POCIS – Current Applications, On-going Research and Future Needs

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U.S. Department of the Interior
U.S. Geological Survey
OUTLINE

State of technology

What types of information can you get

Current/recent application

Calibration

PRCs

Bioindicator tests

Future needs
Polar Organic Chemical Integrative Sampler (POCIS)

The POCIS was designed to sequester and concentrate waterborne polar organic chemicals.

It consists of a microporous polyethersulfone membrane enveloping various solid phase sorbents and/or mixtures of sorbents.

Its versatility allows for the sequestering medium and membranes to be tailored to specific applications.

Recommend using the “pharmaceutical” configuration containing Oasis HLB for most applications.

Exploded view of the uptake process in POCIS

Sorbent particles

Contaminant molecule

Pore Size

0.1 \( \mu \)m

Membrane

\sim 130 \mu m thickness
General Processing Scheme for POCIS

1. Exterior Cleaning
2. Solvent Extraction & Chemical Recovery
3. Enrichment and Fractionation
4. Transport to lab sealed in airtight can
5. Deployed POCIS
6. Chemical Analysis
7. Bioassay/Toxicity testing
Sampling Characteristics of POCIS and SPMDs

Alvarez et al. 2007 Ch. 8 in Passive Sampling Techniques. Comprehensive Analytical Chemistry, vol 48, Elsevier
<table>
<thead>
<tr>
<th>SPMDs</th>
<th>POCIS</th>
</tr>
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<tbody>
<tr>
<td>Priority Pollutant PAHs</td>
<td>Pharmaceuticals including</td>
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<tr>
<td>(also, some alkylated PAHs)</td>
<td>Acetaminophen, Carbamazepine, Azithromycin,</td>
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<tr>
<td></td>
<td>Erythromycin, Sulfas drugs (antibiotics)</td>
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<tr>
<td>Certain heterocyclic aromatics</td>
<td>Tetracycline antibiotics</td>
</tr>
<tr>
<td>Organochlorine Pesticides</td>
<td>Illicit drugs (methamphetamine, MDMA)</td>
</tr>
<tr>
<td>Several Current-Use Pesticides including</td>
<td>Several natural and synthetic hormones</td>
</tr>
<tr>
<td>Pyrethroids and Endosulfan</td>
<td>17β-estradiol, 17α-ethynylestradiol</td>
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<tr>
<td></td>
<td>metabolites: estrone and estridol</td>
</tr>
<tr>
<td>PCB Congeners</td>
<td>Triazine herbicides including</td>
</tr>
<tr>
<td>Chlorinated dibenzodioxins including</td>
<td>Atrazine and its metabolites</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>Various polar pesticides including</td>
</tr>
<tr>
<td>Chlorinated dibenzofurans including</td>
<td>Acetochlor, Alachlor, Chlorpyrifos, Diazinon,</td>
</tr>
<tr>
<td>2,3,7,8-TCDF</td>
<td>Dichlorvos, Diuron, Isoproturon, Metolachlor</td>
</tr>
<tr>
<td>Perfluorinated Compounds</td>
<td>Various household and industrial products and</td>
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<tr>
<td>PFOS, telomer alcohols</td>
<td>degradation products including</td>
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<tr>
<td>Flame Retardants</td>
<td>Alkyl phenols (nonyl phenol), Benzophenone,</td>
</tr>
<tr>
<td>PBDEs</td>
<td>Caffeine, DEET, Indole, Tricosan</td>
</tr>
<tr>
<td>Tributyl Tin</td>
<td>Perfluorinated Compounds</td>
</tr>
<tr>
<td>Nonyl phenol</td>
<td>PFOS, PFOA</td>
</tr>
<tr>
<td>Essentially, compounds with log $K_{ow} &gt; 3.0$</td>
<td>Essentially, compounds with log $K_{ow} \leq 3.0$</td>
</tr>
</tbody>
</table>
**What type of information can you get from the POCIS?**

With sampling rate data –

- Quantitative measurements of contaminant water concentrations
- Plus everything under the “Without sampling rate data” list

Without sampling rate data –

- Qualitative measures of contaminant water concentrations
- Relative differences between sites
- Identification of chemicals (is it there? YES / NO )
- Bio-mimic assessment of an organism’s exposure to chemicals
Current / Recent Applications – Wastewater Monitoring

- Tinkers Creek, OH
- Potomac River Basin, MD and VA
- Assunpink Creek, NJ
- Mad River, OH
- Fourmile Creek, IA
- Boulder Creek, CO
- Santa Ana River, CA
- Las Vegas / Lake Mead, NV
- Ozark Caves, MO
- Eagle Bluffs, MO
- Golden Gate National Park, CA
- Ozark Caves, MO
- Boulder Creek, CO
Current / Recent Applications - Drugs from WWTPs

Also Detected:
nonylphenol polyethoxylate and alcohol polyethoxylate surfactants
PFOA and PFOS

Azithromycin (antibiotic)

Illegal Drugs

Jones-Lepp et al. 2004 Arch Environ Contam Toxicol 47, 427-439
Current / Recent Applications - Agricultural Monitoring

POCIS were deployed Summer 2004 in the drainage basins of 3 agricultural areas.

