Environmental Chemistry

QUANTIFICATION OF PHARMACEUTICALS, PERSONAL CARE PRODUCTS, AND PERFLUOROALKYL SUBSTANCES IN THE MARINE SEDIMENTS OF PUGET SOUND, WASHINGTON, USA

EDWARD R. LONG,*† MARGARET DUTCH,‡ SANDRA WEAKLAND,† BHARAT CHANDRAMOULI,† and JONATHAN P. BENSIN†

‡Environmental Assessment Program, Washington State Department of Ecology, Olympia, Washington, USA
†AXYS Analytical Services, Sidney, British Columbia, Canada

(Submitted 30 December 2012; Returned for Revision 20 February 2013; Accepted 5 April 2013)

Abstract: Concentrations of 119 pharmaceuticals and personal care products (PPCPs) and 13 perfluorooalkyl substances (PFASs) in marine sediments measured throughout Puget Sound (n = 10) and Bellingham Bay (n = 30), Washington, USA, are reported. These data are among the first measurements of PPCPs and PFASs in marine sediments from the Pacific Northwest and provide a comparison to previous measurements of these chemicals in influent, effluent, and biosolids from municipal wastewater treatment plants throughout the region. The concentrations of both PPCPs and PFASs in sediments from Puget Sound and Bellingham Bay ranged from very low to non-detectable for most compounds. Only 14 of the 119 PPCPs and 3 of 13 PFASs were quantifiable in sediments. Diphenhydramine (an antihistamine) was most frequently detected (87.5% of samples), with a maximum concentration of 4.81 ng/g dry weight and an estimated mean detected concentration of 1.68 ng/g. Triclocarban (an antibacterial) was detected in 35.0% of the samples, with a maximum concentration of 16.6 ng/g dry weight. Perfluorooalkyl substances were detected in 2.5% of analyses. Perfluorobutanoate, perfluorooctane sulfonate, and perfluorooctane sulfonamide were detected in 7, 5, and 1 sample(s) each, respectively, with the highest concentrations observed for perfluorooctane sulfonate (1.5 ng/g). Detected concentrations were often highest within the industrial harbor in Bellingham Bay and near the cities of Seattle and Bremerton. Environ Toxicol Chem 2013;32:1701–1710. © 2013 SETAC

Keywords: Puget Sound Sediments Pharmaceuticals Personal care products Perfluorooalkyl substances

INTRODUCTION

Contamination and toxicity of sediments in Puget Sound

Surveys throughout Puget Sound during the 1980s demonstrated that sediments and demersal fishes in the industrialized harbors and maritime waterways were contaminated with mixtures of metals and organic compounds [1,2]. In addition, sediments were toxic in multiple laboratory tests, and some demersal fish had high incidences of lesions and tumors [1,2]. Chemical analyses of metals, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides were conducted using state-of-the-science methods available in the 1980s.

Since 1989, the Washington State Department of Ecology has monitored the quality of sediments in Puget Sound annually as part of the Puget Sound Ecosystem Monitoring Program and since 1997 as part of its Urban Waters Initiative ([3]; www.ecy.wa.gov/programs/eap/psamp/index.htm). These monitoring surveys are performed to determine spatial status and temporal trends in sediment quality by measuring levels of chemical contaminants, toxic responses in laboratory bioassays, and the structure of the sediment-dwelling invertebrate communities. This approach is commonly referred to as the sediment quality triad [4].

Previous and current sediment chemical monitoring includes analyses for metals, PAHs, PCBs, phthalate esters, phenols, chlorinated benzenes, chlorinated pesticides, texture (i.e., grain size) percentage of organic carbon, and additional organic compounds [3]. In 2010, suites of pharmaceuticals and personal care products (PPCPs) and perfluorooalkyl substances (PFASs) were added to the analyte list to begin establishing a baseline for these chemicals in Puget Sound sediments.

PPCPs in the environment

Since the 1990s, there has been growing interest in the presence of PPCPs in the environment [5–7]. These substances include thousands of prescription pharmaceuticals, over-the-counter medicines, illicit drugs, nutritional supplements, diagnostic agents, shampoos, soaps, fragrances, and lotions [8]. Following use, PPCPs and their transformation products may enter the environment as a result of incomplete degradation during wastewater treatment. Continuous discharge of these chemicals can result in their accumulation in receiving environments [9].

