

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

environment. PFCs, used in products for their non-stick properties

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.,

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.

Enalapril

Hydrocodone

Betamethason

DEET

**List 5 - Acid Extraction** 

in Positive Ionization

2004; Lubliner et al., 2010; Prakash, Baker, and Dinglasan-Panlilio,

(e.g., cookware, roofing, clothing), are persistent, bioaccumulative, and

which through human use are continuously released into the

Introduction



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

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#### **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 0.1m<sup>2</sup> stainless steel double vanVeen grab sampler. The top 2 to 3 cm were analyzed for grain size, TOC, toxicity, and chemistry (including PPCPs and

#### **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).

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

#### **Personal Care Products and Pharmaceuticals**

Ciprofloxacin Clarithromycin

Cloxacillin

Erythromycin-H20 Lomefloxacin Miconazole Ofloxacin Ormetoprim Oxacillin Oxolinic acid Penicillin G Penicillin V Roxithromycin

Sarafloxacin Sulfachloropyridazir Sulfamerazine Sulfamethazine Sulfamethizole Sulfamethoxazo

Perfluoroundecanoate (PFUnA) Perfluorododecanoate (PFDoA)

Perfluorooctanoate (PFOA) Perfluorononanoate (PFNA Perfluorodecanoate (PFDA)

**List 3 - Acid Extraction** Fluticasone propionate in Negative Ionization 10-hydroxy-amitriptyline Gemfibrozi Glipizide Glyburide Norfluoxetine Hydroclorothiazide Norverapamil Paroxetine Prednisolone Prednisone Naproxen Triclocarban Promethazine Triclosan Propoxyphene Warfarin Propranolol Sertraline List 4 - Basic Extraction Simvastatin Trenbolone Albuterol **Amphetamine** Trenbolone acetate Atenolol Valsartan Atorvastatin Verapamil Cimetidine Clonidine

Perfluorooctanesulfonamide (PFOSA)

Triamterene Diphen-Triclocarban (anti-bacterial hydramine Triclocarban anti-fungal, Diphenhydramine household (antihistamine Undetected Undetected disinfectants, soaps) sleep aid -0.01 - 0.85 0.255 - 0.267 Benadryl, Nytol, 0.268 - 0.279 1.15 - 1.46 Tylenol PM) 0.280 - 0.295 0.296 - 0.309 1.58 - 1.78 0.310 - 0.322 1.79 - 2.00 0.323 - 0.364 2.01 - 2.18 0.365 - 0.502 **2.19 - 2.66** 0.503 - 0.818 Figure 1. Figure 3. Perfluorobutanoate Verapamil 4-Epitetracycline (PFBA) (in photo film) Amitriptyline • Amphetamine sulfonamide (PFOSA) tetracycline Azithromycin Concentration Concentration (Scotchgard) Concentration Miconazole Perfluorosulfonate Undetected Undetected Oxytetracycline 0.00 - 1.49 Norverapamil 0.00 - 1.49 Undetecte (PFOS) (PFOSA breakdown) 1.50 - 3.50 1.50 - 3.50 0.1 3.51 -6.00 3.51 -6.00 0.2 6.01 - 9.00 6.01 - 9.0 0.6 21.70 21.70 46.90 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.

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.

Figure 6. Concentrations of Perfluorinated Chemicals detected in sediments at 10 long-term monitoring stations throughout Puget Sound and 30 stations in Bellingham Bay.

# YS Analytical Services Ltd.

#### 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)	Stations	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
,	0	1	

#### 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.