Suspended particulate matter transport of polycyclic aromatic hydrocarbons in the lower Columbia River and its estuary

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Abstract

Analysis of suspended particulate material (SPM) collected from the Columbia River and its estuary in 2007–2008 revealed the ubiquitous presence of polycyclic aromatic hydrocarbons (PAHs) from several distinct sources. The two dominant ones were: (1) a suite of non-alkylated, three to five-ringed compounds derived from high temperature combustion and (2) perylene, a compound of diagenetic origin. A particle-selective, hydrodynamic trapping process explains how both PAH types become concentrated on both a particle weight and organic carbon basis in the estuarine turbidity maximum (ETM) by as much as 10 times relative to the river-borne particle source. The ETM is a transient sedimentary feature at the land-to-sea interface of river-dominated estuarine systems which, in the case of our study region, is located remotely from the likely site of initial PAH input. Particle normalized concentrations for PAH of notable environmental concern, such as fluoranthene, chrysene, and benzo[a]pyrene, exceeded the EPA-defined threshold effects level in all cases and were typically at, or above, the probable effects level. Comparison with results from studies for other waterways around the world indicates PAH concentrations in ETM-trapped particles from the Columbia River estuary are higher than those documented for SPM in waters of many far more industrialized and populated regions. Our refined understanding of PAH behavior in the Columbia River and its estuary should prove valuable for reliably modeling the transport and dispersal mechanism that is characteristic of other hydrophobic, particle associated persistent organic pollutants prevalent in this system, and for other river-dominated estuarine systems.

The use of natural and man-made chemicals has substantially contributed to worldwide economic development and growth. However, these benefits have been realized without the guidance of 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 freshwater and marine aquatic environments, adverse impacts include fishery and recreational closures, a loss of biodiversity, and unsafe drinking water, thereby limiting the benefits these environments once provided to human society. In response, the Clean Water Act of 1972 initiated measures to mitigate point source discharges of contaminants into waterways. While these regulations have seen some success, water quality issues persist as significant levels of fertilizers, fossil fuel contaminants, consumer products, and industrial waste still find their way into many waterways. The approach to restoring water quality today needs to focus on managing pollutants discharged from non-point sources, such as urban runoff and atmospheric fallout deposition (U.S. Ocean Commission 2004).

Effective management of persistent organic pollutant (POPs) inputs is one major challenge. POPs have been released into the environment for decades, owing to the central role they have played in pest control (e.g., dichlorodiphenyltrichloroethane or DDT) and industry (e.g., polychlorinated biphenyls or PCBs, polybrominated diphenylethers or PBDEs). Their molecular structure makes them resistant to processes of chemical and biological degradation which explains how they can be transported long distances, bioaccumulate in the fatty tissues of organisms, and in some cases biomagnify. With regard to management, the ubiquity of POPs is well known, but incomplete understanding remains regarding their mechanism of transport, exposure pathways, and fate in each ecosystem of concern. A more holistic understanding is a desirable goal because it would allow 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 (U.S. Ocean Commission 2004; Schwarzenbach et al. 2006; LCREP 2007).

The lower Columbia River and its estuary, located between the states of Oregon and Washington, represents an

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environment where POPs are widespread (McCarthy and Gale 2001; Johnson et al. 2007a, 2007b). Polycyclic aromatic hydrocarbons (PAHs), DDT, PCBs, and PBDEs have been detected there in the tissue and stomach contents of juvenile Chinook salmon. The highest concentrations are typically reported for samples from sites adjacent to industrialized regions, such as Portland, Oregon. In some of the juvenile salmon, concentrations of DDT, PAHs, and PCBs have approached or exceeded health effect thresholds—the point where sublethal impacts on growth, development, reproduction, immune function, and behavior become prevalent (Johnson et al. 2007b). Currently, it is unclear as to where and how these organisms have become exposed to POPs within the Columbia River and its estuary. Using PAHs as model contaminants and tracers, our study investigates how riverborne suspended particulate matter (SPM) transport and selective hydrodynamic trapping in estuarine turbidity maxima (ETM) functions as a mechanism of organism exposure to POPs.

The ETM is a complex, transient sedimentary feature characterized by high levels of SPM that occurs in most river-dominated estuaries (Simenstad et al. 1994). The formation of this feature is shaped by tidal forces pushing in-flowing salt water beneath out-flowing river water, creating a hydrodynamic trap for settling particles (Jay et al. 2007; Park et al. 2008). The ETM typically does not occur at a fixed location in an estuary. It follows the leading edge of the salt wedge, moving up and down river on the flood, and ebb tide, respectively. The strength and magnitude of the ETM varies over time and is controlled by the tidal energy (i.e., spring vs. neap forcing), river discharge rate, and patterns of estuarine circulation and stratification (e.g., Small and Prahl 2004; North et al. 2005; Jago et al. 2006). For example, in San Francisco Bay, variations in SPM concentrations are primarily a result of the spring-neap tidal cycle, where values increase from enhanced resuspension during the spring tide and decrease due to deposition on the bed during neap tide (Schoellhamer et al. 2007).

In many estuaries, the ETM hosts a relatively large zooplankton biomass compared to upriver (e.g., Morgan et al. 1997). This characteristic makes the ETM a feeding ground for larval and juvenile fish (Suzuki et al. 2008). For example, striped bass in the Chesapeake Bay system release eggs upriver, which are transported to the ETM by river-to-estuary circulation patterns. This process places juvenile fish in a zone of abundant zooplankton prey and optimal salinity for growth (North et al. 2005). In the Columbia estuary, the ETM traps particles and their associated chemical constituents during neap tide conditions and erodes them during spring tide conditions (Reed and Donovan 1994; Small and Prahl 2004). Depending on the river discharge rate, the trapped particles reside in the estuary for $\sim$ 2 weeks to 4 weeks, whereas the residence time of water is much shorter, typically only a few days (Crump and Baross 2000). These

particles play an important role in the food web of the estuary because zooplankton consume the particulate organic matter as a primary food source (Morgan et al. 1997). The zooplankton are linked to higher trophic levels, such as fish, making the ETM a region of high biological activity (Simenstad et al. 1994; Crump and Baross 2000). It is possible and likely that POPs are attached to and concentrated in the particles trapped by the ETM. Consequently, consumers feeding within the ETM and subsequently their predators are at increased risk to contaminant exposure.

The hypothesis of this study is that PAHs and, by analogy, other POPs introduced upstream within the Columbia River Basin are transported effectively via SPM to the estuary where they are trapped particle-selectively by the ETM, leading to their increased concentration on a bulk particle basis. The objectives are: (1) to characterize the overall composition of SPM-associated PAHs delivered by the Columbia River to its estuary; (2) to identify the primary sources contributing to the overall observed composition; (3) to assess the role that the ETM plays as a site for concentrating PAHs by means of particle selective, hydrodynamic trapping; and (4) to determine how the measured concentrations of the PAHs on SPM in this transient sedimentary feature fit within the sediment quality criteria thresholds set for them as recognized priority pollutants.

Materials and methods

Study area

As part of the Center for Coastal Margin Observation and Prediction (CMOP) program, SPM samples were collected from eight sites during a 2 week cruise (16 August 2007–29 August 2007) aboard the RV *Barnes* (Fig. 1; Table 1). The sampling sites in the mainstem Columbia were located downriver from the port of Vancouver (B), downriver from the confluence with the Willamette River (C), at Columbia City (D) and at Beaver Army Terminal (or BAT, E). Those in the Columbia River estuary (CRE) were located in the south (F) and north (G) channels, and near the mouth (H). The sampling site in the Willamette River was located downriver from Portland Harbor (A).

