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Contaminants of legacy and emerging concern in largescale suckers (*Catostomus macrocheilus*) and the foodweb in the lower Columbia River, Oregon and Washington, USA☆

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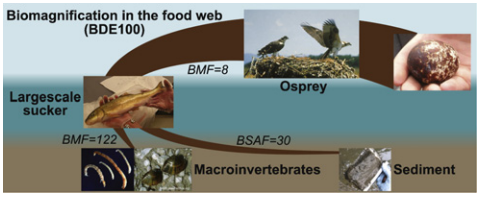
HIGHLIGHTS

- Several contaminant classes were detected at all sites and in nearly all largescale sucker tissues sampled.
- Contaminant concentrations were highest in fish livers, followed by brain, stomach, gonad, and fillet.
- Contaminants in sediments, fish tissues, and osprey eggs increased moving downstream along an exposure gradient.
- Contaminant concentrations exceeded environmental quality benchmarks in some cases.
- Biomagnification of BDE47, 100, 153, and 154 occurred in largescale suckers and osprey eggs.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated occurrence, transport pathways, and effects of polybrominated diphenyl ether (PBDE) flame retardants and other endocrine disrupting chemicals (EDCs) in aquatic media and the foodweb in the lower Columbia River. In 2009 and 2010, foodweb sampling at three sites along a gradient of contaminant exposure near Skamania (Washington), Columbia City (Oregon) and Longview (Washington) included water (via passive samplers), bed sediment, invertebrate biomass residing in sediment, a resident fish species (largescale suckers [*Catostomus*

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macrocheilus]), and eggs from osprey (*Pandion haliaetus*). This paper primarily reports fish tissue concentrations. In 2009, composites of fish brain, fillet, liver, stomach, and gonad tissues revealed that overall contaminant concentrations were highest in livers, followed by brain, stomach, gonad, and fillet. Concentrations of halogenated compounds in tissue samples from all three sites ranged from <1 to 400 nanograms per gram of wet tissue. Several chemical classes, including PBDEs, organochlorine pesticides, and polychlorinated biphenyls (PCBs), were detected at all sites and in nearly all fish tissues sampled. In 2010, only fish livers were sampled and inter-site concentration differences were not as pronounced as in 2009. Chemical concentrations in sediments, fish tissues, and osprey eggs increased moving downstream from Skamania to the urbanized sites near Columbia City and Longview. Numerous organochlorine (OC) pesticides, both banned and currently used, and PBDEs, were present at each site in multiple media and concentrations exceeded environmental quality benchmarks in some cases. Frequently detected OC compounds included hexachlorobenzene, pentachloroanisole, dichlorodiphenyltrichloroethane (DDT) and its degradates, chlorpyrifos, and oxyfluorofen. Biomagnification of BDE47, 100, 153, and 154 occurred in largescale suckers and osprey eggs. Results support the hypothesis that contaminants in the environment lead to bioaccumulation and potential negative effects in multiple levels of the foodweb.

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1. Introduction

The Columbia River is the principal source of hydroelectric power and water for irrigation and municipal uses in the Pacific Northwest and is invaluable as a scenic-recreational area and tribal fishery. The river has been extensively altered and its habitat, wildlife, and fisheries must deal with physical stresses such as increased water temperatures, excessive dissolved gases, diminished summer flows, and loss of fish rearing habitats. Further, the biota is also subjected to physicochemical stresses from contaminants discharged in agricultural and urban stormwater runoff. There is an urgent need to investigate the vulnerability of the Columbia River foodweb to the quantity, spatial patterns, transfer, and accumulation rates of chemicals of emerging and legacy concern (Naiman et al., 2012).

For the last few years, the U.S. Geological Survey (USGS) has been conducting a study of contaminants in the lower Columbia River (LCR) and their effects on parts of the foodweb. This work, dubbed the Columbia River Contaminants and Habitat Characterization (ConHab) study, has focused on areas within the LCR below Bonneville Dam (RM 146.1). This is the largest remaining free-flowing reach and supports a variety of culturally significant anadromous and resident fish populations and other aquatic and terrestrial organisms. The Willamette River basin, where about 2.5 million people – roughly two-thirds of Oregon's population – reside, joins this reach of the river. As such, the river in this area is heavily urbanized and severely altered. Several fish species in the area are First Foods for Native American populations (CRITFC, 2011) that depend on these resources and are disproportionately exposed to fishborne contaminants due to their high fish consumption rate (ODEQ, 2008a,b).

In the early 2000s, concentrations of polybrominated diphenyl ether (PBDE) flame retardants doubled in fish in the upper Columbia River every 1.6 years (Rayne et al., 2003). These chemicals inhibited osprey reproduction in terms of young produced per nest and concentrations in eggs increased rapidly, with the highest concentrations in downstream areas (Henny et al., 2009, 2011). Flame retardant chemicals are widespread in the LCR and in juvenile salmon tissues, especially near urban and industrial areas (LCREP, 2007). In some species of vertebrates, PBDEs alter thyroid function, reduce sperm counts, and delay sperm maturation by interfering with androgen synthesis (Kuriyama et al., 2005). Contaminants of emerging concern (CECs), which include PBDEs, are present in many waters of the U.S. (Kolpin et al., 2002; Focazio et al., 2008), including effluent reaching the Columbia River (Morace, 2012) and in sediments of the LCR (Nilsen et al., 2014), and some of those compounds accumulate in fish tissue (Brooks et al., 2005; Ramirez et al., 2009; Schultz et al., 2010).

The interdisciplinary ConHab study investigated the chemical fate and effects of multiple contaminant classes in aquatic environmental media and in several levels of the foodweb in the LCR. Previous studies have attempted to link contaminant concentrations with effects in fish in large aquatic systems, including the Mississippi River Basin (Schmitt, 2002), Rio Grande Basin (Schmitt et al., 2005), Columbia River Basin (Hinck et al., 2006a), Yukon River Basin (Hinck et al., 2006b), the Colorado Basin (Hinck et al., 2007), and San Francisco Bay (Brar et al., 2010), among others. The primary objective of the ConHab study was to sample representative members of the foodweb at sites with a chemical exposure gradient and use biomarkers to assess physiological effects of contaminants on organisms to investigate links between environmentally relevant chemical concentrations and organism health. This paper specifically addresses fish tissue chemical concentrations and bioaccumulation up the trophic levels sampled.

1.1. Site description

The ConHab study focused on the lower tidally influenced portion of the Columbia River from Bonneville Dam, the lowermost dam on the Columbia, to the mouth (Fig. 1). Contaminants can enter the lower Columbia River from many sources, including municipal and industrial permitted discharges, atmospheric deposition, urban and industrial nonpoint pollution, and runoff from agricultural and forested areas (Fuhrer et al., 1996; LCREP, 2007). In addition to inputs from the lower Columbia region, contaminants may also be transported to the lower river from areas of known contamination above Bonneville Dam, e.g., the Yakima (Fuhrer et al., 2004) and Snake (Clark et al., 1998) Rivers.