The toxicity of PPCPs to plants, invertebrates, and fish has been demonstrated in laboratory bioassays; however, adverse toxicological, biological, and ecological effects of PPCPs in the environment are largely unknown [6,10]. It is possible that these substances occur in the environment as complex mixtures and that their toxicological effects are additive or synergistic, despite their differing individual modes of action [11]. Although most PPCPs are not expected to cause lethal effects in the environment because they occur at very low concentrations, they can reach non-target organisms through unexpected routes. As such, they may elicit toxicological modes of action other than what is expected from their intended use in humans and livestock [12]. Recent studies indicating endocrine disruption in juvenile salmon from Puget Sound [13] and evidence of vitellogenin
production, histopathological lesions, and other estrogen-
induced disorders in male English sole from urban bays in
Puget Sound [14] may indicate aquatic species are exposed to
docrine disrupting substances such as PPCPs.

Previous studies in the Pacific Northwest have reported
detectable concentrations of PPCPs in various media sampled.
These include wastewater effluent, wells and creeks in Sequim,
Washington, USA [15]; water and salmon from the lower
Columbia River [16]; urban streams in the Tualatin River basin
in Oregon, USA [17]; surface and groundwater near Liberty Bay,
Washington, USA [18]; municipal wastewater influent, effluent,
and biosolids in Puget Sound [8]; and reclaimed wastewater and
groundwater in the Puget Sound region [19]. The present study is
the first to measure concentrations of PPCPs in sediments
collected from Puget Sound.

PFASs in the environment

Perfluoroalkyl substances (PFASs; also known as perfluori-
nated compounds or PFCs) are a diverse class of anthropogenic
chemicals that have been manufactured since the 1950s [20,21].
Perfluoroalkyl substances have been used in stain-resistant
coatings for clothing and carpet, refrigerants, paints, adhesives,
anesthetics, waxes, and polishes. The global distribution
of PFASs was only recently identified in the early 2000s
[22,23].

Perfluoroalkyl acids (PFAs; i.e., CF₃CnF₂₃R, where n typically
ranges from 3–13 and R is typically COOH or SO₃H)
are the most commonly measured and detected PFASs in
the environment. The environmental occurrence of PFASs may arise
from direct application in commercial products or processes (e.g.,
aqueous film-forming foams and fluoropolymer manufacturing),
but can also occur from the degradation of commercial precursor
substances (i.e., PFFA-precursors) [24,25].

Risks to marine wildlife associated with current PFAS
exposure levels are not well defined, but PFASs are persistent in
the environment. Those PFASs with perfluoroalkyl chain
lengths greater than 7 carbons are bioaccumulative [26]. High
concentrations of these chemicals have been detected in the
tissues of molluscs, fish, birds, mink, and otter in the Great Lakes
(US and Canada) [27], in the serum of harbor seals in San
Francisco Bay (CA, USA) [28], and in freshwater oligochaetes
exposed to contaminated sediments [29].

In Washington State, 13 PFASs were measured in surface
waters, wastewater treatment plant effluents, fish fillet com-
posites, and fish liver composites in rivers and lakes sampled
statewide, as well as in osprey eggs from the Lower Columbia
River [30]. As with PPCPs, the present study is the first to measure concentrations of PFASs in sediments collected from
Puget Sound.

Study objectives

The objective of the present study was to establish baseline
levels of PPCPs and PFASs in Puget Sound sediments, which
will facilitate comparisons through long-term monitoring. The
present study was not intended to be a comprehensive and
thorough assessment Sound-wide; rather, it was intended as a
first-step, exploratory survey from which a database could be
developed for the Sound.

MATERIALS AND METHODS

Field sampling

Sampling was conducted during April and June 2010 at 40
locations. Ten were fixed, long-term monitoring stations selected
to represent major regions of the Sound [31] (Figure 1). Thirty stations were selected from a probabilistic random
design in Bellingham Bay, an urban region of the Sound that
receives wastewaters from a variety of sources (Figure 2).
The spatial extent of detectable contamination was calculated
as the sum of the areas represented by each sampling station
in Bellingham Bay that had a detectable concentration, as in
previous studies of Puget Sound sediments [32,33].

