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Passive samplers accurately predict PAH levels in resident crayfish

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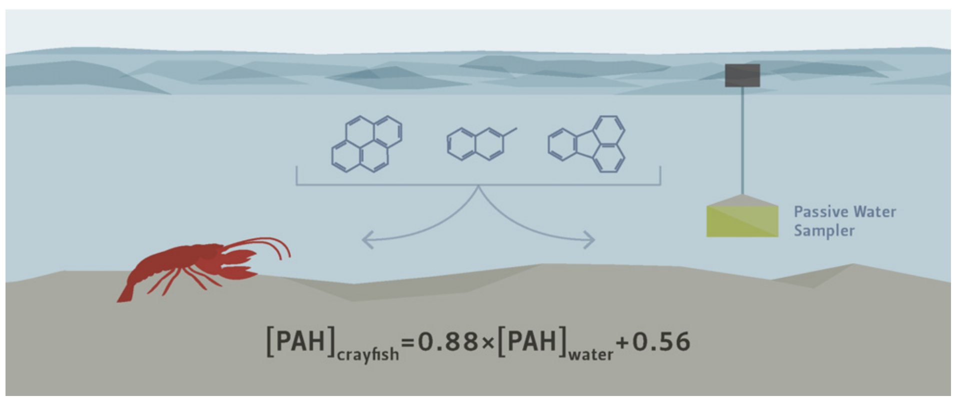
HIGHLIGHTS

- Passive water samplers predict [PAH] in crayfish within a factor of 2, on average.
- The simple model could be adapted to predict risks of eating other shellfish.
- Eating viscera significantly increases cancer risk, compared to eating just tails.
- $\sum$PAH in crayfish were unchanged after 10 years in Superfund areas pre-remediation.
- $\sum$PAH in crayfish were higher after 10 years, upriver of an urban Superfund site.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination of resident aquatic organisms is a major concern for environmental risk assessors. However, collecting organisms to estimate risk is often prohibitively time and resource-intensive. Passive sampling accurately estimates resident organism contamination, and it saves time and resources. This study used low density polyethylene (LDPE) passive water samplers to predict polycyclic aromatic hydrocarbon (PAH) levels in signal crayfish, *Pacifastacus leniusculus*. Resident crayfish were collected at 5 sites within and outside of the Portland Harbor Superfund Megasite (PHSM) in the Willamette River in Portland, Oregon. LDPE deployment was spatially and temporally paired with crayfish collection. Crayfish visceral and tail tissue, as well as water-deployed LDPE, were extracted and analyzed for 62 PAHs using GC–MS/MS. Freely-dissolved concentrations (C_{free}) of PAHs in water were calculated from concentrations in LDPE. Carcinogenic risks were estimated for all crayfish tissues, using benzo[a]pyrene equivalent concentrations (BaP_{eq}). $\sum$PAH were 5–20 times higher in viscera than in tails, and $\sum BaP_{eq}$ were 6–70 times higher in viscera than in tails. Eating only tail tissue of crayfish would therefore significantly reduce carcinogenic risk compared to also eating viscera. Additionally, PAH levels in crayfish were compared to levels in crayfish collected 10 years earlier. PAH levels in crayfish were higher upriver of the PHSM and unchanged within the PHSM after the 10-year period. Finally, a linear regression model predicted levels of 34 PAHs in crayfish viscera with an associated R-squared value of 0.52 (and a correlation coefficient of 0.72), using only the C_{free} PAHs in water. On average, the model predicted PAH concentrations in crayfish tissue within a factor of 2.4 ± 1.8 of measured concentrations. This affirms that passive water sampling accurately

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estimates PAH contamination in crayfish. Furthermore, the strong predictive ability of this simple model suggests that it could be easily adapted to predict contamination in other shellfish of concern.

1. Introduction

Resident aquatic organism contamination is often of concern at sites with environmental pollution. This is especially true when local communities rely on these organisms for food or income. However, characterizing the risk associated with consuming organisms can be challenging. Collecting enough organisms to assess contamination requires specific knowledge about the organism and the local ecosystem, and it is often prohibitively time and resource-intensive. Harvesting large numbers of organisms can also have adverse impacts on local ecosystems. Accurately assessing resident organism contamination is important for improving both human health risk assessments and ecological risk assessments (Bayen et al., 2009; Boehm et al., 2005). Using a predictive approach to assess organism concentrations is attractive because it requires substantially less time and fewer resources than collecting organisms.

In the past 25 years, passive sampling has been gaining momentum as a useful tool for measuring trace levels of contaminants (O'Connell et al., 2014; Petty et al., 2000). Passive samplers measure time-integrated concentrations of the freely dissolved concentration (C_{free}) of contaminants in water. Passive samplers are relatively low-cost, and they do not require energy or maintenance while deployed. Infusing passive samplers with performance reference compounds (PRCs) before deployment further improves their ability to accurately assess contaminant levels (Huckins et al., 2006).

