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Tiffany Gregg for the degree of Master of Science in Marine Resource Management presented on June 19, 2009.
Title: Investigation of Polycyclic Aromatic Hydrocarbons (PAHs) transport by Suspended Particulate Matter (SPM) in the lower Columbia River and its Estuary.

Abstract approved:

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Fredrick G. Prahl

This study aims to improve knowledge of how suspended particulate matter (SPM) affects hydrophobic contaminant transport in the lower Columbia River and its estuary, using polycyclic aromatic hydrocarbons (PAHs) as model compounds. It is hypothesized that PAHs are transported to the estuarine turbidity maximum (ETM), a prime feeding zone in the Columbia estuary, where organisms encounter and consume contaminants adhered to particles as part of their diet. During a CMOP (Center for Coastal Margin Observation and Protection) cruise aboard the RV *Barnes* in August 2007, water samples were collected from sites throughout this study region. In addition, bi-monthly water samples were collected over a one-year period in coordination with the USGS NASQAN program. The PAH content and composition was analyzed in all samples and interpreted in perspective with the SPM concentration and particulate organic carbon content of the SPM.

Results show that the dominant source of PAH to the study region is a characteristic suite of compounds derived from high temperature combustion. Perylene, a compound of yet to be determined natural origin, represents a PAH of comparable quantitative significance. These compounds are transported via riverborne SPM to the estuary and hydrodynamically trapped in the ETM with the trapping process operating somewhat differently between the two sources. The concentration of individual combustion PAHs measured in SPM from the Columbia River and its estuary exceed the thresholds of concern stipulated by environmental protection policies. Surprisingly, measured PAH levels are similar to those measured in other, far more industrialized river and estuarine systems around the world.

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Investigation of Polycyclic Aromatic Hydrocarbons (PAHs) transport by Suspended Particulate Matter (SPM) in the lower Columbia River and its Estuary

by
Tiffany Gregg

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Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Tiffany Gregg, Author

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Investigation of Polycyclic Aromatic Hydrocarbons (PAHs) transport by Suspended Particulate Matter (SPM) in the lower Columbia River and its Estuary

Chapter 1: Introduction

The use of natural and manmade chemicals has substantially contributed to worldwide economic development and growth. However, these benefits have been realized without an effective chemical management strategy that can mitigate the true cost of releasing chemicals into the environment and the consequential degradation of air, soil, and water quality. In aquatic and marine environments, adverse impacts include fishery closures, recreational closures, a loss of biodiversity, and unsafe drinking water, thereby limiting the services these environments once provided to human society. In response, the Clean Water Act of 1972 initiated measures to mitigate point source discharge of contaminants into waterways. While these regulations have seen some success, water quality continues to plummet as fertilizers, oil and gas components, consumer products, and industrial waste still persist in waterways. The pathway to restoring water quality today will focus on managing pollutants discharged from nonpoint sources, such as urban runoff and air deposition (U.S. Ocean Commission, 2004).

One challenge will be to effectively manage persistent organic pollutants (POPs). These chemicals have been released into the environment for decades, owing to the central role they have played in pesticide control (e.g. dichlorodiphenyltrichloroethane or DDT) and industry (e.g. polychlorinated biphenyls or PCBs). The chemical structure of POPs makes them resistant to chemical, biological, and photolytic degradation processes and is the reason they have the ability to travel long distances, bioaccumulate in the fatty tissues of organisms, and in some cases biomagnify. With regards to management, the ubiquity of POPs is well known, but there is less understanding of POP transport, distribution, fate, and exposure pathways in each ecosystem of concern. Such knowledge is valuable because it allows resource managers to develop contaminant transport models that can aid in determining the most appropriate monitoring stations, predict zones where organisms may be at high risk to contaminant exposure, and assist in mitigation planning (Schwarzenbach et al., 2006; LCREP, 2007; U.S. Ocean Commission, 2004).

The lower Columbia River and estuary, located between Oregon and Washington, is one environment where POPs are widespread (Johnson et al., 2007; McCarthy and Gale, 2001). Here, polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), PCBs, and DDT have been detected in the bodies and stomach contents of juvenile Chinook salmon. The highest concentrations were measured from sampling sites adjacent to industrialized regions, such as Portland, Oregon. In some of the juvenile salmon, concentrations of PCBs, PAHs, and DDT approached or exceeded health effect thresholds where sublethal impacts on growth, development, reproduction, immune function, and behavior become prevalent (Johnson et al., 2007). Currently, it is unclear as to where and how organisms, such as juvenile salmon, are exposed to POPs within the Columbia River and estuary. This study addresses the possibility of suspended particulate matter (SPM) functioning as a POP transport mechanism and exposure pathway, which is evaluated using Polycyclic Aromatic Hydrocarbons (PAHs) as model contaminants.

Polycyclic Aromatic Hydrocarbons (PAHs) are included on the U.S. EPA list of priority pollutants due to potential carcinogenic and mutagenic health impairment some pose on exposed organisms, including humans (Boonyatumanond et al., 2006). PAHs are derived from three sources: 1) petrogenic (crude oil and refined products), 2) pyrogenic (incomplete combustion of fuels by both natural and anthropogenic processes), and 3) diagenetic transformation of natural biogenic precursors. Potential anthropogenic inputs of PAHs to the Columbia include atmospheric deposition of vehicle emissions, industrial fossil fuel burning, field burning, forest fires, urban runoff, smelting plants, waste incinerators, pulp mills, and petroleum product spills (Boonyatumanond et al., 2006; Xiao-Jun Luo et al., 2006; Yunker et al., 2002). In the Columbia estuary, the primary exposure route for aquatic/marine organisms to high molecular weight PAHs is likely through dietary consumption of carrier particles. This study investigates how the hydrodynamics of the estuarine turbidity maximum (ETM) may trap PAH carrier particles, thereby increasing the likelihood that organisms feeding within the ETM are also consuming these compounds with possible deleterious impact on them and higher trophic levels.

The estuarine turbidity maximum (ETM) is a complex transient sedimentary feature occurring in most tidal estuaries as a region characterized by high levels of suspended particulate material (SPM). ETM formation is shaped by tidal forces pushing salt water beneath outflowing river water, which through the dynamics of mixing creates a hydrodynamic particle trap (Park et al., 2008; Jay et al., 2007). The ETM is not stationary; it follows the leading edge of the salt wedge, moving upriver with the flood tide and downriver with the ebb tide. The strength and magnitude varies over time and is controlled by the energy of the tide (spring vs. neap), flow of the river, estuarine circulation, wind, and water density (e.g. Small and Prahl, 2004; Crump et al, 1999; North et al., 2005; Jago et al., 2006). For example, in the San Francisco Bay variations in SPM are primarily a result of the spring-neap tidal cycle, where SPM increases from resuspension during spring tide and deposits on the bed during neap tide (Schoellhamer et al., 2007).

In many estuaries, the ETM contains a relatively large zooplankton biomass compared to up-river. This characteristic allows the ETM to serve as feeding grounds for larval and juvenile fish (Suzuki, et al., 2008). For example, the Chesapeake Bay striped bass releases eggs up-river, which are transported to the ETM by river to estuary circulation patterns. This process places larvae in a zone of abundant zooplankton prey and optimal salinity for growth (North et al., 2005). In the Columbia estuary, the ETM traps particles during neap tide conditions and erodes particles during spring tide conditions. The trapped particles reside in the estuary for 2-4 weeks, whereas the residence time of water is only a few days (Crump et al., 1999). These particles play an important role in the estuary's food web, because zooplankton consume the organic matter associated with the particles as a primary food source (Morgan and Simenstad, 1997). The zooplankton are linked to higher trophic levels, such as fish and shrimp, making the ETM a region of high biological activity (Crump et al., 1999). It is possible that POPs are attached to the particles that the ETM selectively traps. If this is the case, consumers feeding within this region are at increased risk to contaminant exposure. Subsequently, the predators of ETM consumers are also potentially exposed to POPs through consumption of their prey.

The hypothesis motivating this study is that PAHs and other POPs detected in the Columbia Basin are transported via SPM to the estuary where they can be trapped, potentially selectively, by the estuary's ETM. The key objectives of the study were: 1) to characterize the overall composition of PAH in SPM from the Columbia River and its estuary; 2) to identify the primary sources contributing to this composition; 3) to track the behavior of PAH compounds within the estuarine SPM throughout the dynamics of neap and spring tidal focing; and 4) to determine if measured concentrations of the PAH on SPM fall above or below sediment quality criteria thresholds for compounds that are recognized priority pollutants.

Chapter 2: Materials and Methods

2.1 Study Area

Water samples were collected from eight sites during a two week cruise (August 16-29, 2007) aboard the *RV Barnes*, directed by the Center for Coastal Margin Observation and Prediction (CMOP) (Figure 2.1). The Columbia River sampling sites were located downriver from the port of Vancouver (hereafter referred to as Vancouver), downriver from the confluence of the Columbia and Willamette Rivers (hereafter referred to as Confluence), at Columbia City, and at Beaver Army Terminal (hereafter referred to as Beaver). The site on the Willamette River was located downriver from Portland Harbor (hereafter referred to as Portland) (Figure 2.1).

Sampling also took place throughout neap (August 20-24, 2007) and spring (August 26-29, 2007) tidal cycles at three locations within the estuary: the North Channel, South Channel, and estuary mouth (Figure 2.2). The North Channel is open to the ocean, but does not extend into the river, whereas the South Channel, a shipping channel maintained by the Army Corps of Engineers, is open to the ocean and connects with upriver ports. Estuary sampling focused on capturing the formation and disintegration of spring and neap tide ETMs. The boat was anchored at station prior to flood tide and conductivity, temperature, depth (CTD profiles) were obtained every 15-30 minutes to monitor water column structure and bottom turbidity. When a sharp increase in bottom turbidity was detected, bottom samples were collected at ~40 minute intervals until turbidity declined.

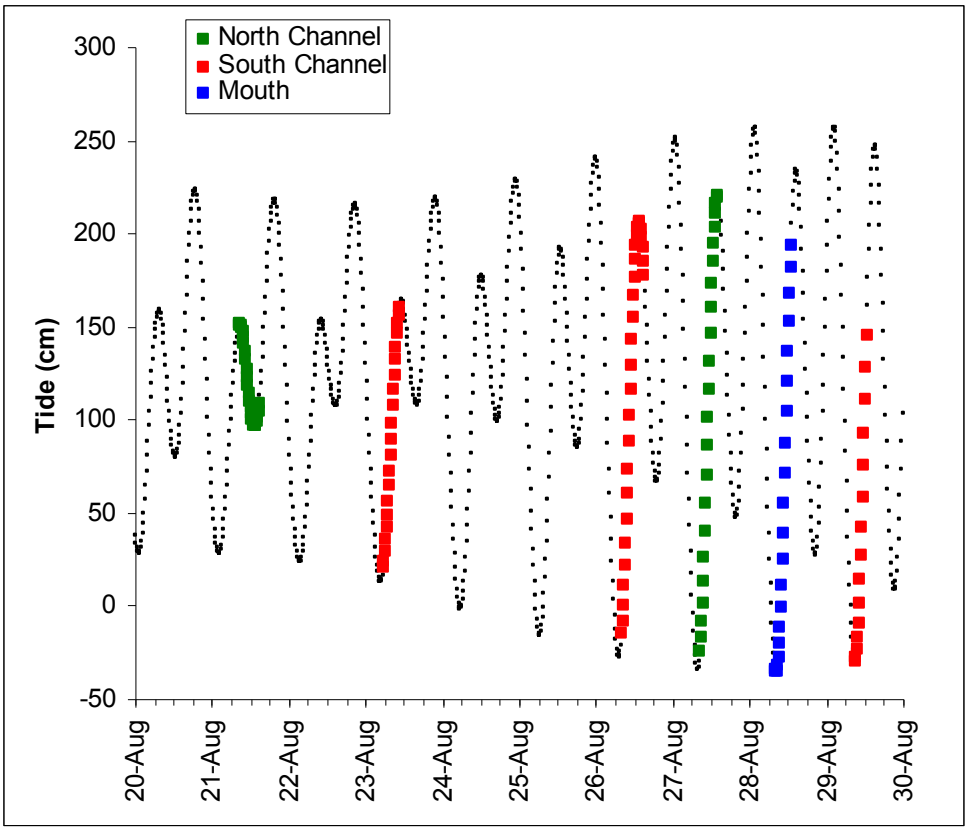
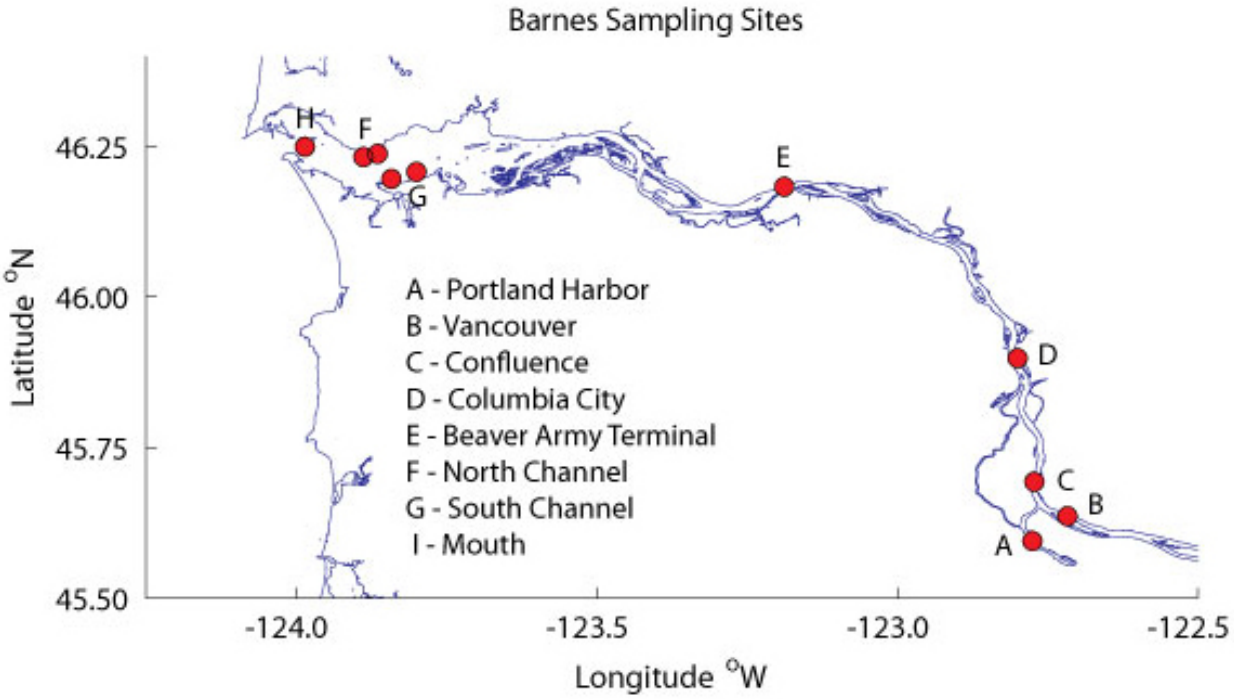


Figure 2.1: Neap (August 23-25, 2007) and spring (August 26-29, 2007) tidal cycles in the Columbia estuary showing when samples were collected.