SPM sampling was done throughout neap (20 August 2007–24 August 2007) and spring (26 August 2007–29 August 2007) tidal cycles at all three locations within the estuary (F, G, H: Fig. 1). The North Channel is open to the ocean, but does not extend far upriver; whereas the South Channel, also open to the ocean, is an active shipping channel, maintained by a regular dredging program to assure commercial connection with upriver ports. Our sampling in the estuary focused on capturing SPM from bottom waters during periods of ETM formation and disintegration. The vessel was anchored on station prior to flood tide and profiles of conductivity—temperature—depth (or CTD) along with transmissometry were obtained every 15–30 min to
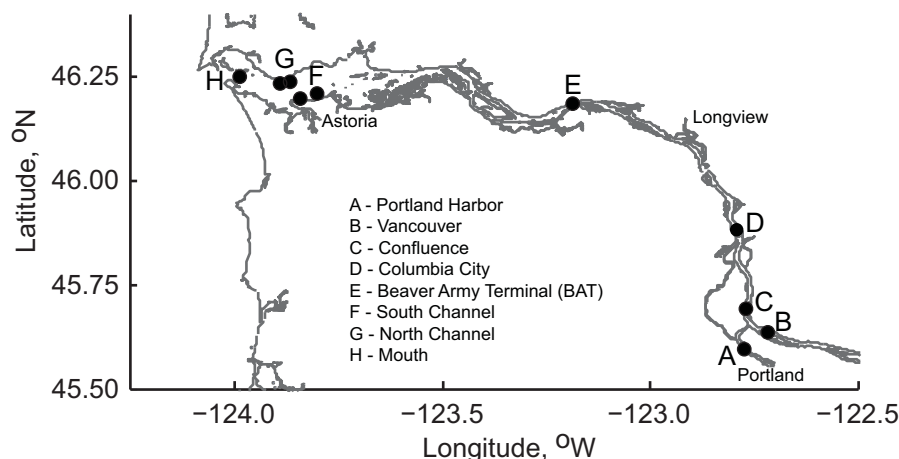
Fig. 1. Map identifying the location of eight sampling sites in the Columbia River and its estuary. More specific information about sampling at these sites is provided in Table 1.

monitor water column structure and bottom turbidity. When a sharp increase in bottom turbidity was detected, bottom samples were collected at ∼ 40 min intervals until sensor values declined.

SPM samples were also collected approximately bimonthly from October 2006 to January 2008 in conjunction with the National Stream Quality Accounting Network (NASQAN) project of the U.S. Geological Survey (USGS) Water Science Center in Portland, Oregon. BAT (E, Fig. 1) is the NASQAN sampling site in the lower Columbia River drainage. It is the first upriver location above the saltwater intrusion where the channel is narrow and uninterrupted by islands. As such, it provides the best sample representation for SPM and its associated PAH content that is introduced to the estuary by river discharge. This sampling site was established in 1972 and is the only long-term monitoring site remaining in the Columbia River and its estuary (Morace 2006).

Water collection and filtration

SPM samples were collected aboard the RV *Barnes* from near-surface (1 m below) and near-bottom (1 m above) locations using an airlift pump (50 mm PVC suction hose, ∼ 115 L

min^{-1}) attached to a CTD profiler. Once the CTD was lowered to the desired depth, water was pumped up and collected in 20 L Nalgene HDPE carboys. To eliminate or at least minimize the potential of particle sampling bias, the carboys were vigorously shaken to ensure homogenization before immediately removing the volume of water needed to obtain samples for analysis of SPM concentration, PAH composition and content, and particulate organic carbon (POC) content. Filtration volumes ranged from 1 L to 2 L for SPM, 3 L to 6 L for PAH, and 100–300 mL for POC samples.

For SPM and PAH analyses, sample water was transferred into a stainless steel cylinder and pressure filtered with nitrogen gas (20 psi) through Teflon tubing and an in-line filter (Prahl et al. 1984; Prahl et al. 1997). SPM and PAH samples were filtered through preweighed, 90 mm polycarbonate membrane filters (1.0 μm pore size, Poretics) and 90 mm glass fiber (GF/C, Whatman) filters (∼1.2 μm pore size), respectively. A follow-up rinse of the filtration cylinder was done in each case to assure quantitative transfer of particles to the sample filter. POC samples were vacuum filtered through pre-combusted (450°C for 4 h) 25 mm GF/F filters (0.8 μm pore size, Whatman). All filters for PAH and POC analysis were folded in half, wrapped in precleaned

Table 1. Location of sites sampled in the Columbia River and its estuary during a cruise aboard the RV *Barnes* in August 2007.

Site label	Site name	Latitude	Longitude	Date sampled
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	8/19
E	Beaver Army Terminal (BAT)	46° 10.99′N	123° 11.28′W	8/19
F	South Channel	∼46° 12.45′N	∼123° 47.99′W	8/20, 23, 26, 29
G	North Channel	∼46° 14.25′N	∼123° 51.87′W	8/21, 24, 27
H	Mouth	46° 14.95′N	123° 59.13′W	8/22, 28

aluminum foil and stored frozen at $-20°C$ until analysis at Oregon State University. SPM filters were folded in half, placed in a plastic Petri dish and, as soon as possible, oven-dried at $\sim 50°C$. After drying and allowing for equilibration at the temperature and humidity of the laboratory, the filters were reweighed and the SPM concentration (mg L^{-1}) was calculated from the determined mass and the volume of water filtered (Prahl et al. 1997).

The SPM collection method was altered during bimonthly sampling at BAT because the boat used by the USGS for NASQAN was not equipped with the same CTD and pump system as the RV *Barnes*. A large volume battery-powered, submersible impeller pump (20 mm silicone hose, 20 L min^{-1}) was used instead to collect water from ~ 1 m below the surface. 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 (≤ 3 h) back to the laboratory to isolate by filtration, as described above, samples for PAH and SPM analysis. POC samples were not collected during the bimonthly sampling at BAT.

PAH extraction

The procedure for extracting and isolating the particle-bound PAH mixtures on glass fiber filters are described elsewhere (Shi et al. 2005). In brief, the wet sample filters were cut into many pieces with a clean razor blade to increase the surface area available for extraction. Samples were then packed into a 10 mL stainless steel extraction chamber and, after adding 10 μL of a mixed perdeuterated PAH recovery standard, extracted using a Dionex ASE-200. The recovery standard, made up in iso-octane, was comprised of three compounds (d10-phenanthrene, d10-fluoranthene, d12-benzo[a]pyrene), prepared at a concentration of 1 ng μL^{-1} each. The ASE-200, set to 1500 psi and 100°C, sequentially extracted samples with 100% methanol (3x) and then a 3:1 v/v mixture of methylene chloride and methanol (4x). The combined extraction volumes were partitioned using a separatory funnel into hexane which was subsequently dried over anhydrous sodium sulfate granules (overnight). This procedure yielded a total lipid extract solution which was concentrated to a small volume (~ 2 mL) using a Turbo Vap II and, after quantitative transfer using methylene chloride to a small glass vial (with Teflon-lined cap), subsequently taken to just dryness under a gentle stream of prepurified nitrogen gas.

