Passive samplers such as PDB, DGT and POCIS for monitoring groundwater quality: A field trial

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Context of the work

> **Groundwater is characterised by**
  
  • Low water flow
  • Sampling using a well
  • Well purged before groundwater sampling (representativity of sample)

> **Few applications of passive samplers in groundwater by comparison with surface waters**
  
  • Some publications on the use of equilibrium passive samplers in groundwater (Passive Diffusive bags PDB) (USGS works)

  • Only few publications (Gustavson et al., 2000, Vrana et al., 2005) about integrative passive sampling in groundwater:
    — SPMD only
    — It is more likely that SPMD uptake is limited by groundwater flow.

  • More recently, preliminary tests of PDB, ceramic dosimeters, Sorbicells in groundwater in polluted sites (INERIS, METROCAP project, May 2011)

Applicability of such tools in groundwater?
Objectives

> To perform preliminary tests to study of the applicability of passive sampling in groundwater
  • Comparison between passive sampling and classical sampling in a groundwater
  • Demonstration of the advantages and drawbacks of passive samplers on a case study

> Study done in 2010 under Aquaref programme (report available on the web site of AQUAREF)
The study site: criteria of choice & description

> **Choice criteria**
  - Presence of several types of pollutants which can be targeted by available passive samplers
  - Concentrations at envoirnemental levels
  - Difficulties to find a site which has multi pollutant’s

> **Site selected: A drinking water supply site presently closed**
  - Presence of volatile organic compounds and polar pesticides & metals at low concentrations
  - Well: 6m of depth and 80 mm of diameter
Selected compounds & passive samplers

> Types of compounds
  • Polar pesticides – 60 compounds
  • Pharmaceuticals -15 compounds
  • VOC – 54 compounds
  • Metals – 11 compounds

> Types of Passive samplers
  • POCIS (Polar Organic Compound Integrative Sampler)
  • PDB (Passive Diffusive Bag)
  • DGT (Diffusive Gradient in Thin film)
General methodology of sampling

- 4 campaigns of about 15-20 days duration
- Classical sampling with a twister pump at 3m before and after purging (3* volume of the well)
- Measurement of physico chemical parameters before and after purging
- Deployment of passive samplers in replicates on a plastic chain at 2 depths

**Piezometric level: 1,4 m**

- Passive samplers: 2 POCIS, 2 PDBs
  - (depth of 2 m - 60 cm in water column)
- Spot sampling (before and after purging)
  - (depth of 3m - 1,6 m in the water column)
  - Passive samplers: 3 DGT

- Passive samplers : 2 POCIS, 2 PDBs
  - (depth of 4,5 m - 3,1 m in the water column)
Passive Diffusive Bags (PDB) / VOC sampling

- LDPE bag with desionised water (Exposmeter)
- Equilibrium passive sampler
- At the end of exposure, transfert of water in flasks
- Analysis of VOC by ITEX/GC/MS
- Comparison with classical sampling (before and after purging) at the retrieval of PDB.
Example of PDB concentrations at two depths

**Campaign 4**

- **1,1 Dichloroethene**
- Ethane, 1,1-dichloro-
- 1,2 dichloroethene CIS
- Chloroform
- Ethane, 1,1,1-trichloro-
- Trichloroethylene
- Tétrachloroéthylène

<table>
<thead>
<tr>
<th></th>
<th>Mean PDB 2m (n=2)</th>
<th>Mean PDB 4,5 m (n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (µg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1 Dichloroethene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane, 1,1-dichloro-</td>
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<tr>
<td>1,2 dichloroethene CIS</td>
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<tr>
<td>Chloroform</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane, 1,1,1-trichloro-</td>
<td></td>
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<tr>
<td>Trichloroethylene</td>
<td></td>
<td></td>
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<tr>
<td>Tétrachloroéthylène</td>
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</tr>
</tbody>
</table>
Comparison between PDB and classical sampling (4 campaigns: C1 C2 C3 C4; after purging)
PDB > Conclusion

