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APPROVED :

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Urban rivers with a history of industrial use can exhibit spatial and temporal variations in contaminant concentrations that may significantly affect risk evaluations and assessment of remediation efforts. To more effectively estimate human and ecological health risks, we evaluated the spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in an urban river using low-density polyethylene passive sampling devices (PSDs). PSDs simulate cell membranes and lipid tissue and accumulate only freely dissolved, and thus, bioavailable contamination. Using PSDs and high-pressure liquid chromatography we measured bioavailable concentrations of 15 priority pollutant PAHs over five years along 18.5 miles of the lower Willamette River including the Portland Harbor Superfund megasite. This area contains several PAH sources including coal tar and creosote sites, which underwent remediation during this study. Additional potential sources of PAHs include combined sewer overflows, urban runoff, atmospheric deposition and petroleum product leaks and spills. Results reveal increased urban bioaccessible PAH loading during wet seasons and high rain events, successful capping of the McCormick and Baxter Superfund site, increased bioavailable PAHs during dredging operations, and the potential for using PSDs for source apportionment. PAH concentrations, loads, and congener ratios changed significantly depending on location, river flow, precipitation, and contaminant removal activities. Our research demonstrates that human and ecological risk varies significantly by season and remediation technique. Additionally, our refined analytical method eliminated 80% of organic solvents and 100% of chlorinated solvents from the sampling method and also reduced labor and cost. Health professionals can apply the findings and refined technology to more effectively assess exposure to pollution.

SPATIAL AND TEMPORAL VARIATIONS OF BIOAVAILABLE POLYCYCLIC AROMATIC HYDROCARBONS IN THE LOWER WILLAMETTE RIVER

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

Gregory J. Sower, Author

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This work is dedicated to my wife, Marianne.
We’re a long way from Burley, Cuteness.

Spatial and Temporal Variations of Bioavailable Polycyclic Aromatic Hydrocarbons in the Lower Willamette River

Chapter 1 - Introduction

The dose makes the poison. This paraphrased observation by Paracelsus is the fundamental tenet of toxicology and succinctly states the concept that a compound's toxicity is not constant, but dependent on other parameters. Originally this meant the quantity of the compound. Today we know the dose effects may also depend on timing (acute and chronic as well as lifestage), the method of exposure (absorption, ingestion, congenital, etc.) and on a compound's bioavailability. The bioavailable fraction is that portion of the total concentration capable of toxic insult: the external dose. As not all of an environmental toxin's concentration may be accessible to organisms, it is important to determine where, when, and how much toxic contamination is biologically available. One way to estimate how much contamination is accessible to organisms is to use a sampling method capable of screening for the bioavailable fraction. In Chapter 2, the ability to measure, evaluate and apportion contamination using semipermeable membrane passive organic sampling technology is demonstrated.

Originally developed as a 2-compartment model, the semipermeable membrane device (SPMD) mimics cellular membranes and lipid tissues. Cell membranes, which have pores of ~9.5 angstroms in diameter *(1)*, are mimicked by the low-density polyethylene (LDPE) tubing which has transient cavities of ~10 angstroms *(2)*. Triolein, or tri-oleic acid, a triglyceride (molecular formula: $C_{57}H_{104}O_6$), is inserted into the LDPE tubing to replicate lipid tissue of organisms and serve as the contaminant sink. Water concentrations of organic contaminants can be back-calculated from quantities accumulated in field deployed SPMDs. These were initially derived by performing laboratory uptake rate experiments with flow-through systems for target analytes and then applying these rates to the field deployed SPMD results. This is the approach we used for the study in Chapter 2. During this study the technology advanced and the use of performance/ permeability reference compounds (PRCs) became a more precise and accurate method of determining uptake rates *(3, 5, 6)*. PRCs are compounds of the same class and similar K_{ow} of the target analytes that will not be encountered in the deployment location. The most common selections are perdeuterated compounds spiked into the triolein before insertion into the SPMD, or, as developed by Booij *et al. (3)*, infused into the LDPE by soaking it in a spiked methanol solution. PRCs allow sampling rates to be calculated from the amount of PRC remaining after deployment and assuming uptake rates are equivalent to loss rates (see Table A2.5 for details).

The PRC approach presented two problems for our analytical methods. First, we used GC and HPLC without mass spectrometry so perdeuterated compounds could not be differentiated. Second, the spiked methanol approach was time consuming and solvent and labor intensive considering the number of samplers required for the field study. To address the first issue we chose a reference compounds not found during our initial (pre-PRC) sampling: dibenz(ah)anthracene. For the second issue, rather than soak the LDPE in spiked methanol, we fortified the tubing prior to heat sealing using a pipet to dispense PRCs in a small volume (100 µL) of solvent *(4)*.

Experiments by Booij *et al. (3)* suggest that the LDPE itself constituted a sufficient sink acting as both membrane and lipid fraction due to the tubing's thickness. In Anderson *et al. (4)*, we evaluated SPMDs and triolein-free, lay-flat polyethylene tubing samplers (LFTs) in side-by-side field trials and found minimal differences in performance. Removing the triolein from the sampler allowed substantial modification of the extraction method. We eliminated the use of dichloromethane, reduced labor and expense, saved time, and increased recoveries by skipping the gel-permeation chromatography and its associated solvent evaporation and transfers previously used to remove triolein. Ultimately, we advanced the science and technology of environmental passive sampling by producing a simpler, cheaper, "greener," device.

The SPMDs and LFTs used in our research accumulate contaminants over the duration of the deployment, usually two to three weeks. But a single sample from a single location in a river almost assuredly fails to represent the fluctuations present in natural systems seasonally or spatially. Extended exposures increase sampler target analyte concentrations and thus increase sensitivity and allow a time-integrated average to be calculated across the deployment duration. Multiple deployments and multiple locations then build a spatial and temporal picture of concentration and load fluctuations spanning seasons and years.

SPMDs and LFTs accumulate many organic compounds, but this work focuses on one class: polycyclic aromatic hydrocarbons (PAHs). PAHs are composed of carbon rings fused at two carbons and many have mutagenic and carcinogenic properties. Of particular interest are the 16 PAHs listed by the US EPA as priority pollutants (Figure 1.1). PAHs are created naturally and anthropogenically as a result of incomplete combustion of organic material (pyrogenic), through intense geologic pressure (petrogenic), and, in limited amounts, by certain organisms (biogenic). The relative abundance of the various PAH congeners varies by source and can result in a unique chemical profile or 'fingerprint.' Common sources of urban PAHs include manufactured gas plant coal tar, creosote, internal combustion engine emissions, and petroleum product leaks and spills. While this research is limited to PAHs, the passive sampling uptake principles would also affect other organic compounds with similar thermodynamic properties.

The severe liability component of the Comprehensive Environmental Response, Compensation and Liability Act, also known as Superfund, has driven research in apportioning contaminant sources. However, few studies have evaluated source apportionment using SPMDs *(7, 8)* or the effectiveness of remediation practices such as dredging *(9)*. Chapter 2 reports the results of applying established source apportionment techniques to SPMD data from multiple sources, pre- and post-remediation of two sites as well as background, thereby advancing the utility of SPMD technology for environmental forensics.

After characterizing the environmentally relevant dose, the next step is to determine if the dose could elicit a response. In Chapter 3, the refined sampler technology is applied as a biological surrogate for predicting potential ecological and human health risk endpoints of the study area. Established models provided methods to estimate impacts based on either water concentrations or mass:mass concentrations. The samplers also provided a way to proof the models by comparing the results to water quality criteria and guidance values. Measuring bioavailable concentrations with passive samplers and applying the results to ecological and human health assessments is a novel approach to evaluating the dose-response relationship in natural systems.

The Oregon State University's Department of Environmental & Molecular Toxicology's mission statement declares its emphasis on the "advancement and application of science and technology to raise environmental quality and human health to the highest attainable level." The research presented herein advances the technology of passive sampling through the application of forensic methods, refinement of the sampler, and advancement of this technology in evaluating remediation effectiveness. Applying this technology advances science by demonstrating the seasonal effects on contamination, the impacts of remediation techniques on pollutant bioavailability, and using existing models to recognize threats to environmental quality and human health.

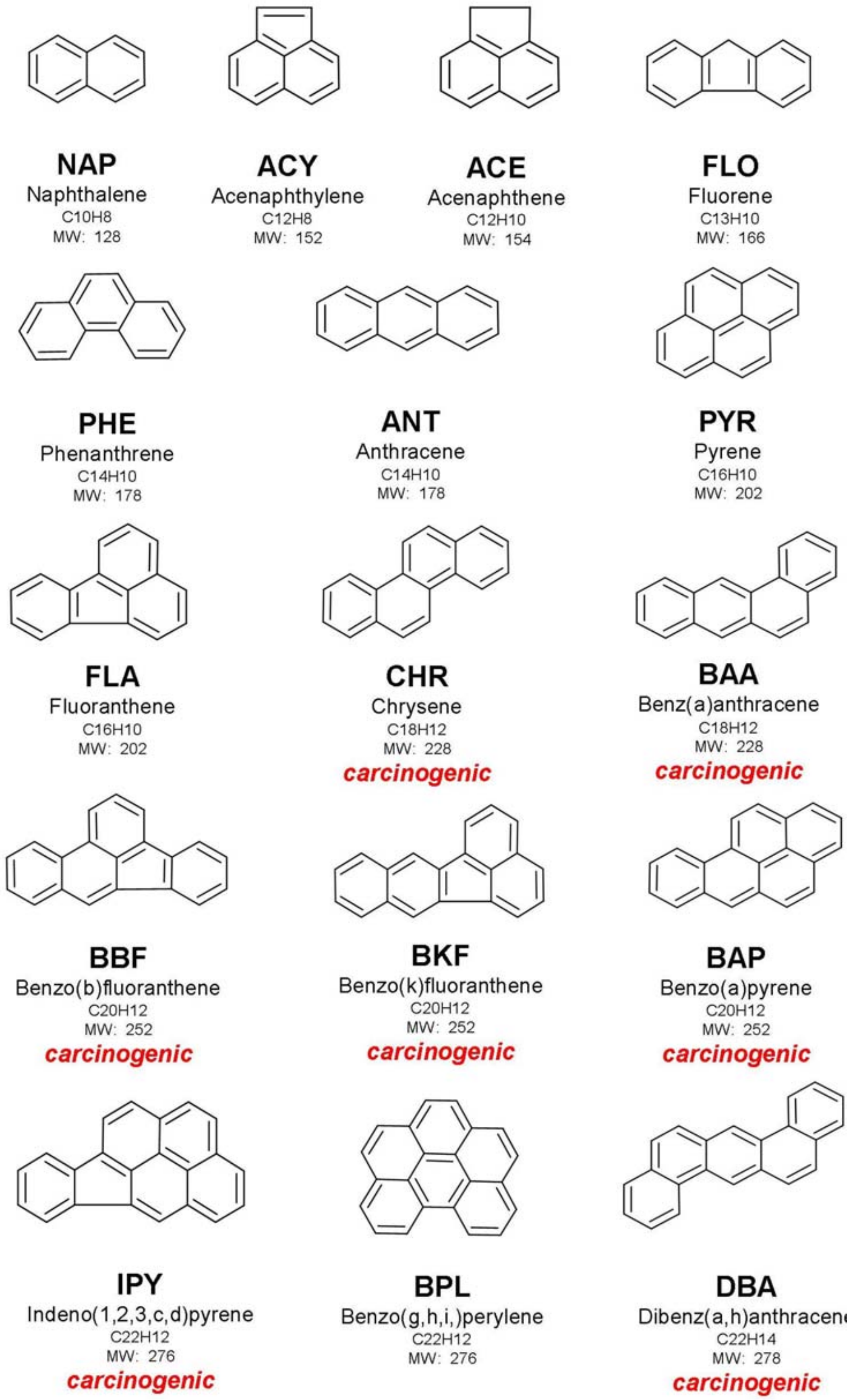

Figure 1.1 US EPA 16 Priority Pollutant PAHs

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Chapter 2 - Spatial and temporal variation of bioaccessible PAHs in an urban river undergoing Superfund remediation

2.1 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 included the Portland Harbor Superfund megasite (river miles, or RM, 3.5 to 9.2), a heavily industrialized stretch of the Willamette containing several PAH sources. These sources include coal tar at RM 6.3 west and an additional Superfund site, McCormick and Baxter, at RM 7 east consisting largely of creosote contamination. Remediation operations took place at both sites during this study. Additional potential sources of PAHs include combined sewer overflows, urban runoff, atmospheric deposition and petroleum product leaks and spills. Study results reveal increased urban bioaccessible PAH loading during wet seasons, successful capping of the McCormick and Baxter Superfund Site, increased bioavailable PAHs during remediation dredging operations, and the potential for using passive sampling devices for source apportionment.

2.2 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 bioaccessible 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 determine in highly impacted areas 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-aklylated, 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 site 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 m^3 of coal tar was removed from the GASCO site at river mile 6.3 west *(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 upriver and downriver bioaccessible PAH concentrations and loads differ significantly from the Superfund area? Do seasonal or heavy rains, or fluctuating river flows, affect concentrations, loads or their sources? Have recent remediation efforts cleaned up the worst areas? To more accurately assess risk to human and ecological health and gauge the effectiveness of Superfund cleanup operations, episodic effects and the spatial and temporal occurrence of PAH contamination must be known. The objectives of this study are to determine spatial and temporal variations of bioaccessible PP PAHs including the effects of precipitation. Additionally, we assessed the remediation of two PAH contaminated sites on the lower Willamette River and the ability of SPMDs to apportion PAH sources.

2.3 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 A1.1). 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) and on west and east sides of the river channel. Surrounding area land use consists of urban (residential and commercial – upriver sites), industrial (Superfund area), and undeveloped (downriver sites). This stretch of the Willamette contains PAH sources that include urban runoff from area drains, parking lots, combined sewer overflows (CSOs) and atmospheric deposition. Creosote and coal tar contaminated sites as well as petroleum industry operations are located within the Superfund area. During 2005 and 2006 SPMDs were located at RMs 7w and 8 only. 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 (Figure A1.2).