In addition to sampling aboard the *RV Barnes*, water samples were collected approximately bi-monthly from February 2007 to February 2008 in conjunction with the US Geological Survey's (USGS) National Stream Quality Accounting Network (NASQAN) project operating out of Portland, Oregon. The Columbia River sampling site for the NASQAN project is located at Beaver, near Quincy, OR (Figure 2.1). It is the first upriver location above the saltwater intrusion where the channel is narrow and uninterrupted by islands. Therefore, it provides the best sample representation of the SPM and associated PAHs entering the estuary from the river. The Beaver site was established in 1972 and is the only long-term monitoring site remaining in the Columbia River and estuary (Morace, 2006).



Site Label	Site Name	Latitude	Longitude	Dates Sampled (2007)
A	Portland	45° 35.70' N	122° 46.51' W	8-18
B	Vancouver	45° 38.18' N	122° 43.04' W	8-18
C	Confluence	45° 41.60' N	122° 46.33' W	8-18
D	Columbia City	45° 54.38' N	122° 48.41' W	8-18
E	Beaver	46° 10.99' N	123° 11.28' W	8-19
F	North Channel	46° 14.25' N	123° 51.87' W	8-21,8-24,8-27
G	Sourth Channel	46° 12.45' N	123° 47.99' W	8-20,8-23,8-26,8-29
H	Mouth	46° 14.95' N	123° 59.13' W	8-22, 8-28

Figure 2.2: Map of *RV Barnes* sampling sites within the Columbia estuary (A-C), lower Columbia River (D-G), and Willamette River (H). The letters associated with each sampling site are more specifically defined in the table by latitude and longitude as well as the date of sampling.

2.2 Water Collection and Filtration

While aboard the *RV Barnes*, water samples were collected from near-surface (1 m below) and near-bottom (1 m above) locations using an airlift pump (50 mm PVC suction hose) attached to a CTD profiler. Once the CTD was lowered to the desired depth, water was pumped onto the deck and collected in 20 L Nalgene carboys. The carboys were vigorously shaken to ensure homogenization before measuring the volume of water needed to obtain samples for PAH, SPM, and particulate organic carbon (POC) analysis. Filtration volumes ranged from 3-6 L for PAH, 1-2 L for SPM, and 100-300 mL for POC samples.

For PAH and SPM analyses, a known volume of water was transferred into a stainless steel cylinder and pressure filtered with nitrogen gas (20 psi) through Teflon tubing to a filter (Prahl et al., 1984). SPM samples were filtered through pre-weighed 90 mm polycarbonate membrane filters (1.0 μm pore size) and PAH samples were filtered through 90 mm glass fiber (GF/C) filters (~1.2 μm pore size). POC samples were vacuum filtered by CMOP colleagues through precombusted (450°C for 4 hours) 25 mm GF/F filters (0.8 μm pore size). All filters were wrapped in pre-cleaned foil and frozen at -15°C until analyzed chemically in the laboratory at Oregon State University.

During USGS bimonthly sampling at Beaver, the water collection method was altered, because the boat was not equipped with the same sampling devices as the *RV Barnes*. A battery-powered, submersible impeller pump was used to collect water from ~1 meter below the surface. In order to gain a sense of fluvial particle input to the estuary, water was collected from three sampling sites evenly distributed across the width of the channel. Approximately 16 L of water was collected from each site and transported quickly (≤ 3 hrs) back to the laboratory at Oregon State University to filter for SPM and PAH concentrations. POC samples were not collected with the USGS.

2.3 Suspended Particulate Matter (SPM) Extraction

SPM filters were oven-dried at 50°C for 24 hours. After drying, the filters were re-weighed and the concentration (mg/L) of material on the filters was calculated from the determined mass and volume of water filtered (Ko and Baker, 2004; Sullivan et al., 2001).

2.4 Polycyclic Aromatic Hydrocarbon (PAH) Extraction

The procedures for processing glass fiber filters containing PAH mixtures have been described elsewhere (Shi et al., 2005; modified U.S. EPA methods 3510C (separatory funnel liquid-liquid extraction), 3630C (silica gel cleanup). To summarize, filters containing particle-bound PAHs were chopped with a clean razor blade to increase the surface area available for extraction. Samples were extracted using a Dionex ASE 200 after adding 10 μL of a mixed perdeuterated PAH recovery standard. The recovery standard was comprised of d10-phenanthrene, d10-fluoranthene, and d12-benzo[a]pyrene, each prepared at a concentration of 1 ng/μL in iso-octane. The ASE, set to 1500 psi and 100°C, sequentially extracted samples with 100% methanol (3x) and then by a 3:1 ratio of methylene chloride to methanol (4x). ASE sample extracts were partitioned into hexane with a separatory funnel and dried overnight over anhydrous sodium sulfate granules. This process yields a total extractable lipid (TEL) fraction that was concentrated to a small volume (~2 mL) using a Turbo Vap II and subsequently taken to dryness under a gentle stream of pre-purified nitrogen gas (EPA Method 3510C).

PAHs were isolated from the TEL reside using a silica gel-packed glass column (7g, silica gel 60, particle size 0.063-0.200mm, EMD). The silica gel support was activated at 220°C for 24 hours and deactivated with water by 5% before use. The column was eluted by gravity first with hexane (35 mL, discarded) and sequentially with 10% methylene chloride in hexane (40 mL) to collect a PAH fraction. The latter fraction was concentrated to a small volume (~2 mL) with nitrogen (Turbo Vap II), transferred quantitatively to small vials lined with Teflon caps, and then slowly reduced to near dryness using a gentle stream of pre-purified nitrogen.

2.5 Gas Chromatography Mass Spectrometry (GCMS) Analysis

Identification and quantification of PAHs was accomplished using a Hewlett Packard 5890A Series II gas chromatograph equipped with an HP-1 fused silica capillary column (30 m x 0.25 mm, 0.25 μm film thickness) and a Hewlett Packard 5971 mass selective detector. Helium was used as the carrier gas at a constant flow rate of 1 mL/min. The oven was temperature programmed starting at 100°C, ramped immediately to 300°C at a rate of 5°C/min and then held isothermal for a total time of 65 minutes (EPA Method 8270C).

PAH sample extracts were dissolved in iso-octane containing d12-chrysene (~1 ng/μL) as an internal standard. A total of 15 PAH compounds were monitored in selective ion mode (SIM) by retention time and at the following characteristic mass fragments: m/z = 178 (phenanthrene), 188 (d10-phenanthrene), 192 (methylphenanthrenes), 202 (fluoranthene, pyrene), 212 (d10-fluoranthene), 228 (benzo[a]anthracene, chrysene), 240 (d12-chrysene), 252 (benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene, perylene), 264 (d12-benzo[a]pyrene), and 274 (tetrahydrochrysenes). An external standard containing 7 PAH standards and 4 perdeuterated standards in iso-octane was used to obtain retention time criteria for peak identification. For PAH compounds not added to the standard (methylphenanthrenes, benzo[a]anthracene, tetrahydrochrysenes), a known archived sample containing these compounds was run to obtain retention times and confirm peak identification. A GCMS trace obtained from analysis of a Portland surface sample is shown in Figure 2.2. The general pattern of PAH retention times is representative of samples collected throughout the study region. The peak area from each detected compound was used in Equation 1 below to solve for PAH concentration in units of micrograms per g dry sediment.

The relative response factor in reference to d12-chrysene was used to convert peak area to PAH concentration. The external standard was run before and after every 3-4 PAH sample runs to compensate for fluctuations in GCMS performance (EPA Method 8270C). The sample PAH concentration in ng/g sediment was calculated using:

$$C_{PAH} = \left\{ RRF_{PAH} \left[\frac{1}{SW} \left(\frac{C_{is} \times V_{is}}{A_{is}} \times A_{smp} \times V_{smp} \right) \right] \times \frac{1}{\%R} \right\} \qquad \text{(Equation 1)}$$

where, C_{PAH} is the sample PAH concentration (ng PAH/g sediment), RRF_{smp} is the relative response factor of the sample, SW is the suspended sediment weight (g), C_{is} is the concentration of the internal standard (ng/μL), V_{is} is the volume of the internal standard (μL), A_{is} is the peak area of the internal standard, A_{smp} is the peak area of the sample, V_{smp} is the volume of the sample (μL), and %R is the percent recovery.

Quality control was monitored by calculating the percent recovery (%R) of three deuterated PAHs spiked into samples prior to ASE extraction (d10-phenanthrene, d10-fluoranthene, and d12-benzo[a]pyrene). The recovery data of samples collected from upriver *Barnes* sites, estuarine *Barnes* sites, and over the USGS time series at Beaver are shown in Appendices IA, IB, and IC, respectively. Phenanthrene and methylphenanthrenes were recovery-corrected with d10-phenanthrene. Fluoranthene, pyrene, and retene were corrected with d10-fluoranthene and all remaining PAHs were corrected with d12-benzo[a]pyrene. Analysis of replicate samples showed a 17% error in the quantification of PAH samples (Table 2.1). No PAH were detected in analysis of blank filters indicating no contamination of samples occurred during filter processing on board the ship or during the chemical workup procedure.

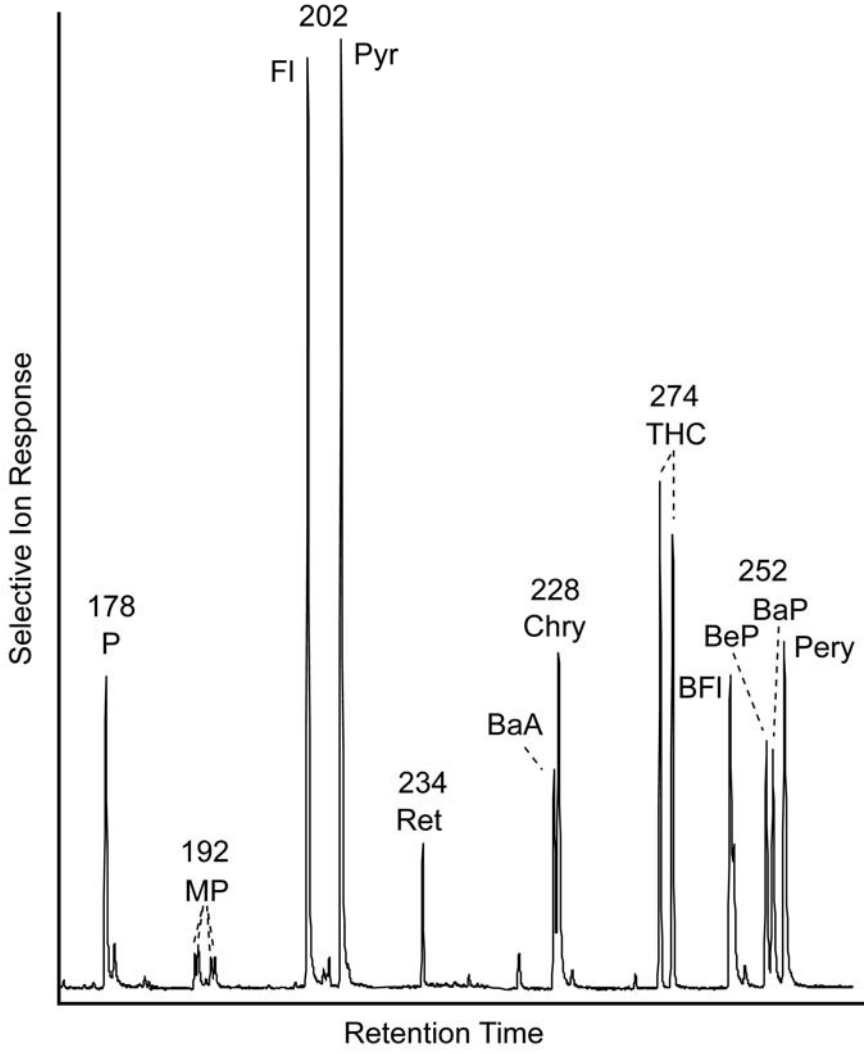


Figure 2.2: GCMS trace from Portland that is representative of samples collected throughout the study region. P- phenanthrene (m/z 178), MP- methylphenanthrenes (m/z 192), fl- fluoranthene and Pyr- pyrene (m/z 202), Ret- retene (m/z 234), BaA- benzo[a]anthracene and Chry- chrysene (m/z 228), THC- tetrahydrochrysenes (m/z 274), BFl- benzofluoranthenes, BeP- benzo[e]pyrene, BaP- benzo[a]pyrene and Pery- perylene (m/z 252).

Table 2.1: PAH concentrations of replicate sediment samples collected from Young's Bay, located in the intertidal region of the Columbia River Estuary. Analysis was used to estimate confidence in PAH quantitation.