> Detection of 7 molecules of the 54 which were analysed at low concentrations (<6 µg/L)

> Slight stratification in the piezometer, probably due to a vertical distribution of compounds in the water column (stratification in accordance with volatility)

> PDB results in good agreement with classical sampling results (before or after purging)
POCIS - Polar organic compound integrative sampler

- POCIS with phase in OASIS HLB (Exposmeter) for groundwater

- Elution with methanol followed by HPLC/MS/MS analysis

- TWAC estimation: TWAC = m/(Rst)

TWAC: Time Weight Average Concentration
m: accumulated mass
Rs: Sampling rate from literature (L/d/g of Pocis)
t: time duration (days)

- Comparison with the average concentration in water samples during the campaign
Pesticide concentrations in water samples over the 4 campaigns

Before and after purging concentrations of the same order (except for atrazine (C2) and DEA (C3, C4))

Slight variation of concentrations in groundwater
POCIS/pesticides: accumulated mass (ng/g) during the 4 campaigns

No « logical results » between time duration and accumulated mass, variation of water flow ??
Factor of 4 to 50 between TWAC and Water concentration.

Rs found in literature are not applicable to this site.
Factor of 2-3 between TWAC and water concentration
As accumulation is not reproducible from a campaign to another, POCIS does not allow to follow the pesticide concentrations in groundwater
### Pharmaceuticals : qualitative information (screening)

#### Classical sampling  Passive sampling

<table>
<thead>
<tr>
<th>Pharmaceuticals</th>
<th>Water Campaigns 1,2,3,4</th>
<th>POCIS campaign 1</th>
<th>POCIS campaign 2</th>
<th>POCIS campaign 3</th>
<th>POCIS campaign 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>FENOFIBRIC ACID</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>CARBAMAZEPINE</td>
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<td>+</td>
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<td>BROMAZEPAM</td>
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<tr>
<td>SULFAMETHOXAZOLE</td>
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<td>DICLOFENAC</td>
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<tr>
<td>OXAZEPAM</td>
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<td>+</td>
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</tr>
</tbody>
</table>

**Detection of compounds not detected by classical sampling**
POCIS >Conclusion

> Qualitative information
  • screening of pesticides and pharmaceuticals
  • Improvement of the screening performance in comparison with classical approach

> Quantitative information
  • Sampling rate from litterature are not applicable to this site
    — Accumulation from a campaign to another is not reproducible
    — Is water flow sufficient to ensure a constant concentration at the surface of POCIS ?
    — Is water flow constant over the 4 campaigns ? (probably not due to the starting of the drinking water supply unit)

> Others results more promising in other sites
DGT – Diffusive Gradient in Thin film

- Classical DGT used except for one campaign for which 3 types of DGT used with different thickness, 0.76, 1.18 et 1.95 mm (DGT Research)
- Estimation of the diffusion boundary layer according the publication (Kent W. Warnken et al., 2006)
- Elution by HNO3 followed by ICP/MS analysis
- Estimation of the TWAC in water:

\[
C_{\text{DGT}} = \frac{M\left(\frac{\Delta g}{D_{\text{gel}}} + \frac{\delta}{D_{w}}\right)}{At}
\]

- Comparison with the average concentration in metals in water samples during the campaign
### Metal concentrations in water samples & influence of purging