The three areas selected for detailed foodweb investigations in 2009 and 2010, from highest to lowest contaminant levels, were the Columbia River near Longview (river mile 66), near Columbia City (river mile 82), and near Skamania (river mile 140). The sites were located far enough apart to avoid feeding range overlap between sites. The Longview site is located in the heart of the Port of Longview, and is influenced by the Cowlitz River (Fig. 1). On the Oregon side at this location, effluent from two local wastewater-treatment plants (WWTPs) enters the Columbia River upstream and downstream of the Longview sampling area. The Columbia City site is bracketed by two small Oregon cities, St. Helens on the upstream end and Columbia City on the downstream end. The Multnomah Channel drains into the Columbia River at the upstream end of this site. The WWTP at St. Helens serves only 10,000 people but has a fairly large design flow (45 million gallons per day) because of the paper mill aeration pond collocated with the treatment plant. Lake River, which receives much of the stormwater runoff from Vancouver, Washington, via Vancouver Lake, enters the Columbia River just upstream of the Multnomah Channel. The Skamania site is the most upstream site. It is located just downstream of Bonneville Dam and it is upstream of the urban areas of Portland and Vancouver. Because of past studies showing lower levels of contamination at this site (Fuhrer et al., 1996; Morace, 2006; Johnson et al., 2006), it was chosen as a lower-exposure reference site for the study. There are no known

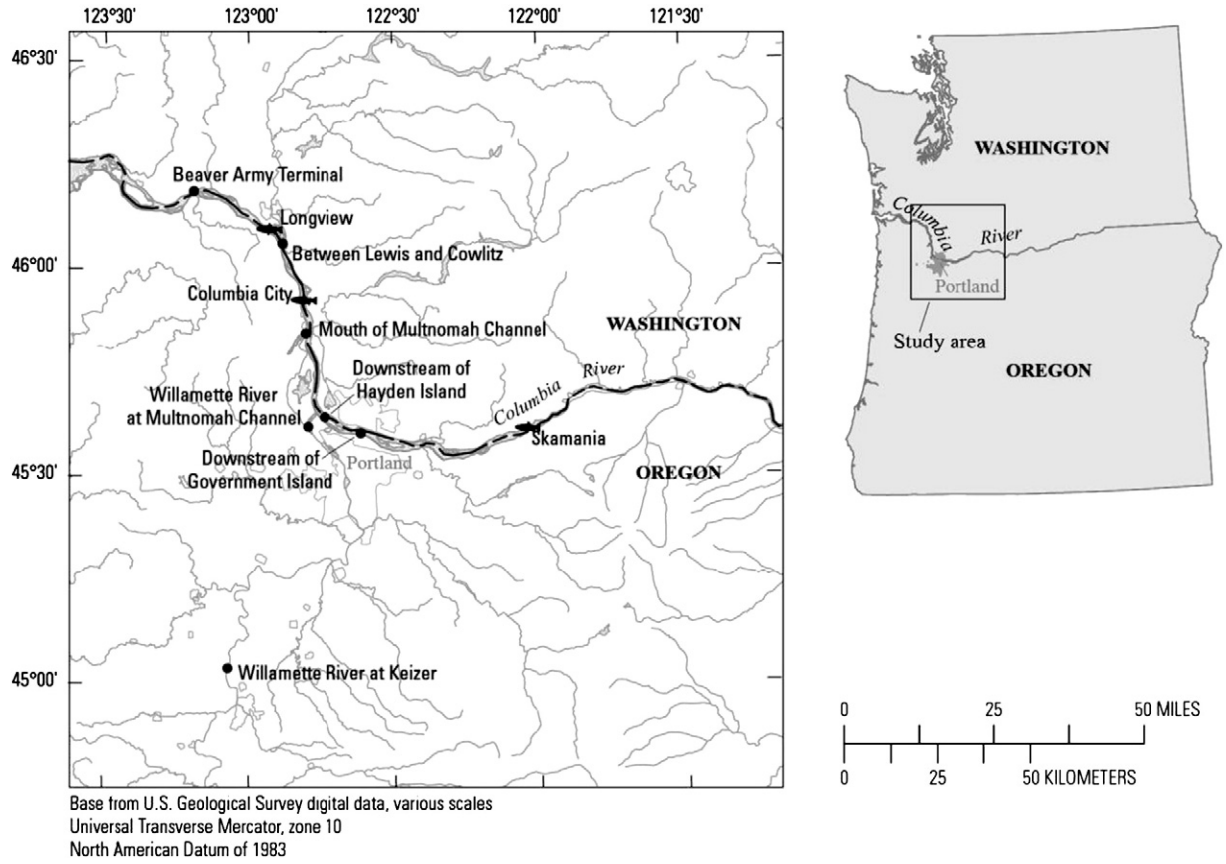

Fig. 1. Map of the region with inset of the study area. The three Lower Columbia River study area locations are indicated by a fish symbol: Skamania, Columbia City, and Longview. (Map courtesy of NWRC and USGS Science Publishing Network, Lafayette Publishing Service Center, Louisiana, USA).

inputs of potential contamination near the site except for what may be delivered from upstream.

2. Materials and methods

2.1. Collection, shipment, and storage of samples

Sampling equipment was free of materials that might leach interferences, absorb compounds of interest, or potentially contaminate or degrade the tissue samples. Field-sampling procedures followed those typically used to collect samples for trace organic compound analyses (Ward and Harr, 1990; Lane et al., 2005). Some of the compounds that were determined in this study are also found in commonly used products, such as soaps, electronics, and textiles; therefore, precautions were followed to avoid contamination (Lewis and Zaugg, 2003).

The sampling tools were cleaned with Liquinox® and methanol before each sample was collected to prevent cross-contamination between samples. Tissue and sediment samples were stored in certified organics-free (I-CHEM® brand) jars. Samples were frozen in the field as soon as possible after collection and shipped on wet or dry ice via overnight service to the USGS National Water Quality Laboratory (NWQL) in Denver, CO where they were analyzed for several organic contaminant classes.

Largescale suckers were sampled by electroshocking on 4–7 May, 2009, and on 3–5 May, 2010. In 2009, 16 individual males were collected in Skamania, 15 males in Columbia City, and 15 males in Longview; in 2010, 15 males were collected in Skamania, 14 males in Columbia City, and 15 males in Longview. Fish were euthanized using MS-222 (tricaine methane sulphonate; Cat. No. E10521, Sigma-Aldrich, St. Louis, MO, USA) and dissected on site to provide tissues for several different analyses (Jenkins et al., 2014–in this issue; Torres et al., 2014–in this issue).

For fish tissue contaminant analyses in 2009, gonad, brain, fillet, stomach, and liver tissues were dissected from male fish and analyzed. Male fish were the major focus of contaminant analyses because males may be more susceptible to certain contaminants than females (Lema et al., 2008; Muirhead et al., 2006). To contain costs while still assessing different tissue types, like tissues from fish caught at each site were composited and homogenized before analysis; therefore, each data point is a composite of organs from all fish caught as described above. In 2010, only livers were analyzed from each male fish collected at each site. This was done to allow statistical comparisons of liver contaminant burdens between sites and since concentrations were highest in livers in 2009. Classes of target compounds included selected fire retardants, anthropogenic waste indicator (AWI) compounds (e.g., triclosan and methyl-triclosan), pesticides, and others (Appendix A, Table A1).

Sediments were collected in 2009 from each field site using a depth-based generalized random tessellation stratified (GRTS) sampling pattern (Stevens and Olsen, 2004) on each of five transects within the site. Samples from each transect were composited to limit analytical costs. Benthic invertebrates were picked from each composited sediment sample, and then sediment organic matter (SOM) targeted for chemical analysis was separated from the bulk sediment using a 64-micron sieve. The sediment sampling design and results are described in detail elsewhere (Counihan et al., 2014–in this issue).

At each study site, a single protective canister containing three SPMDs was deployed for a period of 30 days. The SPMDs were processed according to established procedures including dialytic recovery of the sequestered analytes, enrichment/fractionation using

size exclusion chromatography, and fractionation using adsorption chromatography (Alvarez et al., 2008, 2012; Huckins et al., 2006). Detailed methodology was described by Alvarez et al. (2014–in this issue).

