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Estimating risk at a Superfund site using passive sampling devices as biological surrogates in human health risk models

Sarah E. Allan, Gregory J. Sower, Kim A. Anderson *

Environmental and Molecular Toxicology Department, Oregon State University, Corvallis, OR, USA

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ABSTRACT

Passive sampling devices (PSDs) sequester the freely dissolved fraction of lipophilic contaminants, mimicking passive chemical uptake and accumulation by biomembranes and lipid tissues. Public Health Assessments that inform the public about health risks from exposure to contaminants through consumption of resident fish are generally based on tissue data, which can be difficult to obtain and requires destructive sampling. The purpose of this study is to apply PSD data in a Public Health Assessment to demonstrate that PSDs can be used as a biological surrogate to evaluate potential human health risks and elucidate spatio-temporal variations in risk. PSDs were used to measure polycyclic aromatic hydrocarbons (PAHs) in the Willamette River; upriver, downriver and within the Portland Harbor Superfund megasite for 3 years during wet and dry seasons. Based on an existing Public Health Assessment for this area, concentrations of PAHs in PSDs were substituted for fish tissue concentrations. PSD measured PAH concentrations captured the magnitude, range and variability of PAH concentrations reported for fish/shellfish from Portland Harbor. Using PSD results in place of fish data revealed an unacceptable risk level for cancer in all seasons but no unacceptable risk for non-cancer endpoints. Estimated cancer risk varied by several orders of magnitude based on season and location. Sites near coal tar contamination demonstrated the highest risk, particularly during the dry season and remediation activities. Incorporating PSD data into Public Health Assessments provides specific spatial and temporal contaminant exposure information that can assist public health professionals in evaluating human health risks.

1. Introduction

Urban rivers that are used by local residents for recreational purposes such as boating, and sport or subsistence fishing are often heavily polluted. Public Health Assessments inform the public about the relative risks of these activities in a specific area by providing information about potential exposures and the likelihood that those exposures could lead to adverse health effects. A Public Health Assessment develops an estimated human exposure dose based on environmental and contaminant data for a specific site and existing regulatory standards (ATSDR, 2005) (for more information about Public Health Assessments please see Section 1 in Supplementary information). Currently, exposure due to consumption of resident organisms is based on tissue contaminant data from fish or shellfish harvested in the area. However, obtaining organisms for analysis can be difficult, usually requires destruction of the organism and often provides limited specific spatial or temporal information (Huckins et al., 2006). Studies have highlighted spatial and temporal variations in contamination and exposure (Ko and Baker, 2004; Brown and Peake, 2006) and others have called for their consideration in risk assessments (Linkov et al., 2002). Recently, developing methodology for more accurately assessing exposure has become a priority for risk assessment (Birnbaum, 2010). Passive sampling devices (PSDs) can be strategically deployed to address spatial and temporal issues in bioavailable contaminant concentrations, an issue that has been shown to significantly affect risk (Huckins et al., 2006).

PSDs, such as semipermeable membrane devices (SPMDs), simulate biological membranes and lipid tissue and thus sequester only the freely-dissolved or bioaccessible fraction of lipophilic organic contaminants. Huckins et al. (2006) reviewed over 30 studies with side-by-side comparisons of SPMDs with organisms and found good correlations with finfish and bivalves, though few studies have investigated PAHs specifically (Peven et al., 1996; Baussant et al., 2001; Verweij et al., 2004; Boehm et al., 2005; Ke et al., 2007). Correlations between PAHs in SPMDs and organisms

Abbreviations and definitions: PSD, passive sampling device; LFT, lipid-free tubing PSD; RM, River Mile on the Willamette River, Oregon. River miles are measured from the confluence of the Willamette River with the Columbia River; $\sum_{16}$PAH, sum of 16 PAH compounds.

* Corresponding author. Address: Environmental and Molecular Toxicology Department, Oregon State University, ALS 1007, Corvallis, OR 97331, USA. Tel.: +1 541 737 8501; fax: +1 541 737 0497.

E-mail address: kim.anderson@oregonstate.edu (K.A. Anderson).

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have been found in terrestrial and aquatic systems, although investigators observed differences in the composition of the PAHs sequestered by organisms and PSDs (Baussant et al., 2001; Ke et al., 2007; Tao et al., 2008). Baussant et al. (2001) found that lower molecular weight PAHs predominated in caged finfish while Ke et al. (2007) measured higher concentrations of PAHs in SPMDs compared to tissue from caged carp. While these studies demonstrate that PSD concentrations can be correlated to organism tissue concentrations, they do not link the PSD concentrations to human health risks.

Recent lab and field trials have resulted in simpler and cheaper variants of SPMDs (Adams et al., 2007; Sower and Anderson, 2008; Allan et al., 2009). These PSDs are constructed from low density polyethylene lay-flat tubing without triolein and designated lipid-free tubing samplers, or LFTs. PSDs, such as the LFT used in this study, offer numerous advantages over using organisms for environmental assessment including simplicity, low cost, fast and minimal extraction and clean-up procedure, no metabolic activity and no organisms are destroyed. Though numerous physical, physiological and ambient factors affect concentrations in organisms, all accumulate contaminants like PSDs: from water across biological membranes (Huckins et al., 2006). Also, unlike organisms, PSDs spiked with performance reference compounds provide chemical specific calibrations of time-integrated, bioavailable concentrations that can be standardized across studies (Huckins et al., 2006; Adams et al., 2007). Using PSDs to determine the time integrated water concentration of contaminants is well established, however, this is the first demonstration of the direct application of PSD data for assessing potential human health risks from consumption.