<table>
<thead>
<tr>
<th>Concentration (ng/L)</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
<th>U</th>
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<tbody>
<tr>
<td><strong>Campaign 1</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Beginning before purging</td>
<td>1159</td>
<td>129</td>
<td>947</td>
<td>7559</td>
<td>39</td>
<td>44</td>
<td>997</td>
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<tr>
<td>After purging</td>
<td>839</td>
<td>124</td>
<td>635</td>
<td>1726</td>
<td>6</td>
<td>16</td>
<td>999</td>
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<tr>
<td>End</td>
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<td></td>
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<tr>
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<td>130</td>
<td>445</td>
<td>4305</td>
<td>55</td>
<td>33</td>
<td>1093</td>
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<tr>
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<td>877</td>
<td>123</td>
<td>280</td>
<td>1627</td>
<td>20</td>
<td>50</td>
<td>1107</td>
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<td></td>
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<tr>
<td>Beginning before purging</td>
<td>1480</td>
<td>135</td>
<td>435</td>
<td>2020</td>
<td>33</td>
<td>25</td>
<td>965</td>
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<td>After purging</td>
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<td>10</td>
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<td></td>
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<tr>
<td>Beginning before purging</td>
<td>3017</td>
<td>140</td>
<td>583</td>
<td>5720</td>
<td>23</td>
<td>20</td>
<td>980</td>
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<tr>
<td>After purging</td>
<td>900</td>
<td>130</td>
<td>280</td>
<td>1653</td>
<td>6</td>
<td>20</td>
<td>1037</td>
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<td><strong>Campaign 3</strong></td>
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<td>Beginning before purging</td>
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<td>140</td>
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<td>After purging</td>
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<td>280</td>
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<td>Beginning before purging</td>
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<td>403</td>
<td>4973</td>
<td>18</td>
<td>67</td>
<td>1043</td>
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<tr>
<td>After purging</td>
<td>843</td>
<td>120</td>
<td>243</td>
<td>1063</td>
<td>6</td>
<td>50</td>
<td>1067</td>
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<tr>
<td><strong>Campaign 4</strong></td>
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<td>243</td>
<td>1063</td>
<td>6</td>
<td>50</td>
<td>1067</td>
</tr>
</tbody>
</table>

**Low concentrations of metals in groundwater**

- **Ni, Zn**: High Influence of purging
- **Co, U**: Concentrations are constant - No influence of purging
- **Pb, Cu, Cd**: Concentrations are constant over the 4 campaigns - low influence of purging
Estimation of the diffusive boundary layer

- Low flow in comparison with surface water
- The DBL was calculated according Kent W. Warnken et al., 2006 by using DGT with several gel thickness
- **Rough** estimation of the DBL:

<table>
<thead>
<tr>
<th>Al</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.8</td>
<td>0.6</td>
<td>1</td>
<td>0.7</td>
<td>1</td>
<td>1.3</td>
<td>1.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

\( \delta = 1 \text{ mm} \)
TWAC vs spot sampling analysis

Average concentration in water samples over the 4 campaigns before purging
Average concentration in water samples over the 4 campaigns after purging

Ni, Zn : overestimation of water concentration probably due to the water quality before purging
TWAC vs spot sampling analysis

Good reproducibility from a campaign to another
Co, Pb, U : probable influence of the speciation
Cd : little overestimation, influence of the water quality before purging
Cu : influence of the water quality before purging
DGT conclusions

> The DBL does not seem to be negligible for this site
  • Need to get more data in other sites

> Representativity of water in the well & local pollution
  • all the more so as the well was not very deep (influence of runoff ??)
  • Depends on the elements

> Speciation : is there any interest to know the « bioavailable fraction » in groundwater ?
Conclusion on this case study: applicability of passive sampling in groundwater

> **Limits which are identified**
  - Representativity of water in the well & local pollution especially for metals all the more so as the well was not very deep
  - Pollution by the deployment system
  - Variation of the water flow & direction of the flow?

> **Qualitative tool**
  - Screening of molecules
  - Deployment at several depths to estimate vertical variability

> **Quantitative tool**
  - PDB powerful tool
  - Influence of the water flow especially for POCIS
Perspectives: Applicability of passive samplers in groundwater

> Need to investigate the applicability on other sites

> Identification of conditions (water flow) for which passive sampling is applicable for quantitative information

> Acquisition of specific sampling rates
  - Use of PRC: difficult in groundwater used for drinking water supply
  - Experimental calibration system representative of groundwater → ORIGAMI PROJECT (ANR 2012-2015)
  - In situ calibration: need of « model groundwater site »