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 cm^2, contains 1 mL of ≥ 95% pure triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol) and has a total weight of 4.5 g.

2.3.1 Chemicals and solvents PAH standards (purities ≥ 99%) were obtained from ChemService, Inc. (West Chester, PA, USA). SPMDs were fortified with dibenz[a,h]anthracene as a performance/permeability reference compound during 2004-2006 deployments. 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, and indeno123(cd)pyrene (IPY). Cleanup and extraction solvents were pesticide or Optima® grade from Fisher Scientific (Fairlawn, NJ, USA).

2.3.2 Sample collection and extraction From 2002 to 2006 samplers were deployed in multiple 14 to 21 day events during the dry season of each year (July and/or August) through the beginning of the wet season (October and/or November). 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. Five SPMDs were loaded into a stainless steel cage at 10 sites (Figure A1.1) and suspended 3 meters above the river bottom with an anchor-cage-float system described elsewhere *(19)*. The use of performance and permeability reference compounds in SPMDs for calculating contaminant uptake has been recommended *(20)* but were used in our study only in the 2004-2006 sampling seasons. To maintain comparable data, temperature adjusted sampling rates from the literature *(21)* were used for all events (formula provided in Appendix 1).

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 (Figure A1.4). In addition, grab samples were taken 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)(Figure A1.5).

SPMD field cleanup and laboratory extraction were performed as previously described *(22)* 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.

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. 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.

2.4 Results and discussion

Our study addressed the bioaccessible priority pollutant PAH variation by concentration, daily load, congener ratios and profiles, and water chemistry. The results included 5 years of data in summer (dry) and fall (wet), defined by the precipitation and river flow as well as episodic events of high precipitation during the dry season. The wet season flow averaged > 300 m^3/s and precipitation averaged > 3 mm for the sampling event. Quality control resulted in duplicate sites average RSD equaling 15%, and target compounds in blanks were either non-detect or below levels of quantitation. Results are recovery corrected using method surrogates. Remediation events at RMs 7 east (e) and 6.3 west (w) were also evaluated and the potential role of passive sampling devices in source apportionment is demonstrated.

2.4.1 Spatial distribution of bioaccessible PAHs and water chemistry Analysis revealed, not surprisingly, the Superfund area 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 2.1 and Table 2.1**,** Kruskal-Wallis one-way analyses on ranks combined with Dunn's method of pairwise multiple comparison). Superfund sites were also higher in bioaccessible 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 Superfund area sites (Figure 2.1).

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, a former pesticide manufacturing facility site and organochlorine pesticide hot spot. PAH contamination may be from sites upriver that were not captured by east side RM 8 samplers or fill used to stabilize banks *(23)*, or some other source of PAHs. The GASCO site at RM 6.3w was a significant source of PAHs and, due to tidal influence, appears to have temporarily contributed to upriver contamination at RM 7w as discussed later in this article.

The only spatial differences in water chemistry parameters were specific conductivity at the downriver site and higher ORP at upriver sites than Superfund sites (187 vs. 155 mV, $n = 94$, $P = 0.015$, Kruskal-Wallis one-way analysis on ranks). The highest ORP measurements were at RM 18.5, the confluence of Johnson Creek, a large urban watershed, with the Willamette. Significant differences in parameters that might affect the freely dissolved fraction of PAHs *(24)* occurred in TSS (upriver 3.4 mg/L, Superfund 7.4, downriver 7.9, degrees of freedom = 10, $P < 0.001$, two-way ANOVA with Holm-Sidak pairwise comparison) and TDS (upriver 78 mg/L, Superfund 85, downriver 107, P = 0.004). However, an increase in solids would be expected to lower freely dissolved, high molecular weight, high K_{ow} compounds *(24, 25)* and this was not observed. Local soil and sediment remediation activities may have disturbed sediment and allowed the dissolution of particulate-bound contamination; a situation SPMDs are uniquely suited to detect. No significant spatial differences in other water chemistry parameters were found (Tables A1.4 and A1.5).

2.4.2 Temporal variation of bioaccessible PAHs 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. 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. 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 ± 136 m^3/s, dry = 262 ± 20 m^3/s). These data reflect not only increased deposition, but also an increased bioaccessible PAH loading during the wet season; however, neither low molecular weight (LMW) nor high molecular weight (HMW) PAHs differed significantly between seasons as observed by Motelay-Massei *et al. (4)*.

As expected if increased precipitation flushed urban PAHs and particulates in to the river, TOC was significantly higher in the wet season (2.8 vs.1.6 mg/L, t-test, n = 8, $\alpha = 0.05$, P = 0.03). DOC also averaged higher in the wet season but was not statistically significant. There were not enough TDS and TSS samples to make a comparison between seasons. Specific conductivity dropped in the urban area during the wet season as did pH and nitrate while ammonium showed no change and dissolved oxygen increased as expected with decreasing water temperature (Table A1.4). Together with flow and precipitation, these data demonstrate that the seasonal delineation is not arbitrary but consistent with expected seasonal changes.

Unlike the upriver sites, the Portland Harbor Superfund megasite, excluding RM 7w, did not have significantly different ΣPAH loads or concentrations between seasons. Upriver wet season PAHs were likely due to non-point sources such as urban runoff and atmospheric deposition *(4, 12, 13, 26, 27)* which may include an increased biomass burning for 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 2.1). 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 2.1). 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 ΣPAH 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. (29)* 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; for example, PAH sources such as creosote, coal tar, or asphalt, a standard local practice *(23)*.

Temporal variation in water chemistry at Superfund and downriver sites showed some similarities with upriver sites. Like the upriver sites, they experienced lower wet season specific conductivity and higher dissolved oxygen, but no significant difference in other parameters. No differences were statistically distinguishable for RM 7w.

2.4.3 High rain events Brown and Peake *(12)* and Gasperi *et al. (27)* found that increased precipitation or related activities like street cleaning in urban areas can increase PAH concentrations and loads in runoff. Because SPMDs were deployed for periods ranging from 14 to 21 days, time-integration necessarily assumes a constant concentration; 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). Additionally, while flow during these events increased significantly from a dry season/no rain median of 249 to 278 m^3/sec (Mann-Whitney rank sum, n = 27, $P < 0.001$), this is still significantly lower than the wet season median of 335 m^3/sec (n = 28, $P < 0.001$). TOC, DOC, TSS, and TDS grab samples did not show significant differences between dry season and rain event samples, however, sample size was low (n = 5). While high rain event concentrations and loads during the dry season was not significantly higher than the wet season, the load was significantly different than dry season/no rain medians due to the river flow. That wet season concentrations at upriver sites did not significantly differ from the dry season, but loads did is explained by the dilution effects of increased river flow combined with the deposition of accumulated urban PAHs *(12, 27)*.

2.4.4 McCormick and Baxter Superfund Site remediation Vrana *et al. (8)* and Cornelissen *et al. (28)* demonstrated the use of passive samplers to evaluate contaminant diffusion from sediments into overlying water. 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 bioaccessible PAH concentrations from an average of 440 ± 422 ng/L in 2003 to 8 ± 3 ng/L in 2005 (Table 2.2). 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 (Figure A1.2). Samplers positioned near observed seeps had the highest ΣPAH concentrations and loads in 2003, but not in 2005 which were below upriver levels demonstrating remediation success *(30)*. 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 successfully accumulated the post-cap low levels of freely dissolved toxic contamination.

2.4.5 RM 7 west during GASCO remediation Using aerobic bioslurry experiments, Ghosh *et al. (31)* found PAHs associated with coal tar pitch were 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 remediation efforts at RM 6.3w from August to October of 2005 removed >11,500 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 7w 1000 m upstream during this activity have significantly higher mean bioaccessible concentrations (2.9 ± 0.5 µg/L) than pre- and post-remediation samples (1.0 ± 1.1 µg/L, t-test, n = 18, P = 0.002). Samples deployed during tar remediation also had significantly higher mean bioaccessible 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 2.2). Coal tar PAHs may be less bioaccessible *in-situ (7)*, but it is clear that dredging readily desorbed PAHs and greatly increased the bioaccessibility 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 also 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 *(29)*.

2.4.6 Source apportionment using ratios Because SPMDs accumulate compounds over the course of days or weeks they offer more discrete sourcing information than sediments and increased sensitivity over water 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)*. Luellen and Shea *(32)* 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. SPMD FLA/PYR ratios ranged 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 differed 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 2.1) suggests an increased pyrogenic input not found in the dry season. Atmospheric PAHs are 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 2.1). 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 PAH ratios differ significantly (Table 2.1, $P < 0.001$) 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 ΣPAH 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 did not vary significantly by season nor before or after the remediation events at RM 7e and RM 6.3w. However, median FLA/PYR was 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 were 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)*.

2.4.7 Source apportionment using PCA 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 2.2). 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 2.2). 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 2.2). 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 2.2 and Table A1.2). 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.

2.4.8 Threats to aquatic life and human health There are no US EPA Water Quality Criteria 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 (Table A1.1). 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 (Figure A1.5).

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.

2.5 Acknowledgments

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2.6 Supporting information

Supporting figures and tables including area maps and site descriptions, additional data, congener profiles, and PCA graphs are available in Appendix 1.

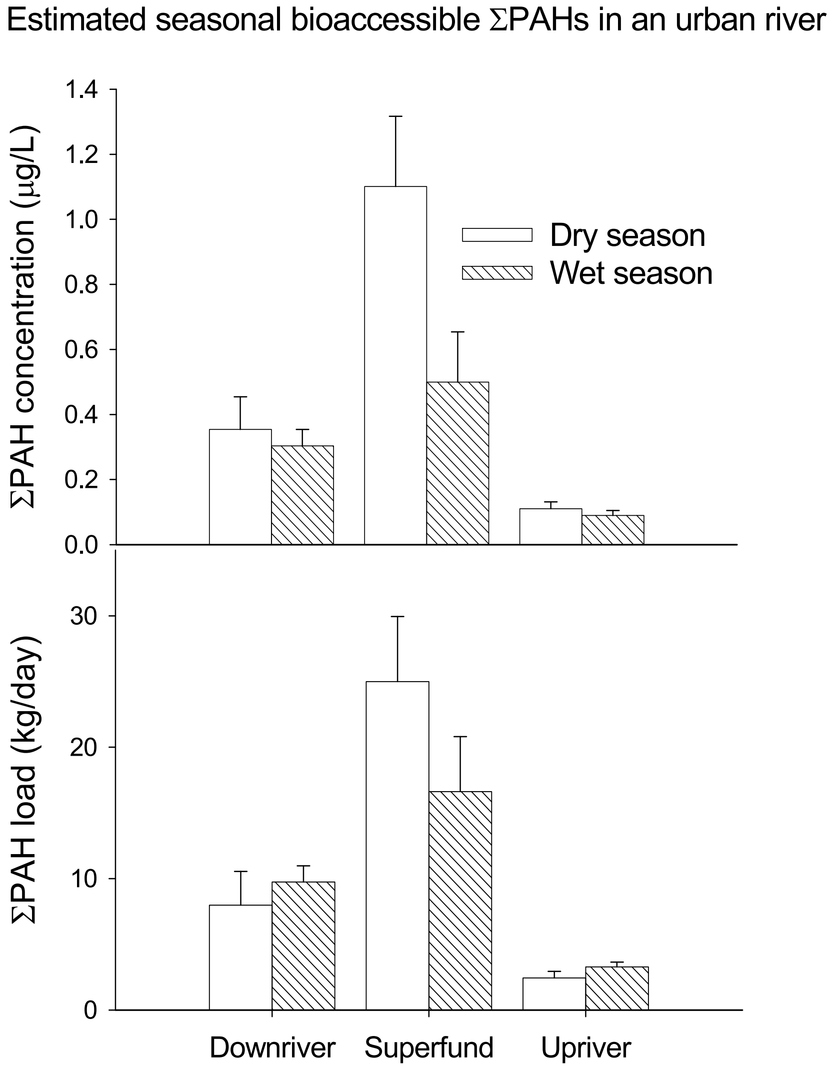

Figure 2.1 SPMD estimated PAH loads and concentrations by season and area

The Superfund megasite estimated bioaccessible ΣPAH 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. Sites include 1 downriver, 4 Superfund, and 5 upriver.

Table 2.1 Spatial and temporal variation of median ΣPAH estimates by SPMD in an urban river[1]

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	0.3	2.8	0.005*	44	0.3	0.93	0.004*
dry	27	51		1.1		22		0.74	
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	0.008*	9.7	0.2	113	0.1	1.03	0.32
dry	28	658		15		140		0.98	
w/o RM 7 west	33	273		7.5		101		0.97	
wet	15	207	0.1	7.5	0.8	76	0.5	1.02	0.7
dry	18	374		7.6		112		0.95	
RM 7 east									
pre-cap	13	338	<0.001*	7.6	<0.001*	32	<0.001*	1.23	<0.001*
post-cap	16	7		0.2		0.6		0.76	
RM 7 west	18	1170		26		262		1.02	
wet	8	331	0.02*	13	0.04*	212	0.1	1.07	0.2
dry	10	1867		39		528		1.02	
Downriver	16	269		7.4		53		0.89	
wet	6	270	0.8	9.3	0.1	57	0.9	0.99	0.1
dry	10	259		6.1		50		0.78	

[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 $\alpha = 0.05$.

Table 2.2 Effectiveness of McCormick and Baxter and GASCO remediation activities

Site and Activity	Season	Concentration average ±1SD (ng/L) N	BAA	BAP	Carcinogenic	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

[a] These number are Water Quality Triggers and only apply to River Mile 6.3 west during tar removal activities.
[b] From the McCormick and Baxter second 5-year review*(30)*.

