



RECONNAISSANCE OF PHARMACEUTICALS AND WASTEWATER INDICATORS IN STREAMBED SEDIMENTS OF THE LOWER COLUMBIA RIVER BASIN, OREGON AND WASHINGTON¹

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ABSTRACT: One by-product of advances in modern chemistry is the accumulation of synthetic chemicals in the natural environment. These compounds include contaminants of emerging concern (CECs), some of which are endocrine disrupting compounds (EDCs) that can have detrimental reproductive effects. The role of sediments in accumulating these types of chemicals and acting as a source of exposure for aquatic organisms is not well understood. Here we present a small-scale reconnaissance of CECs in bed sediments of the lower Columbia River and several tributaries and urban streams. Surficial bed sediment samples were collected from the Columbia River, the Willamette River, the Tualatin River, and several small urban creeks in Oregon. Thirty-nine compounds were detected at concentrations ranging from <1 to >1,000 ng [g sediment]⁻¹ dry weight basis. Concentrations and frequencies of detection were higher in tributaries and small urban creeks than in the Columbia River mainstem, suggesting a higher risk of exposure to aquatic life in lower order streams. Ten known or suspected EDCs were detected during the study. At least one EDC was detected at 21 of 23 sites sampled; several EDCs were detected in sediment from most sites. This study is the first to document the occurrence of a large suite of CECs in the sediments of the Columbia River basin. A better understanding of the role of sediment in the fate and effects of emerging contaminants is needed.

(KEY TERMS: environmental impacts; endocrine disruption; environmental sampling; organic chemicals; point source pollution; nonpoint source pollution; and streambed sediment.)

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INTRODUCTION

Modern chemistry has produced numerous compounds that facilitate everyday life and improve health through human and veterinary medicine. One by-product of these advances is the accumulation of synthetic chemicals in the natural environment.

Contaminants enter the aquatic environment from many pathways, including, for example, treated industrial and municipal wastewater and private septic systems, untreated sewage overflows resulting from storm surges, biosolids applied to land as fertilizer, landfill leachate, unintended cross-connections of storm and sewer systems, illegal dumping, and aquaculture.

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Some of these chemicals of emerging concern (CECs) include pharmaceuticals, fragrances, detergents, disinfectants, plasticizers, preservatives, and other chemicals present in wastewater and agricultural and urban runoff. These chemicals are sometimes referred to as pharmaceuticals and personal care products (PPCPs) (Ramirez *et al.*, 2009) and/or anthropogenic waste indicator (AWI) compounds. Some of these are endocrine disrupting compounds (EDCs) that have detrimental reproductive effects in fish (e.g., Brian *et al.*, 2007; Silva de Assis *et al.*, 2013) and in humans (Guillette, 1995; Solomon and Schettler, 2000; Hotchkiss *et al.*, 2008; Bergman *et al.*, 2013). EDCs mimic and block natural hormones in the body and disrupt normal function and development (Natural Resources Defense Council, 1998).

Although little is known about the environmental transport pathways and fate of many of these compounds, some sorb to sediments. Several hydrophilic compounds that are weak sorbates have been shown to migrate through riverbed sediments (Labadie *et al.*, 2007). Once in the aquatic environment, in waters and/or sediments, CECs may present an exposure risk to aquatic organisms (Anderson *et al.*, 2012), although toxicity levels are largely unknown (Burton, 2013). Although PPCP concentrations in surface waters are rapidly diluted they have been measured in rivers and streams nationwide (Kolpin *et al.*, 2002), and their continual release into water can create a chronic exposure or pseudo-persistence (Han *et al.*, 2010). Streambed sediments can act as a source and/or a sink for CECs, depending on the compound, physicochemical conditions, and time scale. Accumulation in sediments is one of the mechanisms by which some CECs may persist in the aquatic environment and enter the food web through benthic organisms (Nakata *et al.*, 2007).

Sediments provide a historic record and have long served as a tool for assessing presence and fate of legacy organic contaminants (e.g., Knezovich and Harrison, 1987). The contamination of sediments with medium polar contaminants has not been extensively studied (Richardson *et al.*, 2005). Some information has been obtained on specific compounds in sediments within limited geographic regions; for example, synthetic musks in Germany (Fromme *et al.*, 2001), the Great Lakes (Peck and Hornbuckle, 2003, 2006), and in China (Zeng *et al.*, 2008), antibiotics in Germany (Löffler *et al.*, 2005) and in Colorado (Kim and Carlson, 2007), surfactants in Cadiz Bay (Lara-Martín *et al.*, 2006), biocides in Chesapeake Bay, Maryland (Miller *et al.*, 2008), and UV stabilizers in Japan (Nakata *et al.*, 2009).

