Pharmaceuticals and Personal Care Products (PPCPs) & Perfluorinated Chemicals (PFCs) in Puget Sound Sediments

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I. Introduction

PPCPs and PFCs released into the environment by human activity are of growing concern. While environmental and human-health effects of PPCPS are not well known, they are by design bioactive chemicals which through human use are continuously released into the environment. PFCs, used in products for their non-stick properties (e.g., cookware, roofing, clothing), are persistent, bioaccumulative, and toxic and can cause cancer, liver, kidney, and reproductive problems.

Recent studies have documented measureable levels of PPCPs and PFCs in ground, fresh, and estuarine waters, and biota in Puget Sound and Washington watersheds (Furl and Meredith, 2010; Johnson et al., 2004; Lubliner et al., 2010; Prakash, Baker, and Dinglasan-Panlilio, 2011). Effects on reproduction in English Sole measured in Elliott Bay may be attributed to exposure to these chemicals (Johnson et al., 2008).

PPCPs and PFCs have never been measured in Puget Sound sediments.

II. Study Questions

- Are PPCPs and PFCs present in Puget Sound sediments?
- If PPCPs and PFCs are present in Puget Sound sediments, which ones have measurable concentrations, where are they located, and in what concentrations are they found?

III. Sampling Locations

In April, 2010, sediments were collected for two ongoing Puget Sound monitoring programs. Ten long-term ambient monitoring stations were sampled from locations throughout Puget Sound for the Puget Sound Assessment and Monitoring Program. Thirty randomly-selected stations were also sampled from Bellingham Bay, using a probabilistic sampling design developed for the Washington State Department of Ecology's Urban Waters Initiative.

IV. Methods

Sediment Collection

Sediments were collected with a 0.1m² stainless steel double vanVeen grab sampler. The top 2 to 3 cm were analyzed for grain size, TOC, toxicity, and chemistry (including PPCPs and PFCs).

Chemical Analyses

Sediments were tested for the presence of 119 PPCPs and 13 PFCs (**Table 1**). Analyses were conducted by AXYS Analytical Services Ltd., Sidney, BC, Canada, using AXYS Method MLA-075 (an extension of USEPA 1694) for PPCPs and MLA-041 for PFCs. These methods use high performance liquid chromatography with positive and negative electrospray ionization modes and tandem mass spectrometry (HPLC/ESI-MS/MS).

V. Results - PPCPs

PPCPs were detected in <2% (91 of 5536) of all results, while 12% (14 of 119) of all chemicals were detected. The concentration and distribution of PPCPs at the 40 stations are displayed in **Figures 1-5**.

Detected chemical	Function	No. Bell. Bay Stations (of 30)	No. Long-term Stations (of 10)	Ratio: Result / Est. Det. Limit
Diphenhydramine	antihistamine	28	7	1.1-8.5
Triclocarban	antibacterial	9	5	1.0-5.9
Triamterene	diuretic	12	2	1.0-2.7
Verapamil	calcium channel blocker	5	1	1.1-1.5
Amphetamine	stimulant	4	1	1.2-2.2
Azithromycin	antibiotic	2	1	1.0-1.1
Oxytetracyclin	antibiotic	2		1.4-1.8
4-Epitetracycline	antibiotic	1		1.0
Amitriptyline	antidepressant		1	1.6
Anhydrochlortetracycline	antibiotic	1		1.0
Ibuprofen	anti-inflammatory	1		1.5
Miconazole	antifungal	1		1.0
Norverapamil	calcium channel blocker	1		1.2
Propoxyphene	pain reliever	1		4.7

Analytical Challenges

Low surrogate recoveries and quantitation issues occurred during PPCP analyses. Performance studies conducted by AXYS suggest that silicate/humic acid interactions in the sediment matrix may transform fluoroquinolone analytes into a form not captured and quantified during analysis. Some PPCP analyses appear to be heavily matrix dependent, and the use of matrix spikes and matrix spike duplicates is critical for matrix-specific troubleshooting with these samples.

VI. Results - PFCs

PFCs were detected in <3.6% (13 of 359) of all results, while 23% (3 of 13) of all chemicals were detected. The three PFCs detected included perfluorobutanoate, perfluorooctanesulfonamide, and perfluorooctanesulfonate, chemicals (and break-down products) used in the manufacturing of photo film and Scotchgard ™. The concentration and distribution of PFCs at the 40 stations are displayed in **Figure 6**.

Detected chemical	No. Bellingham Bay Stations (of 30)	No. Long-term Stations (of 10)	Ratio: Result / Est. Quant. Limit
Perfluorobutanoate (PFBA)	6	1	1.1-2.3
Perfluorooctanesulfonate (PFOS)	1	4	1.1-7.9
Perfluorooctanesulfonamide (PFOSA)	0	1	1.9

VII. Summary/Conclusions

- A PPCP/PFC baseline has been established for sediments at 10 long-term stations and 1 major urban bay in Puget Sound.
- PPCPs/PFCs were detected in sediments from both urban and nonurban locations in limited numbers and at low levels.
- Environmental effects of PPCPs and PFCs in sediments are not well known. Further work is necessary to determine effects of chronic, low-level PPCP/PFC exposure on aquatic life.
- Similar PPCP/PFC baseline surveys are recommended for the other major urban bays in Puget Sound.

Table 1. Personal Care Products and Pharmaceuticals and Perfluorinated Chemicals measured in sediments at 10 long-term monitoring stations throughout Puget Sound and 30 stations in Bellingham Bay.