PSDs are particularly useful in areas where point sources are significant contributors to contamination and where seasonal fluctuations in contaminant concentrations are suspected. To this end, the Portland Harbor Superfund megasite on the Willamette River in Portland, Oregon (river miles or RM 3.5–9.2) is an ideal model system for examining the application of PSD data to Public Health Assessments to elucidate potential exposures and risks in an urban river. Portland Harbor is an industrialized area containing several PAH point sources including coal tar and a remediated former creosoting plant, which is its own Superfund site within the larger harbor site. Additional sources of PAHs in the lower Willamette include ship, train and vehicle emissions, combined sewer overflows, urban runoff, atmospheric deposition and petroleum product leaks and spills. Additionally, significant seasonal flow and precipitation fluctuations occur on the river and seasonal variations in contamination concentrations have been observed (Sower and Anderson, 2008).

The Willamette River is used extensively for both sport and subsistence fishing. Eating contaminated fish from the harbor is considered the most significant health risk from chemical contamination at the site (ATSDR, 2006). Although fish advisories have been issued for some areas, based on exposure to other industrial contaminants, the most recent Public Health Assessment could not evaluate risk from exposure to PAHs due to insufficient fish data. Of 39 species of resident fish in this area, eight constitute the most likely to be caught and consumed by local sport and subsistence fishers, including walleye, black crappie, white crappie, smallmouth bass, pikeminnow, yellow bullhead, carp and largescale sucker. Clams and crayfish are also commonly harvested for consumption. Details about resident fish as well as fish consumption data for different population groups is available in the Portland Harbor Public Health Assessment (ATSDR, 2006).

The purpose of this study is to apply PSD data in a Public Health Assessment to demonstrate that PSDs can be used as a biological surrogate to elucidate spatial and temporal variations in potential human health risks. To achieve this, the PSD mass concentrations of PAHs were substituted for fish tissue contaminant concentrations. The spatial and temporal distribution of PSD measured PAH concentrations were applied to cancer and non-cancer human health risk assessment models.

2. Methods

2.1. Study area

The study area was the lower 18.5 miles of the Willamette River, up to its confluence with the Columbia River. Samplers were placed at 13 sites on west (W) and east (E) sides of the river channel from 2004 to 2006 (Fig. 1). The sites were located upriver (RMs 18.5E, 17E, 15.5E, 13W, and 12E), downriver (RM 1E) and within the Portland Harbor Superfund megasite (RMs 3.5E, 3.5W, 5W, 6.5W, 7W, 7E and 8E). Residential and commercial uses dominate the upriver area whereas the Superfund megasite area is heavily industrialized and contains PAH point sources including creosote and coal tar contaminated sites at RMs 7E and 6.3W respectively. In addition, urban runoff and combined sewer overflows affect the area. Undeveloped or agricultural areas predominate downriver from the harbor.

The study period overlapped with remediation activities that were carried out at RM 6.3 from August to October, 2005. During this time submerged tar from a manufactured gas plant (MGP) site was removed by dredging and a cap was placed over the contaminated sediment. The temporal effects of this remediation activity are analyzed separately from the seasonal data and serve to highlight the importance of having specific spatial and temporal data for effective risk assessment in areas affected by sporadic peaks in contaminant inputs.

2.2. Chemicals and solvents

PAH standards (purities $\geqslant$99%) were obtained from ChemService, Inc. (West Chester, PA, USA) and Pesticide or Optima® grade cleanup and extraction solvents from Fisher Scientific (Fairlawn, NJ, USA) were used. The 16 target analytes, which correspond to the USEPA 16 priority PAHs, included naphthalene, acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene benzo(ghi)perylene, and indeno(1,2,3-c,d)pyrene.

2.3. Sample collection, extraction and analysis

LFT passive samplers were constructed and fortified with performance reference compounds (PRCs) using methods described in Sower and Anderson (2008) Briefly, additive-free, 2.7 cm wide, low-density polyethylene membrane (Barefoot) from Brentwood Plastic, Inc. (St. Louis, MO, USA) was cleaned with hexanes, cut into 100 cm strips, fortified with dibenz(ah)anthracene as a PRC and heat sealed at both ends.

From 2004 to 2006 samplers were deployed in multiple 21-d events during July or August ("dry season") and October or November ("wet season"). This period represents the transition from the lowest precipitation and river 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 m above the river bottom at each site with an anchor–cage–float system described elsewhere (Sethajintanin and Anderson, 2006).

A YSI® sonde was used during sampler deployment and retrieval to collect water chemistry data including temperature, pH, specific conductivity, and oxidative-reductive potential (ORP). LFT