Various methods have been developed to screen for large suites of compounds having diverse chemical and physical properties in aqueous media (e.g., Trenholm *et al.*, 2006). Reconnaissance efforts have been made

over the last decade to assess the presence of some CECs in natural waters (Kolpin *et al.*, 2002; Cahill *et al.*, 2004; Murray *et al.*, 2010). Methods capable of analyzing a large suite of CECs in solid media have been published (Burkhardt *et al.*, 2005, 2006; Kinney *et al.*, 2006a, b; Chiaia-Hernandez *et al.*, 2013). Here we present a small-scale reconnaissance of CECs in bed sediments of the lower Columbia River and several tributaries and urban creeks in northwest Oregon.

METHODS

Study Site

The Columbia River is the fourth largest by volume in the nation and drains a 295,000 square-mile basin that comprises land in seven states and one Canadian territory. The Columbia River Basin provides important hydroelectric power generation, anadromous fisheries, large recreational areas and scenic beauty, and valuable habitat for wildlife and fish. This study focused on the lower tidally influenced portion of the Columbia River from downstream of Bonneville Dam, the lowermost dam on the Columbia, to near the mouth, including several tributaries and urban creeks (Figure 1; Table 1). Contaminants can enter the lower Columbia River and tributaries from many sources, including municipal and industrial permitted discharges, atmospheric deposition, urban and industrial nonpoint pollution, and runoff from agricultural and forested areas (Fuhner *et al.*, 1996; LCREP, 2007).

Sample Collection

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

Surface sediment (top 1-3 cm) was collected from the lower Columbia River, the Willamette River, the Tualatin River, and several small urban creeks (Figure 1; Table 1). The National Oceanic and Atmospheric Administration (NOAA) and the Oregon Department of Environmental Quality (ODEQ)

collected Columbia River sediment from Pt. Adams to Warrendale in summer 2005. Each sediment sample represents a homogenized composite of three petite Ponar or Van Geen bottom grabs. At the NOAA sites (river mile [RM] 4, 54, 82, 101, 141), three samples were taken at ~3-m intervals from a shallow, near-shore area of approximately 10-m diameter. The ODEQ sample sites (RM 66, 68, 102, 110) were randomly selected and not targeted to a specific environment. These latter samples were also composites of three individual grab samples per site. The U.S. Geological Survey (USGS) collected sediment samples at the tributary sites in winter 2007 as composites of three to five grab samples per site parallel to shore and approximately two meters apart, depending on terrain. Shallow water depositional areas were selected and site locations were targeted upstream and downstream of several area wastewater treatment plants (WWTPs). However, many of the small tributary sites were close enough to the tributary mouth that mixing could occur with the main stem of the river.

In all cases, the sampling tools were cleaned with Liquinox® and methanol before each sample was collected to prevent cross-contamination between samples. Sediment samples were stored in certified organic-free glass jars and were frozen in the field as soon as possible after collection. Frozen samples were transported to the Oregon Water Science Center (ORWSC) by USGS, NOAA, and/or ODEQ personnel and maintained frozen at ORWSC until shipment. All samples were shipped from the ORWSC on wet or dry ice via overnight service to the USGS National

Water Quality Laboratory (NWQL) in Denver, Colorado where they were analyzed for several organic contaminant classes.

TABLE 1. Sample Site Names and Locations.

Site Name	River Mile	Location
<i>Columbia Basin Tributary Sites</i>		
CS2	n/a	Columbia Slough at Smith and Bybee Park
CS1	n/a	Columbia Slough at Portland Rd
W5	n/a	Willamette R at Morrison Street Bridge
Jo	n/a	Johnson Cr at Willamette R confluence
W4	n/a	Willamette R d/s Kellogg WWTP
Ke	n/a	Kellogg Cr at Willamette R confluence
W3	n/a	Willamette R u/s Kellogg WWTP
W2	n/a	Willamette R d/s Tryon Creek WWTP
Tr	n/a	Tryon Cr at Willamette R confluence
W1	n/a	Willamette R u/s Tryon WWTP
T2	n/a	Tualatin R d/s Durham WWTP
T1	n/a	Tualatin R at Fanno Cr
Fa2	n/a	Fanno Cr near Tualatin R confluence
Fa1	n/a	Fanno Cr at Durham City Park
<i>Columbia River Mainstem Sites</i>		
C1	4	At Point Adams
C2	54	At Beaver Army Terminal
C3	66	d/s Cowlitz R and Longview WWTP
C4	68	At Cowlitz R
C5	82	At Columbia City
C6	101	At Willamette R
C7	102	u/s Willamette d/s Columbia Blvd WWTP
C8	110	u/s Willamette R and Columbia Blvd WWTP
C9	141	At Warrendale

