tables 4.15 and 4.16 in reference 1). The data from the 1980's seemed to indicate that various metals may be elevated in Presque Isle Bay. However, much of these data from the 1980's probably are not trustworthy, and the variable results are probably due to analytical problems. More recent work, that probably were performed using more reliable procedures, suggest that these parameters are of less concern (6), with the possible exceptions of nitrosamines and arsenic. Presque Isle Bay sediment concentrations of nitrosamines (up to 26 mg/kg) and arsenic (up to 234 mg/kg) are high enough to cause histopathological lesions, including tumors, in demersal fish (6). Nitrosamines are known carcinogens in fish (6). Inorganic arsenic, as reduced arsenite, is classified as a human carcinogen; however, it is not known to cause cancer in fish (42).



There was no violation of FDA action levels (or of AOC fish consumption guidelines) in fish collected in Presque Isle Bay and Lake Erie in 1987-1990 for 11 different contaminants (pesticides, PCB, and metals, including mercury; PAH was not monitored) (1). The 1993 study sponsored by USEPA that found significantly elevated levels of PAH in the sediment near the mouths of Mill Creek and Cascade Creek did not find pesticide or PCB concentrations above standard EPA method detection limits (6). Arsenic was found to be the only metal with elevated concentrations in the sediment from some locations. However, several species of fish collected in 1995 from Presque Isle Bay contained <0.08 to 0.477 mg/kg wet wt. total arsenic in soft tissues (7). These concentrations are typical for freshwater fish from uncontaminated environments. However, the concentration of mercury in a sample of bowfin collected in Misery Bay in 1995 contained 0.812 mg/kg mercury (7). This concentration, although slightly lower than the FDA action level for mercury of 1 mg/kg, is higher than the Risk Based Concentration (RBC) developed by EPA Region III (43) for mercury in edible tissues of fish consumed by man (0.41 mg/kg as either inorganic or methylmercury).

Several potential environmental contaminants, other than PAHs, were determined in water, tissue, and sediment during the Presque Isle Bay study sponsored by PADEP in 1993 (6). Composite fish fillet tissue from 5 locations in Presque Isle Bay were analyzed for a series of persistent chlorinated pesticides, polychlorinated biphenyls (PCB), and series of metals (6), and the target analytes were either not detected or only detected at low levels. Metals and nitrosamines were determined in sediment samples. The arsenic concentrations, which were as high as 200 mg/kg in sediments from one location, were well above background levels, and the only metal that was present at concentrations high enough to be of concern (6). Dissolved inorganic arsenate and arsenite are toxic to fish and, at high concentrations, may cause histopathological lesions. The analyses performed on these sediments did not include arsenic speciation; therefore it is not known what fraction of the total sediment arsenic was in a bioavailable form that could have adverse affects. The nitrosamine concentrations appear to exhibit seasonal variability in Presque Isle Bay, and in the early spring of 1992 the levels were below what is commonly regarded as levels of concern. In the summer of 1993, there were some locations where sediment nitrosamine concentrations were above those that could contribute to liver tumor formation (up to 26.2 mg/kg). The nitrosamine concentrations were, however, highly variable, not only by season but also by location within the Bay, and no location was consistently elevated in replicate samplings. The 1994 survey and analyses did not confirm the earlier nitrosamine results — no significant nitrosamine elevation was observed (3). Other chemical contaminants that could be present in Presque Isle Bay and could contribute to the degradation of environmental quality in the bay, but which have not been analyzed or detected by the methods used, include butyltin compounds (used in antifouling paints on boats and ships) and polychlorinated dibenzodioxins (byproducts of steel manufacture and waste incineration). These chemicals are highly toxic to aquatic organisms at extremely low concentrations (low parts per billion).



### 4.0 BIOLOGICAL CHARACTERIZATION STUDIES

#### 4.1 FISH TUMOR STUDIES

Two studies of tumor incidence in fish from Presque Isle Bay were reviewed for this report. One study was conducted by PADEP in 1992 and 1993, and was designed to first assess the applicability of the brown bullhead (*Amieurus nebulosus*), a catfish that forages in and ingests sediments, as an indicator species for Presque Isle Bay and then to determine the incidence of tumors in brown bullheads in Presque Isle Bay (6). Attempts were also made to correlate tumor incidence and animal responses with the presence of chemical contaminants in the sediments of the Bay, or the tissue or bile of the fish.

The second fish tumor study was also sponsored by PADEP and was performed in 1995 (7). In this study both brown bullheads and bowfin (*Amia calva*) from Presque Isle Bay were surveyed for tumor incidence. Additionally, a reference population of brown bullheads was sampled from a nearby reservoir thought to be free of significant levels of pollution, such as PAH. Results of these studies were discussed briefly in Section 3 of this report in relation to concentrations of PAHs in sediments from the Bay. They will be discussed here in relation to the health of aquatic biological resources of Presque Isle Bay.

Brown bullheads tagged in Presque Isle Bay nearly always were recaptured in the bay, indicating that these fish are for the most part resident and do not make frequent migrations out of the bay (6). They tend to move freely throughout the bay, concentrating in shallow vegetated areas in the lagoon system of the northern bay in the spring and fall, and moving into deeper water along the south shore in other seasons. The brown bullheads used in the tag/recapture study had a 61 percent incidence of skin tumors. However, 82.2 percent of the fish captured at the mouth of Mill Creek, a source of contaminated freshwater inflow to the bay, contained tumors. Because of the limited migrations undertaken by these fish, it is probable that they encountered the causative agent(s) for the tumors from the water, sediments, or food with which they came into contact in the bay. However, because of the latency of tumor formation following exposure to tumor causing agents, such as some PAHs, it is difficult to correlate the geographic incidence of tumors with the geographic distribution of potential tumorogenic chemicals in sediments (6).

The latency of tumor induction is supported by the observation that there is a direct correlation in Presque Isle Bay brown bullheads between body length (and presumably age) and the incidence of tumors (6). No brown bullheads shorter than 200 mm had tumors and more than 80 percent of brown bullheads larger than 350 mm had tumors. The larger fish probably are 10 to 14 years old. Age related tumor incidences in brown bullheads have been noted elsewhere in Lake Erie (40).

A lower incidence of tumors, particularly liver carcinomas, was observed in closely related yellow bullheads from the bay (6) and in distantly-related bowfins (7) than in brown bullheads. The differences in incidence of tumors in the three species may be related to differences in the rate of metabolism of PAHs and differences in the metabolites formed (only a small fraction of the metabolites of a few PAHs are carcinogenic) by the three species. Yuan *et al.* (35) reported that liver microsomes of brown bullheads metabolize benzo(a)pyrene more rapidly and produced a higher proportion of carcinogenic metabolites than do liver microsomes of channel catfish. Where the two species occur together in contaminated sediment environments, brown bullheads nearly always have a higher incidence of tumors than channel catfish. A similar difference in metabolic capability and tumor incidence was observed in English sole and starry flounder from Puget Sound, WA (44, 45). If this explanation of the differential tumor incidence in brown and yellow bullheads and bowfins is true, it is strong circumstantial evidence that PAHs are the cause of



some of the tumors in bullheads from Presque Isle Bay. High molecular weight, pyrogenic PAHs in sediments have been implicated in tumor induction in several species of freshwater and marine fish (33, 45, 46).

Nitrosamines are primary carcinogens and do not have to be metabolically activated to cause cancer. They may have a shorter latency period for cancer production in fish than PAHs do. Nitrosamines, which may occur seasonally at high concentrations in Presque Isle Bay sediments, may contribute to the incidence of tumors in brown bullheads from the bay.

However, although high incidences of tumors have been reported in fish from 19 of 43 Areas of Concern in the Great Lakes Basin Ecosystem including 7 out of the 9 Areas of Concern in Lake Erie (47), the causative agent or agents for the tumors still is not understood. For example, the high incidence of tumors in brown bullheads and walleye from the Detroit River could not be correlated to concentrations of PAH in sediments and stomach contents of the fish (48). There is a low incidence of tumors in brown bullhead and walleye from lower Green Bay and its tributaries despite heavy contamination of the environment and fish with chlorinated compounds, including PCDDs, PCDFs, and PCBs, and arsenic (49). A high incidence of tumors in sauger and walleye from Torch Lake, Michigan, can not be attributed to any chemical contaminants in the lake (50). Lake water and sediments are not mutagenic and rainbow trout eggs and fry exposed to lake sediments for long periods of time did not develop tumors. Although the cause of the tumors is thought to be chemicals, the identity of the chemicals is unknown.

In a preliminary assessment, an examination of 100 brown bullheads from Presque Isle Bay revealed that 64 percent had skin tumors and 22 percent had liver tumors, most of the latter of which were classified as cancerous (6). Field and laboratory studies confirmed that the tumors in the fish were not caused by a virus. They probably were caused by one or more chemicals. A subsequent analysis of 3,236 brown bullheads (about 10 percent of the population) from Presque Isle Bay in 1992 revealed a tumor incidence of 60.8 percent. This tumor incidence is as high as or higher than incidences in brown bullheads from other urbanized coastal waters of the Great Lakes (32, 47).

It is certain metabolites of some PAHs, not the parent PAHs themselves, that are carcinogenic (8, 46). Benzo(a)pyrene is the best-known of the carcinogenic PAHs. The 7,8,9,10-diol epoxides are the most carcinogenic benzo(a)pyrene metabolites (8). PAH metabolites that do not bind to tissue macromolecules, such as DNA, to form DNA adducts (the suspected proximate carcinogens), are conjugated with sulfate or glucuronide and excreted, primarily in the bile via the gall bladder of fish. Thus, accumulation of PAH metabolites in the bile is an indication that PAH metabolism is taking place in the fish, but is difficult to correlate with induction of tumors in the fish. At best, the presence of metabolites of carcinogenic PAHs, such as benzo(a)pyrene, in the bile indicates that the fish are metabolizing carcinogenic PAHs and, in the processes, could be producing carcinogenic DNA adducts. Accumulation of metabolites of non-carcinogenic PAHs, such as naphthalenes and phenanthrenes, in bile is not itself indicative of exposure to potentially carcinogenic PAHs. However, non-carcinogenic and carcinogenic PAHs often co-occur in contaminated sediments of water bodies near urban/industrial centers; thus, the presence of any PAH metabolites in fish bile is suggestive of recent exposure to potentially carcinogenic PAHs.

Bile from some of the brown bullheads examined for tumors was analyzed for metabolites of 2-ring (naphthalene equivalents), 3-ring (phenanthrene equivalents) and 4- through 6-ring (benzo(a)pyrene equivalents) PAHs. Tumor-free fish from Misery Bay contained less than 0.113  $\mu\text{g/g}$  benzo(a)pyrene equivalents in their bile; bile of tumored fish from Point locations and severely tumored fish from Lagoon locations in Presque Isle Bay contained means of 0.241  $\mu\text{g/g}$  and 0.248  $\mu\text{g/g}$  total benzo(a)pyrene equivalent metabolites, respectively (6). A large number of fish was examined for tumors and bile PAH



metabolites in the 1995 study (7). Twenty four brown bullheads without tumors contained a mean of 0.418  $\mu\text{g/g}$  of benzo(a)pyrene metabolites in their bile (range, 0 to 2.08  $\mu\text{g/g}$ ). Sixty-four bullheads collected at the same locations and times and containing one or more of three epithelial tumors or abnormal pigmentation contained a mean of 0.689  $\mu\text{g/g}$  benzo(a)pyrene equivalent metabolites in their bile (range, 0.008 to 6.37  $\mu\text{g/g}$ ). In two sampling locations (Lagoon and Sara's Cove) where there were sufficient numbers of clean and tumored brown bullheads to make comparisons, metabolite concentrations were higher in bile of tumored than of non-tumored fish (Figures 3-11 and 3-12). Younger fish contained lower concentrations of metabolites in their bile than older fish did. Thus, age related differences in tumor incidence probably contributed to the differences in tumor incidence and bile metabolite concentrations in the brown bullheads.

Muscle tissues of brown bullheads were analyzed for several metals, PCBs, and pesticides (6). None of the target chemicals were present in the fish tissues at concentrations that are likely to be toxic to the fish. For the most part, concentrations of contaminants in tissues were comparable to those in tissues of the same or similar species from clean freshwater environments. Five brown bullhead muscle samples from the bay were analyzed in 1995 (7). Most metals were present at concentrations below the method detection limits. Lead, mercury, copper, and arsenic were detected at low concentrations, similar to those in muscle tissue of brown bullhead from the Eaton Reservoir reference site. Traces of alpha-BHC, 4,4'-DDE, and Aroclor-1260 also were detected.

Sediment samples from Presque Isle Bay also were analyzed. Some sediment samples collected in 1993 contained elevated concentrations of nitrosamines (up to 26 mg/kg) and arsenic (up to 199 mg/kg). As discussed above, both nitrosamines and arsenic are known carcinogens in some animals. These chemicals may have contributed to the high incidence of tumors in brown bullheads in Presque Isle Bay. Arsenic concentrations in muscle tissue of several species of fish from Presque Isle Bay ranged from less than 0.08 to 0.477 mg/kg (7). These concentrations are below concentrations that might be toxic to the fish themselves and well below natural concentrations in muscle tissues of marine fish (42). However, they are above the risk-based concentrations (RBC) for fish tissues destined for consumption by man of 0.0018 mg/kg wet weight for carcinogenicity of arsenic and 0.41 mg/kg for systemic effects of arsenic (43). However, nearly all the arsenic in fish tissues is in non-toxic and non-carcinogenic organic forms that are not readily converted to toxic inorganic arsenite (42).

The evidence presented here supports the hypothesis that high molecular weight, carcinogenic, PAHs in sediments near the south shore of the Bay contribute to the high incidence of tumors in brown bullheads from Presque Isle Bay. The PAHs are derived primarily from pyrogenic sources probably in and around the city of Erie, PA.

### 4.2 BENTHIC MACROFAUNAL COMMUNITY STRUCTURE

The benthic macrofaunal community in Presque Isle Bay was characterized as part of the 1994 Presque Isle Bay sediment quality evaluation performed by Battelle as EPA Work Assignment 107 (3). The species composition, abundances, and distribution of sediment-dwelling aquatic animals were determined at eight of the 21 sampling stations in the bay.

Sediments from the eight stations were classified as sandy clayey silt, except Station PIB18, which was nearly 100 percent sand. Small differences in sediment texture affected the abundances of species and individuals among stations. However, at all stations except the sandy station, Station PIB18, the density of benthic fauna (number of animals per meter<sup>2</sup>) was high, ranging from 1,580 to 12,080 individuals/m<sup>2</sup>. The



benthic fauna were dominated by oligochaete worms and chironomid insect larvae, typical of moderately fine-grained freshwater sediments.

There was not a clear and consistent relationship between individual benthic community parameters and concentrations in sediments of total PAHs or nitrosamines (Table 4-1). The benthic faunal community was sparse at Station PIB18 where the sediment was sandy. Among the other stations, the station where the total PAH concentration was highest (Station PIB09, 40.65 mg/kg total PAHs) had the lowest density of benthic fauna. Stations at which sediments contained more than 10,000 individuals/m<sup>2</sup> contained 12.27 and 22.68 mg/kg total PAHs. Highest concentrations of nitrosamines were in sediments containing low to moderate numbers of benthic fauna.

**Table 4-1. Concentrations of Clay, Total PAHs, and Total Nitrosamines and Benthic Community Parameters at Eight Stations in Presque Isle Bay Sampled in 1994 (3)**

Station	Clay (%)	Total PAH (mg/kg) <sup>a</sup>	Total Nitrosamines (mg/kg) <sup>a</sup>	No. of Species	No. of Individuals	Density (No./m <sup>2</sup> )
01	12.4	15.01	0.066	15	83	1,660
07	19.2	26.86	0.108	16	92	1,840
08	23.2	22.68	0.086	33	509	10,180
09	15.8	40.65	0.131	17	79	1,580
11	19.8	29.19	0.452	25	166	3,320
18	0	1.69	0.004	6	56	1,120
19	4.2	12.27	0.052	23	604	12,080
20	6.9	9.97	0.042	30	193	3,860

<sup>a</sup> Concentrations are on a dry weight basis.

However, if the overall similarity of the benthic communities in sediments at different stations, as indicated by a numerical classification dendrogram (Figure 3-1 in reference 3), is compared to clay and total PAH concentrations in sediments (Table 4-1 in this document), some patterns emerge. The benthic faunal communities at the three stations with the lowest percent clay (Stations PIB18, PIB19, AND PIB20) were distinctly different from the communities at the other five stations. Among the five stations where sediments contained more than 10 percent clay, the benthic communities at the two stations containing the highest concentrations of total PAHs (29.19 mg/kg at Station PIB11 and 40.65 mg/kg at Station PIB09) were more similar to one another than to communities at the other three stations. The station containing the third highest concentration of total PAH (26.86 mg/kg at Station PIB07) was more similar to the two stations with the highest PAH concentration than to the two other stations with lower sediment PAH concentrations. There was no clear relationship between nitrosamine concentrations in sediments and community parameters (Table 4-1). These results suggest that PAHs in the sediments of Presque Isle Bay are influencing the community structure of the local benthic fauna. However, sediment texture has a greater influence than PAHs on community structure and the apparent relationship between community parameters and concentrations of PAHs in sediments may be due to a direct correlation between percent clay and concentrations of PAH in sediments.



In order to determine if PAHs in surface sediments could be contributing to differences in benthic community structure in different regions of Presque Isle Bay, ranges of measured concentrations of individual PAHs in surficial sediments were compared to published lowest effects levels (LEL) for freshwater sediments (51) or effects range-median (ERM) concentrations for marine sediments (52) if LEL values were not available. Most of the low molecular weight, primarily petrogenic PAHs were present in the sediments at concentrations below the LEL or ERM concentrations (Table 4-2). Highest toxic units (concentration in sediment/LEL) were observed for anthracene and phenanthrene. A toxic units value (sometimes called hazard quotient) above 1 indicates that the sediment PAH could be toxic to some benthic organisms. The risk increases as the toxic units value increases. Highest concentrations of these low molecular weight PAHs were in surface sediments from Station PIB10 off Cascade Creek. Anthracene is rare in crude and refined oils, but is common in pyrogenic PAH assemblages from some sources. Phenanthrene is common in both petrogenic and pyrogenic PAH assemblages.

**Table 4-2. Comparison of Concentration Ranges of Individual and Total PAHs in Surface Sediments from Presque Isle Bay with Published Freshwater Sediment Lowest Effect Levels (LEL) (51). The resulting ranges of toxic units (concentration in sediments/LEL) also are given.**

Chemical	Concentration Range (mg/kg) <sup>a</sup>	LEL (mg/kg) <sup>a</sup>	Toxic Units
<b>Low MW PAHs</b>			
Naphthalene	0.002 - 0.34	2.10 <sup>b</sup>	<0.01 - 0.16
Methylnaphthalene	0.001 - 0.47	0.67 <sup>b, c</sup>	<0.01 - 0.70
Acenaphthene	0.001 - 0.18	0.50 <sup>b</sup>	<0.01 - 0.36
Acenaphthylene	0.001 - 0.26	0.64 <sup>b</sup>	<0.01 - 0.41
Fluorene	0.001 - 0.23	0.19	0.01 - 1.21
Anthracene	0.002 - 0.47	0.22	0.01 - 2.14
Phenanthrene	0.005 - 2.02	0.56	0.01 - 3.61
<b>High MW PAHs</b>			
Fluoranthene	0.013 - 3.68	0.75	0.02 - 4.91
Pyrene	0.013 - 3.77	0.49	0.03 - 7.69
Benz(a)anthracene	0.004 - 1.98	0.32	0.01 - 6.19
Chrysene	0.008 - 2.25	0.34	0.02 - 6.62
Benzo(k)fluoranthene	0.002 - 0.97	0.24	0.01 - 4.04
Benzo(a)pyrene	0.003 - 2.07	0.37	0.01 - 5.59
Indeno(1,2,3-cd)pyrene	0.004 - 2.76	0.20	0.02 - 13.80
Dibenz(a,h)anthracene	0.001 - 1.00	0.06	0.02 - 16.67
Benzo(g,h,i)perylene	0.004 - 2.30	0.17	0.02 - 13.53
Total PAHs	0.24 - 26.28	4.00	0.06 - 6.57

<sup>a</sup> Concentrations are on a dry weight basis, and include the three stations outside the Bay.

<sup>b</sup> No LEL available; the marine sediment ERM value was used (52).

<sup>c</sup> ERM value is for 2-methylnaphthalene.



Sediments from a few stations contained concentrations of high molecular weight, primarily pyrogenic PAHs well above the LEL concentrations (Table 4-2). The value for maximum toxic units tended to increase with increasing molecular weight and ring number of the PAHs. Highest values for toxic units were for dibenz(ah)anthracene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene, all predominantly pyrogenic PAHs. The toxic units for total PAHs in surficial sediments ranged from 0.06 to 6.57. Thus, concentrations of individual high molecular weight PAHs and total priority pollutant PAHs in some sediments from Presque Isle Bay are high enough to cause adverse effects in benthic fauna, if the PAHs were in bioavailable forms.

Stations with the highest PAH concentrations in surface sediments are clustered along the south shore of the bay, particularly near the mouth of Cascade Creek and to the southwest. One of the stations where sediment contained high PAH concentrations is PIB07 in the central basin of the bay. These are the stations that cluster close to one another in the benthic community numerical classification dendrogram (Figure 3-1 in reference 3). However, sediments from these stations also contained the highest proportions of clay. Thus, there is a link between elevated concentrations of pyrogenic PAHs and clay on the one hand and altered benthic faunal communities in Presque Isle Bay on the other. It is unclear which factor is more important.

Considering the high values for toxic units of individual and total PAHs in sediments from some locations in Presque Isle Bay, it is surprising that benthic communities were altered to only a small degree. The lack of effects as great as predicted from the LEL comparisons may be due in part to the forms of pyrogenic PAHs in the bay sediments. Most of the benzo(a)pyrene and other high molecular weight PAHs in aquatic sediments are derived from combustion sources and so are present in a not readily exchangeable form, primarily associated with particles. They are bound to sediment particles more strongly than predicted by equilibrium partitioning theory. Readman *et al.* (53) used a linear free energy sediment-water exchange model to simulate the partitioning and exchange of individual unalkylated (primarily pyrogenic) PAHs between the surface mixed layer of sediment and the overlying water of the Tamar River Estuary, England. They showed that the concentrations of PAHs in the sediments are between two and five orders of magnitude greater than those expected from equilibrium partitioning with concentrations of PAHs in the associated water. These results indicate that most of the pyrogenic PAHs in the sediments are chemically inert. Sorptive exchange with the water and, therefore, bioavailability of the PAHs to marine organisms appears to be restricted by the existence of occluded and other micro-morphologically inert forms of humic acid-bound or particle-bound PAHs. Similar results have been obtained for sediments in Boston Harbor, Massachusetts (54).

Arsenic concentrations in some surface sediments also were higher than the LEL value of 6.0 mg/kg dry wt (7). In particular, sediments from Stations 5 and 6 of the Presque Isle Bay tumor study contained arsenic concentrations ranging from 20.1 to 126.6 mg/kg and 49.3 to 199 mg/kg, respectively. These arsenic concentrations correspond to toxic units values ranging from 3.35 to 33.2. Station 5 is in the central basin of the bay; station 6 is close to shore east of Cascade Creek. The chemical form(s) and bioavailability of arsenic in the sediments is not known; therefore, it is uncertain if arsenic may be contributing to the altered benthic faunal communities at these locations. Large seasonal variations in arsenic concentrations in the sediments (7) and the likelihood that the sediments are anoxic at least for part of the year suggests that the sediment arsenic is relatively mobile and is readily released from the sediments in soluble, potentially bioavailable forms on a seasonal basis. In anoxic freshwater sediments which usually do not contain high concentrations of sulfur, arsenic is reduced to arsenite and usually is present as arsenolite ( $\text{As}_2\text{O}_3$ ) which is moderately toxic and tends to migrate upward to be released into the overlying water column in a bioavailable form (42). Thus, high concentrations of arsenic in Presque Isle Bay sediments could contribute to altered benthic community structure in some parts of the bay.



### 4.3 PLANKTON CHARACTERIZATION

A plankton population assessment was also performed for the 1994 Presque Isle Bay sediment quality evaluation performed by Battelle as EPA Work Assignment 107 (3); the abundance, classification, and diversity of both the phytoplankton and zooplankton communities were determined. The samples were collected at four stations within the Bay. The stations were PIB10 near the south shore east of Cascade Creek, PIB12 near the north shore of the Bay, PIB18 near the mouth of Mill Creek, and PIB20 in Misery Bay.

The phytoplankton and zooplankton communities of Presque Isle Bay are fairly typical of those in near-shore areas of Lake Erie. Differences in community structure among the four stations can be attributed to differences in water depth and particularly abundance of attached macrophytes. The recent introduction of the zebra mussel to the bay may have contributed to a decline in phytoplankton abundance, particularly at shallow locations in the bay. Reduction of phytoplankton abundance probably has led to a reduction in the abundance of zooplankton that feed on phytoplankton. The plankton community in Presque Isle Bay is typical of a eutrophic freshwater system. The slow flushing rate of the bay combined with large inputs of organic matter, as indicated by the high concentrations of organic matter in most sediments, contribute to eutrophication of the bay. There is no evidence that phytoplankton or zooplankton communities have been adversely affected by chemical contamination of sediments in the bay. There are no reliable data on concentrations of potentially toxic metals and organic contaminants in the bay waters. Therefore, it is not possible to determine if concentrations of any contaminants are high enough in solution in the water column to cause adverse effects in the plankton community.

### 4.4 TOXICITY STUDY

The toxicity of surface sediments collected at 12 stations was measured using a 10-day static renewal acute toxicity test with the amphipod *Hyaella azteca*. The toxicity study was a part of the 1994 Presque Isle Bay sediment quality evaluation performed by Battelle as EPA Work Assignment 107 (3).

Sediments from four stations caused mortality among the amphipods that was significantly greater than that among controls. These stations were PIB01 in the southwest corner of the bay, PIB07 in the central basin, PIB08 near the north shore, and PIB20 in Misery Bay. There was no correlation between toxicity of the sediment to benthic amphipods and concentrations in the sediment of total PAHs or other organic contaminants. No attempt was made to correlate sediment toxicity to arsenic concentrations. The sediment toxicity stations and the tumor study stations (6) where sediment arsenic was measured do not correspond well, so it is difficult to make comparisons. However, toxicity study Station PIB11 corresponds approximately to tumor study Station 5. Station 5 sediments contained 20.1 to 126 mg/kg arsenic. Survival of amphipods in Station PIB11 sediment was not statistically significantly different from survival of amphipods in control sediments. Therefore, sediment arsenic does not appear to be contributing to the observed sediment toxicity. The only significant correlation observed was between sediment toxicity and percent total organic carbon in the sediments (3). During sediment storage, organic matter in sediments may break down releasing ammonia. The ammonia is highly toxic to benthic amphipods and may have contributed to the observed toxicity of the four sediments to the amphipods.