One partially incubated osprey egg was randomly collected from each of 5 nests within each study site to determine contaminant concentrations. Collection procedures were described in detail by Henny et al. (2011). Egg analysis was described in detail by Gauthier et al. (2008). Remains of fish collected from nest sites indicated that largescale suckers were the dominant prey species (Henny et al., 2011).

2.2. Laboratory analysis of fish tissue and sediment

All samples received at the NWQL were frozen at −20 °C and thawed just prior to sample preparation. All tissue samples were thoroughly homogenized using a blender specially fitted with glass, stainless steel, and Teflon® parts. A laboratory reagent/sand blank and a spiked sample were prepared with each set (up to 10 environmental samples), and 50 μL of surrogate solution (see Appendix A) were added to each sample. Spike samples were fortified with 100 μL of solution containing all the method compounds at 2 nanograms per gram. The compounds of interest (see Appendix A, Table A1) were extracted from 0.5 to 1.5 g of homogenized tissue sample (by wet weight), or 5 to 10 g of homogenized sediment sample (by wet weight) using a pressurized liquid extraction (PLE) system (Dionex ASE ™ 200, Sunnyvale, Calif., USA). The sample extracts were prepared similarly to the procedure outlined by Burkhardt et al. (2005). PLE settings, extract cleanup procedures, surrogate spiking solution, and internal standard solutions are described in Appendix A.

The method compounds were separated in sample extracts by capillary column gas chromatography (GC) and detected by negative ion mass spectrometry (MS), with ammonia as the reaction gas, using selected ion monitoring (Agilent Technologies, Model 5975 GC/MS; see Appendix A for GC and MS conditions). Sample results are reported in nanogram per gram for tissues on a wet weight basis and for sediments on a dry weight basis. The qualitative identification of compounds detected by the mass spectrometer can be verified, although not necessarily reliably quantified, at concentrations less than the method quantitation limit. Any such detection is reported as an estimated concentration only (Appendix C).

2.3. Quality assurance/quality control

The final method as well as the environmental samples was validated against a comprehensive set of performance-based quality control parameters including laboratory blanks, matrix spikes, replicate samples, and surrogate recovery. Laboratory blanks analyzed as part of this study for tissues and sediments (N = 7) consisted of reagent grade sand carried through the extraction, cleanup, and analysis steps. Recoveries in laboratory-spiked samples (N = 6) for method validation ranged from 45 to 156% for fish tissue, 33 to 126% for invertebrate tissue, and 46 to 179% for bed sediment (Appendix A). Mean recoveries of surrogates in these method validation environmental samples were 71%, 102%, and 85% for fish tissue, 77%, 70%, and 69% for invertebrate tissue, and 74%, 96%, and 79% for bed sediment for dibromooctafluorobiphenyl, DDT-d_8, and PCB 202-$^{13}C_{12}$, respectively. Thirty percent of samples were run in replicate and RSDs for compounds detected in multiple repeat measures of a sample were 23% for pesticides, 13% for polychlorinated biphenyls (PCBs), and 17% for PBDEs. Where replicates were analyzed, measureable concentrations of compounds were detected in both replicates. Equivalent blanks, matrix spikes, and all other laboratory QC procedures were followed in both years.

The limit of detection (LOD) was calculated as the amount of analyte in the spiked sample that produced a signal greater than three times the background signal. Method detection limits (MDLs) were determined for each compound (Table A1) by spiking 7 replicates of representative sediment with a mixture of the compounds fortified at 0.1 nanogram per gram and 8 replicates of representative tissue with a mixture of the compounds fortified at 0.5 nanogram per gram. For each set of spiked samples, the sample standard deviation was computed and the MDL calculated from the following formula:

$$\mathrm{MDL} = S \times t_{(n-1,1-\alpha=0.99)},$$

where

S standard deviation of replicate analyses, in nanograms per gram, at the lowest spike concentration;
n number of replicate analyses; and
$t_{(n-1,\ 1-\alpha=0.99)}$ Student's t-value for the 99-percent confidence level with $n-1$ degrees of freedom.

2.4. Statistics

Numerical comparisons of concentrations measured on composite tissue samples at each site in 2009 were based on calculated relative standard deviations (RSDs) based on laboratory method variability. Contaminant concentrations in individual fish livers collected in 2010 were not normally distributed and were transformed to log base 10. Non-detections were assigned a value of zero and a constant of 1.0 was added to each concentration before determining the log to avoid zeros and values less than one. Calculated means of the normalized values were analyzed by one-way ANOVA for each contaminant. Significant F values were followed by the Tukey–Kramer honestly significant difference test to identify specific differences between the sites (Appendix B, Table B1). We performed all statistical analyses using JMP Release 7 software (SAS Institute, Inc., Cary, NC), and the accepted level of significance for all tests was $p < 0.05$. The extreme studentized deviate test was used to identify outliers (extreme studentized deviate [ESD] Z = absolute value [mean-value] / standard deviation, where the critical Z for N = 15 is 2.55; Barnett and Lewis, 1994).

2.5. Calculations

Biomagnification factors (BMFs) and biota-sediment bioaccumulation factores (BSAFs) were calculated as follows for BDE47, 100, 153, and 154, which had frequency of detection sufficient to facilitate comparisons between different media and trophic levels.

$$\mathrm{BMF} = \mathrm{CB}/\mathrm{CD}$$

where CB = chemical concentration in biota (wet weight); CD = chemical concentration in organism's diet (mass chemical per kg of food).

$$\mathrm{BSAF} = \mathrm{CB}/\mathrm{CS}$$

where CS = chemical concentration in sediment (wet weight).

3. Results and discussion

3.1. Chemical concentrations in fish tissues 2009

Concentrations of halogenated compounds in tissues sampled in 2009 ranged from <1 to >400 ng g^{-1} wet tissue weight. The PBDEs, organochlorine pesticides (including DDT and its degradates [ΣDDT]), and PCBs were detected at all sites in nearly all organs tested. These contaminant concentrations generally showed an increasing trend moving

downstream, with lowest concentrations for most contaminants in Skamania fish and highest concentrations in Longview fish (Fig. 2). Chemical concentrations were highest in livers, followed by brain, stomach, gonad, and fillet. The PBDE congeners most frequently detected and at the highest concentrations were BDE47 > 100 > 154 > 153.

Fish tissue analysis provides bioavailable concentrations that are closer to the site of toxic action than concentrations in water or sediment (i.e., the tissue-residue approach [Meador et al., 2008]), and comparisons to available benchmarks provide relevant context for the concentrations measured. Environmental quality guidelines do not exist for all of the chemicals analyzed in this study. The U.S. Food and Drug Administration (FDA) established deleterious substance guidelines for human health for some of the compounds (U.S. FDA, 2001). All of the chlorinated pesticides and PCBs analyzed in this study were well below the established FDA guidelines for human health. However, several compounds exceeded Oregon Department of Environmental Quality (ODEQ) acceptable tissue levels (ATLs) for carcinogens in fish tissues for human consumption and/or wildlife consumption (Table 1). The ΣDDT exceeded ODEQ ATLs for chemicals in whole fish consumed by wildlife (specific to egg development in osprey and eagles) in most tissues at all sites. The ΣDDT concentrations also exceed the ATLs for carcinogens in fish fillet for human consumption in many tissues, including fillet at all sites. The ΣPCB concentrations exceeded the ATLs for carcinogens in fish fillet for human consumption in many tissues at all sites, including fillet at Columbia City.