Note: R, river; d/s, downstream; u/s, upstream; Cr, creek; WWTP, wastewater treatment plant

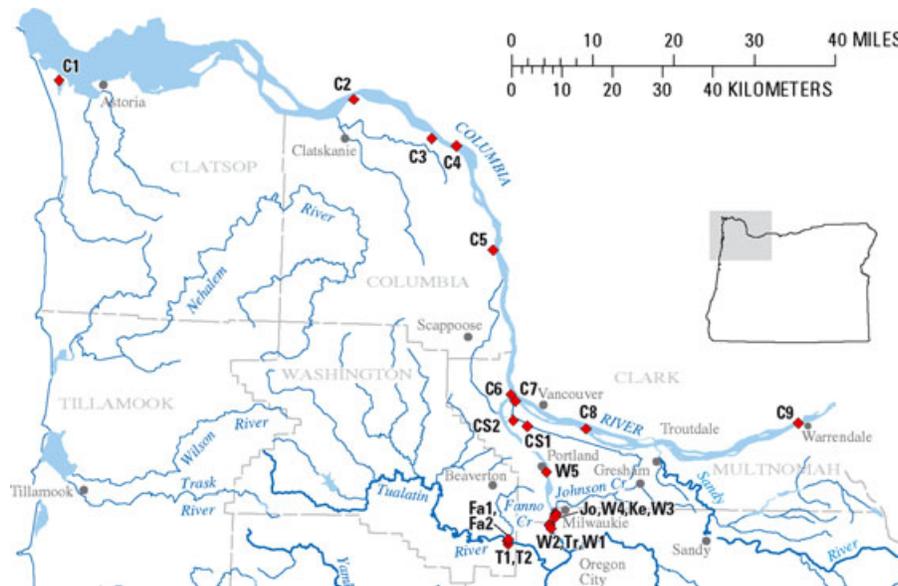


FIGURE 1. Sampling Site Locations in the Lower Columbia River and Selected Tributaries. Refer to Table 1 for explanation of site name abbreviations.

Analytical Methods

All samples received at the NWQL were frozen at -20°C and thawed just prior to sample preparation. The compounds of interest (Table 2) were extracted from 5-10 g of homogenized sediment sample (by wet weight) using a pressurized liquid extraction (PLE) system (Dionex ASE PLE™ 200; Sunnyvale, California) and were prepared for instrumental analysis using methods as previously described (Kinney *et al.*, 2006a, b). Extracts were analyzed for 20 human-use pharmaceuticals using the instrumental analysis procedure of Furlong *et al.* (2008), modified to improve specificity and sensitivity by replacing the single-quadrupole mass spectrometry component of that method with a functionally superior triple-quadrupole mass spectrometry (MS/MS) analysis, operated in positive electrospray ionization (ESI) mode (Furlong *et al.*, 2012). The liquid chromatographic (LC) separation was the same as used in Furlong *et al.* (2008) and two unique precursor/product ion transitions were monitored for identification and quantitation. All values below the level of the lowest standard ($0.005\text{ ng}/\mu\text{l}$) were considered nondetections. Extracts were then reanalyzed by LC-MS/MS to screen for 10 antidepressant compounds after methods by Schultz *et al.* (2010).

A separate extraction was performed on all samples for analysis of 62 AWI compounds; these extracts were prepared and analyzed by positive ESI gas chromatograph-mass spectrometry (GC-MS) using methods previously described (Burkhardt *et al.*, 2005, 2006). Sample results are reported in nanogram per gram sediment 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 (“E” in Tables A1 and A2). Measured concentrations that were above the method detection limits (MDLs) but less than five times a value detected in the blank were not reported as a quantitative value (“detected” in Tables A1 and A2).

The volatile content of each sediment sample was determined by loss on ignition (LOI) after drying (Fishman and Friedman, 1989). LOI can not only provide an estimate of organic carbon content in a sample (Heiri *et al.*, 2001) but can also vary with clay content (Abbaslou *et al.*, 2013). For this reason, the LOI data are reported as percent volatile fraction as opposed to sediment organic carbon.

