USGS
science for a changing world

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

1

OUTLINE

State of technology

What types of information can you get

Current/recent application

Calibration

PRCs

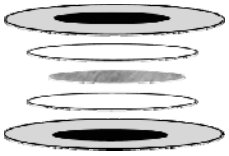
Bioindicator tests

Future needs

USGS

2

Polar Organic Chemical Integrative Sampler (POCIS)



Exploded 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.

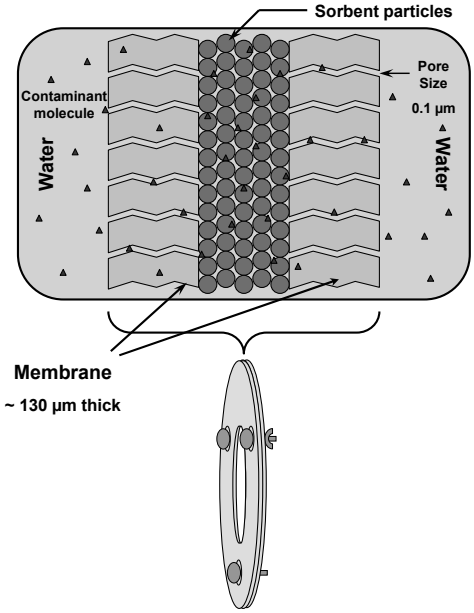
Recommend using the “pharmaceutical” configuration containing Oasis HLB for most applications.

USGS

Alvarez et al. 2004 *Environ Toxicol Chem* 23:1640-1648

3

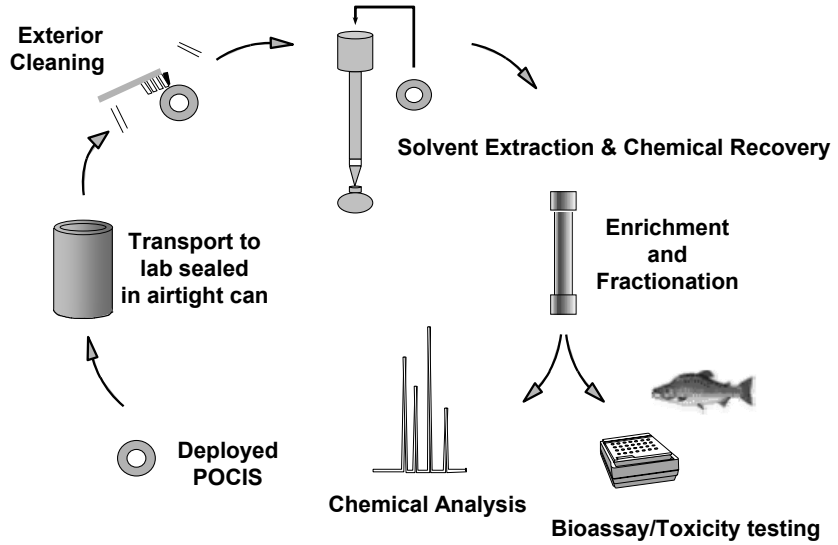
Exploded view of the uptake process in POCIS



USGS

4

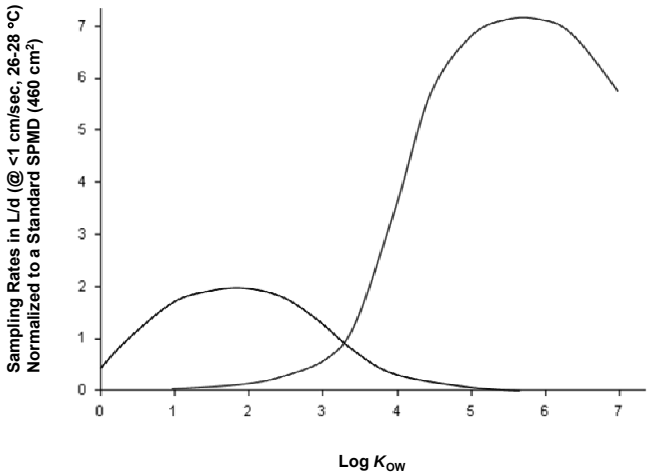
General Processing Scheme for POCIS



USGS

5

Sampling Characteristics of POCIS and SPMDs



USGS

Alvarez et al. 2007 Ch. 8 in *Passive Sampling Techniques. Comprehensive Analytical Chemistry*, vol 48, Elsevier

