Laboratory Calibration and Field Deployment of the Polar Organic Chemical Integrative Sampler (POCIS) for Pharmaceuticals and Personal Care Products

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Pharmaceuticals as Pollutants

- numerous drugs
- intended biological effects in target organisms
- portions excreted unchanged
- sewage treatment removes pathogens
- continuous unregulated discharge
- non-target organisms chronically exposed

Daughton & Ternes Environ. Health Perspect. 107 (1999) 907. http://www.ehponline.org/members/2005/113-10/spheres.html.

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Non-target Organisms

from a recent review
(Fent *et al*. 2006 Aquatic Toxicology)

- **acute effects**
  - **scenario unlikely unless a concentrated spill**
- **effluent/surface concentrations**
  - **generally 100× < chronic LOEC in lab organisms**

→ chronic effects not extensively studied

http://www.galab.de/laboratories/services/environment/pharmaceuticals.html

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Characterizing Exposure

- **grab/composite water samples**
  - **laborious**
  - **captures snapshot**
  - **may miss important events**

- **passive sampling**
  - **low maintenance**
  - **provides time weighted average**
  - **characterizes chronic exposure**

SPMD for nonpolar organics

http://www.est-lab.com/img/spmd_onspider_250.jpg

Polar Organic Chemical Integrative Sampler (POCIS)

- **sequesters polar organics from water**
  - **pharmaceuticals & pesticides**
- **field usage mainly qualitative (ng/POCIS)**
- **requires calibration to be quantitative**

← single POCIS

Alvarez, Doctoral Thesis, University of Missouri Columbia, Columbia, MO, 1999.
U.S. Patent 6,478,961 – Petty, Huckins, Alvarez, November 12, 2002.
Alvarez *et al.* Environ. Toxicol. Chem. 23 (2004) 1640.
Jones-Lepp *et al.* Arch. Environ. Contam. Toxicol. 47 (2004) 247.

Polar Organic Chemical Integrative Sampler (POCIS)

- **calibrated for uptake of 6 drugs**
- **aqueous boundary layer controlled uptake**
- **resistant to biofouling**

Alvarez et al. Environ. Toxicol. Chem. 23 (2004) 1640.
Jones-Lepp et al. Arch. Environ. Contam. Toxicol. 47 (2004) 247.
Alvarez et al. Chemosphere 61 (2005) 610.

Research Goals

1) to carry out lab based calibration of POCIS to characterize uptake of several common pharmaceuticals and personal care products (PPCPs)

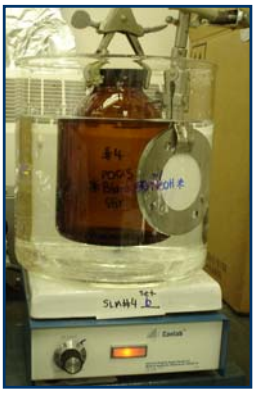
2) to use field deployments for demonstration of the utility of the calibrated sampling rates

Calibration Experiment

POCIS exposed to 33 common PPCPs

A) flowing conditions (25 days, 4 renewals)

B) quiescent conditions (29 days, 3 renewals)



setup:

- **3L water per vessel (spiked at 1 ng/mL)**
- **3 separate vessels per condition**
- **protected from light**
- **regular water samples analyzed to monitor uptake**

controls:

1. **no drug** (monitor for contamination)
2. **no POCIS** (monitor for dissipation)

Alvarez, Ph.D. Thesis, University of Missouri-Columbia, Columbia, MO, 1999.

Measuring Uptake

assuming first order kinetics for uptake:

$$C_w(t) = C_{w(o)}e^{-kt}$$

$C_w(t)$ = aqueous concentration of PPCP at time,t
$C_{w(o)}$ = initial aqueous concentration of PPCP

