Comparison between the polar organic chemical integrative sampler and the solid-phase extraction for estimating herbicide time-weighted average concentrations during a microcosm experiment

N. Mazzella, T. Debenest, F. Delmas

To cite this version:
Comparison between the polar organic chemical integrative sampler and the solid-phase extraction for estimating herbicide time-weighted average concentrations during a microcosm experiment.

Nicolas Mazzella*, Timothée Debenest, François Delmas

Unité de recherche Réseaux, Epuration et Qualité des Eaux, Groupement CEMAGREF de Bordeaux
50 Avenue de Verdun, Gazinet, 33612 Cestas Cedex. FRANCE
Contacts:

*Corresponding author.

E-mail: nicolas.mazzella@cemagref.fr; mazzelladibosco@yahoo.fr
Phone: +335 57 89 27 18
Fax: +335 57 89 08 01
Abstract

Polar organic chemical integrative samplers (POCIS) were exposed for 9 days in two different microcosms that contained river waters spiked with deethylterbuthylazine, terbuthylazine and isoproturon. The experiment was performed with natural light and strong turbulence (flow velocities of about 15-50 cm s\(^{-1}\)) for reproducing natural conditions. The concentrations were kept relatively constant in the first microcosm (2.6-3.6 µg L\(^{-1}\)) and were variable in the second microcosm (peak concentrations ranged from 15-24 µg L\(^{-1}\) during the 3 day pulse phase). The time-weighted average (TWA) concentrations were determined with both POCIS and repetitive grab sampling followed by solid phase extraction. The results showed a systematic and significant overestimation of the TWA concentrations with the POCIS most probably due to the use of sampling rates derived under low flow scenario. The results showed also that peak concentrations of pollutants are fully integrated by this passive sampler. Even if the POCIS should not provide very accurate concentration estimates without the application of adequate sampling rate values or the use of performance reference compounds, it can be a really useful tool for detecting episodic or short-term pollution events (e.g. increased herbicide concentrations during a flood), which may be missed with classical and low frequency grab sampling.

Keywords: GC-MS, phenylureas, triazines, passive sampler, water monitoring.
1. Introduction

The European framework directive in the field of water policy 2000/60/EC seeks to prevent deterioration, to enhance and to restore bodies of surface water, to achieve good chemical and ecological status of such water and to reduce pollution from discharges and emissions of hazardous substances. The evaluation of surface water chemical status requires reliable concentration estimates of various organic pollutants such as herbicides. For this purpose, two approaches can be considered: active sampling (grab or automated) or passive sampling. Grab and low frequency sampling (every week or month) is the easiest and most common method, however, it seldom accurately tracks concentration fluctuations of targeted compounds in natural aqueous environments. Time-weighted average (TWA) concentrations can be estimated by the collection of several repetitive grab samples with automatic samplers. However, the use of such equipment is often physically and logistically difficult, and it generates a large number of samples with a corresponding increase in analytical cost. For monitoring polar herbicides in freshwater, the use of polar organic chemical integrative samplers (POCIS) allows estimates of TWA concentrations (Alvarez et al., 2004; Alvarez et al., 2005). Nevertheless, the accuracy and the precision of these passive samplers for determining the ambient concentrations in rivers have not been fully demonstrated.

This work assessed POCIS reliability for sampling selected polar herbicides (deethylterbuthylazine, terbuthylazine and isoproturon) in natural aqueous environments. We spiked triplicates of POCIS with the chemicals of interest and determined their elimination into river water after 9 days. Afterwards, the POCIS were immersed within two microcosms filled with the same river water but fortified at different concentration level; a relatively constant
concentration and pulsed concentration event scenarios were considered. In fact, transient, high environmental concentration events were simulated in one microcosm in order to determine the capacity of the POCIS for integrating short-term large concentration increases. We also studied the effects of turbulence and the eventual biofouling on both the precision and accuracy of TWA concentrations estimated with the POCIS.
2. Experimental

