ANNEXE 7 : Conférences présentées au colloque final de restitution des résultats, à Nantes le 23 novembre 2011

**General aspects:**
*Objectives, design, field campaigns*

C. Miège, N. Mazzella, D. Munaron, C. Tixier, S. Lardy-Fontan, B. Lepot, S. Schiavone, C. Berho, JP Ghestem, M Coquery

**Final Workshop**
*Passive Sampler Intercomparison Exercise*

C. Miège, N. Mazzella, S. Schiavone, A. Dabrin, M. Coquery: Carnagref - 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
Planning

- Year 1 (2009):
  - Constitution of an organisation committee
  - Configuration of the exercise
  - Prospection/searching for participants

- Year 2 (2010):
  - Realization of the 3 in situ campaigns
  - Centralisation of final results on the web site

- Year 3 (2011):
  - Data treatment
  - Valorisation and communication on the results (report to participants, conference at IPSW 2011, final workshop, final report for Aquaref, scientific papers)

General objectives

The assessment of the potential role and efficiency of passive samplers for water pollutants measurements in surface and coastal water in the frame of the WFD:

- to evaluate the comparability and variability of measurements of selected priority substances with passive samplers
- to evaluate the suitability of these samplers implemented in different aquatic environments to sample selected substances
- to demonstrate the applicability of such tools to water basin managers and routine laboratories
How to design the intercomparison exercise? (1)

1/ PS not used in France by routine lab. for monitoring programs, (especially for continental waters)
   nowrap>necessity to limit to expert lab.

2/ Necessity to have enough data per tool/molecule/site for satisfying statistical data treatment (for evaluation of the TWAC and its uncertainty and comparison of various tools)
   nowrap>necessity to find foreign lab.

How to design the intercomparison exercise? (2)

3/ None detailed guideline per PS, each expert lab. has its own sampling and analytical strategy (exposure conditions, analytical treatment, quality control, PRC, calculation of TWAC, …)
   nowrap>Choice to let expert lab. proceed as they are used to

4/ Some participants are very far away from the location of the in situ campaigns
   nowrap>They could either come and prepare their own PS before exposure or they send us the detailed procedure and let us prepare their own PS before exposure
How to design the intercomparison exercise? (3)

5/ Choice of the molecules:
- Selection of priority molecules (WFD, OSPAR, good ecological status)
- Metals / Hydrophilic Organics / Hydrophobic Organics
- Selection of pesticide metabolites
- Detected in the selected sites
- Possible to be sampled by PS
- Possible to be analysed by central lab.

6/ Choice of the tools:
- Cover the most known tools: DGT, SPMD, POCIS
- Let the possibility for other tools to be compared (chemcatcher, SR, MESCO, ...)

7/ Choice of the sites:
- to test the influence of various physico-chemical field conditions for some tool/molecule/site ➔ marine and continental water sites
- In relatively contaminated area to be sure to quantify the studied pollutants
- Well known by organising lab.
- Easy to access, protected from vandalism

24 expert laboratories participated

- 11 national and 13 international lab. (Czech republic, Germany, Italy, Netherlands, Norway, Slovakia, Spain, Sweden, United Kingdom, United States)

- AZTI-Foundation (ES).
- BRGM (FR).
- Cefas (UK).
- Cermaqref (FR).
- Deltares/TNO (NL).
- Ecole des Mines d’Alès (FR).
- EDF R&D/UNHE (FR).
- Environment Agency, National Laboratory Service (UK).
- IFREMER (FR).
- Labogua (ES).
- ALS Scandinavia AB (SW). LEESU (FR).
- LPTC Bordeaux (FR).
- Marine Scotland - Science (UK).
- NJIVA (NO).
- T. G. Mazowetz Water Research Institute, Public Research Institution (CZ).
- UFZ - Department of Ecological Chemistry, Helmholtz Centre for Environmental Research (DE).
- Universita di Cagliari (IT).
- University of Rhode Island (USA).
- Water Research Institute (SK)
Various tools and exposure systems

- Exposure system (cage or support): Commercially available or home made
- PS and main characteristics:

<table>
<thead>
<tr>
<th>Substances</th>
<th>Tools and main characteristics</th>
</tr>
</thead>
</table>
| Metals     | * DGT: binding agent (Cladion-100) with open pore or restrictive diffusive gels (thickness: 0.8 mm)  
            | * Chemcatcher (metals) |
| PAHs       | * SPMD: standard, 460 cm²  
            | * LDPE, from 80 to 490 cm²  
            | * Chemcatcher (apolar), C18 : 15.9 and 17.4 cm²  
            | * SR-5, 160 or 600 cm²  
            | * MESCO: LDPE membrane, silicone phase  
            | * CFIS (PDMS) |
| Pesticides | * FOCUS: both pesticide and pharmaceutical configurations  
            | * Chemcatchers (polar), C18, SDB-XC and SDB-RPS: 15.9 cm²  
            | * SR: 5 cm²  
            | * MESCO: cellulose membrane, silicone phase |

