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Spatial and temporal trends in occurrence of emerging and legacy contaminants in the Lower Columbia River 2008–2010

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HIGHLIGHTS

- SPMDs and POCIS were used to track trends in contaminant concentrations.
- Contaminant profiles were related to surrounding land-use.
- Temporal trends are poorly defined while chemical loadings followed rainfall levels.

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ABSTRACT

The Lower Columbia River in Oregon and Washington, USA, is an important resource for aquatic and terrestrial organisms, agriculture, and commerce. An 86-mile stretch of the river was sampled over a 3 year period in order to determine the spatial and temporal trends in the occurrence and concentration of water-borne organic contaminants. Sampling occurred at 10 sites along this stretch and at 1 site on the Willamette River using the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) passive samplers. Contaminant profiles followed the predicted trends of lower numbers of detections and associated concentrations in the rural areas to higher numbers and concentrations at the more urbanized sites. Industrial chemicals, plasticizers, and PAHs were present at the highest concentrations. Differences in concentrations between sampling periods were related to the amount of rainfall during the sampling period. In general, water concentrations of wastewater-related contaminants decreased and concentrations of legacy contaminants slightly increased with increasing rainfall amounts.

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1. Introduction

The Columbia River provides important hydroelectric power generation, valuable recreational and tribal fisheries, extensive recreational areas and scenic beauty, and habitat for wildlife and fish. The lower Columbia River below Bonneville is the largest remaining free-flowing reach not impounded by hydroelectric dams in the Columbia Basin, and is critical to the viability of culturally significant fish populations (anadromous and resident), as well as a myriad of other aquatic and terrestrial organisms. Fish, wildlife, and human populations along the lower Columbia River are exposed to an ever-growing variety of contaminants as a result of increasing urbanization, industrialization and agricultural development (Nilsen and Morace, 2014–in this issue).

The work presented here is part of the US Geological Survey's (USGS) Columbia River Contaminants and Habitat Characterization (ConHab, http://or.water.usgs.gov/proj/Conhab/) joint effort to address how emerging contaminants, such as polybrominated diphenyl ether flame retardants (PBDEs) and endocrine disrupting compounds (EDCs), impact fish, osprey, and other wildlife in the basin. One of the purposes of the ConHab project is to fill knowledge gaps associated with the occurrence and bioaccumulation of PBDEs and EDCs to improve the ability of management agencies to evaluate the actions that are the most likely to result in improving river and estuarine conditions for salmonids and other organisms. The presence and effects of these emerging contaminants are important issues that have high scientific and public visibility and potentially important implications for people, fish, and wildlife in the Columbia River Basin.

Recent studies (Lower Columbia River Estuary Partnership, 2007; Johnson et al., 2006) have quantified PBDE contamination in the lower Columbia River using semipermeable membrane devices (SPMDs). The patterns of PBDE contamination observed in these SPMDs matched those observed in juvenile salmon collected during the same time period. Additionally, anthropogenic wastewater indicators, including some EDCs, were measured in the water column (Lower Columbia River Estuary Partnership, 2007) and in bed sediment (Nilsen et al., 2007).

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In general, a higher proportion of these compounds were detected in the bed sediment than in the water column and at higher concentrations. The connection between these results in the environment (water and sediment) and in salmon is complicated by the migratory nature of salmon.

Passive sampling devices and a combination of chemical analyses and an *in vitro* assay were used in this study to help assess the presence of organic industrial and wastewater compounds (OWCs) entering the Lower Columbia River. The passive samplers integratively sample organic environmental contaminants over prolonged periods concentrating these contaminants considerably over ambient water concentrations making it easier to detect compounds at low levels. Two of the most widely used and studied passive samplers are the SPMD and the polar organic chemical integrative sampler (POCIS). SPMDs consist of a nonporous layflat polyethylene membrane tube containing a neutral lipid (triolein). They are designed to mimic key aspects of the bioconcentration process, which results in elevated contaminant concentrations after exposure to trace hydrophobic organic contaminants (compounds with moderate to high octanol–water partition coefficients [K_{ow}] greater than 3) in aquatic environments. The POCIS is designed to mimic an organism's exposure to hydrophilic organic contaminants with low to moderate K_{ow} (less than 3), and consists of a solid-phase sorbent or mixture of sorbents contained between two sheets of a microporous polyethersulfone (PES) membrane. Sampling of compounds with both of these passive samplers is integrative (*i.e.*, extracted residues are constantly accumulated without significant losses back into the environment) and analyte concentrations are reported as time-weighted average values (Alvarez et al., 2004, 2007; Huckins et al., 2006). These time-weighted average concentrations are important as they provide a measure of exposure to resident fish species which were collected as part of the larger ConHab study (Jenkins et al., 2014–in this issue; Nilsen et al., in this issue-b; Torres et al., in this issue).