2.1. Chemicals and materials

Acetonitrile supragradient, methanol gradient and water gradient (HPLC grade) were purchased from ICS-Science Groupe (Gradignan, France), ethyl acetate (HPLC grade) was provided by Riedel-de Haën (Saint-Quentin-Fallavier, France). 1 mL empty polypropylene solid-phase extraction (SPE) tubes with polyethylene (PE) frits (20 μm porosity) and Oasis HLB bulk sorbent (60 μm) were purchased from Supelco (Saint-Quentin-Fallavier, France) and Waters (Guyancourt, France), respectively. Hydrophilic polyethersulfone (PES) SUPOR 100 Membrane Disc Filters (0.1 μm, 90 mm membrane diameter) were purchased from Pall (Saint-Germain-en-Laye, France). Oasis HLB cartridges (6 mL, 500 mg, 60 μm) were provided by Waters (France). Pharmaceutical POCIS were provided by Exposmeter (Tavelsjö, Sweden). All analytical standards (purity ≥ 98%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany): deethylterbuthylazine (DET), terbuthylazine, isoproturon and atrazine d5.

2.2. Solid-phase extraction of water

Preconcentration of the analytes from water samples was accomplished by using SPE with Oasis HLB cartridges. Prior to SPE, 200-mL water samples (pH adjusted to 7) were filtered using GF/F glass microfibre filters (0.7 μm pore size). Afterwards, 10 μL of a stock solution (acetonitrile) containing 100 ng μL⁻¹ of atrazine d5 (surrogate), was added to the water samples, resulting in fortification level of 5 μg L⁻¹. SPE was conducted using a VisiPrep 12-port manifold.
(Supelco, France). The conditioning, extraction and rinsing steps were carried out under a 53.33 kPa vacuum. The SPE cartridges were successively washed with 10 mL of methanol, conditioned with 10 mL of HPLC grade water, loaded with 200-mL water samples, then rinsed with 20 mL of HPLC grade water and dried with a stream of nitrogen for 30 minutes. Elutions were achieved with 5 mL of methanol. The 5-mL extracts were blown under a gentle stream of nitrogen and dissolved within 1 mL of ethyl acetate prior to the GC-MS analyses. The final concentration of the surrogate was about 1 mg L$^{-1}$ after SPE extractions. The recoveries (Table 1) were optimized with the extraction of 200 mL of both tap and river waters fortified with 5 µg L$^{-1}$ of DET, terbuthylazine, isoproturon and atrazine d5 ($n=10$).

2.3. Recoveries from POCIS

“Pharmaceutical” POCIS (Alvarez et al., 2004) contains 200 mg of Oasis HLB sorbent enclosed between two polyethersulfone (PES) membranes. The membrane-sorbent-membrane layers are compressed between two holder washers (5.1 cm I.D., 8.9 cm O.D.). The total exchanging surface area of the membrane (both sides) is approximately 41 cm$^2$ and the surface area per mass of sorbent ratio is approximately 200 cm$^2$ g$^{-1}$. After the exposure in water, each POCIS was opened and the sequestration medium (i.e. Oasis HLB) was transferred in a 50 mL glass beaker with 2×20 mL washes of HPLC grade water. The sorbent was transferred into a 1 mL empty SPE tube with a PE frit and packed under vacuum by using a Visiprep SPE Manifold. Afterwards, another polyethylene frit was added to the top of the SPE cartridge. All the cartridges were washed with 20 mL of HPLC grade water and dried with a stream of nitrogen for 30 minutes. Elutions were achieved with 5 mL of methanol. 10 µL of a stock solution (acetonitrile) containing 100 ng µL$^{-1}$ of atrazine D5 was added before the evaporation of the methanol with a
gentle stream of nitrogen. The final extract was dissolved within 1 mL of ethyl acetate prior to the GC-MS analyses.

Table 1. Analytical parameters and sampling rates of DET, terbuthylazine and isoproturon.

