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Spatial and temporal variation of freely dissolved PAHs in an urban river undergoing Superfund remediation

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Abstract

Urban rivers with a history of industrial use can exhibit spatial and temporal variations in contaminant concentrations that may significantly affect risk evaluations and even the assessment of remediation efforts. Concentrations of 15 biologically available priority pollutant polycyclic aromatic hydrocarbons (PAHs) were measured over five years along 18.5 miles of the lower Willamette River using passive sampling devices and HPLC. The study area includes the Portland Harbor Superfund megasite with several PAH sources including remediation operations for coal tar at RM 6.3 west and an additional Superfund site, McCormick and Baxter, at RM 7 east consisting largely of creosote contamination. Study results show that organoclay capping at the McCormick and Baxter Superfund Site reduced PAHs from a pre-cap average of 440 ± 422 ng/L to 8 ± 3 ng/L post-capping. Results also reveal that dredging of submerged coal tar nearly tripled nearby freely dissolved PAH concentrations. For apportioning sources, fluoranthene/ pyrene and phenanthrene/anthracene diagnostic ratios from passive sampling devices were established for creosote and coal tar contamination and compared to published sediment values.

Introduction

Urban rivers are often plagued by organic contaminants that, depending on their concentrations, may pose a threat to human and ecological health. Attempts to remediate point sources, or “hot spots,” can re-suspend or release pollutants, particularly the freely dissolved and thus bioavailable fraction, and contaminate nearby areas and increase risk (1). Often the remediation results are uncertain because the contaminant concentration observed depends on the timing and method of sample collection (1–5). To more accurately assess seasonal or temporal variations in risk as well as remediation effectiveness at Superfund sites a time-integrated sampling method with good sensitivity is required.

Studies of urban aquatic systems often use sediment samples or water grab samples to evaluate concentrations, though each has limitations. For example, sediment analyses may overestimate the contribution of high molecular weight compounds of limited bioaccessibility (6, 7) and also encompass too broad a time frame that can be difficult to

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Supporting information

Supporting figures and tables including area maps and site descriptions, additional data, congener profiles, and PCA graphs are available at <http://pubs.acs.org>.

determine in highly impacted area such as harbors (8). Water grab samples offer only a “snapshot” and while multiple samples can be interpolated, this increases field and laboratory costs. Additionally, the dissolved fraction of target analytes in a grab sample may be too low for detection or quantitation. Semipermeable membrane devices (SPMDs), however, address bioaccessibility, sensitivity and time-integration issues by sequestering only the freely dissolved fraction over days or weeks (9–11) and have been recommended for remediation assessment (1).

The Willamette River in Portland, Oregon, like many urban rivers, has been the site of heavy industrial use including manufactured gas plants (MGP), creosoting operations and urban traffic, as well as petroleum product leaks and numerous combined sewer overflows (CSOs); all known sources of polycyclic aromatic hydrocarbon (PAH) contamination (5, 12–14). PAHs are a class of organic compounds with varying mutagenic and/or carcinogenic properties. The U.S. Environmental Protection Agency (USEPA) priority pollutants (PP) include 16 parent, or non-alkylated, PAHs that create a congener profile or ‘fingerprint’ with varying toxic potential (15). By analyzing congener ratios (12, 15, 16) and applying multivariate statistical techniques (4, 8, 17) this profile can also help reveal the source material.

In 2000, the area between river miles 3.5 and 9.2 was designated the Portland Harbor Superfund megasite and during our study a sediment cap was placed over 23 acres of creosote contaminated sediment in 2004 at the McCormick and Baxter Superfund site at river mile 7 east. In 2005, over 11,500 m³ of coal tar was removed from river mile 6.3 west, the GASCO site within the Portland Harbor megasite (18). Populated by benthic and pelagic, resident and migratory fish, this stretch of the Willamette is frequented by sport and subsistence anglers as well as recreational boaters.