Sediment Wt. (g)	Young's Bay PAH Concentrations (ng/g sediment)					
	Phen	Fluor	Pyr	Ret	Chry	Pery
0.1	3661	1940	2745	4597	2832	6703
0.5	3507	2187	2826	5662	2450	4337
1.0	3234	1528	2133	4329	1704	3843
1.4	3071	1754	2343	4600	2150	4164
1.5	4245	2088	2657	6527	1826	4741
Average	3544	1899	2541	5143	2192	4757
Std. Dev.	455	264	292	927	461	1135
% Error	13%	14%	12%	18%	21%	24%
% Error in Quantitation = 17%						

2.6 Particulate Organic Carbon and Nitrogen Extraction

POC samples were processed by CMOP colleagues aboard the *RV Barnes*. At OSU, the frozen filters were removed from their foil storage wrappers, defrosted and fumed with concentrated hydrochloric acid for (24 hours) to remove any inorganic carbon, then oven-dried (50°C for 24 hours) (Hedges and Stern, 1984). The dried filters were packed into pre-cleaned silver boats, manually pelletized with forceps and then wrapped in an additional layer of pre-cleaned tin foil. Samples prepared in this way were analyzed on a Carlo Erba NA-1500 elemental analyzer using acetanilide as a calibration standard, described elsewhere (Verardo et al., 1990).

Chapter 3: Results

3.1 PAH Correlation

The measured concentrations of 12 PAHs detected all samples collected from upriver *Barnes* sites, estuarine *Barnes* sites, and over the USGS time series at Beaver are shown in Appendices IIA, IIB, and IIC, respectively. To reduce the number of compounds discussed, correlation matrices were made for the 54 samples collected aboard the *Barnes* (Table 3.2 a) and the 23 samples collected with the USGS (Table 3.2 b). The Pearson correlation coefficients presented in Tables 3.2 are a measure of the linear dependence between two PAH compounds. A value of 1.0 is a perfect correlation, where x increases as y increases. The following t-test equation was used to evaluate the significance of correlation coefficients that were less than 1.0:

$$t = \frac{r}{\sqrt{\frac{1-r^2}{N-2}}} \qquad \text{(Equation 2)}$$

where N is the sample size (54 for Barnes and 23 for USGS) and r is the Pearson correlation coefficient (Till, 1974). Using this equation, an r value of 0.8 or greater has less than a 0.000001 probability of being uncorrelated and thus interpreted as more than sufficient for making source assignments. Within the *Barnes* and USGS datasets, eight out of the twelve PAHs had r values ≥0.8 (phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene) indicating that these compounds were derived from the same source.

Scatter plots were constructed to visualize the relationships defined by correlation results in Table 3.1 and to further assist with appropriate source groupings for the PAHs. A plot of fluoranthene versus pyrene indicates that in nearly all samples analyzed within the study region, the concentration these two PAH was effectively 1:1 (Figure 3.1a). Past studies have found that this criterion is indicative of a combustion source (LaFlamme and Hites, 1978; Blumer and Youngblood, 1975). A scatter plot of phenanthrene to methylphenanthrenes shows that the data is mostly distributed along a relationship of 0.25:1 and 0.5:1 (Figure 3.1b). Past studies have determined that MP:P ratios within this range are typical of combustion, whereas a relationship of 1:1 or greater is typical of petroleum. The scatter plots reveal a pyrogenic source and indicate that the eight

correlated PAHs identified in Table 3.1 can be grouped together. The concentrations of these PAHs were summed and will henceforth be referred to as the sum of combustion PAHs (∑COMB). Methylphenanthrenes (MPs) is a compound associated with petroleum and burning, but it did not meet the correlation coefficient criteria (≥ 0.8) and was not included in the ∑COMB.

The remaining three PAHs (retene, tetrahydrochrysenes, perylene) were not highly correlated with ∑COMB or with one another. Figure 3.2 (a-c) shows scatter plots which identify the samples that reduce the correlation. Different origin, specific particle association and subsequent environmental behavior are the ascribed reasons for the reduced correlation. Perylene is a diagenetic product that has not been associated with an anthropogenic process. Tetrahydrochrysenes and retene are natural derivatives of wood that can be released into the environment through anthropogenic burning and forest fires.

Table 3.1: Correlation matrix of A) 54 samples collected aboard the *Barnes* and B) 23 samples collected from Beaver with the USGS. The correlation coefficients highlighted in red are greater than or equal to 0.8 and statistically significant (P<<0.001).

A)	Phen	MP	Fluor	Pyr	Ret	BaA	Chry	THC	BFl	BeP	BaP	Pery
Phen	1											
MP	0.6	1										
Fluor	**0.9**	0.4	1									
Pyr	**0.9**	0.4	**1.0**	1								
Ret	0.5	0.2	0.6	0.6	1							
BaA	**0.8**	0.7	0.7	0.7	0.4	1						
Chry	**0.9**	0.4	**0.9**	**0.9**	0.6	0.8	1					
THC	0.5	0.2	0.5	0.5	0.3	0.6	0.5	1				
BFl	**0.9**	0.7	**0.8**	**0.8**	0.5	**1.0**	**0.8**	0.5	1			
BeP	**0.8**	0.4	**0.9**	**0.9**	0.6	0.7	**0.9**	0.5	**0.8**	1		
BaP	**0.9**	0.4	**1.0**	**1.0**	0.6	0.7	**0.9**	0.4	**0.8**	**1.0**	1	
Pery	0.3	0.2	0.1	0.1	0.1	0.4	0.3	0.1	0.4	0.2	0.2	1

B)	Phen	MP	Fluor	Pyr	Ret	BaA	Chry	THC	BFl	BeP	BaP	Pery
Phen	1											
MP	0.5	1										
Fluor	**0.9**	0.3	1									
Pyr	**0.9**	0.4	**1.0**	1								
Ret	0.2	0.1	0.1	0.1	1							
BaA	**0.8**	0.2	**1.0**	**0.9**	0.0	1						
Chry	**0.8**	0.3	**1.0**	**1.0**	0.0	**1.0**	1					
THC	0.4	0.3	0.3	0.3	0.7	0.2	0.3	1				
BFl	**0.8**	0.3	**1.0**	**1.0**	0.1	**1.0**	**1.0**	0.3	1			
BeP	**0.8**	0.3	**1.0**	**1.0**	0.1	**1.0**	**1.0**	0.3	**1.0**	1		
BaP	**0.8**	0.2	**1.0**	**1.0**	0.0	**1.0**	**1.0**	0.1	**1.0**	**1.0**	1	
Pery	0.6	0.4	0.5	0.5	0.4	0.3	0.4	0.5	0.4	0.5	0.4	1

*Phen- phenanthrene, MP- methylphenanthrenes, Fluor- fluoranthene, Pyr- pyrene, Ret- retene, BaA- benzo[a]anthracene, Chry- chrysene, THC- tetrahydrochrysenes, BFluor- benzofluoranthenes, BeP- benzo[e]pyrene, BaP- benzo[a]pyrene, Pery- perylene.

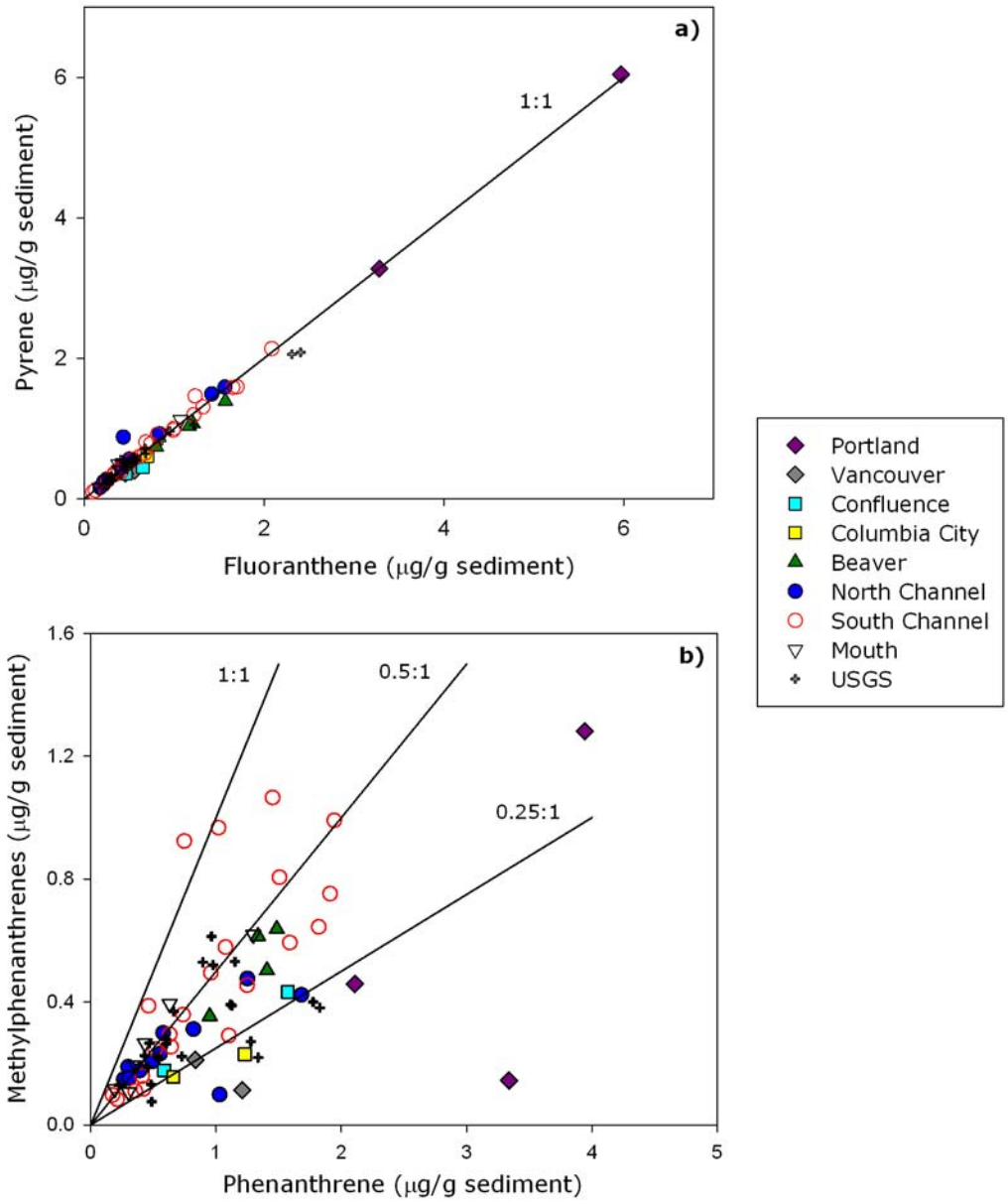


Figure 3.1: Scatter plots used in grouping 12 PAHs by similar source: a) fluoranthene to pyrene and b) methylphenanthrenes to phenanthrene. Solid lines are representative of relationships, e.g. a 1:1 relationship.

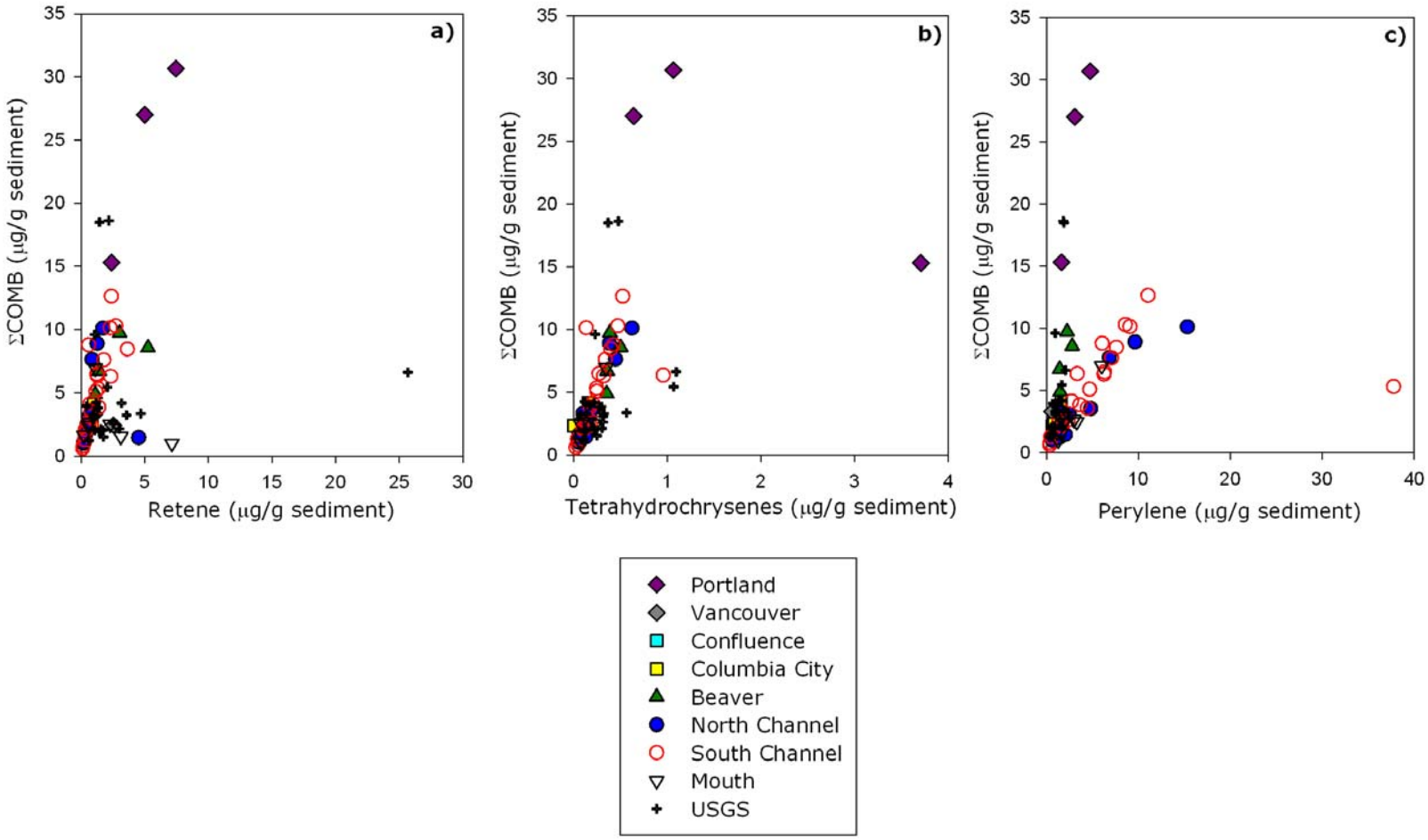


Figure 3.2: Scatter plots of ∑COMB versus a) retene, b) tetrahydrochrysenes, and c) perylene.