Earlier sediment bioassays performed by the US Army Corps of Engineers for dredged material from the inner and outer harbor channels and areas around the docks in Presque Isle Bay showed low to moderate toxicity (2). Sediments from the harbor basin were the most toxic. Subsequent analyses of sediments from this area have revealed high concentrations of PAHs at a few sites. However, the sediments evaluated by



the Army Corps of Engineers were subsequently dredged and disposed of offsite, so comparability to sediments now in the harbor basin is unlikely.

The lack of correlation between concentrations of total PAHs and possibly arsenic in the sediments and the toxicity of the sediments to benthic amphipods suggests that the PAHs and arsenic in the sediments were not present in mobile, bioavailable forms. Landrum *et al.* (55) have shown that the bioavailability of PAHs from Great Lakes sediments decreases as the length of time the sediments have been contaminated increases. This effect was greater for high molecular weight than low molecular weight PAHs. The PAHs apparently become tightly bound to sediment organic matter and are not easily released into solution in the sediment interstitial water or overlying water column (56). As discussed above pyrogenic PAHs, because of their tight binding to soot particles, also have a much lower than predicted bioavailability to benthic organisms (57). Thus, the PAHs in Presque Isle Bay sediments may have a limited bioavailability to benthic marine organisms. These results suggest that percent clay and TOC in sediments, but not PAH concentrations, were the main contributors to altered community and apparent toxicity of Presque Isle Bay sediments.



### 5.0 CONCLUSIONS

PAH have been identified as a class of contaminants of potential concern for the Presque Isle Bay sedimentary environment. USEPA requested that Battelle review several documents and data concerning PAH contamination of bay sediments and incidences of tumors in fish from the bay to gain a better understanding of the PAH contamination of Presque Isle Bay and its possible effects.

PAH concentrations in Presque Isle Bay surface sediment are higher than in sediments from most coastal environments, including those of the Great Lakes. However, the PAH concentrations are not surprisingly or uncommonly high considering the urban nature of the area, and the physical characteristics of the Bay. For instance, the sediment PAH concentrations in Presque Isle Bay are comparable to the concentrations measured in sediments from Boston Harbor and in much of Narragansett Bay. However, concentrations of total PAHs in sediments from many locations in the southern and central parts of Presque Isle Bay are higher than the "high" concentration of total PAHs (1.73 mg/kg dry wt) identified in coastal sediments, including those from the Great Lakes, in the NOAA National Status and Trends Program.

There is a relationship between concentrations of PAH metabolites in the bile and the incidence of surface and liver tumors in brown bullheads from Presque Isle Bay. However, this relationship is partially obscured by the direct correlation between the incidence of tumors and the ages of the fish. However, the PAH metabolite concentrations measured in fish from Presque Isle Bay (and Eaton Reservoir) appear to be no higher than concentrations in fish bile from other urban bays and estuaries. PAH metabolite concentrations and tumor incidences were much lower for bowfin than for brown bullheads from Presque Isle Bay and the closely-related yellow bullheads had lower tumor incidences than brown bullheads, suggesting large inter-species differences in ability to metabolize PAH to produce mutagenic metabolites. The recent publication by Yuan *et al.* (34) supports this hypothesis.

The relationship between concentrations of PAH metabolites, even those of carcinogenic PAHs such as benzo(a)pyrene, in bile and tumors in fish is unclear. The PAH metabolite data demonstrate recent exposure of the fish to bioavailable forms of PAHs in the ambient water, food, and sediments, but the concentrations of metabolites in bile is only a moderate indication of the risk of tumors in the fish. However, the available data do support the hypothesis that PAH may contribute to the high incidence of tumors in bullheads in Presque Isle Bay.

Benthic communities and plankton communities in Presque Isle Bay are typical of those in coastal waters of Lake Erie. Benthic communities were altered slightly in a few locations where concentrations of sediment PAHs were high. The sediments containing the highest concentrations of PAHs also contained the highest concentrations of clay. The benthic communities may have been affected more by low sediment grain size than by high concentrations of PAHs. Sediment bioassays did not indicate that sediments containing high concentrations of PAHs were more toxic than sediments containing low PAH concentrations. The PAHs in the sediments apparently are tightly bound to sediment organic matter and inert particles, rendering them only slightly bioavailable to benthic fauna. Sediment grain size probably was the main factor causing differences in benthic community structure in different regions of the bay.

Several other chemical contaminants have been measured in sediments from Presque Isle Bay as part of several studies. Only arsenic was present in some sediments at concentrations high enough that it could be toxic to benthic organisms. The forms of arsenic in the sediment are not known. However, if the sediments are anoxic or hypoxic and do not contain high concentrations of sulfur, the arsenic may be present in a mobile, bioavailable form that may be toxic to benthic organisms. There are several environmental toxins



## CONCLUSIONS

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that were not measured in sediments from Presque Isle Bay that could have contributed to the high incidence of tumors in brown bullheads from the bay. The most prominent of these are polychlorinated dibenzodioxins and dibenzofurans. These compounds are highly mutagenic and toxic. If present, they could contribute to the production of tumors in brown bullheads.

The available evidence indicates that PAHs and possibly arsenic and nitrosamines in sediments may contribute to the high incidence of tumors in brown bullheads and the altered benthic community structure in some parts of the bay. Other contaminants, nutrient enrichment (eutrophication), and the biological characteristics of brown bullheads could also contribute to these biological effects.

Most of the PAHs in sediments from Presque Isle Bay are of pyrogenic origin. Petrogenic PAHs also are present in the sediments. The pyrogenic PAHs probably are derived from deposition of airborne particles (soot) from various combustion sources, runoff from roadways particularly via combined sewer overflows (CSOs), and from various historic or current industrial sources, such as iron and steel plants, coke ovens, coal-fired power plants, and manufactured gas plants. Engine exhaust from small boats in the bay may also contribute large amounts of pyrogenic and petrogenic PAHs to the sediments. The lower molecular weight, petrogenic PAHs usually are derived in urban estuaries from runoff from land and treated sewage effluents as well as spills of refined petroleum products on the land. The PAH concentrations observed in sediments from inside the bay compared to those from outside the Bay, and the apparent concentration gradients in the Bay away from the City of Erie, clearly indicate that the sources of PAHs are on the south, city side of the bay.

The data in the Battelle report to EPA indicate similar general locations for the elevated concentrations of PAHs in sediments as earlier reports have indicated. The data do not indicate the presence of major point sources of pollution, other than the two creeks entering the south side of the bay. The area near the mouth of Cascade Creek clearly had elevated PAH, and the data suggest that Mill Creek/Garrison Run is another major source of PAH. These two creeks, the docking operations, and other direct discharges on the city side probably are today's main contributors of PAH to Presque Isle bay sediments.

Until late 1990, the Pennsylvania Electric Company operated the Front Street Station, a coal fired power plant, on the southern shore of the eastern boat basin (1). Coal pile runoff and atmospheric deposition from this plant probably have contributed PAHs to the Bay until recently. Several old industrial sites and waste disposal locations, such as old landfills in town and the Old United Tank Farm, are also potential sources for PAH runoff. The past coking operations at what is currently the Erie Coke plant (previously Kopper's Coke and Interlake Steel Corporation) at the Pennsylvania Fuel Gas site, has produced large amounts of coke tar, some of which could still be present in land fills at the site. The Erie Coke plant is still in operation and a potential active source. Coal tars produced by coal coking contain very high concentrations of pyrogenic PAHs and could clearly be a source of some of the PAHs in the area of Mill Creek. The GAF asphalt shingles plant is another manufacturer on the shore of the Bay that handles large quantities of materials that are high in PAH (asphalt). The Erie wastewater treatment plant sludge incinerator flue gas discharge is another potential source of PAHs. However, the operations at these possible point sources may be such that the PAH are well contained, and most of the PAHs being discharged to Presque Isle Bay probably are from nonpoint sources.

Because most of the drainage basin for Presque Isle Bay is a developed, urban area, the Bay receives high concentrations of nonpoint pollutants from urban runoff, including untreated industrial, commercial, and residential wastewater which escapes from CSOs in the City's sewer systems (1). Many portions of the City's wastewater collection system contain CSOs that receive surface runoff during and after precipitation events and discharge it to the creeks and bay. The inflow of surface runoff often exceeds the capacity of



the treatment plant, and untreated wastewater escapes to the Bay through dozens of CSOs, the majority of which discharge to the Mill Creek/Garrison Run drainage system. Additionally, separate storm sewers exist which convey surface runoff directly to the Bay or to tributary streams draining to Presque Isle Bay. A surface sheen is often observed at the mouth of Mill Creek, where elevated PAH concentrations are found in sediments [and where brown bullheads congregate (1, 2)], indicating sources of PAHs upstream that are discharged to the Bay through Mill Creek.

It is important not to underestimate the potential significance of pollution that can enter Presque Isle Bay in urban runoff, storm drains, and an old CSO system. Large numbers of storm drains and CSOs discharge directly to Presque Isle Bay or indirectly through Mill Creek/Garrison Run and Cascade Creek. These two streams contribute two-thirds of the water flow to Presque Isle Bay, much of which may be heavily contaminated with urban (and possibly industrial) pollutants.

This probable source of contamination to the Bay has been addressed through the 1989 Consent Decree between the Pennsylvania Department of Environmental Resources and the City of Erie, which required a series of remedial actions and future planning for the sewerage disposal needs of Erie and surrounding municipalities. The multi phase sewerage system upgrade includes the construction of a new sewerage treatment plant outfall, construction of a large overflow retention facility, construction to eliminate CSOs, and improvements in the handling of wet weather flow capacity constraints. Although all the technical details of the infrastructure improvements have not been finalized, it is clear that the intent is to significantly reduce the pollution being discharged to Presque Isle Bay through the sewerage system.

Based on the available data one cannot conclusively determine when the "peak" of PAH input to the Bay occurred, or that, indeed, the peak has occurred. However, unless there are significant unidentified discharges of PAH from a few undetermined point sources, such as the Erie Coke plant, it is likely that the time of greatest PAH contamination of surface sediments in Presque Isle Bay is past and that, for the most part, progressively cleaner sediments are being deposited in the Bay. The anticipated CSO system improvements should further reduce the contaminant levels in sediments deposited in the years to come. Nevertheless, significant amounts of PAH are part of today's urban environment and it is unlikely that the PAH concentrations in the surface sediment in Presque Isle Bay will decline rapidly in the near future, particularly considering the physical characteristics of Presque Isle Bay (i.e., the significant urban drainage into the Bay and the slow flushing of the Bay).

None of the information reviewed for this report suggests that direct remediation of the Bay sediment would improve the environmental quality of the Bay. On the contrary, this could potentially cause significant acute (and possibly long-term) damage to this relatively confined system. The best approach for improving environmental quality in the bay is through actions to decrease mass loadings to the bay of chemical contaminants, particularly PAH, in point-source runoff from Erie, PA. The infrastructure improvements that are planned for the city of Erie, are the most appropriate and significant steps that can be taken to produce long term improvements to the quality of Presque Isle Bay sediments. One should, however, not expect anything but a fairly slow recovery of the Presque Isle Bay environment, considering the physical characteristics of the Bay and the associated slow flushing time.

### *Recommendations*

The CSO and other infrastructure improvements that are planned for the city of Erie are likely to produce significant improvements in Presque Isle Bay sediment quality in the long term, and may be sufficient to restore the Bay to a desirable level of environmental quality. Additional environmental investigations may therefore not be warranted at this point, but the following are recommendations and other possible studies for consideration.



- The proposed infrastructure improvements include the possible segregation of CSO flow from the “standard” storm drain flow. The sewerage containing CSO streams would be treated at the sewerage treatment plant while the flow from urban runoff would continue to be discharged into Presque Isle Bay without treatment. While this approach would likely remove the majority of the contamination currently discharged to the Bay, a considerable (and unknown) amount of PAH could continue to be diverted to the Bay. Street and other urban runoff during storm events contain significant amounts of PAH, most of which is typically flushed through the system in the first 15 to 30 minutes. If the improved sewerage and drainage system could be constructed to at least accommodate treatment of this initial “flush”, considerable additional reductions in PAH inputs to the Bay could potentially be realized. This could possibly be done by constructing a holding facility to capture the initial runoff flow during a storm (which should not allow for dilution of the initial volume once the holding facility is full), which could then be gradually diverted to the treatment plant. Alternatively, it may be feasible to plan on treating the storm drain flow as the normal mode of operation, and only divert the storm runoff stream (but **not** combined sewerage) when the maximum capacity of the plant is reached — it is possible that this would allow for treatment of the runoff flow from the most critical initial 15–30 minutes, before storm water diversions would be necessary.
- It may be useful to confirm that PAH inputs have indeed peaked by better mapping the history of PAH input. This could be accomplished by collecting sediment cores to at least 100 cm in length from 6–8 locations (for dating and PAH analysis), and analyzing them in sections of about 10 years/sample back to 1930, and in 50 year segments before that. Arsenic speciation, and possibly dioxin, analysis of the surface sediments could be included to provide additional potentially valuable information.
- The surprisingly similar tumor rates and PAH metabolite levels in brown bullheads from Presque Isle Bay and the supposedly uncontaminated Eaton Reservoir warrants further study. Such additional studies should include comparable chemical analyses of the sediments in both locations, as well as studies of the fish.
- The brown bullhead population in Presque Isle Bay is composed primarily of old individuals, assuming a representative cross section of the fish population was collected in the latest PADEP tumor study (7); recruitment of juveniles to the bay seems to be low. It is possible that chemicals in the bay are causing reproductive impairment. Studies of fish reproduction and recruitment to the Bay could be performed to gain further understanding of these observations. DNA adducts of PAHs could be analyzed in brown bullhead tumors as a clue to the causes of tumors in the fish.



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**Appendix A. WA107 Surface Sediment PAH Data**



WA107 - FINAL DATA  
Battelle Ocean Sciences

PAH IN SURFACE SEDIMENT

Station ID	PIB01	PIB02	PIB02-D	PIB03	PIB03-D	PIB04	PIB05	PIB06	PIB07	PIB08	PIB09	PIB10
Battelle ID	QJ77	QJ78	QJ83	QJ79	QJ80	QJ81	QJ82	QJ84	QJ85	QJ86	QJ87	QJ88
Depth (ft)	28-Jun-94	28-Jun-94	28-Jun-94	28-Jun-94	28-Jun-94	28-Jun-94	06-Aug-94	28-Jun-94	28-Jun-94	28-Jun-94	28-Jun-94	29-Jun-94
Matrix	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
Sample Size (g)	20.02	17.82	19.99	34.22	33.78	19.82	19.03	19.12	17.71	15.91	20.37	22.43
Percent Moisture (%)	61.3	64.8	60.4	33.6	34.3	60.9	62.4	62.1	64.9	68.2	59.4	55.4
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
naphthalene	0.1243	0.1785	0.1698	0.0117	0.0119	0.1958	0.2296	0.2229	0.2160	0.2165	0.2622	0.2921
C1-naphthalenes	0.1508	0.2144	0.2142	0.0154	0.0162	0.3199	0.3199	0.2925	0.2687	0.3042	0.3977	0.4673
C2-naphthalenes	0.2131	0.3118	0.3224	0.0267	0.0274	0.3486	0.4738	0.4318	0.3771	0.4552	0.5506	0.6297
C3-naphthalenes	0.2319	0.3306	0.3414	0.0366	0.0396	0.3690	0.4601	0.4699	0.3848	0.4522	0.5577	0.6624
C4-naphthalenes	0.2340	0.3388	0.3485	0.0472	0.0551	0.4154	0.3433	0.4296	0.3782	0.4197	0.4571	0.5980
biphenyl	0.0280	0.0418	0.0432	0.0031	0.0027	0.0458	0.0481	0.0499	0.0471	0.0509	0.0570	0.0562
acenaphthylene	0.0640	0.0904	0.0999	0.0063	0.0073	0.1021	0.1122	0.2618	0.1093	0.1422	0.1126	0.1389
acenaphthene	0.0644	0.0916	0.0888	0.0048	0.0045	0.1377	0.0956	0.0964	0.0878	0.0812	0.1806	0.1600
dibenzofuran	0.0775	0.1002	0.0952	0.0076	0.0073	0.1375	0.1417	0.1276	0.1265	0.1074	0.1725	0.1738
fluorene	0.1186	0.1545	0.1497	0.0133	0.0144	0.1989	0.1711	0.1639	0.1626	0.1318	0.2155	0.2305
C1-fluorenes	0.0679	0.0859	0.0928	0.0089	0.0117	0.1122	0.1084	0.1189	0.0938	0.1000	0.1416	0.1596
C2-fluorenes	0.1347	0.1572	0.1662	0.0308	0.0303	0.2228	0.2228	0.2128	0.1873	0.1978	0.2594	0.2596
C3-fluorenes	0.2609	0.3655	0.3365	0.0495	0.0528	0.3849	0.4798	0.4387	0.3321	0.3856	0.4660	0.4847
phenanthrene	0.6524	0.9314	0.9164	0.0652	0.0668	1.1982	1.0875	0.9876	0.8594	0.7920	1.8295	2.0219
anthracene	0.1372	0.2003	0.2068	0.0131	0.0120	0.3248	0.3147	0.3256	0.2482	0.1990	0.4081	0.4669
C1-phenanthrenes/anthracenes	0.4059	0.5622	0.5563	0.0615	0.0636	0.7808	0.7713	0.6954	0.6251	0.8073	1.0209	1.1620
C2-phenanthrenes/anthracenes	0.4272	0.5629	0.5497	0.0923	0.0912	0.7298	0.8479	0.7413	0.6830	0.6523	1.0191	1.0243
C3-phenanthrenes/anthracenes	0.3791	0.4307	0.4318	0.0884	0.0934	0.5643	0.8246	0.6741	0.5855	0.5644	0.6953	0.7549
C4-phenanthrenes/anthracenes	0.3103	0.4303	0.5004	0.0738	0.0772	0.5949	0.8509	0.5914	0.6405	0.4435	0.5947	0.8997
dibenzothiophene	0.0564	0.0790	0.0771	0.0065	0.0066	0.1086	0.0939	0.0996	0.0849	0.0782	0.1293	0.1399
C1-dibenzothiophenes	0.0612	0.0802	0.0794	0.0109	0.0128	0.1074	0.1089	0.1003	0.0857	0.0826	0.1093	0.1241
C2-dibenzothiophenes	0.1087	0.1228	0.1327	0.0238	0.0255	0.1409	0.2320	0.1970	0.1650	0.1653	0.2664	0.2396
C3-dibenzothiophenes	0.1176	0.1365	0.1498	0.0300	0.0305	0.2036	0.2778	0.2633	0.2144	0.2266	0.2867	0.2876
fluoranthene	1.2406	1.7056	2.3126	0.1325	0.1386	2.1530	2.4896	2.1234	2.6662	1.7404	3.6683	3.6815
pyrene	1.2874	1.8055	2.5121	0.1412	0.1467	1.9182	2.4121	2.3451	3.2150	1.9352	3.4408	3.7654
C1-fluoranthenes/pyrenes	0.7141	0.9557	0.9333	0.0638	0.0913	1.2691	1.6004	1.3320	1.1763	1.0661	1.4081	1.8984
benz[a]anthracene	0.6152	0.8720	0.8371	0.0568	0.0523	1.1887	1.1516	1.1079	1.0662	0.8790	1.9373	1.9803
chrysene	0.7771	1.0377	0.9769	0.0882	0.0903	1.2300	1.3581	1.2419	1.2383	1.0548	1.9956	2.2475
C1-chrysenes	0.3969	0.4562	0.4771	0.0488	0.0498	0.7081	0.8345	0.7301	0.7141	0.5701	1.1061	0.9460
C2-chrysenes	0.3325	0.3930	0.4213	0.0522	0.0555	0.5273	0.7254	0.6160	0.6485	0.5580	1.1806	0.7570
C3-chrysenes	0.2035	0.2512	0.2295	0.0345	0.0428	0.3357	0.5260	0.3909	0.4165	0.3404	0.6263	0.4116
C4-chrysenes	0.1625	0.1682	0.1436	0.0187	0.0191	0.2115	0.3239	0.3354	0.2969	0.2882	0.6758	0.4166
benzo[b]fluoranthene	1.2829	1.7485	1.6333	0.1310	0.1298	2.2845	2.3619	2.3243	2.1760	1.9428	3.3510	3.6800
benzo[k]fluoranthene	0.3611	0.5046	0.4679	0.0388	0.0392	0.6311	0.7413	0.6900	0.5943	0.5790	0.7837	0.9668
benzo[e]pyrene	0.6436	0.8742	0.8112	0.0700	0.0703	1.0743	1.2608	1.1879	1.1369	0.9761	1.6043	1.4920
benzo[a]pyrene	0.7147	0.9991	0.9456	0.0648	0.0633	1.2601	1.3535	1.3486	1.2959	1.0872	2.0410	2.0714
perylene	0.3305	0.3798	0.3508	0.0855	0.0867	0.5044	0.5019	0.4985	0.4964	0.4132	0.5921	0.5544
indeno[1,2,3-c,d]pyrene	0.7361	0.9825	0.9520	0.0743	0.0744	1.3062	1.3731	1.4086	1.3419	1.1496	2.7570	1.7590
dibenz[a,h]anthracene	0.1694	0.2330	0.2238	0.0156	0.0156	0.3123	0.3533	0.3171	0.3122	0.2692	0.9997	0.4003
benzofg,h,i]perylene	0.6161	0.8452	0.8077	0.0659	0.0669	1.0912	1.1641	1.2230	1.1014	0.9702	2.2959	1.4371
Total PAH (all):	15.01	20.21	21.10	1.93	1.99	25.66	29.15	27.23	26.86	22.68	40.65	39.90
Total PAH (16 EPA):	8.96	12.38	13.30	0.92	0.93	15.53	16.77	16.19	16.69	13.17	26.28	25.30



WA107 - FINAL DATA  
Battelle Ocean Sciences

PAH IN SURFACE SEDIMENT

Station ID	PIB11	PIB12	PIB13	PIB14	PIB15	PIB16	PIB18	PIB19	PIB20	PIB21	PIB22
Bottle ID	OJ89	OJ90	OJ91	OJ92	OJ93	OJ94	OJ95	OJ96	OJ97	OJ98	OJ99
Depth (ft)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Analysis Date	06-Aug-94	29-Jun-94	29-Jun-94	30-Jun-94	30-Jun-94	30-Jun-94	30-Jun-94	01-Jul-94	01-Jul-94	21-Jun-94	01-Jul-94
Matrix	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
Sample Size (g)	18.78	16.34	20.29	20.30	21.88	20.83	40.65	32.82	10.06	40.48	39.29
Percent Moisture (%)	63.5	67.6	59.4	59.9	56.8	58.6	19.7	34.4	70.7	20.7	21.6
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
naphthalene	0.2277	0.1532	0.2470	0.3418	0.2264	0.2266	0.0031	0.3419	0.1279	0.0017	0.0077
C1-naphthalenes	0.2628	0.2013	0.2895	0.3773	0.2244	0.2306	0.0034	0.1545	0.1314	0.0013	0.0089
C2-naphthalenes	0.4260	0.2894	0.4193	0.5408	0.3482	0.3351	0.0066	0.2202	0.1905	0.0016	0.0152
C3-naphthalenes	0.4339	0.2918	0.4361	0.5621	0.3730	0.3561	0.0136	0.2431	0.1991	0.0033	0.0269
C4-naphthalenes	0.4709	0.2880	0.4418	0.4505	0.3419	0.3612	0.0186	0.1843	0.1544	0.0037	0.0350
biphenyl	0.0395	0.0342	0.0503	0.0667	0.0382	0.0401	0.0009	0.0254	0.0224	0.0000	0.0013
acenaphthylene	0.0882	0.0947	0.1172	0.1419	0.1048	0.1096	0.0065	0.0560	0.0636	0.0007	0.0019
acenaphthene	0.0811	0.0629	0.0920	0.1135	0.0878	0.0677	0.0059	0.0461	0.0274	0.0005	0.0011
dibenzofuran	0.1255	0.0864	0.1152	0.1169	0.0976	0.1006	0.0042	0.0793	0.0497	0.0005	0.0032
fluorene	0.1702	0.1152	0.1409	0.1664	0.1352	0.1124	0.0082	0.1031	0.0581	0.0010	0.0032
C1-fluorenes	0.1172	0.0885	0.1030	0.1184	0.0953	0.0926	0.0056	0.0448	0.0513	0.0011	0.0052
C2-fluorenes	0.2473	0.1466	0.1982	0.2160	0.1810	0.1551	0.0107	0.0923	0.0951	0.0043	0.0163
C3-fluorenes	0.5473	0.2723	0.3129	0.3509	0.3001	0.2894	0.0181	0.1617	0.1709	0.0079	0.0379
phenanthrene	1.0241	0.6790	0.8311	1.1624	0.9107	0.6845	0.0787	0.9909	0.3346	0.0054	0.0216
anthracene	0.2454	0.1634	0.2495	0.2864	0.2483	0.2106	0.0196	0.1717	0.0915	0.0018	0.0039
C1-phenanthrenes/anthracenes	0.7111	0.4580	0.5925	0.7411	0.5855	0.5309	0.0410	0.3433	0.2840	0.0061	0.0301
C2-phenanthrenes/anthracenes	0.7314	0.5194	0.6484	0.7212	0.6025	0.5850	0.0364	0.3157	0.3164	0.0112	0.0476
C3-phenanthrenes/anthracenes	0.8691	0.4464	0.4321	0.5520	0.5313	0.5241	0.0293	0.2314	0.2917	0.0128	0.0527
C4-phenanthrenes/anthracenes	0.7646	0.3816	0.4157	0.6583	0.5248	0.4054	0.0343	0.1969	0.2179	0.0075	0.0319
dibenzothiophene	0.0908	0.0595	0.0801	0.0888	0.0837	0.0712	0.0055	0.0521	0.0305	0.0006	0.0028
C1-dibenzothiophenes	0.1006	0.0639	0.0609	0.0715	0.0623	0.0515	0.0051	0.0304	0.0373	0.0012	0.0062
C2-dibenzothiophenes	0.2322	0.1321	0.1750	0.1824	0.1651	0.1610	0.0103	0.0739	0.0913	0.0045	0.0144
C3-dibenzothiophenes	0.3213	0.1545	0.1883	0.1893	0.2040	0.2011	0.0123	0.0722	0.1199	0.0043	0.0168
fluoranthene	2.0061	1.4552	1.6774	2.1582	2.1920	2.7715	0.1707	1.4129	0.6738	0.0129	0.0359
pyrene	2.2424	1.5859	1.8579	2.4126	1.9853	1.4978	0.1806	1.3257	0.7505	0.0126	0.0425
C1-fluoranthenes/pyrenes	1.5468	0.8301	0.8258	1.1804	1.1042	0.9374	0.0849	0.4663	0.4915	0.0076	0.0273
benz[a]anthracene	1.1588	0.7180	0.9613	1.2859	1.0026	0.7811	0.0907	0.5631	0.3928	0.0041	0.0154
chrysene	1.3812	0.9107	0.9921	1.4233	1.1584	0.7690	0.0962	0.6309	0.5077	0.0078	0.0296
C1-chrysenes	0.8839	0.4844	0.7160	0.7111	0.5713	0.5650	0.0399	0.2322	0.2942	0.0047	0.0207
C2-chrysenes	0.7220	0.4277	0.7273	0.5745	0.5108	0.5386	0.0326	0.1795	0.3068	0.0061	0.0290
C3-chrysenes	0.5893	0.2619	0.3916	0.3928	0.3113	0.3826	0.0195	0.1370	0.2118	0.0036	0.0209
C4-chrysenes	0.3119	0.2652	0.4370	0.3488	0.2487	0.3353	0.0185	0.1066	0.1594	0.0000	0.0195
benzo[b]fluoranthene	2.5818	1.6380	1.9709	2.3773	1.9210	1.3420	0.1527	0.8551	0.8040	0.0074	0.0290
benzo[k]fluoranthene	0.8281	0.4775	0.4111	0.6391	0.4997	0.3786	0.0500	0.2141	0.2385	0.0023	0.0078
benzo[e]pyrene	1.2491	0.8112	0.8227	1.1069	0.9156	0.6839	0.0725	0.3882	0.4102	0.0050	0.0177
benzo[a]pyrene	1.4515	0.9058	1.0115	1.4391	1.1176	0.8325	0.0964	0.5024	0.4397	0.0032	0.0136
perylene	0.5135	0.3198	0.3244	0.4421	0.3785	0.3438	0.0299	0.1681	0.1845	0.0091	0.0246
Indeno[1,2,3-c,d]pyrene	1.5461	0.8740	1.3326	1.3481	1.0157	1.0130	0.0861	0.4139	0.4570	0.0037	0.0140
dibenz[a,h]anthracene	0.4182	0.2224	0.5194	0.3292	0.2514	0.2549	0.0209	0.1067	0.1175	0.0010	0.0034
benzo[g,h,i]perylene	1.4355	0.8121	1.6855	1.1046	0.8301	0.8268	0.0705	0.3351	0.3982	0.0037	0.0137
Total PAH (all):	29.19	18.28	23.30	27.49	22.49	18.16	1.69	12.27	9.97	0.18	0.76
Total PAH (16 EPA):	16.89	10.97	14.10	16.73	13.69	9.88	1.14	8.07	5.48	0.07	0.24