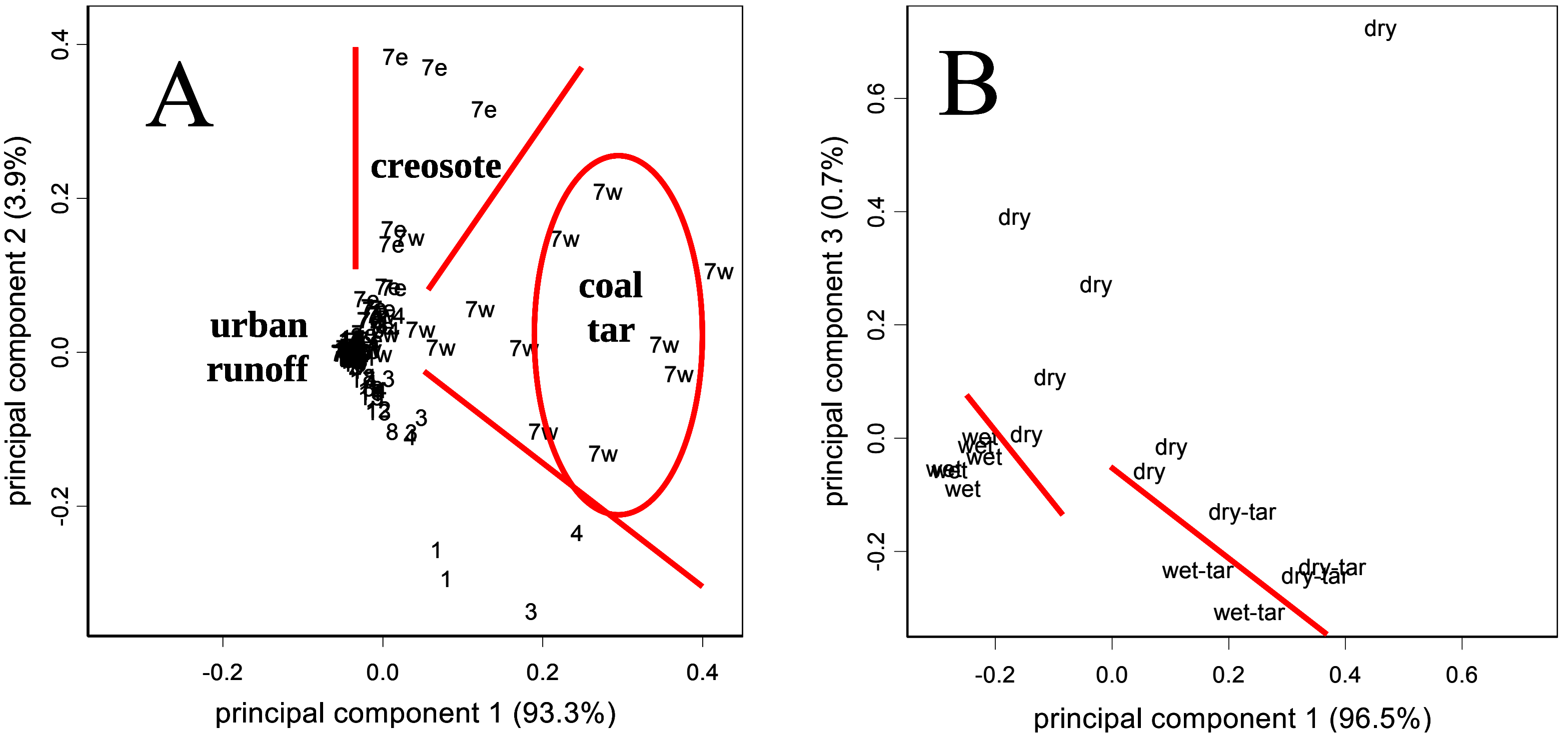

Figure 2.2 PCA plots of spatial and temporal distribution of all sites (A) and RM 7 west seasonal variation (B) *Panel A.* Spatial and temporal distribution of all sites using congener profiles comprised of 14 PAHs labeled by river mile (n = 141). For RM 7 locations, e and w denote east and west side 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.

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Chapter 3 - Using passive sampling devices as biological surrogates in ecological and human health risk models.

3.1 Abstract

Passive sampling devices constructed of polyethylene lay-flat tubing (LFTs) mimic biomembranes and lipid tissues and measure the bioaccessible fraction of lipophilic contaminants. We used LFTs to measure polycyclic aromatic hydrocarbons (PAHs) within the first 18.5 miles of the Willamette River including the Portland Harbor Superfund megasite. Basing our approach on an existing public health assessment (PHA) for this area, we substituted the mass-to-mass concentrations of these LFTs for fish tissue concentrations normally used to calculate health risks from consumption. Unlike the original PHA, our study area included not only the superfund megasite but also sites upriver and downriver, for three years and during three seasons. The PHA could not evaluate PAHs due to insufficient data, but LFT results reveal no unacceptable risk for non-cancer endpoints; however, all sites show an unacceptable risk level for cancer regardless of season. Estimated cancer risk varied by several orders of magnitude based on location within the Superfund megasite and season, especially at sites near coal tar contamination. These sites demonstrated the highest risk, particularly during the dry season and during remediation activities. Incorporating LFT data into health assessments can help fill data gaps to evaluate potential contaminant exposures by providing specific spatial and temporal data.

3.2 Introduction

Urban rivers that are used by local residents for recreational purposes such as boating, sport and subsistence fishing often contain highly polluted areas. In an attempt to inform the public about the relative risks of these activities, public health assessments (PHAs) provide information about potential exposures and the likelihood that those exposures could lead to adverse health effects. A PHA develops an estimated human exposure dose based on site environmental and contaminant data as well as existing regulatory standards and using the assessors' professional judgment. Exposure due to consumption is usually based on tissue contaminant data from harvested resident fish and/or shellfish, however, tissue concentrations vary substantially depending on species, age, sex, health, and range, resulting in significant sample variation and little specific spatial or temporal information *(1)*. Several studies have highlighted the potential spatial and temporal variation of contamination and exposure *(2, 3)* and others have called for their consideration in risk assessments *(4)*. To address these issues and reduce variation, caged fish or shellfish (biomonitoring organisms or BMOs) may be strategically deployed to determine bioavailable contaminant concentrations based on bioaccumulation factors (BAFs) *(1, 5)*. However, as observed by Burkhard *et al. (5)* BAFs are site- and species- specific and thus require field data or modeling to compare across studies.

Deploying BMOs insures that only the bioavailable fraction is collected; an issue that has been shown to significantly affect risk *(1, 6, 7)*. The development of passive sampling devices (PSDs) such as semipermeable membrane devices (SPMDs) which simulate biological membranes and lipid tissue and thus sample only the bioaccessible fraction *(1)* provides a standardized approach. Huckins *et al. (1)* reviewed over 30 studies with side-by-side SPMD to BMO comparisons and found good correlations with finfish, though fewer studies have investigated PAHs *(8-13)*. Of these, Baussant *et al. (8)* found caged mussels and SPMDs to accumulate similar PAH profiles in a laboratory study. However, in field exposures Boehm *et al. (9)* and Peven *et al. (10)* found mussels accumulate more high molecular weight PAHs than SPMDs. The Baussant *et al. (8)* study also included caged finfish (turbot, *Scophthalmus maximus*) in which lower molecular weight PAHs predominated. Using caged crucian carp (*Carassius carassius*) tissue concentrations, Ke *et al. (13)* found SPMDs sequestered higher concentrations of PAHs overall. Verweij *et al. (11)* significantly correlated SPMD PAH concentrations to carp biliary metabolites, considered a better indication of finfish PAH exposure than tissue concentrations *(14, 15)*. Biliary PAH metabolites may better reflect an organism's exposure; however, because they do not reflect tissue concentrations they do not translate to human health risk from consumption. Filets, on the other hand, may not accurately reflect whole fish concentrations or exposure. While these studies demonstrate that PSD concentrations can be correlated to organism exposure, they do not link the PSD concentrations to human or ecological health risk. Certain PSDs reflect not only exposure but also potential tissue concentrations and provide a standard from which a risk assessor may qualify health hazards.

Recent lab and field trials have resulted in simpler, cheaper versions of SPMDs *(16, 17)*. Made of polyethylene lay-flat tubing (LFT) without triolein, LFTs offer numerous advantages over BMOs: simplicity, low cost, fast and minimal extraction procedure, no metabolic activity and no organisms are destroyed. LFTs could be used to determine both water concentration as well as potential health effects from consumption. And though species, age, sex, health, and range affect concentrations in organisms, all accumulate contaminants from water across their biological membranes *(1)*. And unlike BMOs that determine organism-specific chemical concentrations, LFTs spiked with performance reference compounds (PRCs), provide chemical-specific calibrations of time-integrated, bioavailable concentrations for the deployment duration that are standardized across studies *(1, 16, 18)*.

LFTs are particularly useful in areas where point sources are significant contributors to contamination and where seasonal fluctuations in contaminant concentrations are suspected. The Portland Harbor Superfund megasite on the Willamette River in Portland, Oregon (river miles, or RM, 3.5 to 9.2) is a heavily industrialized area containing several PAH point sources including coal tar at RM 6.3 west and an additional remediated former creosoting plant and Superfund site, McCormick and Baxter, at RM 7 east. Additional sources of PAHs in the lower Willamette include combined sewer overflows, urban runoff, atmospheric deposition and petroleum product leaks and spills. The lower Willamette experiences significant seasonal flow and precipitation fluctuations and is an important resource for local sport and subsistence fisherman. Of 39 species of fish inhabiting this area, eight constitute the most likely to be caught and consumed, along with freshwater mussels and crayfish *(19)*. The difficulty in harvesting numerous species across many miles and several seasons makes the lower Willamette a good model to evaluate using LFTs and consumption guidelines to generate a baseline or standard concerning potential exposures in an urban river. The purpose of this study is to evaluate the use of LFT data in a public health assessment to determine if LFTs effectively serve as a screening tool and help communicate potential ecological and human health risks. To achieve this, spatial and temporal distribution of LFT measured PAH concentrations in the lower Willamette River are evaluated using ecological and human health risk assessment models.

3.3 Materials and methods

The study area consists of the first 18.5 miles of the Willamette River. Samplers were placed from river miles (RM) 1 to 18.5 (Figure A2.1) from 2004 to 2006. The locations on west and east sides of the river channel (noted by w and e, respectively) include points upriver (at RMs 18.5e, 17e, 15.5e, 13w, and 12e), downriver (RM 1e) and within the Portland Harbor Superfund megasite (RMs 3.5e, 4w, 5w, 6.5w, 7w, 7e and 8e). Duplicate samplers were placed at RMs 7w and 8e. Land use in the surrounding areas consists of urban (residential and commercial – upriver sites), industrial (Superfund area), and undeveloped/agricultural (downriver site). The stretch of the Willamette upriver from the Portland Harbor Superfund area contains PAH sources that include urban runoff from area drains, parking lots, and combined sewer overflows. Within the Superfund area, however, there are known PAH point sources including creosote and coal tar contaminated sites (RMs 7e and 6.3w, respectively) as well as petroleum industry operations in addition to urban runoff and overflows. LFT samplers were constructed and fortified with PRCs using methods described in Anderson *et al. (17)*. Briefly, additive-free, 2.7 cm wide, low-density polyethylene membrane (Barefoot) was purchased from Brentwood Plastic, Inc (St. Louis, MO, USA), cleaned with hexanes and cut into 100cm strips, fortified with dibenz(ah)anthracene as a PRC and heat sealed.

3.3.1 Chemicals and solvents PAH (purities ≥ 99%) standards were obtained from ChemService, Inc. (West Chester, PA, USA). All cleanup and extraction solvents were pesticide or Optima® grade from Fisher Scientific (Fairlawn, NJ, 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 indeno123(cd)pyrene (IPY).

3.3.2 Sample collection and extraction From 2004 to 2006 LFT samplers were deployed in multiple 21 day events during July or August (dry season) through October or November (wet season). This period represents the transition from the lowest precipitation and flows of the year to relatively high precipitation and flows. In 2006 two sampling events were added from May through June, the transition from high to low flow. Stainless steel cages were loaded with five LFTs and suspended 3 meters above the river bottom at each site with an anchor-cage-float system described elsewhere *(20)*.

Water chemistry data including temperature, pH, specific conductivity, and oxidative-reductive potential (ORP) were collected during sampler deployment and retrieval using a YSI® sonde. LFT field cleanup and laboratory extraction were performed as previously described *(21)*. Quality control consisted of duplicate samplers, field blanks, trip blanks and field cleanup blanks. Laboratory quality control included reagent blanks, high and low concentration fortifications, and unexposed fortified LFTs.

After extraction, samples were solvent exchanged into acetonitrile and analyzed by HPLC with diode-array and fluorescence detectors. Diode-array 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. Data analysis was performed using Microsoft Excel® 2003, SigmaStat® for t-tests and rank sum tests, and SigmaPlot® for graphing.

3.3.3 Calculations and models Water concentrations were calculated with equations provided in Huckins *et al. (1)* with a brief summary provided in Appendix 2. LFT mass:mass concentrations were calculated based on average LFT mass and instrument reported data.

Exposures and human health endpoints were calculated using the approach in the Portland Harbor PHA *(19)*. The LFT mass concentrations were substituted for the fish tissue contaminant concentrations while all other variables were as stated in the PHA. The non-cancer endpoint used the LFT mass concentrations of the lower molecular weight PAHs not recognized as carcinogens by the EPA. The cancer endpoint used the LFT mass concentrations of the carcinogenic PAHs (list). The equation variables and default values are the same as those used in the ATSDR PHA *(19)* and are summarized in Tables A2.1 and A2.2. Equation 3.1 was used to calculate exposure where C is the mass concentration (LFT substituted for fish), CF is a conversion factor, EF and ED are exposure frequency and duration, respectively, BW is body weight and AT is the averaging time.

$$Exposure = \frac{C \times CF \times IR \times EF \times ED}{BW \times AT} \qquad \text{Eq. 3.1}$$

The ingestion rate (IR) is from the Portland Harbor PHA that evaluated local sport and subsistence angling populations. These rates may not apply to other areas.