3.2 Combustion PAHs (∑COMB)

The mean concentration of combustion PAH (∑COMB) in bottom and surface samples collected aboard the *Barnes* is provided in Tables 3.2a and 3.2b, respectively. Highest ∑COMB concentrations were measured in particles from bottom waters of Portland and the lowest in particles from surface waters of the estuary. Values for the three uppermost Columbia River sampling sites (Vancouver, Confluence, and Columbia City) were relatively constant. Those at Beaver were not equivalent to the other Columbia River sites. The mean ∑COMB concentrations at the surface and bottom of Beaver exceeded the other Columbia River sites by 34% and 66%, respectively. The three estuary sites (North Channel, South Channel, and Mouth) also showed little variability. On average, concentrations in bottom waters of the estuary exceeded those in the surface by 72%. Mean ∑COMB concentration was similar between the estuary and Beaver bottom sampels (18% higher at Beaver) (Figure 3.3).

3.3 Suspended Particulate Matter (SPM) Concentrations

Mean bottom and surface SPM concentrations from the eight sampling sites are shown in Tables 3.2a and 3.2b, respectively. Portland SPM concentrations at the surface and bottom were similar and elevated over measurements in the Columbia River. SPM in the estuary behaved differently. Measurements from surface waters of the estuary were similar to Columbia River values. However, the mean SPM concentration in bottom waters of the estuary (33.9 ± 5.5 mg/L) exceeded the bottom mean in the Columbia River by 79% (Figure 3.3). These high SPM values are attributed to estuary sampling taking place throughout the formation and disintegration of ETMs.

Table 3.2a: Bottom SPM and PAH Means from *Barnes* sampling sites

Site	SPM (mg/L ± SD)	PAH Concentrations (µg/g dry ± SD)			
		∑Comb	Ret	ThChry	Pery
Portland	17.8 ± 5.0	28.8 ± 2.6	6.2 ± 1.7	0.9 ± 0.3	3.9 ± 1.2
Vancouver	6.4	2.4	2.5	0.0	1.0
Confluence	9.2	2.1	0.4	0.0	0.6
Columbia City	7.9	2.3	0.9	0.0	0.8
Beaver	5.6	6.7	1.4	0.4	1.4
North Channel	28.2 ± 17.6	5.0 ± 3.4	1.4 ± 1.3	0.3 ± 0.2	5.5 ± 4.9
South Channel	39.1 ± 22.0	6.1 ± 3.2	1.5 ± 0.9	0.3 ± 0.2	7.3 ± 8.3
Mouth	34.3 ± 19.5	5.3 ± 3.0	1.4 ± 1.0	0.3 ± 0.2	6.3 ± 6.5

Table 3.2b: Surface SPM and PAH Means from *Barnes* sampling sites

Site	SPM (mg/L ± SD)	PAH Concentrations (µg/g dry ± SD)			
		∑Comb	Ret	ThChry	Pery
Portland	16.2	15.3	2.4	3.7	1.6
Vancouver	7.6	3.3	1.0	0.2	0.6
Confluence	6.4	3.8	1.0	0.2	1.3
Columbia City	7.8	4.2	1.0	0.2	1.6
Beaver	7.1 ± 0.9	5.7 ± 2.7	2.1 ± 1.8	0.3 ± 0.1	1.7 ± 0.8
North Channel	6.9 ± 2.4	1.4 ± 0.6	0.3 ± 0.1	0.1 ± 0.0	1.1 ± 0.5
South Channel	8.2 ± 6.0	1.8 ± 1.5	0.4 ± 0.3	0.1 ± 0.1	1.1 ± 1.0
Mouth	10.0 ± 3.7	1.4 ± 0.3	3.5 ± 3.5	0.1 ± 0.0	1.3 ± 0.2

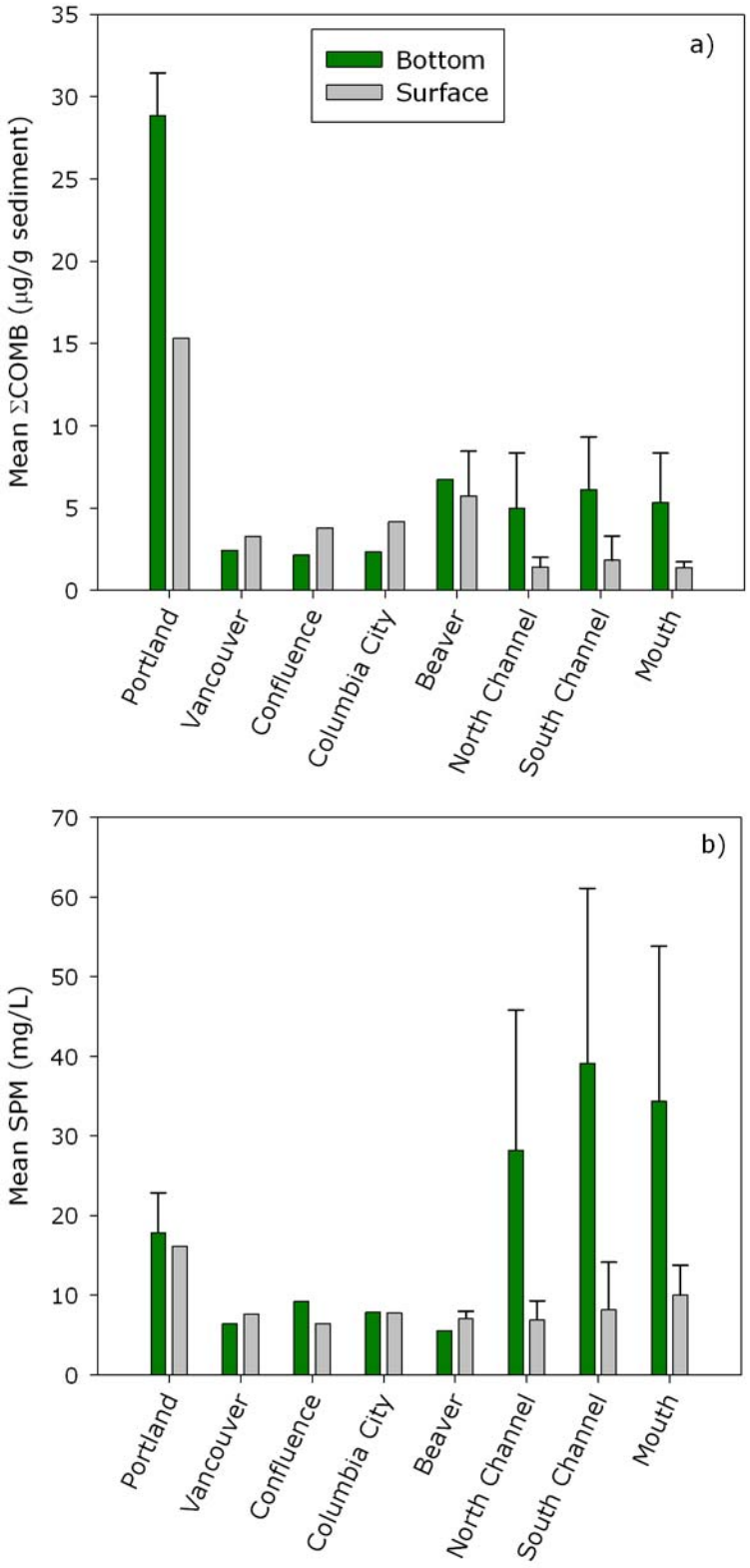


Figure 3.3: a) Mean (± SD) ∑COMB and b) SPM (± SD) concentrations measured in surface and bottom waters at the Barnes sampling sites, August 2007.

3.4 Retene, Tetrahydrochrysenes, and Perylene

Mean bottom and surface concentrations for retene, tetrahydrochrysenes, and perylene are shown in Tables 3.2a and 3.2b, respectively. Retene levels were highly variable between sites and in samples collected from the same site. Thirteen samples had retene concentrations that exceeded 2.0 μg/g, but these samples were not site specific and were measured at both the surface and bottom. Throughout the study region, tetrahydrochrysenes were present at very low concentrations, making their accurate quantification very difficult. Perylene levels were low at the surface of all sites. Bottom concentrations were high at all three estuary sites and at Portland. The mean perylene concentration in SPM from bottom waters of the estuary bottom was 82% greater than that in SPM from surface waters of the estuary and 39% greater than that in SPM waters at Portland.

3.5 Estuarine Turbidity Maximum (ETM) Trapping

Estuary samples were collected from August 20-23, 2007 to capture neap tide ETMs and from August 26-29, 2007 to capture spring tide ETMs (Figure 2.2). Turbidity was visualized onboard the *Barnes* as the CTD was lowered from the surface to the bottom. In general, an ETM was approaching the anchored boat when bottom turbidity increased by ~3-4 NTU (Nephelometric Turbidity Units) in a 30 minute time span. Since the boat was anchored during sampling, there was only ~2 hours to catch the ETM as it passed under the boat and progressed upriver. It is unknown if the collected samples collected capture the peak of the ETM, because the sampling process would often exceed 40 minutes.

Figure 3.4 shows how concentrations (both /g dry sediment and /gOC) for ∑COMB and perylene vary versus SPM (plotted as its inverse). This graphical method represents the ETM as an endmember to the mixing curve and places the more particle-rich or turbid water towards the origin of the plot (Prahl et al., 1997). The ETM is defined to be ≥40 mg/L (or 0.25 L/mg SPM). At the estuary bottom, ∑COMB and perylene concentrations increase in vicinity of the ETM reference line. In comparison to bottom samples, surface SPM is clearly lower and surface samples are generally less concentrated in ∑COMB and perylene. The ∑COMB concentrations in the river (represented by Beaver) are approximately equal to concentrations measured at the estuary bottom. However, the concentration of perylene on SPM in estuary bottom waters is, on average, 73% greater than perylene concentrations on SPM in the river.

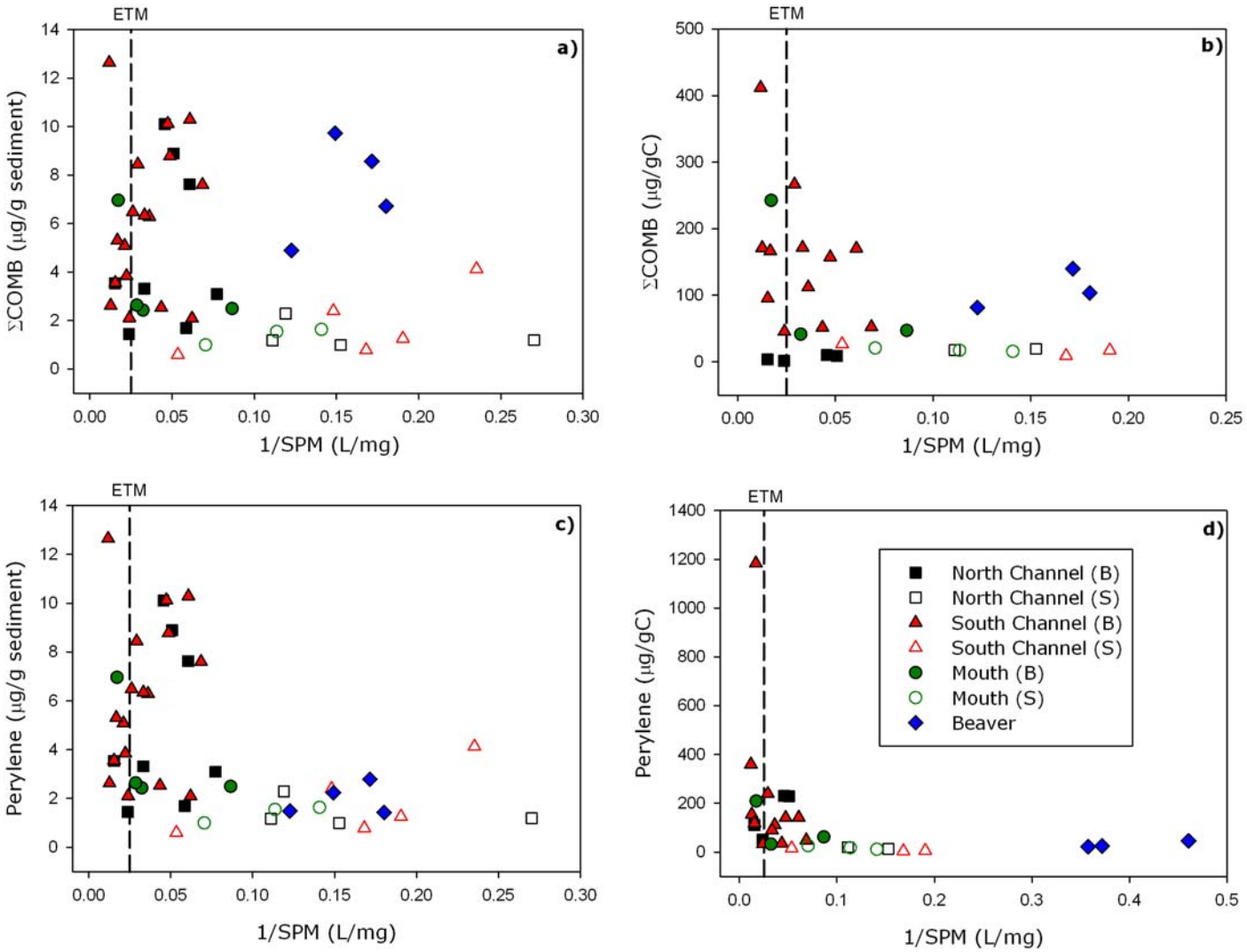


Figure 3.4: a) ∑COMB (/g) b) ∑COMB (/gC) c) Perylene (/g) d) Perylene (/gC) plotted versus the inverse of SPM concentration (i.e., L/mg).