## **Appendix B. WA107 Sediment Core PAH Data**



WA107 - FINAL DATA  
Battelle Ocean Sciences

PAH IN SEDIMENT CORES

Station ID	PIB01-C1	PIB01-C2	PIB03-C1	PIB03-C2	PIB04-C1	PIB04-C2	PIB05-C1	PIB05-C2	PIB06-C1	PIB06-C2	PIB07-C1	PIB07-C2	PIB08-C1
Bottle ID	O157-1	O158	O155	O151	O150	O156	O154	O179	O139	O132-R	O134	O133	O180
Depth (ft)	0.0 - 1.75	1.75 - 3.3	0.0 - 1.9	1.9 - 4.0	0.0 - 2.0	2.0 - 3.6	0.0 - 2.0	2.0 - 4.0	0.0 - 2.0	2.0 - 4.0	0.0 - 0.5	2.0 - 4.2	0.0 - 1.75
Analysis Date	3-Aug-94	2-Jul-94	2-Jul-94	2-Aug-94	2-Aug-94	2-Jul-94	3-Aug-94	12-Jul-94	3-Aug-94	11-Jul-94	12-Jul-94	12-Jul-94	2-Jul-94
Matrix	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
Sample Size (g)	30.16	39.14	19.32	40.59	30.94	34.42	24.92	35.86	30.80	33.26	21.06	31.46	23.04
Percent Moisture (%)	42.5	22.3	61.5	22.6	39.7	33.7	51.8	33.0	40.5	34.1	58.7	37.8	54.9
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
naphthalene	0.0385	0.0034	0.0915	0.0013	0.0194	0.0037	0.0585	0.0063	0.0454	0.0056	0.1890	0.0052	0.0505
C1-naphthalenes	0.0423	0.0098	0.1160	0.0028	0.0244	0.0106	0.0781	0.0171	0.0547	0.0149	0.2094	0.0148	0.0507
C2-naphthalenes	0.0571	0.0158	0.1999	0.0074	0.0342	0.0203	0.1019	0.0786	0.0690	0.0265	0.0408	0.0310	0.0613
C3-naphthalenes	0.0833	0.0281	0.2102	0.0151	0.0610	0.0329	0.1185	0.0786	0.0856	0.0663	0.3141	0.0664	0.0508
C4-naphthalenes	0.0840	0.0397	0.1638	0.0000	0.0596	0.0458	0.1326	0.1213	0.0873	0.1049	0.2598	0.1017	0.0413
biphenyl	0.0045	0.0003	0.0122	0.0000	0.0025	0.0008	0.0076	0.0000	0.0054	0.0000	0.0375	0.0019	0.0033
acenaphthylene	0.0148	0.0000	0.0421	0.0000	0.0042	0.0000	0.0225	0.0000	0.0143	0.0000	0.1086	0.0000	0.0138
acenaphthene	0.0112	0.0000	0.0526	0.0000	0.0054	0.0006	0.0171	0.0000	0.0096	0.0000	0.0461	0.0000	0.0177
dibenzofuran	0.0249	0.0019	0.0585	0.0000	0.0106	0.0048	0.0301	0.0035	0.0249	0.0043	0.0939	0.0037	0.0258
fluorene	0.0225	0.0007	0.0942	0.0016	0.0090	0.0025	0.0262	0.0014	0.0224	0.0000	0.0850	0.0011	0.0290
C1-fluorenes	0.0287	0.0056	0.0640	0.0060	0.0186	0.0175	0.0296	0.0121	0.0266	0.0000	0.0821	0.0136	0.0163
C2-fluorenes	0.0781	0.0248	0.0845	0.0000	0.0487	0.0429	0.0708	0.0586	0.0613	0.0000	0.1642	0.0430	0.0249
C3-fluorenes	0.1065	0.0504	0.2038	0.0000	0.0706	0.0560	0.1449	0.0896	0.1223	0.0000	0.3136	0.0724	0.0538
phenanthrene	0.0846	0.0060	0.3585	0.0068	0.0370	0.0183	0.1749	0.0119	0.0861	0.0136	0.3279	0.0104	0.1317
anthracene	0.0255	0.0008	0.0796	0.0000	0.0096	0.0010	0.0522	0.0000	0.0288	0.0000	0.1345	0.0000	0.0314
C1-phenanthrenes/anthracenes	0.1111	0.0271	0.2953	0.0168	0.0748	0.0583	0.1783	0.0592	0.1237	0.0587	0.3450	0.0545	0.0947
C2-phenanthrenes/anthracenes	0.1693	0.0738	0.3382	0.0349	0.1356	0.1065	0.2404	0.1277	0.1912	0.1116	0.4895	0.1084	0.1099
C3-phenanthrenes/anthracenes	0.1578	0.0841	0.2771	0.0382	0.1363	0.1020	0.2414	0.1529	0.1813	0.1533	0.4726	0.1131	0.0898
C4-phenanthrenes/anthracenes	0.1016	0.0604	0.2306	0.0201	0.0846	0.0521	0.1595	0.0922	0.1172	0.0930	0.3963	0.0748	0.0563
dibenzothiophene	0.0096	0.0028	0.0445	0.0011	0.0052	0.0039	0.0160	0.0031	0.0109	0.0035	0.0408	0.0024	0.0131
C1-dibenzothiophenes	0.0179	0.0082	0.0516	0.0039	0.0122	0.0148	0.0267	0.0157	0.0184	0.0153	0.0494	0.0135	0.0144
C2-dibenzothiophenes	0.0406	0.0236	0.0903	0.0000	0.0282	0.0243	0.0637	0.0345	0.0458	0.0367	0.1360	0.0293	0.0264
C3-dibenzothiophenes	0.0493	0.0231	0.1020	0.0000	0.0321	0.0208	0.0726	0.0363	0.0715	0.0396	0.1582	0.0293	0.0311
fluoranthene	0.2371	0.0055	0.9330	0.0036	0.1030	0.0079	0.4016	0.0058	0.2198	0.0057	1.0055	0.0056	0.3284
pyrene	0.1965	0.0079	0.8713	0.0056	0.0876	0.0080	0.3517	0.0081	0.1982	0.0065	0.7040	0.0061	0.2992
C1-fluoranthrenes/pyrenes	0.1340	0.0183	0.5651	0.0128	0.0692	0.0179	0.2443	0.0259	0.1580	0.0251	0.5290	0.0207	0.1498
benz[a]anthracene	0.1171	0.0063	0.4907	0.0017	0.0514	0.0039	0.2145	0.0020	0.1327	0.0000	0.5534	0.0000	0.1461
chrysene	0.1531	0.0259	0.6367	0.0104	0.0752	0.0246	0.2652	0.0268	0.1725	0.0205	0.6385	0.0210	0.1633
C1-chrysenes	0.1353	0.0368	0.3747	0.0159	0.0894	0.0308	0.2145	0.0409	0.1725	0.0317	0.7304	0.0284	0.1219
C2-chrysenes	0.1569	0.0713	0.3623	0.0267	0.1051	0.0560	0.2380	0.0879	0.2321	0.0682	0.9724	0.0653	0.1159
C3-chrysenes	0.0951	0.0415	0.2333	0.0160	0.0669	0.0294	0.1699	0.0615	0.1599	0.0504	0.6030	0.0453	0.0709
C4-chrysenes	0.0725	0.0292	0.1586	0.0000	0.0399	0.0266	0.1013	0.0396	0.1006	0.0000	0.5258	0.0249	0.0618
benzo[b]fluoranthene	0.2289	0.0072	0.8996	0.0033	0.1030	0.0078	0.3869	0.0086	0.2519	0.0065	1.1323	0.0068	0.2421
benzo[k]fluoranthene	0.0743	0.0012	0.3450	0.0009	0.0303	0.0012	0.1371	0.0010	0.0850	0.0000	0.3896	0.0008	0.0799
benzo[e]pyrene	0.1253	0.0129	0.5806	0.0049	0.0597	0.0109	0.2150	0.0133	0.1420	0.0100	0.6376	0.0095	0.1466
benzo[a]pyrene	0.1075	0.0028	0.6144	0.0012	0.0485	0.0019	0.2261	0.0017	0.1308	0.0000	0.6652	0.0000	0.1588
perylene	0.3774	0.3177	0.2744	0.0490	0.4424	0.3174	0.5270	0.6325	0.4754	0.4930	0.7201	0.4305	0.1972
indeno[1,2,3-c,d]pyrene	0.1178	0.0028	0.5612	0.0012	0.0550	0.0028	0.2039	0.0030	0.1322	0.0000	0.9590	0.0021	0.1300
dibenz[a,h]anthracene	0.0259	0.0011	0.1296	0.0000	0.0123	0.0010	0.0481	0.0010	0.0313	0.0000	0.2327	0.0000	0.0309
benzo[g,h,i]perylene	0.0896	0.0113	0.5490	0.0019	0.0413	0.0091	0.1537	0.0108	0.1275	0.0078	0.8458	0.0076	0.1520
Total PAH (all):	3.81	1.10	11.84	0.31	2.40	1.20	6.16	1.93	4.43	1.49	16.57	1.46	3.63
Total PAH (16 EPA):	1.54	0.08	6.75	0.04	0.69	0.09	2.74	0.09	1.69	0.07	8.02	0.07	2.00



WA107 - FINAL DATA  
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PAH IN SEDIMENT CORES

Station ID	PIB08-C2	PIB09-C1	PIB09-C2	PIB10-C1	PIB10-C2	PIB10-C3	PIB11-C1	PIB11-C2	PIB11-C3	PIB12-C1	PIB12-C2	PIB13-C1
Bottle ID	0187	0145	0149	0147	0146	0130	0143	0142	0138	0159	0161	0177
Depth (ft)	1.75 - 3.1	0.0 - 1.7	1.7 - 3.3	0.0 - 0.5	0.5 - 2.0	2.0 - 3.0	0.0 - 0.5	0.5 - 1.75	1.75 - 4.1	0.0 - 1.6	1.6 - 3.0	0.0 - 1.9
Analysis Date	26-Jul-94	3-Aug-94	2-Aug-94	3-Aug-94	3-Aug-94	12-Jul-94	3-Aug-94	3-Aug-94	2-Aug-94	2-Jul-94	2-Jul-94	12-Jul-94
Matrix	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
Sample Size (g)	36.02	21.35	33.62	32.87	28.86	34.37	20.59	22.28	31.85	23.51	37.29	22.57
Percent Moisture (%)	29.4	57.5	34.6	36.6	42.8	31.9	59.1	56.3	38.1	54.0	28.9	55.0
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
naphthalene	0.0046	0.3816	0.0200	0.4359	0.3531	0.0541	0.2800	0.2508	0.0121	0.1332	0.0010	0.2368
C1-naphthalenes	0.0122	0.4679	0.0322	0.6404	0.4456	0.0844	0.2505	0.2296	0.0200	0.1478	0.0008	0.2230
C2-naphthalenes	0.0269	0.5573	0.0441	0.6721	0.5669	0.1316	0.2932	0.2610	0.0341	0.2032	0.0000	0.2830
C3-naphthalenes	0.0694	0.6400	0.0690	0.6831	0.7079	0.1613	0.3421	0.3278	0.0625	0.1757	0.0000	0.2830
C4-naphthalenes	0.1229	0.5750	0.0798	0.4975	0.6720	0.1555	0.3269	0.2726	0.0808	0.1181	0.0000	0.1728
biphenyl	0.0000	0.0822	0.0030	0.0586	0.0656	0.0114	0.0434	0.0285	0.0030	0.0217	0.0000	0.0343
acenaphthylene	0.0000	0.1562	0.0028	0.0909	0.1850	0.0199	0.1565	0.0939	0.0026	0.0641	0.0003	0.0716
acenaphthene	0.0000	0.1275	0.0027	0.1386	0.3847	0.0278	0.1094	0.0348	0.0042	0.0375	0.0003	0.0660
dibenzofuran	0.0067	0.1717	0.0128	0.1841	0.2474	0.0393	0.1509	0.0945	0.0106	0.0710	0.0003	0.0692
fluorene	0.0062	0.2194	0.0076	0.2030	0.5675	0.0432	0.2077	0.0807	0.0070	0.0920	0.0004	0.1271
C1-fluorenes	0.0184	0.1627	0.0192	0.1230	0.2493	0.0346	0.1382	0.0654	0.0196	0.0490	0.0000	0.0792
C2-fluorenes	0.0589	0.3244	0.0489	0.1583	0.3568	0.0675	0.2370	0.2944	0.0542	0.0571	0.0000	0.1371
C3-fluorenes	0.1256	0.6438	0.0713	0.4147	0.6257	0.1192	0.5790	0.2944	0.0650	0.1785	0.0000	0.2459
phenanthrene	0.0218	1.1312	0.0332	1.5575	3.5300	0.2200	1.0879	0.3739	0.0287	0.3972	0.0011	0.3419
anthracene	0.0000	0.3584	0.0075	0.2942	0.7766	0.0498	0.3507	0.1412	0.0084	0.1001	0.0005	0.1112
C1-phenanthrenes/anthracenes	0.0911	0.8492	0.0811	0.7890	1.7378	0.1926	0.6607	0.3610	0.0760	0.2698	0.0020	0.3646
C2-phenanthrenes/anthracenes	0.1652	1.0295	0.1300	0.7418	1.3666	0.2290	0.6593	0.4728	0.1287	0.3282	0.0035	0.4423
C3-phenanthrenes/anthracenes	0.1974	1.0679	0.1300	0.5799	1.1821	0.1999	0.5745	0.5628	0.1415	0.2841	0.0049	0.4023
C4-phenanthrenes/anthracenes	0.1040	0.8357	0.0830	0.6350	1.4763	0.1427	0.5255	0.4717	0.0882	0.2020	0.0025	0.2766
dibenzothiophene	0.0043	0.1077	0.0055	0.0825	0.2021	0.0195	0.0961	0.0405	0.0056	0.0387	0.0002	0.0373
C1-dibenzothiophenes	0.0165	0.1346	0.0149	0.0830	0.1805	0.0234	0.0962	0.0555	0.0126	0.0352	0.0006	0.0494
C2-dibenzothiophenes	0.0389	0.3044	0.0300	0.1576	0.3179	0.0417	0.2130	0.1564	0.0291	0.0893	0.0000	0.1303
C3-dibenzothiophenes	0.0395	0.4248	0.0338	0.1861	0.3914	0.0405	0.2936	0.2709	0.0310	0.1082	0.0000	0.1526
fluoranthene	0.0131	2.2678	0.0725	2.5906	5.4155	0.3888	2.3510	0.7356	0.0672	0.5948	0.0028	1.0616
pyrene	0.0118	2.0688	0.0577	2.1388	4.3284	0.3100	2.1416	0.5996	0.0529	0.5845	0.0028	0.9425
C1-fluoranthenes/pyrenes	0.0305	1.7510	0.0635	1.3378	2.8076	0.2410	1.4377	0.4714	0.0602	0.4840	0.0030	0.5371
benz[a]anthracene	0.0034	1.2888	0.0348	1.2113	3.0663	0.1894	1.3576	0.5619	0.0418	0.3272	0.0013	0.4528
chrysene	0.0290	1.5430	0.0564	1.3944	3.4012	0.2258	1.6917	0.6382	0.0689	0.3790	0.0031	0.5460
C1-chrysenes	0.0398	1.3130	0.0699	0.7684	1.9711	0.2109	1.1013	0.7953	0.0790	0.3471	0.0028	0.5067
C2-chrysenes	0.0767	1.4545	0.1074	0.6300	1.6256	0.2439	1.0603	0.9902	0.0977	0.3656	0.0045	0.6264
C3-chrysenes	0.0686	1.0737	0.0658	0.4293	1.0348	0.1449	0.7849	0.7035	0.0644	0.2966	0.0000	0.3743
C4-chrysenes	0.0452	0.8241	0.0418	0.4555	0.8172	0.1140	0.6684	0.4700	0.0271	0.2366	0.0000	0.4765
benzo[k]fluoranthene	0.0096	2.3451	0.0592	2.0529	4.7434	0.3000	2.6283	0.9144	0.0642	0.5859	0.0026	0.8357
benzo[k]fluoranthene	0.0015	0.6729	0.0177	0.6817	1.6123	0.1075	0.5404	0.2674	0.0195	0.2116	0.0007	0.2633
benzo[e]pyrene	0.0124	1.2598	0.0386	1.0151	2.2042	0.1659	1.3753	0.4906	0.0409	0.3936	0.0019	0.4485
benzo[a]pyrene	0.0019	1.3760	0.0295	1.2437	2.8108	0.1890	1.4891	0.4330	0.0304	0.3094	0.0010	0.4818
perylene	0.0350	0.6070	0.0425	0.3665	0.8322	0.5193	0.4263	0.6731	0.5546	0.2819	0.0069	0.2786
indeno[1,2,3-c,d]pyrene	0.0035	1.2261	0.0300	1.0877	2.2578	0.1778	1.4564	0.5630	0.0294	0.3605	0.0014	0.5116
dibenz[a,h]anthracene	0.0011	0.3014	0.0068	0.2425	0.5734	0.0435	0.2591	0.1387	0.0073	0.0957	0.0004	0.1392
benzo[g,h,i]perylene	0.0097	1.1188	0.0253	0.9898	1.9025	0.1532	1.0065	0.4196	0.0262	0.3487	0.0017	0.4441
Total PAH (all):	1.88	33.25	2.17	28.04	57.99	5.83	29.45	14.99	2.26	9.41	0.06	13.30
Total PAH (16 EPA):	0.12	16.58	0.46	16.35	35.91	2.50	17.11	6.31	0.47	4.62	0.02	6.64



**WA107 - FINAL DATA**  
Battelle Ocean Sciences

**PAH IN SEDIMENT CORES**

Station ID	PIB13-C1(D)	PIB13-C2	PIB13-C2(D)	PIB14-C1	PIB14-C2	PIB14-C3	PIB15-C1	PIB15-C2	PIB15-C3	PIB18-C1	PIB18-C2	PIB18-C3
Battelle ID	O144	O178	O148	O175	O135	O137-R	O153	O152	O131-R	O172-1	O180-R	O176-R
Depth (ft)	0.0 - 1.9	1.9 - 4.0	1.9 - 4.0	0.0 - 1.0	1.25-2.0	2.0 - 4.25	0.0 - 1.83	1.83 - 4.0	8.0 - 6.75	0.0 - 0.5	0.5 - 2.0	2.0-3.5
Analysis Date	3-Aug-94	12-Jul-94	2-Aug-94	12-Jul-94	12-Jul-94	12-Jul-94	2-Aug-94	2-Aug-94	12-Jul-94	1-Sep-94	12-Jul-94	12-Jul-94
Matrix	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
Sample Size (g)	23.67	30.62	30.87	22.16	25.75	33.58	23.97	34.18	39.25	10.40	36.02	37.29
Percent Moisture (%)	54.3	40.8	41.4	56.6	50.1	33.6	52.8	34.2	24.6	79.6	29.7	25.6
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
naphthalene	0.2782	0.0591	0.0497	0.5103	0.2498	0.0133	0.2511	0.0068	0.0058	0.0906	0.0082	0.0032
C1-naphthalenes	0.2499	0.0503	0.0385	0.4765	0.2507	0.0274	0.2168	0.0150	0.0147	0.1046	0.0145	0.0086
C2-naphthalenes	0.2851	0.0782	0.0508	0.6319	0.3232	0.0531	0.2472	0.0273	0.0332	0.2125	0.0292	0.0206
C3-naphthalenes	0.3236	0.1106	0.0721	0.6484	0.3417	0.0914	0.2824	0.0470	0.0699	0.1557	0.0436	0.0425
C4-naphthalenes	0.3156	0.1326	0.0998	0.5457	0.3311	0.1124	0.2613	0.0556	0.1124	0.1112	0.0795	0.0625
biphenyl	0.0397	0.0117	0.0090	0.0876	0.0317	0.0027	0.0196	0.0000	0.0000	0.0096	0.0000	0.0000
acenaphthylene	0.1179	0.0209	0.0103	0.2281	0.0925	0.0000	0.0762	0.0000	0.0000	0.0601	0.0000	0.0000
acenaphthene	0.0661	0.0164	0.0134	0.1636	0.0635	0.0037	0.0500	0.0000	0.0000	0.0289	0.0038	0.0000
dibenzofuran	0.1138	0.0356	0.0306	0.1921	0.1328	0.0081	0.0904	0.0044	0.0035	0.0446	0.0038	0.0024
fluorene	0.1345	0.0318	0.0256	0.2594	0.1148	0.0061	0.0940	0.0032	0.0028	0.0699	0.0050	0.0000
C1-fluorenes	0.0911	0.0321	0.0270	0.1909	0.0900	0.0223	0.0822	0.0142	0.0190	0.0508	0.0153	0.0000
C2-fluorenes	0.1574	0.0675	0.0584	0.3122	0.1670	0.0585	0.2013	0.0336	0.0498	0.1216	0.0410	0.0000
C3-fluorenes	0.3360	0.1179	0.0940	0.6531	0.3559	0.0728	0.3123	0.0487	0.0823	0.1922	0.0643	0.0000
phenanthrene	0.6575	0.1251	0.0757	1.3175	0.3763	0.0305	0.4416	0.0178	0.0181	0.2862	0.0155	0.0082
anthracene	0.2246	0.0475	0.0312	0.3595	0.1658	0.0059	0.1635	0.0023	0.0000	0.0887	0.0000	0.0000
C1-phenanthrenes/anthracenes	0.4389	0.1692	0.1127	0.7656	0.3931	0.0839	0.4097	0.0535	0.0597	0.2538	0.0483	0.0328
C2-phenanthrenes/anthracenes	0.5220	0.2329	0.1372	0.8414	0.5675	0.1437	0.6032	0.0893	0.1169	0.2239	0.1013	0.0684
C3-phenanthrenes/anthracenes	0.4685	0.2121	0.1459	0.6541	0.6008	0.1495	0.6735	0.1009	0.1390	0.1792	0.1191	0.0832
C4-phenanthrenes/anthracenes	0.3737	0.1538	0.1028	0.5870	0.5163	0.0968	0.5828	0.0496	0.0864	0.2050	0.0707	0.0471
dibenzothiophene	0.0613	0.0165	0.0082	0.1066	0.0419	0.0047	0.0487	0.0032	0.0030	0.0192	0.0029	0.0018
C1-dibenzothiophenes	0.0684	0.0227	0.0141	0.1193	0.0534	0.0144	0.0636	0.0096	0.0132	0.0345	0.0111	0.0089
C2-dibenzothiophenes	0.1674	0.0459	0.0328	0.2394	0.1452	0.0301	0.1969	0.0277	0.0318	0.0853	0.0311	0.0193
C3-dibenzothiophenes	0.2232	0.0444	0.0413	0.2627	0.2277	0.0342	0.3173	0.0292	0.0302	0.0880	0.0334	0.0202
fluoranthene	1.2983	0.3188	0.2260	2.4517	0.9309	0.0562	1.0660	0.0181	0.0059	0.6233	0.0089	0.0043
pyrene	1.1455	0.2714	0.1859	2.1844	0.6245	0.0478	0.9529	0.0163	0.0068	0.5156	0.0094	0.0038
C1-fluoranthenes/pyrenes	0.8695	0.2185	0.1368	8.8489	0.5358	0.0731	7.7383	0.0306	0.0219	0.3595	0.0197	0.0128
benz[a]anthracene	0.7104	0.1789	0.1351	1.0990	0.6057	0.0338	0.6246	0.0084	0.0000	0.2298	0.0030	0.0000
chrysene	0.8557	0.1882	0.1517	1.3820	0.5711	0.0474	0.7441	0.0323	0.0237	0.3288	0.0215	0.0133
C1-chrysenes	0.7560	0.2200	0.1591	5.3458	0.8925	0.0661	0.6725	0.0428	0.0324	0.2141	0.0298	0.0197
C2-chrysenes	0.7895	0.2503	0.1885	5.8062	1.2652	0.0972	0.8077	0.0709	0.0728	0.1835	0.0646	0.0417
C3-chrysenes	0.5474	0.1454	0.1277	4.4219	0.8509	0.0655	0.5301	0.0489	0.0278	0.0857	0.0343	0.0271
C4-chrysenes	0.4086	0.1367	0.0816	4.0000	0.9393	0.0000	0.2786	0.0000	0.0000	0.0795	0.0000	0.0000
benzo[b]fluoranthene	1.2378	0.2743	0.2092	1.8289	1.0336	0.0495	1.0167	0.0179	0.0068	0.5736	0.0088	0.0039
benzo[k]fluoranthene	0.1780	0.0933	0.0696	0.6039	0.3001	0.0150	0.3394	0.0041	0.0000	0.1916	0.0028	0.0000
benzo[e]pyrene	0.5019	0.1541	0.1176	1.1356	0.5834	0.0309	0.5246	0.0167	0.0100	0.2729	0.0093	0.0057
benzo[a]pyrene	0.7355	0.1790	0.1199	1.1427	0.6519	0.0275	0.5893	0.0073	0.0000	0.2781	0.0028	0.0000
perylene	0.3207	0.5459	0.5198	0.5777	0.8026	0.5425	0.5160	0.4575	0.4137	0.2254	0.4303	0.2510
indeno[1,2,3-c,d]pyrene	0.6329	0.1577	0.1068	0.9831	0.8535	0.0228	0.5161	0.0068	0.0017	0.3165	0.0044	0.0014
dibenz[a,h]anthracene	0.1350	0.0403	0.0277	0.4965	0.2214	0.0059	0.1313	0.0000	0.0000	0.0646	0.0028	0.0000
benzo[g,h,i]perylene	0.3873	0.1399	0.0771	0.9106	0.7887	0.0250	0.4957	0.0128	0.0074	0.1689	0.0101	0.0049
Total PAH (all):	17.23	5.35	3.91	53.37	18.08	2.27	16.23	1.43	1.52	7.43	1.40	0.92
Total PAH (16 EPA):	8.80	2.14	1.51	15.92	7.64	0.39	7.55	0.15	0.08	3.92	0.11	0.04