For the non-cancer endpoint each contaminant's exposure was divided by a reference dose (RfD) or minimum risk level (MRL) and summed to give a hazard quotient (Equation 3.2). A ΣHQ that exceeds one is considered an unacceptable risk.

$$\Sigma Hazard\ Quotient = \frac{Exposure}{Rfd\ or\ MRL} \qquad \text{Eq. 3.2}$$

To determine excess cancer risk the sum of the contaminants exposure was multiplied by the slope factors (Equation 3.3). Slope factors for carcinogenic PAHs were normalized to benzo(a)pyrene. An excess cancer risk greater than one in one million ($1x10^{-6}$) was considered unacceptable.

$$ExcessCancerRisk = Exposure \times SlopeFactor \qquad \text{Eq. 3.3}$$

Potential ecological risk was estimated by applying an approach developed by Neff *et al. (22)* for sediment PAHs. This model was chosen because it estimates toxicity of PAH assemblages based on the dissolved concentration. For each compound a hazard quotient is determined based on the compound concentration in solution (originally, pore water, but calculated water column concentration in this study) divided by the toxicity value (Table A2.3) (Equation 3.4). The HQs of each compound are summed for a hazard index (HI) (Equation 3.5). A hazard index greater than 1 represents PAH concentrations with unacceptable toxicity.

$$HQ = \frac{[PAH]_{LFT}}{toxicity\ value} \qquad \text{Eq. 3.4}$$

$$HI = \Sigma HQ \qquad \text{Eq. 3.5}$$

The model assumes PAH toxicities are additive and the chronic toxicity values equal the acute values divided by five.

3.4 Results and discussion

Our study addresses the bioaccessible priority pollutant PAH variation by PSD estimated concentration, ecological hazard quotients, non-cancer hazard quotients, excess cancer risk. The results include 3 years of data in summer (dry) and fall (wet), as well as a two spring (wet) deployments defined by river flow. The wet season is defined as flow > 300 m^3/s;

median flows were 494 m^3/s for wet and 246 m^3/s for dry (n= 111, P<0.001). Results for water chemistry parameters support the seasonal delineation. The dry season had higher temperature (22 vs. 16 °C), higher specific conductivity (0.1 vs. 0.08 mS/cm), lower ORP (139 vs. 196mV, all n = 17, P <0.05), but no difference in pH (7.4, P=0.9).

A coal tar contaminated sediment remediation project at RM 6.3w was also evaluated. Quality control resulted in duplicate sites average RSD equaling 29%. When naphthalene, the compound with the highest amount of variability, is removed from the ΣPAH concentrations, RSD drops to 19%. Target compounds in blanks were either non-detect or below levels of quantitation. Results are recovery corrected. An assumption concerning the risk models in this study is that the LFTs are at equilibrium. Huckins *et al. (1)* (page 162) stress that partition-coefficient similarities with BMOs may only be assessed when both the sampler and the BMO have attained equilibrium (i.e., no longer in a linear uptake phase). However, this study attempts to determine the suitability of LFTs in public health assessment estimates, not correlations with BMOs. If LFTs are not at equilibrium then they underestimate mass concentrations, exposures and health endpoints. The lack of equilibrium does not affect reported water concentrations as the calculations use PRCs to account for this. Because LFTs were positioned 3 meters above the sediment, concentrations may best reflect exposure of organisms residing in the water column. Benthic organisms such as crayfish and mussels may be exposed to higher concentrations due to higher sediment PAH concentrations.

3.4.1 Model validation Each of the risk models was evaluated by using the US EPA water quality criteria (WQC) or guidance values as inputs. When the carcinogenic PAH WQC for human health for the consumption of water + organism and organism only (0.0038 μg/L and 0.018 μg/L, respectively) are applied to the cancer model the results are well below the 1x10-6 excess cancers threshold for average and high consumption (Table A2.4). The human health cancer model is based on slope factors with equivalencies to BAP and considered additive. The concentration of BAP equivalent PAHs required to exceed the excess cancer threshold is 1.3 μg/L for average consumption and 16 μg/L for high.

The human health non-cancer assessment models the effects of low molecular weight PAHs of which only three have WQC for consumption: ACE, FLO, and PYR (Table A2.4). At the highest allowable concentration, each compound still resulted in hazard quotients at least an order of magnitude below the non-cancer risk threshold of one. If all three compounds were at the maximum allowable concentration (consumption of organism only), then the non-cancer high consumption estimate would receive a hazard index of 0.3, still one-third of the unacceptable ΣHQ. Also considered additive in toxicity by the model, but with varying WQC concentrations, a threshold ΣPAH concentration could not be determined.

The ecological risk model developed by Neff *et al.(22)* was evaluated using Oregon water quality guidance values for protection of freshwater aquatic organisms for three PAHs: NAP, ACE, and FLA. The acute concentration limits for ACE and FLA both cause the model acute hazard quotients to exceed one (Table A2.4). The ACE chronic value also exceeds one for the model's chronic HQ (FLA does not have a chronic guidance value). Of note are the extremes to which FLA values exceed the threshold. An acute hazard quotient of 72 and a chronic HQ of 362 suggest that either the water quality guidance values are insufficient to protect aquatic organisms or the model substantially overestimates toxicity for dissolved PAHs as molecular weight increases, or some combination thereof. These results should be considered when evaluating the model outputs.

3.4.2 Spatial variations of concentrations LFTs are established for determining bioavailable organic contaminant water concentrations *(16, 17)*. A Kruskal-Wallis one-way analysis on ranks of 110 observations reveals the Superfund median ΣPAH concentrations of 11.4 ng/L to be significantly higher than upriver sites (3.1 ng/L, $P<0.001$), but not downriver sites (6.5 ng/L). The upriver area does not exhibit significant variation between sites, but Superfund sites do. None of the sites averages are in excess of the human health WQC for consumption of water + organism or organism only (3.8 ng/L and 18 ng/L, respectively) for the carcinogenic PAHs, though some sites did exceed the threshold seasonally or during specific sampling events (Figure 3.1).

Stout *et al. (23)* note that storm water contributes the most to sediment PAHs over time, and Brown and Peake *(2)* as well as Gasperi *et al. (24)* found that water flushing of urban streets creates a PAH contamination spike. Significant urban runoff outfalls are located at RM 18.5, RM 12 and between samplers at RM 7w and RM 6.5w. Neither RM 18.5 nor RM 12 are significantly higher in PAH concentrations than other upriver sites ($P = 0.2$). Samplers at RMs 7w, 6.5w and 5w are consistently the most contaminated sites, while sites downriver decrease in concentration and upriver Superfund samplers at RM 7e and 8e are consistently lower in concentration (Figure 3.1).

Cornelissen *et al. (25)* and Vrana *et al. (26)* have demonstrated that PSDs effectively sample contamination released from sediment to the overlying water column; however, highly contaminated sediments do not necessarily correspond to high exposure in the water column *(11)*. The outfalls at RMs 18.5 and 12 do not vary from other upriver sites, but RMs 7w and 6.5 (sites that bracket an outfall) are the highest in the Superfund area; therefore, either that outfall delivers an inordinate amount of PAHs compared to others, or sediment contamination is seeping into the water column. Known coal tar sediment contamination at RM 6.3w could explain the concentrations, however, after removal of most of the contamination in 2005, 2006 PAH concentrations at these sites remain high.

The site downriver from the Superfund megasite, RM 1, is not significantly different in concentration from the Superfund sites. While the Portland Harbor PHA only sampled within the Portland Harbor Superfund sites, our data demonstrate that the downriver site has similar concentrations and could pose similar health risks.

3.4.3 Spatial variations of ecological and human health risk Rather than calculate back from LFT water concentrations to mass and introduce unnecessary complexity and potential uncertainty, LFT concentrations are based on the mass of contaminant collected versus the mass of the sampler. This mass:mass concentration treats the LFT as a direct biological surrogate and represents the amount of contaminant an organism would be exposed to through equilibrium partitioning and without metabolism. All areas exceed the established threshold of one excess cancer risk in 1,000,000 (1×10^{-6}) although none of the sites average above the 3.8 ng/L EPA water quality criteria for consumption of water and organism. Excess cancers at the Superfund megasite and RM1 downriver (1.3×10^{-5} and 1.7×10^{-5}, average consumption, respectively) were significantly higher than upriver sites (4.5×10^{-6}, $n = 111$, $P<0.001$). Within the Superfund area there can be five times greater risk between banks (RMs 7e and 7w). Non-cancer risk by PAHs was also higher at Superfund and downriver sites than urban areas ($P<0.001$) with RMs 7w, 6.5w, and 5w exhibiting the highest hazard quotients, though all were below one by more than two orders of magnitude.

Concerning ecological health, no NAP, ACE, and FLA concentrations exceeded freshwater water quality guidance values. No sites exceeded the Neff *et al. (22)* toxicity model to LFT concentrations of freely dissolved water column PAHs, an acute or chronic hazard index of one. The Superfund megasite experienced the highest average hazard indices; RM 7w and RM5 had the highest indices recorded (5.6×10^{-3} and 2.0×10^{-3}, respectively).

3.4.4 Temporal variations of concentrations and risk Brown and Peake *(2)* and Ko *et al.* *(3)* have observed higher PAH concentrations with increasing seasonal precipitation and flows and though no seasonal difference in concentrations presented in upriver sites, wet season ΣPAH loads were significantly higher (231 g/day wet, 60 g/day dry, n = 37, P = 0.01). However, both upriver and Superfund sites experienced significantly higher concentrations of carcinogenic PAHs but during the dry season (Table 3.1). The decreased upriver wet season carcinogenic PAH concentrations are probably due to dilution because there is no difference in loads between seasons (10.3 and 10.0 g/day, wet and dry, respectively, n = 37, P = 0.8). Motelay-Massei *et al.(27)* found that cool temperatures and increased precipitation increased the vapor phase fraction and atmospheric deposition of lower molecular weight PAHs which would explain the higher wet season PAH loads in this study.

The Superfund megasite has dry season carcinogenic PAH concentrations more than seven times higher than the wet season (2.3 vs. 0.31 ng/L, dry and wet respectively, n = 64, P<0.001) but no significant difference in loads (499 g/day dry vs. 359 g/day wet, P= 0.8). Eliminating the outlier samples taken during tar remediation, the area between RM 7w and 6.5w appears to drive this difference in the dry season with ΣPAH loads of 671 g/day versus the wet season 315, however, this is not significant (n = 16, P=0.19). Seasonal loads at RM 7e and 8e do not vary significantly but are lower (204 g/day dry and 228 g/day wet, n=22, P= 0.3) and downriver sampler concentrations decrease from the peaks at RM 6.5 and 7w (Figure 3.1). Lower concentrations at RM 7e and 8 do not preclude an upriver west bank source for RM 7w contamination. Given the difference between seasonal concentrations and loads and their lack of similarity to RMs 7e and 8, dilution is unlikely and contaminant diffusion from sediments into overlying water is probably responsible for high concentrations and loads in samplers at RMs 7w and 6.5 *(25, 26)*.

Though upriver sites experienced a significant increase in carcinogenic PAH concentrations during the dry season and increased lower molecular weight PAH loading in the wet season, these did not translate into significantly different cancer risks (Table 3.1). The increased PAH concentrations in the Superfund area did result in significantly elevated dry season risk. Both non-cancer HQs increased (P=0.004) as did excess cancers (P<0.001), however the non-cancer HQs remained below unacceptable risk levels (Table 3.2). The cancer model predicts almost four times as many cancers from dry season concentrations in the Superfund area compared to wet season. But at RM 7w the excess cancer risk from average consumption of LFT measured mass concentrations is a seven-fold increase during the dry season from 7.8×10^{-6} to 6.0×10^{-5} ($n = 18$, $P = 0.005$). Seasonal information could be useful to public health officials when constructing a health assessment or determining where to post warning signs.

While no sites exceeded the ecological health model hazard index of one, significant differences in risk between seasons were observed, but only in the Superfund area. Excluding sample events during tar remediation, Superfund wet season acute and chronic HIs are 1.8×10^{-4} and 9.1×10^{-4}, respectively while dry season HIs are significantly higher: 5.9×10^{-4} and 2.9×10^{-3} ($n=45$, $P<0.001$). An ANOVA finds sites at RM 7w and downriver significantly higher than RMs 7e and 8 ($n=23$, $P = 0.02$) during the dry season. RM 6.5 dry season HIs are the highest non-tar events recorded (1.7×10^{-3} and 8.7×10^{-3}, acute and chronic, respectively, $n=23$) and take place only in 2006 after remediation. Remediation at RM 6.3 of coal tar contamination removed significant quantities; however the area remains a higher risk than surrounding areas, particularly in the dry season. The contamination may be from within riverbank sediments and higher wet season flows could inhibit groundwater movement into the river due to hydraulic pressure and bank storage.

3.4.5 Effects of remediation activities While remediation of contaminated sites is desirable, few studies have investigated the effectiveness of dredging as a contamination removal method *(28)*. Dredging of a MGP coal tar contaminated site at RM 6.3w removed more than 11,500 m^3 of submerged tar contamination from August to October 2005. Previous studies had reported varying bioavailability for MGP coal tar PAHs *(6, 7)* and this operation provided an opportunity to evaluate the effects of dredging on coal tar PAH bioavailability.

Using *Hyalella azteca* assays, Kreitinger *et al.(7)* demonstrated that MGP sediment PAHs were much less bioavailable than expected. However, Ghosh *et al.(6)* found coal tar pitch associated PAHs released more readily than those bound to carbonaceous coal in aerobic bioslurry experiments. Contaminant desorption upon sediment disturbance is likely regardless as Boehm *et al. (9)* found that simply digging holes in marine sediments to position BMOs and SPMDs resulted in higher PAH concentrations than sites where holes were not dug. Because of tidal influence by the Columbia River on the lower Willamette, uncontained contamination can be pushed upriver. LFT samplers downstream at RM 5w and upstream at RM 7w during this period accumulated significantly elevated ΣPAH and carcinogenic PAH concentrations (Table 3.1). September 2005 samples, the middle of the dredging activity, from RM 7w down to RM 1 are the highest concentrations of ΣPAHs and carcinogenic PAHs recorded during this study (Figure 3.1). The median bioavailable ΣPAH water concentration pre- and post-tar removal is significantly lower (16 ng/L) than the tar removal median (101 ng/L, n=28, $P<0.001$). Bioavailable carcinogenic PAHs also increased from a median 0.9 ng/L pre- and post-tar to 3.7 ng/L during the removal ($P<0.004$). The September 2005 LFT carcinogenic PAHs at RMs 7w and 5 were the highest observed during this study at 71 ng/L and 20ng/L, respectively. At RM 5, CHR and BAA exceed US EPA WQC limit of 3.8 ng/L for the consumption of water and organism, while at RM 7w BBF and BAP exceeded this limit and CHR and BAA exceeded the 18 ng/L limit for the consumption of organisms.

