Development of adapted versions of Polar Organic Chemical Integrative Samplers (POCIS) for alkylphenols and their derivatives

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Interest of passive sampling

• Spatial and temporal variability
• Low concentration
• Complex mixture
• Matrice effects

Spot sampling is a snapshot of contamination at the time of sampling
Interest of passive sampling

Passive sampling allow accessing to Time Weighted Average (TWA) concentration on sampling period

- Integrative tools
- Simplification of sampling
- Preconcentrator tools (allow detecting water concentration above LOD)
Theory of passive sampling

- The accumulation of compounds follows a first order kinetic
- The water concentration is assessed from the sorbent concentration

\[ C_s = C_w \left( \frac{k_u}{k_e} \right) (1 - e^{-k_e t}) \]

\[ C_s: \text{concentration in sorbent (ng/g)} \]
\[ C_w: \text{concentration in water (ng/L)} \]
\[ k_u: \text{uptake rate constant (L/g/d)} \]
\[ k_e: \text{elimination rate constant (d}^{-1}) \]
Theory of passive sampling

To plot concentration factor ($C_f$) in function of time, Uptake rate constant were determined by linear regression

$$C_f = \frac{C_S}{C_W} = k_u t$$

$C_s(t) = C_w k_u t$

$C_s$: concentration in sorbent (ng/g)
$C_w$: concentration in water (ng/L)
$k_u$: uptake rate constant (L/g/d)
Range of application of principal passive samplers

APs, class of interest:
- regulatory perspectives
- Environmentaly

Pharmaceutical configuration of POCIS

Easy, sensitive and modular tool

EE2: 4.12
Gemfibrozil: 4.77
Amitriptyline: 4.92
Alkylphénols (APs)

- **4-nonylphenol (4-NP)**
  - CAS: 84852-15-3
  - Log $K_{ow}$: 5.99<sup>a</sup>

- **4-t-octylphenol (4-t-OP)**
  - CAS: 140-66-9
  - Log $K_{ow}$: 5.50<sup>a</sup>

- Listed on Water Framework Directive
- The 4-NP is a mixture of isomers:
  - Branched alkyl group
  - 3 to 6% in ortho position, 90 to 93% in para
- The 4-t-OP isomer is the most widely used
- Formed by biodegradation of APEOs
- Used in industries such as additives or antioxydants in the production of plastic (80% 4-NP and 20% 4-t-OP)

<sup>a</sup>: calculated by KOWWIN
Alkylphénols derivatives

Nonylphenol monoethoxylate (NP1EO)
CAS: 26027-38-3
Log $K_{OW}$: 5.58<sup>a</sup>

Nonylphenol diethoxylate (NP2EO)
CAS: 26027-38-2
Log $K_{OW}$: 5.30<sup>a</sup>

Nonylphenoxy acetic acid (NP1EC)
CAS: 3115-49-9
Log $K_{OW}$: 5.80<sup>a</sup>

- Anthropogenic origin
- NPEOs are amphiphilic compounds and non ionic surfactants
- NPEOs represent 80 to 85% of APEOs

<sup>a</sup>: calculed by KOWWIN
Laboratory calibrations

- Determination of kinetic exchanges and parameters
- Exposure under controlled conditions:
  - Contamination with flow through system (conc: 5-10 μg/L)
  - Constant flow
  - Constant temperature (20°C)
- Analysis of water every two days ($C_w$)
- Analysis of POCIS ($C_s$)
Kinetic accumulation in POCIS

First type of accumulation: Linear trends

**Equation of model:** \( C_f = 1.33 \times t \) \((R^2 = 0.89)\)

- \( k_u = 1.33 \text{ L/g/d} \)
- \( R_s = 0.27 \text{ L/d} \)

Literature values:
- \( R_s = 0.12 \text{ L/d} \) \(^1\)
- \( R_s = 0.06 \text{ L/d} \) \(^2\)

**Equation of model:** \( C_f = 1.20 \times t \) \((R^2 = 0.92)\)

- \( k_u = 1.20 \text{ L/g/d} \)
- \( R_s = 0.24 \text{ L/d} \)

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Kinetic accumulation in POCIS

Second type of accumulation: exponential trends

- Accumulation with lag effect*
- Integrated uptake is not achieved
- Sampling rates variable over exposure time

*Time required for the compounds cross the water boundary layer and the membrane
Kinetic accumulation in POCIS

Determination of pseudo kinetic parameters

- Reasoning only on the linear part of exponential trend
- Utake rate constant is determined by linear regression
- They must be used carefully
- The lag time is over 5 days.
Kinetic accumulation in POCIS

Determination of pseudo kinetic parameters

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Equation of model</th>
<th>$R^2$</th>
<th>$k_u$ (L.g$^{-1}$.d$^{-1}$)</th>
<th>$R_s$ (L.d$^{-1}$)</th>
<th>$\tau_0$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-NP</td>
<td>$C_f=-4.94 + 0.79t$</td>
<td>0.94</td>
<td>0.79</td>
<td>0.16</td>
<td>6.22</td>
</tr>
<tr>
<td>NP1EO</td>
<td>$C_f=-7.29 + 1.29t$</td>
<td>0.95</td>
<td>1.29</td>
<td>0.25</td>
<td>5.62</td>
</tr>
<tr>
<td>NP2EO</td>
<td>$C_f=-8.19 + 1.27t$</td>
<td>0.99</td>
<td>1.27</td>
<td>0.25</td>
<td>6.47</td>
</tr>
</tbody>
</table>
Kinetic accumulation in POCIS