WA107 - FINAL DATA  
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PAH IN SEDIMENT CORES

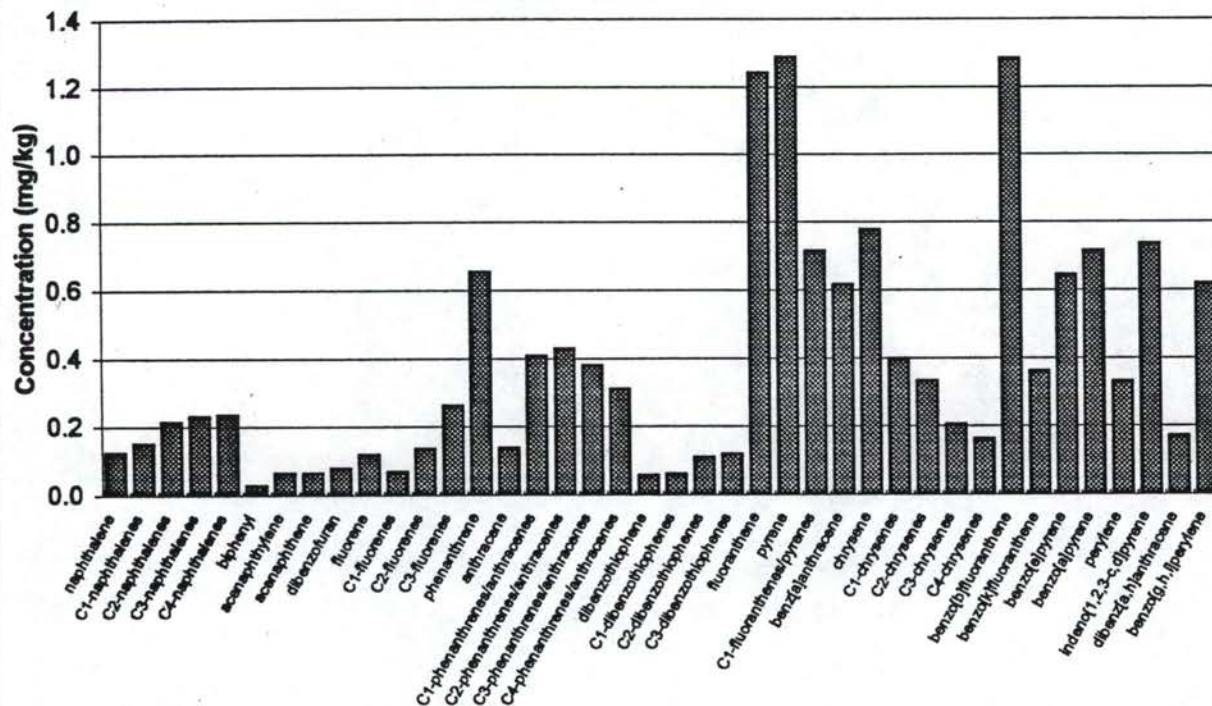
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Bottle ID	O171	O174	O140	O162	O164	O163	O168	O165	O169	O173-R	O168	O170
Depth (ft)	3.5-5.0	0.0-2.0	2.0-3.5	0.0-2.0	2.0-3.0	3.0-4.25	0.0-2.5	2.5-5.0	0.0-2.0	2.0-2.5	0.0-0.9	0.9-3.5
Analysis Date	28-Jul-94	12-Jul-94	2-Aug-94	2-Jul-94	3-Jul-94	3-Jul-94	28-Jul-94	28-Jul-94	28-Jul-94	2-Aug-94	28-Jul-94	28-Jul-94
Matrix	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
Sample Size (g)	41.72	40.77	41.24	42.03	41.01	39.88	20.45	30.38	41.22	42.26	40.41	40.42
Percent Moisture (%)	17.8	19.5	19.0	16.9	20.1	21.9	59.6	41.4	21.5	19.2	20.9	19.3
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
naphthalene	0.0014	0.0968	0.0006	0.1503	0.0808	0.0073	0.1727	0.0055	0.0021	0.0008	0.0042	0.0026
C1-naphthalenes	0.0030	0.0436	0.0000	0.0802	0.0561	0.0041	0.1348	0.0129	0.0014	0.0000	0.0063	0.0049
C2-naphthalenes	0.0045	0.0531	0.0000	0.1271	0.1087	0.0058	0.1821	0.0279	0.0033	0.0000	0.0121	0.0104
C3-naphthalenes	0.0092	0.0969	0.0000	0.1293	0.1736	0.0091	0.1758	0.0558	0.0079	0.0000	0.0230	0.0205
C4-naphthalenes	0.0154	0.0762	0.0000	0.0830	0.1230	0.0169	0.1617	0.0522	0.0112	0.0000	0.0447	0.0630
biphenyl	0.0000	0.0094	0.0000	0.0113	0.0072	0.0007	0.0226	0.0019	0.0001	0.0000	0.0000	0.0008
acenaphthylene	0.0000	0.0285	0.0000	0.0237	0.0158	0.0014	0.0956	0.0000	0.0007	0.0000	0.0000	0.0000
acenaphthene	0.0000	0.0597	0.0019	0.0338	0.0305	0.0030	0.0348	0.0009	0.0016	0.0000	0.0037	0.0009
dibenzofuran	0.0005	0.0253	0.0000	0.0401	0.0284	0.0022	0.0684	0.0053	0.0009	0.0000	0.0045	0.0028
fluorene	0.0003	0.0436	0.0000	0.0608	0.0605	0.0032	0.0523	0.0041	0.0014	0.0000	0.0062	0.0035
C1-fluorenes	0.0026	0.0442	0.0000	0.0345	0.0434	0.0065	0.0409	0.0147	0.0030	0.0000	0.0103	0.0086
C2-fluorenes	0.0091	0.0537	0.0000	0.0702	0.0959	0.0148	0.0000	0.0443	0.0104	0.0000	0.0313	0.0326
phenanthrene	0.0242	0.1100	0.0000	0.0984	0.1563	0.0269	0.0000	0.1034	0.0330	0.0000	0.0797	0.0847
anthracene	0.0019	0.4422	0.0013	0.4553	0.3480	0.0273	0.2215	0.0146	0.0085	0.0032	0.0210	0.0132
C1-phenanthrenes/anthracenes	0.0000	0.1037	0.0000	0.0802	0.0723	0.0074	0.1134	0.0011	0.0023	0.0011	0.0069	0.0034
C2-phenanthrenes/anthracenes	0.0094	0.2421	0.0032	0.2189	0.2598	0.0330	0.2749	0.0589	0.0148	0.0084	0.0516	0.0459
C3-phenanthrenes/anthracenes	0.0285	0.2223	0.0000	0.2030	0.3441	0.0580	0.4003	0.1315	0.0325	0.0175	0.1093	0.1092
C4-phenanthrenes/anthracenes	0.0389	0.1882	0.0000	0.1533	0.2639	0.0563	0.3991	0.1614	0.0449	0.0258	0.1440	0.1497
dibenzothiophene	0.0292	0.1658	0.0000	0.1324	0.1772	0.0318	0.2378	0.1184	0.0336	0.0149	0.1371	0.1059
C1-dibenzothiophenes	0.0005	0.0294	0.0000	0.0289	0.0283	0.0022	0.0174	0.0028	0.0009	0.0007	0.0031	0.0025
C2-dibenzothiophenes	0.0022	0.0209	0.0000	0.0288	0.0441	0.0069	0.0346	0.0132	0.0035	0.0028	0.0098	0.0095
C3-dibenzothiophenes	0.0082	0.0411	0.0000	0.0637	0.1040	0.0154	0.0878	0.0281	0.0105	0.0000	0.0285	0.0277
fluoranthene	0.0115	0.0422	0.0000	0.0735	0.1105	0.0208	0.0000	0.0353	0.0140	0.0000	0.0411	0.0378
pyrene	0.0014	0.5692	0.0012	0.7157	0.4215	0.0433	0.8749	0.0110	0.0214	0.0121	0.0553	0.0279
C1-fluoranthenes/pyrenes	0.0022	0.4755	0.0014	0.6016	0.3705	0.0365	0.7679	0.0095	0.0225	0.0115	0.0659	0.0262
benz[a]anthracene	0.0082	0.3222	0.0000	0.2890	0.2739	0.0291	0.6109	0.0276	0.0210	0.0096	0.0550	0.0316
chrysene	0.0000	0.2695	0.0000	0.2888	0.1943	0.0204	0.6669	0.0043	0.0077	0.0036	0.0202	0.0084
C1-chrysenes	0.0071	0.2611	0.0026	0.3580	0.2406	0.0326	0.8015	0.0265	0.0141	0.0085	0.0361	0.0307
C2-chrysenes	0.0103	0.4145	0.0042	0.1386	0.1422	0.0338	0.7185	0.0314	0.0129	0.0104	0.0507	0.0373
C3-chrysenes	0.0215	0.5042	0.0000	0.1068	0.1343	0.0361	0.6903	0.0679	0.0189	0.0135	0.0826	0.0692
C4-chrysenes	0.0153	0.3107	0.0000	0.0774	0.0936	0.0208	0.4628	0.0450	0.0115	0.0106	0.0504	0.0549
benzo[b]fluoranthene	0.0000	0.2575	0.0000	0.0447	0.0569	0.0163	0.3755	0.0000	0.0000	0.0000	0.0327	0.0336
benzo[k]fluoranthene	0.0018	0.3007	0.0007	0.4091	0.2499	0.0249	1.1616	0.0113	0.0113	0.0049	0.0276	0.0118
benzo[e]pyrene	0.0002	0.1077	0.0000	0.1353	0.0738	0.0079	0.1487	0.0019	0.0036	0.0012	0.0080	0.0029
benzo[a]pyrene	0.0031	0.2027	0.0010	0.2121	0.1392	0.0158	0.2250	0.0112	0.0077	0.0040	0.0206	0.0134
perylene	0.0000	0.2593	0.0000	0.2335	0.1072	0.0137	0.6254	0.0011	0.0032	0.0024	0.0056	0.0015
indeno[1,2,3-c,d]pyrene	0.0975	0.0742	0.0097	0.1125	0.1332	0.0492	0.5748	0.3867	0.0191	0.0179	0.1287	0.1478
dibenz[a,h]anthracene	0.0005	0.1728	0.0000	0.1999	0.0965	0.0090	0.6150	0.0045	0.0039	0.0016	0.0111	0.0038
benzo[g,h,i]perylene	0.0002	0.0643	0.0000	0.0501	0.0258	0.0027	0.1240	0.0009	0.0010	0.0000	0.0028	0.0011
	0.0017	0.1900	0.0005	0.1838	0.1007	0.0098	0.5841	0.0089	0.0037	0.0015	0.0137	0.0067
Total PAH (all):	0.37	6.99	0.03	6.54	5.59	0.76	12.98	1.54	0.43	0.19	1.45	1.25
Total PAH (16 EPA):	0.02	3.44	0.01	3.98	2.49	0.25	7.08	0.11	0.11	0.05	0.29	0.14



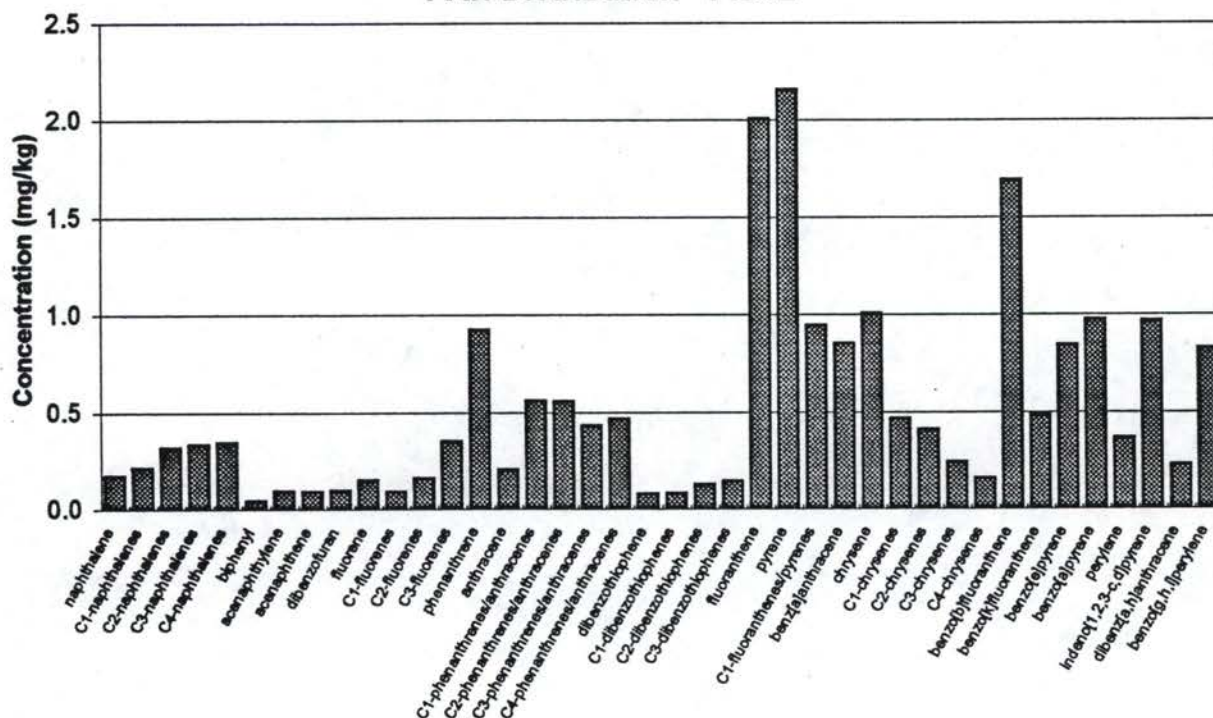
**Appendix C. PAH Distribution Plots for WA107 Surface Sediment Samples**



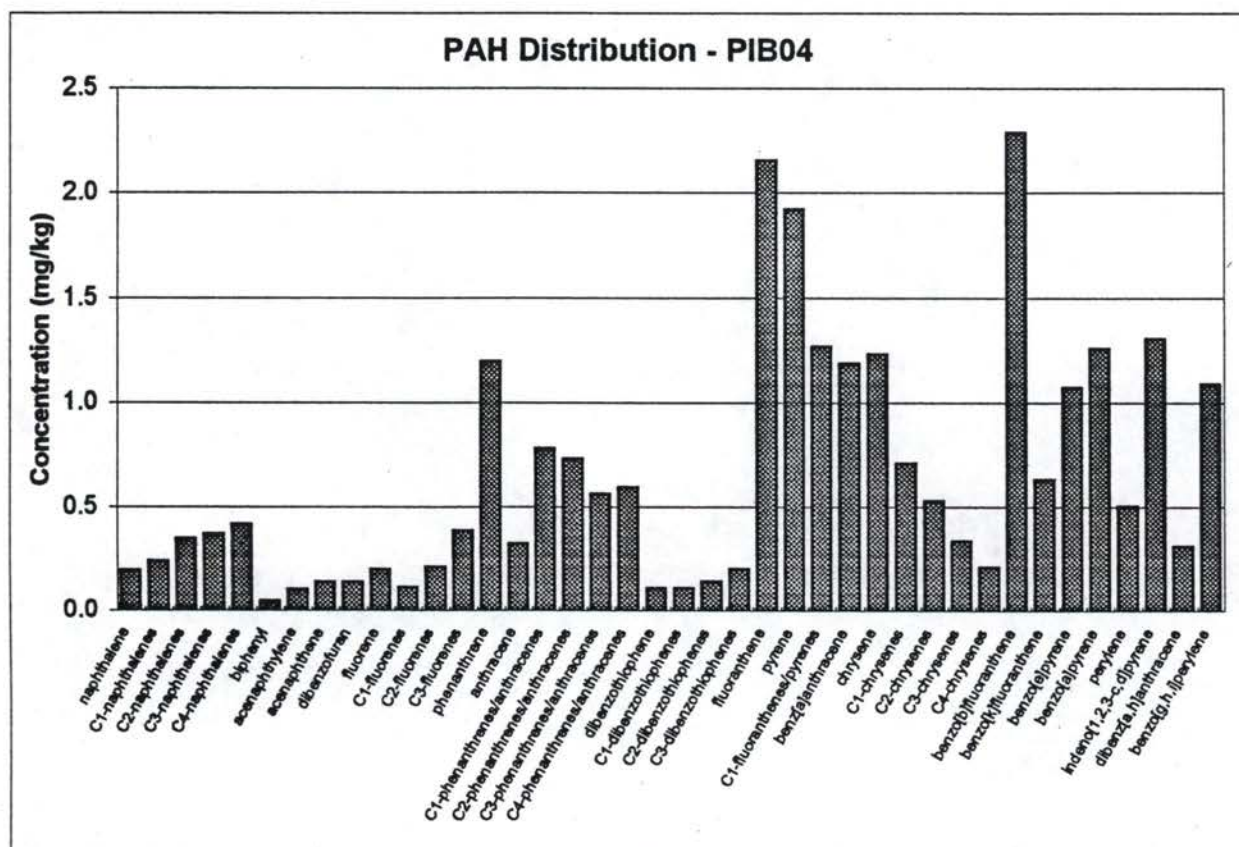
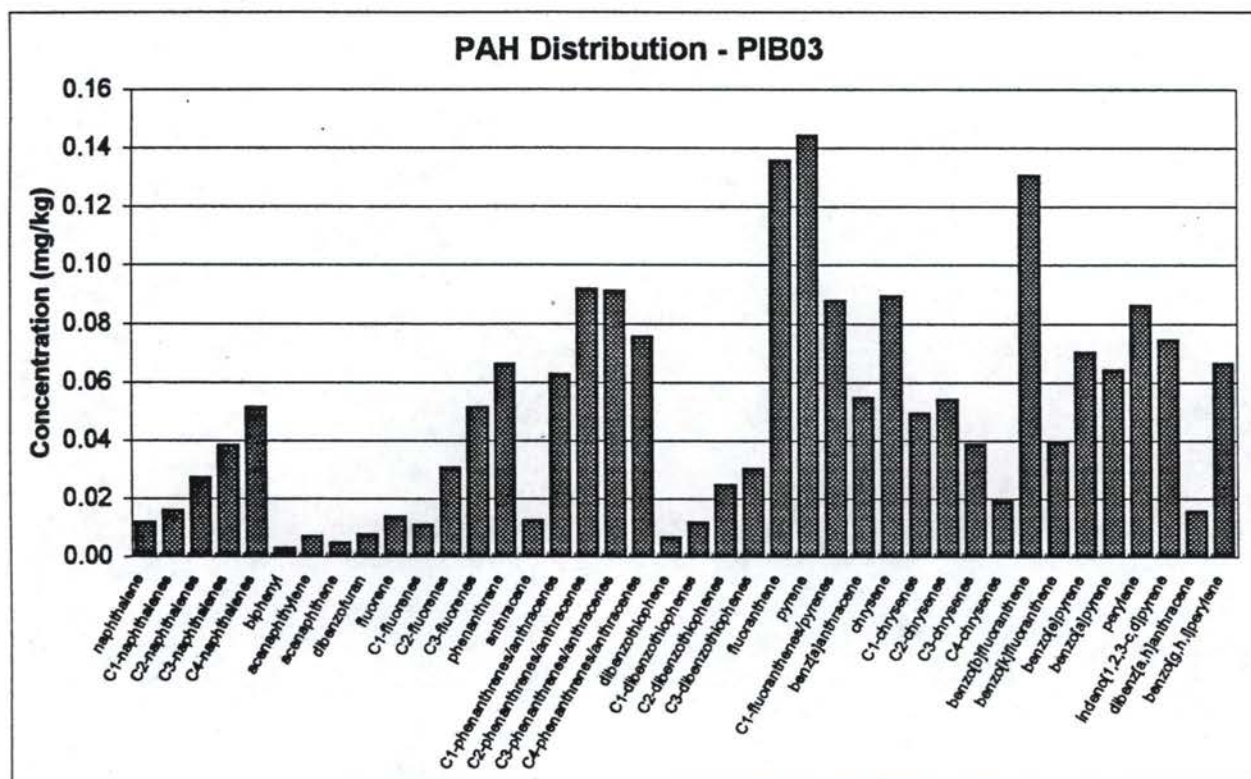
PAH Distribution - PIB01



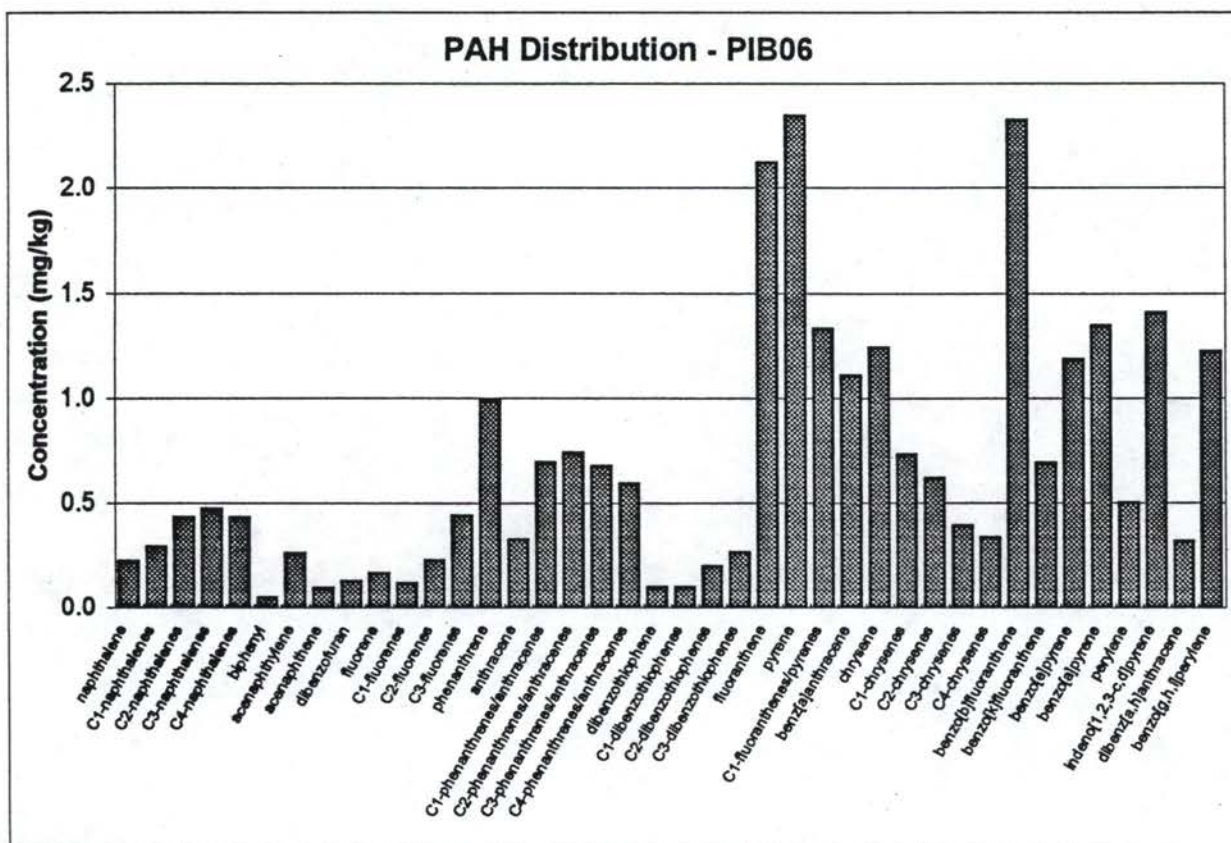
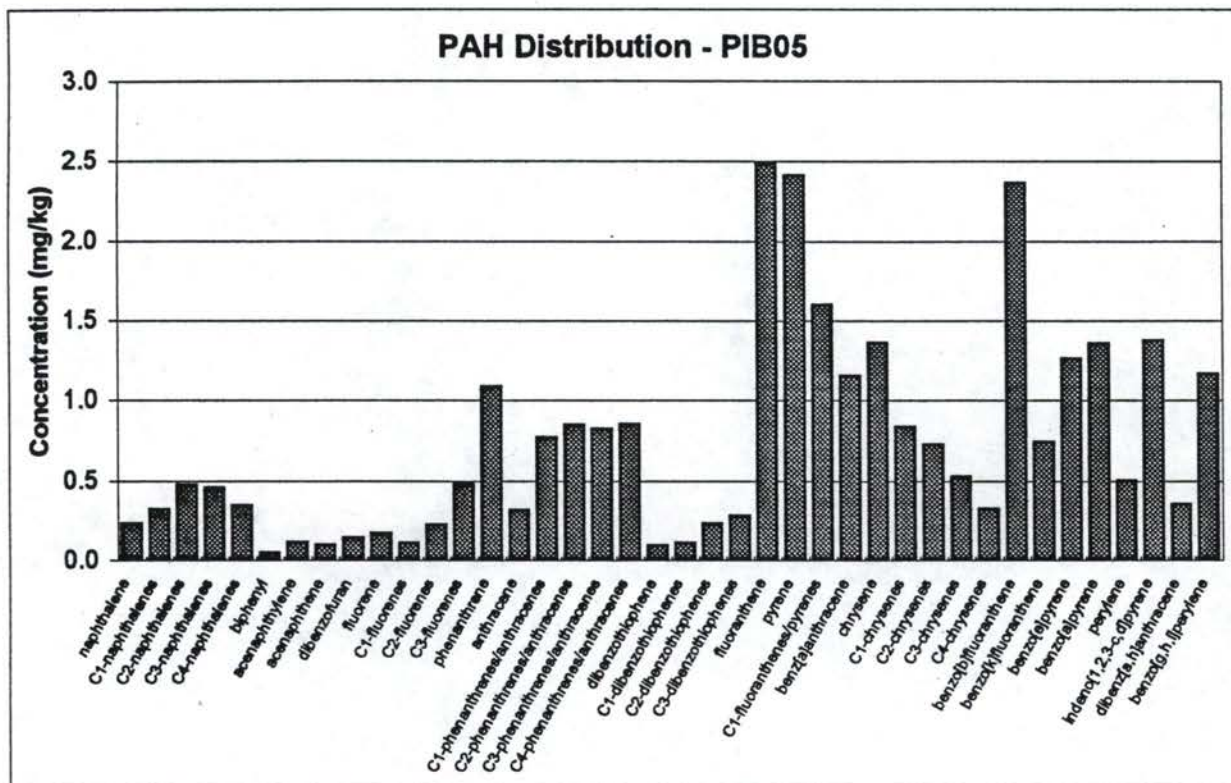
PAH Distribution - PIB02