While the tar removal had a significant effect on concentrations and the resulting cancer and non-cancer exposures (Table 3.2) the short duration would be expected to have an immediate and more substantial effect on aquatic organisms. The highest HIs occurred during the tar removal action at RM 6.3 when RM 7w upriver peaked at 5.6×10^{-3} and downriver at RM 5 peaked at 2.0×10^{-3}. Though fish kills were observed within the containment area, none were observed outside the barriers, consistent with the LFT and model results that, while the highest recorded in the study, were still below acute and chronic thresholds *(29)*. Alternately, resident species may have avoided the site during high concentrations.

LFT captured the re-suspended PAHs desorbed from particulates demonstrating that dredging increased the bioavailable fraction resulting in increased potential health effects. While this study evaluated PAHs, sediments contaminated with organic compounds of similar partitioning properties (e.g., PCBs, PBDEs and OC pesticides) would be expected to produce similar results when dredged. Overall, LFTs demonstrated the ability of PSDs to provide excellent spatial and temporal data for conducting ecological and human health assessments and providing increased resolution in risk analysis.

3.5 Acknowledgments

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3.6 Supporting information

Supporting figures and tables including area maps and site descriptions, and additional data are available in Appendix 2.

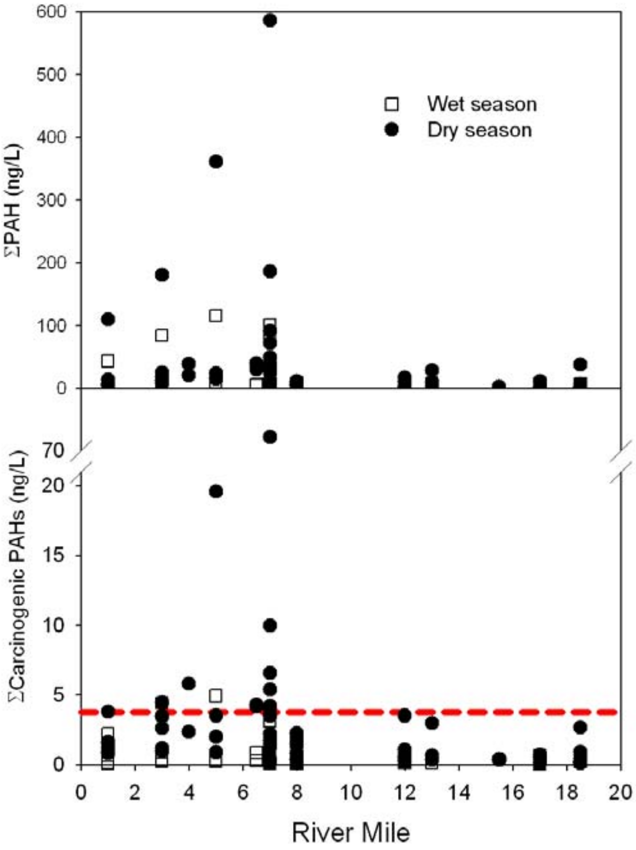

Figure 3.1 LFT estimated PAH concentrations by river mile and season

Red dashed line represents the Water Quality Criteria limit (3.8 ng/L)

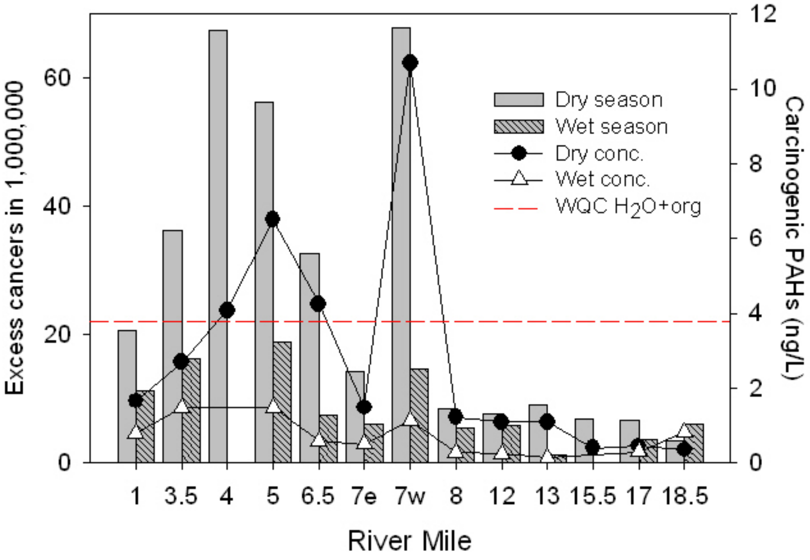

Figure 3.2 Estimated excess cancers and PAH concentrations by river mile and season

Table 3.1 Median PAH concentrations and estimated human health risks

							Non-cancer hazard quotient			Excess cancer risk		
		Concentrations					Consumption			Consumption		
River location and season	N	ΣPAHs in water (ng/L)	P-value[2]	carcinogenic PAHs in water (ng/L)	P-value[2]	ΣPAHs in PSD (ng/g)	Average	High	P-value[2]	Average	High	P-value[2]
Upriver	37											
wet	13	3.2	0.84	0.25	0.015*	4.8	2.0x10^{-4}	1.3x10^{-3}	0.07	3.8x10^{-6}	3.1x10^{-5}	0.31
dry	24	3		0.42		7.2	4.0x10^{-4}	3.3x10^{-3}		5.6x10^{-6}	4.6x10^{-5}	
Superfund Megasite	64											
wet	28	5.7	<0.001*	0.31	<0.001*	8.5	9.3x10^{-4}	7.6x10^{-3}	0.004*	6.7x10^{-6}	5.4x10^{-5}	<0.001*
dry	36	25		2.3		33	3.3x10^{-3}	2.7x10^{-2}		2.6x10^{-5}	2.1x10^{-4}	
Superfund no tar events	45											
wet	22	5.1	<0.001*	0.26	<0.001*	8.3	3.6x10^{-4}	3.0x10^{-3}	<0.001*	6.5x10^{-6}	5.3x10^{-5}	<0.001*
dry	23	20		2.3		29	2.9x10^{-3}	2.4x10^{-2}		2.2x10^{-5}	1.8x10^{-4}	
RMs 7w & 5	28											
no tar	19	16	<0.001*	0.92	0.004*	19	1.1x10^{-3}	8.5x10^{-3}	0.02*	1.5x10^{-5}	1.2x10^{-4}	<0.001*
tar	9	101		3.7		116	4.5x10^{-3}	3.7x10^{-2}		9.1x10^{-5}	7.4x10^{-4}	
Downriver	10											
wet	4	3.8	0.17	0.41	0.17	12	3.4x10^{-4}	1.5x10^{-2}	0.11	9.1x10^{-6}	7.4x10^{-5}	0.18
dry	6	8		1.4		23	1.9x10^{-3}	2.8x10^{-3}		1.8x10^{-5}	1.5x10^{-4}	

[1] Mann-Whitney rank sum tests within location between seasons.

[2] P-values are for comparisons between seasons

*indicates significance at $\alpha = 0.05$.

Table 3.2 Median PAH concentrations and estimated ecological risk[1]

				Ecological Risk Hazard Index		
River location and season	N	ΣPAHs in water (ng/L)	P-value[2]	Acute	Chronic	P-value[2]
Upriver	37					
wet	13	3.2	0.84	$1.2\text{x}10^{-4}$	$6.0\text{x}10^{-4}$	0.9
dry	24	3		$9.0\text{x}10^{-5}$	$4.0\text{x}10^{-4}$	
Superfund Megasite	64					
wet	28	5.7	<0.001*	$2.0\text{x}10^{-4}$	$1.0\text{x}10^{-3}$	<0.001*
dry	36	25		$6.2\text{x}10^{-4}$	$3.0\text{x}10^{-3}$	
Superfund no tar events	45					
wet	22	5.1	<0.001*	$1.8\text{x}10^{-4}$	$9.1\text{x}10^{-4}$	<0.001*
dry	23	20		$5.9\text{x}10^{-4}$	$2.9\text{x}10^{-3}$	
RMs 7w & 5	28					
no tar	19	16	<0.001*	$4.6\text{x}10^{-4}$	$2.0\text{x}10^{-3}$	0.01*
tar	9	101		$8.0\text{x}10^{-4}$	$4.0\text{x}10^{-3}$	
Downriver	10					
wet	4	3.8	0.17	$2.7\text{x}10^{-4}$	$1.0\text{x}10^{-4}$	0.7
dry	6	8		$2.8\text{x}10^{-4}$	$1.0\text{x}10^{-4}$	

[1] Mann-Whitney rank sum tests within location between seasons.

[2] P-values are for comparisons between seasons

*indicates significance at $\alpha = 0.05$.

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Chapter 4 - Conclusion

When estimating dose, the bioavailable concentration and timing of potential toxicant exposure need to be considered. Using PSDs as a standard comparable across sites and studies, this research revealed the spatial and temporal differences an urban river might expect. General urban areas can expect an increase in low molecular weight bioavailable PAH loading in a cool, wet season while dry season heavy rains deliver temporary higher concentrations and loads. Sites with sediment-based contamination may not be a constant seep, but could change substantially depending on river flows as well as riverbank and upland conditions. At McCormick & Baxter sediment capping was effective at preventing short term contamination of the water column, but long term effectiveness is as yet undetermined. However, pre-and post-remediation baselines were set and the foundation laid for continued monitoring. Slightly upriver at the GASCO site, dredging removed substantial amounts of contamination but short term effects were significant. If containment systems are not sufficient during dredging, the results of sediment disturbance include resuspension, transport and increased bioavailability of organic contamination.

If multiple species or ecosystem exposures are being investigated, then samplers such as SPMDs and LFTs are ideal because they do not metabolize contaminants. Metabolism affects compounds differently, but PSDs reflect an unadulterated signature potentially revealing issues not found when sampling organisms or totals. For example, fish tissues may not have revealed the wet season increase in low molecular weight PAHs due to up regulation of metabolizing enzymes. Additionally, sampling fish might not have exposed the increased bioavailability of resuspended contamination because of site avoidance during the high concentration episodes. However, PSDs estimate the potential exposure of less mobile species that cannot escape the resulting plume.

Our research also advanced forensic methods in source apportionment by demonstrating that low molecular weight PAH ratios such as fluoranthene/pyrene and phenanthrene/anthracene are applicable to PSDs. The application of principal component analysis demonstrated the ability to discern similar sources such as urban runoff, coal tar and creosote through PSD analyte profiles. An increased congener profile that includes alkylated PAHs, retene, dibenzothiophene and other diagnostic compounds may further refine source apportionment capabilities.

Progress was made in risk assessment as well. The studies demonstrated seasonal risk variability of several orders of magnitude as well as the short term impacts of remediation. Armed with PSD data of high spatial and temporal resolution, health professionals can better communicate risk to affected populations.

In accordance with the Environmental and Molecular Toxicology department's mission, we advanced science and technology through hypothesis driven research guided by clearly defined objectives. PSDs provide an estimated dose based on bioavailability rather than the simple presence of a contaminant, and the ecological and human health risk assessment models provide an estimated response to the measured contamination. Analysis of five years of PSD data from a model urban river provided answers to questions relevant beyond the studies' specific analytes and field sites in an effort to raise environmental quality and human health to a higher level.

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APPENDICES

Appendix 1- Supporting Information: Spatial and temporal variation of bioaccessible PAHs in an urban river undergoing Superfund remediation.

A1.1 Data analysis

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

$$C_{water} = \frac{C_{SPMD} \bullet V_{SPMD}}{R_S \bullet t} \quad \text{Eq. A1.1}$$

where V_{SPMD} is the volume of the sampler and t is the time in days. Loads were calculated using USGS flow estimates.

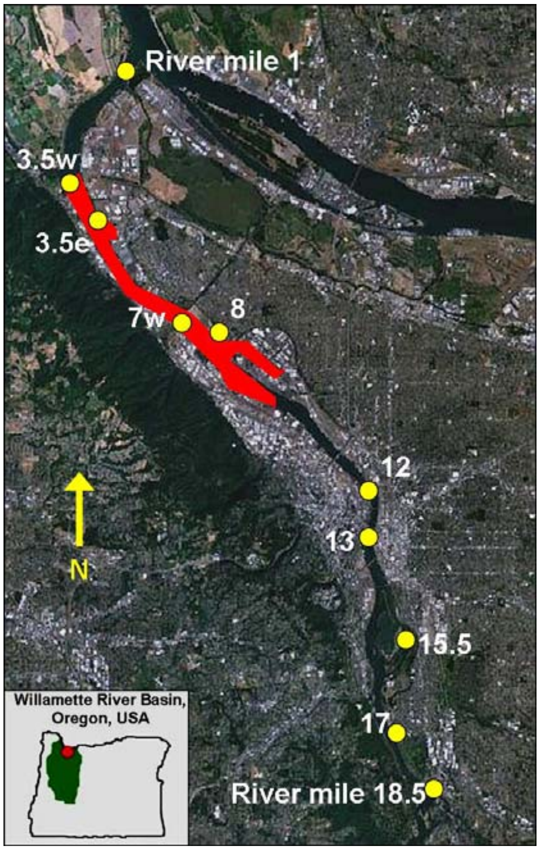

Figure A 1.1 Lower Willamette River SPMD sampling sites.
Yellow circles are the approximate sites of SPMD samplers on the Willamette River (north flowing). The Portland Harbor Superfund site is in red. The McCormick and Baxter Superfund site is on the east bank at river mile 7.