Quality Assurance/Quality Control

Environmental samples were validated against a comprehensive set of performance-based quality

control parameters including laboratory blanks, matrix spike recoveries, replicate samples, and surrogate recoveries. Laboratory blanks for the pharmaceutical method ($n = 3$) and the AWI method ($n = 4$) consisted of reagent grade sand carried through the extraction, cleanup, and analysis steps (Tables A3 and A4). Recoveries for compounds detected during this study in spiked samples ($n = 3$) analyzed as part of this study ranged from 18 to 123% for the pharmaceutical method and 15 to 94% for the AWI method (Supporting Information). Mean recoveries of surrogate spike mixtures added to the environmental samples prior to instrumental analysis ($n = 6$) were 39, 54, 27, and 30% for carbamazepine- d_{10} , cotinine- d_3 , fluoxetine- d_5 , and codeine- d_6 , respectively, for the pharmaceutical method and 85, 105, and 34% for decafluorobiphenyl, fluoranthene- d_{10} , and d_8 -bisphenol A, respectively, for the AWI method. MDLs are included in the Supporting Information.

Statistics

To identify co-occurrence of the compounds with one another and/or with percent volatile fraction, compounds that were detected at more than 75% of sites were compared (Supporting Information). These compounds were not normally distributed and therefore their concentrations were normalized 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 (Osborne, 2002). Pairwise correlations were performed on normalized values of all measured concentrations (Table 3). We performed all statistical analyses using JMP Release 7 software (SAS Institute, Inc., Cary, North Carolina).

RESULTS AND DISCUSSION

Tributary Sites

Pharmaceutical Compounds. Pharmaceutical uses and some common trade names are listed in Table 2. Cotinine, codeine, caffeine, trimethoprim, thiabendazole, diphenhydramine, diltiazem, dehydronifedipine, miconazole, azithromycin, and three antidepressant compounds, venlafaxine, fluoxetine, citalopram, and the antiepileptic carbamazepine, were detected in samples at concentrations ranging from <1 to $150\text{ ng}/\text{g}$ (Supporting Information). Cimetidine was detected at or below the level of the lowest standard. 1,7-dimethylxanthine, acetaminophen, albuterol,

TABLE 2. Categories, Uses, Trade Names, Known (K) or Suspected (S) Endocrine Disrupting Potential, pK_a (pharmaceuticals) or $\log K_{ow}$ (all others), and Reference for pK_a or $\log K_{ow}$ Value for CECs Detected.

Category Name	Compound (generic)	Use or Source	Trade Name	Endocrine Disrupting Potential ²	$pK_a/\log K_{ow}$	Reference
Pharmaceutical	Azithromycin	Antibiotic	Zithromax ^{®1}	—	8.74	Drug Bank ³
	Miconazole	Antifungal	—	—	6.5	Beggs (1992)
	Thiabendazole	Veterinary anthelmintic	Mertect [®]	—	4.64	Drug Bank
	Trimethoprim	Antibiotic	Bactrim [®]	—	6.6	Da Silva <i>et al.</i> (2011)
	Caffeine	Stimulant	—	—	14	Moffatt (1986)
	Cotinine	Nicotine metabolite	—	—	4.37	Schepers and Walk (1988)
	Carbamazepine	Antiepileptic, antidepressant	Tegretol [®]	—	13.9	Da Silva <i>et al.</i> (2011)
	Citalopram	Antidepressant	Cipramil [®]	—	9.78	Drug Bank
	Fluoxetine	Antidepressant	Prozac [®]	—	9.8	Drug Bank
	Sertraline	Antidepressant	Zoloft [®]	—	9.85	Drug Bank
	Venlafaxine	Antidepressant	Effexor [®]	—	8.91	Drug Bank
	Dehydromefepipine	Antianginal metabolite	—	—	—	—
	Diltiazem	Antihypertensive	Cardizem [®]	—	7.5	Sateesha <i>et al.</i> (2010)
	Cimetidine	Antacid	Tagamet [®]	—	6.8	Da Silva <i>et al.</i> (2011)
	Codeine	Analgesic	—	—	8.2	Drug Bank
	Diphenhydramine	Antihistamine	Benadryl [®]	—	8.87	Drug Bank
	Fragrance	Indole	Fragrance in coffee	—	—	2.14
Acetophone		Fragrance in detergent and tobacco, flavor in beverages	—	—	1.58	NWQL
Personal care product	Skatol	Fragrance, present in feces and coal tar	—	—	2.6	NWQL
	Tonalide (AHTN)	Synthetic fragrance	—	S	5.8	NWQL
	Galaxolide (HHCB)	Synthetic fragrance	—	S	5.9	NWQL
	Triclosan	Disinfectant, antimicrobial	—	S	4.76	NWQL
	Benzophenone	Fixative for perfumes and soaps	—	S	3.18	NWQL
	<i>d</i> -Limonene	Fungicide, antimicrobial, antiviral, fragrance	—	—	4.57	NWQL
	Methyl salicylate	Liniment, food, beverage, UV-absorbing lotion	—	—	2.55	Hansch and Leo ⁵
	Isoquinoline	Flavor and fragrance	—	—	2.08	NWQL
	Butylated hydroxyanisole (BHA)	Food additive, preservative, antioxidant	—	K	3.5	NWQL
	Industrial	Bisphenol A	Manufacturing resins, antioxidant, flame retardant	—	K	3.32
Phenol		Manufacturing, disinfectant	—	—	1.46	NWQL
Anthraquinone		Manufacturing, seed treatment, bird repellent	—	—	3.39	NWQL
1,4-Dichlorobenzene		Moth repellent, fumigant, deodorant	—	S	3.44	NWQL
Isophorone		Solvent, resin	—	—	1.7	NWQL
Para-cresol		Wood preservative	—	S	1.94	NWQL
Carbazole		Manufacturing, explosives, lubricants	—	—	3.72	NWQL
4-Tert-octylphenol		Nonionic detergent metabolite	—	K	4.12	NWQL
Para-nonylphenol		Nonionic detergent metabolite	—	K	3.28	NWQL