PAHs were isolated from the total lipid extract residue using a silica gel-packed glass column (7 g, silica gel 60, particle size 0.063–0.200 mm, EMD Chemicals, Inc.). Before use, the silica gel support was activated at 220°C for 24 h and deactivated 5% with water. To collect a PAH fraction, the total lipid extract residue was loaded using a minimum volume of hexane (~ 1 mL) onto the column, which was then eluted by gravity first with hexane (35 mL, discarded), and

subsequently with 10% methylene chloride in hexane (40 mL). The PAH fraction was concentrated to a small volume (~ 2 mL) with nitrogen (Turbo Vap II), transferred quantitatively using methylene chloride to a small vial (with Teflon-lined cap), and then slowly reduced to just dryness again using a gentle stream of pre-purified nitrogen.

Gas chromatography-mass spectrometry (GC-MS) analysis

PAH identification and quantification was accomplished using a Hewlett Packard 5890A Series II gas chromatograph equipped with an HP-1 fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness) and a Hewlett Packard 5971 mass selective detector. The carrier gas (helium) was supplied at a constant flow rate (1 mL min^{-1}). The GC oven was temperature programmed immediately from 100°C to 300°C at a rate of 5°C min^{-1} and then held isothermal for a total analysis time of 65 min.

PAH fractions were dissolved in iso-octane containing d12-chrysene (~ 1 ng μL^{-1}) as an internal GC standard. Fifteen PAH compounds were monitored in selective ion mode using the following characteristic mass fragments: $m/z = 178$ (phenanthrene), 188 (d10-phenanthrene), 192 (methylphenanthrenes), 202 (fluoranthene, pyrene), 212 (d10-fluoranthene), 228 (benz[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 PAHs and 4 perdeuterated PAHs in iso-octane was used to obtain retention time criteria for peak identification. For PAH compounds not present in the standard (methylphenanthrenes: $m/z = 192$; benz[a]anthracene: m/z: 228; tetrahydrochrysenes: m/z: 274), a known archived sample containing these compounds was run to obtain retention times and confirm peak identification. Figure 2 shows a Gas chromatography-mass spectrometry (GC-MS) trace obtained from analysis of an SPM sample collected in surface waters of the Willamette River at Portland (A, Fig. 1). The PAH compositional pattern illustrated is representative of that present in samples collected throughout the study region.

The relative response factor of d12-chrysene was used to convert a given PAH peak area to concentration. The external standard was run before and after every three to four sample runs to compensate for fluctuations in GC-MS performance. The concentration of a given PAH in a sample (C_{PAH}, units: ng per g dry weight of SPM) was calculated using the following expression:

$$C_{\text{PAH}} = \frac{\text{RRF}_{\text{PAH}} \left[\frac{C_{\text{is}} \times V_{\text{is}}}{A_{\text{is}}} \times A_{\text{PAH}} \times V_{\text{smpl}} \right]}{\text{SW} \times \%R} \quad (1)$$

RRF_{PAH} is the response factor of the given PAH relative to the internal GC standard d12-chrysene (determined through independent GC/MS analysis of an external standard mixture), C_{is}, V_{is}, and A_{is} are the concentration (ng μL^{-1}),
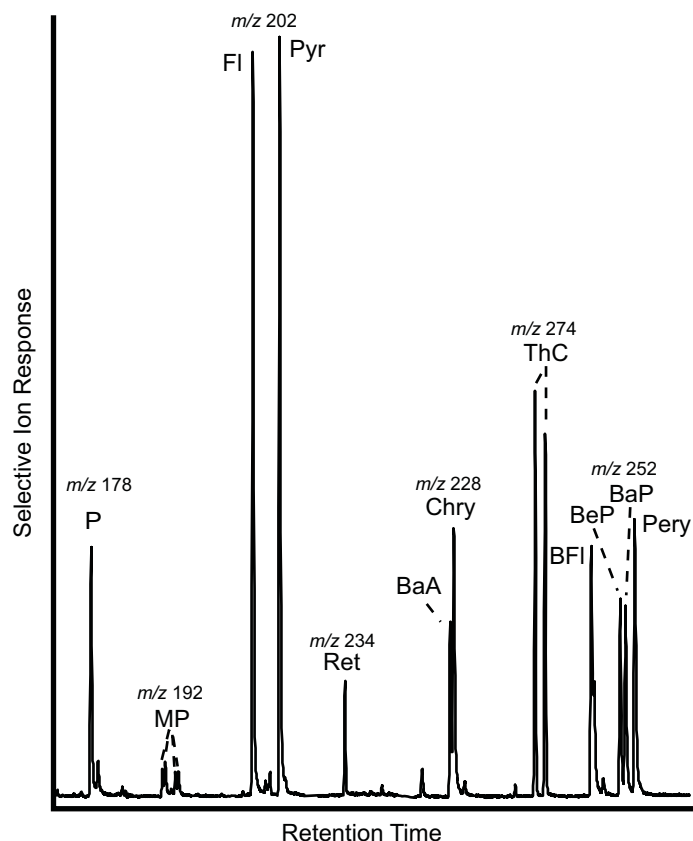
Fig. 2. GC-MS trace for an SPM sample from Portland, representative of the PAH composition in samples collected throughout the study region. P, phenanthrene (*m/z* 178); MP, methylphenanthrenes (*m/z* 192); Fl, fluoranthene and Pyr, pyrene (*m/z* 202); Ret, retene (*m/z* 234); BaA, benz(a)anthracene and Chry, chrysene (*m/z* 228); THCs, tetrahydrochrysenes (*m/z* 274); BFl, benzofluoranthenes; BeP, benzo(e)pyrene; BaP, benzo(a)pyrene; and Pery, perylene (*m/z* 252).

dilution volume (μL), and peak area, respectively, of the internal GC standard, A_{PAH} is the peak area for the given PAH, V_{smpl} is the sample dilution volume, SW is the dry weight (g) of SPM analyzed and %R is the percent recovery of the most appropriate perdeuterated PAH tracer added to each ASE extraction.

The uncertainty of quantitation was minimized by measuring the percent recovery (%R) of the three perdeuterated PAHs spiked into each sample prior to ASE extraction (d10-phenanthrene, d10-fluoranthene, and d12-benzo[a]pyrene) and correcting the measured PAH concentration for tracer recovery. Phenanthrene and methylphenanthrenes were recovery-corrected using %R results for the tracer, d10-phenanthrene. Fluoranthene, pyrene, and retene were corrected using d10-fluoranthene results and all remaining PAHs were corrected using d12-benzo[a]pyrene results. Analysis of true replicate samples showed the precision of PAH quantitation by our method was $\leq \pm 17\%$ (see table 2.1 in Gregg 2009). PAHs were not detected in blank filters indicating no sample contamination occurred during filter

processing on board the ship or during the chemical workup and analysis procedure in the laboratory.

Particulate organic carbon

At OSU, the frozen filters for POC analysis were removed from their foil storage wrappers, defrosted, and fumed with concentrated HCl (24 h) to remove all inorganic carbon. On oven drying (50°C for 24 h), the filters were manually pelletized using forceps, packed into precleaned silver boats, and wrapped in an additional layer of precleaned aluminum foil. Samples prepared in this way were analyzed on a Carlo Erba NA-1500 elemental analyzer using acetanilide as the calibration standard. Further details of this method are described elsewhere (Sullivan et al. 2001).

Results

PAH sources

The concentrations of the 12 PAHs detected in all SPM samples (Fig. 2) collected from upriver and estuarine sites during the RV *Barnes* cruise and at BAT as part of the USGS NASQAN time series are available in the appendices of a published Masters thesis (Gregg 2009). To reduce the number of compounds discussed, a correlation matrix was made for the 54 samples collected aboard the RV *Barnes* and the 23 samples collected with the USGS (Gregg 2009). Within the total dataset, eight (phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene) of the twelve PAH displayed Pearson r-values ≥ 0.8, indicating their likely derivation from the same source.

