

Initial Study of the Occurrence of PPCPs and EDCs in Seattle

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Outline

- Background information
- Goals of the study
- Target compounds and methods
- Occurrence data
- Conclusions

Emerging trace-level organic contaminants

- **Endocrine disruptors in general**
 - Species that mimic natural hormones
- **Pharmaceuticals and personal care products (PPCP)**
 - Human and veterinary drugs, fragrances, sunscreens, supplements, etc.
- **Industrial and household chemicals**
 - Flame retardants, deicing agents, plasticizers (e.g. bisphenol A in polycarbonates)



Existing information on EDC/PPCP in the Metropolitan Seattle area

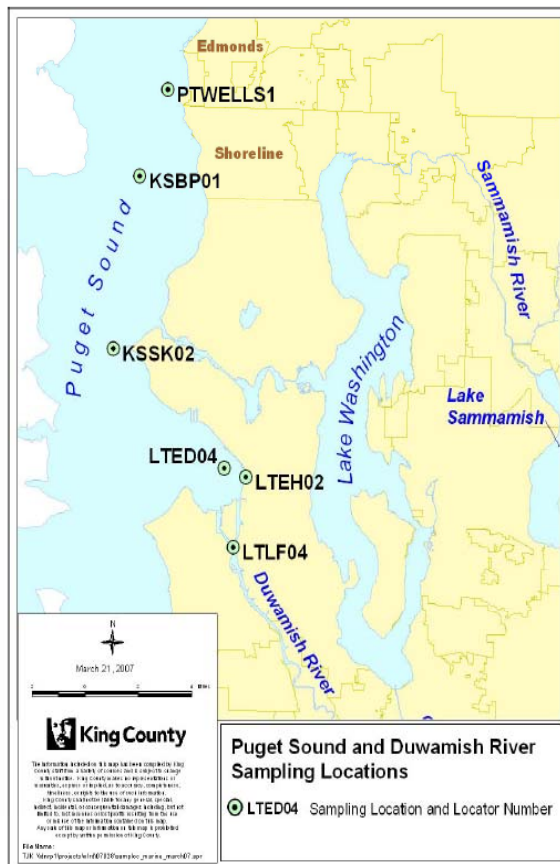
(Survey of Endocrine Disruptors in King County Surface Waters. King County Science Section Report, 2007,

<http://green.kingcounty.gov/wlr/waterres/streamsdata/reports/Endocrine-disrupting-compounds.htm>)

Table 8. EDCs and associated analytical Method Detection Limits ($\mu\text{g/L}$)

Chemical	Method Detection Limit (MDL)	Reporting Detection Limit (RDL)
Benzyl Butyl Phthalate	0.010	0.025
Bis(2-Ethylhexyl)Phthalate	0.010	0.025
Diethyl Phthalate	0.010	0.025
Di-N-Butyl Phthalate	0.010	0.025
Di-N-Octyl Phthalate	0.010	0.025
Dimethyl phthalate	0.050	0.100
Bis(2-ethylhexyl)adipate	0.100	0.500
Bisphenol-A	0.100	0.500
Estradiol	0.010	0.025
Estrone	0.010	0.025
Ethinylestradiol	0.010	0.025
Methyltestosterone	0.010	0.025
4-Nonylphenol (total)	0.100	0.500
Progesterone	0.010	0.025
Testosterone	0.010	0.025
Vinclozolin	0.010	0.025

Selected sampling locations in the King County 2007 study



Existing information on EDC/PPCP in the Metropolitan Seattle area

(Survey of Endocrine Disruptors in King County Surface Waters.
King County Science Section Report, 2007,
[http://green.kingcounty.gov/wlr/waterres/streamsdata/reports/
Endocrine-disrupting-compounds.htm](http://green.kingcounty.gov/wlr/waterres/streamsdata/reports/Endocrine-disrupting-compounds.htm))

- Prior King County study
 - Analytical method - GC/MS
 - Immunoassay testing for estradiol and ethynyl estradiol
- This exploratory study
 - Very different list of compounds
 - HPLC/MS/MS method
 - Considerably more sensitive and reliable for hydrophilic compounds

Goal of this study

- Determine the occurrence of several groups of EDC/PPCP in Seattle area
- Marine waters
 - Puget Sound
- Fresh water sites
 - Industrial sites
 - Duwamish River
 - Urban lakes
 - Lk. Washington, Green Lake, Lk. Union
 - Urban streams
 - Thornton Creek