Personal Care Products and Pharmaceuticals

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

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

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

List 4 - Basic Extraction in Positive Ionization
Albuterol
Amphetamine
Atenolol
Atorvastatin
Cimetidine
Clonidine
Codeine
Cotinine
Enalapril
Hydrocodone
Metformin
Oxycodone
Ranitidine
Triamterene

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

Perfluorinated Chemicals

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

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

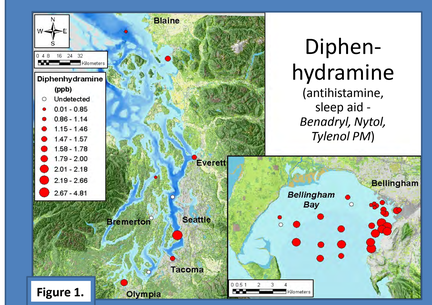


Figure 1.

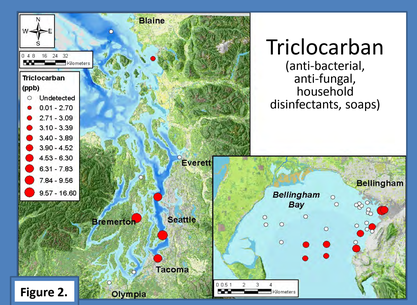
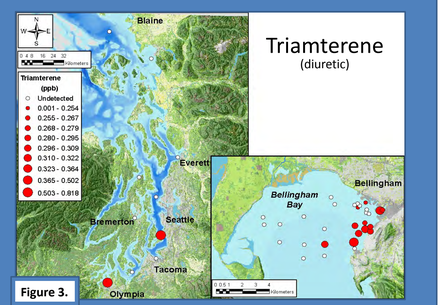


Figure 2.



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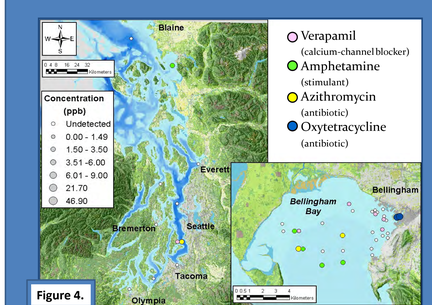

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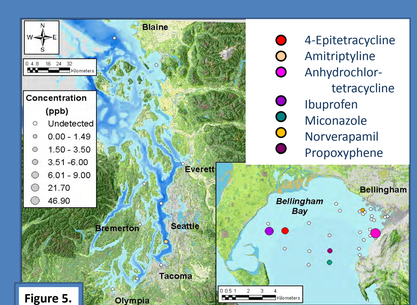

Figure 5.

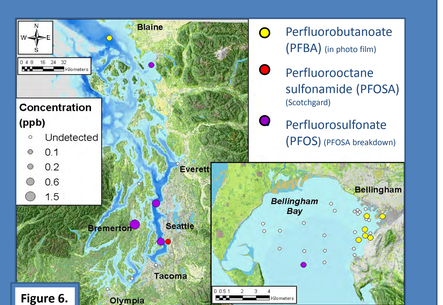

Figure 6.

Figures 1-5. Concentrations of Personal Care Products and Pharmaceuticals detected in sediments at 10 long-term monitoring stations throughout Puget Sound and 30 stations in Bellingham Bay.
Figure 6. Concentrations of Perfluorinated Chemicals detected in sediments at 10 long-term monitoring stations throughout Puget Sound and 30 stations in Bellingham Bay.

Literature Cited: Furl, C. and C. Meredith. 2010. Perfluorinated Compounds in Washington Rivers and Lakes. Washington State Department of Ecology. Publication No 10-03-034. 47 p. + app. http://www.ecy.wa.gov/biblio/1003034.html; **Johnson, A., B. Carey, and S. Golding, 2004.** Results of a Screening Analysis for Pharmaceuticals in Wastewater Treatment Plant Effluents, Wells, and Creeks in the Sequim-Dungeness Area. Washington State Department of Ecology. Publication No 04-03-051. 24 p. + app. www.ecy.wa.gov/biblio/0403051.html; **Johnson, L., D. Lomax, M. Myers, O. Olson, S. Sol, S. O'Neill, J. West, T. Collier. 2008.** Xenoestrogen exposure and effects in English sole (Parophyrs vetulus) from Puget Sound, WA. Aquatic Toxicilogy 88:29-38; **Lubliner, B., M. Redding, and D. Ragsdale. 2010.** Pharmaceuticals and Personal Care Products in Municipal Wastewater and Their Removal by Nutrient Treatment Technologies. Washington State Department of Ecology. Publication No 10-03-004. 52 p. + app. http://www.ecy.wa.gov/biblio/1003034.html; **Prakash, S., J. Baker, and J. Dinglasan-Panlilio, 2011.** Perfluorinated acids in surface waters from Puget Sound. Platform presentation at Pacific Northwest Society of Environmental Toxicology and Chemistry, April 15, 2011, Vancouver, WA.

General information and all data generated during these surveys can be accessed from Ecology's Marine Sediment Monitoring website: **www.ecy.wa.gov/programs/eap/psamp/index.htm.** The poster was prepared for the 2011 Salish Sea Ecosystem Conference, October 25-27, 2011, in Vancouver, British Columbia, and can be found online at **www.ecy.wa.gov/biblio/1103051.html**.