Sediment samples were collected using multiple deployments
of a double 0.1 m² vanVeen grab sampler, and the upper 2 cm to
3 cm (i.e., sediment depth from 0 to 2–3 cm) were selected for
chemical analyses. Samples at each station were composited,
homogenized, and shipped on ice to AXYS Analytical Services
(Sidney, BC, Canada) for analysis.

Extraction, treatment, and analysis of samples

A total of 119 PPCPs (Table 1) were extracted from
sediments using US Environmental Protection Agency
(USEPA) method 1694 [34]. The PPCPs were originally
selected by the USEPA as being compounds of emerging
concern, especially from wastewater treatment plant water
and biosolid discharges. Briefly, extractions were carried out
at pH 2.0 for analytes in lists 1, 2, and 3 and pH 10 for analytes
in list 4. Prior to extraction, samples were adjusted to the
appropriate pH and spiked with isotopically-labeled surrogates.
Samples were extracted repeatedly by sonication with acetoni-
trile, and the combined supernatants were adjusted to the
appropriate pH with acetonitrile. The PPCPs were quantified
in positive ionization mode by liquid chromatography–mass
spectrometry (LC/MS–MS) using positive and negative
ionization in multiple reaction monitoring mode. The analytical
method reported PFASs as a total of linear and branched
isomers.

A total of 13 PFASs (Table 1) were extracted from sediments using in-house methods developed by AXYS Analytical
Services. After spiking with isotopically labeled standards,
samples were extracted by shaking once with dilute acid (aq),
than twice with methanolic ammonium hydroxide. The super-
natants were combined, diluted with water, and treated with
ultra-pure carbon powder. The resulting solution was processed
by solid phase extraction using weak anion exchange
cartridges (150 mg, 6 cm; OASIS WAX). The final extract was
spiked with recovery standard and then analyzed by LC/MS–MS
under negative ionization in multiple reaction monitoring
mode.

Quality assurance/quality control

Samples were extracted in batches of up to 22 samples, which
included 1 procedural blank and 1 spiked reference sample (per
batch). A total of 5% of the test samples within a batch were
analyzed in duplicate. In all instances, analytes were quantified
by isotope dilution (in cases where an exactly matched,
isotopically labeled standard was available) or an internal
standard approach (in cases where an exactly matched,
isotopically labeled standard was unavailable). Calibration
curves were run initially (1/x weighted linear regression, \( r^2
>0.985 \)) after which a mid-level standard was run after every 20
samples to monitor potential drift in instrument response.
Detection limits were set at 1 ng/g to 1,000 ng/g dry weight for
PPCPs and 0.1 ng/g dry weight for PFASs. For both methods,
internal standard selection for compounds without an
isotopically labeled analog was based on structural similarity and method development data that indicated good fit.

Data summary and analysis

Because PPCPs and PFASs were often present at concentrations at or below method detection limits, regression on order statistics (ROS) [35] were used to estimate minimum, mean, and median concentrations in cases where both detectable and nondetectable concentrations were observed. The incidence, or number and percentage of stations with PPCP and PFAS concentrations, was calculated for each detected chemical for both the long-term stations and the Bellingham Bay stations. The spatial extent, or area (km²) and percentage of area with detected PPCP and PFAS concentrations, was also calculated for Bellingham Bay per the Urban Waters Initiative study design [3]. The method reporting limits (MRLs) generated with these analyses were based on the higher of the reported estimated detection limit (EDL) or estimated quantitation limit (EQL) values. The EDL (sample-specific detection limit) was calculated using MassLynx 4.1 software and verified by the

Figure 1. Ten long-term sediment sampling locations in Puget Sound, Washington, USA.
chemist analyzing the samples. The EQL was based on the lowest calibration standard used to calibrate the instrument. Both EDL and EQL were prorated for the final extract volume, initial sample weight, and percentage of solids.

RESULTS AND DISCUSSION

The present survey of Puget Sound sediments provides a baseline of data establishing recent levels of PPCPs and PFASs in both an urban bay and at ambient stations representing varied habitats. These data are compared with data from other studies to gain a perspective on the levels of these chemicals in marine sediments compared with other environmental media and geographic locations. This survey did not extend throughout all regions of Puget Sound; as a result, it is not possible to draw comprehensive conclusions regarding the spatial distribution or patterns of PPCP and PFAS contamination Sound-wide. However, the data indicated a few interesting patterns within Bellingham Bay and among the 10 long-term stations. Often, the concentrations of these chemicals were highest in the inner harbor of Bellingham Bay and near Seattle, but they did not always co-occur or co-vary with one another.

