PHARMACEUTICALS AND PERSONAL CARE PRODUCTS DETECTED IN STREAMBED SEDIMENTS OF THE LOWER COLUMBIA RIVER AND SELECTED TRIBUTARIES

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INTRODUCTION

Modern chemistry has produced numerous compounds that facilitate everyday life and save lives through human and veterinary medicine. One byproduct of these advances is the accumulation of these synthetic chemicals in the natural environment. The compounds include pharmaceuticals, synthetic fragrances, detergents, disinfectants, plasticizers, preservatives, and others present in wastewater and agricultural and urban run-off, and are commonly referred to as “pharmaceuticals and personal care products” (PPCPs). Included also are endocrine disrupting compounds (EDCs) that have detrimental reproductive effects in fish (e.g., Brian et al 2007) and in humans (Guillette 1995). 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 in recent years to assess the presence of some of these compounds in natural waters (e.g., Kolpin et al. 2002, Cahill et al. 2004). The first methods capable of analyzing these compounds in solid media were recently published (Burkhardt et al. 2005, 2006, Kinney et al. 2006a,b). To date, published studies using these methods have primarily focused on biosolids, irrigated soils, and test materials. Here we present a small-scale reconnaissance of PPCPs in natural bed sediments of the lower Columbia River and several tributaries and urban creeks.

METHODS

Surface sediment samples were collected from the Columbia River (CR), the Willamette River, the Tualatin River, and several small urban creeks. Sampling sites were targeted upstream and downstream of several area wastewater treatment facility effluents. Samples underwent accelerated solvent extraction (ASE) and were prepared for instrument analysis using methods previously described (Kinney et al. 2006a,b). Extracts were analyzed for 20 pharmaceutical compounds by liquid chromatography-mass spectrometry (LC-MS) in positive electrospray ionization (ESI) mode. These same extracts were also analyzed separately by LC-MS/MS to confirm identities and then re-analyzed by LC-MS/MS using different instrument parameters to screen for 13 antidepressant compounds. A separate ASE was performed on all samples for 61 wastewater indicator compounds; these extracts were prepared and analyzed by positive

electron impact gas chromatograph-mass spectrometry (GC-MS) using methods previously described (Burkhardt et al. 2005, 2006).

RESULTS

Caffeine, trimethoprim, thiabendazole, diphenhydramine, diltiazem, and four anti-depressant compounds, venlafaxine, fluoxetine, citalopram and carbamazapine were detected in samples at concentrations ranging from 2 to 150 ng g^{-1} sediment. Additionally, codeine, cotinine, dehydronifedipine, miconazole, azithromycin and cimetidine were detected at or below the level of the lowest standard, which ranged between ~0.4 and 28 ng g^{-1} sediment, depending on the compound.

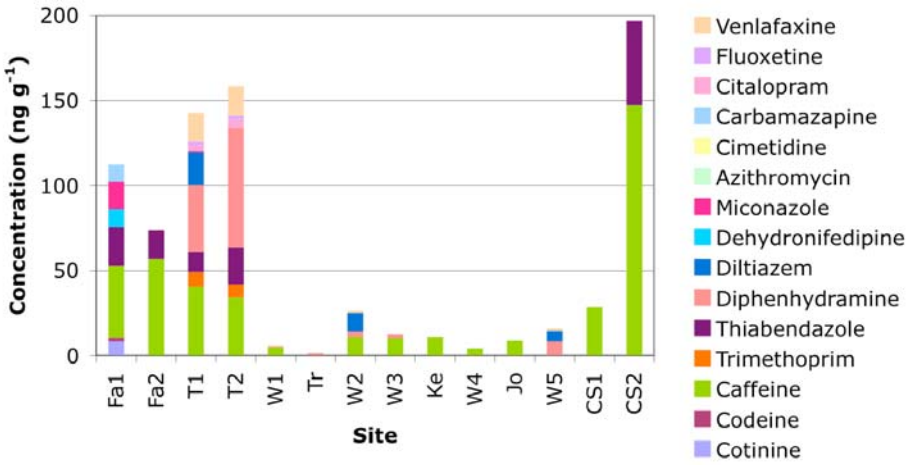

Figure 1. Pharmaceuticals detected in sediments of the tributary sites displayed from furthest upstream (far left) toward the Columbia River. Fa = Fanno Creek, T = Tualatin River, W = Willamette River, Tr = Tryon Creek, Ke = Kellogg Creek, Jo = Johnson Creek, CS = Columbia Slough.