Given the Willamette’s industrial history and significant seasonal variation in flow, questions arise concerning the concentrations of PAHs available to aquatic life and, ultimately, human exposure. Do recent remediation approaches effectively clean up the worst areas? Do seasonal or heavy rains, or fluctuating river flows, affect dissolved PAH concentrations, loads or their sources and complicate remediation efforts? To more accurately gauge the effectiveness of Superfund cleanup operations, the spatial and temporal occurrence of PAH contamination must be known. The objectives of this study were to assess the remediation approaches of two PAH contaminated sites on the lower Willamette River and determine spatial and temporal variations of freely dissolved PP PAHs including the effects of precipitation.

Materials and methods

The study area consists of the first 18.5 miles of the Willamette River. Samplers were placed from RM 1 to 18.5 at 10 sites with duplicates at 1 and 18.5 for a total of 12 samplers per deployment from 2002 to 2004 (Figure 1 and Table 1). These included sites upriver (at RMs 18.5, 17, 15.5, 13, and 12), downriver (RM 1) and within the Portland Harbor Superfund megasite (RMs 8, 7, 3.5 east, and 3.5 west) on west and east sides of the river channel (designated w and e, respectively). Surrounding area land use consists of urban (residential

and commercial – upriver sites), industrial (Superfund area), and undeveloped (downriver sites). During 2005 and 2006 SPMDs were located at RMs 7w and 8 only. This stretch of the Willamette contains PAH sources that include urban runoff from area drains, parking lots, CSOs and atmospheric deposition. Creosote and coal tar contaminated sites as well as petroleum industry operations are located within the Superfund area. In 2003 and again in 2005, 17 additional samplers were placed at the McCormick and Baxter Superfund site at RM 7e for 3-week deployments prior to and after placement of a 23-acre sand and organoclay sediment cap in 2004 (Supporting Information Figure S1).

Sample collection and extraction

From 2002 to 2006 samplers were deployed in 14 or 21 day events during the dry season of each year through the beginning of the wet season (Table 1). The wet season is defined as flow > 300 m³/s and precipitation > 3 mm for the sampling event. This period represents the transition from the lowest precipitation and flows of the year to relatively high precipitation and flow. In 2006 two 3-week sampling events were added in the spring prior to the beginning of the dry season. At each site five SPMDs were loaded into a stainless steel cage and suspended 3 meters above the river bottom with an anchor-cage-float system described elsewhere (19). The five SPMDs from each site were extracted together as one sample to increase detection capabilities.

Standard SPMDs were purchased from Environmental Sampling Technologies (St. Joseph, MO, USA). A standard SPMD consists of a 91–106 cm segment of 2.5 cm wide low-density polyethylene lay-flat tube having a wall thickness of 70–95 µm and a surface area of 450 cm², contains 1 mL of 95% pure triolein (1,2,3-tri[*cis*-9-octadecenoyl]glycerol) and has a total weight of 4.5 g.

Chemicals and solvents

PAH standards (purities 99%) were obtained from ChemService, Inc. (West Chester, PA, USA). Target analytes included naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLO), anthracene (ANT), phenanthrene (PHE), fluoranthene (FLA), pyrene (PYR), chrysene (CHR), benz(a)anthracene (BAA), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), benzo(ghi)perylene (BPL), and indeno(1,2,3-*cd*)pyrene (IPY). Cleanup and extraction solvents were pesticide or Optima® grade from Fisher Scientific (Fairlawn, NJ, USA).

Water quality data included temperature, pH, dissolved oxygen, specific conductivity, oxidative-reductive potential (ORP) and nitrate and ammonium concentrations, and were collected at each site during sampler deployment and retrieval using a YSI® sonde. Additionally, grab samples were also taken at sampler deployment and retrieval at certain sites for analysis of total and dissolved organic carbon (TOC and DOC), as well as total suspended and total dissolved solids (TSS and TDS). The two measurements were averaged for each sampling event and results are summarized in Supporting Information.

SPMD field cleanup and laboratory extraction were performed as previously described (20) and in accordance with standard operating procedures and standard analytical methods. Quality control consisted of field blanks, trip blanks and field cleanup blanks. Laboratory

quality control included reagent blanks, high and low concentration fortifications, and unexposed fortified SPMDs. Quality control resulted in duplicate sites average RSD equaling 15%, and target compounds in blanks were either non-detect or below levels of quantitation.