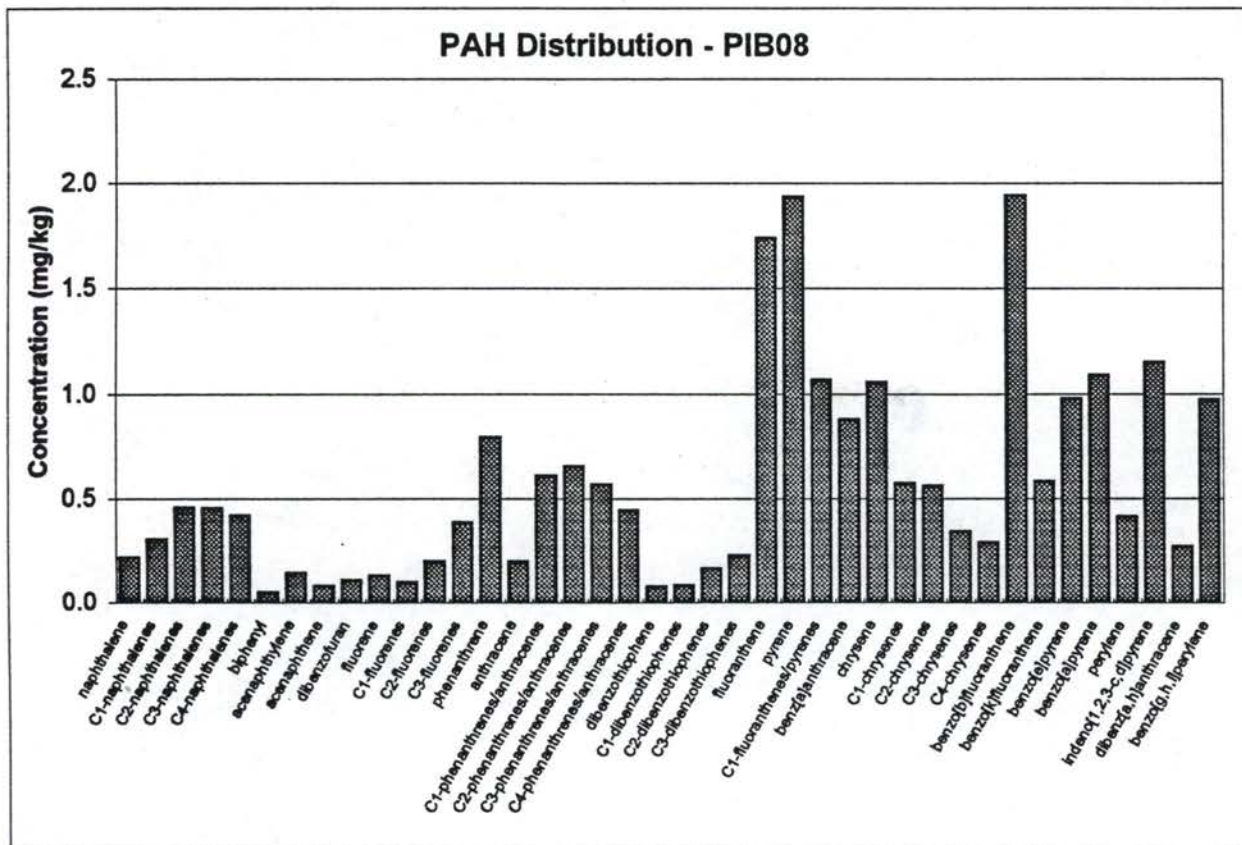
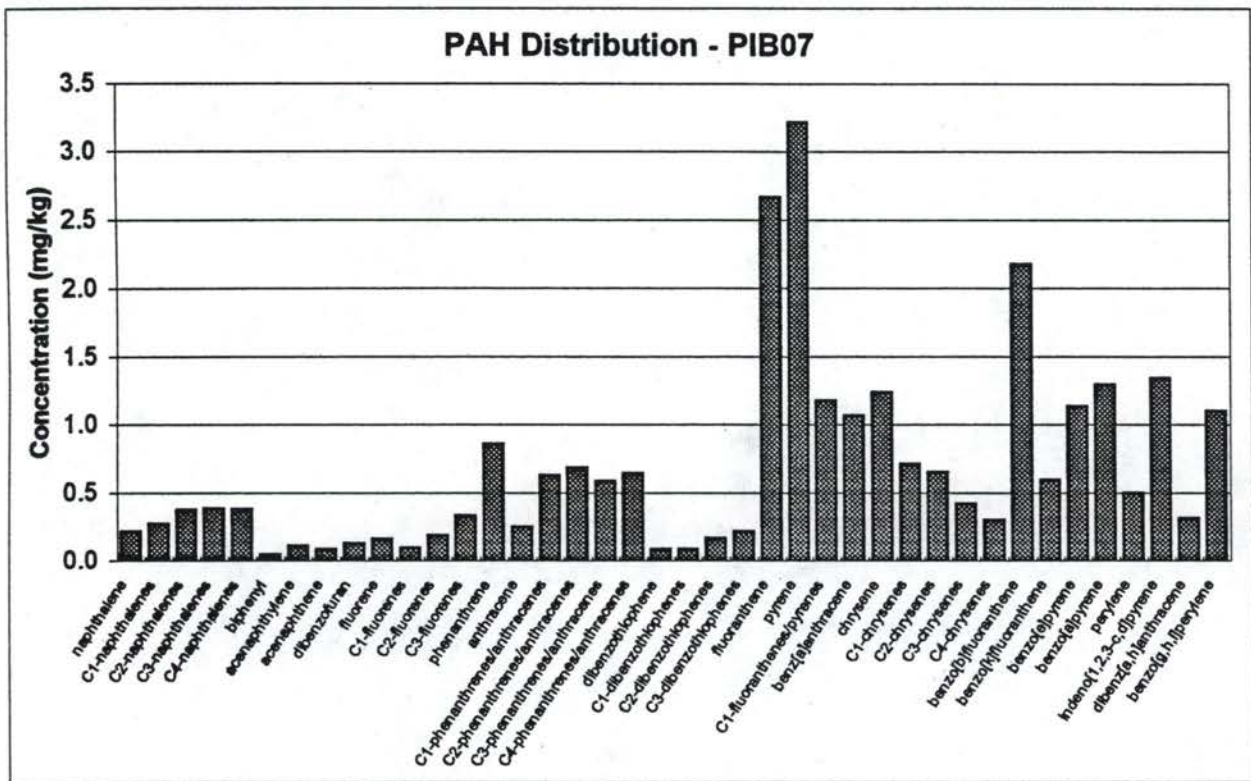




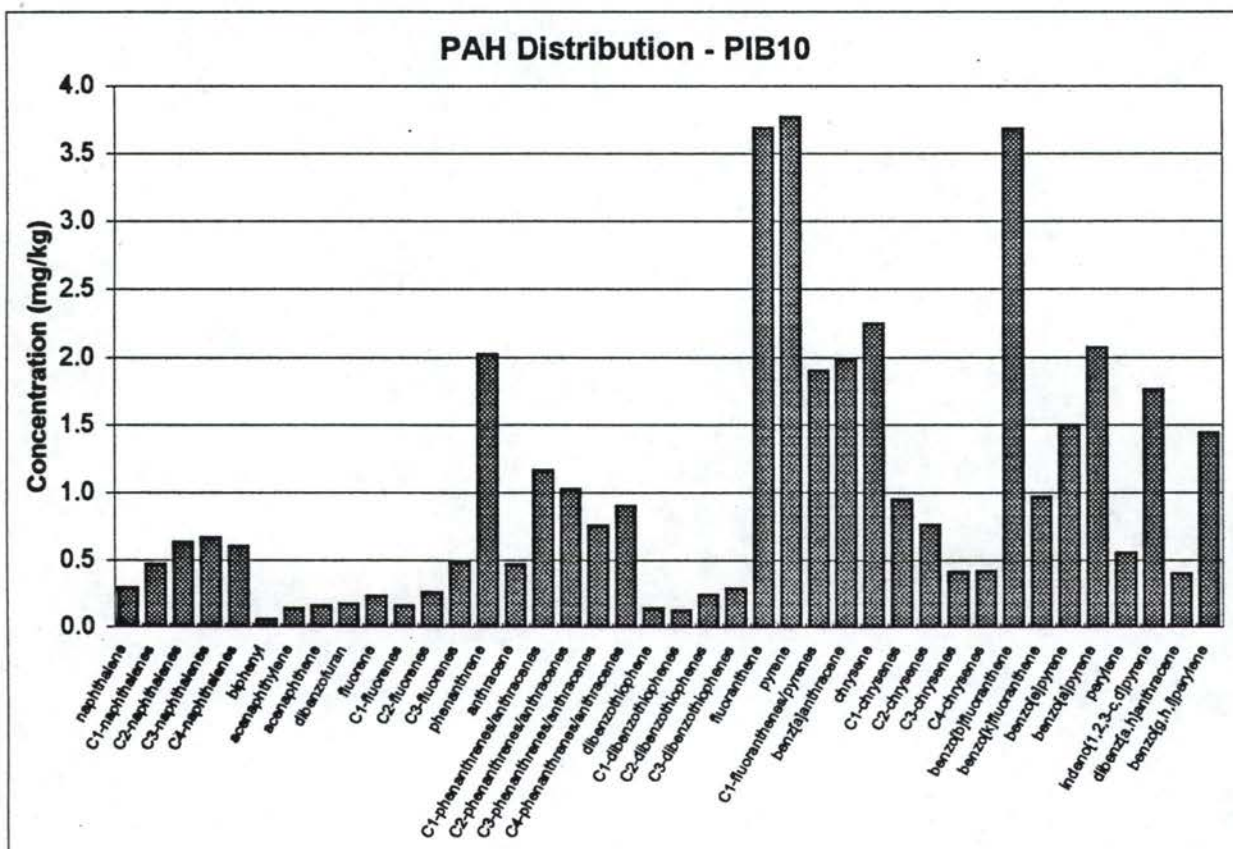
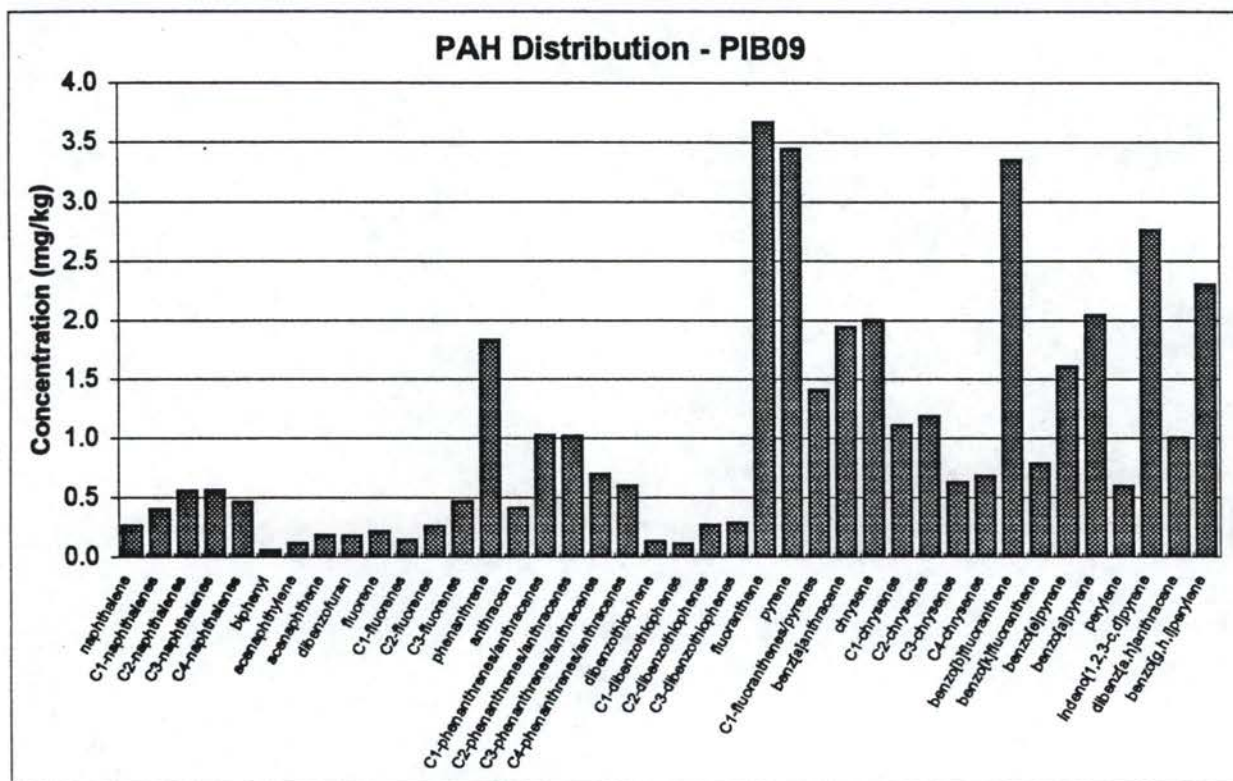




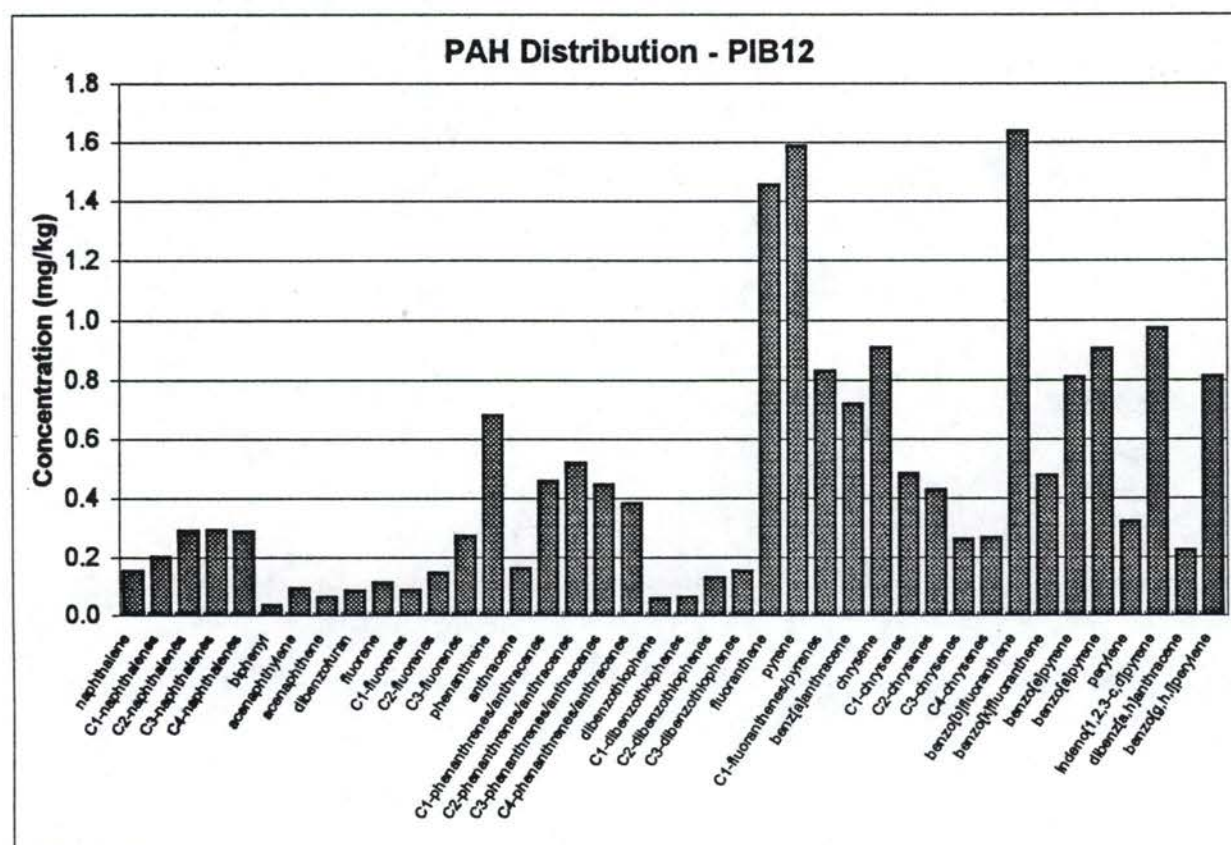
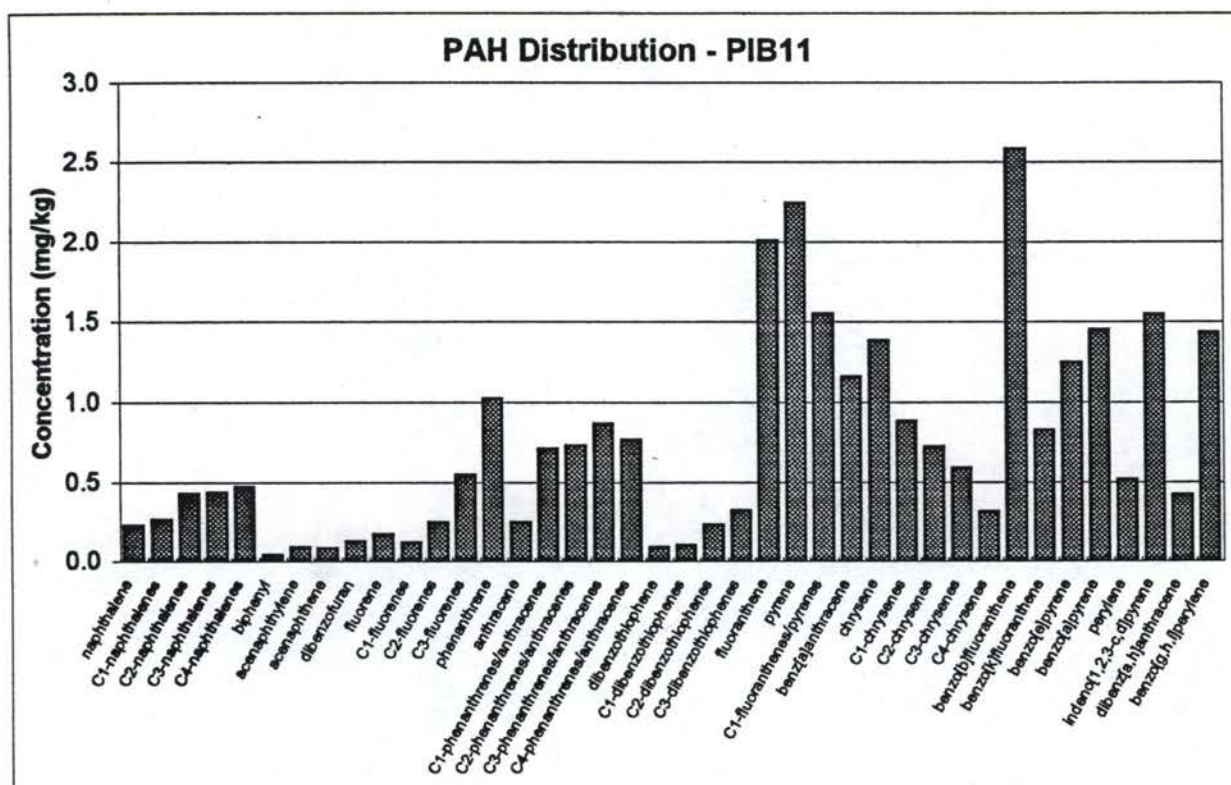




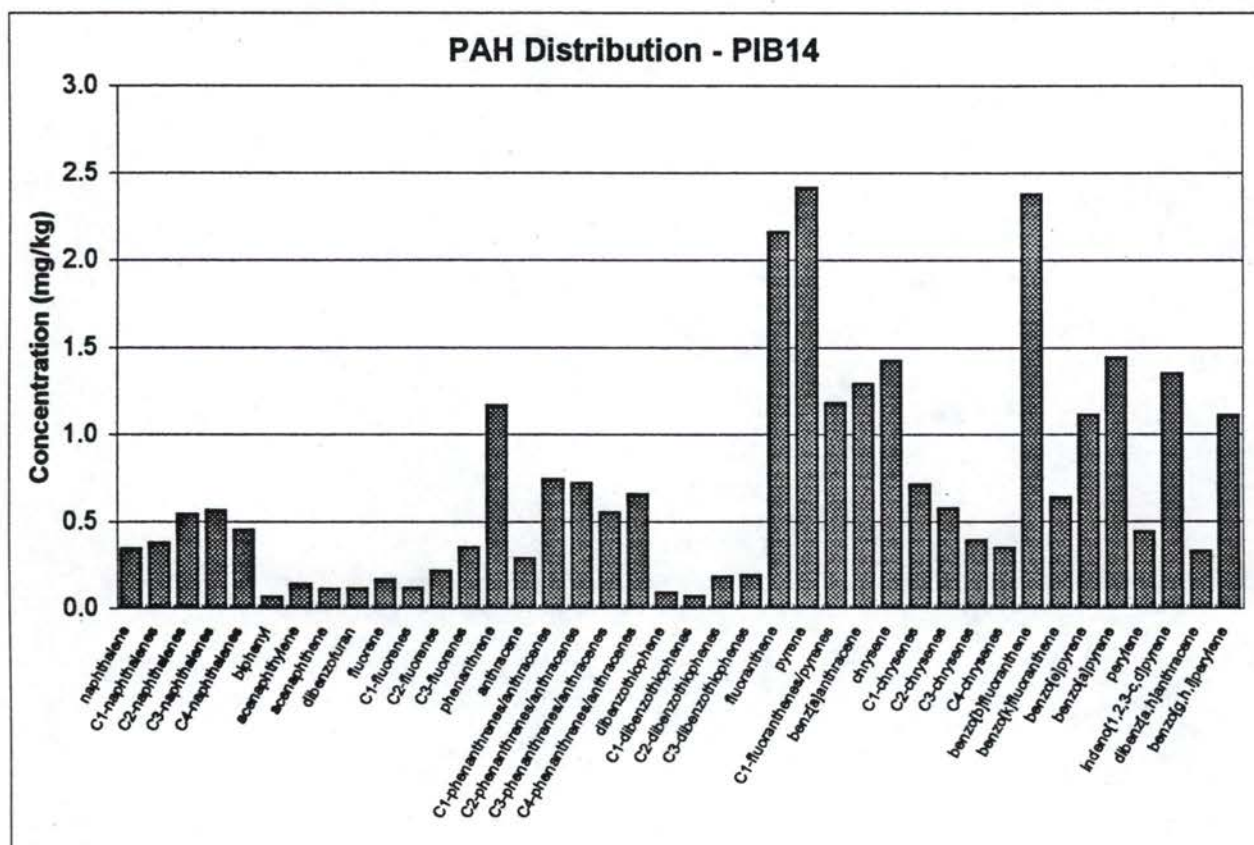
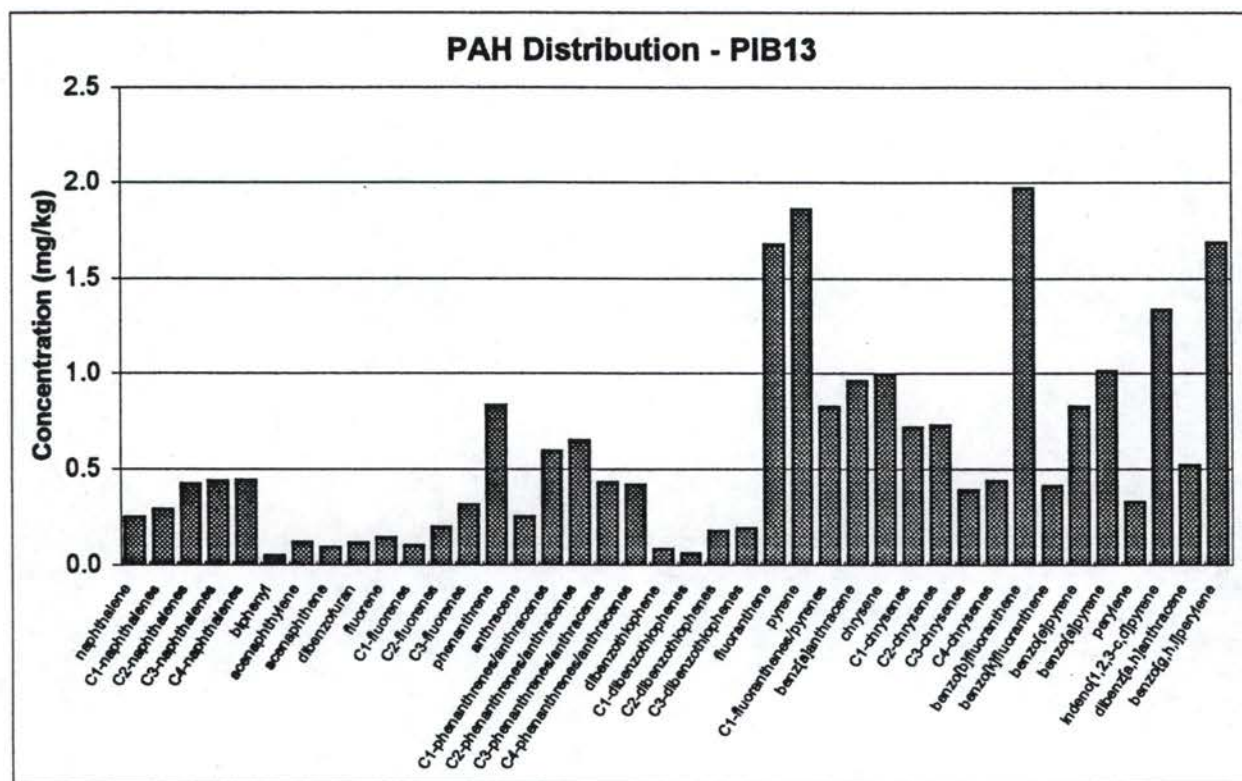