PPCPs

Among the 40 samples and 119 analytes (a total of 4760 analyses), 14 PPCPs were detected in 86 analyses, an incidence of 1.8%. Concentrations among the 14 detectable PPCPs ranged from 0.13 ng/g to 46.90 ng/g dry weight. Minimum, mean, and median concentrations estimated with ROS ranged from 0.05 ng/g to 1.23 ng/g, 0.09 ng/g to 3.22 ng/g, and 0.08 ng/g to 1.57 ng/g, respectively (Table 2). The estimated areas in Bellingham Bay affected by detected concentrations of PPCPs ranged from 0.19 km² (norverapamil) to 36.32 km² (diphenhydramine), representing 0.5% and 87.9% of the total survey area, respectively (Table 3).

Diphenhydramine, an antihistamine, was detected in the greatest number of stations (35 of 40, or 87.5%), with concentrations ranging from 0.61 to 4.81 ng/g (Table 2). The highest concentration of diphenhydramine (4.81 ng/g) was observed at long-term station 38, a deep, central Puget Sound station between Seattle and Tacoma (Supplemental Data, Figure S1) and tended to decrease considerably in less populous sites further north and south of this location. Similarly, in Bellingham Bay, concentrations of diphenhydramine were generally higher (>2.0 ng/g) within the industrialized area of the harbor (nearest to the wastewater treatment plant) and decreased toward the center of the bay. Maximum concentrations reported in the present study were lower than those reported from sediments in 5 locations nationwide (20–50 ng/g) [36]. Diphenhydramine has been associated with multiple toxicological outcomes in aquatic biota, ranging from increased mortality to reduced growth and reproduction [37].
Triclocarban, a disinfectant, was detected in 14 of the 40 samples, an incidence of 35.0%. Concentrations ranged from 0.13 to 16.6 ng/g (Table 2). The highest concentrations of triclocarban were observed at long-term station 38 in the deep central Puget Sound basin (16.6 ng/g) and station 34 in Sinclair Inlet near the city of Bremerton (13.2 ng/g) (Supplemental Data, Figure S2). Relatively high concentrations of triclocarban (>6 ng/g) were also detected in central and inner Bellingham Bay.

Sample concentrations of triclocarban near the reporting limit for the present project should be considered carefully because of a possible low-level laboratory background below the low calibration limit of the method. In analyses conducted by AXYS in solid matrices in 2010, triclocarban was detected in method blanks below the method reporting limit approximately 50% of the time. The Washington State Department of Ecology’s Manchester Environmental Laboratory personnel performed a quality assurance evaluation of the data AXYS generated. The USEPA Contract Laboratory Program 5-times rule [38] was used to assess background contribution. With this rule, results less than 5 times the amount found in the associated method blank were reported as not detected, and results greater than 5 times the associated method blank were reported as detected. Most of the results near the method reporting limit would have been reported as not detected had the Manchester Environmental Laboratory applied a 10-times rule, which is sometimes used for common lab contaminants. However, the concentration and spread in the background levels observed at AXYS indicates that applying a 10-times criterion may result in false negatives.

Table 1. Personal care products and pharmaceuticals (PPCPs) and perfluoroalkyl substances (PFASs) analyzed in Puget Sound, Washington, USA, sediments in April and June 2010
Table 2. Numbers of samples with detected concentrations\(^a\), ranges in MRLs, and summary statistics for detected and estimated concentrations of PPCPs and PFASs in 40\(^b\) sediment samples from Puget Sound, Washington, USA.