Target species

Typical use/origin	Compound	Classification
anti-bacterial and anti-fungal	Triclocarban	PCP
anti-bacterial and anti-fungal	Triclosan	PCP
antibiotic	Erythromycin	P
antibiotic	Sulfamethoxazole	P
antibiotic (urinary)	Trimethoprim	P
anti-depressant	Fluoxetine	P
anti-epileptic	Dilantin	P
anti-epileptic, anti-convulsant	Carbamazepine	P
vascular dementia, ED, other	Pentoxifylline	P
anti-hyperlipidemic	Gemfibrozil	P
anti-hypertensive	Atenolol	P
anti-hypertensive	Metoprolol	P
anti-hypertensive	Propranolol	P
anti-inflammatory	Ibuprofen	P
anti-inflammatory	Naproxen	P
anti-pyretic, analgesic	Acetaminophen	P
anti-pyretic, analgesic	Diclofenac	P
X-ray contrast medium	Iopromide	P
steroid hormone	E1	P/EDC
steroid hormone	E2	P/EDC
steroid hormone	E3	P/EDC
steroid hormone	Progesterone	P/EDC
steroid hormone, contraceptive	EE2	EDC
steroid hormone, contraceptive	Mestranol	P/EDC
sunscreen agent	Oxybenzone	PCP
herbicide	Atrazine	herbicide
insect repellent	DEET	PCP
natural alkaloid	Caffeine	food product
plastic component (polycarbonate)	Bisphenol-A	EDC

Marine sampling site

- Puget Sound
 - Golden Gardens park
 - Near West Point treatment plant (shore)
 - Elliott Bay (near the aquarium)
 - Hiram Chittenden locks