6

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

USGS

7

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

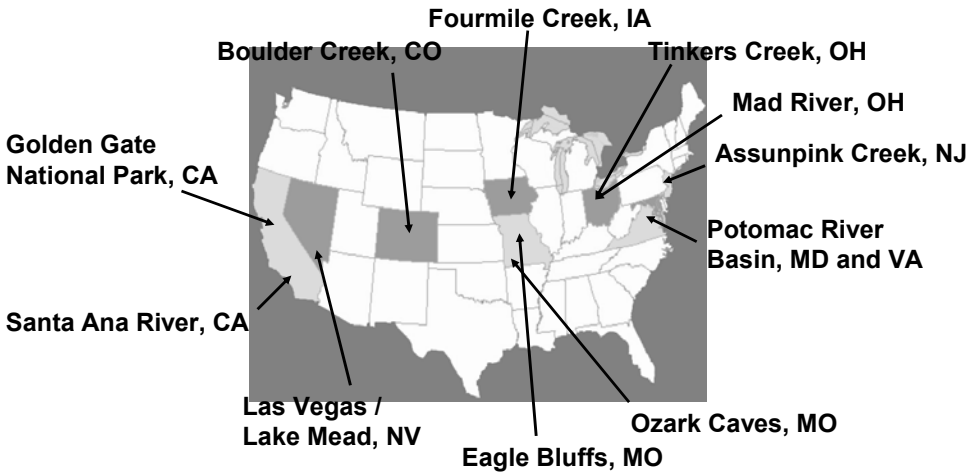
Without sampling rate data –

- 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

USGS

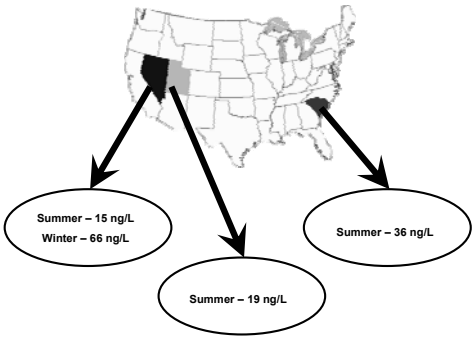
8

Current / Recent Applications – Wastewater Monitoring



USGS

Current / Recent Applications - Drugs from WWTPs



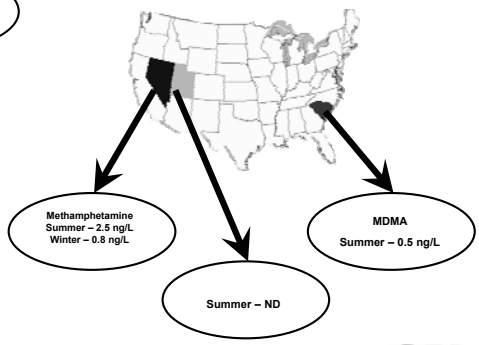
Azithromycin (antibiotic)

Also Detected:

nonylphenol polyethoxylate and alcohol polyethoxylate surfactants

PFOA and PFOS

Illegal Drugs



USGS

Jones-Lepp et al. 2004 *Arch Environ Contam Toxicol* 47, 427-439

ORD

10

Current / Recent Applications - Agricultural Monitoring

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

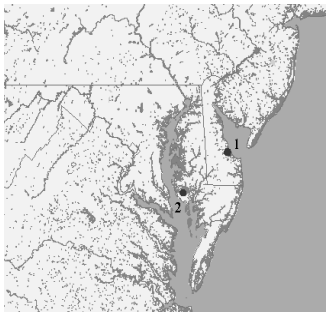
Pesticides and degradates which were commonly found included:

- Acetochlor
- Alachlor
- Atrazine
- Desethylatrazine
- Desisopropylatrazine
- Fipronil
- Metochlor
- Simazine
- Trifluralin