¹Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

²From Burkhardt *et al.* (2006)

³Drug Bank Open Data Drug and Drug Target Database, <http://www.drugbank.ca/>, accessed January-June 2013.

⁴Spreadsheet from the USGS National Water Quality Laboratory (NWQL) e-mailed to lead author in September 2009.

⁵Hansch, C. and A. Leo. The Log P Database. Claremont, CA: Pomona College, 1987.

TABLE 3. Pairwise Correlations between Compounds with Fewer Than 25% Nondetects and Percent Volatile Fraction. For the compounds included, all data were considered in this analysis.

	% Volatile										Diethyl			AWI			
	Phenol	d-Limonene	Acetophenone	Para-Cresol	Indole	Skatol	Phthalate	Cholesterol	Beta-Sitosterol	Stigmastanol	Total	Phthalate	Skatol	Cholesterol	Beta-Sitosterol	Stigmastanol	Total
Phenol	0.772**																
d-Limonene	0.696**	0.694**															
Acetophenone	0.685**	0.923**	0.648**														
Para-cresol	0.802**	0.880**	0.610**	0.782**													
Indole	0.774**	0.837**	0.698**	0.782**	0.796**												
Skatol	0.826**	0.908**	0.805**	0.851**	0.922**	0.922**											
Diethyl	0.314	0.322	0.259	0.381	0.396	0.353	0.315										
phthalate	0.822**	0.712**	0.638**	0.831**	0.724**	0.839**	0.061										
Cholesterol	0.815**	0.858**	0.726**	0.905**	0.666**	0.802**	0.176	0.850**									
Beta-sitosterol	0.687**	0.856**	0.671**	0.743**	0.712**	0.818**	0.358	0.701**	0.806**								
Stigmastanol	0.881**	0.924**	0.739**	0.829**	0.875**	0.950**	0.289	0.887**	0.920**	0.843**							
AWI total	0.374	0.348	0.482**	0.351	0.437*	0.461*	-0.101	0.452*	0.328	0.396							
Pharmaceutical																	
total																	

*p < 0.05.
 ***p < 0.01.

erythromycin, ranitidine, sulfamethoxazole, and warfarin were not detected.

Sites with highest concentrations and numbers of detections tended to have relatively moderate to high percent volatile content and proximity to WWTP effluent (Figure 2). The sites on the Tualatin River and Fanno Creek were the most urbanized and probably had higher sediment retention. Rounds *et al.* (2009) detected several of the same compounds in influent at the Durham WWTP headworks as were measured in sediment at the Tualatin River and Fanno Creek sites for this study; however, only two of the same compounds, namely, carbamazepine and cotinine, were detected in the Durham WWTP effluent. Carbamazepine has been shown to be a persistent contaminant in wastewater-influenced surface water (Miao *et al.*, 2005; Guo and Krasner, 2009) and in sediment (Stein *et al.*, 2008). Four of the same compounds (caffeine, cotinine, carbamazepine, and codeine) were also detected in water samples from the Tualatin River and/or Fanno Creek (Rounds *et al.*, 2009) as were detected in sediments. The Rounds *et al.* (2009) study of water samples represents a very short time period