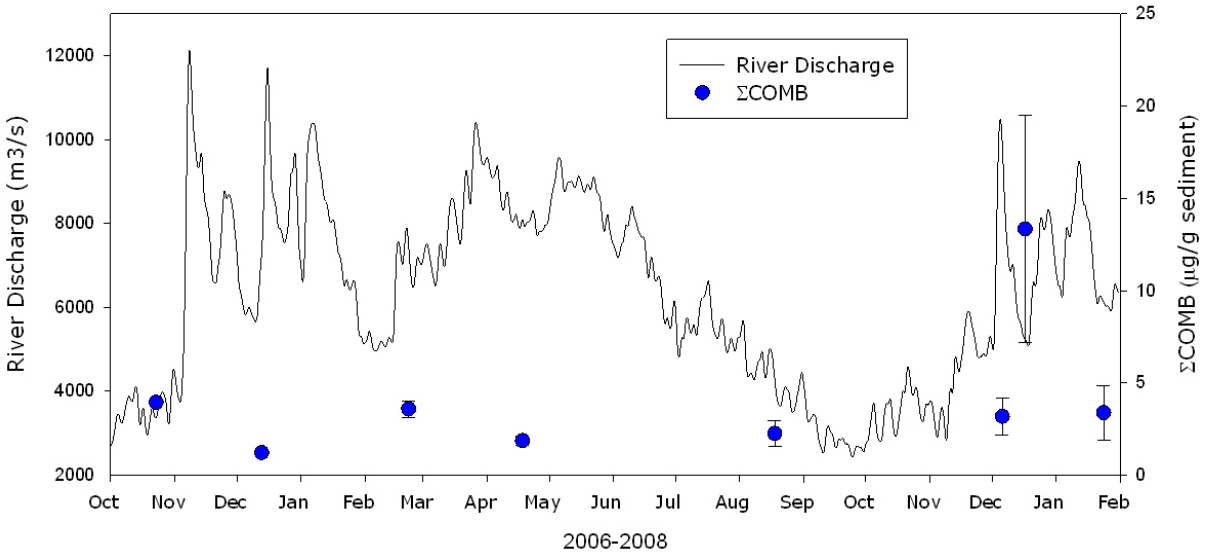
3.6 Bi-monthly Combustion PAH Concentrations (∑COMB) at Beaver

Figure 3.5 shows fluctuations in ∑COMB concentration measured bi-mothly at Beaver in cooperation with the U.S Geological Survey's NASQAN (National Stream Quality Accounting Network) program. The transport of PAHs on SPM is continuous throughout the year. There is a gap in sampling from August to December 2007, because funding for the NASQAN project was temporarily brought to a close. The highest PAH pulse occurred in December 2007 and the lowest level was measured in December 2006. River flow at Beaver was also plotted in Figure 3.5 to assess whether or not PAH levels increased as flow increased, but there was not any detection of a clear pattern.

3.7 Sediment Quality Guidelines for PAHs

Sediment quality guidelines were used to evaluate the level of risk associated with exposure to PAHs in SPM (threshold values for contaminants adsorbed to SPM do not exist). The two guidelines used were the threshold effect level (TEL), defined as the contaminant concentration level at which no adverse effects are likely to occur, and the probable effects level (PEL), defined as the contaminant concentration level at which adverse impacts in organisms are expected to occur frequently (MacDonald et al., 2000). PELs and TELs have been calculated for five PAHs known to cause adverse impacts in organisms: phenanthrene, fluoranthene, pyrene, chrysene, and benzo[a]pyrene (MacDonald et al., 2000).

For each sampling site, the measured surface and bottom concentrations of these five PAHs were compared to the corresponding TEL and PEL values (Table 3.3 and Figure 3.6). Portland is not included in Figure 3.6 because concentrations greatly surpassed the other sites making comparisons difficult. However, Table 3.3 shows that all five TELs and PELs were exceeded at Portland. In the Columbia River and estuary, TELs were always exceeded on SPM in both surface and bottom waters. The phenanthrene PEL was exceeded at all sites, except in waters at the surface of the estuary (Figure 3.6 a). The pyrene and chrysene PEL were exceeded in SPM from both the surface and bottom waters of Beaver, while samples from estuary bottom waters fall slightly below (Figure 3.6 c,d). The fluoranthene and benzo[a]pyrene PELs were not exceeded at any of the Columbia River and estuary sites (Figure 3.6 b,e).



Date	Mean ∑COMB (µg/g ± SD)	Mean SPM (mg/L ± SD)	River Discharge (m^3/s)
10/23/2006	3.94	3.2	3370
12/13/2006	1.22	11.3	7306
2/22/2007	3.59 ± 0.45	25.8 ± 5.5	7476
4/18/2007	1.88 ± 0.24	14.5 ± 2.1	8099
8/18/2007	2.26 ± 0.71	6.89 ± 1.2	4276
12/6/2007	3.19 ± 1.0	66.1 ± 10.8	9883
12/17/2007	13.3 ± 6.1	10.5 ± 2.8	5239
1/24/2008	3.39 ± 1.5	12.7 ± 3.3	6116

Figure 3.5: Columbia River discharge measured at Beaver compared to fluctuations in ∑COMB PAHs over the year 2007. For each USGS sampling day, the table reports the mean values of ∑COMB, SPM, and river discharge.

Table 3.3: Probable Effects Level (PEL) and Threshold Effects Level (TEL) for five PAHs known to cause adverse impacts in organisms. Abbreviations for each compound are in parentheses. Sample measurements exceeding the TEL are in *italics* and those exceeding the PEL are in red.

A) Surface TEL & PEL Concentrations (µg/g sediment)

PAH Compound	TEL	PEL	Portland	Vancouver	Confluence	Columbia City	Beaver	North Channel	South Channel	Mouth
Phenanthrene (Phen)	0.042	0.52	2.1	1.2	1.6	1.2	1.3	*0.38*	*0.38*	*0.28*
Fluroanthene (Fluor)	0.11	2.4	3.3	*0.56*	*0.65*	*0.70*	*1.2*	*0.25*	*0.32*	*0.24*
Pyrene (Pyr)	0.053	0.88	3.3	*0.40*	*0.45*	*0.60*	1.1	*0.25*	*0.33*	*0.24*
Chrysene (Chry)	0.057	0.86	1.9	*0.34*	*0.43*	*0.57*	1.2	*0.13*	*0.21*	*0.15*
Benzo[a]pyrene (BaP)	0.032	0.78	0.89	*0.064*	*0.098*	*0.20*	*0.52*	*0.074*	*0.12*	*0.098*

B) Bottom TEL & PEL Concentrations (µg/g sediment)

PAH Compound	TEL	PEL	Portland	Vancouver	Confluence	Columbia City	Beaver	North Channel	South Channel	Mouth
Phenanthrene (Phen)	0.042	0.52	3.6	0.83	0.59	0.66	1.4	0.89	0.92	0.75
Fluroanthene (Fluor)	0.11	2.4	6.2	*0.45*	*0.46*	*0.42*	*1.2*	*0.72*	*0.98*	*0.56*
Pyrene (Pyr)	0.053	0.88	6.7	*0.36*	*0.35*	*0.48*	1.0	0.81	0.95	*0.61*
Chrysene (Chry)	0.057	0.86	3.6	*0.15*	*0.18*	*0.19*	1.0	*0.71*	*0.72*	*0.41*
Benzo[a]pyrene (BaP)	0.032	0.78	2.7	*0.17*	*0.093*	*0.033*	*0.47*	*0.42*	*0.46*	*0.24*

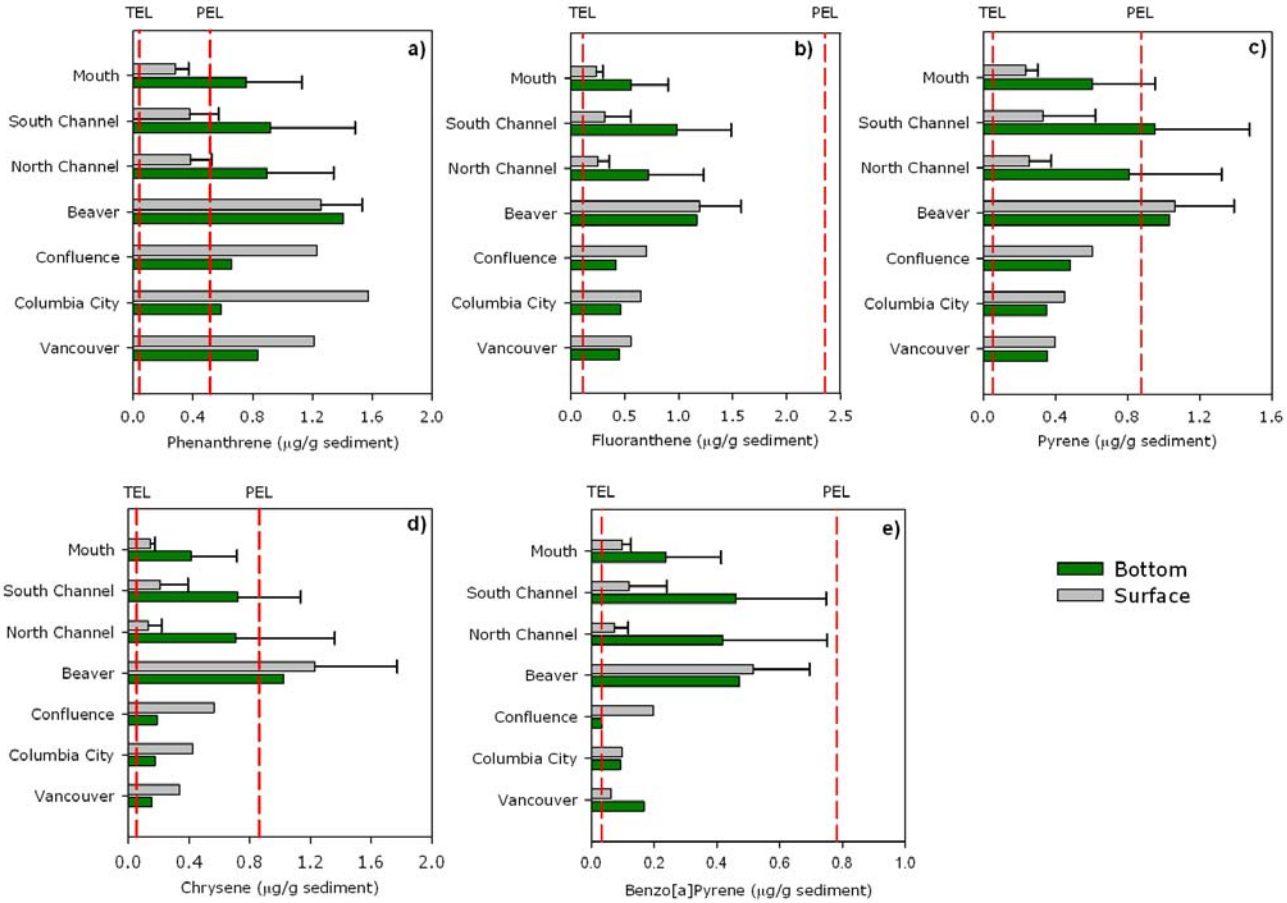


Figure 3.6: Mean (± SD) concentrations of a) phenanthrene b) fluoranthene c) pyrene d) chrysene and e) benzo[a]pyrene measured from *Barnes* sites in comparison to the corresponding threshold effects level (TEL) and probable effects level (PEL) guidelines of these five PAHs.

Chapter 4: Discussion

4.1 PAH Levels and Distribution within Study Region

Particle-bound PAHs were detected at all sites within the study region. The highest concentrations of combustion PAHs on SPM were measured at Portland, Beaver, and estuary bottom waters. The very high concentrations found at Portland were anticipated, because a six mile stretch within Portland Harbor was designated by the U.S. Environmental Protection Agency as a Superfund site in December, 2000 (Sethajintanin et al., 2004). The huge drop in PAH concentrations on SPM from Portland to the Lower Columbia, indicates that the Columbia River is not receiving a significant PAH input from the Willamette River due to low discharge rate at the time of sampling in August, 2007 (~220 m^3/s). A different story would likely be the case during the rainy season when discharge ranges between 500-3,600 m^3/s (USGS Water Data). Figure 4.1 shows the dramatic increase in Willamette River discharge in relation to Columbia River discharge from late October through March.