Scatter plots were constructed to further assist with appropriate source groupings for the PAHs. One for fluoranthene vs. pyrene data indicated that in nearly all samples analyzed within the study region, the quantitative relationship between these two tetracyclic PAHs was effectively 1: 1 (see fig. 3.1a in Gregg 2009). This quantitative relationship is diagnostic of a pyrogenic or high temperature combustion-derived source (Blumer and Youngblood 1975; Laflamme and Hites 1978). A scatter plot of total methylphenanthrenes to phenanthrene (MP/P) showed that the data is almost entirely bounded between a quantitative relationship of 0.25: 1 and 0.5: 1 (see fig. 3.1b in Gregg 2009). MP/P values falling within this range are typical of high temperature combustion-derived PAH, whereas those much greater than 1: 1 best describe the composition of petrogenic sources, e.g., oil and coal (Kawka and Simoneit 1990). Based on these findings, the concentrations for the eight well-correlated PAHs noted above were summed and that value will be referred to subsequently as the total sum of combustion PAHs ($\sum$COMB). Although also seemingly derived from a high temperature source as per the evidence just stated, the distribution for methylphenanthrenes did not meet the correlation coefficient criteria ($r \geq 0.8$) and, therefore, were not included in the definition of $\sum$COMB.

Table 2. SPM and PAH concentrations.

Site (# samples)	SPM (mg L^{-1})	PAH (μg g dry^{-1})			
		ΣCOMB	Ret	ThCs	Pery
(a) Surface waters from RV *Barnes* sampling sites					
Portland (1)	16.2	13.2	2.4	3.7	1.6
Vancouver (1)	7.6	2.1	1.0	0.2	0.6
Confluence (1)	6.4	2.2	1.0	0.2	1.3
Columbia City (1)	7.8	2.9	1.0	0.2	1.6
BAT (3)	6.9 ± 1.2	6.5 ± 2.3	3.1 ± 2.4	0.4 ± 0.1	2.5 ± 0.4
South Channel (5)	8.2 ± 6.0	1.5 ± 1.3	0.4 ± 0.3	0.1 ± 0.1	1.1 ± 0.5
North Channel (4)	6.9 ± 2.4	1.0 ± 0.5	0.3 ± 0.1	0.1 ± 0.0	1.1 ± 0.5
Mouth (3)	10.0 ± 3.7	1.1 ± 0.3	3.5 ± 1.8	0.1 ± 0.0	1.3 ± 0.2
(b) Bottom waters from RV *Barnes* sampling sites					
Portland (2)	17.8 ± 5.0	25.2 ± 3.0	6.2 ± 3.3	0.9 ± 0.3	3.9 ± 1.2
Vancouver (1)	6.4	1.6	2.5	0.0	1.0
Confluence (1)	9.2	1.6	0.4	0.0	0.6
Columbia City (1)	7.9	2.7	0.9	0.0	0.8
BAT (1)	5.6	5.3	1.4	0.4	1.5
South Channel (17)	39.1 ± 22.0	5.0 ± 2.7	1.5 ± 0.9	0.3 ± 0.2	7.3 ± 8.3
North Channel (8)	28.2 ± 17.6	4.1 ± 3.0	1.4 ± 1.3	0.3 ± 0.2	5.5 ± 4.9
Mouth (4)	34.3 ± 19.5	2.9 ± 1.9	1.1 ± 0.8	0.2 ± 0.1	3.5 ± 1.7

The remaining three PAHs (retene, tetrahydrochrysenes, perylene: Fig. 2) were not well correlated ($r \ll 0.8$) with $\sum$COMB or with one another (Gregg 2009). Potential causes for this reduced level of correlation are different origins, distinct particle associations, and consequently different dispersal behavior in the environment. Retene (Ret) and tetrahydrochrysenes (ThCs) are derived by diagenetic transformation of natural products in specific types of woody and non-woody vascular plant tissues (Simoneit 1998). Neither Ret or ThCs necessarily require a high temperature process to form from their natural product precursor (Wakeham et al. 1980), but anthropogenic burning processes and forest fires can facilitate the formation and release of each into the environment (e.g., Oros and Simoneit 2001a,2001b). Perylene (Pery), conversely, is a diagenetic product that has not been associated with an anthropogenic emission process high temperature or otherwise (Marynowski et al. 2013).

Spatial variation in PAH contribution

$\sum$COMB, Ret, ThCs and Pery concentrations in SPM from surface and bottom samples collected aboard the RV *Barnes* are reported in Table 2. Average ΣCOMB measured at the various sampling sites are compared in Fig. 3A. Highest values were evident in SPM from bottom waters in the Willamette River at Portland (25.2 ± 3.0 μg g dry^{-1}) and lowest in surface waters throughout the estuary (1.2 ± 1.4 μg g dry^{-1}). Values measured in SPM collected at the three sites farthest upriver in the mainstem Columbia (Vancouver, Confluence,

and Columbia City) were $\sim$ 6–10x lower than that in the Willamette at Portland, and relatively constant regardless of collection depth (2.4 ± 0.4 μg g dry^{-1}). The value increased by a factor of > 3 at BAT, the mainstem Columbia site located just downstream toward the estuary. On average, the ΣCOMB concentration in SPM from bottom waters at all three sites in the estuary (South Channel, North Channel, Mouth) were comparable, exceeding by a factor of > 3 that measured in surface waters at the corresponding sites and similar to that measured at BAT.

Ret concentrations in SPM were highly variable between sites and in samples collected from the same site (Table 2). ThCs were detectable in SPM throughout the study region, but at concentrations (0.4 ± 0.9 μg g dry^{-1}) typically the lowest of all PAHs. Pery concentration was low in SPM from surface waters throughout the study region but elevated in SPM from bottom waters of the Willamette, and particularly at all three sites in the estuary. The average Pery concentration in SPM from estuarine bottom waters was greater than that in SPM from overlying surface waters by a factor of $\sim$ 5, and greater than that in SPM from Willamette River waters by a factor of $\sim$ 2.