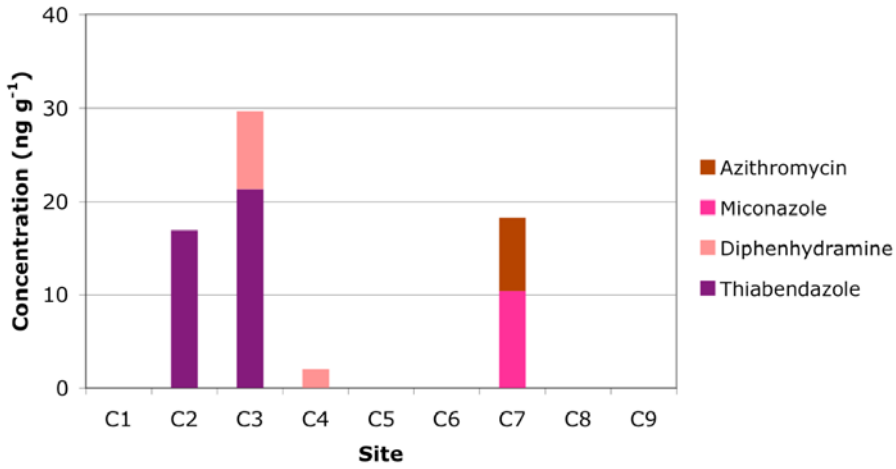

Figure 2. Pharmaceuticals detected in sediments of the Columbia River sites displayed moving downstream from left to right from Warrendale to Point Adams. C1 = Columbia River @ Warrendale, C2 = CR upstream (u/s) of the Willamette, C3 = CR downstream (d/s) of the Willamette, C4 = CR d/s Willamette, C5 = CR @ Columbia City, C6 = CR @ Cowlitz River, C7 = CR d/s Cowlitz, C8 = CR @ Beaver Army Terminal, C9 = CR @ Point Adams.

The largest number of pharmaceutical compounds was found in sediments from the Tualatin River and Fanno Creek (Figure 1). The Willamette River downstream of Tryon Creek (W2) and at the Morrison Street Bridge (W5) had more detections than the other Willamette River sites. Columbia Slough at Smith and Bybee Park (CS2) had only two compounds present, but their concentrations were relatively high. Far fewer compounds were detected in Columbia River sediments, and occurred at lower concentrations (Figure 2). None of the anti-depressants were detected in the Columbia River sediments.

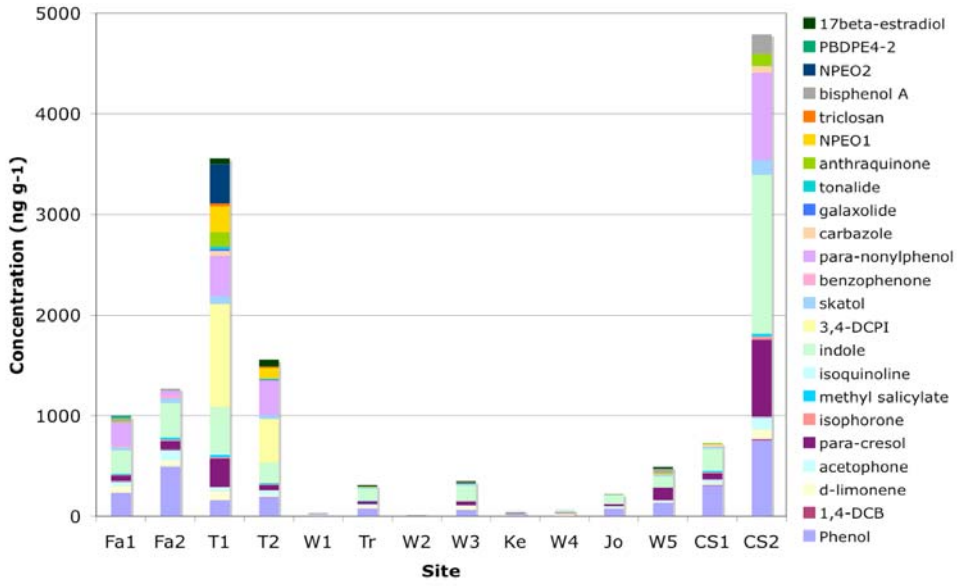

Figure 3. Wastewater indicator compounds detected in sediments of the tributary sites from furthest upstream (far left) toward the Columbia River. Site labels are as in Figure 1. 17β-estradiol should be interpreted as detection only; concentrations not reportable by the method used. Some of these data are preliminary pending re-analysis.