<table>
<thead>
<tr>
<th>Herbicides</th>
<th>DET</th>
<th>Terbuthylazine</th>
<th>Isoproturon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classes</td>
<td>Triazine metabolite</td>
<td>Triazine</td>
<td>Phenylurea</td>
</tr>
<tr>
<td>Retention times (min)</td>
<td>21.85</td>
<td>24.05</td>
<td>12.90&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fragments (m/z)</td>
<td>145, 186&lt;sup&gt;b&lt;/sup&gt;, 201</td>
<td>173, 214&lt;sup&gt;b&lt;/sup&gt;, 229</td>
<td>146&lt;sup&gt;b&lt;/sup&gt;, 161</td>
</tr>
<tr>
<td>SPE recoveries (%)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>95 (3)</td>
<td>100 (7)</td>
<td>106 (5)</td>
</tr>
<tr>
<td>log K&lt;sub&gt;ow&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.98</td>
<td>3.21</td>
<td>2.87</td>
</tr>
<tr>
<td>k&lt;sub&gt;a&lt;/sub&gt; (mL·g&lt;sup&gt;-1&lt;/sup&gt;·d&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1025 (28)</td>
<td>1253 (48)</td>
<td>1088 (51)</td>
</tr>
<tr>
<td>R&lt;sub&gt;s&lt;/sub&gt; (mL·d&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>205 (6)</td>
<td>251 (10)</td>
<td>218 (10)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isoproturon was analyzed as 4-(isopropyl)phenyl isocyanate degradation product (Carabias-Martínez et al., 2003).
<sup>b</sup> Base peak.
<sup>c</sup> Fortification of tap and river waters (±1 S.D, n=10).
<sup>d</sup> log K<sub>ow</sub> for pH=7-8 (Barceló & Hennion, 1997; Hansch & Leo, 1987)
<sup>e</sup> Data (±1 S.D) from (Mazzella et al., 2007)

2.4. GC-MS determination of herbicides

DET, terbuthylazine and isoproturon were analyzed using a TRACE GC 2000 gas chromatograph (Thermo Electron Corporation, MA, USA) equipped with a Zebron ZB-5 (Phenomenex, Le Pecq, France) capillary column (60 m, 0.25 mm, 0.25 μm) and an AS 800 autosampler (Thermo Electron Corporation, MA, USA). The TRACE GC 2000 gas chromatograph was coupled to a GCQ/POLARIS ion trap mass spectrometer (Thermo Electron Corporation, MA, USA). The transfer line was held at 280 °C and the source at 240 °C. Electron impact mass spectra were acquired at 70 eV. Quantitative analysis were acquired in full scan
mode from 100 to 350 amu. The total scan time was set to 0.68 s (6 microscans) and the max ion
time was kept constant at 25 ms. Retention times, and quantitative and characteristic fragments of
DET, terbuthylazine and isoproturon are given in Table 1. Atrazine d5 was used as internal
standard (retention time: 23.30 min, m/z = 205). A volume of 2 μL (samples dissolved within
ethyl acetate) was injected on a splitless injector (270 °C, 138 kPa pressure pulse for 1.2 min).
Helium was used as carrier gas at a constant flow rate of 1 mL min⁻¹. The temperature program
was 40 °C for 1.2 min, then 15 °C min⁻¹ up to 160 °C and 4°C min⁻¹ to 270 °C followed by a 3.3
min isotherm (total running time: 40 min).