Low-density polyethylene (LDPE) is a widely-used material for making passive samplers (Anderson et al., 2008). When LDPE is deployed in water, hydrophobic organic contaminants (HOCs) diffuse into LDPE from the water into the hydrophobic polymer. This process is analogous to passive uptake by a phospholipid membrane into an organism's tissues, making LDPE well-suited to serve as a surrogate for contamination in organisms (Allan et al., 2011; Booij et al., 2006; Fernandez and Gschwend, 2015).

Numerous studies have compared uptake of HOCs in passive samplers and aquatic organisms. Many of these investigated the potential for caged organisms to serve as sampling devices, or "biomonitoring organisms" (BMOs) (Joyce et al., 2015). Many studies have used LDPE filled with triolein as a sampling device, known as semi-permeable membrane devices (SPMDs). Anderson et al. (2008) co-deployed SPMDs with triolein-free LDPE samplers and concluded that the two samplers behaved sufficiently similarly. Thus, the two will be directly compared in the present study.

Booij et al. (2006) reviewed nine studies comparing SPMDs and BMO mussels, concluding that SMPDs yield less variable results, while identifying similar spatial trends. In the same year, Huckins et al. (2006) reviewed over 30 studies comparing SPMDs and BMOs, concluding that there are substantial overarching similarities in HOC accumulation in aquatic organisms and SPMDs.

Recent research has continued to assess passive samplers as replacements for BMOs in assessing water quality (Alvarez et al., 2014; Bourgeault and Gourlay-France, 2013; Burgess et al., 2015; Joyce et al., 2015) and as tools to estimate contaminant levels in resident organisms (Allan et al., 2011; Fernandez and Gschwend, 2015; Forsberg et al., 2014). While some studies have highlighted key differences between contaminant accumulation in passive samplers and organisms (Boehm et al., 2005; Bourgeault and Gourlay-France, 2013), the majority report good agreement between contaminant accumulation in passive samplers and organisms (Allan et al., 2011; Alvarez et al., 2014; Burgess et al., 2015; Fernandez and Gschwend, 2015; Forsberg et al., 2014; Joyce et al., 2015).

Only a few studies have used predictive tools to assess human health risks associated with consuming resident organisms (Allan et al., 2011; Forsberg et al., 2014). Many studies have used predictive tools to assess the accumulation of HOCs in aquatic organisms. These predictive tools often require chemical or physical partitioning data such as bioaccumulation factors or partition coefficients between lipid and water, and including these can increase prediction variability (Axelman et al., 1999; Booij et al., 2006; Huckins et al., 2006). Notably, Fernandez and Gschwend showed that using porewater C_{free} predicted more accurate and less variable tissue concentrations in clams than using the traditional biota-sediment accumulation factor (Fernandez and Gschwend, 2015). However, even when predicting based on C_{free}, they suggested that using previously published values (to estimate lipid-water partitioning coefficients and the fraction of lipids in the clams) may have increased variability in their predictions (Fernandez and Gschwend, 2015). Additionally, in their 2006 review, Huckins et al. noted that lipid-normalizing tissue concentrations has been debated in the literature since the early 1980s (Huckins et al., 2006). It is therefore desirable to have a predictive tool that requires as few additional inputs as possible.

Forsberg et al. (2014) demonstrated that mathematical models may work as well or better than physical or chemical partitioning data when predicting organism concentrations using passive samplers. If organismal concentrations could be reliably predicted using only passive sampler data and mathematical models, this would greatly reduce the time and information needed for a risk assessor to estimate contaminant levels in resident organisms.

Polycyclic aromatic hydrocarbons (PAHs) are pervasive environmental contaminants that pose risks to human health. Some PAHs are pro-carcinogens, which can be metabolically activated through oxidation by P450 enzymes, creating reactive intermediates that can form DNA adducts (Baird et al., 2005). Diet is the main pathway by which nonsmokers are exposed to PAHs (Phillips, 1999; Zelinkova and Wenzl, 2015).

The Portland Harbor Superfund Megasite (PHSM) is located in the Willamette River in Portland, Oregon. Since the Industrial Revolution, Portland Harbor has been subjected to countless sources of pollution that left a legacy of pollutants, including PAHs (Allan et al., 2012; ATSDR, 2006). In 2000, the area between river mile (RM) 3.5 and 9.2 was designated the PHSM. The PHSM was later expanded, stretching from RM 2.0 to 11.8 as of 2013 (LWG, 2013). This area is home to many species that are harvested by local fishermen, including the native signal crayfish, *Pacifastacus leniusculus* (ATSDR, 2006). Crayfish consumption was listed as a main route of exposure to pollutants in the Agency for Toxic Substances and Disease Registry (ATSDR)'s Public Health Assessment (PHA) for the PHSM (ATSDR, 2006; ATSDR, 2011).

It has been previously observed that PAHs accumulate in crayfish (Jewell et al., 1997). This is partly due to crayfish having less efficient cytochrome P450 systems than finfish (Levengood and Schaeffer, 2011). Additionally, signal crayfish in this portion of the Willamette likely spend their whole lives in Portland Harbor due to their small home range. This means they are exposed for much more of their lifespans than organisms that only pass through the PHSM (ATSDR, 2006). The combination of reduced metabolism and increased exposure duration may lead to greater bioaccumulation of pollutants in crayfish than in finfish. A similar dynamic would likely be observed in other shellfish