SR: PDMS sheet

Various sampling and analytical procedures

- Quality controls (those not set by the organizers):
  - Laboratory PS blank or not
  - Internal surrogates or not
  - Correction from field blanks or not

- To calculate TWAC:
  - Rs for organic chemicals: From literature or determined by the participant
  - Various models applied

- Analytical procedures:
  - Metals: ICP-MS or GF/AAS
  - Organic: purification or not
    - GC-MS, GC/MS/MS or HPLC/MS/MS, HPLC/fluo

- PRC used or not
Target substances

- Metals (8): Cd\textsuperscript{**,†}, Ni\textsuperscript{***}, Pb\textsuperscript{*,†}, Zn\textsuperscript{**}, Cu\textsuperscript{**}, Mn, Co, Cr\textsuperscript{**}

- PAHs (16 EPA): naphthalene*,acenaphthylene, acenaphthene, fluorene, phenanthrene†, anthracene**, fluoranthenes†, pyrene†, benzo(a)anthracene†, chrysene†, benzo(b)fluoranthenes†, benzo(a)pyrene†, benzo(k)fluoranthenes*, benzo(ghi)perylene†, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene†

- Pesticides (9): acetochlor, alachlor*, atrazine* and metabolites (DEA / DIA), diuron*, isoproturon*, simazine*, S-metolachlor

Priority molecules: WFD\textsuperscript{*} OSPAR \textsuperscript{†} Good

ecological status: \textsuperscript{†}

Exposure durations

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>PAHs</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>POCIS</td>
<td>SPMD</td>
<td>DGT</td>
</tr>
<tr>
<td>SBSE</td>
<td>LDPE</td>
<td>Chemcatcher</td>
</tr>
<tr>
<td>Chemcatcher</td>
<td>Chemcatcher</td>
<td></td>
</tr>
<tr>
<td>SR</td>
<td>SR (PDMS sheet)</td>
<td>MESCO</td>
</tr>
<tr>
<td>MESCO</td>
<td>CFIS</td>
<td></td>
</tr>
<tr>
<td>14 days</td>
<td>21 days</td>
<td>7 days</td>
</tr>
</tbody>
</table>

Final Workshop - AQUAREF Passive Sampler Intercomparison Exercise, Nantes, 31st November
### 3 sampling sites

<table>
<thead>
<tr>
<th>Coastal waters</th>
<th>Thau (Hérault)</th>
<th>27th April-18th May 2010</th>
<th>Pesticides, PAHs and metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>River waters</td>
<td>Beillant (Charente maritime)</td>
<td>27th May-10th June 2010</td>
<td>Pesticides</td>
</tr>
<tr>
<td></td>
<td>Ternay (Rhône)</td>
<td>17th June-8th July 2010</td>
<td>PAHs and metals</td>
</tr>
</tbody>
</table>

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**Thau site**

*(Hérault, France)*

- PAH, Pesticides, Metals
Thau lagoon: the second largest lake in France, 21 km long, 8 km wide, an area of 7 hectares, mean depth of 4.5 m, max depth of 30 m.

East borders largely industrial
Northern side has villages dedicated to fishing and the production of shellfish

Oyster farming

**Thau site**

- **Lagoon waters: mean during exercise (usual annual ranges)**
  - Temperature: 17.9°C (5-26°C)
  - Salinity: 37.6 PSU (34-39)
  - Suspended solids: 0.89 mg/L
  - Flow velocity: 1.59 cm/s
  - Micropollutants concentrations in the dissolved phase:
    - Metals: >500ng/L for Ni and Cu, ~60 ng/L for Co, < 20 ng/L for the others
    - Pesticides and PAHs: < 3 ng/L

- Preparation of the PS before exposure in laboratory (at 5.5 miles from the exposure site, by boat)

- Description of the exposure area:
  - Former site of oyster farming surrounded with shell farming tables in action
  - A monitoring site of the French mussel watch program (IFREMER)
Former site of oyster farming

Rope to hang up the exposure cages of PS
Signalisation of the exposure cages of PS (tool/lab.)