<table>
<thead>
<tr>
<th>Detected Chemical</th>
<th>Function</th>
<th>No. of detected values</th>
<th>No. of nondetected values</th>
<th>MRL(^c) (ng/g dry wt)</th>
<th>Estimated minimum(^d) concentration (ng/g dry wt)</th>
<th>Minimum detected concentration (ng/g dry wt)</th>
<th>Maximum detected concentration (ng/g dry wt)</th>
<th>Estimated mean(^d) concentration (ng/g dry wt)</th>
<th>Estimated SD(^d) concentration (ng/g dry wt)</th>
<th>Estimated median(^d) concentration (ng/g dry wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PPCP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>Antihistamine</td>
<td>35</td>
<td>5</td>
<td>0.48–5.45</td>
<td>0.61</td>
<td>0.61</td>
<td>4.81</td>
<td>1.68</td>
<td>0.73</td>
<td>1.57</td>
</tr>
<tr>
<td>Triclocarban</td>
<td>Antibacterial</td>
<td>14</td>
<td>26</td>
<td>2.37–5.51</td>
<td>0.13</td>
<td>3.09</td>
<td>16.60</td>
<td>0.24</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td>Triamterene</td>
<td>Diuretic</td>
<td>14</td>
<td>25</td>
<td>0.22–0.63</td>
<td>0.70</td>
<td>0.25</td>
<td>0.82</td>
<td>3.22</td>
<td>3.55</td>
<td>1.37</td>
</tr>
<tr>
<td>Verapamil</td>
<td>Calcium channel blocker</td>
<td>6</td>
<td>33</td>
<td>0.11–1.73</td>
<td>0.05</td>
<td>0.13</td>
<td>0.26</td>
<td>0.09</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>Amphetamine</td>
<td>Stimulant</td>
<td>5</td>
<td>35</td>
<td>1.30–4.95</td>
<td>0.67</td>
<td>1.76</td>
<td>3.21</td>
<td>1.20</td>
<td>0.68</td>
<td>0.83</td>
</tr>
<tr>
<td>Azithromycin</td>
<td>Antibiotic</td>
<td>3</td>
<td>37</td>
<td>1.22–14.6</td>
<td>1.23</td>
<td>1.43</td>
<td>1.60</td>
<td>1.33</td>
<td>0.09</td>
<td>1.31</td>
</tr>
<tr>
<td>Oxytetracyclin</td>
<td>Antibiotic</td>
<td>2</td>
<td>38</td>
<td>4.49–6.24</td>
<td>n/a</td>
<td>6.65</td>
<td>8.87</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>4-Epifluracil</td>
<td>Antibiotic</td>
<td>1</td>
<td>39</td>
<td>4.49–6.29</td>
<td>n/a</td>
<td>6.06</td>
<td>8.06</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Amiatriptyline</td>
<td>Antidepressant</td>
<td>1</td>
<td>39</td>
<td>0.23–2.45</td>
<td>n/a</td>
<td>0.45</td>
<td>0.45</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Anhydrochlorotetracycline</td>
<td>Antibiotic</td>
<td>1</td>
<td>39</td>
<td>11.9–51.0</td>
<td>n/a</td>
<td>46.90</td>
<td>46.90</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Anti-inflammatory</td>
<td>1</td>
<td>39</td>
<td>11.2–15.6</td>
<td>n/a</td>
<td>21.70</td>
<td>21.70</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Miconazole</td>
<td>Antifungal</td>
<td>1</td>
<td>39</td>
<td>1.12–4.14</td>
<td>n/a</td>
<td>1.50</td>
<td>1.50</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Norverapamil</td>
<td>Calcium channel blocker</td>
<td>1</td>
<td>37</td>
<td>0.11–0.30</td>
<td>n/a</td>
<td>0.17</td>
<td>0.17</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Propoxyphene</td>
<td>Pain reliever</td>
<td>1</td>
<td>38</td>
<td>0.24–1.07</td>
<td>n/a</td>
<td>1.74</td>
<td>1.74</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>PFAS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBA</td>
<td>In photo film, degradation product of a variety of PFASs</td>
<td>7</td>
<td>33</td>
<td>0.09–0.10</td>
<td>0.03</td>
<td>0.13</td>
<td>0.23</td>
<td>0.07</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>PFOS</td>
<td>Pre-2002 aqueous film-forming foams, degradation product of perfluorooctane sulfonamides</td>
<td>5</td>
<td>35</td>
<td>0.18–0.23</td>
<td>&lt;0.01</td>
<td>0.20</td>
<td>1.50</td>
<td>0.09</td>
<td>0.27</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>PFOSA</td>
<td>Impurity in pre-2002 ScotchGard formulations, degradation product of a variety of PFASs</td>
<td>1</td>
<td>39</td>
<td>0.09–0.14</td>
<td>n/a</td>
<td>0.18</td>
<td>0.18</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

\(^a\)Field splits and laboratory duplicates not included.

\(^b\)Total number of detected and nondetected sample results is fewer than 40 in a few cases where analyses were rejected.

