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

D.A. Alvarez

USGS, BRD, Columbia Environmental Research Center, Columbia, MO
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 μm

Water

Water

Membrane

~ 130 μm thick
General Processing Scheme for POCIS

Exterior Cleaning

Solv

tent Extraction & Chemical Recovery

Enrichment and Fractionation

Transport to lab sealed in airtight can

Deplo

ed POCIS

Chemical Analysis

Bioassay/Toxicity testing

Chemical Analysis
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><strong>SPMDs</strong></th>
<th><strong>POCIS</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Priority Pollutant PAHs (also, some alkylated PAHs)</td>
<td>Pharmaceuticals including: Acetaminophen, Carbamazepine, Azithromycin, Erythromycin, Sulfur drugs (antibiotics) Tetracycline antibiotics</td>
</tr>
<tr>
<td>Certain heterocyclic aromatics</td>
<td>Illicit drugs (methamphetamine, MDMA)</td>
</tr>
<tr>
<td>Organochlorine Pesticides</td>
<td>Several natural and synthetic hormones</td>
</tr>
<tr>
<td>Several Current-Use Pesticides including</td>
<td>17β-estradiol, 17α-ethynylestradiol</td>
</tr>
<tr>
<td>Pyrethroids and Endosulfan</td>
<td>metabolites: estrone and estriol</td>
</tr>
<tr>
<td>PCB Congeners</td>
<td>Triazine herbicides including: Atrazine and its metabolites</td>
</tr>
<tr>
<td>Chlorinated dibenzodioxins including 2,3,7,8-TCDD</td>
<td>Various polar pesticides including: Acetochlor, Alachlor, Chlorpyrifos, Diazinon, Dichlorvos, Diuron, Isoproturon, Metolachlor</td>
</tr>
<tr>
<td>Chlorinated dibenzofurans including 2,3,7,8-TCDF</td>
<td>Various household and industrial products and degradation products including: Alkyl phenols (nonyl phenol), Benzophenone, Caffeine, DEET, Indole, Triclosan</td>
</tr>
<tr>
<td>Perfluorinated Compounds</td>
<td>Perfluorinated Compounds: PFOS, PFOA</td>
</tr>
<tr>
<td>Flame Retardants</td>
<td>Urobilin (fetal contamination marker)</td>
</tr>
<tr>
<td>PFOS, telomer alcohols</td>
<td></td>
</tr>
<tr>
<td>PBDEs</td>
<td></td>
</tr>
<tr>
<td>Tributyl Tin</td>
<td></td>
</tr>
<tr>
<td>Nonyl phenol</td>
<td></td>
</tr>
<tr>
<td>Essentially, compounds with log $K_{ow}$ ≥ 3.0</td>
<td>Essentially, compounds with log $K_{ow}$ ≤ 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

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

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

Azithromycin (antibiotic)

Summer – 15 ng/L
Winter – 66 ng/L
Summer – 19 ng/L

Illegal Drugs

MDMA
Summer – 0.3 ng/L

MDMA
Summer – ND

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
- Desethylatrazine
- 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>
</tr>
<tr>
<td>carbamazepine</td>
<td>Fryol FR2</td>
<td>triphenyl phosphate</td>
</tr>
<tr>
<td>dehydronifedipine</td>
<td>tri(2-butoxyethyl)phosphate</td>
<td></td>
</tr>
<tr>
<td>diphenhydramine</td>
<td>Nonionic Detergent Metabolites</td>
<td></td>
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<tr>
<td>sulfamethoxazole</td>
<td>4-cumylphenol</td>
<td>5-methyl-1H-benzotriazole</td>
</tr>
<tr>
<td>thiabendazole</td>
<td>4-tert-octylphenol</td>
<td>anthraquinone</td>
</tr>
<tr>
<td></td>
<td>nonylphenol, diethoxy</td>
<td>benzophenone</td>
</tr>
<tr>
<td></td>
<td>Fragrances</td>
<td>caffeine</td>
</tr>
<tr>
<td></td>
<td>3-methyl-1H-indole</td>
<td>cotinine</td>
</tr>
<tr>
<td></td>
<td>HHCB</td>
<td>tributyl phosphate</td>
</tr>
<tr>
<td></td>
<td>indole</td>
<td>triclosan</td>
</tr>
<tr>
<td></td>
<td>methyl salicylate</td>
<td>triethyl citrate</td>
</tr>
<tr>
<td></td>
<td>tonalide</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
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.
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
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Doug Novinger – Missouri Department of Conservation
Akin Babatola – City of Santa Cruz, CA

And Many More That I’m Forgetting, Sorry.