Final Workshop

Passive Sampler Intercomparison Exercise

C. Miège, N. Mazzella, S. Schiavone, A. Dabrin, M. Coquery: Cemagref - Lyon, Bordeaux
C Berho, J-P Ghestem: BRGM – Orleans
J-L Gonzalez, D Munaron, C. Tixier: Ifremer - La Seyne/Mer, Sète, Nantes
B. Lalere, S. Lardy-Fontan: LNE - Paris
B. Lepot: INERIS – Paris
C. Gonzalez: EMA - Ales
Results for polar pesticides

N. Mazzella, D. Munaron, C. Berho
11 expert laboratories

- 6 French and 5 European labs (Germany, Netherlands, UK, Slovakia, Sweden)

- Various strategies:
  - With standard commercial or home-made passive sampler (POCIS, Chemcatchers, ...),
  - With standard commercial or home-made exposure system,
  - Using Rs from literature or calibrated,
  - Using some PRCs
# Passive samplers and exposure durations

<table>
<thead>
<tr>
<th>9 Pesticides/metabolites</th>
<th>Devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>- acetochlor</td>
<td>- 9 POCIS (DIA-d5 as PRC for 2 participants only, mainly HLB receiving phase)</td>
</tr>
<tr>
<td>- alachlor *</td>
<td>- 4 SBSE, Silicone rod/sheet and MESCO</td>
</tr>
<tr>
<td>- atrazine * + DEA / DIA</td>
<td>- 5 Chemcatchers (SDB and C\textsubscript{18})</td>
</tr>
<tr>
<td>- diuron *</td>
<td>- 14 days</td>
</tr>
<tr>
<td>- isoproturon *</td>
<td></td>
</tr>
<tr>
<td>- metolachlor</td>
<td></td>
</tr>
<tr>
<td>- simazine *</td>
<td></td>
</tr>
</tbody>
</table>

* priority substances (WFD)
## Sampling sites and planning

<table>
<thead>
<tr>
<th>Coastal waters</th>
<th>Thau Lagoon (Hérault)</th>
<th>27th April-18th May</th>
</tr>
</thead>
<tbody>
<tr>
<td>River waters</td>
<td>Beillant site (Charente maritime)</td>
<td>27th May-10th June</td>
</tr>
</tbody>
</table>
Water concentration estimates (ng/L) and data treatment methodology

- For Beillant site:

**Means and standard deviations (all participants)**

**Means and standard deviations (without QC outliers)**

**Robust statistic (all participants)**

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For Beillant site:

- Atrazine
  - Number of labs: 12
- Diuron
  - Number of labs: 12

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**Final Workshop – AQUAREF Passive Sampler Intercomparison Exercise, Nantes, 23rd November**
Comparison of pesticides water concentration (ng/L) from various tools and lab.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Number of quantified results</th>
<th>Results/Participants ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Beillant</td>
<td>Thau</td>
</tr>
<tr>
<td>Acetochlor</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Alachlor</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Atrazine</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Diuron</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Metalochlor</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Simazine</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

- Very low concentrations for Thau (sub ng/L except diuron with 2.4 ng/L)

- Very few results for Thau, only diuron data will be presented for this site
Comparison of pesticides water concentration (ng/L) from various tools and lab.

For Beillant site:

\[ x^* \pm S_R \]

10.6 ± 6.7 ng/L (TWAC estimates)

18.3 ± 4.2 ng/L (spot sampling, raw water)

Aberrant values

<table>
<thead>
<tr>
<th>QC</th>
<th>Z score&gt;3</th>
<th>Dispersion (Cochran)</th>
<th>Mean (Grubbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DATA</td>
<td>Dispersion (Cochran)</td>
<td>Mean (Grubbs)</td>
<td></td>
</tr>
</tbody>
</table>

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Comparison of pesticides water concentration (ng/L) from various tools and lab.

For Beillant site:

\[ x^* \pm s_r \]

6.7 \pm 7.4 ng/L

Aberrant values

- QC Z score>3
- Dispersion (Cochran)
- Mean (Grubbs)

DATA
- Dispersion (Cochran)
- Mean (Grubbs)

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Comparison of pesticides water concentration (ng/L) from various tools and lab.

- For Beillant site:

\[ x^* \pm S_R \]

35.9 ± 39.6 ng/L (TWAC estimates)

49.2 ± 18.7 ng/L (spot sampling, raw water)
Comparison of pesticides water concentration (ng/L) from various tools and lab.