Specific information for each sampling site:

River Mile 1: East bank of the river and approximately 100 meters north of the confluence of the Willamette and Columbia slough. The immediate area is undeveloped, however, Columbia slough passes through a highly industrial area with known PAH contamination*(1)*. This site had duplicate samplers.

River Mile 3.5 east and west: Point just south of Sauvie Island (an undeveloped, agricultural island) on the east river bank below industrial area and within the Portland Harbor Superfund site.

River Mile 7 east: The McCormick and Baxter Superfund site. Before and after capping, 17 samplers were placed here, but during placement of the sediment cap a sampler was placed several hundred meters downstream.

River Mile 7 west: Known as the Arkema, Inc. site, it is approximately 50 meters south of the railroad bridge and opposite the McCormick and Baxter Superfund site. A heavily industrialized area, the site is just upriver from a former manufactured gas plant (GASCO)

River Mile 8: This site is positioned just north of the Swan Island shipyards and dry docks.

River Mile 12: Located within downtown Portland on the east side of the river below a major bridge and near an urban drain pipe. The area has residential, commercial and light industrial activity.

River Mile 13: Located on the west side of the river at a vessel moorage at the base of a city park in downtown Portland.

River Mile 15.5: On the east side of the river, east of Ross Island, a sand and gravel quarry site. The immediate area has considerable vegetation and some residences.

River Mile 17: Positioned on the east side of the river offshore of a golf course.

River Mile 18.5: On the east side of the river near the mouth of Johnson Creek which drains a large urban watershed. This area has a boat launch and parking lot and is located below a major commercial area with heavy traffic. This site had duplicate samplers.

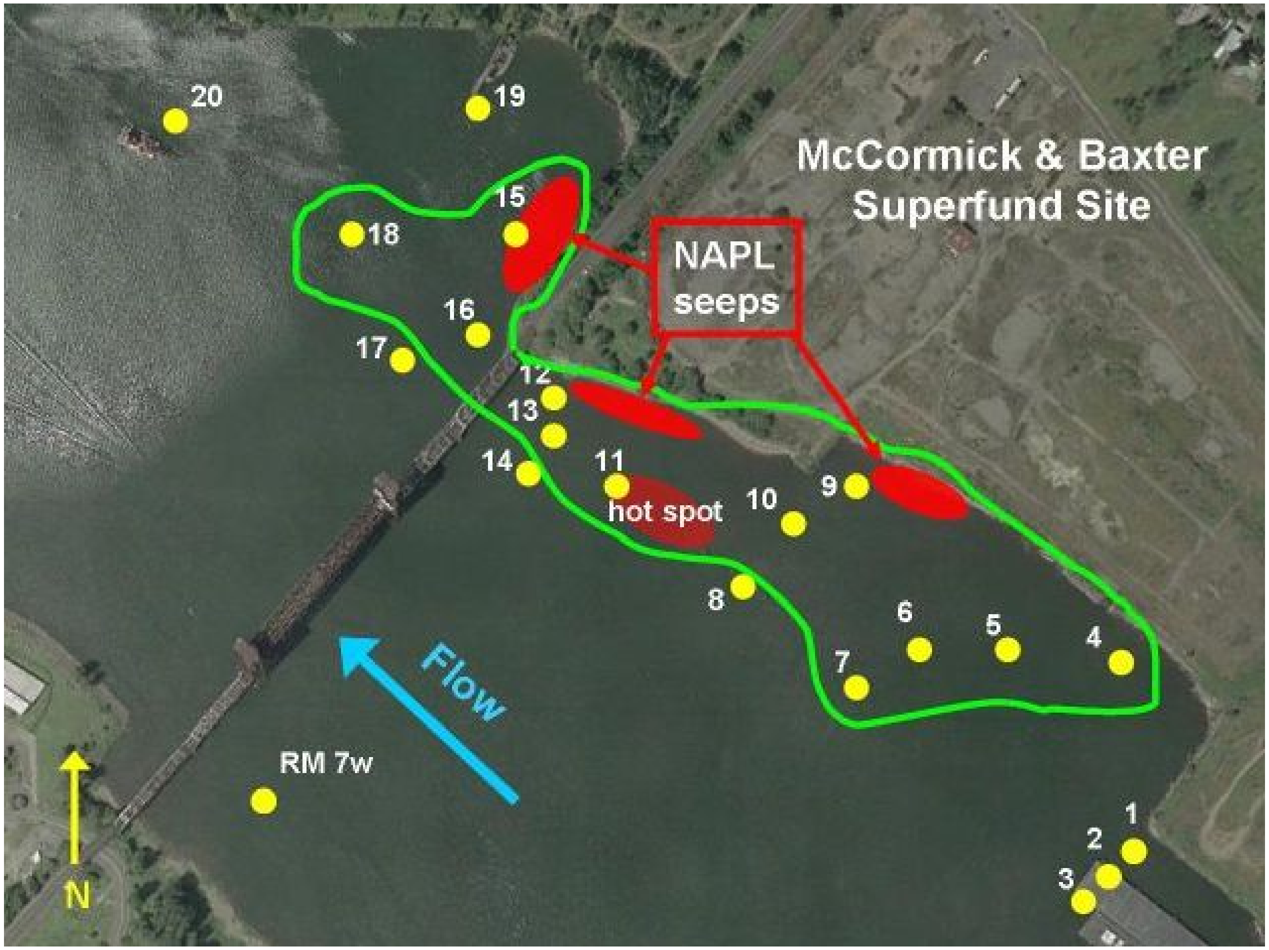

Figure A 1.2 McCormick & Baxter Superfund site sampling sites 2003 and 2005
The green line represents approximate boundary of the sediment cap.

Table A 1.1 Estimated average daily concentrations of LMW PAHs in SPMDs

* Fluorene not included due to analytical issues, ND = non-detect.

River Mile	Season	n	Low Molecular Weight PAHs average concentrations (ng/L)					
			NAP	ACY	ACE	FLO	PHE	ANT
1	dry	10	5 ± 7	7 ± 13	2 ± 4	3 ± 5	14 ± 14	5 ± 10
	wet	6	7 ± 10	5 ± 7	0.7 ± 1	13 ± 17	50 ± 29	5 ± 9
3.5w	dry	4	12 ± 16	11 ± 14	32 ± 34	29 ± 34	100 ± 98	20 ± 25
	wet	2	4 ± 5	8 ± 13	0.7 ± 1	18 ± 26	56 ± 37	9 ± 12
3.5e	dry	5	11 ± 10	18 ± 18	23 ± 19	8 ± 18	68 ± 41	14 ± 14
	wet	3	45 ± 55	15 ± 21	68 ± 102	44 ± 61	132 ± 110	27 ± 34
7w	dry	10	26 ± 34	14 ± 24	68 ± 46	53 ± 59	330 ± 187	80 ± 62
	wet	8	3 ± 5	3 ± 7	19 ± 34	24 ± 30	182 ± 243	44 ± 72
7e	dry	1	15	ND	51	44	68	11 ± 7
	wet	5	45 ± 55	15 ± 21	68 ± 102	44 ± 61	132 ± 110	27 ± 34
	2005	17	0.1 ± 0.3	ND	0.4 ± 0.3	0.4 ± 0.2	1 ± 0.6	0.3 ± 0.2
	2003	15	14 ± 30	11 ± 21	65 ± 102	*	99 ± 64	3 ± 9
8	dry	8	0.4 ± 0.5	4 ± 9	3 ± 5	3 ± 5	13 ± 8	3 ± 6
	wet	5	2 ± 3	4 ± 8	0.2 ± 0.3	5 ± 8	15 ± 17	2 ± 44
12	dry	4	5 ± 6	7 ± 14	1 ± 2	ND	6 ± 7	5 ± 9
	wet	2	6 ± 5	15 ± 21	ND	15 ± 16	14 ± 20	4 ± 4
13	dry	4	8 ± 8	5 ± 11	39 ± 4	ND	6 ± 7	5 ± 9
	wet	3	2 ± 1	9 ± 16	0.5 ± 0.8	9 ± 9	22 ± 19	4 ± 4
15.5	dry	5	5 ± 6	4 ± 10	0.6 ± 1	0.1 ± 0.3	5 ± 6	4 ± 8
	wet	3	3 ± 3	12 ± 22	0.3 ± 0.4	23 ± 20	18 ± 16	3 ± 3
17	dry	5	0.8 ± 0.2	6 ± 13	0.6 ± 1	0.1 ± 0.3	5 ± 5	4 ± 7
	wet	3	4 ± 4	9 ± 16	0.2 ± 0.3	11 ± 16	13 ± 12	3 ± 4
18.5	dry	9	4 ± 7	8 ± 15	1 ± 2	0.4 ± 0.8	5 ± 6	5 ± 8
	wet	5	4 ± 4	5 ± 10	0.3 ± 0.3	4 ± 6	14 ± 13	2 ± 3

Table A 1.2 Estimated average daily concentration of HMW PAHs by SPMD

ND = non-detect

River Mile	Season	n	High Molecular Weight PAHs average daily concentrations (ng/L) as estimated by SPMD								
			FLA	PYR	CHR	BAA	BBF	BKF	BAP	BPL	IPY
1	dry	10	87 ± 74	150 ± 168	20 ± 25	16 ± 19	10 ± 14	3 ± 3	8 ± 13	ND	0.1 ± 0.3
	wet	6	81 ± 26	80 ± 18	ND	18 ± 19	0.2 ± 0.3	4 ± 4	9 ± 20	ND	ND
3.5w	dry	4	285 ± 245	354 ± 352	17 ± 22	47 ± 42	14 ± 21	8 ± 9	28 ± 50	ND	0.1 ± 0.2
	wet	2	83 ± 41	80 ± 28	3 ± 6	29 ± 20	6 ± 11	5 ± 3	14 ± 21	ND	ND
3.5e	dry	5	227 ± 136	319 ± 281	10 ± 23	40 ± 30	15 ± 29	4 ± 4	15 ± 20	ND	ND
	wet	3	114 ± 114	96 ± 52	ND	22 ± 10	4 ± 10	6 ± 3	19 ± 19	ND	ND
7w	dry	10	632 ± 339	625 ± 358	108 ± 74	106 ± 63	30 ± 21	14 ± 12	44 ± 36	0.8 ± 3	15 ± 49
	wet	8	236 ± 292	224 ± 290	34 ± 55	42 ± 54	8 ± 13	4 ± 5	24 ± 29	ND	1 ± 2
7e	dry	1	70	49	ND	9	11	0.7	2	ND	ND
	wet	5	114 ± 114	96 ± 52	ND	22 ± 10	4 ± 10	6 ± 3	19 ± 19	ND	ND
	2005	17	2 ± 0.9	3 ± 1	0.3 ± 0.3	0.4 ± 0.2	ND	ND	ND	ND	ND
	2003	15	120 ± 121	86 ± 78	ND	24 ± 28	5 ± 7	ND	12 ± 14	ND	ND
8	dry	8	69 ± 35	76 ± 533	8 ± 9	10 ± 8	0.8 ± 1	0.7 ± 1	5 ± 5.8	0.1 ± 0.2	2 ± 4
	wet	5	24 ± 11	25 ± 9	0.2 ± 0.4	0.9 ± 1	0.1 ± 0.2	1 ± 2	9 ± 16	ND	0.2 ± 0.4
12	dry	4	39 ± 38	54 ± 58	7 ± 12	5 ± 8	0.2 ± 0.2	0.6 ± 1	4 ± 5.6	ND	ND
	wet	2	14 ± 8	16 ± 4	ND	ND	0.4 ± 0.5	2 ± 2	23 ± 30	ND	ND
13	dry	4	40 ± 35	59 ± 58	6 ± 12	6 ± 10	0.3 ± 0.4	0.8 ± 1	3 ± 4	ND	ND
	wet	3	27 ± 11	24 ± 26	2 ± 3	3 ± 6	ND	3 ± 3	13 ± 22	ND	ND
15.5	dry	5	27 ± 28	37 ± 43	0.1 ± 0.2	3 ± 6	0.2 ± 0.2	0.7 ± 0.8	1 ± 2	ND	ND
	wet	3	20 ± 8	21 ± 11	ND ±	2 ± 4	3 ± 5	2 ± 2	13 ± 21	ND	ND
17	dry	5	19 ± 22	27 ± 26	0.2 ± 0.4	0.4 ± 0.9	0.1 ± 0.1	0.4 ± 0.7	6 ± 9	ND	ND
	wet	3	16 ± 6	16 ± 8	ND	2 ± 4	0.1 ± 0.2	0.8 ± 1	10 ± 18	ND	ND
18.5	dry	9	29 ± 30	36 ± 41	0.3 ± 0.6	3 ± 5	0.4 ± 0.3	0.6 ± 0.6	4 ± 9	ND	ND
	wet	5	21 ± 8	22 ± 11	0.1 ± 0.3	3 ± 6	0.2 ± 0.3	2 ± 2	7 ± 16	ND	ND