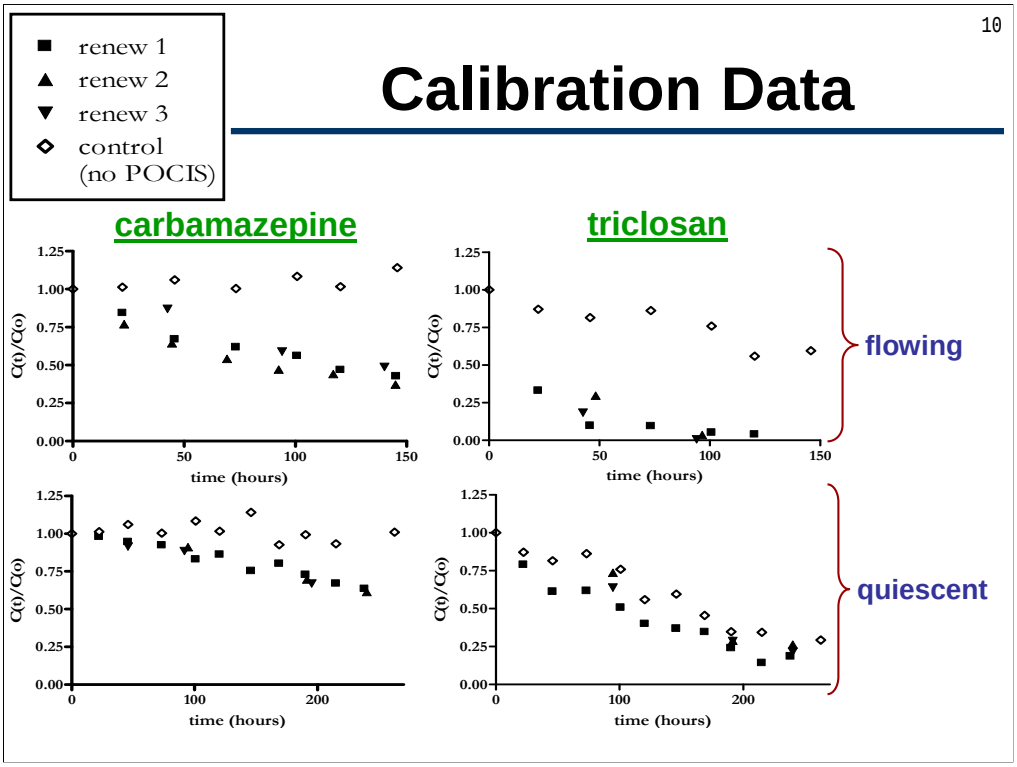
uptake rate constants

- **obtained for each renewal period**
- **averaged for each condition (flowing and quiescent)**

dissipation rate constants

- **similarly obtained for "no POCIS" control**
- **subtracted from uptake rate constants**

Calibration Data



carbamazepine, a commonly used anti-epileptic drug, poorly eliminated in WWTP thus frequently found in surface waters

AND

triclosan, a commonly used antimicrobial agent, also commonly found in surface waters

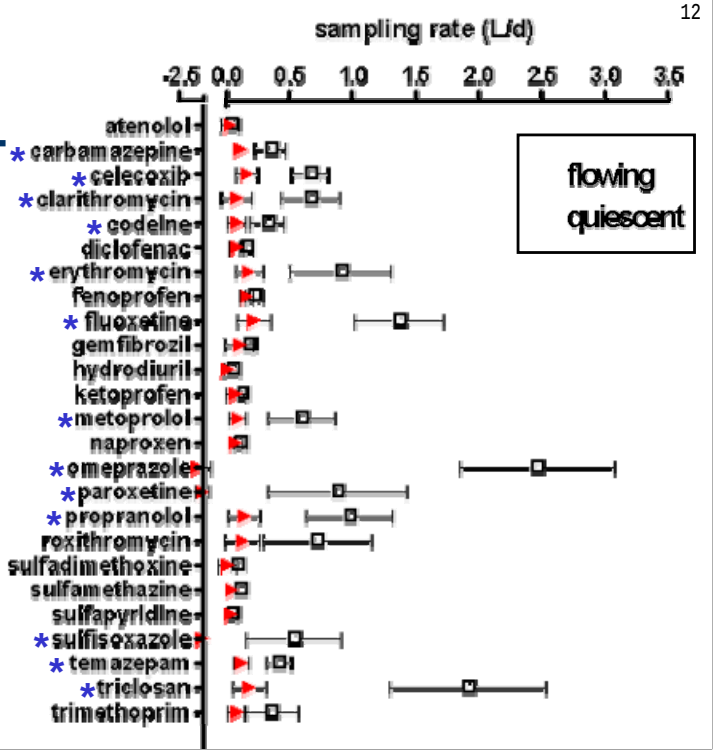
Sampling Rates

sampling rate = $R_s = kV$ where V = 3L water in vessel

- rate = effective L water sampled per day
- 3 flow rates investigated
  - inconclusive for R_S dependence on flow rate
- POCIS calibrated for 25 of 33 drugs
  - reliable data over course of experiment
  - reproducible uptake curves
  - 13 of 25 show boundary layer controlled uptake