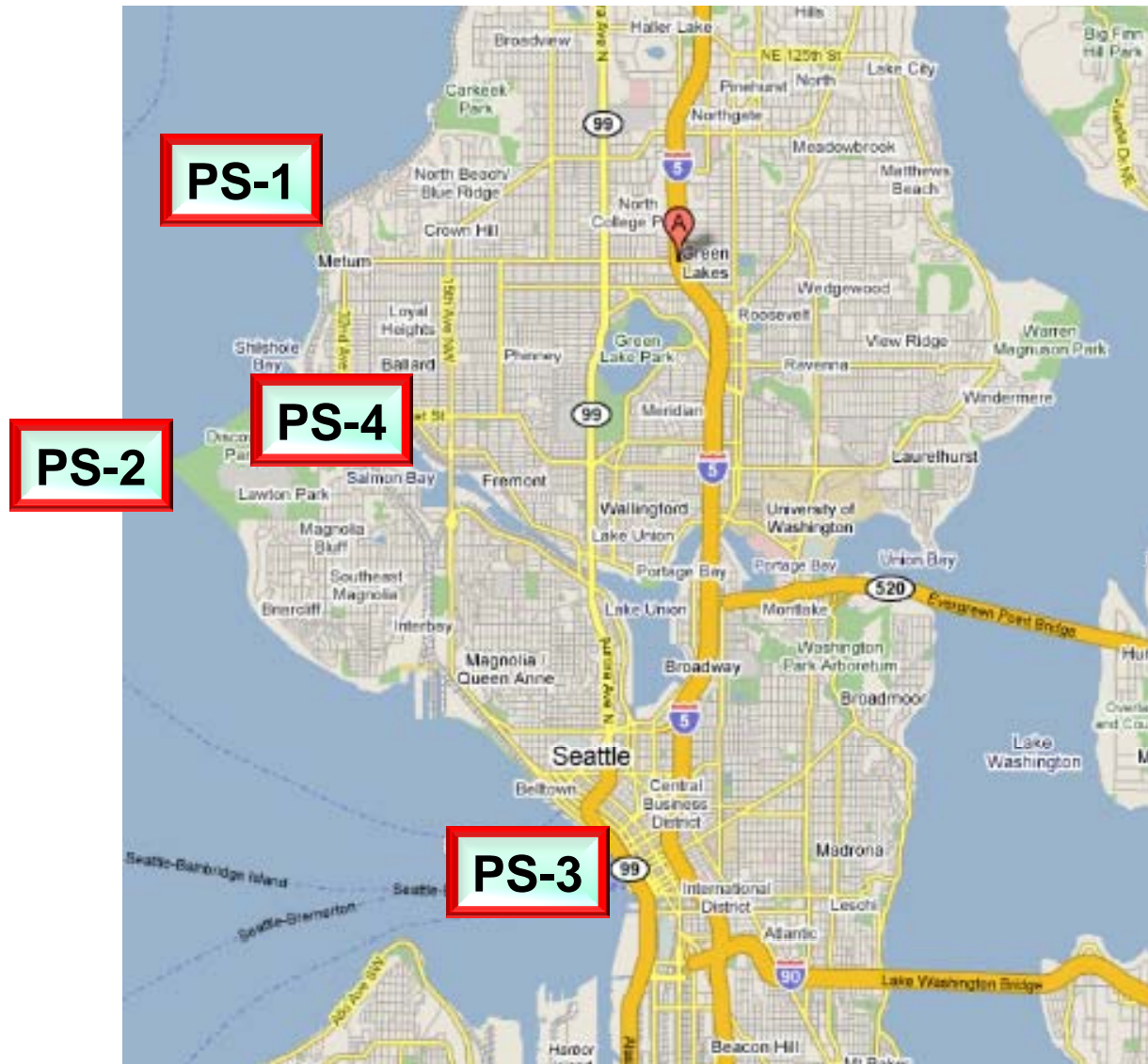


Urban sampling sites

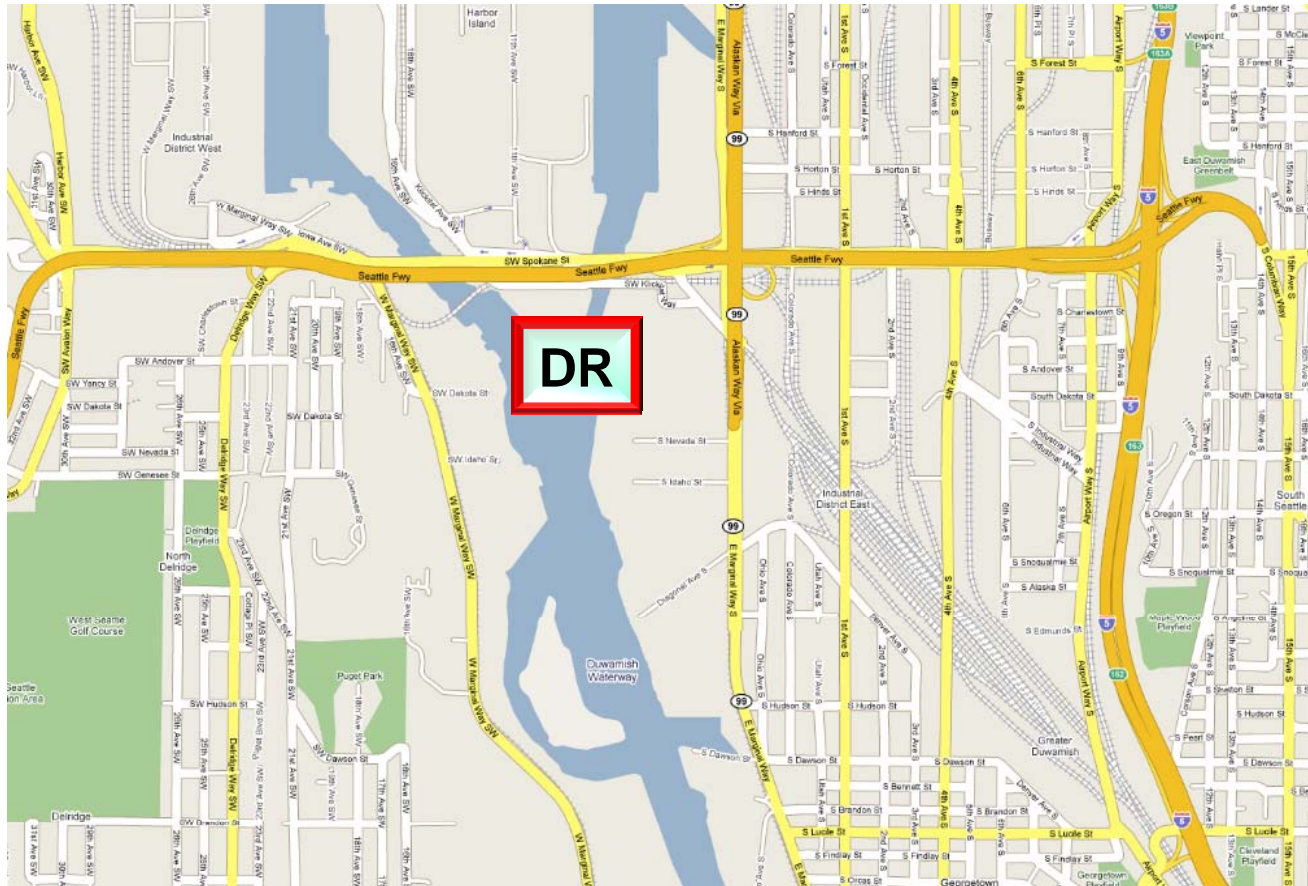
- Lk. Washington
 - Magnuson Park
 - Lake Forest Park
 - Madrona Park
- Thornton Creek
- Lk. Union
 - Gas Works park
 - South Lake park
- Green Lake
- Duwamish River



