Final Workshop
Passive Sampler Intercomparison Exercise

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B. Lepot: INERIS – Paris
C. Gonzalez: EMA - Ales
Results for Metals

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10 expert laboratories

- 5 French and 5 other European countries laboratories (Italy, Spain, United Kingdom, Sweden, Norway)

- Various strategies:
  - Standard commercial or home-made passive samplers (PSs): DGT open pores, DGT restrictive pores, Chemcatcher
  - With home-made exposure systems
  - Analytical treatment
  - Using diffusion coefficients/uptake rates from literature
Passive samplers and exposure durations

<table>
<thead>
<tr>
<th>8 metals</th>
<th>devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium*</td>
<td>DGT (Diffusive Gradient in Thin films)</td>
</tr>
<tr>
<td>Chromium*</td>
<td>Open pores</td>
</tr>
<tr>
<td>Lead*</td>
<td>Restrictive pores</td>
</tr>
<tr>
<td>Nickel*</td>
<td>Chelex-100</td>
</tr>
<tr>
<td>Manganese</td>
<td>Chemcatcher</td>
</tr>
<tr>
<td>Zinc*</td>
<td>Empore chelating disk</td>
</tr>
<tr>
<td>Copper*</td>
<td>7 days</td>
</tr>
<tr>
<td>Cobalt</td>
<td></td>
</tr>
</tbody>
</table>

*Priority substances (WFD)

*Substances of the ecological status

- Tools were exposed in triplicates and field blanks (brought to the field but not exposed in waters) were used
**Sampling sites**

- 2 contrasted environments

<table>
<thead>
<tr>
<th>Environment</th>
<th>Location</th>
<th>Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coastal environment</td>
<td>Thau Lagoon (Hérault)</td>
<td>27 April-5 May 2010</td>
</tr>
<tr>
<td>Continental environment</td>
<td>Rhône River Ternay site</td>
<td>17-24 June 2010</td>
</tr>
</tbody>
</table>

Former site of oyster farming
Spot sampling concentrations

3 spot sampling:
Start, during and at the end of the PSs deployment

**Ternay (Continental Environment) - ICPMS**

**Thau (Coastal environment) - Chelation-Extraction (Danielson et al., 1982) - ICP-MS**
Comparison of passive sampling concentrations from various tools and laboratories

<table>
<thead>
<tr>
<th>Metals</th>
<th>Number of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>12</td>
</tr>
<tr>
<td>Ni</td>
<td>13</td>
</tr>
<tr>
<td>Pb</td>
<td>12</td>
</tr>
<tr>
<td>Cu</td>
<td>13</td>
</tr>
<tr>
<td>Cr</td>
<td>11</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
</tr>
<tr>
<td>Co</td>
<td>8</td>
</tr>
<tr>
<td>Mn</td>
<td>11</td>
</tr>
</tbody>
</table>

- Two times more results were obtained for the exercise at Ternay site than Thau
- Tools were lost or some laboratories did not give results for some metals
- Percentage of results compared with the number of tools:
  - Ternay: from 62 to 100%
  - Thau: from 71 to 100%
Statistical data treatment and methodology

- Arithmetic means and reproducibility standard deviations $S_R$ (ISO 5725-2)

- Robust statistics: ISO 5725-5
  No exclusion from laboratories with outliers results
  Data was processed to minimize the weight of suspect values

- Comparison of:
  - Arithmetic means and $S_R$ with data of all lab.
  - Arithmetic means and $S_R$ after elimination of QC outliers
  - Robust means ($x^*$) and $S_R$ with data of all lab.
Water concentrations (µg/L) for metals – passive samplers

● Ternay site:

- Robust approach allows to decrease the means and the standard deviations
Data dispersion of passive samplers

- Comparison with a classical proficiency testing exercise (analytical):
  - Higher dispersion of PSs data for Pb, Zn, Mn
  - Similar dispersion of PSs for Cd, Cr, Cu
  - Lower dispersion for Ni

- However, much lower concentrations determined by passive samplers

- Moreover, reproducibility for PS includes both analytical and sampling steps

Since analytical variability was low in this exercise (from 8 to 25%, from 4 to 44%), the dispersion was mainly due to PS step
Comparison of passive sampling results from various tool and lab

- For Ternay site:

\[ \bar{x} \pm S_r \]

\[ 0.0053 \pm 0.0031 \mu g/L \text{ (TWAC, robust mean)} \]

RSD 58%

\[ 0.013 \pm 0.002 \mu g/L \text{ (spot sampling)} \]
Comparison of passive sampling results from various tool and lab

- For Ternay site:

<table>
<thead>
<tr>
<th>QC</th>
<th>PSs DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cochran test)</td>
<td>within-laboratory variability</td>
</tr>
<tr>
<td>(Grubbs test)</td>
<td>between-laboratory variability</td>
</tr>
</tbody>
</table>

**Aberrant values**

<table>
<thead>
<tr>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>x* ± S_R</td>
</tr>
<tr>
<td>0.063 ± 0.070 µg/L (TWAC estimates)</td>
</tr>
<tr>
<td>RSD 112%</td>
</tr>
<tr>
<td>0.367 ± 0.629 µg/L (spot sampling)</td>
</tr>
</tbody>
</table>
Comparison of passive sampling results from various tool and lab