2.5. Dissolved organic carbon measurements

The water samples were filtered using GF/F glass microfibre filters (0.7 μm pore size) and
the concentrations of dissolved organic carbon (DOC) were measured using a model 1010 OI
Analytical carbon analyzer with a 1051 auto-sampler (Bioritech, France). The total organic
carbon analyses were performed with an high-temperature persulfate oxidation technology and

2.6. Microcosm experimental design and POCIS exposure

As shown in Figure 3, the POCIS (n=3) were immersed into two different glass
microcosms A and B each filled with 50 L of river water from Anan (southwest part of France).
The river water was characterized by a pH 7.67 and a low dissolved organic carbon content
(DOC = 1.69±0.03 mg L⁻¹). Prior to use, concentrations of isoproturon, DET and terbuthylazine
were determined in the river water. Background concentrations of the chemicals of interest were lower than the LODs (0.05-0.15 µg L\(^{-1}\)). The microcosms A and B were initially spiked with approximately 5 µg L\(^{-1}\) and 25 µg L\(^{-1}\) of test compounds, respectively. Another microcosm with unfortified river water was used as a blank control for the POCIS. During the exposure, concentrations were relatively constant in microcosm A (i.e. standard addition was not required after the initial spiking), whereas the river water was fully changed in microcosm B after 3 days. Turbulent conditions were obtained by using submersible pumps. Flow velocities in the microcosms varied from 15 to 50 cm s\(^{-1}\). The temperature was kept constant (21±1 °C) and the experiment was carried out with natural light. SPE were performed at time zero (t\(_0\)) and every 3 days (t\(_0\), 3-d, 6-d and 9-d), resulting in 4 grab samples per microcosm. Both concentration and standard deviation values were recovery corrected. The time weighted average concentrations (Figure 2) were expressed for 3-day intervals and then for the whole exposure period (9 days). All the triplicates of POCIS were sampled after 9 days of exposure.
Figure 1. Experimental design of microcosms A and B. Triplicate POCI S were immersed into river water for 9 days and exposed to flow velocities ranging from 15 to 50 cm s$^{-1}$.

### 2.7. Spiking of POCIS sorbent with DET, terbuthylazine and isoproturon

A solution of 1 mg L$^{-1}$ of DET, terbuthylazine and isoproturon was prepared in methanol. 50 mL of this solution was added to 5 g of Oasis HLB bulk sorbent and sonicated for 5 min. The solvent was eliminated with a rotary evaporator and the sorbent was dried at 60 °C for 1 h. We obtained 5 g of Oasis HLB bulk sorbent spiked with 10 µg g$^{-1}$ of each of the test chemicals. Three reference cartridges were prepared by transferring 200 mg of the fortified sorbent into 1 mL empty polypropylene SPE tubes with PE frits. The elution (5 mL of methanol) and the GC-MS analysis of the reference cartridges revealed initial concentrations ($C_0$) of 8.3 µg g$^{-1}$ (7.8% RSD), 7.4 µg g$^{-1}$ (4.1% RSD) and 7.7 µg g$^{-1}$ (4.4% RSD) for DET, terbuthylazine and isoproturon, respectively. Three POCIS were prepared with 200 mg of the same fortified sorbent. The POCIS were exposed in a microcosm filled with 50 L of river water. The flow and temperature conditions were as described above. The 3 POCIS were sampled after 9 days of exposure. The sorbents were transferred into 1 mL empty SPE tubes with PE frits, eluted with 5 mL of methanol and dried under a gentle stream of nitrogen (1 µg of atrazine D5 was added as internal standard before the solvent elimination). The extracts were dissolved within 1 mL of ethyl acetate prior to the GC-MS analysis.
Figure 2. Time-weighted average concentrations of DET, terbutylazine and isoproturon (microcosms A and B) calculated from repetitive grab sampling and from POCIS.
3. Theory and modelling

Assuming isotropic exchange, ambient concentrations of the contaminants can be estimated from the amounts of these chemicals within the POCIS. Eq. 1 (Huckins et al., 1993; Huckins et al., 1999; Stuer-Lauridsen, 2005; Vrana et al., 2005):

\[ C_{POCIS} = C_w K_{sw} (1 - e^{-k_e t}) \] (1)