Average SPM concentrations in surface and bottom waters at each of the eight sampling sites (Table 2) are compared in Fig. 3B. Values in surface and bottom waters of the Willamette were similar and a factor of $\sim$ 2 higher than that noted in the mainstem Columbia. The pattern for SPM concentration with depth in estuarine waters differed significantly.
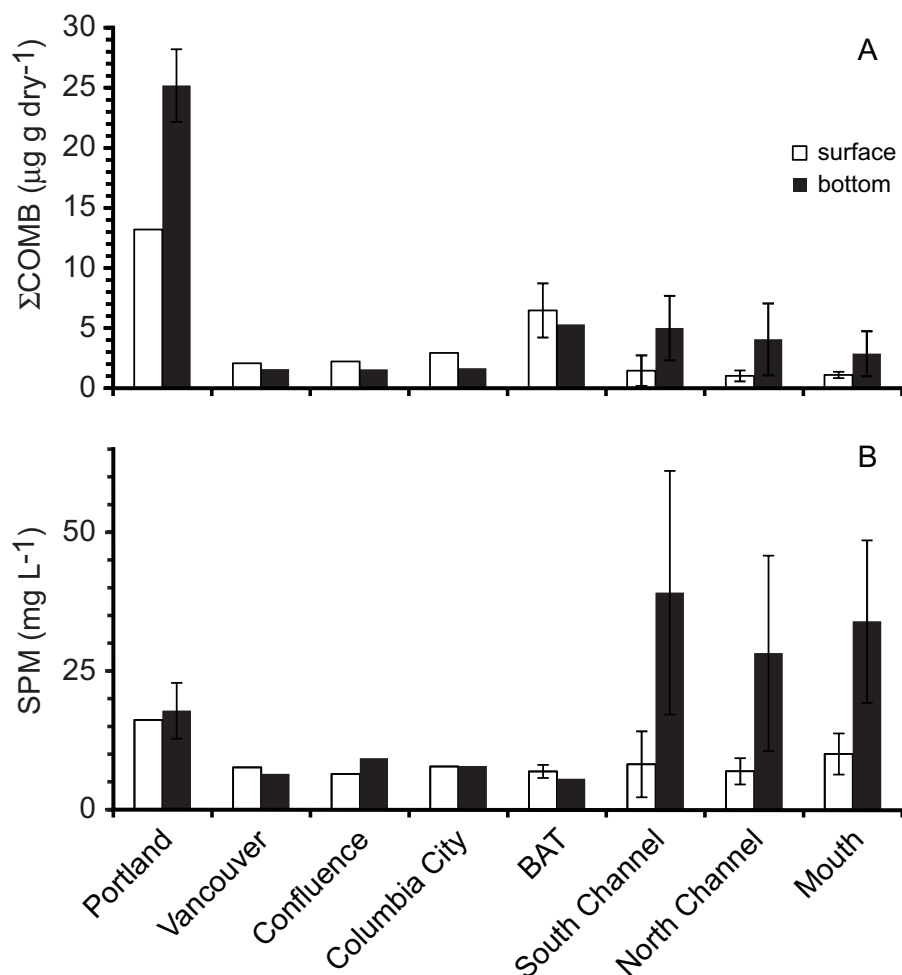
Fig. 3. (A) Mean (± SD) concentration of ΣCOMB and (B) SPM measured in surface and bottom waters at the sampling sites identified in Fig. 1 in August 2007. The data plotted are those reported in Table 2a,b.

Values in surface waters were similar to those throughout the lower Columbia River. However, values in estuarine bottom waters (33.7 ± 5.5 mg L^{-1}) exceeded those in the mainstem Columbia by a factor of ~ 5. Such elevated SPM levels are attributed to sampling done throughout the formation and disintegration of ETM.

Seasonal variation in PAH

The PAH composition and content was analyzed in SPM samples collected approximately bimonthly from Columbia River surface waters at BAT (Fig. 1) over the time period from October 2006 to January 2008 (Table 3). All four putative sources of PAH (ΣCOMB, Ret, ThCs, and Pery) were detectable and quantified in every sample collected. Regardless of source, concentration in μg per g dry sediment spanned a broad range throughout the time series: ΣCOMB $(1.0 - 11.8)$, Ret $(0.42 - 3.2)$, ThC $(0.10 - 0.56)$, Pery $(0.37 - 2.0)$. However, the apparent wide range of variability followed no clear temporal pattern in any case. A positive,

but statistically insignificant, correlation was observed between ΣCOMB and Ret $(r = +0.18, p = 0.33)$, ThCs $(r = +0.67, p = 0.034)$ and Pery $(r = +0.55, p = 0.079)$. And, there was no statistically significant correlation observed between SPM and any type of PAH concentration: ΣCOMB $(r = -0.24, p = 0.28)$ and ThCs $(r = -0.23, p = 0.29)$; Ret $(r = +0.54, p = 0.089)$ and Pery $(r = +0.40, p = 0.16)$.

Discussion

PAH levels and distribution within study region

Finding the highest concentrations for ΣCOMB in SPM from the Willamette at Portland is no surprise given a six mile stretch within Portland Harbor, which brackets our sampling location (A, Fig. 1), was designated in 2000 as a Superfund site (Sethajintanin et al. 2004). The large drop in ΣCOMB values below the Willamette confluence indicates SPM in the lower Columbia River is not predominantly derived from Willamette discharge. This conclusion is reinforced by the measurement of a ΣCOMB value in SPM collected at Vancouver, a site located

Table 3. Seasonal record for SPM and PAH concentrations in surface waters at BAT.

Date (# samples)	SPM mg L^{-1}	PAH (μg g dry^{-1})			
		ΣCOMB	Ret	ThCs	Pery
12 Oct 2006 (1)	3.2	3.5	0.42	0.18	0.68
13 Dec 2006 (1)	11.3	1.0	0.61	0.10	0.37
22 Feb 2007 (6)	25.8 $\pm$ 5.5	2.8 $\pm$ 0.24	1.1 $\pm$ 0.18	0.24 $\pm$ 0.09	1.2 $\pm$ 0.15
18 Apr 2007 (4)	14.5 $\pm$ 2.1	1.4 $\pm$ 0.24	1.5 $\pm$ 0.31	0.18 $\pm$ 0.07	0.65 $\pm$ 0.15
18 Aug 2007 (4)*	6.6 $\pm$ 2.1	6.2 $\pm$ 1.9	2.7 $\pm$ 1.9	0.40 $\pm$ 0.07	2.0 $\pm$ 0.65
6 Dec 2007 (3)	66.1 $\pm$ 10.8	2.5 $\pm$ 0.34	3.2 $\pm$ 0.29	0.17 $\pm$ 0.09	1.9 $\pm$ 0.38
17 Dec 2007 (4)	10.5 $\pm$ 2.8	11.8 $\pm$ 5.8	1.8 $\pm$ 0.68	0.54 $\pm$ 0.38	1.7 $\pm$ 0.49
24 Jan 2008 (4)	12.7 $\pm$ 3.3	2.7 $\pm$ 1.1	2.7 $\pm$ 1.4	0.56 $\pm$ 0.36	1.4 $\pm$ 0.47

*samples collected aboard RV *Barnes*; all others collected collaboratively with USGS.

in the mainstem Columbia above the Willamette confluence, similar to that in SPM collected at the confluence and Columbia City, the next site below. Notably, at the time of sampling in August 2007, Willamette discharge was $\sim$ 220 m^3 s^{-1}, or only $\sim$ 5% of the mainstem Columbia flow. Thus, on a mass balance basis, suspended particle loading of the Columbia River by Willamette discharge is demonstrably minimal, reinforcing the inference made above from simple quantitative intercomparison of PAH concentration in the particles.

Elevated ΣCOMB concentrations in SPM collected further downstream at BAT and in bottom waters of the estuary were unexpected (Fig. 3A). It was assumed 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 in the region (e.g., Barrick and Prahl 1987). In contrast to the portion of our study area proximate to Portland, a more rural landscape surrounds BAT, and the CRE (Jackson and Kimmerling 2003). Longview, Washington is a lightly industrialized, small population center located just upriver of BAT (between E and D, Fig. 1). Astoria, Oregon is located much farther downstream from BAT on the south side of the mid-CRE near sampling site F (Fig. 1). The infrastructure of this small town was once built around the fishing and fish processing industry, with some emphasis on the timber industry. But that focus in recent years has been greatly down-sized and shifted to tourism. The absence of a large downstream gradient in PAH concentration in our study area highlights the likelihood that nondeveloped portions of river—estuary systems are not necessarily isolated from the impact of these compounds and other particle associated POPs. The hydrophobicity and associated physicochemical behavior of such contaminants allows for their potential transport on particles to locations far downfield from their likely sites of introduction into the environment.