- For Ternay site:

Aberrant values

QC
(Cochran test) within-laboratory variability
(Grubbs test) between-laboratory variability

PSs DATA
(Cochran test) within-laboratory variability
(Grubbs test) between-laboratory variability

Ni

\[ x^* \pm S_R \]

0.392 ± 0.139 µg/L (TWAC estimates)
RSD 25%

0.733 ± 0.118 µg/L (spot sampling)
Comparison of passive sampling results from various tool and lab

- For Thau site:

  - TWAC estimates:
    - \(0.027 \pm 0.025 \mu g/L\)
  - Spot sampling:
    - \(0.014 \pm 0.003 \mu g/L\)

**QC**
- (Cochran test) within-laboratory variability
- (Grubbs test) between-laboratory variability

**PSs DATA**
- (Cochran test) within-laboratory variability
- (Grubbs test) between-laboratory variability

- **Cd**

\[ x^* \pm S_R \]

\(0.027 \pm 0.025 \mu g/L\) (TWAC estimates)

\(0.014 \pm 0.003 \mu g/L\) (spot sampling)
Comparison of passive sampling results from various tool and lab

For Thau site:

- For Thau site:

Aberrant values

 QC (Cochran test) within-laboratory variability
 (Grubbs test) between-laboratory variability

PSs DATA (Cochran test) within-laboratory variability
 (Grubbs test) between-laboratory variability

Pb

\[ x^* \pm S_R \]

0.021 ± 0.012 µg/L (TWAC estimates)
RSD 58%

0.019 ± 0.002 µg/L (spot sampling)
Comparison of passive sampling results from various tool and lab

For Thau site:

- Aberrant values

<table>
<thead>
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</table>

\[
x^* \pm S_R
\]

0.261 ± 0.126 µg/L (TWAC estimates)

RSD 48%

0.454 ± 0.152 µg/L (spot sampling)
Comparison of TWAC and spot sampling (Dissolved concentrations)

- 100% of total dissolved Mn was sampled by PSs

- Only 35% of Cu was sampled by PSs

For metals, PSs only «see» a part of total dissolved concentrations, depends on the metal and on the environmental conditions (DOM)
Field blanks for metals (ng/tool)

Ternay: 2 lab. substracted field blanks

Field blanks

Samples (mean)

Cd

Cr

Co

Cu

Mn

Ni

Pb

Zn

17% 1% 17%
Field blanks for metals (ng/tool)

Thau: 1 lab. substracted field blanks

Graphs showing concentrations of various metals (Cd, Cr, Co, Ni, Cu, Mn, Pb, Zn) for different samples and field blanks. Each graph includes a diamond symbol for samples (mean) and a line for field blanks. The graphs indicate the percentage of field blanks relative to samples, with values of 4%, 22%, 0%, and 20%.
Field blanks for metals

Ternay

**Cr**

![Graph showing the relationship between ng/tool (field blanks) and ng/tool (samples) for Cr with a correlation coefficient R = 0.94 (p< 0.05)]

**Zn**

![Graph showing the relationship between ng/tool (field blanks) and ng/tool (samples) for Zn with a correlation coefficient R = 0.88 (p< 0.05)]
Field blanks for metals

- Field blanks are partly responsible for PSs TWAC variability in these exercises:
  
  \[
  Cr, Zn : \text{Ternay} \\
  Cr, Cd : \text{Thau}
  \]

- In other cases, field blanks are high but there is no relationship

- For all metals, there is a need to better determine contamination origin: by discriminating field blanks and lab-blanks
Conclusions and perspectives

- Estimation of water concentrations by passive sampling for metals shows low and satisfying variability, considering various lab, strategies and tools.

- RSD are comparable to analytical interlab. Exercise (SWIFT)

- Since analytical interlab. variability was low in this exercise (from 8 to 44%), the variability was mainly due to PS step

- PSs allow to measure low concentrations

- PSs allow to facilitate the measurement of some metals in saline matrix

- After this exercise, difficult to conclude for use a better tool since only one chemcathcer and two DGT with restrictive pores were used

- For metals, PSs only see a part of total dissolved concentrations, and depends on the metal and the environment

- Contamination of field blanks (in particular for Cr, Cd, Zn, Pb) is partly responsible for DGT TWAC variability
Conclusions and perspectives

- Need to discriminate sources of PS uncertainties for each lab (including steps of assembly, deployment, dismantling, elution, ...) - by obtaining lab-blanks for each laboratory and to compare with field blanks

- Need to compare more precisely Chemcatcher, DGT open and restrictive pores

- Considering WFD:
  - A need of detailed protocols for non expert lab. (to better control blanks)
  - A need to clarify the fraction which is sampled by these tools in contrasted environment and during contrasted conditions
Thanks to the participant lab

- ALS Scandinavia AB (SW)
- AZTI-Foundation (ES)
- BRGM (FR)
- Cefas (UK)
- Cemagref (FR)
- EDF R&D/LNHE (FR)
- IFREMER (FR)
- NIVA (NO)
- Universita di Cagliari (IT)
Thanks to central lab for water analysis

- IFREMER (metals and physico-chemical parameters in Thau site)
- Cemagref of Lyon (metals and physicochemical parameters at Ternay site)
- Ineris for data treatment
Thank you for your attention