Where \( C_{POCIS} \) is the concentration (\( \mu g \ \text{g}^{-1} \)) of the analyte in the sorbent, \( C_w \) the TWA concentration (\( \mu g \ \text{L}^{-1} \)) of the analyte in water, \( K_{sw} \) the POCIS-water partition constant (\( L \ \text{g}^{-1} \)) and \( k_e \) the elimination rate constant (\( d^{-1} \)). Details of the model development and the conditions have been presented and discussed for the semipermeable membrane devices (SPMDs) (Huckins et al., 1993; Huckins et al., 1999) and applied to the POCIS (Alvarez, 1999; Alvarez et al., 2004; Mazzella et al., 2007). If the elimination rate \( k_e \) is negligible compared to the uptake rate \( k_u \) (\( L \ \text{g}^{-1} \ \text{d}^{-1} \) or \( \text{mL} \ \text{g}^{-1} \ \text{d}^{-1} \)), then the POCIS acts as an infinite sink for the chemical of interest and analyte uptake is linear for several weeks (\( t \leq (\ln 2)/k_e \)) (Alvarez et al., 2004). In this case, Eq. 1 can be reduced to:

\[ C_{POCIS} = C_w k_u t \] (2)

If we introduce the mass of the sorbent \( M_{POCIS} \) (g), we can rearrange Eq. 2 to an equivalent relationship with the sampling rate \( R_s \) (mL d\(^{-1} \)), instead of the uptake rate constant \( k_u \):

\[ C_{POCIS} = \frac{C_w R_s t}{M_{POCIS}} \] (3)

Eq. 3 and \( R_s \) values derived from a previous calibration experiment (Mazzella et al., 2007; Table 4) were used for TWA concentration estimates with the POCIS.
4. Results and discussion

4.1. Desorption of DET, terbuthylazine and isoproturon from POCIS

We studied the desorption of DET, terbuthylazine and isoproturon. As reported in Table 5, elimination was negligible (3%) for DET and relatively low for both terbuthylazine and isoproturon (11-12%) after 9 days. These results are in good agreement with previous works indicating a strong retention for some polar herbicides such as atrazine, diazinon, diuron, isoproturon (Alvarez et al., 2004) and simazine (Mazzella et al., 2007). However, the POCIS are frequently deployed for several weeks in the field (Alvarez et al., 2004; Alvarez et al., 2005; Macleod et al., 2007; Matthiessen et al., 2006) and for long exposure times, the desorption phenomena are probably not negligible. In this case we have to investigate the elimination rates in further detail.

Table 2. Desorption of the chemical of interest.

<table>
<thead>
<tr>
<th>Herbicides</th>
<th>( C_{9,d}/C_0 )^a</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>DET</td>
<td>0.97</td>
<td>1.4</td>
</tr>
<tr>
<td>Terbuthylazine</td>
<td>0.88</td>
<td>12.5</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>0.89</td>
<td>18.0</td>
</tr>
</tbody>
</table>

^a Ratio between the concentrations after 9 days and the initial concentrations.

Table 3. Parametric Z-test (critical Z value of 1.960 and 95 % confidence interval) for comparing the time-weighted average (TWA) concentrations calculated from repetitive grab sampling and from the POCIS in the microcosms A and B.
<table>
<thead>
<tr>
<th>Herbicides</th>
<th>DET</th>
<th>Terbutylazine</th>
<th>Isoproturon</th>
<th>DET</th>
<th>Terbutylazine</th>
<th>Isoproturon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcosms</td>
<td></td>
<td>A</td>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Differences (µg L)⁴</td>
<td>0.90</td>
<td>0.77</td>
<td>0.77</td>
<td>0.90</td>
<td>1.77</td>
<td>2.80</td>
</tr>
<tr>
<td>Overestimation (%)</td>
<td>+ 25</td>
<td>+ 29.5</td>
<td>+ 28.5</td>
<td>+ 11</td>
<td>+ 25</td>
<td>+ 49</td>
</tr>
<tr>
<td>Z b (Observed value)</td>
<td>3.402</td>
<td>2.203</td>
<td>1.000</td>
<td>1.372</td>
<td>1.919</td>
<td>2.750</td>
</tr>
<tr>
<td>p-values b (Two-tailed)</td>
<td>0.001</td>
<td>0.028</td>
<td>0.317</td>
<td>0.170</td>
<td>0.055</td>
<td>0.006</td>
</tr>
</tbody>
</table>

⁴ Differences between the means of the TWA concentrations calculated from POCIS and from grab samples.

b Z-tests and p-values were calculated with XLSTAT-PRO (Addinsoft).