Acceptable tissue levels have not been calculated for PBDEs, although PBDEs may have the potential for toxicity similar to PCBs due to their similar chemical structures (Pijnenburg et al., 1995; de Boer et al., 1998; Eriksson et al., 1998). Similar toxicological effects have been shown in mammals (Hallgren et al., 2001), and PBDEs can also affect hormone levels in the thyroid and cause reproductive (Kuriyama et al., 2005) and neurological (Ibhazehiebo et al., 2011) effects. The PBDE concentrations were lower than PCB concentrations in nearly all tissues at Skamania and higher than PCB concentrations in all tissues at Columbia City and Longview (Table 1). Concentrations of PBDEs in fish fillet at Columbia City and Longview were comparable to those measured in fish fillets in the Lower Columbia River in 2005 (Johnson et al., 2006) and higher than at most other Columbia Basin sites sampled in 2005 (Johnson et al., 2006). The ΣDDT concentrations were comparable; while PCB concentrations were within the low end of the range measured in largescale suckers by Hinck et al. (2006a). Chlordane and dieldrin concentrations in our study were lower than those measured previously in largescale suckers in the Columbia River (Hinck et al., 2006a).

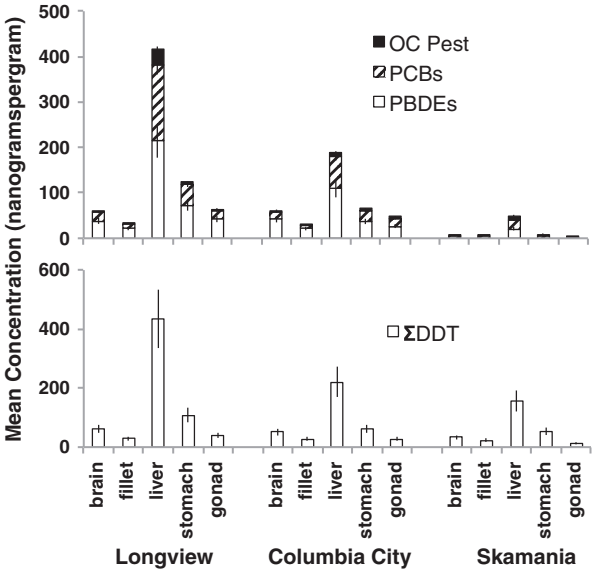

Fig. 2. Contaminant concentrations (nanograms per gram, wet weight) in fish tissue composites for the three sites from 2009 collection. Error bars based on reported %RSD values.

Table 1
Chemical concentrations (nanogram per gram, wet weight) in composites of male fish tissues from 2009 compared to acceptable tissue levels (ATLs) (ODEQ, 2007). Bold values indicate an ATL exceedence. Italicized values indicate no ATL has been established.

		Chlordane[a]	Dieldrin	HCB[b]	ΣDDT[c]	ΣPCB[d]	ΣPBDE[e]
Skamania	Brain	nd	nd	0.499	**33.2**	**5.11**	*nd*
	Fillet	0.678	nd	0.300	**23.0**	4.61	*0.426*
	Liver	1.26	**1.50**	1.37	**157**	**20.0**	*21.0*
	Stomach	0.773	nd	0.540	**53.3**	**5.26**	*0.507*
	Gonad	nd	nd	0.159	12.0	0.976	*0.168*
	Average[f]	0.542	0.300	0.574	**55.7**	**7.20**	*4.42*
Columbia	Brain	0.825	nd	**0.952**	**51.1**	**15.7**	*42.3*
	Fillet	0.477	nd	0.286	**27.0**	**6.67**	*21.2*
	Liver	2.15	nd	**2.85**	**221**	**70.9**	*109*
	Stomach	1.19	nd	**0.937**	**61.2**	**21.6**	*38.0*
	Gonad	0.763	nd	**1.15**	**27.2**	**17.7**	*26.1*
	Average	1.08	nd	**1.24**	**77.5**	**26.5**	*47.2*
Longview	Brain	0.516	nd	0.956	**60.0**	**19.5**	*38.4*
	Fillet	0.610	nd	0.347	**28.2**	**10.4**	*21.6*
	Liver	**6.14**	**2.96**	**3.90**	**434**	**169**	*214*
	Stomach	1.54	nd	1.36	**107**	**44.3**	*73.5*
	Gonad	0.878	nd	0.602	**40.7**	**17.9**	*42.9*
	Average	1.94	**0.592**	**1.43**	**134**	**52.2**	*78.1*

[a] Sum cis and trans.
[b] HCB = hexachlorobenzene.
[c] ΣDDT includes p,p-DDE and p,p-DDD; p,p-DDT not detected.
[d] ΣPCB includes congeners 110, 118, 138, 146, 149, 151, 170, 174, 177, 180, 183, 187, 194, 206; 101 not detected.
[e] ΣPBDE includes congeners 47, 99, 100, 153, 154; 66, 71, 85, 99, 138, 183 not detected.
[f] Calculated average of the five tissues analyzed.

In parts of the developing world – East Asia, for example – PDBE concentrations in the environment have continued to increase in recent years (Wang et al., 2007; Moon et al., 2012). In contrast, PBDE concentrations in the Pacific Northwest may have begun to decline (Henny et al., 2011), likely due to the phase out of several commercial formulations, although more data is needed to confirm this trend. Our results do not unequivocally reflect a decrease compared to earlier data. More trend information could be gained by repeating sampling several years into the future.

3.2. PBDE bioaccumulation in 2009

Bioaccumulation and biomagnification of chemical contaminants adversely affect key species and foodwebs (Naiman et al., 2012). Although the major results of the sediment and osprey portions of the study are described elsewhere (Counihan et al., 2014–in this issue; Henny et al., 2011), we will consider bioaccumulation and biomagnification between trophic levels here. Not all compounds analyzed in this study had a frequency of detection sufficient to facilitate comparisons between different media and trophic levels. In 2009 only PBDEs were analyzed in osprey eggs. The brominated flame retardants were widely detected and were selected to compare across media and trophic levels. Concentrations were higher at the downstream sites than at the upstream site (Table 2), as was observed in previous studies (Johnson et al., 2006; Henny et al., 2011). Concentrations of PBDE congeners were slightly lower in benthic invertebrate biomass than in SOM. Van der Oost et al. (1988) found PBDEs at lower concentrations in plankton and mollusks than in sediment, whereas PBDEs have been shown to bioaccumulate in benthic invertebrate biomass in a receiving environment dominated by municipal wastewater effluent (Dinn et al., 2012).

Our results reflect biomagnification of PBDE congeners 47, 99, 100, 153 and 154 occurring in the foodweb. The congener with the highest concentration in SOM, fish tissue (based on averaged concentrations measured in 5 tissues), and osprey eggs was BDE47, followed by BDE99 in SOM and osprey eggs, and BDE100 in fish tissues. Biotransformation of PBDEs occurs in fish, is species-specific (Wang et al., 2007; Echols et al., 2013), and may contribute to differences in congener concentration patterns. Bioaccumulation at all levels of the foodweb occurred to a greater degree at the downstream sites compared to upstream site (higher BSAFs at Longview and Columbia City), whereas BMFs were higher at Skamania owing to the relatively lower fish concentrations (Table 2). In wastewater treatment plant effluent from 12 cities in the Columbia River basin, PBDE congeners 47, 99, and 100 were detected most frequently and at the highest concentrations (Morace, 2012), indicating one possible pathway for the delivery of these compounds to the system. In previous studies, biomagnification of 9 PBDEs, including BDE47, 99, 100, 153 and 154 was shown to occur in a lake in China (Hu et al., 2010), while a study of another lake in China found biomagnification of only BDE47, 100, and 154 (Wu et al., 2009), and in a Canadian freshwater foodweb only BDE47 and BDE 206 were found to biomagnify (Law et al., 2006). Differences in PBDE biomagnification in published studies likely owe to species-specific metabolism of PBDEs and/or differences in food chain complexity, study site habitat characteristics, and use patterns, among other factors.