Sampling Rates

(significant differences between flowing and quiescent R_s indicated by star)



Undetermined Sampling Rates

caffeine

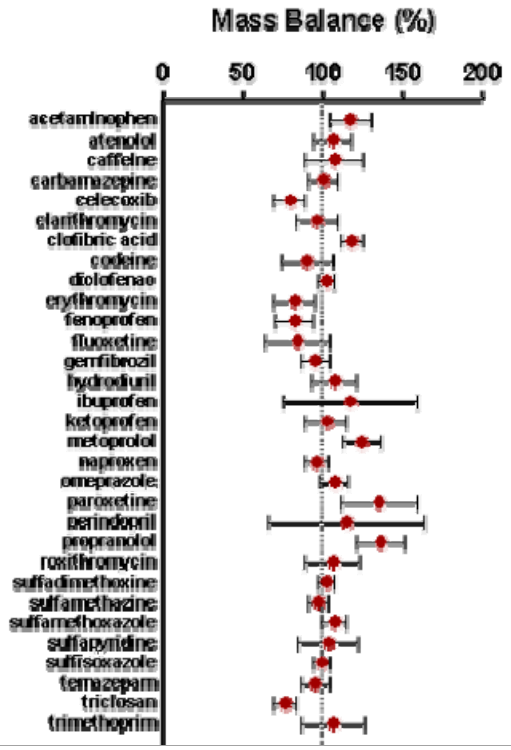
- only 3% dose sequestered
- uptake data scattered
- POCIS not suitable based on this data set

omeprazole, paroxetine, sulfisoxazole

- dissipation comparable to quiescent uptake
- reliable sampling rate could be determined for quiescent water conditions

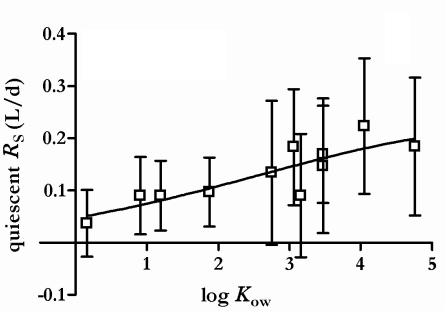
Mass Balance

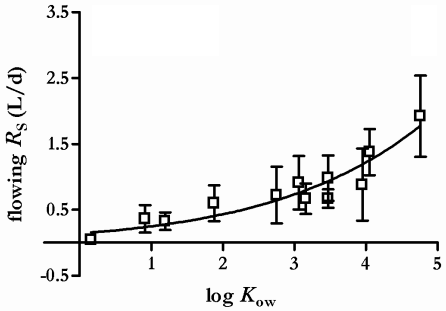
- indicates portion of experimental dose accounted for
- most ~100%
  - reliable accounting
  - no dissipation once sequestered on POCIS

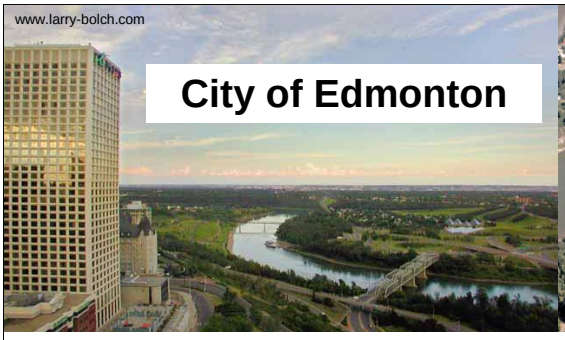


Sampling Rates & PPCP Properties

- no correlation with molecular weight
- correlations with log K_{ow} if classified
- example: cations







Field Deployments

- **grab samples taken at deployment/retrieval**
  - **range of PPCP concentrations**