After extraction, samples were solvent exchanged into acetonitrile and analyzed by HPLC with diode-array and fluorescence detectors. DAD signals were 230 and 254 nm and FLD excitation and emissions were 230 and 332, 405, 460, respectively. Flow was 2.0 mL/min beginning with 40/60% acetonitrile and water and steadily ramping to 100% acetonitrile over a 28 minute run per column maker recommendations. Because the low molecular weight volatile compounds were impacted by the method solvent evaporation steps, SPMD concentrations were recovery corrected with method recovery averages ranging from 35% for NAP to 95% for BPL (Supporting Information Table S1).

The equation established for converting SPMD concentrations (C_{SPMD}) to water concentrations (C_{water}) using laboratory sampling rates (Rs) in L/day is:

$$C_{water} = \frac{C_{SPMD} \bullet V_{SPMD}}{Rs \bullet t} \quad (\text{Eq 1})$$

where V_{SPMD} is the volume of the sampler and t is the time in days. Laboratory sampling rates from the literature were used and temperature corrected using a trendline based on rates at three temperatures: 10, 18, and 26° C (9, 21). Loads were calculated from the concentrations using USGS flow estimates at the Portland station. Data analysis was performed using Microsoft Excel® 2003, SigmaStat® for t-tests and rank sum tests, S+® for principal component analysis and SigmaPlot® for graphing.

Results and discussion

McCormick and Baxter Superfund Site remediation

At RM 7e, the McCormick and Baxter site, 23 acres of creosote contaminated sediments, including NAPL hot spots, were capped with organoclay and articulated concrete block in 2004 to prevent diffusion. SPMDs positioned in the water column and located in the same locations pre- and post-capping revealed a decrease in sum dissolved PAH concentrations from an average of 440 ± 422 ng/L in 2003 to 8 ± 3 ng/L in 2005 (Table 2). Sum carcinogenic PAHs also dropped significantly from an average 44 ± 35 ng/L to 0.8 ± 0.5 ng/L. Additionally, substantial spatial variation within the 2003 SPMDs due to specific NAPL seeps did not appear in 2005 samples (Table 3 and SI Figure S3). Samplers positioned near observed seeps had the highest Σ PAH concentrations and loads in 2003, but not in 2005 which were below upriver levels (22). The cap prevents access to the underlying sediment for sampling, and the low post-cap concentrations would be difficult to quantify using a grab sample. SPMDs accumulated the low levels of freely dissolved contamination post-capping and demonstrated that remediation was successful.

RM 7 west during GASCO remediation

Another remediation approach across the river at the coal tar site had different results. Coal tar remediation efforts at RM 6.3w from August to October of 2005 removed $>11,500 \text{ m}^3$ of submerged tar contamination. The oversight report detailed excessive concentrations of BAA and BAP outside the barrier curtains, and as far as 600 feet downstream (18). Given the tidal fluctuations of the Willamette, this uncontained contamination could also be responsible for RM 7w elevated concentrations upriver. SPMDs deployed at RM 7 west 1000 m upstream during this activity have significantly higher mean concentrations ($2.9 \pm 0.5 \text{ } \mu\text{g/L}$) than pre- and post-remediation samples ($1.0 \pm 1.1 \text{ } \mu\text{g/L}$, t-test, $n = 18$, $P = 0.002$). Samples deployed during tar remediation also had significantly higher mean dissolved carcinogenic PAHs as well as substantially increased BAA, BAP, and ΣPAH loads during remediation, even during the wet season when these values were normally much lower than the dry season (Table 2). Using aerobic bioslurry experiments, Ghosh et al. (23) found PAHs associated with coal tar pitch to be more readily desorbed than those bound to carbonaceous coal. However, *Hyalella azteca* assays by Kreitinger et al. (7) revealed that MGP sediment PAHs were much less bioaccessible than expected. Coal tar PAHs may be less bioaccessible *in-situ* (7), but it is clear that dredging readily desorbed PAHs and greatly increased the dissolved fraction of carcinogenic PAHs as measured by SPMDs.