Pesticides and degradates which were commonly found included:
- Acetochlor
- Alachlor
- Atrazine
- Desethytriazine
- Desisopropylatrazine
- Fipronil
- Metochlor
- Simazine
- Trifluralin

Alvarez et al. 2007 J. Environ. Qual. IN PRESS
Current / Recent Applications - CAFO Activities

Delmarva Peninsula

- 600 million chickens worth more than 2 billion dollars annually (USDA, 1992)
- 1.6 billion pounds of manure per year
- SPMDs and POCIS were deployed during spring/summer 2000 at 3 locations in each refuge
- 17β-estradiol and tetracycline found at sites impacted by poultry litter field application and runoff
- Several pesticides associated with agriculture were also found

1. Prime Hook National Wildlife Refuge
2. Blackwater National Wildlife Refuge
Current / Recent Applications – Comparison to Grab Sampling

Assunpink Creek near Trenton, NJ
Site 1 – 100 yards downstream from WWTP discharge
Site 2 – 2 miles further downstream

POCIS deployed for 54 days
Water samples taken every 14 days
Samples analyzed by LC/MS and GC/MS for selected pharmaceuticals and wastewater-related contaminants

Alvarez et al. 2005 Chemosphere 61:610-622
### Current / Recent Applications – Comparison to Grab Sampling

<table>
<thead>
<tr>
<th>Pharmaceuticals</th>
<th>Fire Retardants</th>
<th>Plasticizers</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetaminophen</td>
<td>Fryol CEF</td>
<td>diethylhexylphthalate</td>
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<tr>
<td>carbamazepine</td>
<td>Fryol FR2</td>
<td>triphenyl phosphate</td>
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<tr>
<td>dehydronifedipine</td>
<td>tri(2-butoxyethyl)phosphate</td>
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<td>diphenhydramine</td>
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<tr>
<td>sulfamethoxazole</td>
<td>Nonionic Detergent Metabolites</td>
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<tr>
<td>thiamizazole</td>
<td>4-cumylphenol</td>
<td>5-methyl-1H-benzotriazole</td>
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<td></td>
<td>4-tert-octylphenol</td>
<td>anthraquinone</td>
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<td></td>
<td>nonylphenol, diethoxy</td>
<td>benzophenone</td>
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<td></td>
<td></td>
<td>caffeine</td>
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<td></td>
<td></td>
<td>cotinine</td>
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<td></td>
<td>Fragrances</td>
<td>tributyl phosphate</td>
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<tr>
<td></td>
<td>3-methyl-1H-indole</td>
<td>triclosan</td>
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<td></td>
<td>HHCB</td>
<td>triethyl citrate</td>
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<td></td>
<td>indole</td>
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<td></td>
<td>methyl salicylate</td>
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<td></td>
<td>tonalide</td>
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<tr>
<td>Pesticides</td>
<td></td>
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<tr>
<td>atrazine</td>
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<td>DEET</td>
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<tr>
<td>diazinon</td>
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<tr>
<td>metolachlor</td>
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<tr>
<td>pentachlorophenol</td>
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<tr>
<td>prometon</td>
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</tbody>
</table>

Chemicals highlighted in green identified in POCIS extracts only
Alvarez et al. 2005 *Chemosphere* 61:610-622
Current / Recent Applications – Pharmaceuticals in UK

A range of therapeutic drug classes were selected based on their prevalent usage and potential risk to the aquatic environment in the United Kingdom.

3 sites located near STWs were sampled over three successive 30 day periods.

7 out of 10 targeted pharmaceuticals were detected including sulfamethoxazole, trimethoprim, propranolol, erythromycin, dextropropoxyphene, diclofenac, and mefenamic acid.

Alvarez et al. 2007 Ch. 8 in Passive Sampling Techniques. Comprehensive Analytical Chemistry, vol 48, Elsevier
Current / Recent Applications - Regulatory Applications

Most emerging contaminants for which POCIS is ideally suited are not currently regulated.

A pilot study by the City of Santa Cruz, CA, using POCIS and SPMDs to monitor effluent from a WWTP has demonstrated the usefulness of this technique once new regulations are made.

For more details on this project, see the poster by Akin Babatola.
Determination of Sampling Rates (Calibration Studies)

Initial tank studies –
Static renewal under stirred and non-stirred conditions
Pharmaceuticals, pesticides, hormones

Current field calibration –
Treated WW effluent under controlled flow, temperature, and light
Wastewater chemicals, pharmaceuticals

Current diluter –
Flow-through system
Agricultural pesticides

USGS
Performance Reference Compounds (PRCs)

PRCs are chemicals added to the sampler prior to deployment. PRC loss rate can be used to account for site-specific environmental factors (i.e., flow and temperature).

POCIS sorbents have a high sorptive capacity making selection of PRC with sufficient fugacity problematic.

Alternatives –

Mini PRC-SPMD mounted in POCIS rings can act as a surrogate for chemicals which are under water boundary layer control.

Use of other chemical reservoirs placed between the PES membranes which are less sorptive (i.e., C18, silicone)

Alvarez et al. 2007 Ch. 8 in Passive Sampling Techniques. Comprehensive Analytical Chemistry, vol 48, Elsevier
Combination with Bioindicator/Toxicity tests

Extracts have been screened using the Microtox acute toxicity assay and the YES. In general, POCIS extracts can be used in conjunction with almost any assay or exposure test.

Standard serial dilution YES assay

Silica gel fractionation/YES/GC-MS identification
Future Research Needs

Optimization of extraction schemes/methods

Different custom configurations for specific chemical classes not easily sampled and/or recovered from the current design

Modeling of the uptake curve
  effects of flow and temperature
  measurement of partition coefficients

Continued determination of sampling rates

Finalization of the PRC approach
Acknowledgements

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Roger Stewart – Virginia DEQ
John Holmes – Friends of the North Fork of the Shenandoah River
Doug Novinger – Missouri Department of Conservation
Akin Babatola – City of Santa Cruz, CA

And Many More That I’m Forgetting, Sorry.