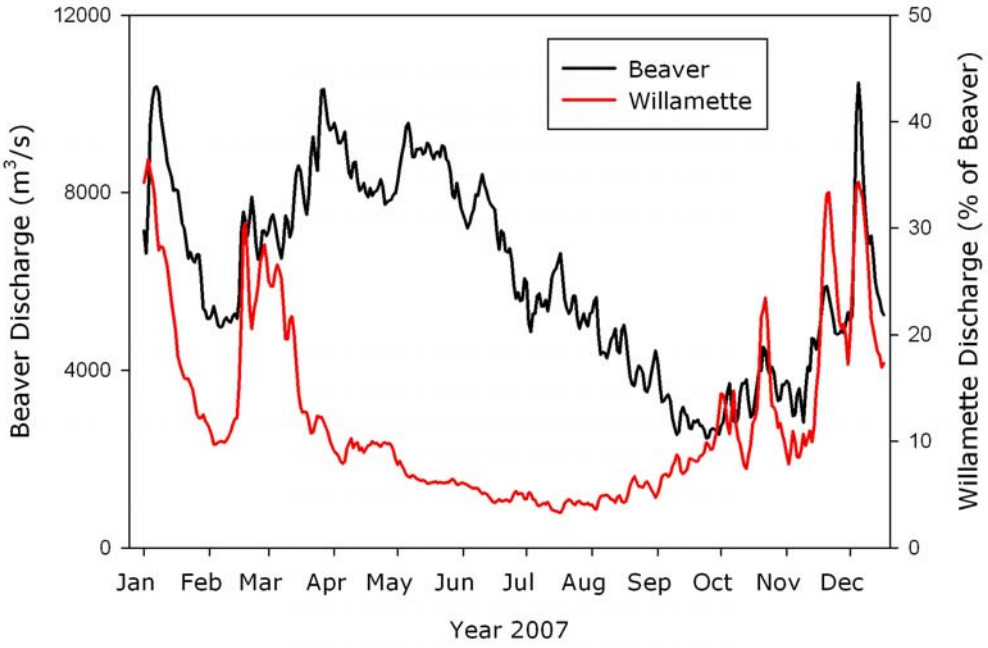


Figure 4.1: Daily river discharge during 2007 from the Columbia River at Beaver and the corresponding percentage of discharge from the Willamette River.

The high PAH concentrations on SPM collected from Beaver and the estuary bottom waters were unexpected (Figure 3.2). It was thought that the three uppermost Columbia River sites (Vancouver, Confluence, and Columbia City) would have higher PAH levels because these sites are located in close proximity to major cities, ports, and industrialized centers- probable sources of combustion derived PAH. The population in Vancouver is ~162K and ~576K in neighboring Portland (US Census Bureau). High tech industry and manufacturing business are drawn to the region, because they benefit from accessibility to numerous transportation options whether it be cargo ship, railroad, interstate, or international air terminals (Oregon Blue Book). All of which are directly or indirectly linked to combustion processes.

In contrast, the landscape surrounding Beaver and the estuary is rural. Longview, WA is the one industrialized center located just upriver of Beaver. Longview has a population of ~36K and the economy primarily runs on timber-based manufacturing (City of Longview). In the estuary, the town of Astoria, Oregon sits near the mouth and has a population of ~10K (US Census Bureau). The economy is driven by fishing and timber harvesting (Astoria & Warrenton). The stark contrast between the surrounding landscapes of the sampling sites reinforces the fact that non-developed waterways are not safe from PAHs, because their chemical behavior allows them to be transported far from their original source.

4.2 Beaver PAH levels over the year 2007

The role of seasonality on PAH levels in the Columbia remains unclear. At Beaver, ∑COMB concentrations in winter (Dec. 06, Feb. 07, Dec. 07, Jan. 08) were both less than and greater than summer levels (August). Higher values during winter months might be expected, because lower temperatures decrease the microbial and photodecomposition of particle attached contaminants. In addition, domestic heating increases in winter, which emits more combustion PAHs to the region (Motelay-Massei et al., 2007).

To gain a sense of whether or not the Columbia has seen a decrease in PAH levels over the last 20 years, PAH levels measured at Beaver were compared to measurements made monthly in 1980 on SPM collected from a site just downstream at the head of the estuary (Tongue Point) (Prahl et al., 1984). This site was located mid-channel and east of Astoria. Only surface samples and two compounds (fluoranthene + pyrene) were compared. Figure 4.2 reveals that surface PAH levels in the Columbia have increased since 1980. The USGS NASQAN program has also detected PAHs in the water and bed sediment at Beaver, but they found concentrations on suspended sediment below the method detection limits (MDLs). The contradicting results brought to light an error in the MDL calculation, revealing that the USGS also has measured PAHs on SPM at levels that are a cause for concern (Morace, 2006).

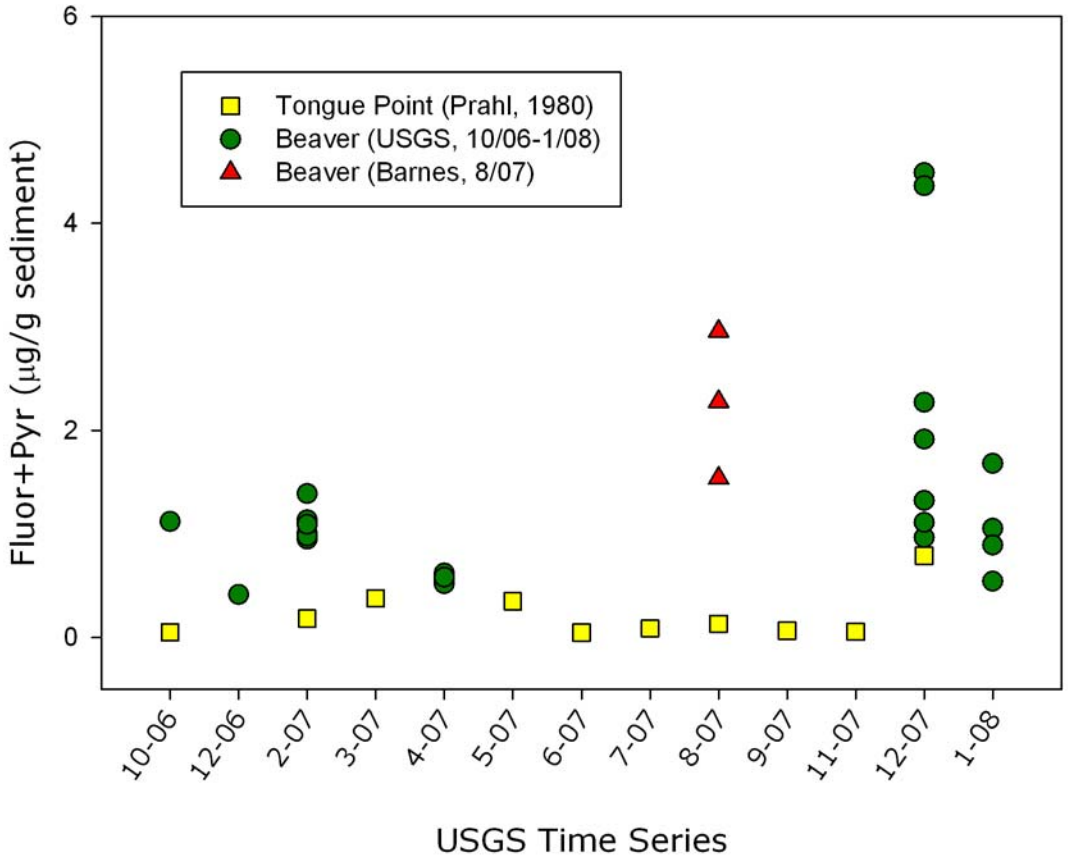


Figure 4.2: Comparison of fluoranthene + pyrene concentrations on SPM at Beaver (2007) versus tongue point (1980).

4.3 ETM Trapping and PAH Concentration

Figure 3.4 reveals that PAH concentrations on SPM in the estuary bottom waters exceed those measured in estuary surface waters. This finding indicates that particles containing PAH are enriched in estuary bottom waters while particle size classes that do not contain PAH are transported more directly offshore. Once in the estuary, the particles containing PAH are selectively trapped by the ETM. These results provide evidence that the ETM traps particles containing combustion-derived PAH. However, the trapping process appears non-selective because the concentration per particle does not increase relative to that noted upriver and PAH levels inside and outside of the ETM boundary (40 mg/L) are not significantly different. A likely reason for the lack of a relationship between increasing SPM and PAH concentrations is that strong ETMs have high energy and could resuspend particles that do not carry PAH, thereby diluting PAH concentrations during an ETM. Increasing the number of samples and frequency of sampling during ETMs would clarify the role of the ETM in trapping and concentrating contaminants of concern.

In the case of perylene, Figure 3.4 suggests that the ETM does selectively trap the particles to which perylene adsorb, thereby concentrating perylene near the bottom of the estuary. Perylene is known to be a digenetic product, but the precursor responsible for its formation remains undetermined. Therefore, it is not known if the precursor for perylene or perylene itself is transported to the estuary. Jiang et al. (2000) suggests the precursor has a terrestrial source, such as fungi, which would supports perylene being delivered to the estuary by riverborne particles. However, it is also possible that the precursor for perylene resides in the estuary and the elevated concentration is due to a local source rather than a function of the ETM.

A major consequence of ETM trapping is that organisms feeding in this sedimentary feature are at risk to exposure from dietary consumption of PAH-containing particles. Consequently, sublethal impacts from exposure could spiral throughout the estuary's food web. Another concern is the effect of SPM concentration on the probability that an organism encounters a contaminated particle. In the Columbia River, an organism would see a mean SPM of ~7 mg/L. If it migrated to the estuary, that SPM mean would increase 3-4x and amplify the likelihood that it encounters and consumes a PAH-contaminated particle.

4.4 Potential Ecosystem Risk

Studies have found that PAHs negatively impact the overall health of exposed organisms. Johnson et al. (2002) measured various health parameters of English Sole living in Puget Sound. Fish were collected from sites where both low and high molecular weight PAHs had been detected in the sediments. These benthic fish were highly susceptible to liver cancer and the development of cancerous lesions when the total PAH reached 1,000 ng/g sediment. Sublethal impacts, such as reproductive impairment, immune dysfunction, and abnormal development were also widespread in the population (Johnson et al., 2002). PAHs have also been found in the stomach contents of juvenile salmon collected between the confluence of the Willamette and Columbia Rivers to Longview, Washington (sites c, d, and e in the current study) (Johnson et al, 2007). Finding PAHs in the stomach is telling that the salmon consumed contaminated prey. Phenanthrene, fluoranthene, pyrene, and chrysene dominated the PAHs present in the stomach contents, which corresponds to the combustion PAHs measured in the present study. The concentrations were similar to those measured from industrialized waterways in the Puget Sound (Duwamish and Hylebos), where exposed fish were found to have reproductive and growth abnormalities.

In order for organisms inhabiting the Columbia River to be adequately protected, PAH concentrations would need to fall below the PEL and approximately equal the TEL. However, PELs were commonly exceeded in SPM from waters at Beaver, the bottom of the estuary, and always exceeded at Portland. The finding of surpassed PELs across the study region serves as a warning sign and suggests the likelihood of significant impairment to the health of the Columbia River ecosystem. This is especially the case in bottom waters of the Columbia estuary where both PAH concentration on SPM and SPM concentrations are high. An understanding of food web linkages between ETM grazers and higher trophic levels coupled with knowledge of seasonal fluctuations in ETM trapping of POPs could improve contaminant risk modeling within the estuary.

4.5 PAH levels across the Globe

To compare PAH levels from this study to other waterways, the concentrations of phenanthrene, fluoranthene, pyrene, and benzo[a]pyrene were averaged over sites located in the Columbia River, estuary, and at Portland. These PAH concentrations were summed and compared to the same set of PAH compounds measured in similar studies (Table 4.1 and Figure 4.3). Figure 4.3a shows the mean combined PAH concentration on SPM from all locations reported in Table 4.1. The PAH concentration on SPM at Portland and the north pollution canal in China greatly surpass the other locations, so they were removed in Figure 4.3b to allow for a better assessment of the differences in PAH levels from one location to the next. A valuable finding is that the PAH levels measured in this study are similar or exceed those measured in other industrialized and/or urban regions of the world. For example, the Seine Estuary is a very populated and industrialized region, supporting Paris, France and its suburbs. The PAH levels measured in the Seine were below those measured in the Columbia River and estuary. The Tianjin region surrounding Bejing, China was the only study location found with PAH levels exceeding those measured in the Columbia River and estuary (Table 4.1).

Table 4.1: Summary of PAH concentrations in SPM (ng/g) from waterways around the globe

Location	SPM range (mg/L)	Mean Concentrations (µg/g sediment)						Max.	Min.	Author	Year
		Phen	Pyr	Fluor	BaP	∑PAH*	Std. Dev.				
Willameter River, Portland USA	14 - 21	3129	5550	5212	2104	15,995	3,067	21,876	9,546	This Study	2009
Columbia River Estuary, USA	3.7 - 65	817	696	668	325	2,506	885	7,286	396	This Study	2009
Daliao River, China	8 - 810	35	137	106	111	388	285	1,392	14	Guo et al.	2007
North Pollution Canal, Tianjin China		9470	2820	3960	2330	18,580	5,356	28,770	8,510	Shi et al.	2005
Chaobi New River, Tianjin China		2100	170	340	30	2,640	1,088	4,140	1,140	Shi et al.	2005
Yongding New River, Tianjin China		4010	560	980	120	5,670	2,138	9,020	2,340	Shi et al.	2005
Hai River, Tianjin China		4330	390	800	20	5,540	2,375	8,550	2,530	Shi et al.	2005
Yellow river, Middle China		869	231	331	54	1,485	694	4,919	213	Sun et al.	2008
Seine Estuary, France		285	100	70	11	1,177		1,986	185	Cailleaud et al.	2007
Pearl River Estuary, China	5 - 42	101	51	47	5	466	192	1,461	171	Luo et al.	2006
Xijiang River, Guangdong South China	3 - 98	176	346	377	278	204	98	538	29	Deng et al.	2006
Susquehanna River, PA USA	2 - 25	439	550	521	339	1,849	521	2,876	822	Ko et al.	2004
Chesapeake Bay, MD USA	2 - 25	306	406	414	206	1,332	172	1,666	998	Ko et al.	2004
Suisun Bay, San Fransico Bay USA	15 - 37	112	247	185	55	599				Domagalski	1993
York River, VA USA	4 - 150	321	392	457	183	1,353	933	8,832	151	Countway et al.	2003

* ∑PAH is the sum of Phen (phenanthrene), Pyr (pyrene), Fluor (fluoranthene), and BaP (benzo[a]pyrene).