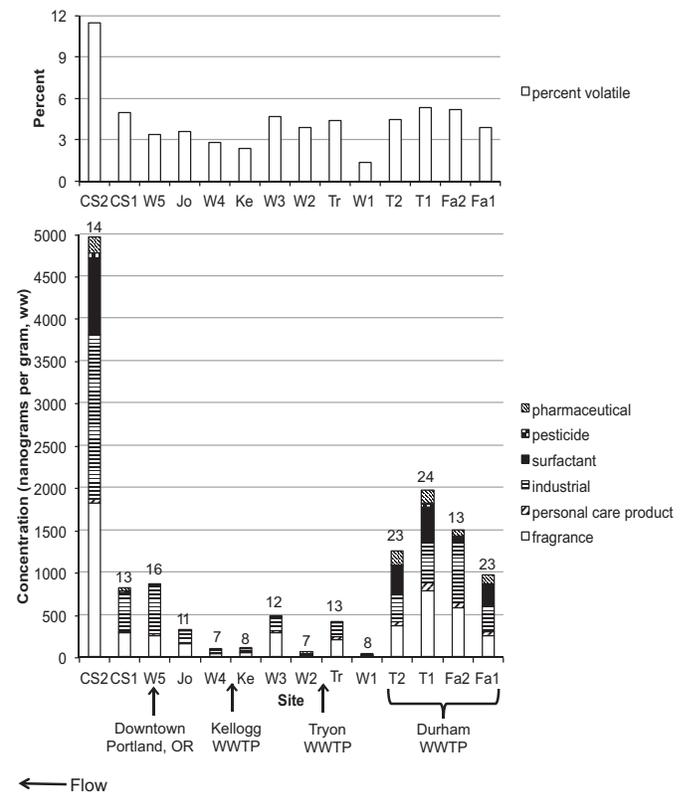


FIGURE 2. Percent Volatile Material (top panel) and Summed Concentrations of Compound Categories (bottom panel) in Bed Sediments of the Columbia River Basin Tributary Sites Displayed from Downstream (left) to Upstream (right). Numbers of individual compounds detected at each site are displayed above each bar (bottom panel). Potential source inputs are indicated by arrows (bottom panel). WWTP, wastewater treatment plant.

while sediment likely acts as an integrator for compounds sourced to the streams over a longer time period. The Willamette River downstream of Tryon Creek (W2) and at the Morrison Street Bridge (W5) had more detections than the other Willamette River sites. Site W2 is downstream of the Tryon Creek WWTP, and site W5 periodically receives combined sewer overflow. Columbia Slough at Smith and Bybee Park (CS2) had only two pharmaceutical compounds present, but their concentrations were relatively high. Percent volatile fraction was the highest at this site and, historically, Columbia Slough received combined sewer overflow from the Columbia Boulevard WWTP. Caffeine persistence in treated effluent depends on the wastewater treatment process (Phillips and Chalmers, 2009). Caffeine was detected at many sites during this study (Supporting Information). This may be due to stormwater runoff of caffeine to streams (Rounds *et al.*, 2009), or may be due to high flows leading to lower hydraulic retention time in treatment facilities, resulting in decreased removal efficiency (Phillips *et al.*, 2012).

Sediment concentrations of concern have not been determined for these compounds. Effects levels have been studied for several of these compounds in water. For instance, 50 percent of a test species of green algae showed growth inhibition at a trimethoprim concentration of 16 mg/l (Lindberg *et al.*, 2007). Several antibiotics have been shown to persist in sediments (Hektoen *et al.*, 1995), but effects levels for sediment concentrations have not been determined. Pharmaceutical compounds with lower solubility ($pK_a > 7$) were more frequently detected in sediments as observed by Da Silva *et al.* (2011), but several compounds with lower pK_a were also observed (Table 2).

Other AWI Compounds. At least two of the other AWI compounds (out of 62 total) were detected at every site; many sites had greater than 10 compounds detected. The content of surfactants and personal care products in sediment at the Tualatin River, Fanno Creek, and Columbia Slough at Smith and Bybee Park (CS2) sites was relatively high, a pattern similar to the pharmaceuticals. The industrial and fragrance categories were detected at more sites (Figure 2). The Willamette River at the Morrison Street Bridge (W5) had, in general, relatively higher numbers of detections and/or relatively larger concentrations compared to the Willamette River sites upstream and downstream of Tryon Creek and downstream of Kellogg Creek. Twenty-five percent of non-pharmaceutical AWI compounds detected had $\log K_{ow}$ values less than 2.5 (Table 2), below which compounds will not easily sorb to sediments; 10% of compounds detected had $\log K_{ow}$ values above 5, allowing efficient sorption during the solids retention

step of wastewater treatment (Pal *et al.*, 2010). Sixty-five percent of non-pharmaceutical AWI compounds detected had $\log K_{ow}$ values within the range of 2.5-5 (Table 2).