Elevated PAH levels returned during the 2006 dry season after coal tar removal at RM 6.3w. As RM 7w PAH loads and concentrations were not impacted permanently either by remediation at RM 6.3w or RM 7e, and because upriver sites do not show this temporal pattern, a different PAH source must contaminate RM 7w. This point source may be PAH-laden fill material such as asphalt, creosote or tar that resists saturation by ground water creating a bank storage situation which is explained later in the temporal analysis (24). Because this observation can significantly affect evaluation of remediation operations, spatial and temporal analysis of PAH contamination in the lower Willamette is necessary to determine the extent of this occurrence.

Spatial distribution of freely dissolved PAHs

Analysis revealed, not surprisingly, that the Portland Harbor Superfund megasite has a significantly higher median ΣPAH concentration (15 target analytes, 418 ng/L) and daily load (11 kg/day) than upriver sites (62 ng/L and 1.8 kg/day), but not the downriver site (269 ng/L and 7.5 kg/day , Figure 2 and Table 2, Kruskal-Wallis one-way analyses on ranks combined with Dunn's method of pairwise multiple comparison). Portland Harbor sites were also higher in dissolved carcinogenic PAHs than other sites (137 vs. 38 ng/L , $P < 0.001$). No upriver sites varied significantly from each other but there was significant variation between Portland Harbor Superfund sites (Figure 2).

Interestingly, the creosote contamination at the McCormick and Baxter Superfund site (RM 7e) did not have the highest levels of PAHs. ΣPAH concentrations and loads were consistently highest in samplers at RM 7w. PAH contamination may be from sites upriver that were not captured by east side RM 8 samplers or fill used to stabilize banks (25), or some other source of PAHs. The GASCO site at RM 6.3w was a significant source of PAH

contamination at RM 7w. However, this site's contamination is further complicated by temporal issues.

Temporal variation of freely dissolved PAHs

Our sampling reveals a higher upriver median daily PAH wet season load than in the dry season (2.8 vs. 1.1 kg/day, respectively, $n = 43$, $P = 0.005$), but no difference in concentration (88 vs. 51 ng/L, wet and dry, respectively, $P = 0.33$). Substantially increased river flows may dilute increased deposition explaining the lack of change in concentration (wet season average flow = $429 \pm 136 \text{ m}^3/\text{s}$, dry = $262 \pm 20 \text{ m}^3/\text{s}$). In a study of nine urban rivers including the Willamette, Stout et al. (26) found that storm water runoff likely contributes the most anthropogenic PAHs to urban river sediments over time. Our data reflect also demonstrate increased deposition as well as increased dissolved PAH loading during the wet season; however, neither LMW nor HMW PAHs differed significantly between seasons as observed by Motelay-Massei et al. (4). Brun et al. (13) and Motelay-Massei et al. (4) found that PAH deposition is greater during seasons with higher precipitation and lower temperatures due to increased vapor phase atmospheric PAHs, particularly of low molecular weight (2–3 ring) PAHs.

Unlike the upriver sites, the Portland Harbor Superfund megasite, excluding RM 7w, does not have significantly different Σ PAH loads or concentrations between seasons. Upriver wet season PAHs are likely due to non-point sources such as urban runoff and atmospheric deposition (4, 12, 13, 26, 27) which may include an increase in residential heating (5). Portland Harbor Superfund PAH sources are predominantly sediment based point sources which contaminate the overlying water regardless of season (28), though RM 7w may be an interesting exception. Also, the significantly higher PAH loading found in the Superfund area (9.7 and 15 kg/day, wet and dry, respectively) is unaffected by the wet season load increase of 1.7 kg/day found upriver (Table 2). Thus, the upriver wet season increase, well below the Superfund median, is hidden and statistically insignificant in the high Superfund loading.