In contrast to our results showing biomagnification of PBDEs in the lower Columbia River, several compounds, including BDE66, BDE183, PCB101, fipronil sulfide, pentachloronitrobenzene, and triclosan, were detected in SOM but not detected in invertebrate biomass or in fish tissues (Appendix C), possibly indicating that these compounds are being metabolized and/or are not bioaccumulating in this foodweb. Although neither triclosan nor methyl triclosan was detected in tissues in this study, these compounds have been shown to bioaccumulate at other sites (Miyazaki et al., 1984; Balmer et al., 2004). As expected based on chemical characteristics, concentrations of PBDEs in water as measured by passive samplers were lower (range ND-1.1 ng L^{-1}; Alvarez et al., 2014–in this issue) than those detected in tissues. As other studies have noted, it is important to consider multiple environmental compartments and trophic levels when assessing contaminant impacts (Mizukawa et al., 2009).

3.3. Chemical concentrations in fish liver tissues 2010

One sample from Skamania was an outlier for all measured contaminants by the ESD test (see Section 2.3 above). Excluding this sample, 11 compounds had statistically different concentrations between sites (Appendix B, Table B1). Ten of these 11 compounds had higher concentration for at least one of the downstream sites compared to Skamania (Fig. 3). Lowest concentrations of PCBs were found at Skamania and PCB concentrations were similar at Longview and Columbia City. Skamania had lower PBDE concentrations than Longview and there were congener-specific differences between Skamania and Columbia City and Columbia City and Longview. Concentration patterns for pesticides and degradates were similar to those for PBDEs, that is, concentrations were lower at Skamania than Longview and there were compound-specific differences between sites.

There are many potential sources of these compounds in the urbanized areas around Columbia City and Longview. For example, anthropogenic waste indicator compounds were detected more frequently and at relatively higher concentrations in treatment plant effluent from Longview than from other cities tested in the Columbia River basin in a previous study (Morace, 2012). Parasite infestation in males analyzed for this study followed the pattern of PDBE concentrations increasing downstream (Torres et al., 2014–in this issue) and it has been shown that PBDEs can compromise immune response in salmonids (Birchmeier et al., 2005) with resulting higher incidence of disease (Arkoosh et al., 2010). Reproductive parameters, including spermatozoan mitochondrial function, viability, apoptosis, and ATP, also showed impairment at the downstream site(s) relative to the upstream site; several parameters, including motility, apoptosis, and ATP were significantly negatively correlated with various contaminant concentrations (Jenkins et al., 2014–in this issue).

Table 2
Geometric means of major PBDE congener concentrations and biota-sediment accumulation factors (BSAFs) and biomagnification factors (BMFs) in the foodweb in 2009.

	Concentration (nanograms per gram, wet weight)				BSAF		BMF	
	SOM	Invertebrate	Average Fish[a]	Osprey Eggs[b]	SOM-invertebrate	SOM LSS	Invertebrate-LSS	LSS-osprey
Longview								
PBDE47	2.63	nd	60.2	175	N/A[c]	22.9	N/A	2.91
PBDE99	1.73	nd	nd	22.5	N/A	N/A	N/A	N/A
PBDE100	0.47	0.12	14.2	106	0.252	30.4	121	7.46
PBDE153	0.19	nd	2.74	37.9	N/A	14.7	N/A	13.8
PBDE154	0.16	nd	0.925	36.0	N/A	5.90	N/A	39.0
Columbia City								
PBDE47	4.33	nd	35.1	131	N/A	8.10	N/A	3.74
PBDE99	3.07	1.83	nd	28.1	0.596	N/A	N/A	N/A
PBDE100	0.84	0.39	9.97	67.3	0.465	11.9	25.6	6.75
PBDE153	0.29	0.40	1.61	21.1	1.38	5.50	4.00	13.1
PBDE154	0.28	0.24	0.579	22.6	0.881	2.09	2.38	39.0
Skamania								
PBDE47	nd	nd	3.24	94.8	N/A	N/A	N/A	29.3
PBDE99	nd	nd	nd	15.2	N/A	N/A	N/A	N/A
PBDE100	0.17	0.13	0.784	42.7	0.779	4.61	5.92	54.5
PBDE153	nd	nd	0.306	12.6	N/A	N/A	N/A	41.3
PBDE154	nd	nd	0.0948	12.6	N/A	N/A	N/A	133

nd (not detected).
SOM (sediment organic matter).
LSS (largescale sucker).
[a] Calculated mean of the five tissues analyzed.
[b] From Henny et al., 2011.
[c] N/A (not applicable) indicates BSAF/BMF not calculated.

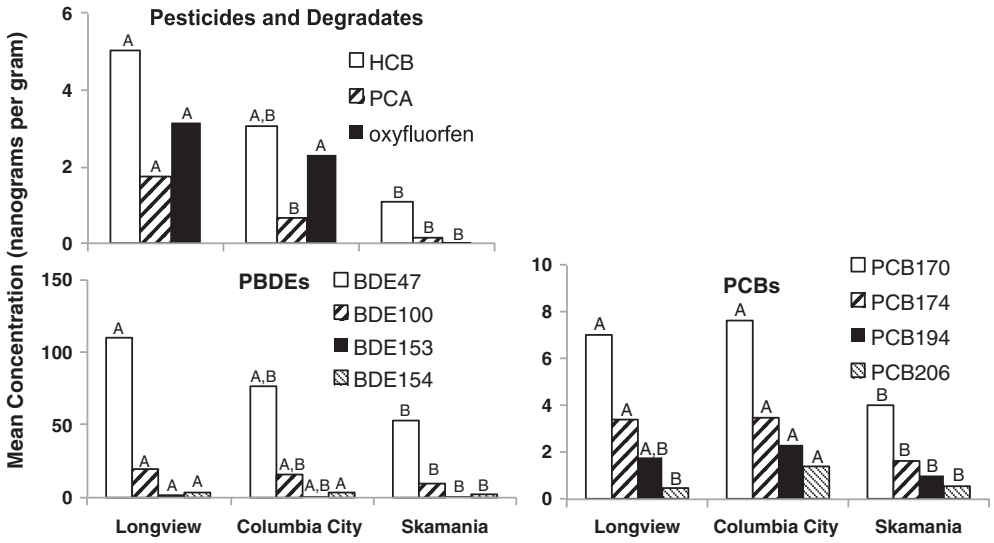

Fig. 3. Mean contaminant concentrations (nanograms per gram, wet weight) in fish liver tissues for the three sites sampled in 2010. Shown are only compounds that had statistically different concentrations between sites. Bars for each contaminant not connected by the same letter are significantly different ($p < 0.05$).

3.4. Comparison of fish tissue concentrations in 2009 and 2010

The different sampling strategies used in 2009 and 2010 each had strengths and weaknesses. The 2009 sampling provided information about concentrations in different fish tissues, as well as allowing assessment of biomagnification in trophic levels; however, the 2009 data did not allow statistical comparisons between sites or to the biomarker data. The 2010 data allowed for statistically robust comparisons, but did not allow the same extent of determination of environmental relevance since benchmarks for wildlife consumption of fish are based on whole body concentrations and those for human consumption are based on fillet. An ideal design would include multiple tissues, abundant sample sizes for males and females, and multiple trophic levels over multiple years. However, the logistical and financial realities nearly always necessitate consideration of the trade-offs. In this case, each year's sampling provided unique information.