Partition between membrane and sorbent

• Sorption in PES membrane during the earlier stage of exposure
• NP1EC and 4-t-OP: less than 20% at 5 days and less than 10% at 15 days
• 4-NP, NP1EO et NP2EO: more than 60% at 5 days and at 50% at 15 days
• The sorbent accumulation start when PES membrane reach a steady state
• The uptake of 4-NP, NP1EO and NP2EO is controlled by PES membranes
POCIS-like. choice of membranes

3 types of membrane were tested but only 2 shown conclusive results

<table>
<thead>
<tr>
<th>Membrane Porosity (Designation)</th>
<th>Polarity</th>
<th>Particularity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 0.1 µm (POCIS-Nylon 0.1 µm)</td>
<td>Hydrophilic</td>
<td>Millipore</td>
</tr>
<tr>
<td>Nylon 30 µm (POCIS-Nylon 30 µm)</td>
<td>Hydrophilic</td>
<td>Millipore</td>
</tr>
</tbody>
</table>

- Nylon polymer have low absorbant power
- The third type of tested membrane is polyethylene
Kinetic accumulation in POCIS-like compounds

**NP1EC**

**4-t-OP**

**NP1EO**

**NP2EO**

**4-NP**

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6th International Passive Sampling Workshop and Symposium, Bordeaux, 26-29 June 2013
Kinetic accumulation in POCIS-like

**NP1EC**

**NP1EO**

**4-t-OP**

**NP2EO**

**4-NP**
Kinetic accumulation in POCIS-like 

NP1EC

4-t-OP

4-NP

NP1EO

NP2EO
Kinetic accumulation in POCIS-like

Any lag effect
Kinetic accumulation in POCIS-like

NP1EC

4-t-OP

4-NP

NP1EO

NP2EO

Lag effect is observed with POCIS- Nylon 0.1µm
Mesocosm validations

- Parameters to know when they are exposed at low concentrations:
  - Kinetic exchanges
  - Integrative aspect
  - TWA concentrations

- Mesocosm validations
  - Semi-controlled conditions
    - 4-Nonylphenol, 4-tert-octylphenol, diuron
  - Analysis of water
  - Replicates of POCIS and POCIS Nylon 0.1 and 30µm

- 2 concentrations tested:
  - EQS level (300 ng/L for 4-NP)
  - 1/3 EQS level (100 ng/L for 4-NP)

- 3 experiments tested:
  - Continuous exposure
  - Accidental exposure
  - Discontinuous exposure
Sampling strategy

- Study the accumulation
- Constant water concentrations
- Determine kinetic parameters
Continuous exposure: accumulated quantities

![Graphs showing concentration over time for POCIS Nylon 0.1µm and 30µm]

- Linear trend
- Lag effect
- Equilibrium-release

R² = 0.91
ku = 0.14 L/j/g
Continuous exposure: accumulated quantities

R² = 0.66  
ku = 0.61 L/j/g

R² = 0.91  
ku = 0.14 L/j/g

No lag effect
Continuous exposure: accumulated quantities

R² = 0.66
ku = 0.61 L/d/g

R² = 0.91
ku = 0.14 L/d/g

Determination of ku not possible
ku labo is employed (1.61 L/d/g)
Continuous exposure: accumulated quantities

Accumulated quantity increases in the following order:

POCIS > POCIS-Nylon 0.1µm > POCIS-Nylon 30µm
Sampling strategy

- Assess integrative aspect
- Peak of contamination
- Estimate TWA concentrations
Accidental exposure: accumulated quantities
Accidental exposure: accumulated quantities

POCIS

4-NP

Thoeretical Injection

POCIS Nylon 0,1µm

POCIS Nylon 30µm

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Accidental exposure: accumulated quantities
Estimated concentration - accidental exposure

Water concentrations snapshot by spot sampling
Estimated concentration-accidental exposure

Average of water concentration at each injection and no-injection periods obtained by spot sampling.

- Injected water concentration
- Integrated average dissolved concentration
Estimated concentration-accidental exposure

4-NP-POCIS

- Mesured conc (ku NQE continuous)
- Injected water concentration
- Integrated average dissolved concentration
Estimated concentration-accidental exposure

4-NP-POCIS

Mesured conc (ku NQE continuous)
Injected water concentration
Integrated average dissolved concentration
Estimated concentration-accidental exposure
Comparison of accumulated quantities between experiments

POCIS and POCIS-Nylon 0.1µm have an integrative behaviour for 4-NP
POCIS have the ability to sample APs and their derivatives

PES membranes prevent to have an use in quantitative tool

Nylon membranes allows eliminating the lag phase observed with POCIS

These tools seem to integrate an accidental contamination

TWA concentrations obtained using these tools are reliable (good agreement with order of magnitude)
Perspectives

✓ More investigation on POCIS-Nylon 30µm

✓ Check sampled fraction by POCIS Nylon 30µm

✓ Apply PRC approach for APs

✓ Field application of these tools
Aknowledgements

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Aquitaine Region

European Community

And you for your attention