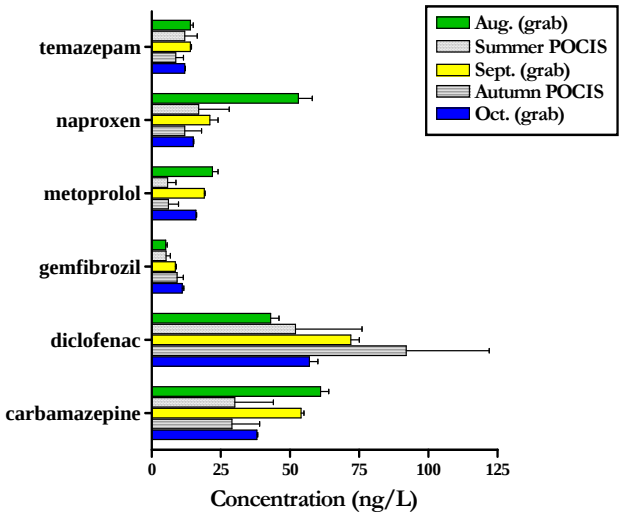
POCIS in the Field

1) POCIS captures information that grab samples may miss.

example: carbamazepine upstream of Edmonton
- **grab samples: 1 L**
- **POCIS: 11±3 L (30 days)**

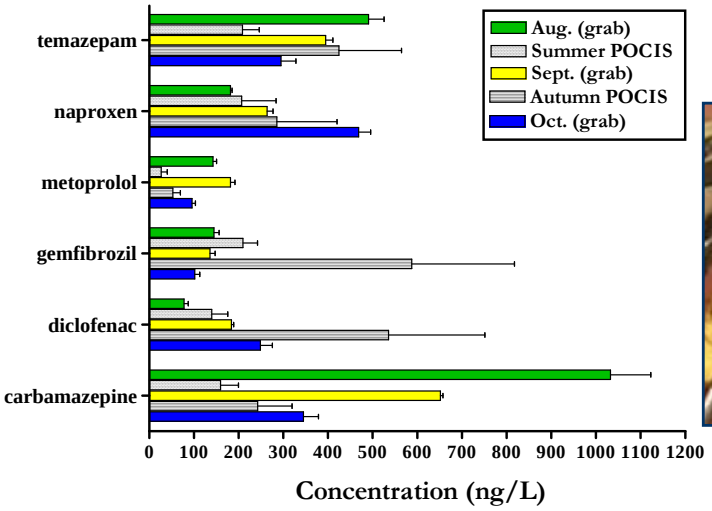
grab (ng/L)	POCIS (ng/L)	grab (ng/L)	POCIS (ng/L)	grab (ng/L)
0.55 ±0.08	0.12 ±0.04	<0.06	0.14 ±0.15	<0.04

2) TWA concentration is generally similar to that derived from grab samples. Sampling rates make sense: downstream of Edmonton



3) Does biofouling have an impact?

Not sure: Lac La Biche WWTP treated effluent

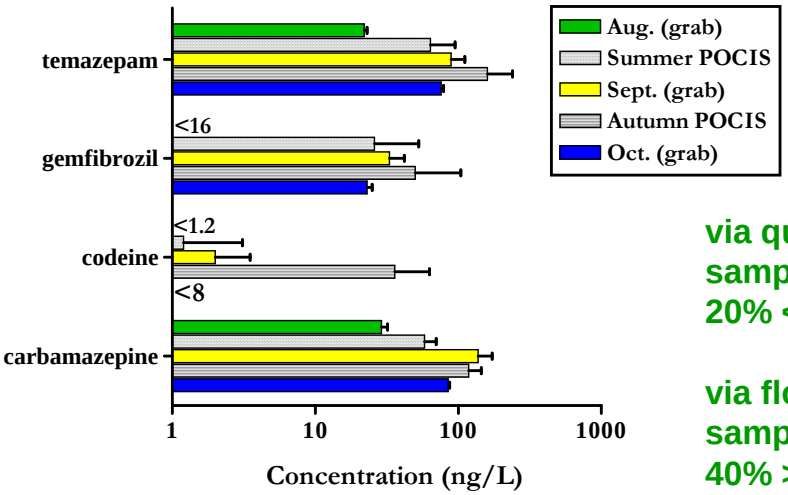


EXTRA INFO

potential biofouling

potential uptake curve not linear for part of the sampling period

4) Is there a flow rate dependence on sampling rate? Not sure: Field Lake



via quiescent sampling rate: 20% < grab

via flowing sampling rate: 40% > grab

Conclusions & Future Work

- **POCIS calibration completed for 25 PPCPs**
  - **some are boundary layer controlled**
  - **potential dependence on log K_{ow}**
- **reasonable for TWA determinations**

- **unanswered questions**
  - **dependence on analyte properties?**
  - **dependence on environmental variables?**

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