When analyzed separately, RM 7w shows a higher concentration and load in the dry season (Table 2). If lower wet season averages were the result of dilution, then RM 7e, the former creosoting operation, would exhibit the same temporal variations in concentration and load but it does not. Also, the Σ PAH wet and dry loads would be expected to remain similar while concentration decreased in the wet season, especially as upriver sites experience an increase in wet season loading. However, because RM 7w wet season loads are significantly lower than dry loads the differences cannot be explained by dilution. An alternative explanation may be a phenomenon described by Winter et al. (24) called bank storage. In this example, the wet season high river flows may create sufficient hydraulic pressure on the sediment contamination preventing discharge and thus storing the contamination in the river bank. For this to occur the area would need to have been capped or filled with material that resists water saturation allowing the higher hydraulic pressure from the river to trap the contamination. Filling banks with PAH-laden asphalt was a common local practice (25).

High rain events

SPMDs yield a time-integrated average for the deployment period; therefore, a high rain event (here defined as precipitation > 12.5 mm in a 24 hr period) must deposit significantly larger amounts to raise the deployment average. And indeed, these sampling events had both higher median concentrations (140 vs. 48 ng/L, $n = 27$, $P = 0.03$) and loads (3.4 vs. 1.0 kg/day, $P = 0.01$). Brown and Peake (12) and Gasperi et al. (27) also found that increased precipitation or related activities like street cleaning in urban areas can increase PAH concentrations and loads in runoff. Additionally, while flow during these events increased significantly from a dry season/no rain median of 249 to 278 m³/sec (Mann-Whitney rank sum, $n = 27$, $P < 0.001$), this is still significantly lower than the wet season median of 335 m³/sec ($n = 28$, $P < 0.001$). While high rain event concentrations and loads during the dry season are not significantly higher than the wet season, the load is significantly different than dry season/no rain medians due to the river flow. That wet season concentrations at upriver sites do not significantly differ from the dry season, but loads do, is explained by the diluting effects of increased river flow combined with the deposition of accumulated urban PAHs (12, 27).

Source apportionment using ratios

Source identification is required to determine the contributions of surrounding contamination versus the contamination under remediation (e.g., at RMs 7w and 7e) and to gauge the remediation effectiveness. Because SPMDs accumulate compounds over the course of days or weeks they offer more discrete sourcing information than sediments and increased sensitivity over grab samples, as well as potentially identifying the source contributing the most bioaccessible contamination. Diagnostic ratios such as FLA/PYR and PHE/ANT are characteristics of congener profiles often used to apportion PAH sources in contaminated harbors (15, 16). Ratios from SPMDs may not be equivalent to sediment ratios due to disparate sampling rates. However, ratios of compounds with very similar sampling rates such as FLA/PYR and PHE/ANT could be very similar to established sediment rates. Luellen and Shea (29) found that SPMDs conserve sterane and hopane ratios demonstrating that traditional PAH profiling techniques may be adapted to SPMDs, though few studies have done this (8).

Given this study area's history at least three PAH sources could be expected, all predominately pyrogenic: urban runoff, creosote, and coal tar. FLA/PYR ratios range from 0.73 to 1.47, all within ranges for pyrogenic sources and well above those expected for most solely petrogenic sources (15). Only the largely urban runoff upriver area differs significantly between seasons with a 0.93 dry season ratio and 0.74 in the wet season, though both are consistent with previously reported ratios for urban runoff (8, 15). The lower values suggest mixing of petrogenic and pyrogenic sources as expected with urban runoff that includes exhaust from fossil fuel combustion and vehicle oil leaks and spills (26). The significantly higher wet season FLA/PYR ratio ($P < 0.004$, Table 2) suggests an increased pyrogenic input not found in the dry season. Atmospheric PAHs are predominantly pyrogenic and as observed by Motelay-Massei et al. (4), increased representation, particularly in SPMDs, could be partially due to increased vapor phase atmospheric PAH deposition caused by cooler temperatures and increased precipitation.