Exposure cages of PS
Same depth for all PS
Preparation of the PS for exposure in laboratory (at 5.5 miles from the exposure site, by boat)
Ternay site
(south of Lyon, Rhône, France)

PAH and Metals

Urban area of Lyon (2,000,000 inhabitants) at around 20 km

Trading site
Ternay site

- **Rhone river waters (mean ± sd on the 3 weeks campaign):**
  - Suspended solids: 14.0 ± 12.1 mg/L (Beillant > Thau)
  - Temperature: 19.8 ± 2.7 °C
  - Flow velocity: 0.217 ± 0.078 m/s (Thau and Beillant)
  - Conductivity: 389 ± 28 μSm/cm
  - Micropollutants mean concentrations in dissolved phase:
    (Metals: from 13 ng/L for Cd to 3.6 μg/L for Mn; PAHs: < 5 ng/L)

- **Preparation of the PS for exposure directly in situ, near the river Rhone (not in laboratory)**

- **Description of the sampling site:**
  - An urban (2 000 000 inhabitants) and industrial area. Lyon is known for its chemical industry located between Lyon and the sampling site.
  - A Rhone river measurement station
  - PS located near the river bank
Folding tables covered with aluminum foils

The exposure cages hanged to the buoy lines

Exp. syst. for SR
Beillant site
(Charente maritime, France)

Pesticides

The watershed area is occupied by almost 80% of agricultural lands

PS exposed in Charente river

376 km long, watershed of about 10 050 km²
Mean annual flow of 68 m³.s⁻¹ (at Beillant, 2008)
Beillant site

- **Charente river waters (mean ± sd on the 2 weeks campaign):**
  - Suspended solids: $7 ± 0.7$ mg/L
  - Temperature: $19.4 ± 1.1°C$
  - Flow velocity: 0.01-0.02 m/s
  - Conductivity: $539.8 ± 10.8 \mu$S/m/cm
  - Pesticide mean concentrations in dissolved phase: 10 to 50 ng/L
    - for DIA, MET, DEA, < LQ for others

- **Preparation of the PS for exposure in laboratory (at 150 km from the exposure site)**

- **Description of the sampling site:**
  - The watershed area is occupied by almost 80% of agricultural lands
  - A very well known site for Centagref Bordeaux
  - PS located near the river bank

---

**Triazine concentrations (2008)**

Background levels and low fluctuations of concentrations
Metabolites (DEA and DIA) are generally more abundant than parent compounds
Phenylurea and chloroacetanilide concentrations (2008)

Applications and detection typically during the spring
The lab. at 150 km from the sampling site

Preparation of PS

Receipt of PS from participants

Access by boat...
Access by boat...

Home made exp. syst. for Chemcatcher

1 buoy line to hang PS
Other aspects:

- A web site
- Water monitoring
- Quality assurance

A web site

To register

To collect results and information (sampling and analytical strategy) from participants
6 central lab. for water analysis

- BRGM (PAH at Ternay),
- Cemagref of Bordeaux (pesticides, physico-chemical parameters at Beillant),
- Cemagref of Lyon (metals, physico-chemical parameters at Ternay),
- EPÖC-LPTC of Bordeaux (pesticides and PAHs at Thau site),
- IFREMER of Sète (physico-chemical parameters at Thau site),
- IFREMER of Nantes (LBCM) (metals at Thau site).

Monitoring of the exposure water conditions

- Ionic composition
- pH, suspended matter, conductivity, salinity (for Thau), DOC, TOC, temperature, water velocity, pluviometry, discharge, dissolved oxygen (for Thau).
- Concentrations of the target compounds in the dissolved and total phases (spot sampling):

<table>
<thead>
<tr>
<th></th>
<th>Beillant</th>
<th>Ternay</th>
<th>Thau</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
<td>/</td>
<td>50 mL Direct analysis by ICP-MS</td>
<td>500 mL Danielson method (1982)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LQ from 0.01 for Cd to 0.5 for Zn</td>
<td>ICP-MS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>LQ from 0.1 ng/L for Cd to 10 for Cu and Zn</td>
</tr>
<tr>
<td><strong>PAHs</strong></td>
<td>/</td>
<td>EL complex</td>
<td>2 L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LLE (dichloromethane)</td>
<td>SPE (C18)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HPLC-FIAX</td>
<td>GC-MS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LQ 0.4 ng/L except ACE and PHE at 2 ng/L</td>
<td>LQ 0.1 ng/L</td>
</tr>
<tr>
<td><strong>Pesticides</strong></td>
<td>50 mL samples</td>
<td>/</td>
<td>2L</td>
</tr>
<tr>
<td></td>
<td>SPE (Basic M6)</td>
<td>/</td>
<td>SPE (Basic M6)</td>
</tr>
<tr>
<td></td>
<td>HPLC-MS-MS</td>
<td>/</td>
<td>HPLC-MS-MS</td>
</tr>
<tr>
<td></td>
<td>LQ from 10 to 20 ng/L</td>
<td>/</td>
<td>LQ from 10 to 20 ng/L</td>
</tr>
</tbody>
</table>
Quality controls and Quality assurance

- Each sampler exposed in triplicate

- 1 field blank per sampler and per site, participants are free to subtract or not this blank from their measurements

- A reference solution to evaluate the accuracy and precision of the instrumental analytical step

- Because of the design of the trial, implementation of QC based on reference PSs (spiked and then distributed to all participants) was not technically possible (too many different PSs studied).

