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Assessing 21st century contaminants of concern using integrative passive sampling devices to obtain more meaningful and cost effective data on impacts from stormwater runoff

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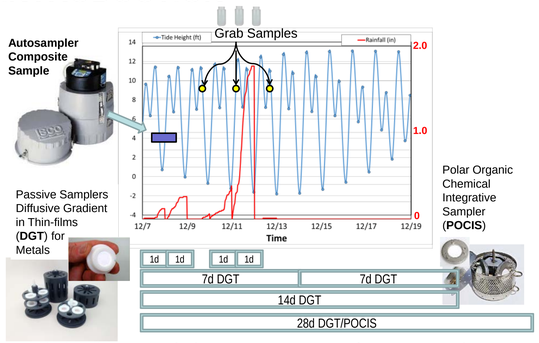
INTRODUCTION

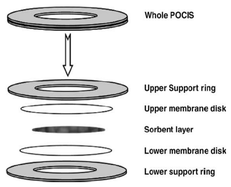


- Grab (and composite) stormwater samples may not be representative of stormwater impacts to the receiving environment, as they may miss the 'pulse' of contaminants.[1]
- Total recoverable metal concentrations used in compliance monitoring are not biologically meaningful for ecological effects
- Composite autosampling has limitations (reliability, cost)
- Integrative passive sampling with Diffusive Gradients in Thin film (DGT) and Polar Organic Chemical Integrative Samplers (POCIS) can provide cost-effective continuous monitoring
- DGTs are being evaluated for end-of-pipe monitoring and value towards assessment of best management practices (BMP) at Naval Base San Diego (NBSD)
- DGTs and POCIS were deployed during ambient monitoring at nearshore locations at Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS&IMF), Naval Base Kitsap (NBK) and reference locations.

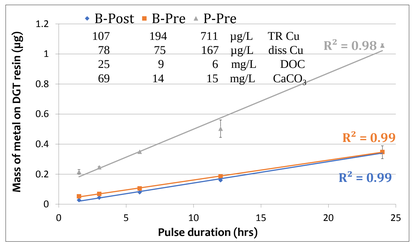
DGT[2] samplers provide a time-averaged concentration of labile (biologically available) metal concentrations following diffusion through a gel layer and permanent binding to a resin layer (Chelex-100).

Cu
Zn
Pb
Cd
Ni

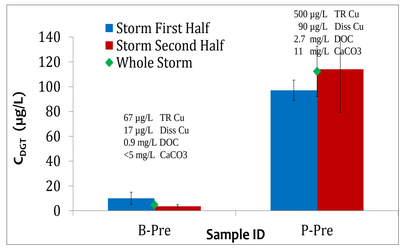
POCIS[3] sample weakly hydrophobic (log K_{ow} ≤4) organic chemicals that bind to a polymeric (hydrophilic-lipophilic-balanced; HLB) sorbent sandwiched between polyethersoulfone (PES) membranes.



RESULTS: San Diego Bay, CA



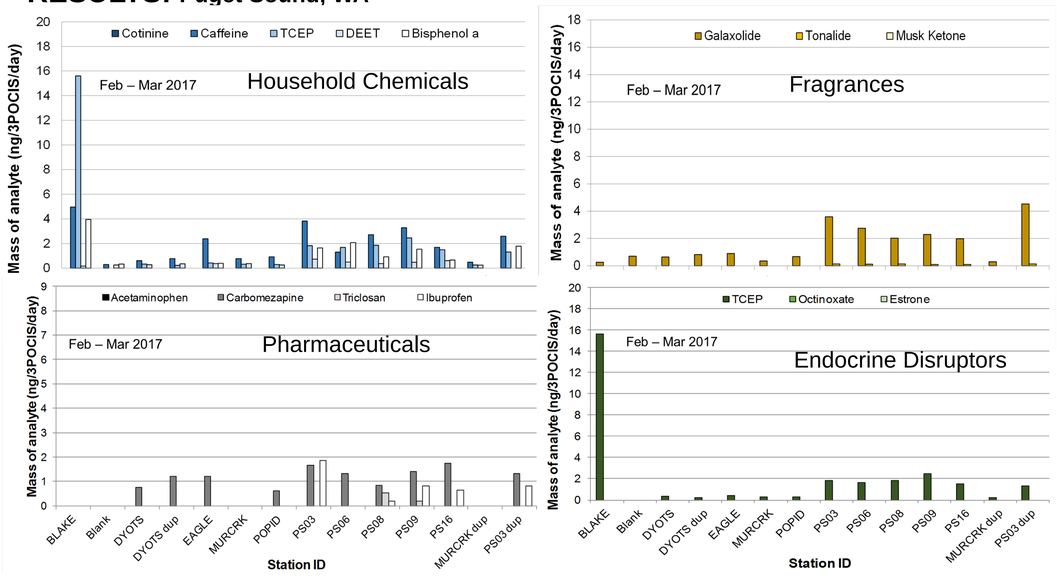
Linear loading of copper on to DGT Chelex-100 resin between 1.5-24 h durations in copper solutions. Shows detectable metal loading during short pulses.