Additionally, residential heating from wood and oil burning has been shown to increase atmospheric deposition of PAHs (5) and would be expected to increase in the colder wet season. Notably, FLA/PYR ratios did not significantly differ in SPMDs that captured a rain event during the dry season. Anthracene levels were often near or below limits of detection and quantitation, therefore PHE/ANT ratios varied substantially within seasons but did not differ significantly between seasons (wet = 44 ± 66 , dry = 28 ± 39 , Table 2). The large variation within seasons may be an artifact of low anthracene levels and/or the result of occasional high petrogenic inputs due to localized, transient contamination.

The creosote contaminated McCormick and Baxter site ratios differ significantly (Table 2, $P < 0.001$) with pre-cap samples near or slightly lower than FLA/PYR ratios reported for creosote (15) while post-cap ratios more closely match the upriver sites of the same season. Water column mixing with upriver petrogenic PAH sources may have caused the slightly lower numbers. Anthracene was sometimes above limits of quantitation at this site, though PHE/ANT ratios demonstrated the same broad spatial variability as pre-capping concentrations and loads. Pre-cap PHE/ANT ratios range from 7.5 to >1000 with an average of 524 ± 1150 , though SPMDs positioned near observed seeps range from 7.5 to 32. According to Neff et al. (15), creosote PHE/ANT ratios (which, unlike this study, include particulate bound fractions of these compounds) range from 0.11 to 4.01 while ratios for petrogenic sources ranges from 14 to >800 due to extremely low anthracene concentrations. Applying these ratios to our SPMD results suggests a petrogenic source; however, post-cap PHE/ANT ratios average 3.8 ± 0.5 , which, considering the greatly reduced Σ PAH concentrations and loads and altered FLA/PYR ratios, demonstrates that the creosote NAPL was the source of these ratios. SPMD sensitivity at low ambient concentrations provided diagnostic ratios that clearly demonstrate that the sediment cap effectively prevents creosote NAPL from seeping into the overlying water.

Across the river at RM 7w, FLA/PYR neither varies significantly by season nor before or after the remediation events at RM 7e and RM 6.3w. However, median FLA/PYR is significantly lower *during* the coal tar remediation at RM 6.3w than before or after it (1.01 vs. 1.07, $n = 18$, $P = 0.04$) and both are below the 1.28 cited in Neff et al. (15) for coal tar. PHE/ANT ratios averaging 3.1 are significantly lower during removal activity than pre- and post-activity sampling (5.9, $P = 0.002$) and closely matches the 3.11 coal tar PHE/ANT ratio reported in Neff et al. (15). Notably, Brown and Peake (12) also report lower PHE/ANT ratios near a gasworks remediation. Also, RM 7e post-cap samples were collected near the end of tar remediation at RM 6.3w and though FLA/PYR do not match, PHE/ANT ratios are similar. One PAH ratio, or even two, is not sufficient for absolute source apportionment, but it does provide additional evidence that RM 7w has contamination distinct from RMs 7e and 6.3w. Further work should be attempted using more PAH congeners, including retene and alkylated, and a broader selection of ratios (5, 13).

Source apportionment using PCA

Because it is uncertain if traditional PAH ratios are preserved in SPMDs, supporting evidence is required for source apportionment. Principal component analysis expresses sample data with respect to similarities and differences, reduces 'dimensions', and provides

graphical representation without *a priori* grouping (17). Using PAH congeners and PCA, Motelay-Massei et al. (4) found increasing suburban atmospheric deposition with increasing precipitation and decreasing temperature due to vapor/particle partitioning. Vrana et al. (8) used SPMDs and PCA to apportion PAH sources near smelter operation in Germany. Using concentrations of the 15 PAHs, PCA did not reveal differences between upriver wet and dry or rain event congener profiles which would be expected if the PAH source changed (Figure 3). Therefore, increased wet season PAHs could be explained by increased urban runoff from precipitation. However, the increased FLA/PYR ratio suggests an increase in pyrogenic contribution at these sites. Atmospheric deposition from residential heating, as expected during the wet season (5, 13), could alter the FLA/PYR ratio but would not necessarily be revealed by this limited congener profile. Retene is an effective marker for seasonal residential wood burning and should be included in future analyses (5).