USGS

Alvarez et al. 2007 *J. Environ. Qual.* IN PRESS

Current / Recent Applications - CAFO Activities



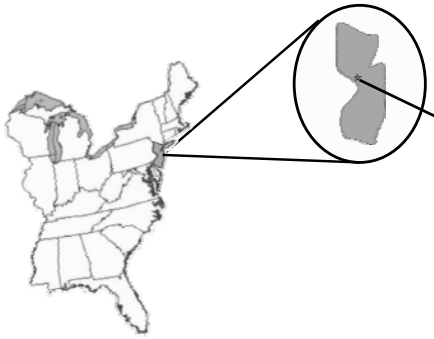
1. **Prime Hook National Wildlife Refuge**
2. **Blackwater National Wildlife Refuge**

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

USGS

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

USGS

Alvarez et al. 2005 *Chemosphere* 61:610-622

13

Current / Recent Applications – Comparison to Grab Sampling

Pharmaceuticals

- acetaminophen
- carbamazepine
- dehydronifedipine
- diphenhydramine
- sulfamethoxazole
- thiabendazole

Pesticides

- atrazine
- DEET
- diazinon
- metolachlor
- pentachlorophenol
- prometon

Fire Retardants

- Fryol CEF
- Fryol FR2
- tri(2-butoxyethyl)phosphate

Nonionic Detergent Metabolites

- 4-cumylphenol
- 4-tert-octylphenol
- nonylphenol, diethoxy

Fragrances

- 3-methyl-1H-indole
- HHCB
- indole
- methyl salicylate
- tonalide

Plasticizers

- diethylhexylphthalate
- triphenyl phosphate

Miscellaneous

- 5-methyl-1H-benzotriazole
- anthraquinone
- benzophenone
- caffeine
- cotinine
- tributyl phosphate
- triclosan
- triethyl citrate

USGS

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.

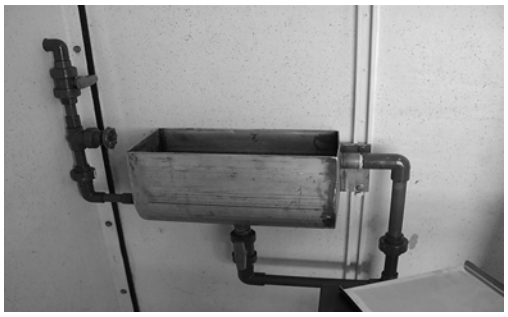
USGS

Alvarez et al. 2007 Ch. 8 in *Passive Sampling Techniques. Comprehensive Analytical Chemistry*, vol 48, Elsevier

Environment Agency

15

Current / Recent Applications - Regulatory Applications



For more details on this project, see the poster by Akin Babatola.

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.

USGS

16

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

17

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)

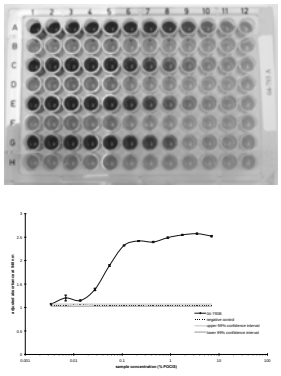
USGS

Alvarez et al. 2007 Ch. 8 in *Passive Sampling Techniques. Comprehensive Analytical Chemistry*, vol 48, Elsevier

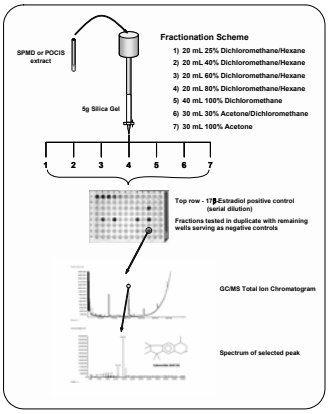
18

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

USGS

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

USGS

Acknowledgements

Jim Petty, Jim Huckins, Walter Cranor, Stephanie Perkins, Vickie Schroeder, Randal Clark, Jon Lebo – USGS CERC

Tammy Jones-Lepp – US EPA

Dominic Getting, Jon Goddard, Anthony Gravell – Environment Agency UK

Andrew Rastall – University of Heidelberg, Germany

Steve Goodbred, John Tertuliani, Dana Kolpin, Paul Stackelberg, Ed Furlong, Mike Meyer, Steve Zaugg, Larry Barber, James Gray, Roger Hothem – USGS

Chris Guy, Fred Pinkney, Beth McGee, Scott Sobiech – US FWS

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.

USGS