\(^c\)The MRL is based on the higher of the reported estimated detection limit or estimated quantitation limit values.

\(^d\)Estimated by regression on order statistics when nondetected data are present [35].

PPCPs = personal care products and pharmaceuticals; PFASs = perfluoralkyl substances; MRL = method reporting limit; SD = standard deviation; PFBA = perfluorobutanoic acid; PFOS = perfluorooctanesulfonate; PFOSA = perfluoro-octanesulfonamide; n/a = too few detected values to calculate using regression on order statistics.
PPCPs and PFASs in Puget Sound sediments

Environ Toxicol Chem 32, 2013 1707

Triamterene, a diuretic, was detected in 14 of 39 samples (with 1 rejected sample), an incidence of 36.0%. Concentrations ranged from 0.25 ng/g to 0.82 ng/g (Table 2). Triamterene was detected at 0.76 and 0.82 ng/g at long-term stations 38 and 49, respectively, and from 0.25 to 0.50 in the industrialized region of Bellingham Bay. Concentrations generally decreased with increasing distance from these stations. The spatial patterns in the concentrations of triamterene were similar to those for triclocarban, with the highest concentrations within inner Bellingham Bay and at 2 stations near Seattle and Olympia (Supplemental Data, Figure S3). Triamterene was not detected at most of the outer Bellingham Bay and long-term stations.

Eleven other PPCPs were detected in Bellingham Bay and at station 38, including amphetamine (a stimulant); azithromycin, oxytetracycline, 4-epitetracycline, anhydrochlortetracycline (antibiotics); verapamil and norverapamil (calcium channel blockers); amitriptyline (an antidepressant); ibuprofen (an anti-inflammatory); miconazole (an antifungal); and propoxyphene (an analgesic). Verapamil, amphetamine, azithromycin, and oxytetracycline were observed at 2 to 6 stations throughout Bellingham Bay and at long-term station 38 (Supplemental Data, Figure S4) at concentrations ranging from 0.05 ng/g estimated and 0.13 ng/g minimum detected to 8.87 ng/g maximum detected values (Table 2). Amitriptyline, anhydrochlortetracycline, ibuprofen, miconazole, norverapamil, propoxyphene, and 4-epitetracycline were detected at 1 station each, primarily in Bellingham Bay (Supplemental Data, Figure S5), at concentrations ranging from 0.17 to 46.90 ng/g (Table 2).

Other PPCPs that were not detected in the present study have been reported elsewhere at low levels. In marine sediments collected in Southern California, the range in concentrations of triclosan was reported as nondetected (<0.6 ng/g) to 1.7 ng/g [39]. Triclosan was not detected in Puget Sound; however, the MRL in this survey was higher (55 ng/g) than in the California study. In sediments from a freshwater stream in North Carolina, the concentrations of the antidepressant fluoxetine (Prozac) ranged from 0.35 to 17.4 ng/g at 4 sites [40]. Fluoxetine was not detected in Puget Sound (MRL = 4.53 ng/g).

To date, there are no effects-based sediment quality criteria or guidelines for pharmaceuticals in the United States. The vast majority of toxicity testing with PPCPs has been conducted with surface water samples or with clean water spiked with individual chemicals and tested in laboratory bioassays. Considerably less work has been conducted with soils and even less with freshwater, estuarine, or marine sediments [41–43]. Further work is necessary to characterize the toxicological effects and environmentally relevant concentrations of PPCPs and mixtures of PPCPs on nontarget organisms.

**PFASs**

Among the 40 samples and 13 analytes (a total of 520 analyses), PFASs were detectable in 13 analyses of Puget Sound sediments, an incidence of 2.5%. Perfluorobutanoate (PFBA), perfluorooctanesulfonate (PFOS), and perfluorooctanesulfonamide (PFOSA) were detected in 7 samples, 5 samples, and 1 sample, respectively (6 long-term stations and 7 Bellingham Bay stations), and were the only congeners detected of the 13 PFASs monitored in the present study (Table 2; Supplemental Data, Figure S6). Detectable concentrations for PFBA, PFOS, and PFOSA ranged from 0.13 ng/g to 1.50 ng/g dry weight. Minimum, mean, and median concentrations for PFBA and PFOS estimated with ROS ranged from <0.01 ng/g to 0.03 ng/g, 0.07 ng/g to 0.09 ng/g, and <0.01 ng/g to 0.05 ng/g, respectively (Table 2). The ranges in concentrations were very small, generally about 1 order of magnitude or less. The stations with detected concentrations of PFBA and PFOS represented areas of 7.37 km² and 1.75 km², equivalent to 17.8% and 4.2%, respectively, of the survey area in Bellingham Bay (Table 3).