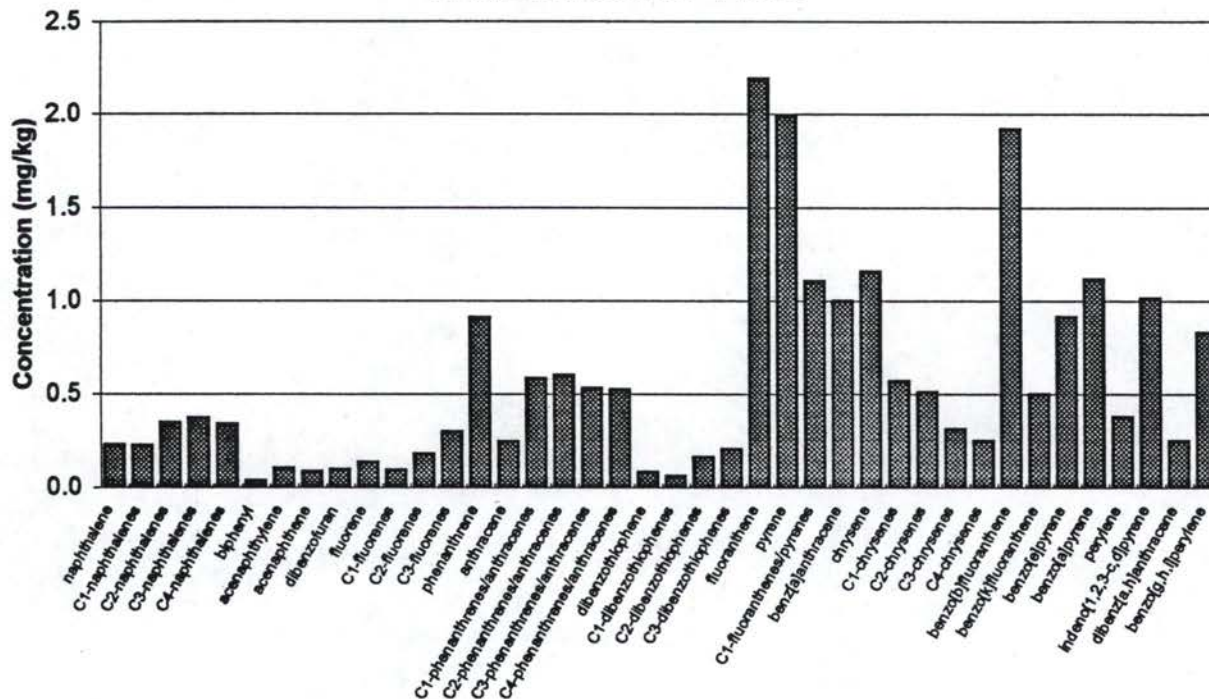




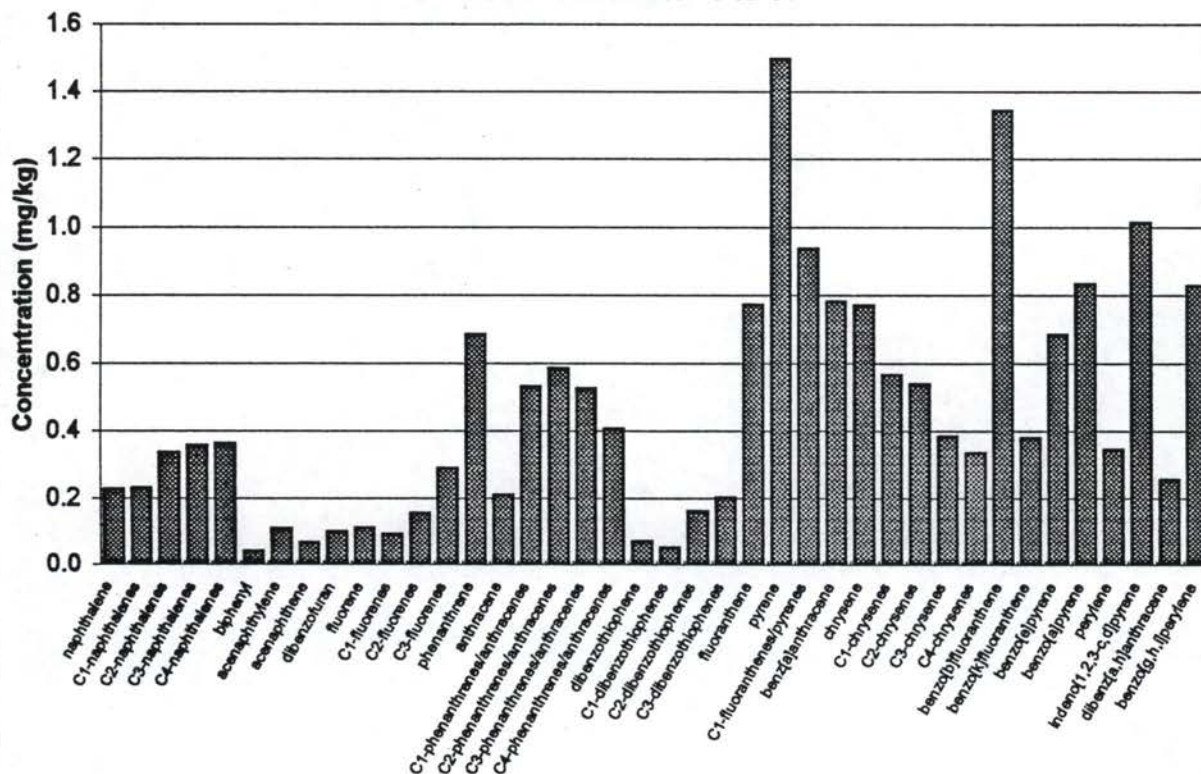




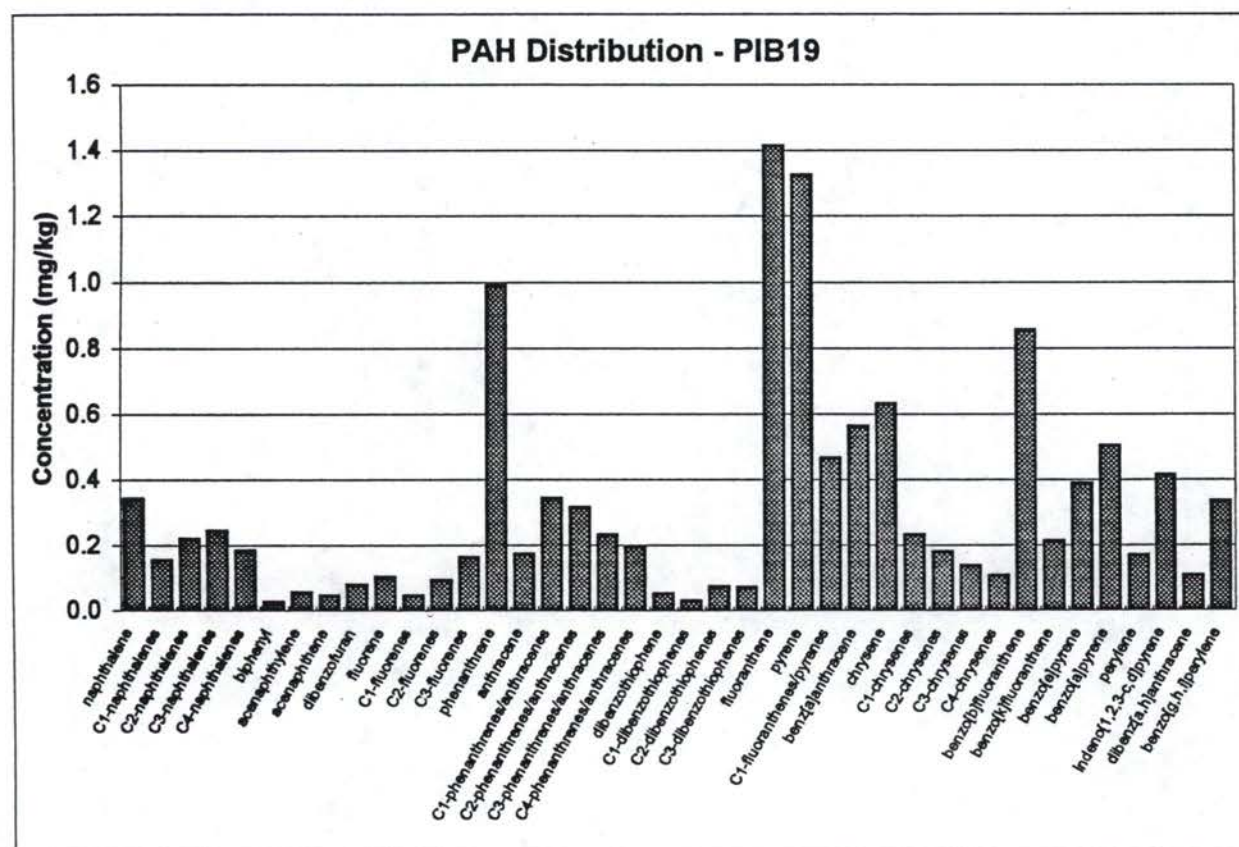
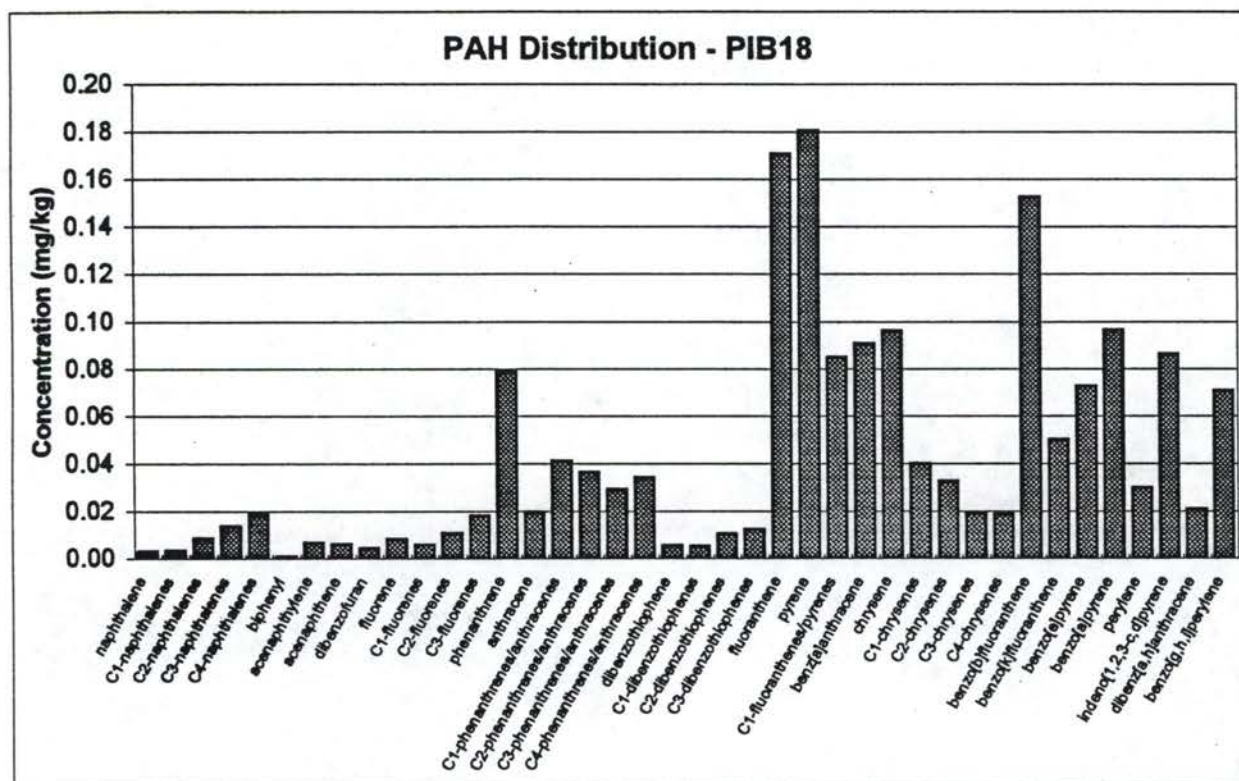
PAH Distribution - PIB15



PAH Distribution - PIB16

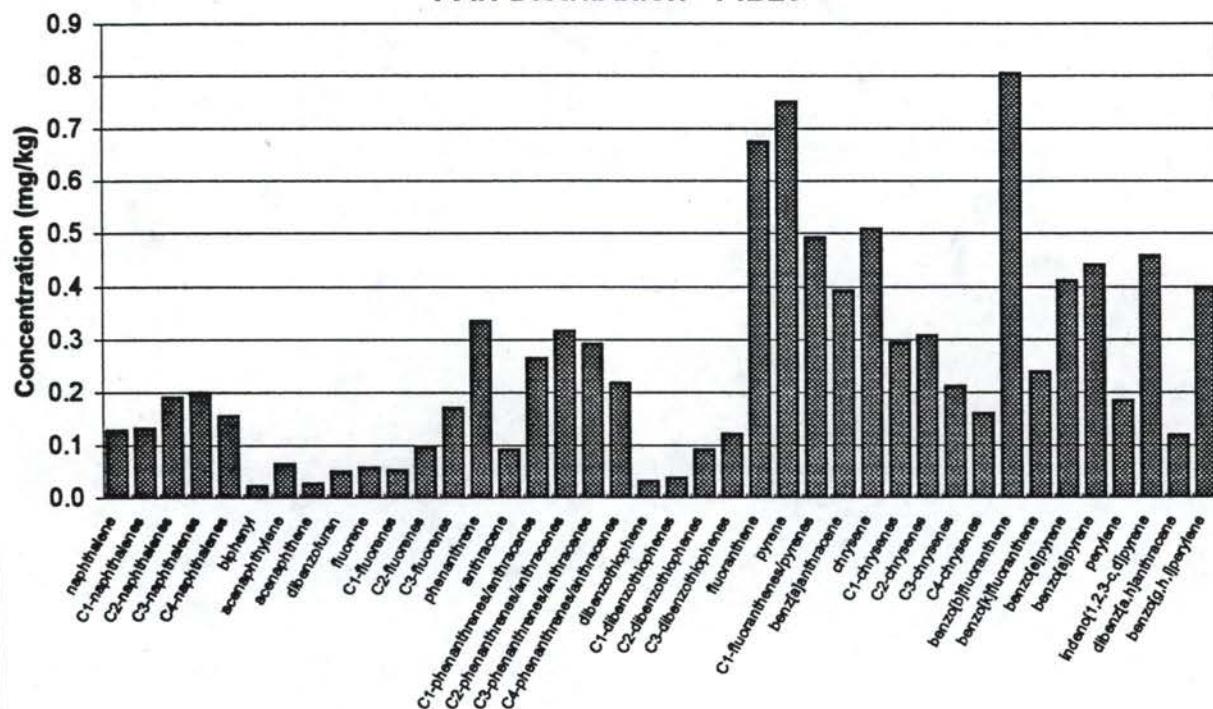




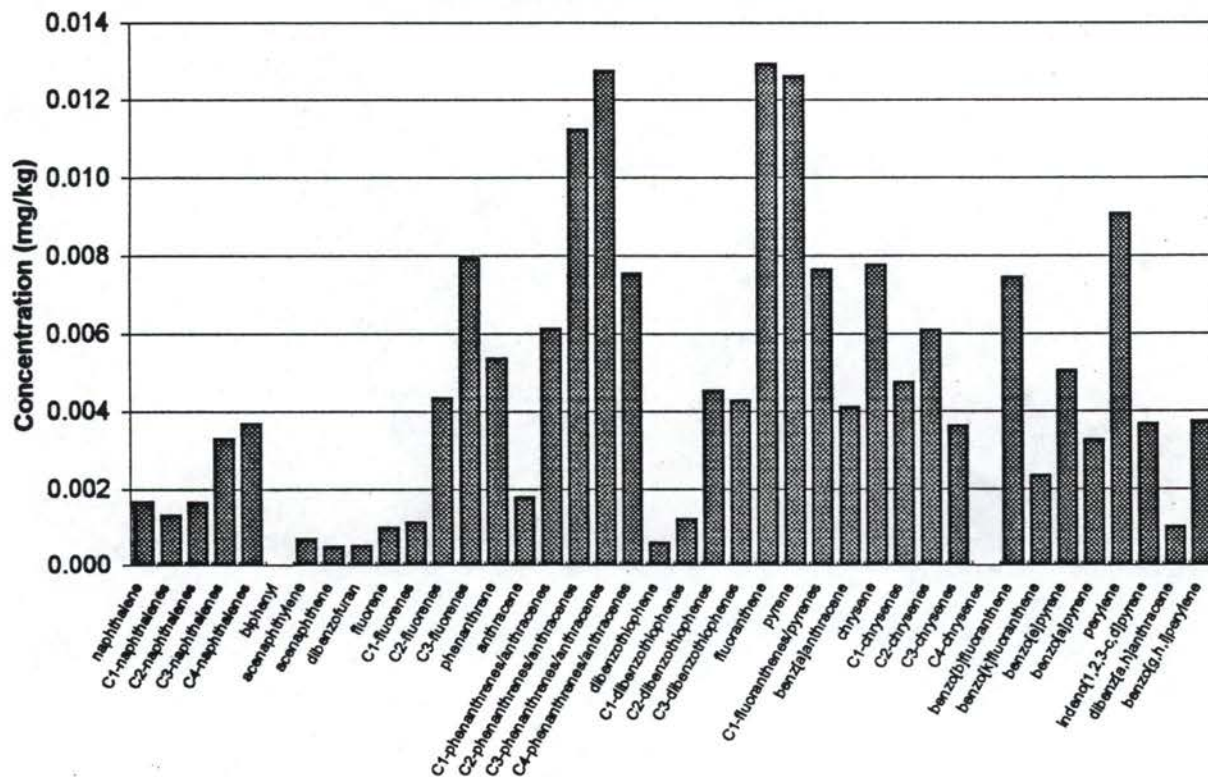




### PAH Distribution - PIB20

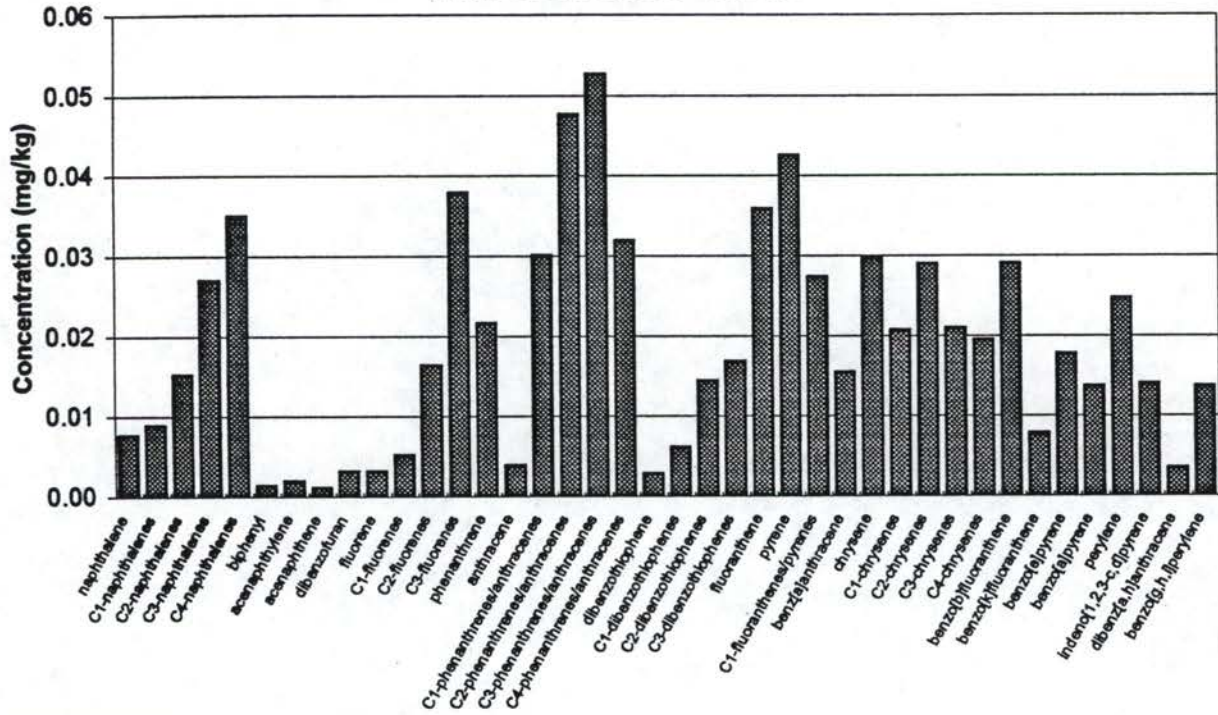


### PAH Distribution - PIB21





PAH Distribution - PIB22

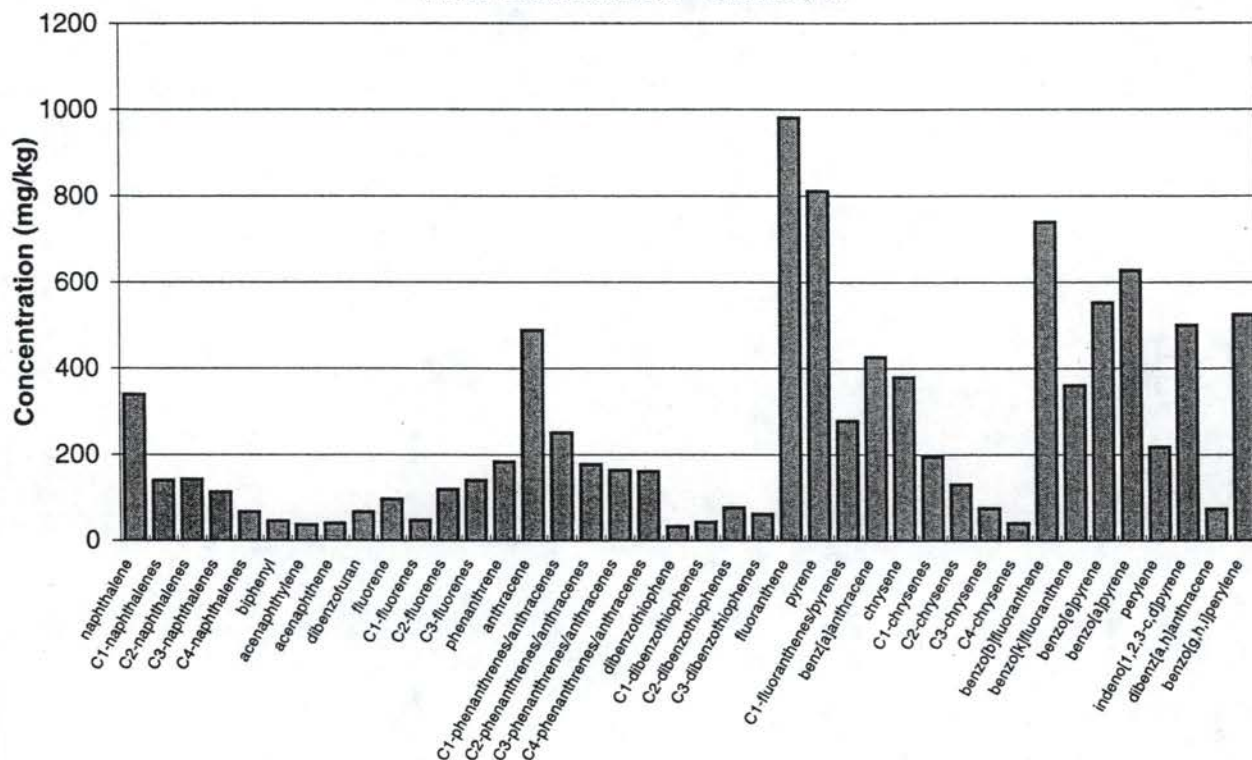




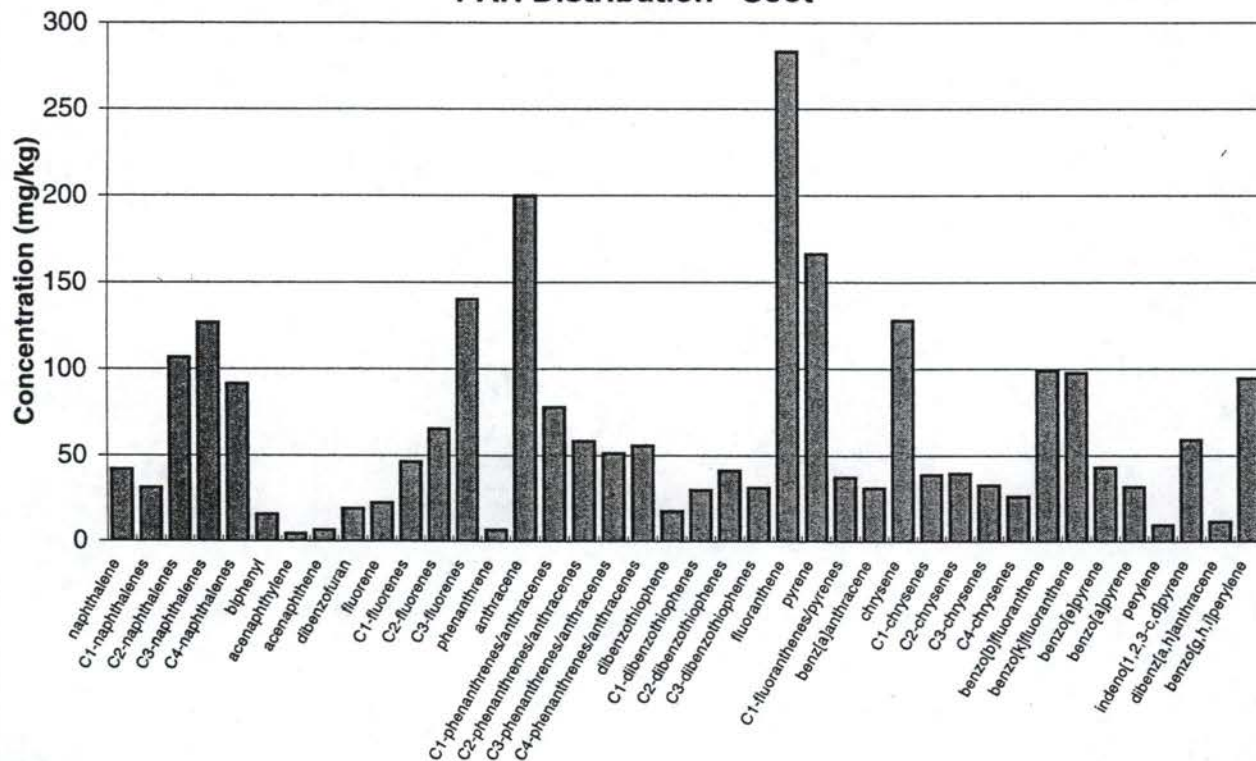
**Appendix D. PAH Distribution Plots for Selected Petroleum  
and Other Hydrocarbon Products**