Liver tissue concentrations can be compared for 2009 and 2010 since livers were analyzed in both years. The inter-site differences in concentrations were not as pronounced in 2010 as in 2009 (Fig. 4). Concentrations for the contaminant categories were more similar between sites in 2010, although 11 chemicals were statistically different between sites, as discussed above. Several factors would need to be further investigated to explain the annual differences, but one possible inference from our data is that hydrologic conditions may play a role in organismal contaminant burden and biomagnification on shorter timescales than expected. For instance, above normal precipitation occurred during the spring of 2010 (Sandvik and Seiders, 2012), and Skamania received roughly twice the rainfall of Columbia City and Longview (Alvarez et al., 2014–in this issue). Precipitation differences and associated runoff appear to have influenced trends in contaminant concentrations in water at these sites (Alvarez et al., 2014–in this issue). Our tissue data may suggest that year-to-year changes in contaminant body burden could also be influenced by hydrologic conditions. Confirmation of this scenario would require estimation of tissue (liver) residence times for the various contaminants.

3.5. Comparison to chemical concentrations in water as measured by passive samplers

The site trends in estimated contaminant concentrations in water averaged over a 30-day period as measured using passive samplers (Alvarez et al., 2014–in this issue) do not always follow the trends observed in fish tissues (Figs. 4 and 5), sediment (Counihan et al., 2014–in this issue), and osprey eggs (Henny et al., 2011). This likely reflects several factors. One is that passive samplers are effective at

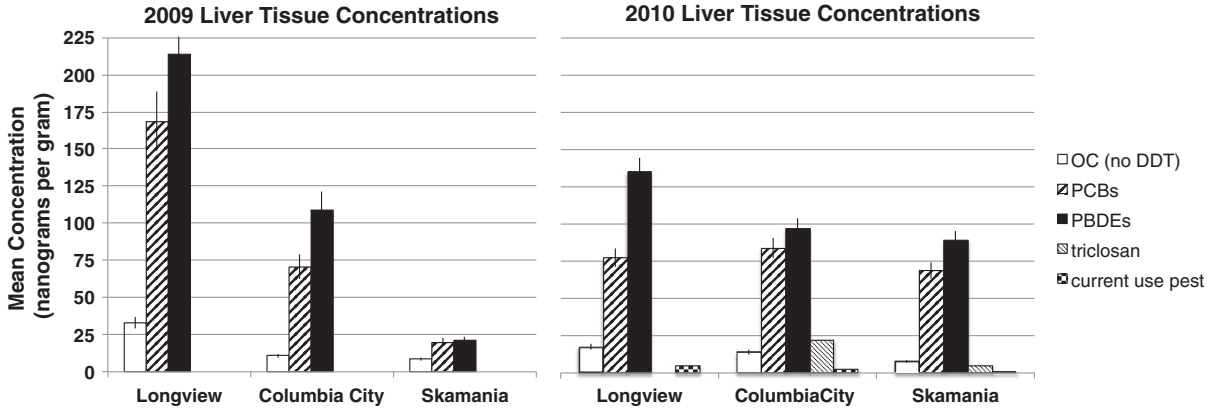

Fig. 4. Comparison of mean contaminant concentrations (nanograms per gram, wet weight) in fish liver tissues sampled in 2009 and 2010 at the three sites.

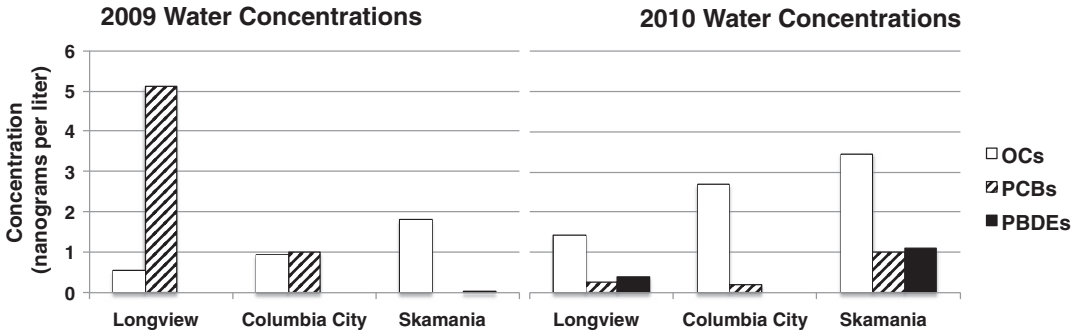

Fig. 5. Estimated contaminant concentrations (nanograms per liter) in water determined from semi-permeable membrane device (SPMD) passive samplers deployed in 2009 and 2010 at the three sites.

integrating contaminant exposure over time, but are spatially constrained to a small point within the foodweb areas, whereas sediments were collected from many locations within each area, and fish move throughout the area. Also, fish generally bioaccumulate contaminants consumed through their diet more readily (Morrison et al., 1997) than by direct uptake from water and sediment. Largescale suckers are bottom feeders, so it follows that fish tissue concentration patterns are similar to those in sediment. These different patterns in the media tested highlight again the importance of assessing multiple environmental compartments and levels of the foodweb for a more accurate understanding of contaminant presence, fate, and potential effects.

4. Conclusions

Numerous organochlorine pesticides, both banned and current-use, including hexachlorobenzene, pentachloroanisole, ΣDDT, chlorpyrifos, and oxyfluorfen, were measured in multiple media and levels of the foodweb at three sites in the lower Columbia River. Biomagnification of PBDE flame retardants occurred in largescale suckers and osprey eggs. BDE47 was the most prevalent PBDE detected in water, sediments, fish tissues, and osprey eggs, but not in invertebrate biomass. Hydrologic conditions may affect fish contaminant body burden and biomagnification. Use of passive samplers in large river systems may require deployment of multiple devices to resolve spatial heterogeneity. Assessing multiple environmental compartments and trophic levels facilitated assessment of physiological effects of contaminants in the foodweb.

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Appendices A–C. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.04.012.