Comparison of first half and second half of ~24 hr storm in comparison with DGT samplers placed for full storm.

Application of a unique DGT approach for real time monitoring of metals in storm drains (above left) in short term (≤ 24 h) exposures at two impervious sites at Naval Base San Diego[4] with focus on BMPs (above right).

RESULTS: Puget Sound, WA



Mass accumulation on POCIS following sampling from sites in Sinclair Inlet and nearby reference sites during Feb. - Mar. 2017 for household chemicals, pharmaceuticals, fragrances, and endocrine disrupting compounds.

Stations (above) within Naval Base Kitsap in Sinclair Inlet and nearby reference locations with varying landuse and runoff regimes (below).

Jurisdiction	Landuse Runoff Regime		StationID
NBK-BREM	Urban/Industrial	Marine/Nearshore	PS03
NBK-BREM	Urban/Industrial	Marine/Nearshore	PS04
PSNS&IMF	Urban/Industrial	Marine/Nearshore	PS06
PSNS&IMF	Urban/Industrial	Marine/Nearshore	PS08
PSNS&IMF	Urban/Industrial	Marine/Nearshore	PS09
PSNS&IMF	Urban/Industrial	Marine/Nearshore	PS11
PSNS&IMF	Urban/Industrial	Marine/Nearshore	PS16
Silverdale Port District	Urban/Commercial	Marine/Nearshore	DYOTS
Illahee Port District	Rural/Residential	Marine/Nearshore	POPIPD
NBK-Bangor	Rural/Industrial	Freshwater/Lake	BLAKE
Bainbridge Island	Rural/Residential	Freshwater/Stream	MURCRK
Bainbridge Island	Urban/Commercial	Marine/Nearshore	EAGLE

Target Chemicals for POCIS

	Analyte Name	Usage	Log Kow	Sampling Rate Studies, L/d
Endocrine Disruptors	Estrone	Hormone	3.6	0.13
	Octinoxate	Sunscreen	5.9	NA – to be determined
	TCEP	Flame Retardant	1.5	NA – to be determined
Household Chemicals	Caffeine	Common Stimulant	-0.63	Equilibrium - 0.74 L/POCIS
	DEET	Insect repellant	2.4	0.22
	Cotinine	Nicotine metabolite	0.07	0.14
	Bisphenol a	Plasticizer	3.6	1.3
Hydrocarbons	4-nonylphenol	Household detergents	6.1	0.12
	Fluoranthene	Aromatic Hydrocarbon	5.0	0.024
Pharmaceuticals	Triclosan	Antimicrobial	5.3	1.7
	Ibuprofen	Anti-inflammatory	0.94	0.33
	Acetaminophen	Pain reliever	0.47	0.11
	Carbamazepine	Seizure treatment	1.9	0.328
	Metformin	Diabetes treatment	-3.25	NA – to be determined
Fragrances	Galaxolide	Soaps, perfumes	5.0	NA – to be determined
	Musk Ketone	Soaps, perfumes	2.51	NA – to be determined
	Tonalide	Soaps, perfumes	5.06	NA – to be determined

Analytical quantitation level (QL, ng extracted from 3 POCIS) and relative stand deviation (RSD) of 6 replicates for analytes of interest.

Analyte	Category	QL	Percent Spiked Recove	RSD
Estrone	EDC - Hormone	<10	75.38%	3.63%
Octinoxate	EDC - Sunscreen	<5	84.63%	3.37%
TCEP	EDC Flame Retardant	<10	101.12%	6.19%
Caffeine	Household	<15	92.20%	6.30%
Cotinine	Household	<5	80.07%	7.99%
DEET	Household - bug repelant	<5	98.13%	4.46%
Bisphenol a	Household - plastic resin	<10	84.12%	9.40%
Nonylphenol	Hydrocarbon - 1 ring	<10	84.47%	4.57%
Fluoranthene	Hydrocarbon - PAH 4 rings	<5	81.07%	4.81%
Triclosan	Medicine - Antibiotic	<10	76.48%	5.03%
Acetaminophen	Medicine - pain	<10	85.72%	4.45%
Ibuprofen	Medicine - pain	<10	90.03%	3.39%
Metformin	Medicine- diabetes	<10	53.48%	20.12%
Carbomezapine	Medicine - sezure	<15	94.10%	8.45%
Galaxolide	Perfume	<5	80.22%	9.31%
Musk Ketone	Perfume	<5	73.43%	9.98%
Tonalide	Perfume	<5	72.53%	11.38%

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CONCLUSIONS

- Integrative passive samplers show promise towards biologically relevant exposure/assessment of stormwater discharges and associated contaminants of concern in receiving water monitoring.
- Highly sensitive, reproducible results that support trace level changes in metal availability (DGT) and weakly hydrophobic (POCIS) contaminants in a marine estuary
- End of pipe sampling promising, but requires additional work to address possible issues associated with low ionic strength rainwater and highly dynamic stormwater discharges
- Passive sampling devices provide supplemental data to reduce costly traditional monitoring
- Surveillance monitoring with passive samplers can be used to finger print likely sources of contamination

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