### PAH Distribution - SRM1941

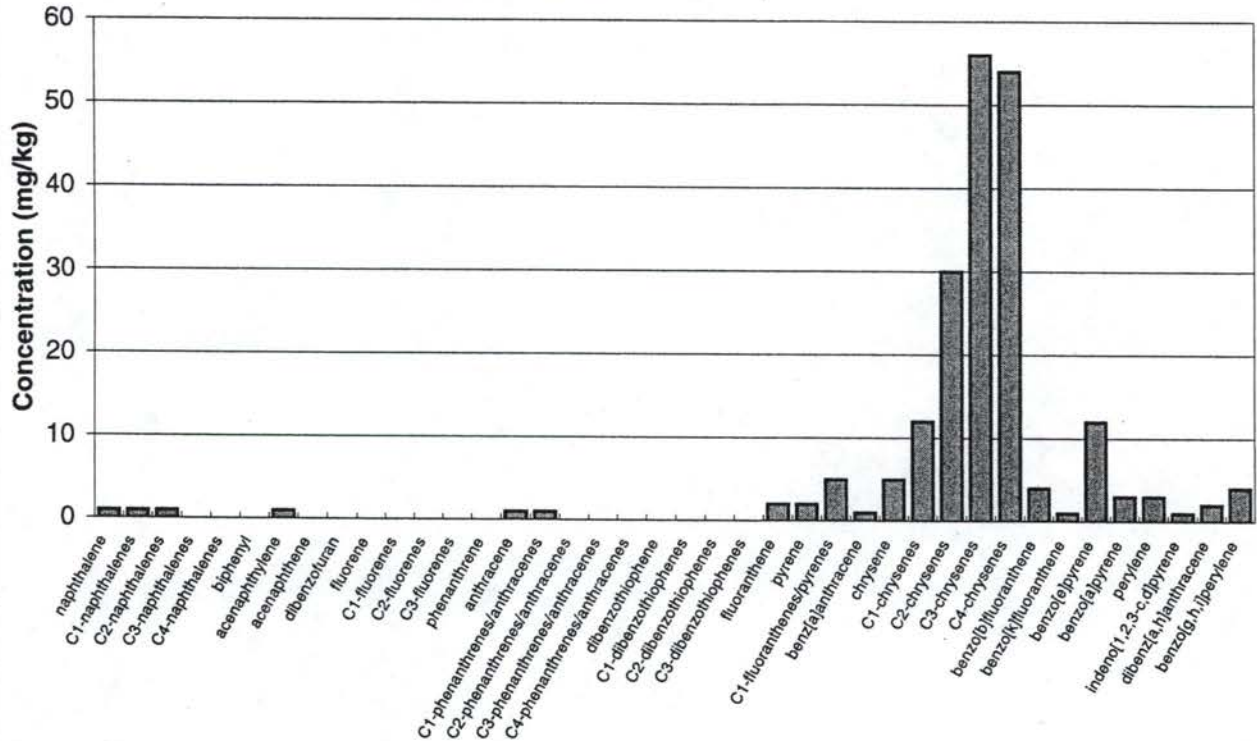


### PAH Distribution - Soot

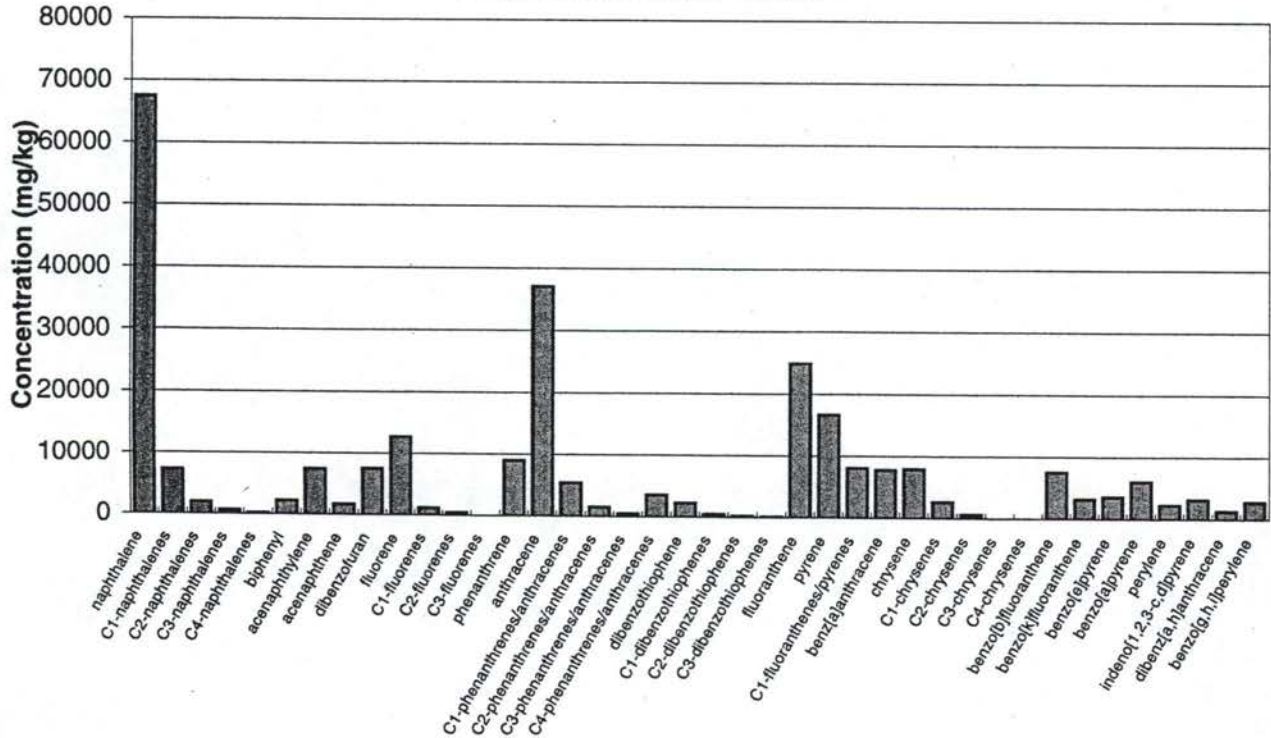




### PAH Distribution - Asphalt

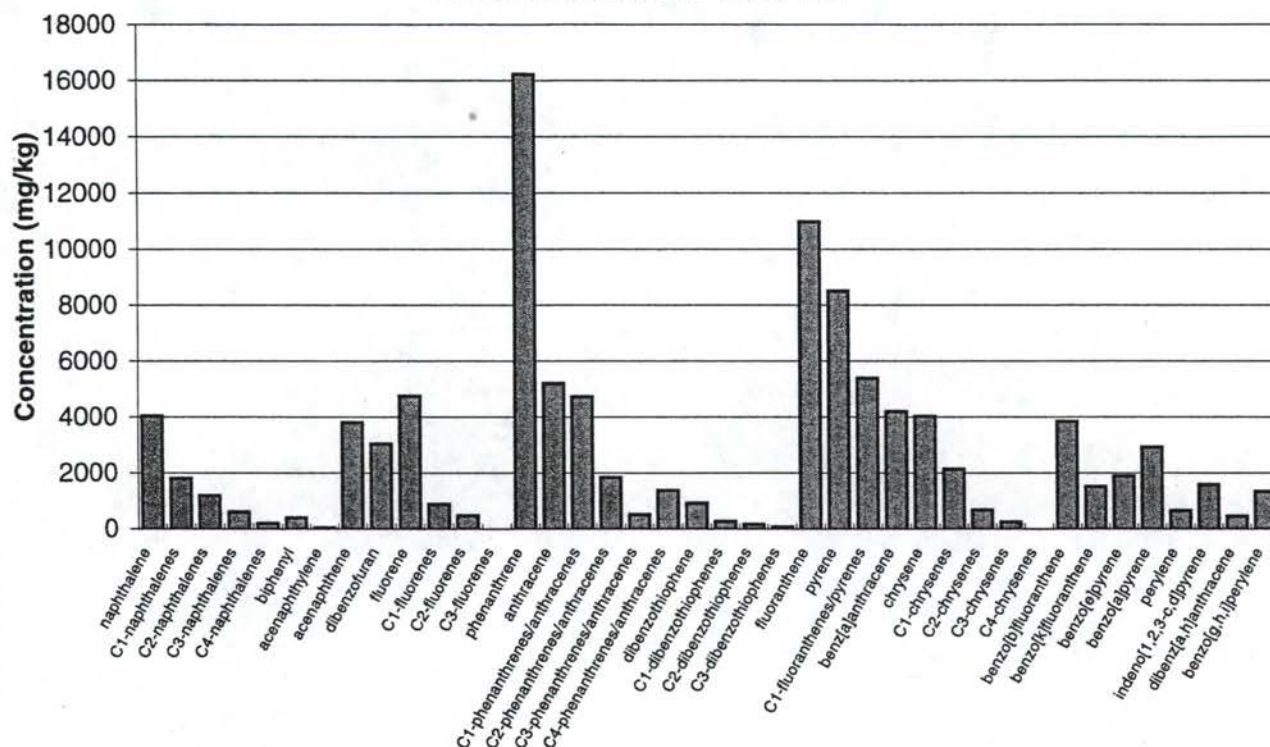


### PAH Distribution - Coke

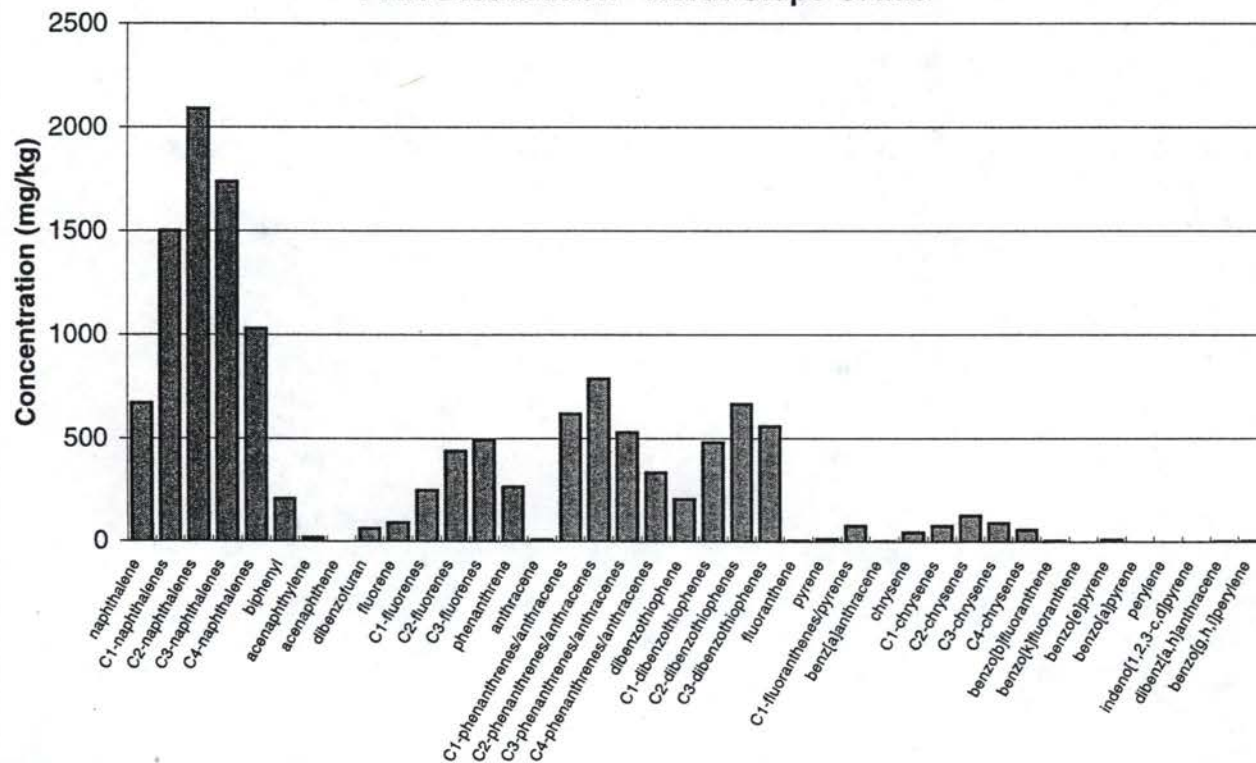




### PAH Distribution - Coal Tar

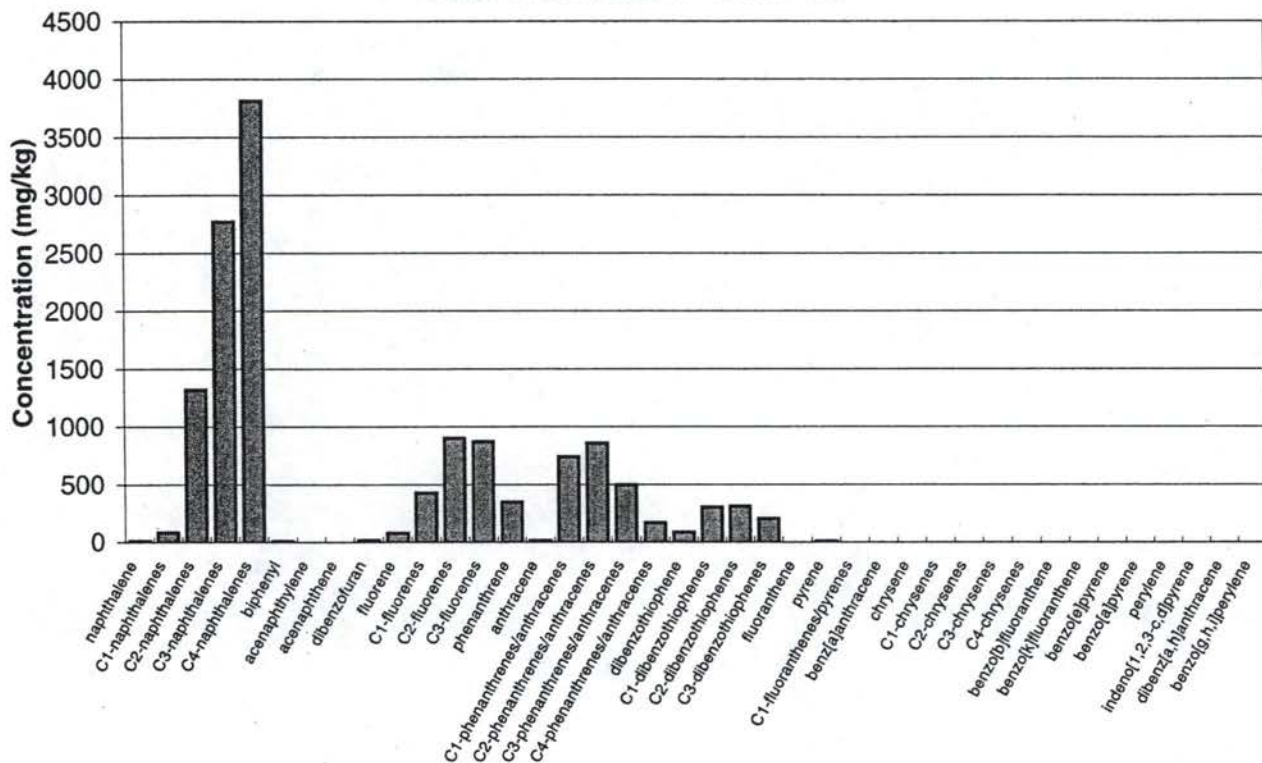


### PAH Distribution - North Slope Crude

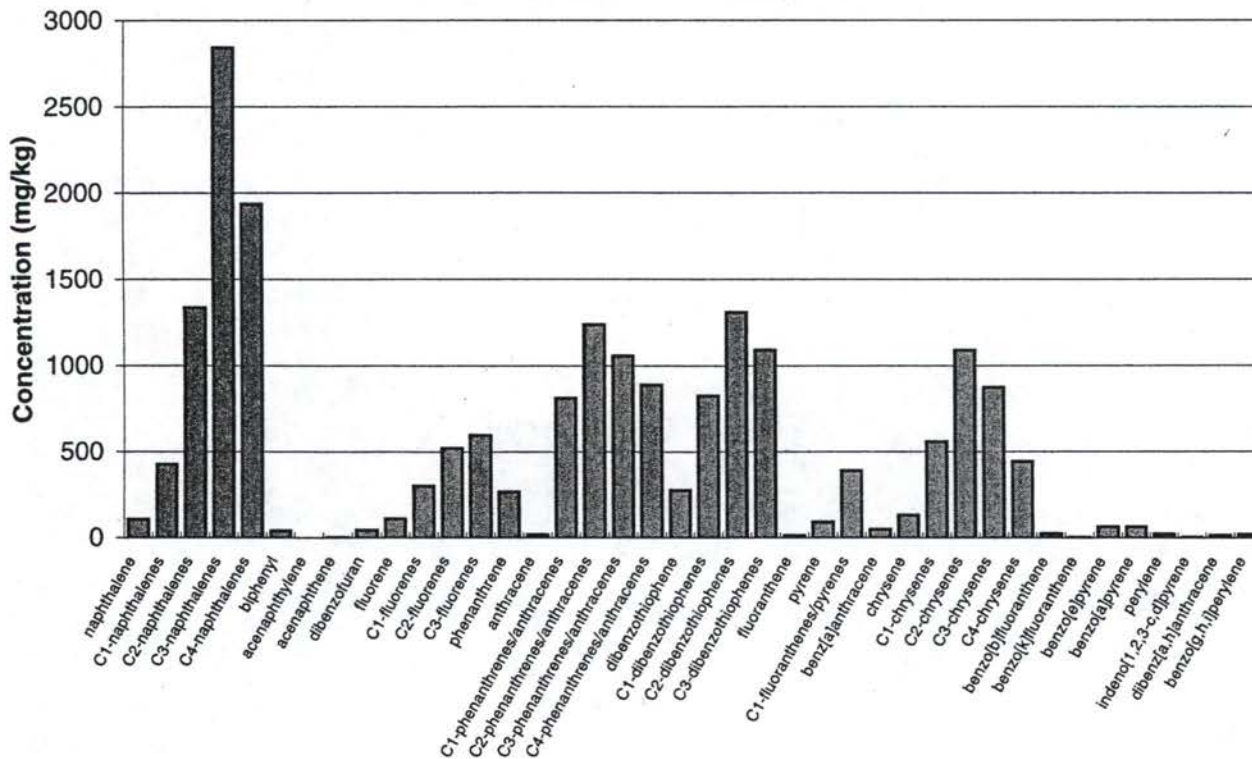




### PAH Distribution - Lube Oil



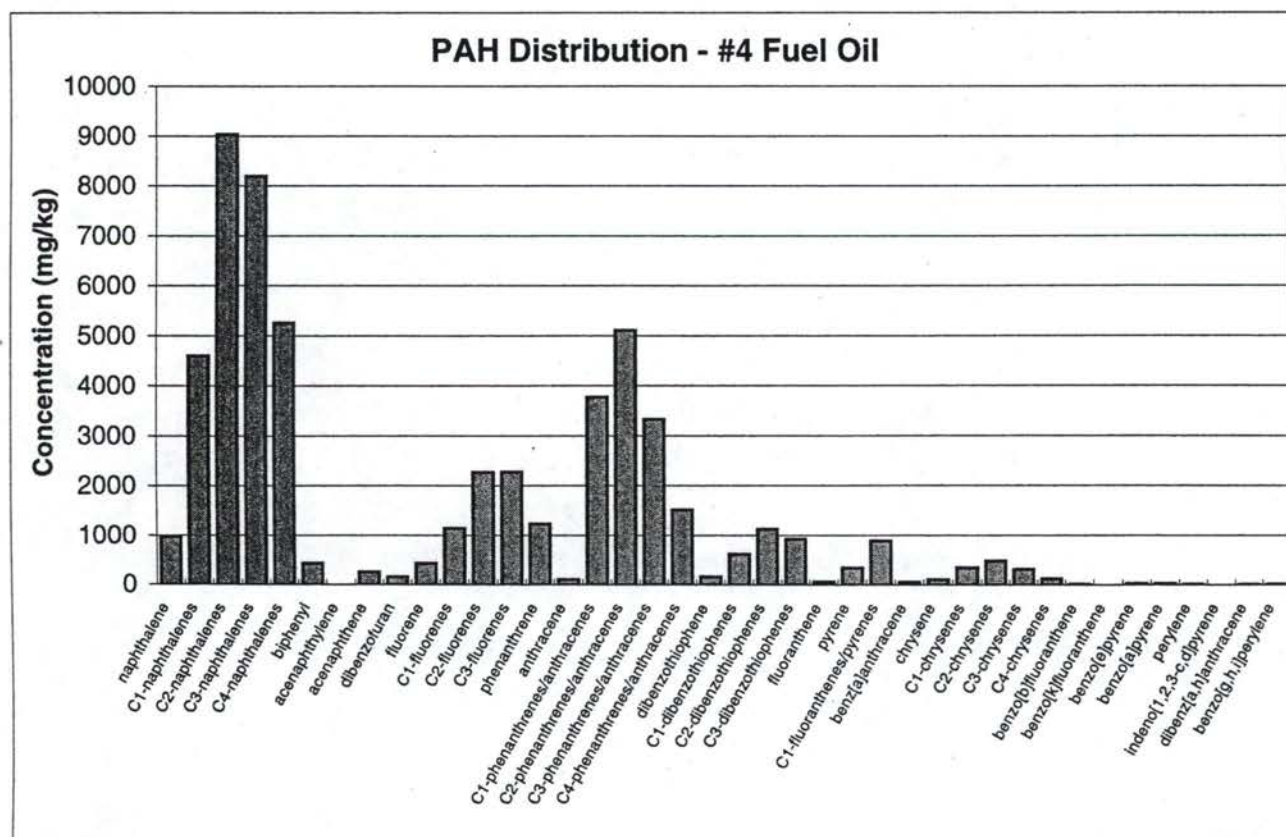
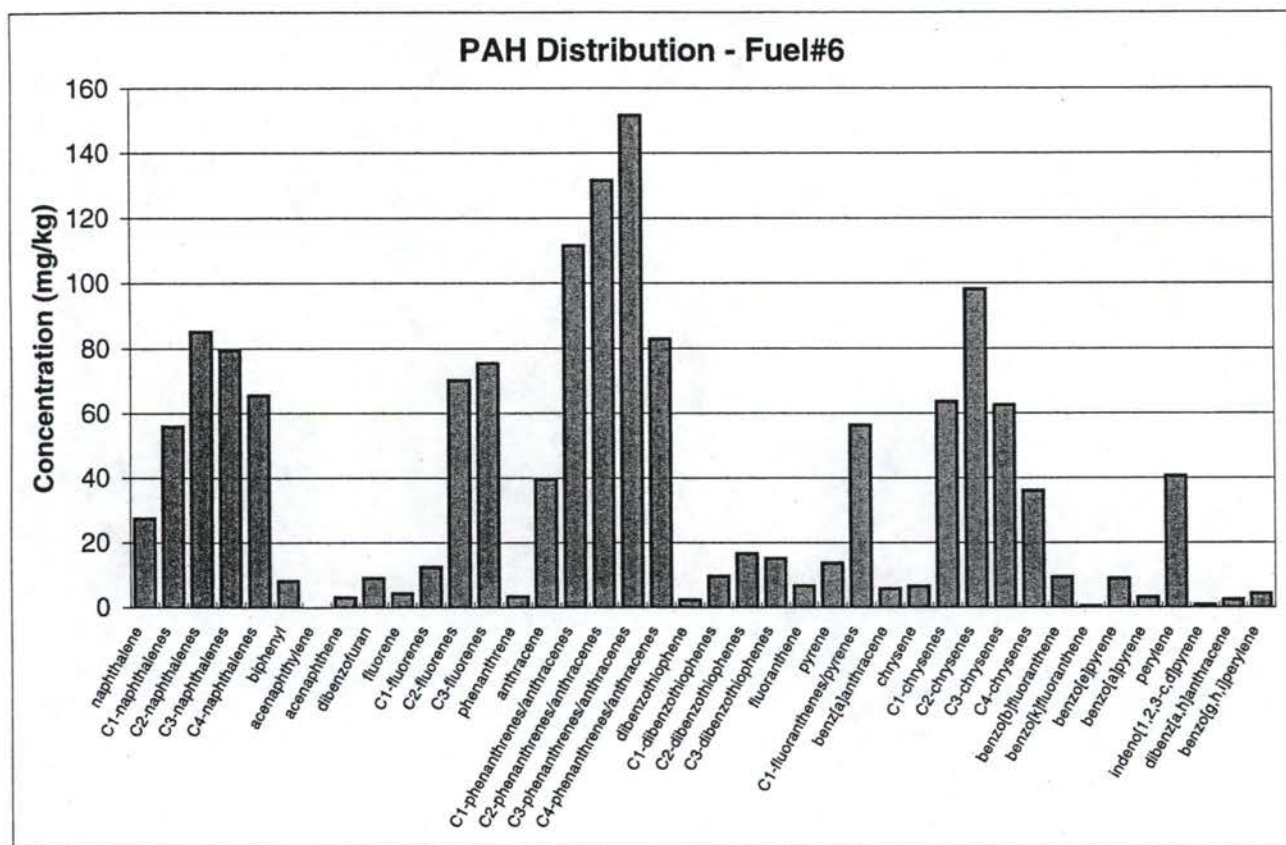
### PAH Distribution - Bunker C