Seasonal variation in PAH levels

The magnitude of seasonal variability in the PAH concentration in SPM from the lower Columbia was assessed by

sampling approximately bimonthly at BAT (Fig. 1) over the time period from October 2006 to January 2008 (see filled squares, Fig. 4). During winter months, a higher concentration of ΣCOMB, the PAH source with greatest potential for municipal input, might be expected because of the greater contribution of Willamette discharge to the lower Columbia and the connectivity of this major tributary with Portland, Oregon. Throughout much of the typically rainy late fall and winter in the Pacific Northwest, the Willamette contributes up to 40% of the water discharge gauged in the mainstem Columbia at BAT (Fig. 4). This level of contribution is almost an order of magnitude higher than that characteristic of the dry summer to early fall period, i.e., $\sim$ 5%. Despite this large seasonal change in the hydrographic character of the lower Columbia drainage basin, however, no significant seasonal variation in the ΣCOMB content of SPM was observed. With one exception in December 2007 (11.8 μg g dry^{-1}), ΣCOMB values were quite uniform throughout the year (Fig. 4), averaging 4.0 $\pm$ 2.2 μg g dry^{-1} (Table 3).

The high ΣCOMB concentration noted at BAT in December 2007 was not associated with either unusually high or low SPM concentrations (see inset in Fig. 4). Furthermore, although the SPM concentration measured at BAT during the sampling period a few weeks earlier (66.1 mg L^{-1}) was $\sim$ 6 times greater than the average for all other times (10.2 $\pm$ 6.2 mg L^{-1}), the ΣCOMB concentration of the particles was not then at all different. Thus, the erosional source of particles leading to periods of increased turbidity is not characterized by an unusual ΣCOMB content (Ruegner et al. 2014).

ETM trapping of PAH

The relationship between concentrations (both per g dry sediment and per g organic carbon) for ΣCOMB (A, B) and perylene (C, D) and SPM concentration (plotted as its inverse) for samples collected at BAT and the CRE during the RV *Barnes* cruise (Table 1) is illustrated in Fig. 5. The 1/SPM (L mg^{-1}) plotting convention is used to most effectively show how the process of concentrating riverborne particles
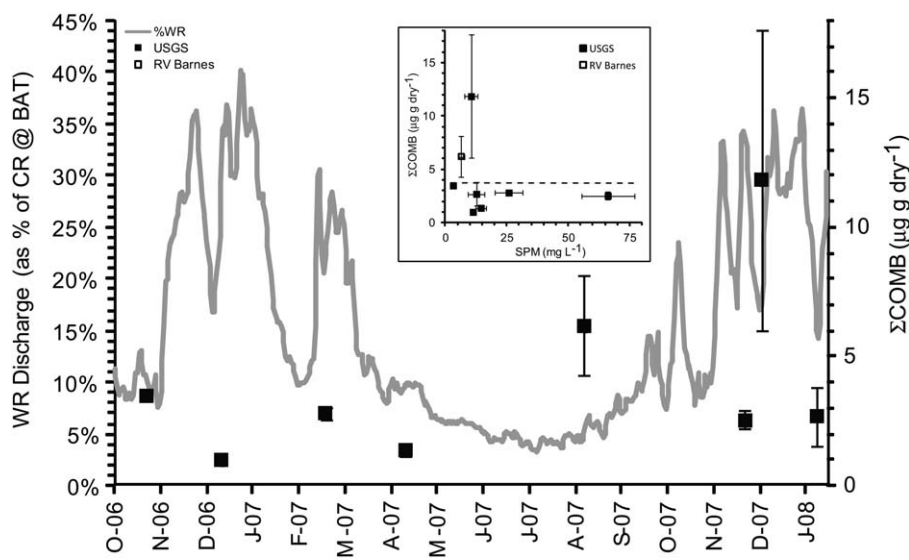
Fig. 4. Graph illustrating how the percent contribution of water discharge from the Willamette River (WR) to total flow in the lower Columbia River (CR) measured at Beaver Army Terminal (BAT) varied over the time period of this study (October 2006 to January 2008). Estimates of this fraction were calculated from USGS data available at: http://waterdata.usgs.gov/usa/nwis/rt. ΣCOMB concentration measured in SPM (μg g dry^{-1}) sampled at BAT in conjunction with the USGS NASQAN program (23 samples, 8 time points) and on a single cruise aboard the RV *Barnes* (Table 1) are plotted for comparison. The inset graph shows a scatter plot of the observed relationship between the concentration of ΣCOMB (μg g dry^{-1}) and SPM (mg L^{-1}) for this same set of samples.

in bottom waters of the estuary (i.e., ETM formation) impacts the PAH concentration measured in bulk suspended particles. Using this means of visualization, particles from more turbid water including the ETM (defined to be ≥ 40 mg SPM L^{-1} or ≤ 0.025 L mg^{-1}) plot toward the origin (Prahl et al. 1997). Notably, the particle-based concentration for both $\sum$COMB and Pery increases as turbidity in estuarine bottom waters increase (or 1/SPM decreases). In contrast, the $\sum$COMB and Pery concentrations of particles in the far less turbid, estuarine surface waters are as much as 10x lower and relatively independent of the SPM concentration.

The apparent "excess" of PAH concentration on SPM in estuarine bottom waters suggests that riverborne particles containing both types of PAH are enriched there, while another class of riverborne particles more depleted in these compounds passes in surface waters more directly through the estuary and offshore. In other words, evidence exists for selective trapping of riverborne PAH-containing particles, once introduced to the estuary, by the ETM (Small and Prahl 2004). Most notably, PAH enrichment is evident not only when concentrations are normalized to dry weight of SPM but also to the organic carbon content of the suspended particles.

The most likely particle carrier for high temperature combustion-derived PAH is some form of black carbon (Hites et al. 1977; Gustafsson et al. 1997). Studies have shown that "black carbon" is commonly found in both modern and ancient environments (Goldberg 1985). However, it is also