Mainstem Sites

Pharmaceutical Compounds. Compared to tributary sites, far fewer compounds were detected in the mainstem Columbia River sediments, and those detected generally occurred at lower concentrations. Pharmaceutical compounds were detected at only four mainstem sites and only four compounds were detected: azithromycin, miconazole, diphenhydramine, and thiabendazole (Table A2). None of the antidepressants were detected in the mainstem sediments. These sediments typically had coarser grain size and lower percent volatile content than sediments from the tributaries. Only two of the mainstem sites had a high percent volatile content and these sites also had the highest number of compounds detected and highest concentrations for most compound classes (Figure 3).

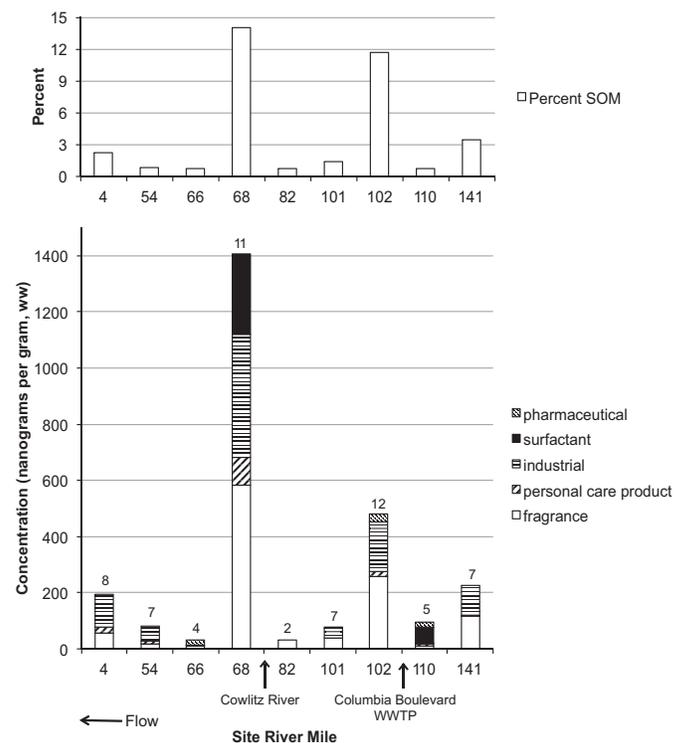


FIGURE 3. Percent Volatile Material (top panel) and Summed Concentrations of Compound Categories (bottom panel) in Sediments of the Mainstem Columbia River Sites Displayed from Downstream (left) to Upstream (right). Numbers of individual compounds detected at each site are displayed above each bar (bottom panel). Potential source inputs are indicated by arrows (bottom panel). WWTP, wastewater treatment plant.

Other AWI Compounds. Although several of these compounds were detected at every Columbia River site, there were in general fewer compounds detected overall and lower concentrations at the mainstem sites compared to the tributary sites. These observations are consistent with the patterns observed for the pharmaceutical compounds. The site at the confluence with the Cowlitz River (RM 68) and the site downstream of the Columbia Boulevard WWTP (RM 102) had the highest number of compounds detected, followed by the site at Point Adams (RM 4). The percent volatile content is widely variable at the sites sampled on the Columbia mainstem, ranging from less than 1% up to 14%. Greater dilution by the large volume of streamflow in the Columbia mainstem and lower percent sedimentary organic matter likely limit contaminant retention.

Endocrine Disrupting Compounds

Notable was the presence of several known or suspected EDCs in sediments (Table 2). Among the tributary sites, the Tualatin River, Fanno Creek, Columbia Slough, and the Willamette River at the Morrison Street Bridge had relatively more compounds and/or higher concentrations of EDCs detected (Table A1). Consistent with the patterns observed for the other classes of compounds, concentrations and detections were generally lower at the Columbia River sites than at the tributary sites. However, at least one EDC was detected at every site sampled except the Columbia River at RM 66 and 82 (Table A2).

