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

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## OUTLINE

State of technology

What types of information can you get

Current/recent application

Calibration

PRCs

Bioindicator tests

Future needs

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## 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.

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

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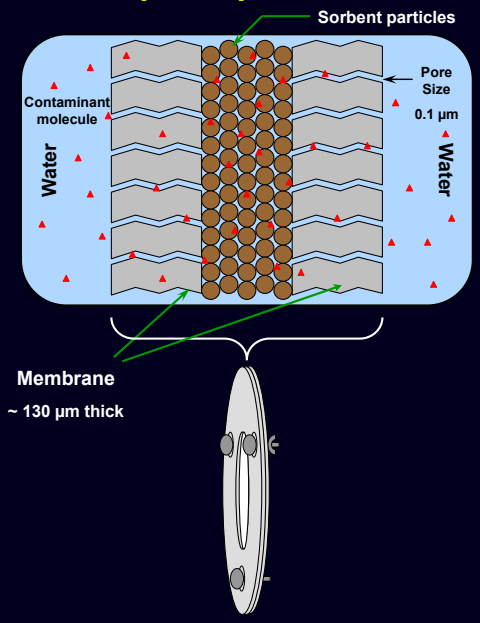
## Exploded view of the uptake process in POCIS

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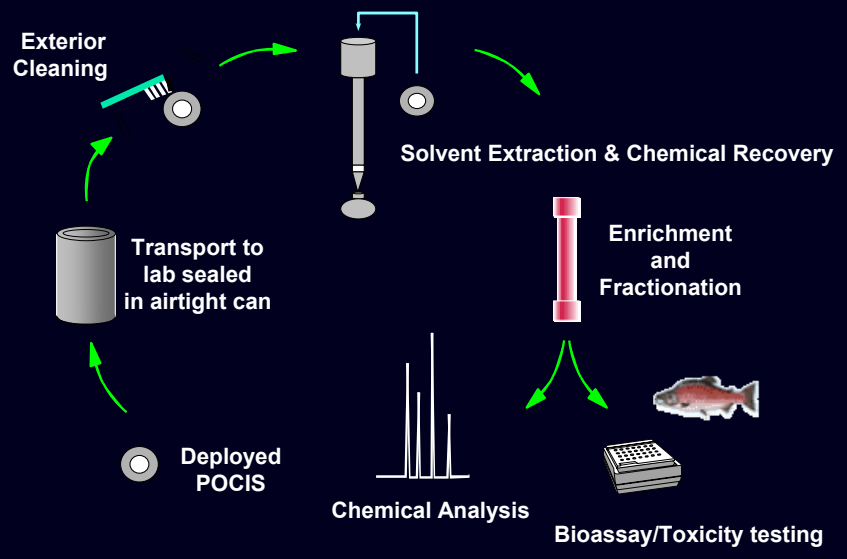
## General Processing Scheme for POCIS

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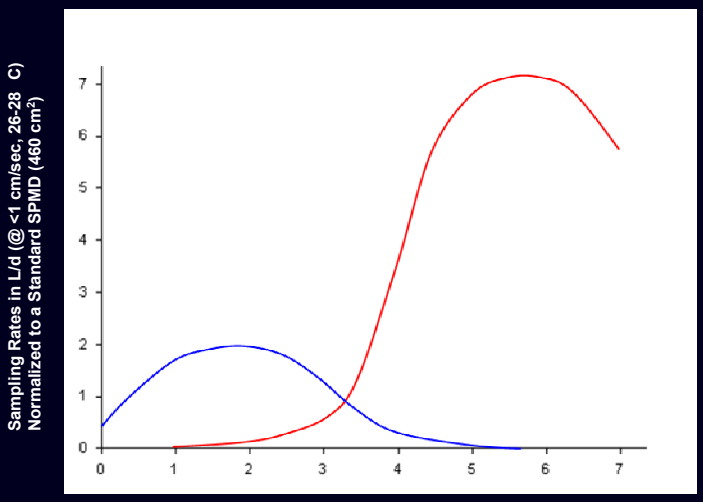
# Sampling Characteristics of POCIS and SPMDs

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

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

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## 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

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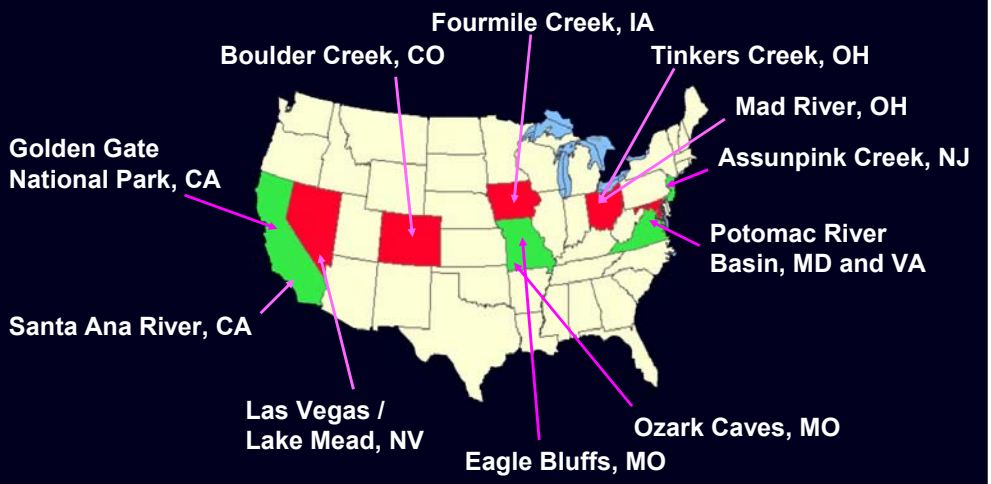
## Current / Recent Applications – Wastewater Monitoring