now known that not all forms of black carbon found in the environment are chemically equivalent (Keiluweit et al. 2010). Keiluweit et al. (2012) analyzed the PAH composition of black carbon (or "biochar") produced in the lab from both grass and wood source material pyrolyzed over a range of temperatures (100–700°C in 100°C increments). A PAH composition closely matching that of ΣCOMB observed in SPM throughout our study region was found in biochar produced at 500°C while biochars produced at lower (400°C) and higher (600°C) were characterized by a PAH signature of significantly different composition and at much lower quantitative yield. Values for ΣCOMB concentrations measured in the biochar produced from pyrolysis of grass and wood at 500°C were 27 μg g^{-1} and 3.2 μg g^{-1}, respectively (Keiluweit et al. 2012). In the case of both source materials, the biochar produced at 500°C was $\sim$ 80% carbon by weight. Notably, the absolute concentration of ΣCOMB measured in SPM from our study region is comparable to that measured in pure biochar from these laboratory experiments if gauged on a per g particle basis (Fig. 5A) and up to 50 times greater if gauged on a per g POC basis (Fig. 5B). Although an excellent match on a qualitative compositional signature basis, either these laboratory produced biochars are not actually indicative of the "black carbon" source that acts as the carrier of the ΣCOMB PAH in our aquatic setting (Van Metre and Mahler 2010), or they are and "weathering" of the biochar has acted somewhere in the environment to preferentially remove mass from the carrier particle, thereby greatly
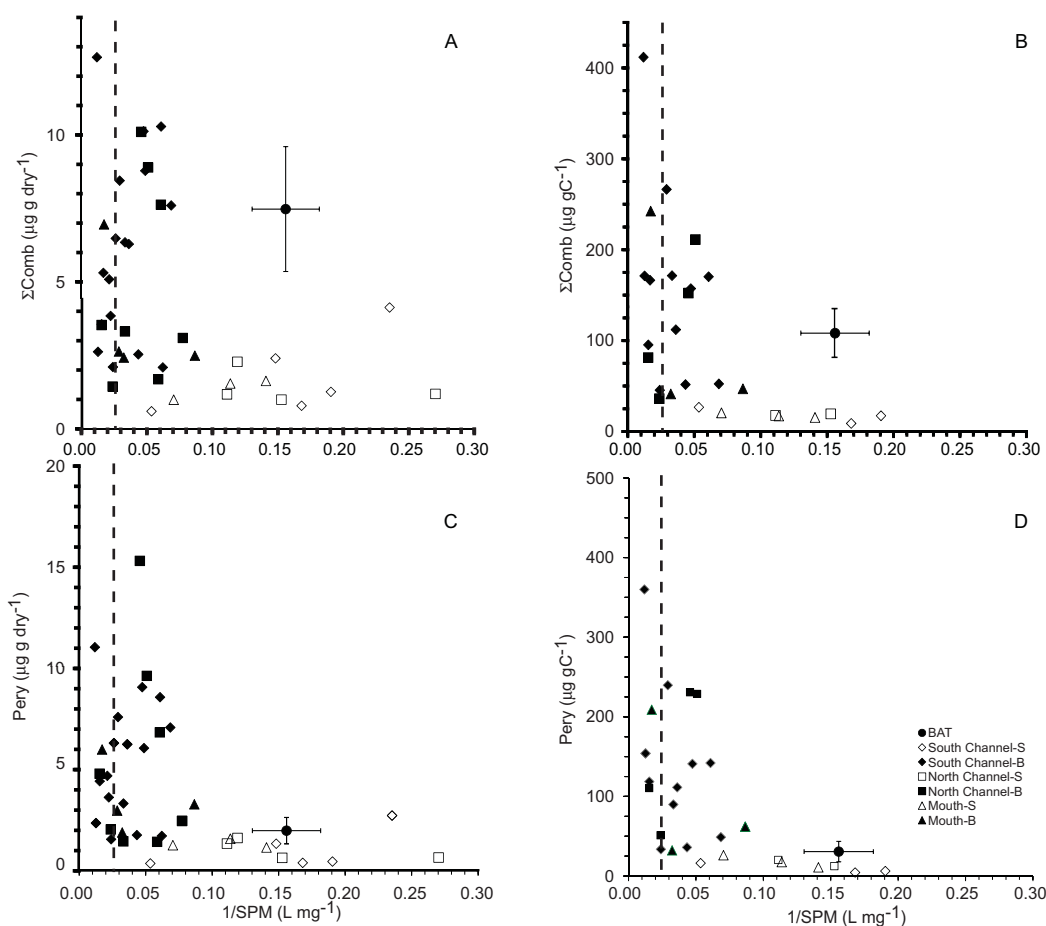
Fig. 5. ΣCOMB and Pery concentration measured per g dry sediment (A,C) and per g POC (B,D) in SPM collected from surface (S) and bottom (B) waters throughout the estuary in August 2007 (Table 1) plotted vs. the inverse of SPM concentration (i.e., L mg^{-1}) for the corresponding sample. For comparison, results from analysis of samples collected upriver at BAT (Fig. 1) in the same time period (Table 1) are also plotted. The data point for BAT represents the mean ($\pm$ 1SD) of measures made on three discrete surface samples and one bottom sample collected over a period of 4 h on the same day.

enriching the more "weatherproof" PAH component on a per particle mass and per organic carbon basis (Fig. 5A,B).

One consequence of concentrating PAHs in the ETM, by whatever means, is that organisms feeding in this environment have increased probability of encountering contaminated food particles and, as such, increased risk of toxicological impact. At the time of our survey cruise, an organism feeding on particles in the lower Columbia River would have encountered an average SPM concentration of $\sim$ 5–10 mg L^{-1}. In comparison, the same organism residing in the estuary and utilizing the ETM for its nutritional benefit would have encountered an SPM level 4–8 times higher.

Potential ecosystem risk

PAHs can negatively impact the overall health of exposed organisms. For example, Johnson et al. (2002) measured various health parameters in English Sole collected from sites in Puget Sound where both low and high molecular weight PAHs were prevalent in sediments comprising their benthic habitat. These flatfish were found to be highly susceptible to development of liver lesions and cancer when the total PAHs reached 1 μg g^{-1} dry sediment. Sublethal impacts, such as reproductive impairment, immune dysfunction, and abnormal development were also widespread in the population.

PAHs have also been found in the stomach contents of juvenile salmon collected in the mainstem Columbia between the Willamette confluence and Longview, Washington (Sites C, D, and E in our study, Fig. 1) (Johnson et al. 2007a, 2007b). This finding indicated that the specimens are exposed to, had encountered and did consume contaminated prey at some close proximity in this river system. Phenanthrene, fluoranthene, pyrene, and chrysene dominated the PAHs present in the stomach contents.

In order for organisms inhabiting the Columbia River to be adequately protected, PAH concentrations on bulk particles would need to fall below the probable effects level
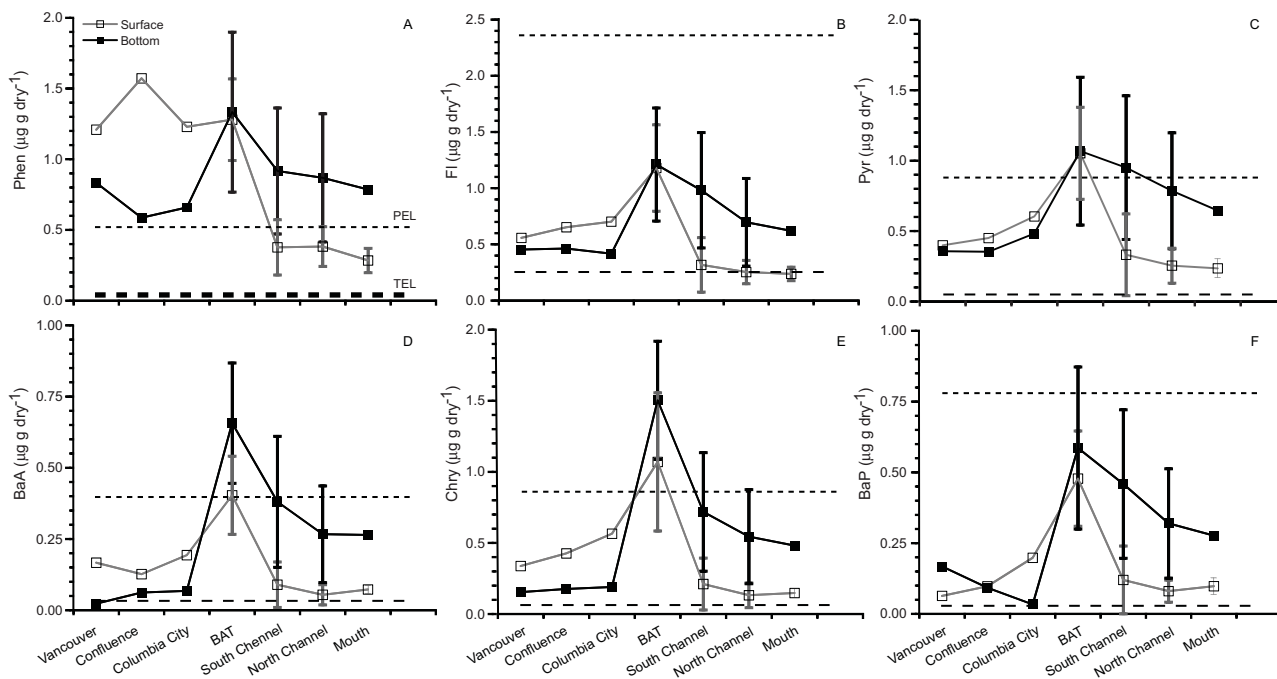
Fig. 6. Mean (± 1SD) concentrations of (A) phenanthrene, (B) fluoranthene, (C) pyrene, (D) benz(a)anthracene, (E) chrysene, and (F) benzo[a]pyrene measured along a transect of river and estuarine sites sampled aboard the RV *Barnes* in August 2007 (see Table 1). The horizontal dashed and dotted lines depict the threshold effects level (TEL) and probable effects level (PEL), respectively, for each PAH (MacDonald et al. 2000).