The consistent observation of PFBA in Bellingham Bay sediments is remarkable considering that sediment–water distribution coefficients ($K_d$, L/kg) for PFASs tend to decrease with decreasing chain length [44], and PFBA was the shortest chain PFAS monitored in the present study. Nonetheless, a

---

Table 3. Incidence and spatial extent of personal care products and pharmaceuticals (PPCPs) and perfluoroalkyl substances (PFASs) in 10 Long-term and 30 Bellingham Bay sediment samples in Puget Sound, Washington, USA

<table>
<thead>
<tr>
<th>Detected chemical</th>
<th>Incidence</th>
<th>Spatial extent a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Long-term stations</td>
<td>Stations with detected values in Bellingham Bay</td>
</tr>
<tr>
<td></td>
<td>No.</td>
<td>Percentage</td>
</tr>
<tr>
<td>PPCP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>7</td>
<td>70.0</td>
</tr>
<tr>
<td>Triclocarban</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triamterene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Varapamil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphetamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Azithromycin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxytetracyclcin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-epitetracyclcin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amitriptyline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrochlorotetracycline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Miconazole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Norverapamil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proproxyphene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFAS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorobutanoate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorooctanesulfonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorooctanesulfonamide</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Spatial extent could not be calculated for the long-term stations, because this study was not based on a probabilistic, random, stratified sampling design [3,31].

---

*Fluoxetine (Prozac) ranged from 0.35 to 17.4 ng/g (Table 2).*
previous study revealed PFBA to be among the major congeners in marine sediments from Tokyo Bay, and in some cases it was absent in pore water but detectable in sediment [45]. The source of PFBA in Bellingham Bay is unclear; however, it is notable that these samples were collected in the vicinity of the Post Point wastewater treatment plant outfall, which serves the city of Bellingham (population ~82,000). Numerous studies have pointed to wastewater treatment plants as significant sources of PFASs to the ambient environment [46–49].

The highest concentration among all PFASs was observed for PFOS (1.50 ng/g) from long-term station 34 in Sinclair Inlet near the city of Bremerton. The city is home to the Puget Sound Naval Shipyard and Naval Base Kitsap, including the former Naval Station Bremerton and Naval Submarine Base Bangor to the north. Perfluorooctanesulfonate is known to have been incorporated into pre-2002 aqueous film-forming foams (AFFF), which are still in use at military bases and airports throughout North America. In the United States, highly elevated levels of PFOS have been reported in groundwater near Naval Air Station Fallon (up to 380 µg/L), Tyndall Air Force Base (up to 2300 µg/L) and Wurtsmith Air Force Base (up to 110 µg/L) [50,51]. The elevated concentrations of PFOS detected in sediments in Sinclair Inlet may indicate past AFFF deployment near this site. Other sites in Puget Sound were also in fairly close proximity to both international and municipal airports, where AFFF may also have been deployed (e.g., Seattle Tacoma International Airport).

Perfluorooctanesulfonamide, which was detected in a single sample south of Seattle (0.18 ng/g) is among a variety of PFASs that have the potential to degrade to PFOS (i.e., PFOS-precursors). The relative importance of PFOS-precursors as a source of exposure to PFOS is of considerable interest, but few data are available on their environmental occurrence. Nonetheless, PFOS-precursors (including PFOSA) have been reported in sediments from Tokyo Bay (Japan) and San Francisco Bay (CA, USA) [45,52] and in some instances have exceeded concentrations of PFOS. While PFOSA was the only PFOS-precursor monitored in the present work, we cannot rule out the occurrence of other PFOS-precursors in sediments of Puget Sound.

Compared with the present study, in which only 3 of the 13 PFASs were detectable, a study of PFAS in sediments from 3 rivers in northern Georgia, USA, reported 10 of 14 were detected [53]. The range in concentrations among the 3 detected chemicals in Puget Sound was 0.13 ng/g to 1.50 ng/g, within the ranges for 10 compounds in Georgia of 0.03 ng/g to 4.66 ng/g. However, the concentrations of PFOS in Puget Sound of 0.20 ng/g to 1.50 ng/g were lower than the range of 1.66 ng/g to 20.18 ng/g in Georgia.