While upriver sites were not readily differentiated by PCA, samplers at RM 7, both east and west, as well as several downriver sites group separately from upriver samples (Figure 3). This demonstrates that the source(s) at RM 7 differs from the upriver source which is consistent with known creosote and tar contamination point sources. Note, however, that post-remediation RM 7e sampling events group with upriver sites, again demonstrating successful remediation. Plotting principal component 1 versus component 3 of RM 7w samples separates wet and dry seasons while the events with tar remediation group strongly though this represents less overall variation (Figure 3). The results suggest that the PAH contamination source changes based on river flow and precipitation, and remediation activities. PC1 represents more HMW PAHs and the tar samples routinely show increases in these compounds compared to the other samples (Figure 3 and Supporting Information Table S3). This demonstrates that sediment re-suspension associated with remediation increases dissolved HMW PAHs normally bound to particulates thus increasing bioaccessibility and, ultimately, risk. Additionally, our data indicate that while coal tar may be responsible for RM 7w contamination during remediation it is not the major contributor to the elevated dry season concentrations and loads, nor is RM 7e. The data are consistent with pyrogenic sources, including creosote, coal tar, asphalt and others, perhaps mixed, that may have been used as fill material and resulted in extreme seasonal variations due to bank storage.

Threats to aquatic life and human health

There are no US EPA Water Quality Criteria (WQC) for PAHs in freshwater systems to estimate risk to aquatic life. Oregon does have Water Quality Guidance values for three PAHs: naphthalene, acenaphthene, and fluoranthene though none of the sampling events exceeded these values (Supporting Information Table S1). The human health WQC for consumption of water and organisms was routinely exceeded for the carcinogenic PAHs, most frequently in the Superfund megasite, though also in upriver sites (Supporting Information Figure S4).

Overall, SPMDs demonstrated the ability of PSDs to provide excellent spatial and temporal data on scales between grab and sediment samples, provide additional source information

and associated risk and bioaccessibility, and reveal the effectiveness of remediation activities.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Yellow circles are the approximate sites of SPMD samplers on the Willamette River (north flowing). The Portland Harbor Superfund megasite is in red. The McCormick and Baxter Superfund site is on the east bank at river mile 7.

Estimated seasonal bioaccessible Σ PAHs in an urban river

Figure 2.

The Superfund megasite estimated dissolved Σ PAH concentration and load is significantly higher than Upriver and Downriver sites in both dry and wet seasons ($n = 110$, $P < 0.001$). Superfund dry season concentrations and loads are significantly higher than the wet season ($n = 51$, $P = 0.008$). Upriver loads are higher during the wet season than the dry season ($n = 43$, $P = 0.005$). Note: error bars represent standard error.

Figure 3.

Panel A. Spatial and temporal distribution of all sites using congener profiles comprised of 14 dissolved PAHs labeled by river mile ($n = 141$). For RM 7 locations, e and w denote east and west side of the river channel, respectively. Variations at RM 7 suggest changes in PAH source from upriver sites and between river banks. *Panel B.* RM 7 west sample PAH congener profiles labeled by season ($n = 18$). Those deployed during the tar removal activity at river mile 6.3 west in 2005 are labeled with “tar” suffix.

Table 1

Sampling event schedule and locations

Year	Dates	Exposure duration (days)	Sampler locations (river mile)
2002	Aug. 7 – 21	14	1, 3.5e, 3.5w, 7w, 8, 12, 13, 15.5, 17, 18.5
	Sept. 11 – 25	14	
	Nov. 7 – 26	19	
2003	Oct. 1 – 15	14	
	Nov. 5 – 19	14	
2004	July 7 – 29	21	
	Aug. 19 – Sept. 9	21	
	Oct. 19 – Nov. 9	21	
2005	Aug. 8 – 29	21	
	Aug. 29 – Sept. 19	21	
	Sept. 19 – Oct. 10	21	
2006	May 18 – June 8	21	Portland Harbor only (7w and 8)
	June 8 – 29	21	
	Aug. 10 – 31	21	
	Aug. 31 – Sept. 21	21	
	Nov. 20 – Dec. 12	21	
McCormick and Baxter Superfund Site			
2003	Oct. 2 – 16	14	7e
2005	Sept. 19 – Oct. 10	21	