References

Alvarez DA, Cranor WL, Perkins SD, Clark RC, Smith SB, 2008. Chemical and toxicologic assessment of organic contaminants in surface water using passive samplers. J Environ Qual 2008;37:1024–33.
Alvarez DA, Rosen MR, Perkins SD, Cranor WL, Schroeder VL, Jones-Lepp TL, 2012. Bottom sediment as a source of organic contaminants in Lake Mead, Nevada, USA. Chemosphere 2012;88:605–11.
Alvarez DA, Perkins S, Nilsen E, Morace J, 2014. Spatial and temporal trends in occurrence of emerging and legacy contaminants in the lower Columbia River 2008–2010. Sci Total Environ 2014;484:322–30. [in this issue].
Arkoosh MR, Boylen D, Dietrich J, Anulacion BF, Ginaylitalo, Bravo CF, et al, 2010. Disease susceptibility of salmon exposed to polybrominated diphenyl ethers (PBDEs). Aquat Toxicol 2010;98:51–9.
Balmer ME, Poiger T, Droz C, Romanin K, Bergqvist P-A, Müller MD, et al, 2004. Occurrence of methyl triclosan, a transformation product of the bactericide triclosan, in fish from various lakes in Switzerland. Environ Sci Technol 2004;38:390–5.
Barnett V, Lewis T, 1994. Outliers in statistical data. Chichester: John Wiley & Sons; 1994.
Birchmeier KL, Smith KA, Passino-Reader DR, Sweet LI, Chernyak SM, Adams JV, et al, 2005. Effects of selected polybrominated diphenyl ether flame retardants on lake trout (*Salvelinus namaycush*) thymocyte viability, apoptosis, and necrosis. Environ Toxicol Chem 2005;24:1518–22.
Brar NK, Waggoner C, Reyes JA, Fairey R, Kelley KM, 2010. Evidence for thyroid endocrine disruption in wild fish in San Francisco Bay, California, USA. Relationships to contaminant exposures. Aquat Toxicol 2010;96:203–15.
Brooks BW, Chambliss CK, Stanley JK, Ramirez A, Banks KE, Johnson RD, et al, 2005. Determination of select antidepressants in fish from an effluent-dominated stream. Environ Toxicol Chem 2005;24:464–9.
Burkhardt MR, Zaugg SD, Burbank TL, Olson MC, Iverson JL, 2005. Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for semivolatile organic compounds, polycyclic aromatic hydrocarbons (PAH), and alkylated PAH homolog groups in sediment. Anal Chim Acta 2005;549:104–16.
Clark GM, Maret TR, Rupert MG, Maupin MA, Low WH, Ott DS, 1998. Water quality in the Upper Snake River Basin, Idaho and Wyoming, 1992–95. U.S. Geological Survey 1998; Circular 1160; 1998. [Available at http://pubs.usgs.gov/circ/circ1160/circ1160.pdf].
Counihan TD, Waite IR, Nilsen EB, Hardiman J, Elias E, Gelfenbaum G, Zaugg SD, 2014. A survey of benthic sediment contaminants in reaches of the Columbia River Estuary based on channel sedimentation characteristics. USA. Sci Total Environ 2014;484:331–43. [in this issue].
CRITFC, 2011. Tribal Pacific Lamprey Restoration Plan for the Columbia River Basin. Portland, OR: Columbia Inter-Tribal Fish Commission; 2011.
de Boer J, Wester PG, Klamer HJC, Lewis WE, Boon JP, 1998. Do flame retardants threaten ocean life? Nature 1998;394:28–9.
Dinn PM, Johannessen SC, Ross PS, Macdonald RW, Whiticar MJ, Lowe CJ, et al, 2012. PBDE and PCB accumulation in benthos near marine wastewater outfalls: the role of sediment organic carbon. Environ Pollut 2012;171:241–8.
Echols KR, Peterman PH, Hinck JE, Orazio CE, 2013. Polybrominated diphenyl ether metabolism in field collected fish from the Gila River, Arizona, USA: levels, possible sources, and patterns. Chemosphere 2013;90:20–7.
Eriksson P, Jakobsson E, Fredriksson A, 1998. Developmental neurotoxicity of brominated flame-retardants, polybrominated diphenyl ethers and tetrabromo-bis-phenol A. Organohalogen Compd 1998;35:375–7.
Focazio MJ, Kolpin DW, Barnes KK, Furlong ET, Meyer MT, Zaugg SD, et al, 2008. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States — II. Untreated drinking water sources. Sci Total Environ 2008;402:201–16.
Fuhrer GJ, Tanner DQ, Morace JL, McKenzie SW, Skach KA, 1996. Water quality of the Lower Columbia River basin — analysis of current and historical water-quality data through 1994. U.S. Geological Survey 1996; Water-Resources Investigations Report 95–4294; 1996. [Available at http://or.water.usgs.gov/pubs_dir/Pdf/columbia_bistate.pdf].

Fuhrer GJ, Morace JL, Johnson HM, Rinella JF, Ebbert JC, Embrey SS, et al, 2004. Water quality in the Yakima River Basin Washington, 1999–2000. U.S. Geological Survey 2004; Circular 1237; 2004. [Available at http://pubs.usgs.gov/circ/2004/1237/pdf/circular1237.pdf].

Gauthier L, Hebert C, Weseloh D, Letcher R, 2008. Dramatic changes in the temporal trends of polybrominated diphenyl ethers (PBDEs) in herring gull eggs from the Laurentian Great Lakes: 1982–2006. Environ Sci Technol 2008;42:1524–30.

Hallgren S, Sinjari T, Håkansson H, Darnerud P, 2001. Effects of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) on thyroid hormone and vitamin A levels in rats and mice. Arch Toxicol 2001;75:200–8.

Henny CJ, Kaiser JL, Grove RA, Johnson BL, Letcher RJ, 2009. Polybrominated diphenyl ether flame retardants in eggs may reduce reproductive success of ospreys in Oregon and Washington, USA. Ecotoxicology 2009;18:802–13.

Henny CJ, Grove RA, Kaiser JL, Johnson BL, Furl CV, Letcher RJ, 2011. Wastewater dilution index partially explains observed polybrominated diphenyl ether flame retardant concentrations in osprey eggs from Columbia River Basin, 2008–2009. Ecotoxicology 2011;20:682–97.

Hinck J, Schmitt C, Echols K, May T, Orazio C, Tillitt D, 2006a. Environmental contaminants in fish and their associated risk to piscivorous wildlife in the Yukon River Basin, Alaska. Arch Environ Contam Toxicol 2006a;51:661–72.

Hinck JE, Schmitt CJ, Blazer VS, Denslow ND, Bartish TM, Anderson PJ, et al, 2006b. Environmental contaminants and biomarker responses in fish from the Columbia River and its tributaries: spatial and temporal trends. Sci Total Environ 2006b;366:549–78.

Hinck J, Blazer V, Denslow N, Echols K, Gross T, May T, et al, 2007. Chemical contaminants, health indicators, and reproductive biomarker responses in fish from the Colorado River and its tributaries. Sci Total Environ 2007;378:376–402.

Hu G-c, Dai J-y, Xu Z-c, Luo X-j, Cao H, Wang J-s, et al, 2010. Bioaccumulation behavior of polybrominated diphenyl ethers (PBDEs) in the freshwater food chain of Baiyangdian Lake, North China. Environ Int 2010;36:309–15.

Huckins JN, Petty JD, Booij K, 2006. Monitors of organic chemicals in the environment — semipermeable membrane devices. New York: Springer Science+Business Media, LLC; 2006 [223 pp.].

Ibhazehiebo K, Iwasaki T, Kimura-Kuroda J, Miyazaki W, Shimokawa N, Koibuchi N, 2011. Disruption of thyroid hormone receptor–mediated transcription and thyroid hormone–induced Purkinje cell dendrite arborization by polybrominated diphenyl ethers. Environ Health Perspect 2011;119:168.

Jenkins JA, Olivier HM, Draugelis-Dale RO, Eilts BE, Nilsen EB, Goodbred SL, 2014. Assessing reproductive and endocrine parameters in male largescale suckers *(Catostomus macrocheilus)* along a contaminant gradient in the lower Columbia River, USA. Sci Total Environ 2014;484:365–78. (in this issue).

Johnson LL, Anulacion BF, Arksooh M, Buzitis J, Bolton J, Boyd D, et al, 2006. In: Lower Columbia River Estuary Partnership, editor. Chemical contaminants and endangered salmon in the Lower Columbia River and Estuary — results of the fish monitoring component of the Lower Columbia River Water Quality Monitoring Project, 2004–2006. Seattle, WA: Northwest Fisheries Science Center; 2006.

Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, et al, 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environ Sci Technol 2002;36:1202–11.

Kuriyama SN, Talsness CE, Grote K, Chahoud I, 2005. Developmental exposure to low dose PBDE 99: effects on male fertility and neurobehavior in rat offspring. Environ Health Perspect 2005;113:149–54.

Lane SL, Radtke DB, Wilde FD, Myers DN, 2005. National field manual for the collection of water-quality data. U.S. Geological Survey 2005; Techniques of Water-Resources Investigations Book 9; 2005. [Available at https://water.usgs.gov/owq/FieldManual/index.html].

Law K, Halldorson T, Danell R, Stern G, Gewurtz S, Alaee M, et al, 2006. Bioaccumulation and trophic transfer of some brominated flame retardants in a Lake Winnipeg (Canada) food web. Environ Toxicol Chem 2006;25:2177–86.