Sediment samples analyzed for 12 PFASs from 13 locations around the perimeters of San Francisco Bay and Monterey Bay (California, USA) displayed a total range of detected concentrations of <0.12 ng/g to 3.94 ng/g dry weight for all samples and all analytes [52]. The majority of their detected concentrations were 0.20 to 0.50 ng/g. These detected concentrations were similar to those for Puget Sound (0.13–1.50 ng/g) for the 3 detected chemicals. The ranges in concentrations of PFOS were similar in California (0.38–3.76 ng/g) and Puget Sound (0.20–1.50 ng/g) but lower than in the Georgia rivers. The range in detected concentrations of 12 PFASs (0.07–1.06 ng/g) in 3 other US areas (inner Baltimore Harbor, MD; Gwynn’s Run, MD; and Willamette River, OR) [52] was also similar to that for Puget Sound.

Perfluorooalkyl substances similar to those quantified in the present study were measured in 2008 in surface waters, wastewater treatment plant effluents, fish fillets, fish livers, and osprey eggs collected from rivers and lakes throughout Washington State [30]. Of the 12 congeners quantified in both studies, 11 were detected in surface waters, 10 in wastewater treatment plant effluent, 9 in osprey eggs, and 4 in fish fillets and livers. The chemical composition of the mixtures of PFASs differed among freshwater sampling stations, as they did in Puget Sound sediments. In all samples PFOS was detected most frequently and at the highest concentrations, and PFOS and PFBA were detected in all but the osprey eggs. While the incidence, or percentage, of analyses with detected PFASs was 2.5% for the sediments measured in this survey, incidence values were higher in surface waters (39.9%), effluent (85.2%), fish fillets (40%), and fish livers (67%).

To the best of our knowledge, there are no effects-based sediment quality criteria or guidelines for PFASs in sediments; however PFOS is known to bioaccumulate and biomagnify in aquatic food webs and may present a hazard to high trophic level organisms [54].

CONCLUSIONS

Detectable concentrations of PPCPs and PFASs in Puget Sound surface sediments occurred in a small minority of samples and analyses at 10 long-term stations around Puget Sound and in Bellingham Bay. The concentrations were very low, either within the ranges or less than results reported for sediments elsewhere and lower than those associated with acute toxicity in laboratory tests for individual chemicals. However, the scientific literature contains very little information on the ecotoxicology of these chemicals in sediment-dwelling organisms; therefore, it is not possible to definitively assess the risk to the resident benthos of Puget Sound. Information from research conducted elsewhere provides evidence that the toxicity of these compounds can be additive or more than additive (i.e., synergistic) when present as mixtures. Nevertheless, along with the results of previous studies in the Pacific Northwest on the presence and concentrations of these substances in surface water, tributary streams, groundwater, wastewater treatment plant influents, effluents, biosolids, fish, and aquatic birds, our data for sediments closes a gap in our knowledge of the ecosystem compartments in which these chemicals occur. Furthermore, our data suggest that the sediments are an important exposure route for these substances to the biota of Puget Sound.

Future work to establish a baseline record of the concentrations of PPCPs and PFASs in sediments in other Puget Sound urban bays and environmental media is required. Such studies will establish a foundation to understand the prevalence and composition of PPCPs and PFASs in the Sound, their potential impact on resident biota, and for use in establishing effects-based sediment quality criteria or guidelines. This information will form an important basis for environmental managers when deciding future regulations regarding the use and discharge of these chemicals in the Puget Sound ecosystem.

SUPPLEMENTAL DATA

Figures S1 to S6. (1.3 MB PDF).

Acknowledgment—The authors thank the following individuals for their role in producing this report: all of the chemists at AXXS Analytical Services who participated in sample analysis; J. Weakland and K. Feddersen, Washington State Department of Ecology’s Manchester Environmental Lab, for their quality assurance review of the data; V. Partridge, Washington State Department of Ecology’s Marine Sediment Monitoring Team, for her
calculations of regression on order statistics for the dataset, and the editors and reviewers for their detailed and helpful comments.

**REFERENCES**