At least one wastewater indicator compound was detected at each site; many sites had multiple compounds present. Many compounds were detected and present at relatively high concentrations in sediments from the Tualatin River and Fanno Creek (Figure 3). Columbia Slough was also a hotspot for detection of wastewater compounds. The Willamette River sites upstream and downstream of Tryon Creek were relatively 'clean' with respect to wastewater compounds. Although several of these compounds were detected at every CR site, there were fewer compounds detected overall and on average lower concentrations at the CR sites than at the tributary sites (Figure 4). These patterns are similar to the pharmaceutical results. The CR sites downstream of the confluence with the Cowlitz River (C6) and the Willamette River (C3) had the most compounds and highest concentrations, followed by the sites at Warrendale (C1) and Pt. Adams (C9).

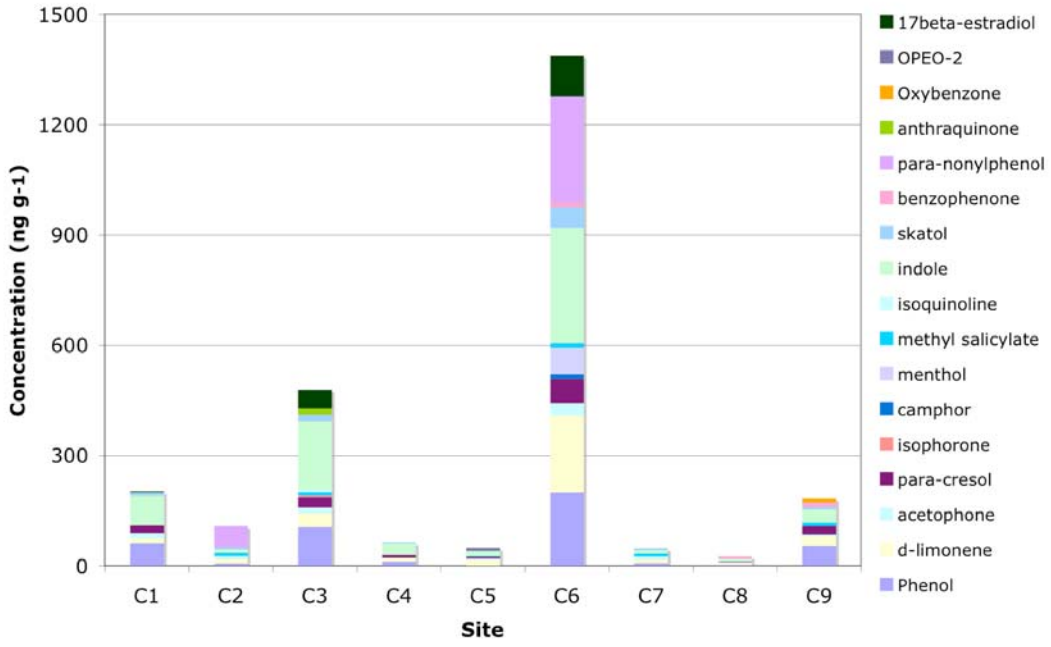

Figure 4. Wastewater indicator compounds detected in sediments of the Columbia River sites displayed moving downstream from left to right from Warrendale to Point Adams. Site labels are as in Figure 2.

Most notable was the presence in sediments of several strictly anthropogenic and known or suspected EDCs: 1,4-dichlorobenzene (DCB), para-cresol, benzo[a]pyrene (not shown), benzophenone, para-nonylphenol, tonalide (AHTN), galaxolide (HHCB), nonylphenol ethoxylate (NPEO), triclosan, bisphenol A, and 17β-estradiol. At least one of these compounds was detected at every site sampled except the CR downstream of the Cowlitz River (C7). The Tualatin River, Fanno Creek, Columbia Slough and the CR at the Cowlitz were hotspots for detections of EDCs. With a few exceptions, similar patterns were observed in concentrations of polycyclic aromatic hydrocarbons (PAHs) and steroid compounds (data not shown). Spatial patterns in concentrations of contaminants in sediments are probably influenced by a combination of factors including contaminant loading, dilution, sedimentary sorption capacity, and compound-dependent characteristics such as its partition coefficient.

IMPLICATIONS

Some of these compounds are known to have detrimental impacts on aquatic life. The effects of others are unknown and require further study. There is an increasing concern in the scientific community about linkages between earth science and public health. This study is the first documented case of the positive occurrence of a large suite of PPCPs in the sediments of this part of the CR Basin. Their very presence raises the possibility of biomagnification through the food web. There is clearly a need for a monitoring strategy for these classes of emerging contaminants, especially because their use and subsequent discharge into the environment is likely to only increase into the future.

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