Puget Sound sampling sites



Duwamish River sampling site



Sampling sites – urban lakes and streams



Analytical procedures

- 4 L containers
 - Clean silanized glassware
- Preconcentration
 - Solid phase extraction
 - 500 mL to 0.5 mL
 - Elution with MTBE/methanol
 - Reconstitution with 80/20 water/methanol
- HPLC/MS/MS analysis
 - ABI-4000 QTrap instrument
 - Shimadzu chromatograph



Analytical procedures

- All samples in triplicates
- Spiked triplicates
 - Spike 10 ng/L of each compound for surface waters
 - Recoveries typically 80 to 100%
 - Lower for fluoxantine, triclocarban
 - Propranolol, metaprolol, oxybenzone

Results

- Groups of compounds
- Antibacterial agents
- Antibiotics
- Antidepressants
- Antihypertensives
- Analgetic and antipyretic
- Steroid hormones
- Others

Occurrence of antibacterial agents in fresh water and marine samples

(all concentrations in ng/L)

Species	MDL (surface water)	MQL (surface water)					TC	GL			DR
			LW-1	LW-2	LW-3	LU-1			LU-2		
Triclosan	0.11	0.30	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
Triclocarban	0.01	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	

Species	MDL (surface water)	MQL (surface water)				
			PS-1	PS-2	PS-3	PS-4
Triclosan	0.11	0.30	<MDL	<MDL	<MDL	<MDL
Triclocarban	0.01	0.04	<MDL	<MDL	<MDL	<MDL

Occurrence of antibiotics in fresh water and marine samples

(all concentrations in ng/L)

Species	MDL (surface water)	MQL (surface water)				TC	GL		
			LW-1	LW-2	LW-3			LU-1	LU-2
Erythromycin	0.03	0.10	<MDL			<MDL	<MDL	<MDL	
Trimethoprim	0.02	0.07	1.0	0.4	0.3	0.4	<MDL	<MDL	
Sulfamethoxazole	0.02	0.06	0.6	2.6	0.4	0.8	0.4	0.3	0.6

Species	MDL (surface water)	MQL (surface water)				
			PS-1	PS-2	PS-3	PS-4
Erythromycin	0.03	0.10	1.5	1.1	1.2	<MDL
Trimethoprim	0.02	0.07	1.2	0.8	0.6	<MDL
Sulfamethoxazole	0.02	0.06	1.9	1.8	1.6	0.6

Occurrence of antidepressants in fresh water and marine samples

(all concentrations in ng/L)

Species	MDL (surface water)	MQL (surface water)	LW		TC	GL	LU		DR
			LW-2	LW-3			LU-1	LU-2	
Carbamazepine	0.01	0.03	<MDL	<MDL	<MDL	0.3	0.3	<MDL	
Dilantin	0.07	0.30	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
Pentoxifylline	0.02	0.07	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
Fluoxetine	0.06	0.20	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	

Species	MDL (surface water)	MQL (surface water)	PS			
			PS-1	PS-2	PS-3	PS-4
Carbamazepine	0.01	0.03	0.4	0.4	0.4	0.4
Dilantin	0.07	0.30		<MDL		
Pentoxifylline	0.02	0.07		<MDL		
Fluoxetine	0.06	0.20		<MDL		

Occurrence of anti-hypertensives in fresh water and marine samples

(all concentrations in ng/L)

Species	MDL (surface water)	MQL (surface water)	LW-1	LW-2	LW-3	TC	GL	LU-1	LU-2	DR
Atenolol	0.08	0.25	0.7	1.0	1.0	1.5	<MDL	<MDL	<MDL	0.7
Metoprolol	0.06	0.20		<MDL		0.5	<MDL	<MDL	<MDL	<MDL
Propranolol	0.02	0.05		<MDL		<MDL	<MDL	<MDL	<MDL	<MDL

Species	MDL (surface water)	MQL (surface water)	PS-1	PS-2	PS-3	PS-4
Atenolol	0.08	0.25	3.2	2.4	2.2	1.0
Metoprolol	0.06	0.20		<MDL		
Propranolol	0.02	0.05	1.8		<MDL	

Occurrence of antipyretics and analgetics in fresh water and marine samples

(all concentrations in ng/L)