- For Beillant site:

$$x^* \pm S_R$$

7.5 ± 4.5 ng/L (TWAC estimates) 14.8 ± 4.7 ng/L (spot sampling, raw water)
Comparison of pesticides water concentration (ng/L) from various tools and lab.

- For Beillant site:

\[ x^* \pm S_R \]

2.1 ± 0.7 ng/L (TWAC estimates)

- Less results, but lower data dispersion
- Quite low concentrations, especially regarding to « spot sampling » LOQs
Comparison of pesticides water concentration (ng/L) from various tools and lab.

- For Thau Lagoon site:

\[ \bar{x} \pm S_R \\
7.5 \pm 6.8 \text{ ng/L} \]

\[ 2.4 \pm 0.3 \text{ ng/L (spot sampling, filtered water)} \]

Very few data... but two labs used the same PRC (DIA-α5)
Comparison of pesticides water concentration (ng/L) from various tools and lab.

For Beillant site

- **Metolachlor**

  - TWAC Passive samplers
  - Mean of spot sampling (raw water)
  - Mean of spot sampling (filtered water)

  \[ n=9 \]

- **DIA**

  \[ n=7 \]

No significant differences between PS TWACs and spot sampling data (both filtered and raw waters)

However, relatively higher data dispersion (e.g. DIA)
Data dispersion for passive samplers

- For Beillant site

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Passive sampler data</th>
<th>SWIFT-WFD Proficiency Testing Exercise (natural water)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Robust mean x ± SD (ng/L)</td>
<td>Robust reproducibility % RSD</td>
</tr>
<tr>
<td>Alachlor</td>
<td>1.8 ± 1.6</td>
<td>84</td>
</tr>
<tr>
<td>Atrazine</td>
<td>6.7 ± 7.5</td>
<td>111</td>
</tr>
<tr>
<td>Diuron</td>
<td>2.1 ± 0.8</td>
<td>36</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>0.4 ± 0.1</td>
<td>36</td>
</tr>
<tr>
<td>Simazine</td>
<td>6.6 ± 5.7</td>
<td>87</td>
</tr>
</tbody>
</table>

- Comparison with a classical proficiency testing: higher dispersion of PS data for some analytes

However, a few results for some analytes (e.g. n=2 for alaclor) and very lower concentrations

Moreover, reproducibility for PS includes both analytical and sampling steps
Comparison of data in ng/tool and ng/L

For Beillant site

Dendrogram

Metolachlor (ng/tool)

50 % of populations in the same group
Comparison of data in ng/tool and ng/L

• For Beillant site

Comparable population size (9 vs 10 populations), but higher number of/smaller groups for ng/L results...

No direct correspondance between data

Higher dispersion?
Comparison of data in ng/tool and ng/L

- For Beillant site

Factorial Discriminant Analysis (atrazine and S-metolachlor)

Outliers (10112, 10115 and 10131) will not be further considered...
**Comparison of data in ng/tool and ng/L**

- **For Beillant site**

  *Number of significantly comparable populations*

  Kruskal-Wallis and Conover-Iman (p=0.05) procedures with outlier exclusion, and then similar samplers (POCIS/chemcatchers)

  ![Diagram showing the comparison of data in ng/tool and ng/L for different compounds.

- Comparable populations decrease with calculations of TWACs...

- Need of harmonization of $R_s$ for a same type of device?
Conclusions

Passive sampling of polar pesticides

• Achievement of ultra-trace levels and TWAC estimates
• POCIS and Chemcatchers (polar configuration) are more suitable
• Quite high data dispersion for some chemicals (e.g. atrazine and simazine), especially in comparison with classical methods…

However:  
- PS techniques combine both analysis and sampling steps
- very low concentration levels (not reached with classical methods)
- contribution of the various calibration data to the whole dispersion

Considering WFD requirements and recommendations

• Investigative monitoring, screening, mapping and determination of trends:
  - Data dispersion may be reduced with harmonization of $R_s$ data
  - More than dispersion, uncertainties must be evaluated

• Surveillance/operational monitoring: good agreement between TWACs and mean concentrations from spot sampling (both raw and filtered waters) for 3 analytes
  - Comparison with more pesticides (and higher log $K_{ow}$ values) is compulsory
Thanks to the participant lab.

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Thanks to the central lab. for water analysis

- Cemagref of Bordeaux (pesticides, physico-chemical parameters in Beillant site)
- ISM-LPTC of Bordeaux (pesticides and PAHs in Thau site)
- IFREMER of Sète (physico-chemical parameters in Thau site)

And also Ineris for data treatment
Thanks for your attention !!