Ranking the EDCs by total concentration of compound measured at all sites and by frequency of detection shows that the four compounds detected at the highest concentrations were also detected at the

highest frequency (Figure 4). Although these data do not identify inputs, some differences in possible sources are likely. For instance, para-cresol may be sourced predominantly from creosote-coated pilings that are located throughout the system, whereas benzophenone, a fixative for perfumes and soaps, is more likely to enter the system with wastewater. Effects levels exist for some of the compounds in water (Pal *et al.*, 2010), but sediment concentrations of concern have not been determined for these compounds. Spatial patterns in concentrations of contaminants in sediments are probably influenced by a combination of factors including contaminant loading, dilution by water volume, sediment sorption capacity, and compound-dependent characteristics such as partition coefficient that partially determine removal efficiency at WWTPs and persistence in the environment.

Compound Correlations

Compounds and compound classes with >75% detections were compared for correlation between each other and to percent volatile fraction. These compounds included phenol, *d*-limonene, acetophenone, para-cresol, indole, skatol, diethylhexyl phthalate, cholesterol, beta-sitosterol, stigmastanol, total AWIs, and total pharmaceuticals. Most compounds were highly correlated with each other and with percent volatile fraction (Table 3). Notable exceptions were diethyl phthalate and total pharmaceuticals. Diethyl phthalate was not statistically correlated with any other compound or percent volatile fraction, perhaps indicating a unique source or behavior in the aquatic environment of this compound compared to the others. None of the individual pharmaceutical compounds was detected at >75% of sites. Total phar-

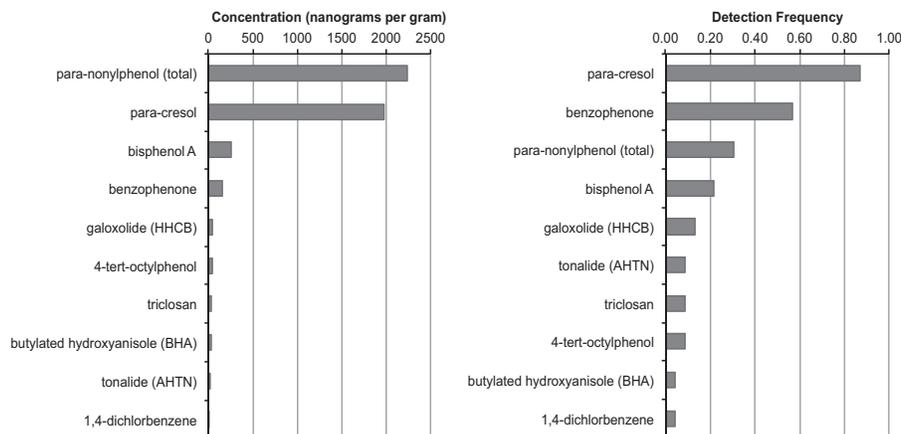


FIGURE 4. Known and Suspected Endocrine Disrupting Compounds Ranked by Total Concentration Measured at All Sites (left) and by Frequency of Detection at Sites (right).

maceuticals had a weaker, but still significant, correlation with five AWI compounds, including *d*-limonene, para-cresol, indole, skatol, and cholesterol. Total pharmaceuticals had no relationship with the other AWI compounds or to percent volatile fraction. This could suggest that pharmaceuticals and the other AWI compounds have different sources, treatment efficiencies, and/or rates of natural attenuation, and/or that adsorption is not occurring by simple hydrophobic partitioning.

CONCLUSIONS

This study is the first documented report of the occurrence of a large suite of CECs in the sediments of the Columbia River Basin. Several of the compounds detected are known to have detrimental impacts on aquatic life, although little is yet known about their sediment concentrations of concern. The effects of many compounds are not understood and require further study. Their presence in this ecosystem raises the possibility of biomagnification through the food web. A monitoring strategy for these classes of emerging contaminants in this and other ecosystems would be valuable, especially because their use and subsequent discharge into the environment is likely to increase into the future. Monitoring the mouths of tributaries and sites downstream of WWTPs would provide important information. Lower order streams appear to pose greater CEC exposure risks to juvenile salmonids and other wildlife. Even on the mainstem Columbia, most sites had at least one EDC present in sediments. Future work is needed to determine effects levels for these compounds and relate sediment concentrations to water column concentrations and/or loads. Future efforts are also needed to understand routes of exposure and bioaccumulation pathways. Sources of these compounds to the environment could likely be reduced through public education and outreach (e.g., USEPA's Design for the Environment program).

SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Table A1. Concentrations (nanograms per gram) in Columbia River Basin tributary sediment samples.

Table A2. Concentrations (nanograms per gram) in Columbia River mainstem sediment samples.

Table A3. Average blank concentrations and average set spike recoveries for the pharmaceutical method compounds.

Table A4. Average blank concentrations and average set spike recoveries for the anthropogenic waste indication compounds.

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