LCREP, 2007. Lower Columbia River Estuary and Ecosystem Monitoring: water quality and salmon sampling report. Portland, OR: Lower Columbia Estuary Partnership; 2007. [Available at http://www.estuarypartnership.org/resource/lower-columbia-river-and-estuary-ecosystem-monitoring-water-quality-and-salmon-sampling].

Lema SC, Dickey JT, Schultz IR, Swanson P, 2008. Dietary exposure to 2,2′,4,4′-tetrabromodiphenyl ether (PBDE-47) alters thyroid status and thyroid hormone-regulated gene transcription in the pituitary and brain. Environ Health Perspect 2008;116:1694–9.

Lewis ME, Zaugg SD, 2003. Processing of water samples: wastewater, pharmaceutical, and antibiotic compounds. U.S. Geological Survey 2003; Techniques of Water-Resources Investigations Book 9, 5.6.1.F; 2003. [Available at http://water.usgs.gov/owq/FieldManual/chapter5/5.6.1.F_v-1.1_4-03.pdf].

Meador JP, McCarty LS, Escher BI, Adams WJ, 2008. The tissue-residue approach for toxicity assessment: concepts, issues, application, and recommendations. J Environ Monit 2008;10:1486–98.

Miyazaki T, Yamagishi T, Matsumoto M, 1984. Residues of 4-chloro-1-(2,4-dichlorophenoxy)-2-methoxybenzene(triclosan methyl) in aquatic biota. Bull Environ Contam Toxicol 1984;32:227–32.

Mizukawa K, Takada H, Takeuchi I, Ikemoto T, Omori K, Tsuchiya K, 2009. Bioconcentration and biomagnification of polybrominated diphenyl ethers (PBDEs) through lower-trophic-level coastal marine food web. Mar Pollut Bull 2009;58:1217–24.

Moon H-B, Choi M, Yu J, Jung R-H, Choi H-G, 2012. Contamination and potential sources of polybrominated diphenyl ethers (PBDEs) in water and sediment from the artificial Lake Shihwa, Korea. Chemosphere 2012;88:837–43.

Morace JL, 2006. Water-quality data, Columbia River Estuary, 2004–05. U.S. Geological Survey 2006; Data Series 213; 2006. [Available at http://pubs.usgs.gov/ds/2006/213/].

Morace JL, 2012. Reconnaissance of contaminants in selected wastewater-treatment-plant effluent and stormwater runoff entering the Columbia River, Columbia River Basin, Washington and Oregon, 2008–10. U.S. Geological Survey 2012; Scientific Investigations Report 2012–5068; 2012. [Available at http://pubs.usgs.gov/sir/2012/5068/].

Morrison HA, Gobas FAPC, Lazar R, Whittle DM, Haffner GD, 1997. Development and verification of a benthic/pelagic food web bioaccumulation model for PCB congeners in western Lake Erie. Environ Sci Technol 1997;31:3267–73.

Muirhead EK, Skillman AD, Hook SE, Schultz IR, 2006. Oral exposure of PBDE-47 in fish: toxicokinetics and reproductive effects in Japanese Medaka (*Oryzias latipes*) and fathead minnows (*Pimephales promelas*). Environ Sci Technol 2006;40:523–8.

Naiman RJ, Alldredge JR, Beauchamp DA, Bisson PA, Congleton J, Henny CJ, et al, 2012. Developing a broader scientific foundation for river restoration: Columbia River food webs. Proc Natl Acad Sci 2012;109:21201–7.

Nilsen EB, Furlong E, Rosenbauer R, 2014. Reconnaissance of pharmaceuticals and wastewater indicators in streambed sediments of the lower Columbia River basin, Oregon and Washington. USA. J Am Water Resour Assoc 2014;50(2):291–301.

ODEQ, 2007. Guidance for assessing bioaccumulative chemicals of concern in sediment. 07-LQ-023A. Oregon Department of Environmental Quality; 2007.

ODEQ, 2008a. Human Health Focus Group Report Oregon Fish and Shellfish Consumption Rate Project. Oregon Department of Environmental Quality; 2008a.

ODEQ, 2008b. Oregon's fish consumption rate — for use in setting water quality standards for toxic pollutants. Draft Memorandum No. Item G 000001. Oregon Department of Environmental Quality; 2008b.

Pijnenburg AM, Everts JW, de Boer J, Boon JP, 1995. Polybrominated biphenyl and diphenylether flame retardants: analysis, toxicity, and environmental occurrence. Rev Environ Contam Toxicol 1995;141:1-26.

Ramirez AJ, Brain RA, Usenko S, Mottaleb MA, O'Donnell JG, Stahl LL, et al, 2009. Occurrence of pharmaceuticals and personal care products (PPCPs) in fish: results of a national pilot study in the U.S. Environ Toxicol Chem 2009;28:2587–97.

Rayne S, Ikonomou MG, Antcliffe B, 2003. Rapidly increasing polybrominated diphenyl ether concentrations in the Columbia River system from 1992 to 2000. Environ Sci Technol 2003;37:2847–54.

Sandvik P, Seiders K, 2012. Washington State Toxics Monitoring Program: evaluation of SPMDs for trend monitoring of PBTs in Washington Waters 2010–2011. Publication No. 12–03–036. Washington: Department of Ecology; 2012.

Schmitt C, 2002. Biomonitoring of environmental status and trends (BEST) program: environmental contaminants and their effects on fish in the Mississippi River Basin. U.S. Geological Survey 2002; Biological Science Report 2002–0004; 2002. [Available at http://www.nwrc.usgs.gov/techrpt/BSR-02-04.pdf].

Schmitt C, Hinck J, Blazer V, Denslow N, Dethloff G, Bartish T, 2005. Environmental contaminants and biomarker responses in fish from the Rio Grande and its U.S. tributaries: spatial and temporal trends. Sci Total Environ 2005;350:161–93.

Schultz MM, Furlong ET, Kolpin DW, Werner SL, Schoenfuss HL, Barber LB, et al, 2010. Antidepressant pharmaceuticals in two U.S. effluent impacted streams: occurrence and fate in water and sediment, and selective uptake in fish neural tissue. Environ Sci Technol 2010;44:1918–25.

Stevens Jr DL, Olsen AR, 2004. Spatially-balanced sampling of natural resources. J Am Stat Assoc 2004;99:262–78.

Torres L, Nilsen E, Grove R, Patiño R, 2014. Health status of largescale sucker (*Catostomus macrocheilus*) collected along a contaminant gradient in the lower Columbia River, Oregon and Washington, USA. Sci Total Environ 2014;484:353–64. [in this issue].

USFDA, 2001. Environmental chemical contaminants and pesticides. In: U.S. Food Drug Administration, editor. Fish and fishery products hazards and controls guidance; 2001. [Washington, DC].

van der Oost R, Heida H, Opperhuizen A, 1988. Polychlorinated biphenyl congeners in sediments, plankton, molluscs, crustaceans, and eel in a freshwater lake: implications of using reference chemicals and indicator organisms in bioaccumulation studies. Arch Environ Contam Toxicol 1988;17:721–9.

Wang Y, Jiang G, Paul KS, Lam AL, 2007. Polybrominated diphenyl ether in the East Asian environment: a critical review. Environ Int 2007;33:963–73.

Ward JR, Harr CA, editors. Methods for the collection and processing of surface-water and bed-material samples for physical analysesU.S. Geological Survey 1990; Open-File Report 90-140; 1990. [Available at http://pubs.er.usgs.gov/publication/ofr90140].

Wu J, Luo X, Zhang Y, Liu J, Yu M, Chen S, et al, 2009. Biomagnification of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls in a highly contaminated freshwater food web from South China. Environ Pollut 2009;157:904–9.