Pharmaceuticals and Personal Care Products (PPCPs) & Perfluoroalkyl Substances (PFASs) in Puget Sound Sediments An Update: 2010 – 2015

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I. Introduction

- PPCPs and PFASs have been detected in the Puget Sound watershed's **ground** and **surface waters** [1,2]; municipal wastewater **influent**, **effluent**, and **biosolids** [3,4]; estuarine **waters** [3–5]; and in estuarine **sediments** collected by Ecology's Marine Sediment Monitoring Team [6–8].
- Results from sediment monitoring in **4 urban bays** and **10 long-term monitoring stations** are summarized and compared here [8].

Objectives

For PPCPs and PFASs in Puget Sound sediments:

- Establish chemical concentration **baselines**.
- Document **spatial patterns** and **gradients** within and among urban bays.
- Calculate the **spatial extent** of chemicals in urban bays.

II. Methods

Sampling locations

- 2010 **Long-term**, n=10
- 2010 **Bellingham Bay**, n=30
- 2013 **Elliott Bay**, n=30
- 2014 **Commencement Bay**, n=30
- 2015 **Bainbridge Basin**, n=33

Sediment collection

- Sediments were collected with a 0.1-m^2 stainless steel double **van Veen grab**.
- The **top 2 to 3 cm** from multiple grabs at each station were combined and homogenized.
- Samples were sent to **AXYS Analytical Services** Ltd., Sidney, BC, Canada for analysis.

Chemical analyses

- Sediments were tested for the presence of **119 PPCPs** and **13 PFASs** (**Table 1**).
- AXYS Method **MLA-075 (USEPA 1694)** for PPCPs and **MLA-041** for PFASs were used, including high-performance liquid chromatography with positive and negative electrospray ionization modes and tandem mass spectrometry.

Literature Cited:

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6. **Long E., M. Dutch, S. Weakland, B. Chandramouli, and J. Benskin. 2013.** Quantification of PPCPs and PFASs in the Marine Sediments of Puget Sound, WA, USA. Environmental Toxicology and Chemistry 32(8):1701-1710.
7. **Dutch, M., S. Weakland, V. Partridge, and K. Welch. 2014.** PPCPs and PFASs in Elliott Bay Sediments: 2013 Data Summary. Washington State Department of Ecology Pub. No. 14-03-049. https://fortress.wa.gov/ecy/publications/SummaryPages/1403049.html
8. **Dutch M., S. Weakland, V. Partridge, D. Burgess, and A. Eagleston.** ***In preparation.*** PPCPs and PFASs in Commencement Bay and the Bainbridge Basin, and a 5-survey comparison.

IV. Summary

- **Baseline established** – Sediment concentrations of 119 PPCPs and 13 PFASs have been measured in 4 urban bays and 10 long-term monitoring stations in Puget Sound.
- **Low occurrence overall** – While many of the parameters tested (1/3 of PPCPs and 1/2 of PFASs) were detected, over 97% of the total results were undetected.
- **4 dominant chemicals** – **Diphenhydramine**, **triclocarban**, **triamterene**, and **PFOS** occurred most frequently, with highest concentrations and greatest spatial coverage.
- **Spatial patterns in urban bays likely reflect proximity to sources, depositional areas** – Occurrence and concentrations were generally greatest near heads of each bay and in deeper, likely depositional areas.
- **Unique chemical signatures in each urban bay.**

III a. Results – Detected chemicals

- **2.5% of PPCP** and **2.6% of PFAS** results were measured in detectable concentrations.
- **43 of 119 PPCPs** and **7 of 13 PFASs** were detected in samples (**Table 1**).
- **Diphenhydramine**, **triclocarban**, **triamterene**, and **PFOS** were detected most frequently.

Table 1. Parameter list with detected chemicals (number of occurrences).

Personal Care Products and Pharmaceuticals

List 1 - Acid Extraction in Positive Ionization
Acetaminophen
Ampicillin 1
Azithromycin (9)
Caffeine (1)
Carbadox (1)
Carbamazepine
Cefotaxime
Ciprofloxacin (1)
Clarithromycin
Clinafloxacin
Cloxacillin
Dehydronifedipine (1)
Digoxigenin
Digoxin
Diltiazem (5)
1,7-Dimethylxanthine
Diphenhydramine (97)
Enrofloxacin (1)
Erythromycin-H20 (11)
Flumequine
Fluoxetine (7)
Lincomycin
Lomefloxacin
Miconazole (17)
Norfloxacin
Norgestimate (1)
Ofloxacin (1)
Ormetoprim
Oxacillin
Oxolinic acid
Penicillin G
Penicillin V
Roxithromycin
Sarafloxacin (2)
Sulfachloropyridazine
Sulfadiazine
Sulfadimethoxine (3)
Sulfamerazine
Sulfamethazine
Sulfamethizole
Sulfamethoxazole (1)
Sulfanilamide
Sulfathiazole
Thiabendazole
Trimethoprim
Tylosin
Virginiamycin