Table A 1.3 Seasonal parameters, concentrations, loads, and other PAH specifics

River Mile	Season	n	precipitation (mm)	river flow (m^3/s)	PAHs (μg/L)	Daily load kg/day	LMW ng/L	HMW ng/L	Carcinogenic μg/L	FLA/PYR
1	dry	10	1.7 ± 1.9	264 ± 21	0.36 ± 0.34	8.0 ± 8.2	38 ± 27	295 ± 308	0.15 ± 0.23	0.79 ± 0.25
	wet	6	3.3 ± 0.2	436 ± 130	0.27 ± 0.10	9.7 ± 3.0	81 ± 59	192 ± 45	0.10 ± 0.11	1.00 ± 0.16
3.5w	dry	4	1.9 ± 2.3	263 ± 26	0.96 ± 0.89	23 ± 23	205 ± 206	754 ± 704	0.26 ± 0.33	0.92 ± 0.32
	wet	2	3.3 ± 0.2	436 ± 146	0.32 ± 0.16	11 ± 4.8	95 ± 89	220 ± 71	0.14 ± 0.11	0.99 ± 0.20
3.5e	dry	5	1.7 ± 2.0	264 ± 23	0.77 ± 0.50	18 ± 13	142 ± 71	630 ± 445	0.19 ± 0.22	0.86 ± 0.26
	wet	3	3.4 ± 0.2	403 ± 115	0.59 ± 0.55	19 ± 19	333 ± 362	262 ± 198	0.08 ± 0.07	1.05 ± 0.66
7w	dry	10	0.8 ± 1.6	255 ± 21	2.15 ± 1.19	48 ± 28	572 ± 338	1575 ± 893	0.48 ± 0.32	1.05 ± 0.14
	wet	8	1.3 ± 1.7	646 ± 546	0.85 ± 1.11	27 ± 28	275 ± 376	573 ± 731	0.23 ± 0.21	1.11 ± 0.12
7e	dry	1	0.1 ± 0.0	234 ± 248	0.33 ± 0.95	6.7 ± 20	189 ± 255	142 ± 699	0.10 ± 0.10	1.41 ± 1.02
	wet	5	3.4 ± 0.2	403 ± 115	0.59 ± 0.55	19 ± 19	333 ± 362	262 ± 198	0.08 ± 0.07	1.05 ± 0.66
	2005	17		316	0.01 ± 0.00	0.2 ± 0.1	3 ± 1	6 ± 2	0.00 ± 0.00	0.73 ± 0.20
	2003	15		262	0.44 ± 0.42	9.9 ± 9.6	4767 ± 2855	247 ± 218	0.04 ± 0.04	N/A
8	dry	8	1.0 ± 1.8	255 ± 24	0.20 ± 0.11	4.4 ± 2.9	27 ± 19	171 ± 107	0.17 ± 0.18	0.98 ± 0.21
	wet	5	2.0 ± 1.8	521 ± 191	0.09 ± 0.07	3.5 ± 2.0	29 ± 38	61 ± 32	0.13 ± 0.10	0.96 ± 0.15
12	dry	4	0.9 ± 1.4	259 ± 23	0.14 ± 0.15	3.2 ± 3.7	25 ± 24	110 ± 123	0.16 ± 0.25	0.77 ± 0.08
	wet	2	3.5 ± 0.4	467 ± 186	0.11 ± 0.11	3.5 ± 2.7	54 ± 67	54 ± 44	0.11 ± 0.09	0.86 ± 0.28
13	dry	4	0.9 ± 1.4	259 ± 23	0.14 ± 0.14	3.3 ± 3.4	27 ± 17	115 ± 120	0.14 ± 0.21	0.71 ± 0.06
	wet	3	3.4 ± 0.3	418 ± 157	0.12 ± 0.07	3.7 ± 1.3	46 ± 34	74 ± 41	0.09 ± 0.11	N/A
15.5	dry	5	1.7 ± 2.0	264 ± 23	0.09 ± 0.10	2.1 ± 2.5	19 ± 21	69 ± 79	0.12 ± 0.21	0.77 ± 0.07
	wet	3	3.4 ± 0.3	418 ± 157	0.12 ± 0.07	4.0 ± 1.7	59 ± 46	62 ± 29	0.08 ± 0.10	0.99 ± 0.20
17	dry	5	1.7 ± 2.0	264 ± 23	0.07 ± 0.07	1.7 ± 1.7	16 ± 19	54 ± 49	0.11 ± 0.20	0.69 ± 0.40
	wet	3	3.4 ± 0.3	418 ± 157	0.09 ± 0.07	2.7 ± 1.7	41 ± 49	45 ± 19	0.08 ± 0.12	1.02 ± 0.15
18.5	dry	9	1.4 ± 1.7	262 ± 21	0.10 ± 0.11	2.3 ± 2.7	23 ± 30	74 ± 77	0.15 ± 0.24	0.84 ± 0.08
	wet	5	3.4 ± 0.3	434 ± 151	0.08 ± 0.05	2.8 ± 1.0	29 ± 30	56 ± 20	0.09 ± 0.09	0.95 ± 0.12

Table A 1.4 Water chemistry data: averages ± 1SD sorted by season and area

Location	Season	Temperature °C	Specific Conductivity mS/cm	Dissolved oxygen mg/L	pH	Oxidation Reduction Potential mV	$NH4^+$ mg/L	$NO3^-$ mg/L
Upriver	wet	9 ± 0	0.1 ± 0.0	12 ± 0.5	6.8 ± 0.4	196 ± 52	0.2 ± 0.03	0.53 ± 0.4
	dry	21 ± 2	0.1 ± 0.1	9 ± 0.6	7.2 ± 0.1	195 ± 44	0.2 ± 0.1	0.97 ± 0.6
Superfund	wet	13 ± 4	0.7 ± 2	10 ± 4	7.3 ± 1.7	197 ± 143	34 ± 115	1.9 ± 2
	dry	21 ± 2	0.1 ± 0.01	9 ± 1	7.3 ± 0.3	167 ± 53	0.2 ± 0.1	1.3 ± 0.7
Downriver	wet	12 ± 5	0.1 ± 0.04	12 ± 0.8	7.2 ± 0.5	197 ± 40	0.7 ± 0.8	2.3 ± 3
	dry	20 ± 1	0.1 ± 0.01	10 ± 1	7.5 ± 0.2	188 ± 50	0.1 ± 0.1	1.4 ± 1
RM 7 west	wet	14 ± 4	1.4 ± 3.4	6 ± 8	8.1 ± 2.0	129 ± 93	80 ± 178	2.5 ± 2
	dry	21 ± 2	0.1 ± 0.01	9 ± 0.8	7.3 ± 0.3	150 ± 53	0.2 ± 0.1	1.5 ± 0.9

Table A 1.5 Water chemistry data: averages ± 1 SD

Location	Season	TOC mg/L	DOC mg/L	TSS mg/L	TDS mg/L
Upriver	wet	2.8 ± 1	2.8 ± 1	3.6	88
	dry	1.7 ± 0.1	1.7 ± 0.2	3.3 ± 1	68 ± 11
Superfund	wet	68 ± 77	1.8	N/A	N/A
	dry	1.6 ± 0.2	1.6 ± 0.3	7.3 ± 1	75 ± 2
Downriver	wet	133	N/A	N/A	N/A
	dry	1.9 ± 0.4	1.8 ± 0.4	8.8 ± 0	97 ± 6
RM 7 west	wet	46 ± 79	1.8	N/A	N/A
	dry	1.6 ± 0.2	1.6 ± 0.3	7.3 ± 1	75 ± 2

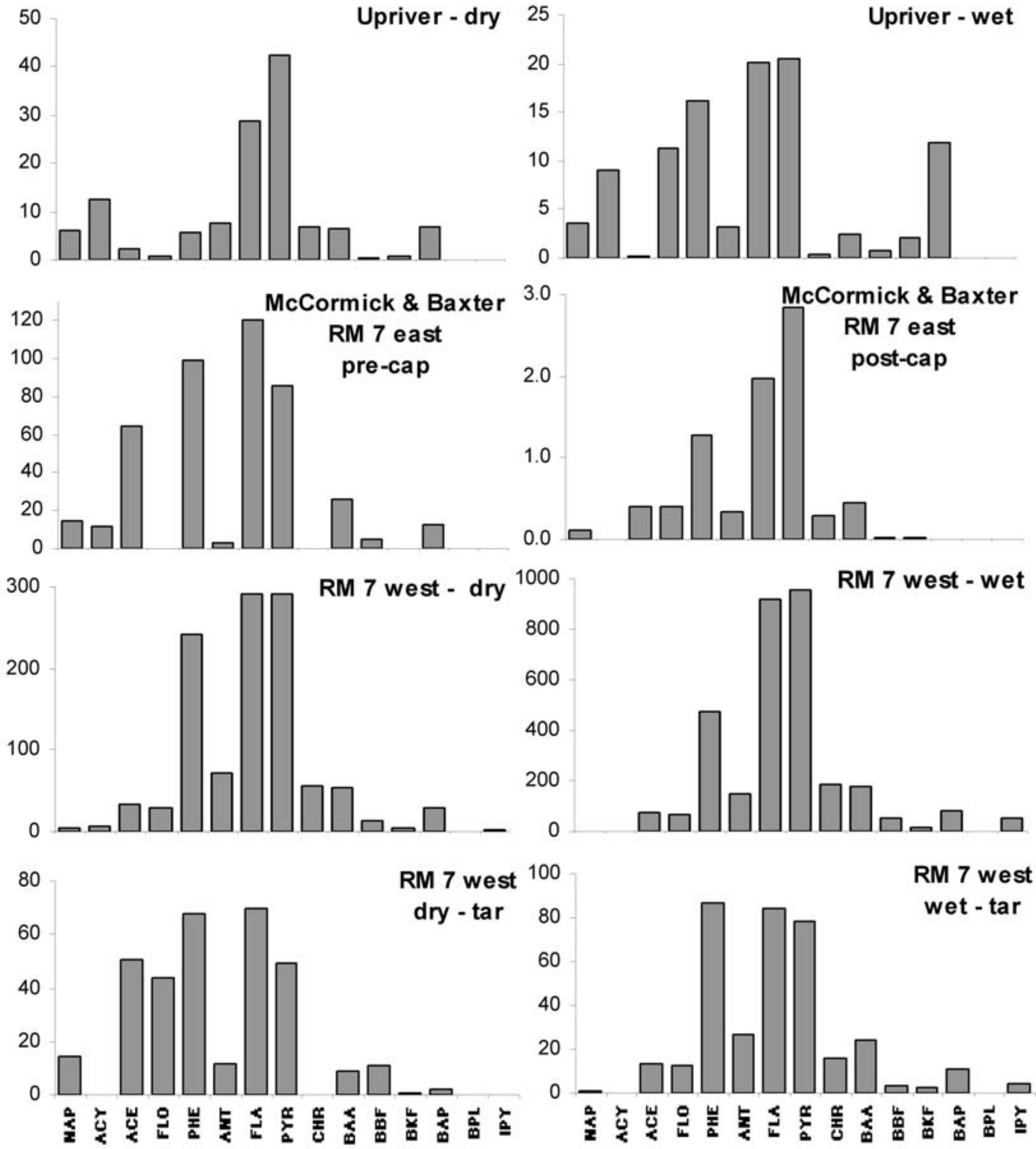

Figure A 1.3 Congener profiles for selected sites and seasons.
Congener concentration profiles (ng/L) of 15 PAHs for dry and wet seasons at upriver and river mile 7 west sites, during tar removal activities downstream from river mile 7 west, and pre- and post-capping at McCormick & Baxter, river mile 7 east. The 'y' axes are not uniform so as to compare the relative congener contributions between sites.

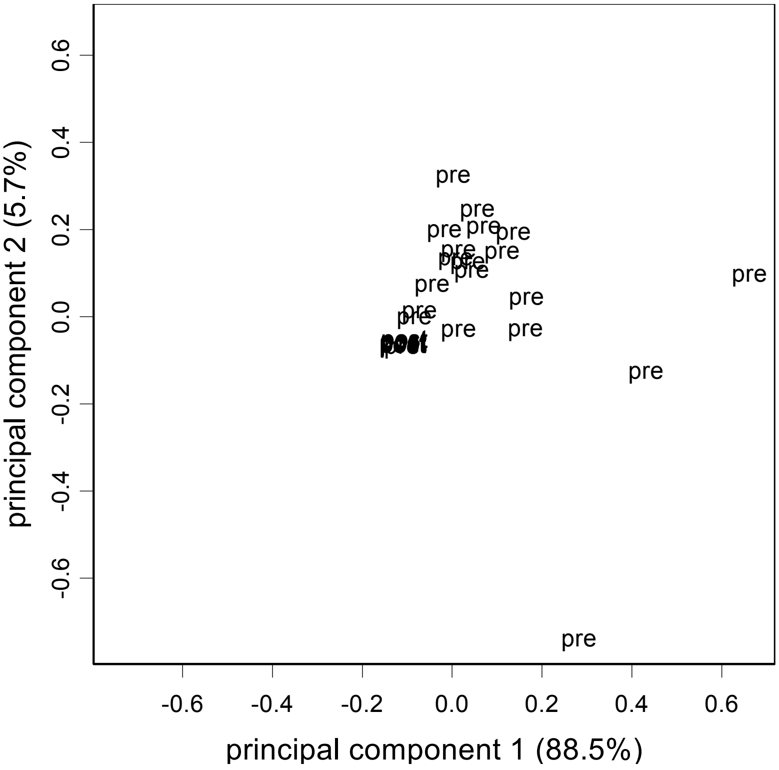

Figure A 1.4 PCA plot for pre- and post-capping samples from the McCormick & Baxter Superfund site.

SPMD PAH congener profiles for pre- and post-remediation at River Mile 7 east (n = 15, pre- and 17 post-). High variability in pre-remediation sites is the result of sampler proximity to various NAPL seeps. See Figure A1.1 for sampler positions.