Table 4. Summary of PAH concentrations in suspended particulate materials (SPM) from rivers and estuaries around the globe.

Location	SPM range (mg L^{-1})	Mean Concentrations (ng g sediment^{-1})								Reference
		Phen	Fl	Pyr	BaP	PAH*	± 1σ	max	min	
Willamette River Portland U.S.A.	14–21	3130	5210	5550	2100	16000	3100	20900	9550	this study
Columbia River U.S.A.	5.6–9.2	1130	800	690	270	2,800	670	5180	1390	this study
Columbia River Estuary U.S.A.	3.7–85	820	670	700	330	2580	890	7290	400	this study
North Pollution Canal Tianjin China	n.r	9470	3960	2820	2330	18580	5356	28770	8510	Shi et al. (2005)
Yongding New River Tianjin China	n.r.	4010	980	560	120	5670	2138	9020	2340	Shi et al. (2005)
Hai River Tianjin China	n.r.	4330	800	390	20	5540	2375	8550	2530	Shi et al. (2005)
Chaobi New River Tianjin China	n.r.	2100	340	170	30	2640	1070	4140	1140	Shi et al. (2005)
Susquehanna River Pennsylvania, U.S.A.	2-25	439	521	550	339	1849	521	2876	822	Ko and Baker (2004)
Yellow River Middle China	n.r.	869	331	231	54	1485	694	4269	217	Sun et al. (2009)
Chesapeake Bay Maryland, U.S.A.	2–25	306	414	406	206	1332	172	1666	998	Ko and Baker (2004)
Seine Estuary France	n.r.	176	377	346	278	1177		1986	185	Cailleaud et al. (2007), Motelay-Massei et al. (2007)
Pearl River Estuary China	5–42	285	70	73	11	439	165	718	185	Luo et al. (2006)
Daliao River China	8–810	35	106	137	111	388	285	1,380	17	Guo et al. (2007)
Suisun Bay, Carquinez Strait, San Fransico Bay, U.S.A.	15–37	44	74	105	30	253	170	599	35	Domagalski and Kuivila (1993)
Xijiang River Guangdong, South China	3–98	101	47	51	5	205	98	454	30	Deng et al. (2006)
York River Virginia, U.S.A.	4–150	44	55	48	23	171	72	276	82	Countway et al. (2003)

*ΣPAH is the sum of Phen (phenanthrene), Fl (fluoranthene), Pyr (pyrene), and BaP (benzo[a]pyrene).
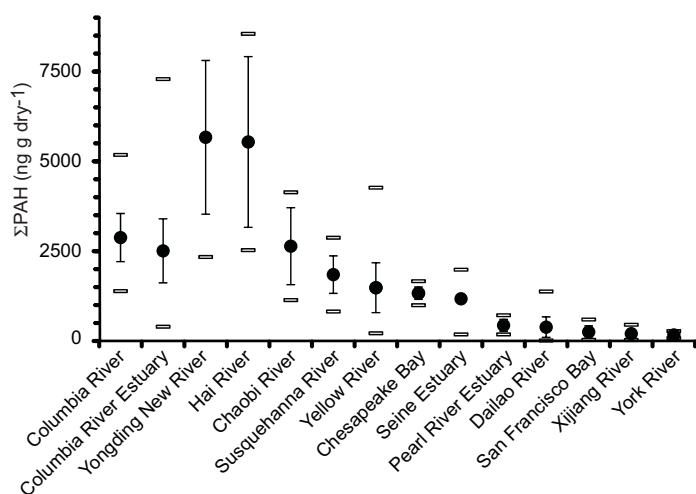n.r., not reported.

Fig. 7. Comparison of mean total PAH (± 1SD, sum of phenanthrene, fluoranthene, pyrene, benzo(a)pyrene) concentration in suspended particulate materials (SPM) for all waterways identified in Table 4 (excluding data for Portland and North Pollution Canal, Tianjin China). Horizontal lines indicate the maximum and minimum values reported for each data set (see references cited in Table 4).

(PEL) and ideally, the threshold effects level (TEL). PEL and TEL are defined respectively as the particulate contaminant concentration level at which adverse impacts in organisms are expected to occur frequently, and at which no adverse effects are likely to occur (MacDonald et al. 2000). PEL values for the suite of three to six ring PAHs (Phen, Fl, Pyr, BaA, Chry, BaP) measured in our study were commonly exceeded in SPM from waters upriver at BAT, the bottom of the estuary, and in all cases from the Willamette River at Portland (Fig. 6). Concentrations surpassing PEL values across the study region serve as a warning and suggest the likelihood of significant impairment to the health of the Columbia River ecosystem. This concern is especially the case in bottom waters of the Columbia estuary where concentrations of both SPM and PAH in SPM are high. Improved understanding of food web linkages between organisms that feed in the ETM and higher trophic levels, coupled with improved knowledge of controls on seasonal fluctuations in the concentrations of PAHs and other POPs in hydrodynamically trapped ETM particles and the bioavailability of such compounds on such transient particulate material (e.g., Brunk et al. 1997), is required to advance contaminant risk modeling and assessment for the CRE and other river-dominated estuarine systems.

Global comparison of PAH levels and its implication

To place PAH concentrations in SPM from our study region into perspective with the case for other waterways around the globe, the concentrations of phenanthrene, fluoranthene, pyrene, and benzo[a]pyrene were averaged for the sites located in the Willamette River at Portland, the mainstem lower Columbia River, and the CRE. These results were also summed and the value compared to equivalent data reported for SPM from the other studies (Table 4). The PAH concentration in SPM from the Willamette River at Portland and the North Pollution Canal in China greatly surpass the other locations, so they were excluded from the data set to allow for a better graphical quantitative sense of the difference in PAH levels from one location to the next.

The PAH levels in SPM from our study region are similar to or exceed those measured in other far more industrialized and/or urbanized regions of the world (Fig. 7). For example, the Seine Estuary is a densely populated and industrialized region, proximate to Paris, France, and its suburbs. Yet, the PAH levels reported there were ~ 50% those in SPM from the Columbia River and its estuary. The Tianjin region surrounding Beijing, China was the only study region where PAH levels in SPM exceeded those measured in the Columbia River and its estuary (Table 4).

Our monitoring of 12 PAHs in SPM from the Columbia River and its estuary has reinforced prior evidence that these compounds have been and continue to be transported via riverborne SPM at significant levels across this land-to-sea margin (Prahl et al. 1984). Once introduced to the estuary, the particles to which high temperature combustion-derived PAHs and perylene are adsorbed are necessarily dispersed through advective transport but trapped and significantly concentrated at least transiently in bottom waters. The ETM trapping phenomenon leads to PAH enrichment on a per particle basis, indicating that the hydrodynamic mechanism must operate on a particle selective basis thereby reinforcing prior findings that PAHs have discrete particle associations within sedimentary materials (e.g., Prahl and Carpenter 1983).

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