List 2 - Tetracyclines in Positive Ionization
Anhydrochlortetracycline (1)
Anhydrotetracycline (1)
Chlortetracycline
Demeclocycline
Doxycycline
4-Epianhydrochlortetracycline
4-Epianhydrotetracycline
4-Epichlortetracycline
4-Epioxytetracycline
4-Epitetracycline (1)
Isochlortetracycline
Minocycline
Oxytetracycline (2)
Tetracycline

List 3 - Acid Extraction in Negative Ionization
Bisphenol A
Furosemide
Gemfibrozil
Glipizide
Glyburide
Hydroclorothiazide
2-hydroxy-ibuprofen
Ibuprofen (1)
Naproxen
Triclocarban (82)
Triclosan
Warfarin

List 4 - Basic Extraction in Positive Ionization
Albuterol (2)
Amphetamine (7)
Atenolol
Atorvastatin
Cimetidine
Clonidine
Codeine (1)
Cotinine (1)
Enalapril
Hydrocodone
Metformin (3)
Oxycodone
Ranitidine
Triamterene (75)

List 5 - Acid Extraction in Positive Ionization
Alprazolam (1)
Amitriptyline (17)
Amlodipine (1)
Benzoylecgonine
Benztropine (2)
Betamethasone
Cocaine (1)
DEET (3)
Desmethyldiltiazem (2)
Diazepam
Fluocinonide
Fluticasone propionate
Hydrocortisone
10-hydroxy-amitriptyline
Meprobamate
Methylprednisolone
Metoprolol
Norfluoxetine
Norverapamil (12)
Paroxetine (1)
Prednisolone (1)
Prednisone
Promethazine
Propoxyphene (1)
Propranolol
Sertraline (14)
Simvastatin (2)
Theophylline
Trenbolone
Trenbolone acetate
Valsartan (1)
Verapamil (17)

Perfluorinated Chemicals

Carboxylic Acids
Perfluorobutanoate (PFBA) (7)
Perfluoropentanoate (PFPeA)
Perfluorohexanoate (PFHxA)
Perfluoroheptanoate (PFHpA)
Perfluorooctanoate (PFOA) (2)
Perfluorononanoate (PFNA)
Perfluorodecanoate (PFDA) (1)
Perfluoroundecanoate (PFUnA) (2)
Perfluorododecanoate (PFDoA) (1)

Sulphonic Acids
Perfluorobutanesulfonate (PFBS)
Perfluorohexanesulfonate (PFHxS)
Perfluorooctanesulfonate (PFOS) (32)
Perfluorooctanesulfonamide (PFOSA) (4)

III b. Results – Occurrence & spatial gradients – all chemicals

- Long-term and Bellingham Bay stations had **fewer chemicals** than stations in Elliott Bay, Commencement Bay, and the Bainbridge Basin.
- In all bays, **larger numbers** of chemicals were detected near the **head of each bay**, likely near **discharge sources**, and in **deeper, depositional** locations (**Figure 1**).

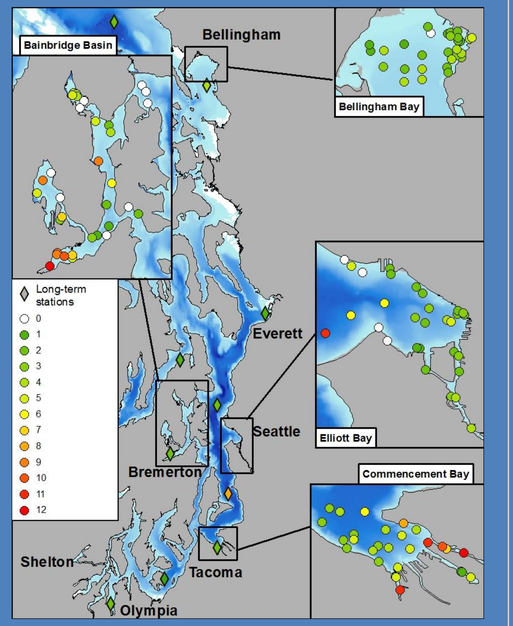

Figure 1. Number of PPCPs and PFASs detected in sediments at 10 long-term monitoring stations and in four urban bays.