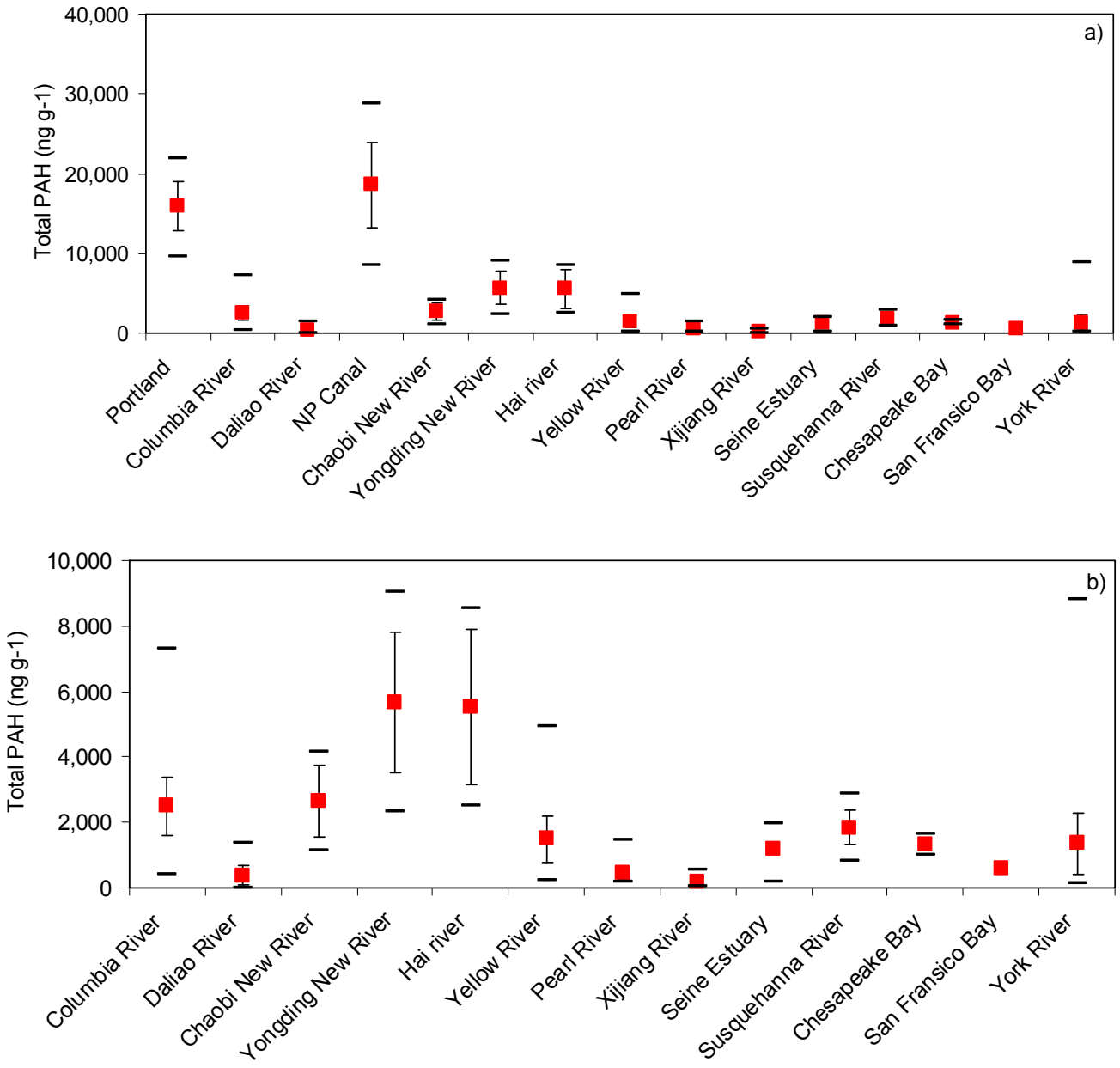


Figure 4.3: Mean total PAH (± SD) from a) all waterways listed in table 4.1 and b) all waterways minus Portland and NP canal. The lines above and below the data points represent maximum and minimum values. The study providing the data for each waterway listed on the x-axis can be found in Table 4.1.

The comparison in Figure 4.3 indicates that across the globe, efforts to manage POPs have been counteracted by rises in population growth, urban sprawl, and corresponding increases in vehicle emissions and industrial/urban runoff (Hwang et al., 2006). Impervious surfaces are a major barrier in reducing POP loads to waterways, because they remove vegetative infiltration, and amplify the concentration of contaminants in runoff. The 2001 Stockholm Convention responded to the threats POPs impose on environmental health and set a goal to reduce and eliminate both pesticide and industrial POPs. As of April 2007, 181 countries have agreed to take steps towards achieving this goal by placing stronger restrictions on point source discharges and improving stormwater management efforts (UNDP, 2007). Yet, recent studies continue to detect high levels of contaminants in waterways.

Chapter 5: Conclusions

Numerous studies have identified the ubiquity of POPs in the air, water, sediment, and biological organisms, but uncertainty surrounding the environmental behavior of these contaminants remains a hurdle (Wu et al, 2008). The monitoring of 12 PAHs on SPM in the Columbia River and estuary has provided evidence that PAHs are transported via SPM from river to estuary. Once in the estuary, the particles to which combustion derived PAHs adsorb are trapped near the bottom but with no clear evidence of the trapping occurring particle selectively. This improved understanding of PAH behavior is indicative of the transport mechanism that is likely traced by other POPs prevalent throughout the Columbia River. It remains unclear as to whether or not the ETM concentrates PAHs. However, it is alarming that PAH levels at the estuary bottom exceed those measured in the more industrialized regions of the Columbia River. An extension of the current study would be useful, because the year to year and seasonal variability in PAHs on SPM remains unknown.

High temperature combustion processes are the primary source of PAH contamination to the study region, according to correlations between PAH signatures. PAHs most likely enter the Columbia Basin from nonpoint sources, including urban and stormwater runoff, industrial discharges, atmospheric deposition, and field burning. Of concern to ecosystem health, is the finding that PAH concentrations across the study region exceeded either TEL or PEL sediment quality guidelines. Additionally, studies from industrialized waterways have measured PAHs on SPM at levels surprisingly similar to this study. These comparisons signify that biological organisms connected to the Columbia are at risk to the sublethal impacts of PAH contamination. Due to high concentrations of both SPM and combustion PAHs, the estuary bottom is one site where there is a high potential for PAHs being transferred into the food web. Beaver is also a likely candidate, however SPM concentrations were less than in the estuary bottom, therefore it would be less likely for an organism to encounter a contaminated particle.

By taking steps to improve the understanding of PAH behavior, this study has progressed towards screening for POPs using a model compound (PAHs) rather than tracing individual compounds. Monitoring for specific substances is coming to a close, because the cost is astronomical and emerging contaminants of concern could be overlooked. It is best to focus on groups of chemicals whose behavior in the environment can be monitored at representative sampling locations. Further studies aimed at improving the knowledge of persistent organic pollutant transport with SPM and the distribution of these contaminants could benefit the development of cost effective management strategies aimed at decreasing contaminant exposure levels to Columbia organisms.

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Appendix IA: Recovery data from upriver *Barnes* sites, sampled in August 2007.

Site	Date/Time	S / B	d10-Phen	d10-Fluor	d12-BaP
Portland	8/18/07 10:18	S	44%	69%	67%
Portland	8/18/07 10:21	B	12%	15%	21%
Portland	8/18/07 10:21	B	134%	263%	213%
Vancouver	8/18/07 9:00	S	45%	69%	65%
Vancouver	8/18/07 9:06	B	127%	198%	205%
Confluence	8/18/07 11:39	S	47%	73%	67%
Confluence	8/18/07 11:42	B	159%	283%	266%
Columbia City	8/18/07 13:33	S	31%	53%	47%
Columbia City	8/18/07 13:35	B	105%	185%	164%
Beaver	8/19/07 7:31	S	42%	99%	87%
Beaver	8/19/07 9:05	S	43%	78%	76%
Beaver	8/19/07 11:01	S	30%	82%	74%
Beaver	8/19/07 7:37	B	44%	87%	58%

*The recovery standard was created on 10/18/2007 using the following concentrations of perdeuterated PAHs, d10-phenanthrene= 1.06 µg/g, d10-fluoranthene= 1.20 µg/g, d12-benzo[a]pyrene= 1.04 µg/g.

Appendix IB: Recovery data from Estuarine *Barnes* sites, sampled in August 2007.

Site	Date/Time	S / B	d10-Phen	d10-Fluor	d12-BaP
NC	8/21/07 8:30	S	198%	283%	270%
NC	8/21/07 14:33	S	215%	302%	299%
NC	8/27/07 10:06	S	99%	155%	151%
NC	8/27/07 13:51	S	112%	164%	199%
NC	8/21/07 8:31	B	50%	82%	59%
NC	8/21/07 11:05	B	46%	81%	80%
NC	8/21/07 11:21	B	53%	88%	93%
NC	8/21/07 14:35	B	54%	86%	96%
NC	8/27/07 8:31	B	28%	44%	41%
NC	8/27/07 9:02	B	21%	29%	28%
NC	8/27/07 9:32	B	21%	32%	32%
NC	8/27/07 13:53	B	17%	27%	25%
SC	8/23/07 5:32	S	156%	209%	221%
SC	8/23/07 10:30	S	155%	214%	212%
SC	8/26/07 8:01	S	109%	167%	130%
SC	8/26/07 15:00	S	99%	157%	164%
SC	8/29/07 9:32	S	186%	318%	333%
SC	8/20/07 10:53	B	13%	48%	56%
SC	8/20/07 11:30	B	22%	54%	63%
SC	8/20/07 12:39	B	27%	58%	61%
SC	8/23/07 7:34	B	34%	50%	52%
SC	8/23/07 7:48	B	76%	115%	97%
SC	8/23/07 8:01	B	68%	109%	110%
SC	8/23/07 9:02	B	56%	85%	71%
SC	8/26/07 9:02	B	45%	62%	64%
SC	8/26/07 10:33	B	49%	60%	63%
SC	8/26/07 11:18	B	39%	54%	51%
SC	8/26/07 12:33	B	14%	23%	22%
SC	8/26/07 13:02	B	7%	40%	44%
SC	8/29/07 10:32	B	77%	121%	109%
SC	8/29/07 11:32	B	76%	133%	116%
SC	8/29/07 12:03	B	76%	126%	109%
SC	8/29/07 13:32	B	78%	130%	124%
SC	8/29/07 15:32	B	84%	146%	126%
Mouth	8/28/07 7:55	S	160%	254%	284%
Mouth	8/28/07 10:30	S	151%	261%	309%
Mouth	8/28/07 13:00	S	162%	263%	289%
Mouth	8/28/07 9:02	B	36%	55%	59%
Mouth	8/28/07 9:32	B	57%	92%	95%
Mouth	8/28/07 10:02	B	51%	84%	81%
Mouth	8/28/07 13:06	B	47%	86%	87%

*The recovery standard was created on 10/18/2007 using the following concentrations of perdeuterated PAHs, d10-phenanthrene= 1.06 µg/g, d10-fluoranthene= 1.20 µg/g, d12-benzo[a]pyrene= 1.04 µg/g.

Appendix IC: Data from USGS time series sampling at Beaver.

Site	Date/Time	S / B	d10-Phen	d10-Fluor	d12-BaP
USGS	10/12/2006	S	101%	234%	281%
USGS	12/13/2006	S	187%	292%	278%
USGS	2/22/2007	S	31%	41%	38%
USGS	2/22/2007	S	32%	43%	41%
USGS	2/22/2007	S	34%	44%	40%
USGS	2/22/2007	S	32%	43%	38%
USGS	4/18/2007	S	41%	63%	64%
USGS	4/18/2007	S	40%	69%	65%
USGS	4/18/2007	S	40%	62%	62%
USGS	4/18/2007	S	41%	63%	58%
USGS	12/6/2007	S	21%	29%	20%
USGS	12/6/2007	S	9%	13%	12%
USGS	12/6/2007	S	2%	69%	61%
USGS	12/6/2007	S	4%	37%	43%
USGS	12/17/2007	S	43%	66%	59%
USGS	12/17/2007	S	38%	57%	55%
USGS	12/17/2007	S	31%	51%	48%
USGS	12/17/2007	S	43%	68%	52%
USGS	1/24/2008	S	87%	135%	100%
USGS	1/24/2008	S	57%	99%	83%
USGS	1/24/2008	S	73%	115%	72%
USGS	1/24/2008	S	31%	51%	31%

*The recovery standard was created on 10/18/2007 using the following concentrations of perdeuterated PAHs, d10-phenanthrene= 1.06 µg/g, d10-fluoranthene= 1.20 µg/g, d12-benzo[a]pyrene= 1.04 µg/g.