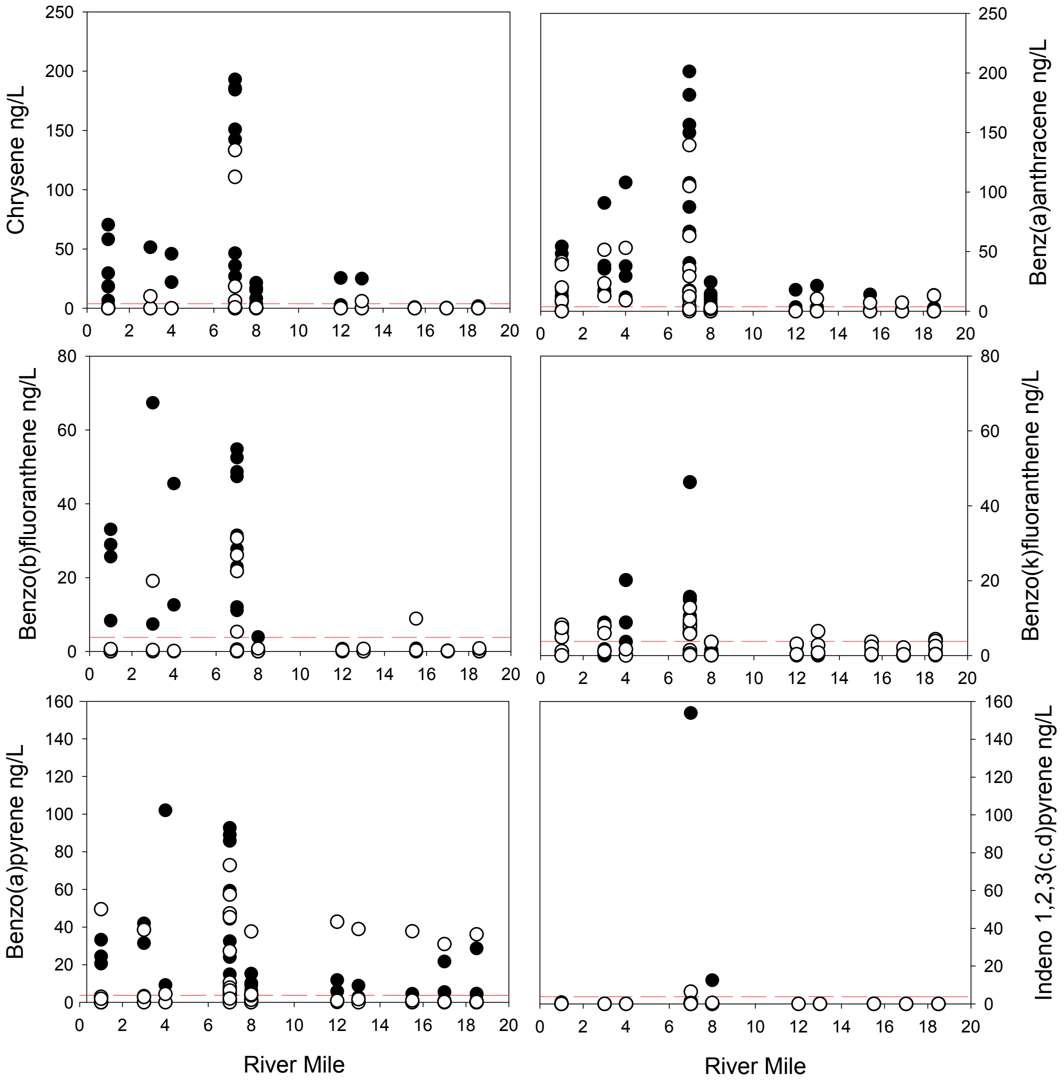

Figure A 1.5 Water quality data for carcinogenic EPA PP PAHs.
Open circles represent the wet season, filled circles the dry. The red dashed lines represent the EPA Water Quality Guidelines for human health for consumption of water and organism (3.8 ng/L).

A1.2 Literature Cited

(1) McCarthy, K., Assessment of the usefulness of semipermeable membrane devices for long-term watershed monitoring in an urban slough system. Environ. Monitor. Assess. 2006, 118, (1-3), 293-318.

Appendix 2 - Supporting Information: Using passive sampling devices as biological surrogates in ecological and human health risk models.

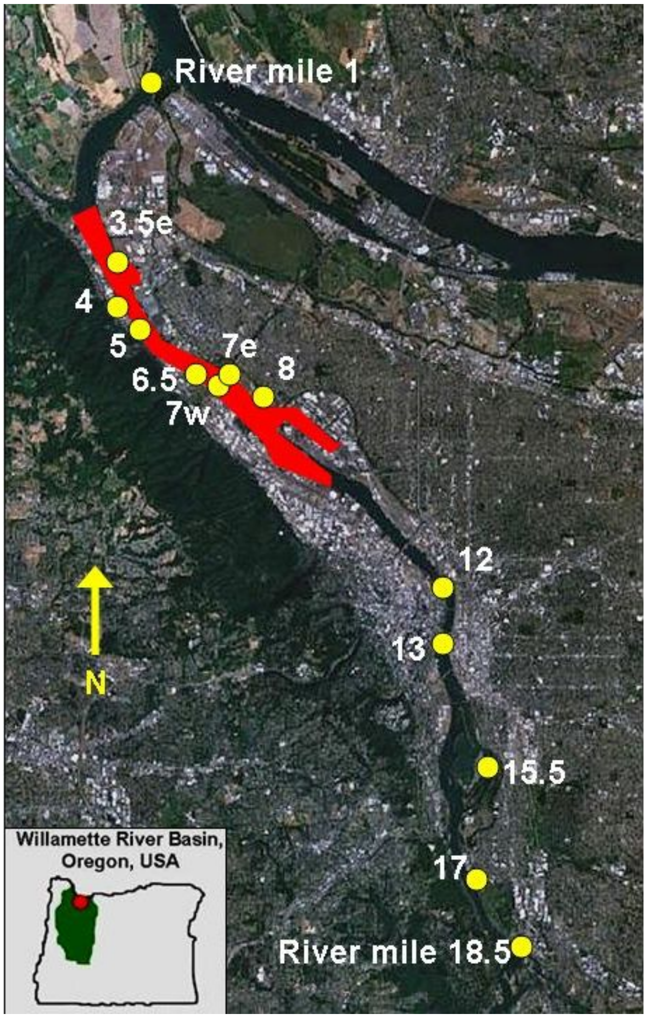

Figure A 2.1 Lower Willamette River LFT sampling sites 2004-2006. Each site is designated by a yellow circle. Not all sites were used every deployment. The red area indicates the approximate boundaries of the Portland Harbor Superfund megasite.

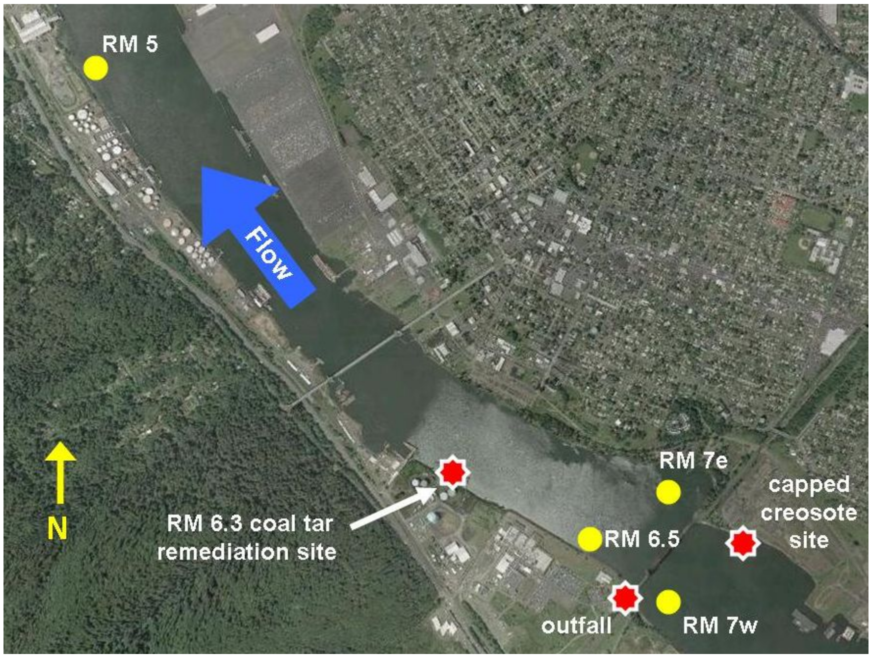

Figure A 2.2 Sampling sites near river mile 6.3 remediation activities.
Dredging of the site took place August to October 2005.
The sampler at RM 6.5 was not in place until May 2006.

Table A 2.1 Chronic oral exposure (mg/kg-day)

Abbrev.	Compound	RfD/ MRL	Cancer slope factor	BAP equivalent	MDL (µg/g)
NAP	naphthalene	0.02			$1.4x10^{-6}$
ACY	acenaphthylene	na			$2.1x10^{-6}$
ACE	acenaphthene	0.6			$1.4x10^{-7}$
FLO	fluorene	0.4			$2.0x10^{-3}$
PHE	phenanthrene	na			$7.1x10^{-7}$
ANT	anthracene	10			$3.9x10^{-7}$
FLA	fluoranthene	0.4			$3.2x10^{-7}$
PYR	pyrene	0.03			$8x10^{-8}$
CHR	chrysene	na		0.01	$9.4x10^{-7}$
BAA	benz[a]anthracene	na		0.1	$3.6x10^{-7}$
BBF	benzo[b]fluoranthene	na		0.1	$8.3x10^{-7}$
BKF	benzo[k]fluoranthene	na		0.01	$1.5x10^{-7}$
BAP	benzo[a]pyrene	na	7.3	1	$3.3x10^{-7}$
DBA	dibenz[ah]anthracene	na			
BPL	benzo[ghi]perylene	na			$1.5x10^{-5}$
IPY	indeno[123cd]pyrene	na		0.1	$1.5x10^{-5}$

Table A 2.2 Parameters and values for calculating exposure and health endpoints

Parameter	#	Units	Description
Concentration (C)	X	μg/g	PSD measured
Conversion Factor (CF)	0.001	kg/g	
Ingestion Rate (IR)	17.5	g/day	Average consumption
Ingestion Rate	142.4	g/day	High consumption
Body Weight (BW)	70	kg	Adult
Exposure Frequency (EF)	365	days/year	Daily consumption
Exposure Duration (ED)	30	years	Area residence time
Averaging Time (AT)	10950	days	30 years (non-cancer)
Averaging Time	25550	days	70 years (cancer)

Table A 2.3 Compound toxicity values for calculating ecological risk[1]

PAH	Acute Toxicity	Chronic Toxicity
NAP	4870	974
ACY	1181	236.2
ACE	1360	272
FLO	730	146
PHE	367	73.4
ANT	300	60
FLA	55	11
PYR	61	12.2
CHR	11	2.2
BAA	9.8	1.96
BBF	14	2.8
BKF	8.6	1.72
BAP	7.6	1.52
BPL	2.4	0.48
IPY	0.64	0.128

[1] Source: Neff et al. for the model and values.

Table A 2.4 Model validations using water quality criteria[1] or guidance values[2]

Ecological Assessment

		Concentration[2]	Hazard Quotient	
		µg/L	acute	chronic
naphthalene	acute	2300	0.5	2.4
	chronic	620	0.1	0.6
acenaphthene	acute	1700	1.3	6.3
	chronic	520	0.4	1.9
fluoranthene	acute	3980	72	362

Human Non-cancer Assessment

		Concentration[1]	Hazard Quotient	
	For the consumption of:	µg/L	average consumption	high consumption
fluoranthene	water+organism	1100	6.9x10^{-4}	5.6x10^{-3}
	organism	5300	3.3x10^{-3}	2.7x10^{-2}
acenaphthene	water+organism	670	2.8x10^{-4}	2.3x10^{-3}
	organism	990	4.1x10^{-4}	3.4x10^{-3}
pyrene	water+organism	830	6.9x10^{-3}	5.6x10^{-2}
	organism	4000	3.3x10^{-3}	2.7x10^{-1}
FLO+ACE+PYR	water+organism		7.9x10^{-3}	6.4x10^{-3}
	organism		3.7x10^{-2}	3.0x10^{-1}

Human Excess Cancers

		Concentration[1]	Excess cancers in 1,000,000	
	For the consumption of:	µg/L	average consumption	high consumption
BAP equivalents	water+organism	0.0038	3.0x10^{-9}	2.4x10^{-8}
	organism	0.018	1.4x10^{-8}	1.1x10^{-7}
	model limit avg	1.3	1.0x10^{-6}	8.1x10^{-6}
	model limit high	16	1.2x10^{-7}	1.0x10^{-6}

[1] US EPA water quality criteria (National Recommended Water Quality Criteria: 2002, EPA-822-R-02-047)

[2] Oregon Water Quality Guidance Values for the application of Oregon's Narrative Toxics Criteria (340-041-0033(1))

Table A 2.5 Calculation of sampling rates (Rs) from PRCs

Adapted from Huckins, J. N., J. D. Petty, et al. (2006). Monitors of organic chemicals in the environment: semipermeable membrane devices. New York, Springer.

Input data

Vs = 4.95 cm^3

exposure duration in days (E) = 21 days

PRC amount in PSD,

at t_0 = 20 ng

at t_E = 9.83 ng

	log K_{ow}s
PRC PCB-82	6.2
DBA	6.75

Log $K_{sw} = a_0 + 2.321(\log K_{ow}) - 0.1618(\log K_{ow})^2$

a_0 = -2.61 for PCBs, PAHs, 4,4'-DDE

a_0 = -3.2 for polar pesticides

(Huckins et al. page 54 equation 3.28)

Step 1. Calculation of PRC R_s

$k_e = -\ln (t_E / t_0) / E =$ 0.0338

$\log K_{sw,\,PRC} =$ 5.56

$R_{s,\,PRC} = V_s \cdot 10^{\log K_{sw,\,PRC}} \cdot k_e =$ 60874 cm3/day » 60.9 L/day

Step 2. Calculation of the relative Rs of analyte and PRC

$\log \alpha = 0.0130 \log K^3_{ow} - 0.3173 \log K^2_{ow} + 2.244 \log K_{ow}$

(Huckins et al. page 60 equation 3.35)

Step 3. Calculate the Rs of the analyte

$R_{s,\,PRC} \cdot (\alpha_{x1} / \alpha_{PRC}) = R_{s,\,x1}$

Step 4. Calculate the aqueous concentrations

$C_{w,\,x1} =$ x_1 accumulation/ $(V_s \cdot K_{sw} (1 - \exp(-(R_s \text{ (mL/d)} \cdot E)/ (V_s \cdot K_{sw}))) * 1000$ = ng/L

Compound	accumulation (ng)	log α	α	Rs (L/d)	Log Ksw	Concentration (ng/L)
PRC	N/A	4.81	65171	60.9	5.56	N/A
DBA calc	1960	4.69	48767	45.6	5.68	**2.485**
DBA meas	1960	4.69	48767	56.8	5.68	**2.086**