4.2. Comparison between solid-phase extraction and POCIS with various conditions

In order to facilitate the comparison between the two approaches, the same sorbent (i.e. Oasis HLB) was used for grab and passive sampling. In regard to the microcosm A, the concentration of DET was relatively constant while a steep decrease of both terbutylazine and isoproturon concentrations was observed between 3 and 6 days (Figure 4). This decrease may be due to the adsorption of isoproturon and terbutylazine on suspended particulate matter since these chemicals are characterized by a higher hydrophobicity (log K<sub>ow</sub>=2.87 and 3.21, respectively) than DET (log K<sub>ow</sub>=1.98). Concerning the microcosm B, we simulated a peak exposure scenario by replacing the initial spiked medium by clear river water after 3 days (Figure 4).

The TWA concentrations (Figure 4) were determined with both SPE of grab samples and the POCIS exposed during 9 days. The results of a parametric test are reported in Table 6 (z-test, p = 0.05). For DET and terbutylazine (microcosm A), the TWA concentrations calculated with the SPE (n=10) and estimated with the POCIS (n=3) were significantly different. In regard to the microcosm B, the reference concentrations (SPE) and the estimated concentrations (POCIS) are
significantly different for isoproturon only. In the other cases (isoproturon in microcosm A and both DET and terbuthylazine in microcosm B), there were no significant differences between the two sampling methods. This may be due to both a slight overestimation (especially for DET in the microcosm B with +11%) and a high standard deviation. Globally, the concentrations were systematically and significantly overestimated with the POCIS (from +11 to +49%; Table 6) in comparison with the SPE procedure. This result is most likely due to the application of inadequate $R_s$ values previously determined during the calibration (Mazzella et al., 2007).

In this study, we used river water with a low DOC content ($1.69 \pm 0.03$ mg L$^{-1}$) and we observed a growth of algae on the glass wall of the microcosms whereas the biofilm formation was barely visible on the membranes of the POCIS. Consequently, we assumed that the PES membranes were probably not affected by the biofouling (Vrana et al., 2005) and the concentration overestimation should be attributed to the higher flow velocities for this experiment (from 15 to 50 cm s$^{-1}$) than for the calibration (2-3 cm s$^{-1}$) (Mazzella et al., 2007).