III c. Results – Concentrations, gradients of most frequently detected chemicals

- Concentrations of **diphenhydramine**, **triclocarban**, **triamterene**, and **PFOS** ranged widely.
- Concentrations were **lower** in Bellingham Bay than in Elliott Bay, Commencement Bay, and the Bainbridge Basin.
- In all bays, **higher** chemical concentrations were detected closer to the **heads of the bays**, likely near **discharge sources**, and in **deeper, depositional locations** (**Figure 2**).

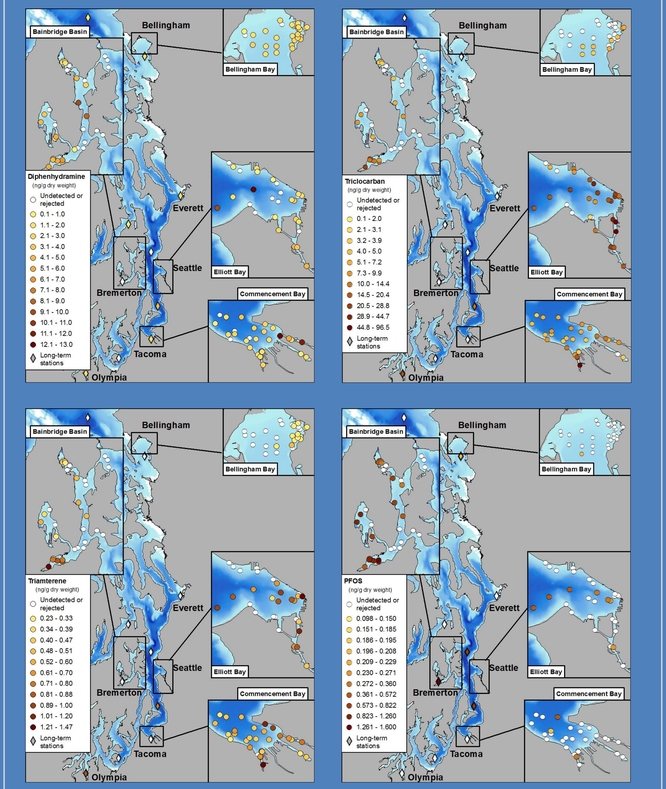

Figure 2. Concentrations (ng/g) of three PPCPs and one PFAS detected most frequently in sediments at 10 long-term monitoring stations and in four urban bays.

III d. Results – Standardized concentrations & spatial extent among study areas

- Standardized chemical concentrations[1] **differed among study areas** but were generally **higher** in Elliott Bay and Commencement Bay (**Figure 3, left**).

  [1] *Concentrations are summarized as percent of the maximum of the weighted means, for comparison among all chemicals and study areas.*
- **Diphenhydramine**, **triclocarban**, **triamterene**, **PFOS** occurred in all 4 bays, with the **highest** combined spatial area (**Figure 3, right**).
- Chemical concentrations and spatial extent values **varied among bays**, giving each a **unique chemical signature.**

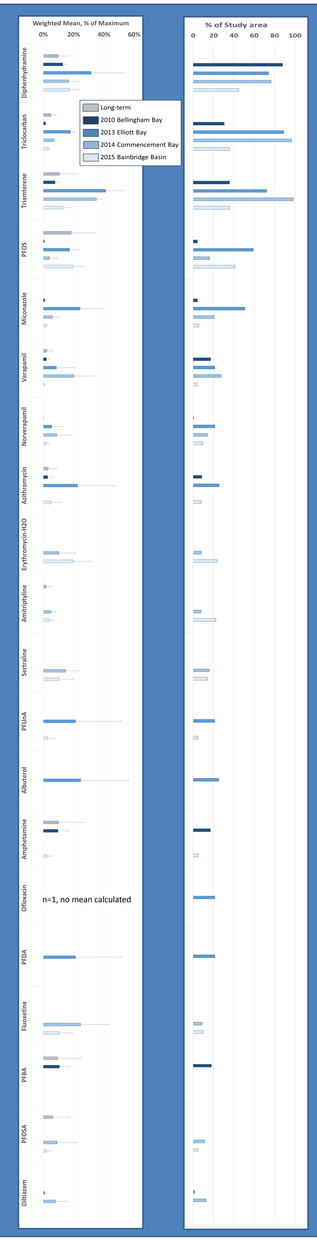

Figure 3. Standardized concentrations (left; as % of the maximum of the weighted means) and spatial extent (right; as % of study area) for 20 most frequently occurring PPCPs and PFASs.

General information about the **Puget Sound Sediment Monitoring Program** and all data generated during these surveys can be accessed from Ecology's Marine Sediment Monitoring website: **https://ecology.wa.gov/Water-Shorelines/Puget-Sound/Sound-science/Marine-sediments**.

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