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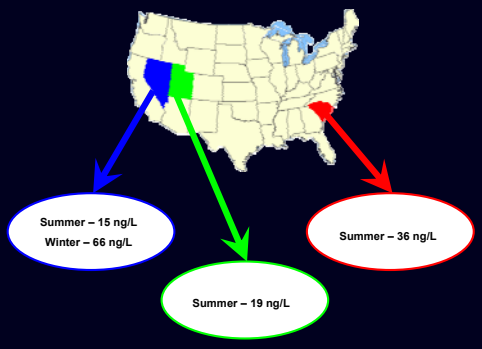
# Current / Recent Applications - Drugs from WWTPs



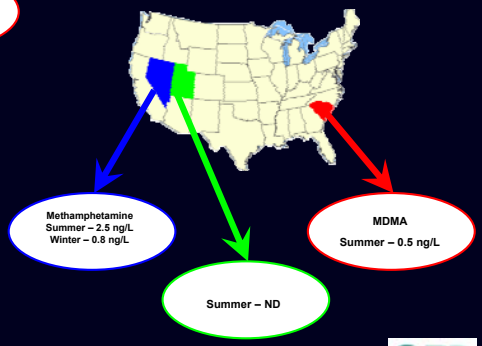

Azithromycin (antibiotic)

**Also Detected:**

nonylphenol polyethoxylate and alcohol polyethoxylate surfactants

PFOA and PFOS

Illegal Drugs

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

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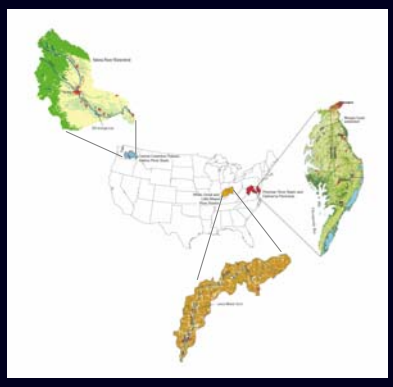
## Current / Recent Applications - Agricultural Monitoring



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

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

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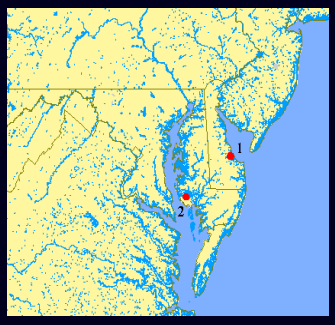
## Current / Recent Applications - CAFO Activities




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

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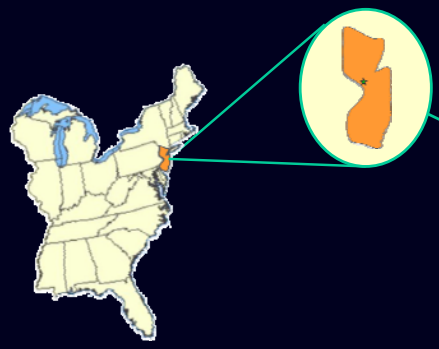
## Current / Recent Applications – Comparison to Grab Sampling



**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**

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

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## 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

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Chemicals highlighted in green identified in POCIS extracts only

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

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## 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.

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

Environment Agency

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## 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.

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## 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

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## 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)

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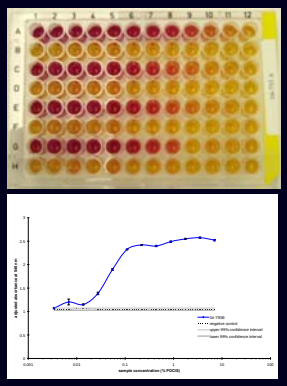
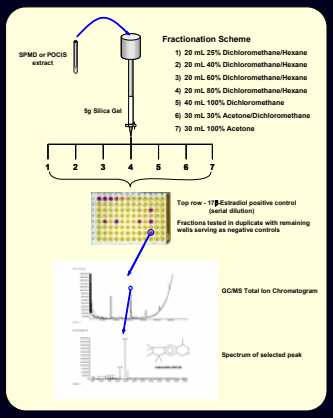
Alvarez et al. 2007 Ch. 8 in *Passive Sampling Techniques. Comprehensive Analytical Chemistry*, vol 48, Elsevier

## 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

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## 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

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## Acknowledgements

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Akin Babatola City of Santa Cruz, CA

And Many More That I'm Forgetting, Sorry.

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