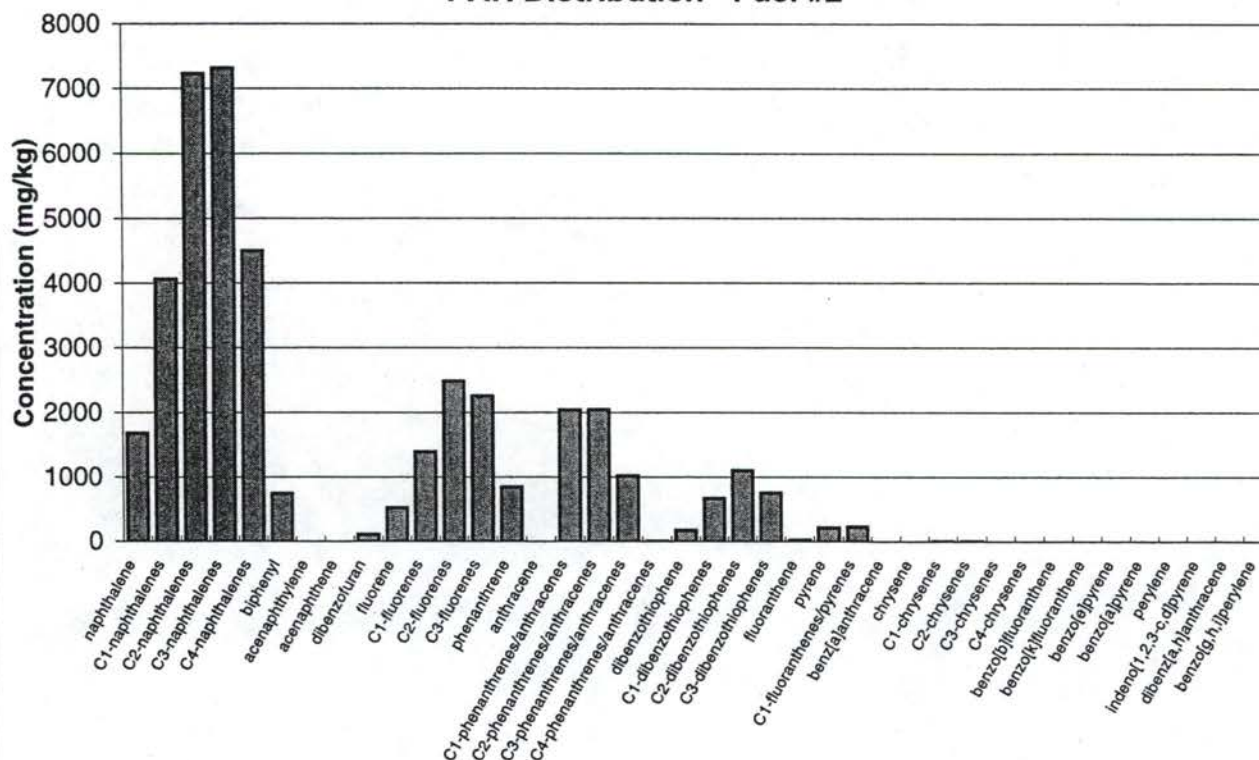




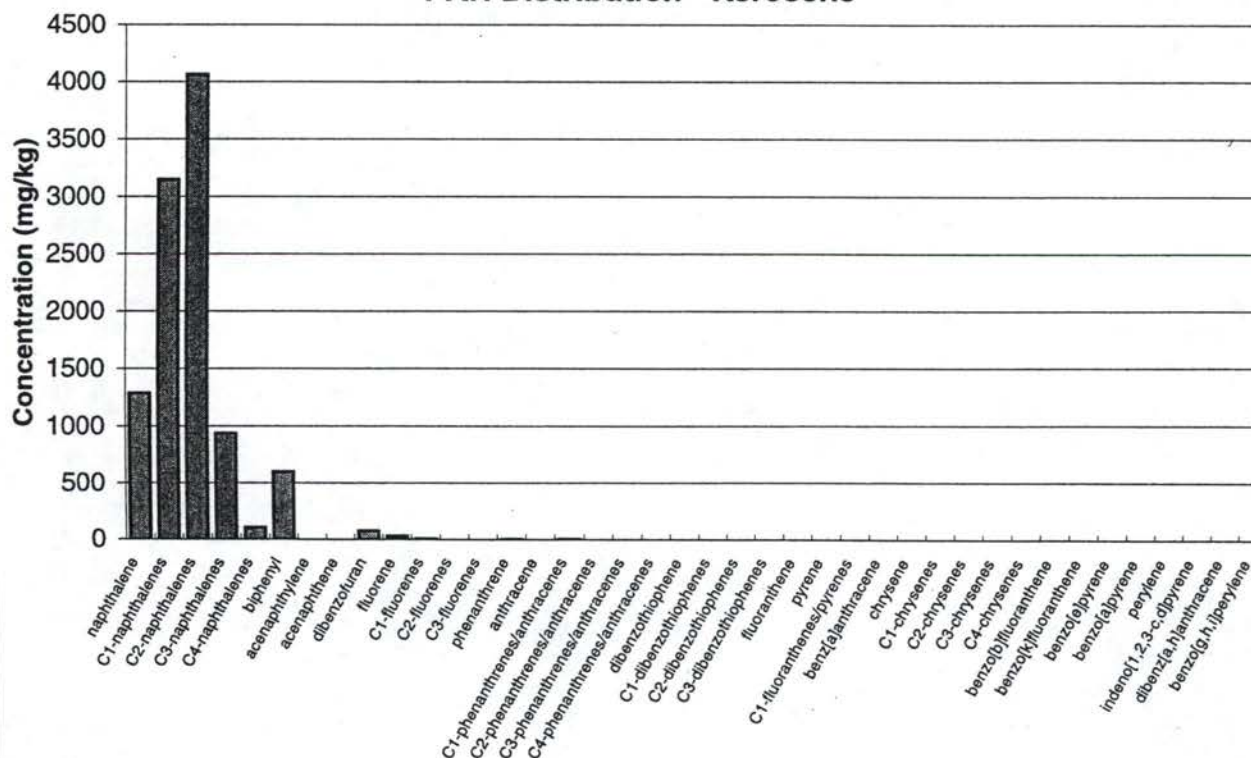




### PAH Distribution - Fuel #2

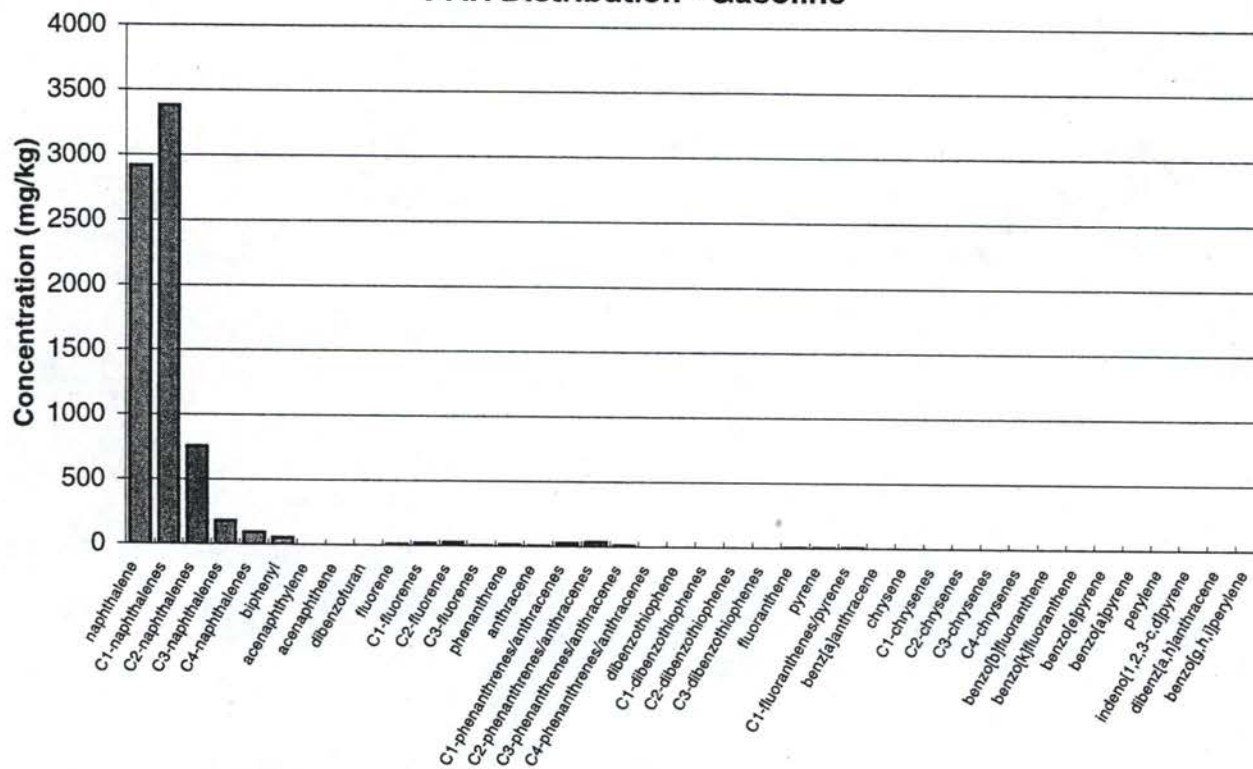


### PAH Distribution - Kerosene

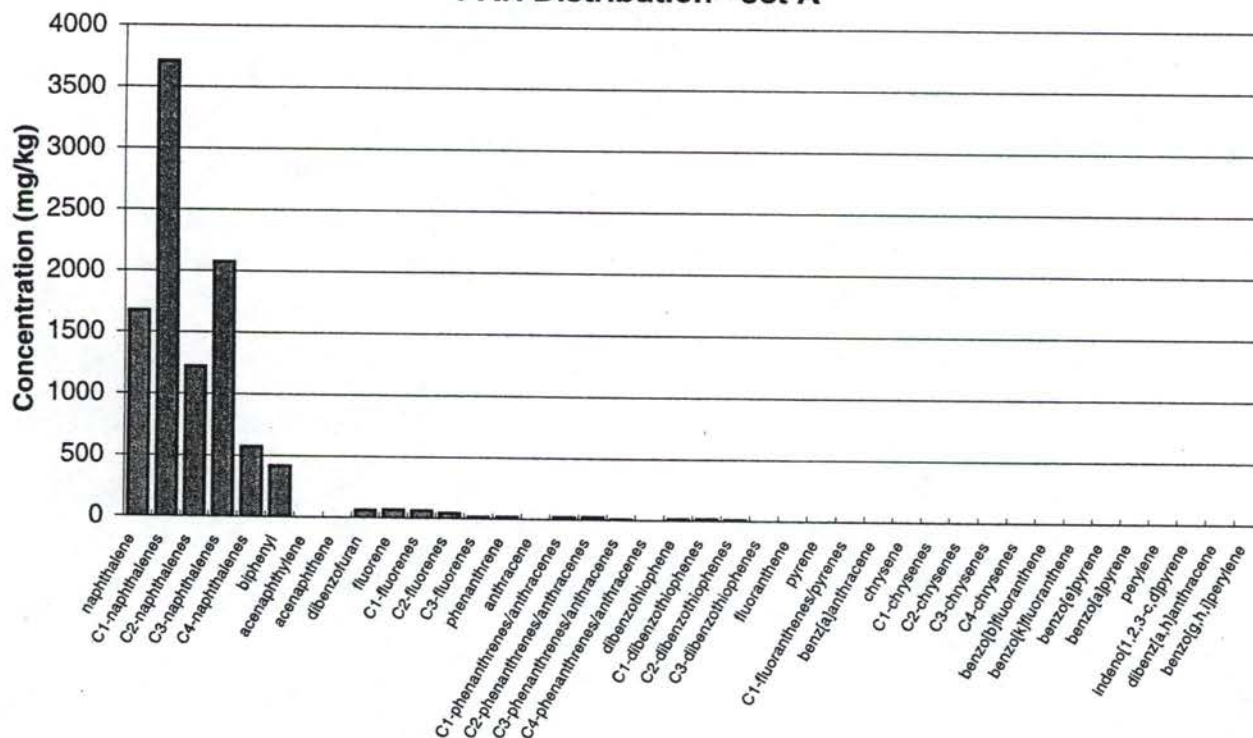




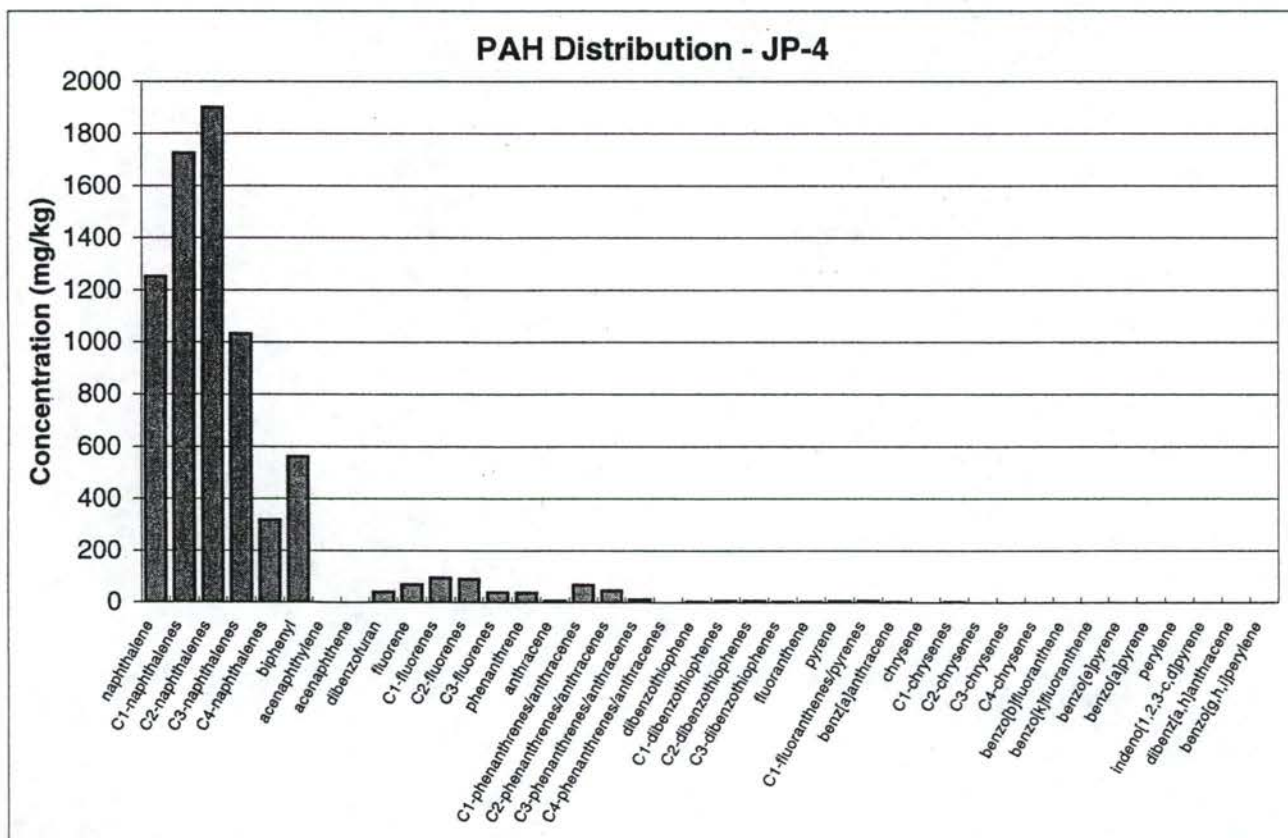
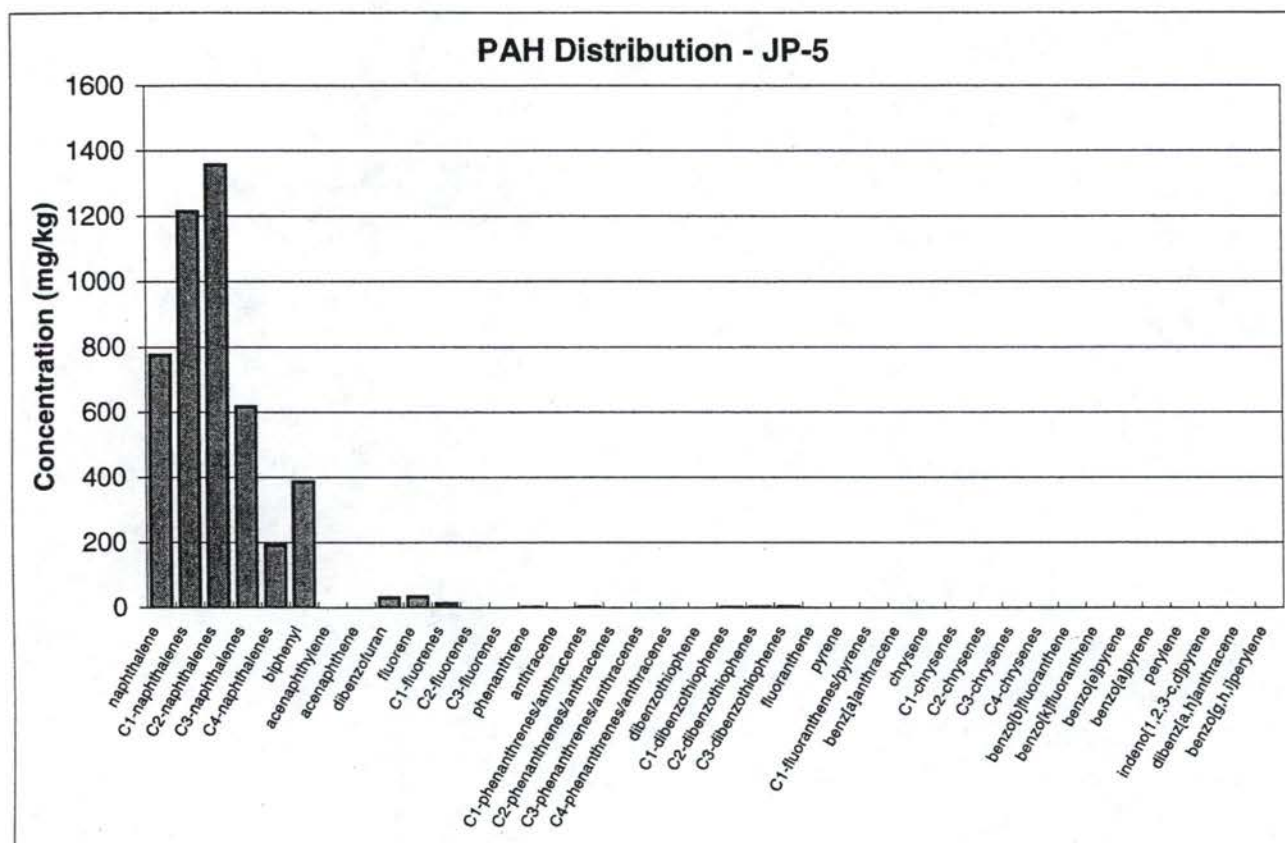
### PAH Distribution - Gasoline



### PAH Distribution - Jet A



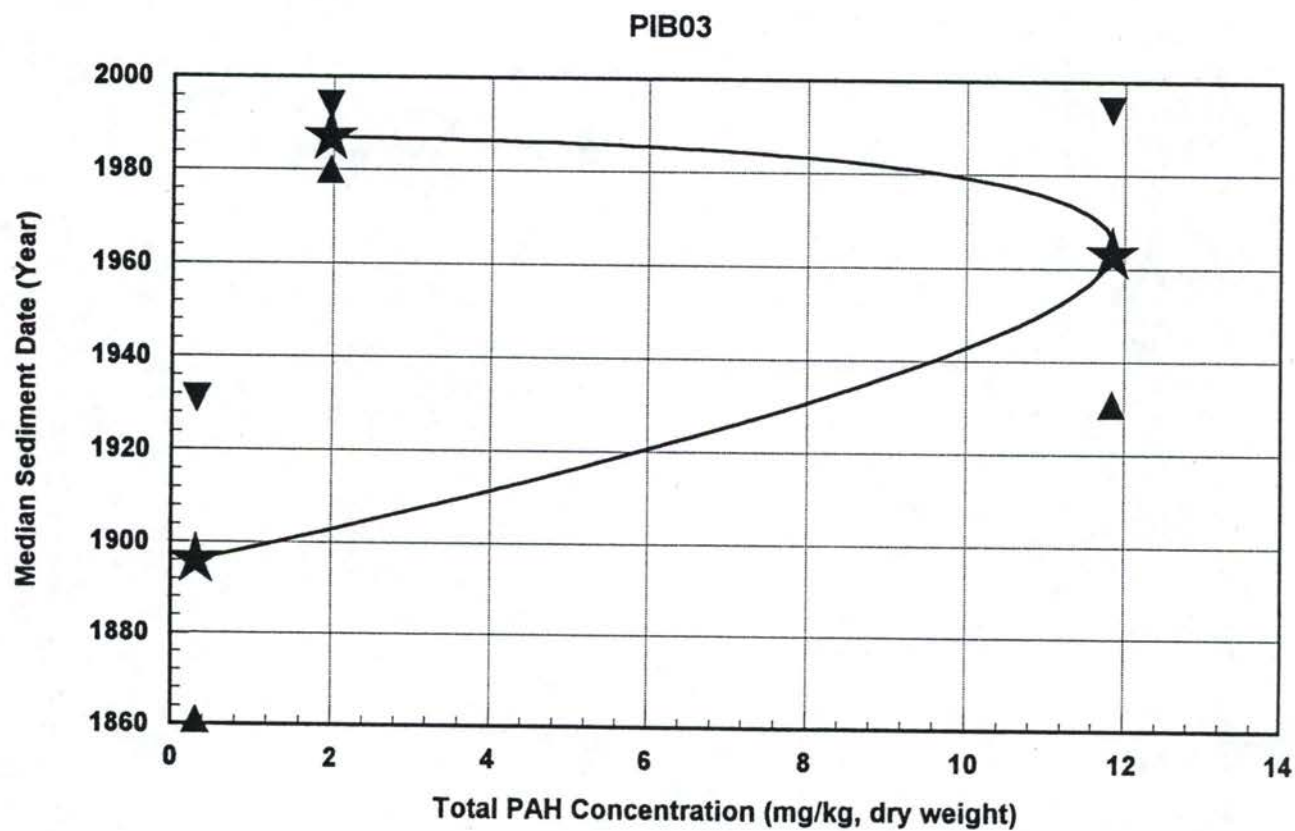
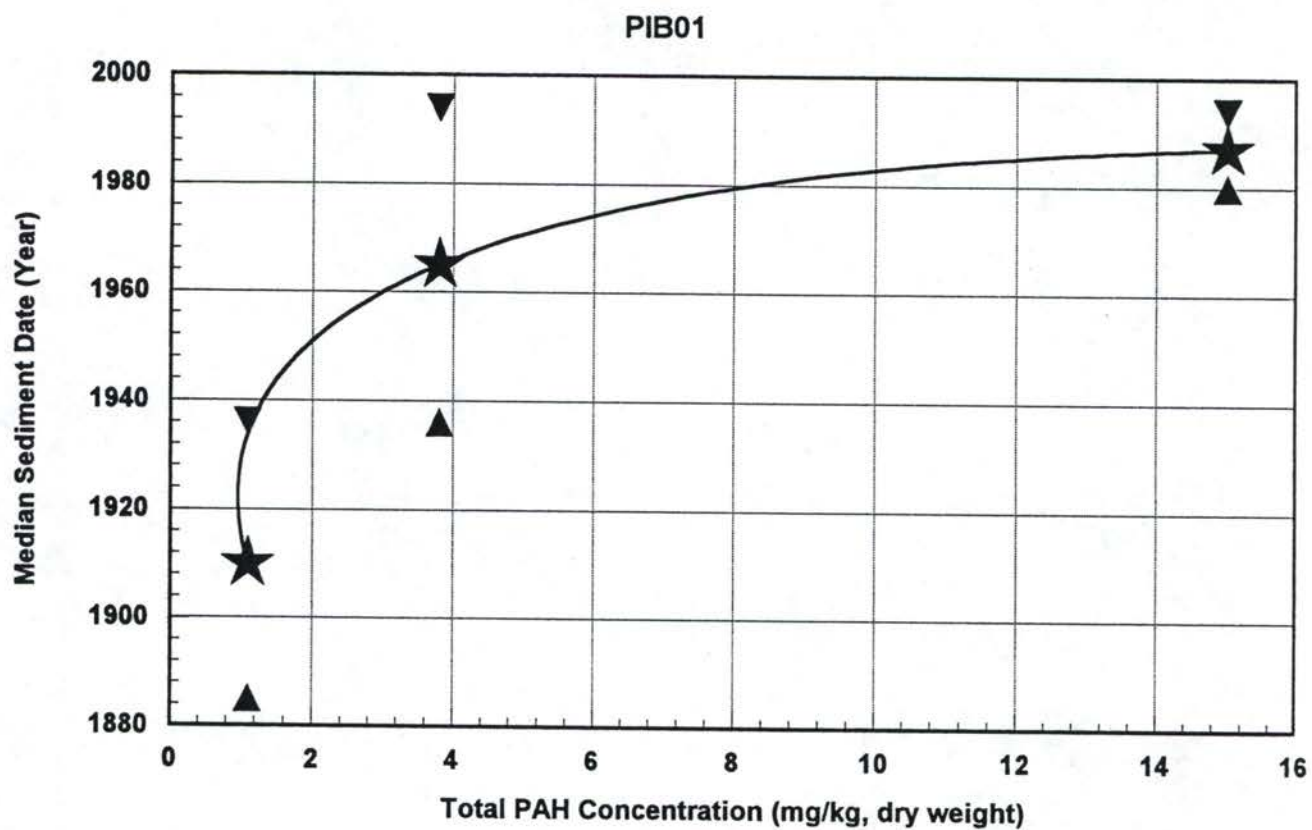






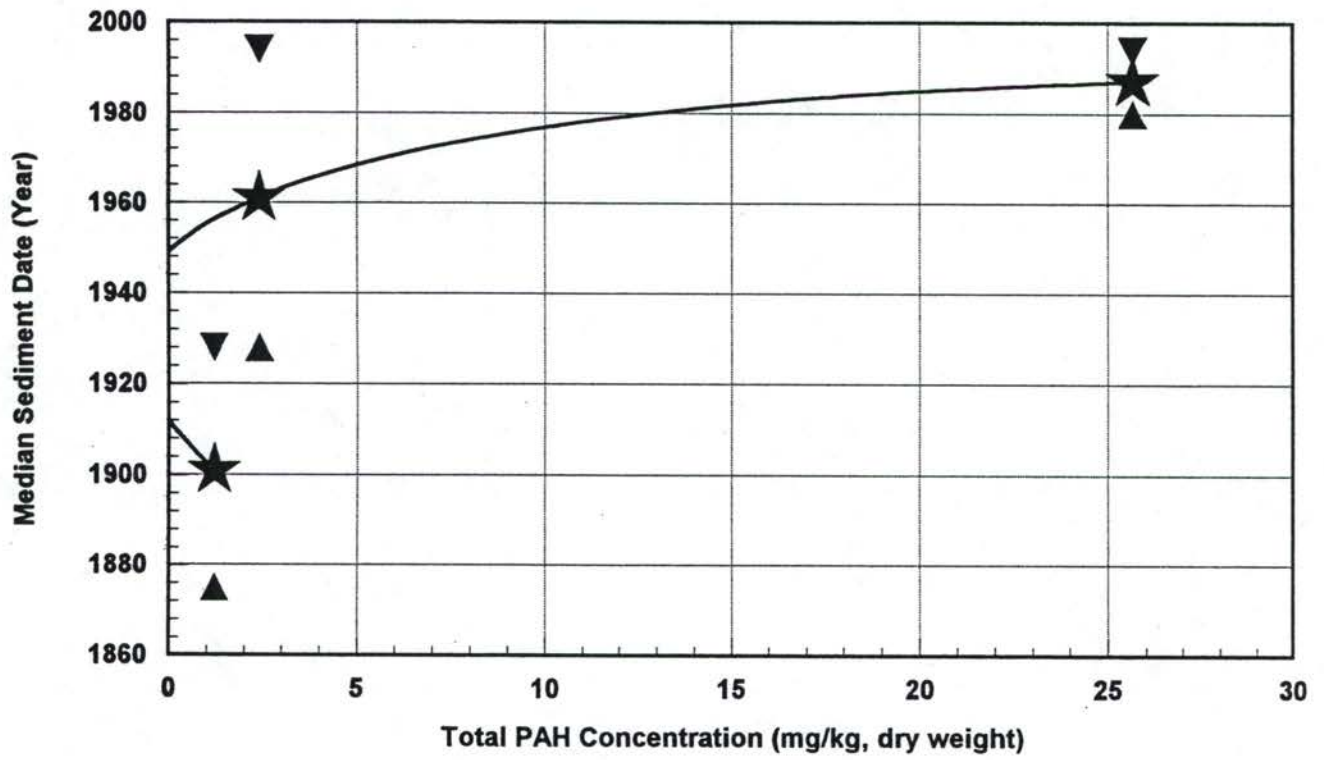
**Appendix E. WA107 Sediment PAH Concentration Profiles  
- Concentration by Sediment Date**







PIB04



PIB05