Species	MDL (surface water)	MQL (surface water)				TC	GL			DR
			LW-1	LW-2	LW-3			LU-1	LU-2	
Acetaminophen	0.25	0.80	<MDL			5.2	<MDL	0.5	0.9	0.9
Diclofenac	0.06	0.20	5.2	4.1	2.1	0.8	<MDL	<MDL		0.6
Ibuprofen	0.15	0.60	<MDL			0.6	0.6	0.8	30.3	0.4
Naproxen	0.20	0.70	0.8	0.6	0.4	4.0	<MDL	1.2	1.0	0.7

Species	MDL (surface water)	MQL (surface water)				
			PS-1	PS-2	PS-3	PS-4
Acetaminophen	0.25	0.80	0.9	0.6	0.7	3.3
Diclofenac	0.06	0.20	0.3	0.3	<MDL	0.4
Ibuprofen	0.15	0.60	<MDL			1.8
Naproxen	0.20	0.70	0.9	0.8	0.7	1.4

Occurrence of steroid hormones in fresh water and marine samples

(all concentrations in ng/L)

Species	MDL (surface water)	ML (surface water)	LW-1	LW-2	LW-3	TC	GL	LU-1	LU-2	DR
Progesterone	0.03	0.12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
E1	0.10	0.35	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
E2	0.08	0.25	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
E3	0.55	1.70	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
EE2	0.14	0.50	<MDL	<MDL	<MDL	1.0	<MDL	<MDL	<MDL	<MDL
Mestranol	0.23	0.80	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

Species	MDL (surface water)	ML (surface water)	PS-1	PS-2	PS-3	PS-4
Progesterone	0.03	0.12	<MDL	<MDL	<MDL	<MDL
E1	0.10	0.35	<MDL	<MDL	<MDL	<MDL
E2	0.08	0.25	<MDL	<MDL	<MDL	<MDL
E3	0.55	1.70	<MDL	<MDL	<MDL	<MDL
EE2	0.14	0.50	<MDL	<MDL	<MDL	<MDL
Mestranol	0.23	0.80	<MDL	<MDL	<MDL	<MDL

Occurrence of other PPCP species in fresh water and marine samples

(all concentrations in ng/L)

Species	MDL (surface water)	ML (surface water)	LW-1	LW-2	LW-3	TC	GL	LU-1	LU-2	DR
Iopromide	0.60	2.00	<MDL			<MDL	<MDL	<MDL		1.0
Gemfibrozil	0.00	0.02	<MDL			2.6	<MDL	0.3	0.9	0.7
Caffeine	0.03	0.11	17.4	17.9	16.2	36.8	180.5	40.5	64.2	14.7
Oxybenzone	0.05	0.20	2.2	2.9	2.4	3.4	26.2	17.4	22.0	1.9
DEET	0.01	0.03	2.8	2.3	2.8	6.2	16.2	6.4	5.2	0.9
Atrazine	0.01	0.03	0.3	0.3	0.3	0.3	<MDL	0.5	0.5	0.0
Bisphenol-A	0.11	0.40	6.6	6.0	1.9	2.9	7.4	4.1	5.0	1.9

Species	MDL (surface water)	ML (surface water)	PS-1	PS-2	PS-3	PS-4
Iopromide	0.60	2.00	2.4	2.3	1.7	<MDL
Gemfibrozil	0.00	0.02	1.2	1.1	0.9	0.4
Caffeine	0.03	0.11	6.5	6.7	27.0	42.4
Oxybenzone	0.05	0.20	3.4	2.5	2.5	3.2
DEET	0.01	0.03	1.1	1.1	0.8	2.7
Atrazine	0.01	0.03	<MDL			0.3
Bisphenol-A	0.11	0.40	1.7	1.3	1.3	4.9

Conclusions

- Multiple EDC/PPCP species are present in marine and fresh water environmental samples
- EDC/PPCP analyses indicate significant contributions of diffuse pollution
 - Caffeine, DEET, oxybenzone, bisphenol A
- Several antibiotics are consistently present, albeit at trace levels
 - Erythromycin, sulfamethoxazol, trimethoprim
- Several other pharmaceuticals are also ubiquitous but the significance of their presence is unknown
 - Acetaminophen, atenolol, carbamazepine, diclofenac, propranolol, ibuprofen, naproxen

Conclusions

- Not much evidence of the presence of steroid estrogens
 - However, there are selected hits
- What is the status and level of EDC/PPCP pollution?
- Mass concentrations tend to be low, but:
 - Only tip of the iceberg?
 - Antibiotics?
 - Selected EDCs (bisphenol A)
- More to be done

Acknowledgements

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- University of Washington for supporting this exploratory research
- King Country