Table 2

Spatial and temporal variation of median dissolved ΣPAH estimates by SPMD in an urban river¹

River location and season	N	concentration (ng/L)	P value ²	load (kg/day)	P value ²	carcinogenic (ng/L)	P value ²	FLA/ PYR	P value ²
Upriver	43	62		1.8		39		0.83	
wet	16	88		2.8		44		0.93	
dry	27	51	0.3	1.1	0.005*	22	0.3	0.74	0.004*
rain event	12	140	0.03*	3.4	0.01*	222	0.3	0.76	0.05
Superfund Megasite	51	418		11		137		1.02	
wet	23	265		9.7		113		1.03	
dry	28	658	0.008*	15	0.2	140	0.1	0.98	0.32
w/o RM 7 west	33	273		7.5		101		0.97	
wet	15	207		7.5		76		1.02	
dry	18	374	0.1	7.6	0.8	112	0.5	0.95	0.7
RM 7 east									
pre-cap	13	338		7.6		32		1.23	
post-cap	16	7	<0.001*	0.2	<0.001*	0.6	<0.001*	0.76	<0.001*
RM 7 west	18	1170		26		262		1.02	
wet	8	331		13		212		1.07	
dry	10	1867	0.02*	39	0.04*	528	0.1	1.02	0.2
Downriver	16	269		7.4		53		0.89	
wet	6	270		9.3		57		0.99	
dry	10	259	0.8	6.1	0.1	50	0.9	0.78	0.1

¹ Mann-Whitney Rank Sum Tests within location between seasons.

² P-values are for comparisons between seasons, except for Upriver rain event which is between dry season with no rain and dry season with rain event.

* indicates significance at $\alpha = 0.05$.

Remediation effectiveness

Table 3

McCormick and Baxter Superfund Site at river mile 7 east averages ± 1 SD, pre- and post-sediment capping compared to Water Quality Criteria and background levels (upriver, wet season averages). River mile 7 west averages ± 1 SD before, during, and after river mile 6.3 west coal tar removal activity.

Site and Activity	Season	N	BAA	BAP	Carcinogenic	Concentration (ng/L)			
						ΣPAH	ΣPAH load (kg/day)	FLA/PYR	
Water quality criteria		N/A	490 ^a	240 ^a	31 ^b	**	N/A	N/A	
River Mile 7 east									
pre-cap		14	26 ± 28	12 ± 14	44 ± 35	439 ± 422	9.9 ± 7.6	1.17 ± 0.40	
post-cap		17	0.44 ± 0.21	ND	0.8 ± 0.5	8.1 ± 3.3	0.22 ± 0.09	0.73 ± 0.20	
background		16	3.1 ± 5.6	7 ± 13	17 ± 18	101 ± 0.6	3.3 ± 1.4	0.96 ± 0.16	
River mile 7 west									
pre-tar removal	wet	3	25 ± 34	16 ± 25	47 ± 36	360 ± 100	13 ± 3	1.12 ± 0.15	
	dry	5	65 ± 49	30 ± 38	181 ± 169	1620 ± 1370	38 ± 35	1.10 ± 0.18	
tar removal	wet	2	122 ± 24	65 ± 11	352 ± 61	2610 ± 360	71 ± 10	1.02 ± 0.01	
	dry	3	180 ± 22	79 ± 18	565 ± 58	3200 ± 380	69 ± 13	0.97 ± 0.04	
post-tar removal	wet	3	6 ± 6	4 ± 2	19 ± 18	160 ± 130	10 ± 3	1.17 ± 0.14	
	dry	2	98 ± 14	28 ± 6	289 ± 53	1870 ± 90	39 ± 2	1.05 ± 0.04	

^aThese number are for the Water Quality Triggers and only apply to River Mile 6.3 west during tar removal activities.

^bFrom the McCormick and Baxter second 5-year review (22).