2. Methods

2.1. Study design/site selection

The work described herein contains both a spatial and temporal component covering approximately 86 river miles and three years of field sampling. Initially, nine locations were sampled during the spring and fall of 2008 along the Lower Columbia River starting at Skamania and ending at Beaver Army Terminal, and one site on the Willamette River at Keizer (Table 1, Fig. 1) to determine the gradient of chemical occurrence under predicted high (spring) and low (fall) flow conditions. The results from this first year reconnaissance study were used to select three sites for more intensive chemical and biological sampling in years 2 and 3. Skamania, with low urban influence, along with Columbia City and Longview, both with moderate to high urban influence, were selected for the intensive studies. Results of the chemical profiles in the water column are discussed in this work. Chemical analyses of the sediments and biota (Nilsen et al., in this issue-b), and the biological measurements (Jenkins et al., 2014–in this issue; Torres et al., in this issue) are reported elsewhere.

2.2. Passive samplers

At each study site and deployment period, a single protective canister containing three SPMDs and three POCIS were deployed. Two of the three SPMDs were fortified with performance reference compounds (PRCs) during construction. The PRCs (phenanthrene-d_{10}, pyrene-d_{10}, PCB congeners 14, 29, and 50) are used to adjust uptake kinetics determined in the laboratory for the *in situ* environmental conditions such as flow, temperature, and the buildup of a biofilm on the sampler's surface (Huckins et al., 2006).

2.3. Processing and analysis

2.3.1. SPMDs

The SPMDs were processed according to established procedures including dialytic recovery of the sequestered analytes, enrichment/fractionation using size exclusion chromatography (SEC), and fractionation using adsorption chromatography (Alvarez et al., 2008, 2012; Huckins et al., 2006). Specific instrument conditions and calibration techniques for the methods described below are reported elsewhere (Alvarez et al., 2008, 2012). One of the two PRC–SPMDs from each canister and field and laboratory blank were designated for the analysis of organochlorine pesticides (OCs), total PCBs, and select PBDEs (congeners 28, 49, 99, 100, and 153). Following dialysis and SEC fractionation, these samples underwent additional cleanup by passing the extracts through a 5 g gravity-flow Florisil column and then on a 5 g gravity-flow silica gel column generating a PCB fraction and an OC/PBDE fraction. Each fraction from the Silica Gel step was analyzed using a Hewlett-Packard®

Table 1
Locations, sampling dates, and precipitation amounts for the study sites in the Lower Columbia River basin.

Site name Coordinates (N, W)	Spring 2008 rainfall (cm)	Fall 2008 rainfall (cm)	Spring 2009 rainfall (cm)	Spring 2010 rainfall (cm)
Willamette River at Keizer 45°02′9″, 123°4′13.3″	4/24/08–5/21/08	9/18/08–10/15/08	–	–
Skamania 45°36′52.8″, 122°2′28.2″	4/23/08–5/20/08 10.8 cm	9/18/08–10/15/08 11.0 cm	4/8/09–5/4/09 17.2 cm	4/1/10–5/4/10 20.6 cm
Downstream of Government Island 45°36′5.9″, 122°36′43.1″	4/21/08–5/21/08	9/16/08–10/14/08	–	–
Downstream of Hayden Island 45°38′27″, 122°44′13.9″	4/21/08–5/21/08	9/16/08–10/14/08	–	–
Willamette River at Multnomah Channel 45°37′2.7″, 122°47′40.2″	4/21/08–5/21/08	9/16/08–10/14/08	–	–
Mouth of Multnomah Channel 45°50′38.7″, 122°48′8.9″	4/21/08–5/19/08	9/16/08–10/14/08	–	–
Columbia City 45°55′11.8″, 122°48′44.4″	4/21/08–5/19/08 4.0 cm	9/16/08–10/14/08 5.8 cm	4/7/09–5/6/09 11.6 cm [a]	3/31/10–5/5/10 5.9 cm [a,b]
Between Lewis and Cowlitz 46°3′37″, 122°52′56.1″	4/22/08–5/19/08	9/17/08–10/14/08	–	–
Upstream Longview 46°5′23.44″, 122°54′47.27″	–	–	–	3/31/10–5/3/10
Longview 46°5′54.9″, 122°56′10.8″	4/22/08–5/19/08 2.7 cm	9/17/08–10/14/08 4.2 cm	4/7/09–5/5/09 9.5 cm	3/31/10–5/3/10 12.3 cm
Beaver Army Terminal 46°11′5.6″, 123°11′15.1″	4/22/08–5/19/08	9/17/08–10/14/08	–	–

[a] Precipitation amounts for Columbia City during the spring 2009 and spring 2010 periods were not available, therefore levels from the adjacent city, St. Helens, OR, were used.
[b] Daily precipitation amounts for the spring 2010 period at St. Helens, OR were not available for 20 of the 36 days.