Appendix IIA: Data from upriver *Barnes* sites, sampled in August 2007

Site	Date/Time	S / B	Salinity (PSU)	SPM (mg/L)	POC (wt%)	PAH Concentrations (µg PAH per g sediment)											
						P	MP	Fl	Pyr	Ret	BaA	Chry	ThC	BFl	BeP	BaP	Pery
Portland	8/18/07 10:18	S	0.05	16.2	4.8%	2.11	0.46	3.28	3.27	2.39	0.99	1.88	3.71	1.80	1.08	0.89	1.63
Portland	8/18/07 10:21	B	0.06	21.4		3.34	0.14	6.38	7.33	7.45	0.47	3.87	1.06	2.04	3.96	3.27	4.76
Portland	8/18/07 10:21	B	0.06	14.3		3.94	1.28	5.97	6.04	5.01	0.99	3.28	0.64	2.69	1.93	2.15	3.09
Vancouver	8/18/07 9:00	S	0.07	7.6	4.8%	1.21	0.11	0.56	0.40	1.04	0.17	0.34	0.16	0.48	0.08	0.06	0.61
Vancouver	8/18/07 9:06	B	0.07	6.4		0.83	0.21	0.45	0.36	2.55	0.02	0.15	0.04	0.30	0.13	0.17	1.04
Confluence	8/18/07 11:39	S	0.07	6.4	5.9%	1.57	0.43	0.65	0.45	0.99	0.13	0.43	0.21	0.35	0.12	0.10	1.32
Confluence	8/18/07 11:42	B	0.07	9.2		0.59	0.18	0.46	0.35	0.39	0.06	0.18	0.05	0.27	0.14	0.09	0.63
Columbia City	8/18/07 13:33	S	0.08	7.8	4.0%	1.23	0.23	0.70	0.60	1.00	0.19	0.57	0.16	0.43	0.24	0.20	1.60
Columbia City	8/18/07 13:35	B	0.08	7.9		0.66	0.16	0.42	0.48	0.86	0.07	0.19	0.00	0.30	0.17	0.03	0.83
Beaver	8/19/07 7:31	S	0.07	5.8	6.1%	1.33	0.61	1.21	1.07	5.25	0.66	1.50	0.50	1.30	0.92	0.59	2.79
Beaver	8/19/07 9:05	S	0.07	6.7		1.48	0.64	1.57	1.39	3.02	0.56	1.58	0.39	1.53	0.98	0.65	2.23
Beaver	8/19/07 11:01	S	0.07	8.2	6.0%	0.95	0.35	0.80	0.74	1.11	0.30	0.61	0.35	0.69	0.50	0.31	1.49
Beaver	8/19/07 7:37	B	0.07	5.6	6.5%	1.41	0.50	1.17	1.03	1.42	0.36	1.02	0.36	0.71	0.55	0.47	1.43

Appendix IIB: Data from Estuarine *Barnes* sites, sampled in August 2007.

Site	Date/Time	S / B	Salinity (PSU)	SPM (mg/L)	POC (wt%)	PAH Concentrations (µg PAH per g sediment)											
						P	MP	Fl	Pyr	Ret	BaA	Chry	ThC	BFl	BeP	BaP	Pery
North Channel	8/21/07 8:30	S	4.4	3.7		0.39	0.18	0.22	0.20	0.23	0.02	0.12	0.05	0.12	0.08	0.04	0.66
North Channel	8/21/07 14:33	S	2.9	6.6	5.1%	0.26	0.15	0.18	0.16	0.18	0.04	0.11	0.06	0.12	0.07	0.05	0.64
North Channel	8/27/07 10:06	S	6.7	8.4		0.58	0.30	0.41	0.44	0.50	0.10	0.25	0.10	0.21	0.16	0.14	1.62
North Channel	8/27/07 13:51	S	14.1	9.0	6.6%	0.30	0.19	0.22	0.23	0.28	0.06	0.04	0.07	0.16	0.10	0.07	1.35
North Channel	8/21/07 8:31	B	26.7	12.9		0.82	0.31	0.50	0.56	0.62	0.12	0.40	0.17	0.23	0.17	0.28	2.47
North Channel	8/21/07 11:05	B	26.9	42.1	4.0%	0.31	0.15	0.22	0.24	4.52	0.09	0.18	0.13	0.18	0.13	0.11	2.05
North Channel	8/21/07 11:21	B	27.4	30.1		1.02	0.00	0.44	0.87	0.89	0.09	0.19	0.10	0.21	0.32	0.18	1.46
North Channel	8/21/07 14:35	B	27.3	17.1		0.49	0.21	0.25	0.27	0.34	0.09	0.20	0.07	0.19	0.11	0.09	1.43
North Channel	8/27/07 8:31	B	9.6	19.7	4.2%	1.25	0.48	1.42	1.49	1.26	0.61	1.10	0.38	1.47	0.84	0.72	9.63
North Channel	8/27/07 9:02	B	8.9	21.9	6.6%	1.68	0.42	1.57	1.59	1.70	0.63	1.23	0.62	1.71	0.95	0.75	15.32
North Channel	8/27/07 9:32	B	12.3	65.2	4.3%	0.55	0.23	0.53	0.54	0.86	0.25	0.40	0.19	0.64	0.34	0.28	4.80
North Channel	8/27/07 13:53	B	30.2	16.5		1.03	0.10	0.84	0.92	0.85	0.36	1.95	0.45	1.02	0.56	0.95	6.84

Appendix IIB Continued:

Site	Date/Time	S / B	Salinity (PSU)	SPM (mg/L)	POC (wt%)	PAH Concentrations (µg PAH per g sediment)											
						P	MP	FI	Pyr	Ret	BaA	Chry	ThC	BFl	BeP	BaP	Pery
South Channel	8/23/07 5:32	S	4.1	5.3	7.3%	0.35	0.11	0.26	0.26	0.27	0.04	0.10	0.04	0.11	0.07	0.07	0.46
South Channel	8/23/07 10:30	S	2.4	6.0	8.8%	0.21	0.08	0.13	0.11	0.17	0.04	0.09	0.04	0.10	0.08	0.03	0.40
South Channel	8/26/07 8:01	S	0.0	6.8		0.52	0.25	0.42	0.39	0.81	0.14	0.34	0.18	0.25	0.21	0.14	1.34
South Channel	8/26/07 15:00	S	5.1	18.7	2.2%	0.17	0.10	0.10	0.09	0.12	0.03	0.07	0.02	0.07	0.05	0.03	0.36
South Channel	8/29/07 9:32	S	0.8	4.3		0.63	0.29	0.69	0.81	0.70	0.21	0.47	0.20	0.62	0.39	0.32	2.73
South Channel	8/20/07 10:53	B	23.1	23.1	4.9%	0.70	0.93	0.38	0.39	0.59	0.12	0.25	0.14	0.31	0.19	0.15	1.77
South Channel	8/20/07 11:30	B	22.9	20.5		0.23	1.06	1.23	1.46	0.59	0.52	1.04	0.43	1.44	0.82	0.82	6.06
South Channel	8/20/07 12:39	B	23.9	41.7	4.6%	0.46	0.39	0.33	0.35	0.45	0.10	0.25	0.12	0.32	0.17	0.12	1.56
South Channel	8/23/07 7:34	B	20.0	14.6	14.5%	1.51	0.81	1.22	1.19	1.78	0.49	0.83	0.34	1.20	0.68	0.48	7.08
South Channel	8/23/07 7:48	B	21.8	44.9		0.74	0.36	0.62	0.59	1.39	0.24	0.49	0.17	0.56	0.36	0.25	3.63
South Channel	8/23/07 8:01	B	22.1	27.7	5.6%	1.08	0.58	1.00	1.00	2.32	0.43	0.74	0.32	0.99	0.61	0.43	6.25
South Channel	8/23/07 9:02	B	22.1	30.1	3.7%	0.96	0.49	0.82	0.91	1.26	0.37	0.70	0.96	0.95	1.15	0.50	3.33
South Channel	8/26/07 9:02	B	10.4	16.5	6.0%	1.94	0.99	1.65	1.58	2.73	0.64	1.18	0.47	1.62	0.98	0.69	8.58
South Channel	8/26/07 10:33	B	12.2	84.9	3.1%	1.82	0.64	2.09	2.13	2.38	0.81	1.73	0.52	1.87	1.07	1.12	11.05
South Channel	8/26/07 11:18	B	11.9	79.3	1.5%	0.42	0.12	0.41	0.43	0.50	0.16	0.32	0.14	0.42	0.26	0.21	2.36
South Channel	8/26/07 12:33	B	11.9	34.3	3.2%	1.59	0.59	1.32	1.30	3.63	0.54	1.04	0.40	1.29	0.76	0.59	7.60
South Channel	8/26/07 13:02	B	12.2	47.3		1.01	0.97	0.74	0.78	1.16	0.32	0.62	0.25	0.76	0.48	0.36	4.69
South Channel	8/29/07 10:32	B	8.0	21.1	6.4%	0.31	0.59	1.70	1.59	2.28	0.68	0.40	0.13	1.99	0.97	0.89	9.08
South Channel	8/29/07 11:32	B	6.8	38.3		1.25	0.45	0.99	0.97	1.23	0.40	0.78	0.27	0.97	0.62	0.50	6.31
South Channel	8/29/07 12:03	B	7.1	59.8	3.2%	1.10	0.29	0.67	0.64	1.34	0.30	1.20	0.24	0.65	0.41	0.34	37.76
South Channel	8/29/07 13:32	B	11.1	16.1		0.41	0.16	1.00	0.32	0.33	0.13	0.25	0.10	0.33	0.16	0.13	1.73
South Channel	8/29/07 15:32	B	21.3	64.9	3.7%	0.12	0.25	0.54	0.56	0.78	0.23	0.42	0.26	0.54	0.35	0.27	4.43
CR Mouth	8/28/07 7:55	S	10.4	8.8	9.0%	0.30	0.11	0.26	0.26	3.12	0.07	0.17	0.08	0.23	0.14	0.11	1.59
CR Mouth	8/28/07 10:30	S	11.0	14.2	4.8%	0.19	0.12	0.17	0.16	7.13	0.06	0.11	0.08	0.15	0.09	0.07	1.27
CR Mouth	8/28/07 13:00	S	22.6	7.1	10.5%	0.36	0.19	0.28	0.29	0.21	0.09	0.16	0.07	0.21	0.13	0.12	1.16
CR Mouth	8/28/07 9:02	B	15.4	30.9	5.9%	0.66	0.00	0.38	0.49	0.54	0.11	0.21	0.08	0.27	0.19	0.12	1.90
CR Mouth	8/28/07 9:32	B	15.4	35.0		0.43	0.26	0.41	0.40	0.62	0.19	0.31	0.15	0.45	0.25	0.19	2.98
CR Mouth	8/28/07 10:02	B	19.2	58.1	2.9%	1.30	0.62	1.07	1.12	1.12	0.46	0.86	0.34	1.08	0.58	0.50	6.00
CR Mouth	8/28/07 13:06	B	32.2	11.6	5.3%	0.63	0.39	0.38	0.41	2.28	0.14	0.27	0.23	0.33	0.18	0.14	3.29

Appendix IIC: Data from USGS time series sampling at Beaver

Site	Date	S / B	Salinity (PSU)	SPM (mg/L)	POC (wt%)	PAH Concentrations (µg PAH per g sediment)											
						P	MP	Fl	Pyr	Ret	BaA	Chry	ThC	BFl	BeP	BaP	Pery
USGS	10/12/06	S	-	3.2	-	0.47	0.27	0.58	0.54	0.42	0.27	0.55	0.18	0.72	0.43	0.39	0.68
USGS	12/13/06	S	-	11.3	-	0.22	0.13	0.22	0.19	0.61	0.06	0.15	0.10	0.18	0.11	0.08	0.37
USGS	2/22/07	S	-	23.5	-	0.90	0.53	0.48	0.47	0.98	0.14	0.45	0.14	0.40	0.23	0.20	1.13
USGS	2/22/07	S	-	23.5	-	0.96	0.61	0.55	0.59	1.26	0.18	0.46	0.30	0.56	0.35	0.21	1.25
USGS	2/22/07	S	-	21.2	-	0.60	0.26	0.48	0.52	0.94	0.19	0.40	0.32	0.56	0.31	0.23	0.97
USGS	2/22/07	S	-	21.2	-	0.60	0.28	0.48	0.50	0.98	0.19	0.41	0.32	0.38	0.30	0.22	0.97
USGS	2/22/07	S	-	32.8	-	1.11	0.39	0.68	0.71	1.18	0.13	0.60	0.12	0.39	0.21	0.41	1.29
USGS	2/22/07	S	-	32.8	-	0.98	0.52	0.54	0.55	1.35	0.16	0.41	0.28	0.64	0.33	0.20	1.30
USGS	4/18/07	S	-	15.7	-	0.46	0.19	0.31	0.25	1.06	0.11	0.31	0.11	0.31	0.16	0.13	0.57
USGS	4/18/07	S	-	13.4	-	0.48	0.13	0.26	0.26	1.74	0.04	0.23	0.25	0.18	0.04	0.03	0.52
USGS	4/18/07	S	-	16.8	-	0.53	0.22	0.30	0.32	1.70	0.10	0.24	0.22	0.28	0.14	0.11	0.87
USGS	4/18/07	S	-	12.1	-	0.54	0.21	0.31	0.27	1.44	0.08	0.20	0.13	0.29	0.12	0.10	0.64
USGS	12/6/07	S	-	72.5	-	1.33	0.22	0.68	0.64	3.17	0.12	0.43	0.22	0.25	0.40	0.33	1.68
USGS	12/6/07	S	-	53.7	-	0.00	0.00	0.41	0.56	2.99	0.11	0.35	0.22	0.39	0.19	0.15	1.72
USGS	12/6/07	S	-	72.2	-	0.66	0.37	0.57	0.54	3.56	0.13	0.33	0.07	0.36	0.35	0.28	2.35
USGS	12/17/07	S	-	8.7	-	1.28	0.27	1.22	1.05	1.08	1.19	1.30	0.23	1.83	0.92	0.82	0.95
USGS	12/17/07	S	-	14.5	-	1.77	0.40	2.41	2.08	1.43	1.73	2.54	0.37	3.71	2.16	2.09	1.89
USGS	12/17/07	S	-	10.4	-	1.83	0.38	2.31	2.05	2.18	1.87	2.67	0.48	3.65	2.11	2.13	1.83
USGS	12/17/07	S	-	8.6	-	1.12	0.39	0.95	0.96	25.67	0.35	0.76	1.09	1.43	0.64	0.40	2.05
USGS	1/24/08	S	-	12.1	-	0.73	0.22	0.53	0.52	4.68	0.17	0.55	0.56	0.43	0.30	0.12	1.87
USGS	1/24/08	S	-	14.5	-	0.43	0.22	0.28	0.26	1.55	0.11	0.44	0.30	0.30	0.21	0.11	0.77
USGS	1/24/08	S	-	15.8	-	1.15	0.53	0.86	0.82	2.05	0.42	0.82	1.07	0.65	0.55	0.18	1.65
USGS	1/24/08	S	-	8.3	-	0.49	0.07	0.47	0.42	2.55	0.21	0.41	0.31	0.01	0.34	0.28	1.49