As suggested by some authors (Alvarez et al., 2004), the solute mass transfer is mainly controlled by the aqueous boundary layer. In other words, the sampling rates depend on the flow velocities and the turbulence. Some works (Gunold et al., In Press) showed for Empore SDB-XC disks that the influence of flow velocity on the sampling rates seems to play a minor role for hydrophilic substances such as herbicides. However, the authors performed calibrations only at relatively high flow velocities (13.5 cm s$^{-1}$ and 40 cm s$^{-1}$) and they did not use diffusion-limiting membranes. The comparison with the POCIS is tenuous but such data indicates an increase of the sampling rates with flow velocity until a certain threshold only. For polar chemicals sampled with Empore SDB-RPS disks, Vermeirssen et al. (Vermeirssen et al., 2008) observed an increase of accumulated amounts with increasing flow velocities (from 2.6 to 37 cm s$^{-1}$). Their results showed also curvilinear uptakes and earlier equilibriums for polar chemicals at flow...
velocities higher than 10 cm s\textsuperscript{-1}, indicating a rapid increase of $k_e$ with flow velocity. However, a direct comparison is still difficult since no diffusion-limiting membrane was used in this work as well. If bulk flow rates in test microcosms are good predictors of chemical uptake rates in boundary layer controlled passive samplers, then the relative differences in TWA concentrations obtained from SPE and POCIS approaches should be relatively constant as shown in Figure 4 and Table 6 for microcosm A. Regarding to microcosm B, the results were more variable with overestimates ranging from +11% to +49%. We observed during the POCIS calibration a slight and variable increase in sampling rates occurring in the first five days (Mazzella et al., 2007). Such a phenomenon is generally reduced with the POCIS presoaking (Alvarez, 1999) but it can explain the variation of the sampling rates during the 3 day pulse experiment only. In this case, short-term pollution peaks may be imprecisely integrated by the POCIS if such a phenomenon occurs at the beginning of the exposure. Lastly, the concordance between the reference SPE measurements and the POCIS concentration estimates could obviously be improved with the application of microcosm-calibrated $R_s$. We can also use an appropriate performance reference compounds (PRCs). The PRC approach was successfully developed and applied for the SPMDs (Booij et al., 2002; Huckins et al., 2002) and in a previous work (Mazzella et al., 2007) we suggested the use of the deisopropylatrazine as PRC since we observed isotropic exchanges and a strong release of this chemical from the POCIS sorbent after only 10 days. The application of such a PRC will be further investigated with in situ experiments.

In general, there is a paucity of studies on the uptake of short-term fluctuations with passive samplers (Greenwood et al., 2007), especially for polar compounds. For the microcosm B (Figure 4), unlike SPE of grab samples, passive samplers do not instantaneously reflect changes in the environmental concentrations of chemicals, as response time must be considered. However,
the results showed that the peaks of DET, terbuthylazine and isoproturon concentrations were integrated by the POCIS. The largest differences in values derived from the two approaches should be observed for comparisons where the time resolution for grab samples is low (i.e., several days or some weeks between samples) and the concentrations measured change relatively fast such as observed for microcosm B. Such conditions are frequently observed with small drainage basin (≤ 1000 km²) and in this case the POCIS may be a really useful tool for detecting episodic and short-term events (e.g. herbicide concentration increase during a rise in the water level) which may be missed with classical and low frequency grab sampling.
5. Conclusion

The POCIS method likely works well when appropriate sampling rates for analytes are available. Unfortunately, the PRC approach for in situ calibration is not fully developed for POCIS, which necessitated the use of sampling rates for test compounds measured at lower flow velocities than the present study. Use of these inappropriate sampling rates for calculating water concentrations of analytes from POCIS concentrations resulted in an expected systematic and significant overestimation of water concentrations relative to SPE grab samples. Although, POCIS derived water concentrations estimates were significantly overestimated relative to SPE grab samples, the bias in the concentration values was not large as they ranged from 11 to 49% greater. Further studies with various real-world conditions (i.e. quiescent or highly turbulent environments, variable temperature, occurrence of organic matter and biofouling, etc.) are compulsory for determining the reliability of the POCIS for a quantitative approach.

Acknowledgements

The authors would like to thank B. Mechin, B. Delest, M. Bonnet and M. Boudigues for their skilful technical assistance.
Tables

Table 4. Analytical parameters and sampling rates of DET, terbuthylazine and isoproturon.

Table 5. Desorption of the chemical of interest.

Table 6. Parametric Z-test (critical Z value of 1.960 and 95% confidence interval) for comparing the time-weighted average (TWA) concentrations calculated from repetitive grab sampling and from the POCIS in the microcosms A and B.
Figures

Figure 3. Experimental design of microcosms A and B. Triplicate POCIS were immersed into river water for 9 days and exposed to flow velocities ranging from 15 to 50 cm s\(^{-1}\).

Figure 4. Time-weighted average concentrations of DET, terbuthylazine and isoproturon (microcosms A and B) calculated from repetitive grab sampling and from POCIS.
References