A questionnaire measuring satisfaction will be sent to you
The authors thank the French National Agency for Water and Aquatic Environments (ONEMA) via AQUAREF for its financial support.

Thank you for your attention!!
QA/QC in the AQUAREF inter comparison exercise

Summary

1. Schedule from data-base conception to participant reporting

2. Position QA/QC in trial from basic concepts to final implemented strategy

3. Data-base overview

4. Statistical treatment

5. Reference solutions from conception to assignation of the final value

6. Presentation of results (QC solution A, field blank) and discussion

7. Conclusion and perspectives
QA/QC in the AQUAREF inter comparison exercise

Schedule
From database conception to participant reporting

General organization of the collaborative trial

⚠️ It is not a proficiency test

QA/QC Schedule : main steps

- Database
  - Development of a single support (for each family of scientists and each site)
  - Database validation

- Instructions
  - For results reporting
  - For reference solution supplies

- Reference solutions
  - Stability and homogeneity

- Verification data collected
  - For the exercise solutions
  - For all participants' control data

- Data Correction
  - To achieve consistency among the participants

- QA/QC Statistical treatment

- Reporting to participants

March to July 2010
April to September 2010
October to November 2010
November 2010
December to February 2011
May 2011
QA/QC in the AQUAREF inter comparison exercise

From basic concepts to the final implemented strategy

From basic concepts... (1)

- Quality and comparability of data;
- Representativity of data;
- Rationalization of costs of monitoring;
- Evaluation of capabilities and competencies;

**METROLOGIC INFRASTRUCTURE** → QA/QC
From basic concepts... (2)

Certified Reference Material
Standards of high purity
Reference solution

Calibration of instrumentation

Uncertainties

TRACEABILITY to S.I.

Comparability

Uncertainties

AQUAREF

CRM matrix

EIL with reference value

Accuracy:
Trueness + Precision

WFD
Directive
QA/QC
QUALITY of DATA

Final Workshop - Passive Sampler Intercomparison Exercise, November 23rd 2011

From basic concepts... (3)

AQUAREF

TRACEABILITY

Calculating value

Certified Reference value

Reference value from NMI

Consensual value from experts laboratories

Consensual value from participating laboratories

Final Workshop - Passive Sampler Intercomparison Exercise, November 23rd 2011
From basic concepts ... (4)

Measurement chains

Various types of pollutants
- PAHS (16 EPA)
- Pesticides (8)
- Metals (

Various types of devices

Various types of sites of deployment
- Relevance with the objectives of the inter comparison exercise;
- State of knowledge;
- Analytical capabilities;
- Acceptable costs

Various types of analytical preparation
- Solvent desorption
- Thermo desorption

Various types of instrumental analysis
- LC-Fluo/DAD/UV
- GC-MS
- LC-HSNS
- GC-MS
- ILP-MS
- GF-AAS

... To the final implemented QA/QC strategy (5)

Various types of pollutants
- PAHS (16 EPA)
- Pesticides (8)
- Metals (

REFERENCE PS $\rightarrow$ DEMONSTRATION of ACCURACY+UNCERTAINTIES

Various types of devices

Each PS pre-deployed $\rightarrow$ DEMONSTRATION of precision, minimum

Various types of

Analytical extract of PS $\rightarrow$ DEMONSTRATION of precision, minimum

Various types of

Relevant PS pre-deployed $\rightarrow$ DEMONSTRATION of precision, minimum

REFERENCE SOLUTIONS $\rightarrow$ ESTABLISHMENT of TRACEABILITY

Various types of instrumental analysis
- LC-Fluo/DAD/UV
- GC-MS
- LC-HSNS
- GC-MS
- ILP-MS
- GF-AAS
... To the final implemented QA/QC strategy (7)

Various types of pollutants
- PAHs (16 EPA)
- Pesticides (8)
- Metals ()

Various types of devices
- Field Blank
- Replicates

Various types of sites of deployment
- Ternary site
- Thau site
- Brilliant site
- Thau site

Various types of analytical preparation
- Dialysis
- Sonication
- Solvent desorption
- Thermo desorption

Reference solutions
- Mineralisation
- Acid Extraction

Various types of instrumental analysis
- LC-Flow/DAD/UV
- GC-MS
- LC-MS/MS
- GC-MS
- ICP-MS
- GF-AAS

QA/QC in the AQUAREF inter comparison exercise

Data base overview
Data base Overview (1)

www.ineris.fr/eil/passivesamplers.php

Data base Overview (2)
QA/QC in the AQUAREF inter comparison exercise

Statistical treatment

Statistical treatment of QC A (1)

- According to the standards and guidelines
  - ISO 5725-5 (1998) « Accuracy (trueness and precision) of measurement methods and results – Part 5 : Alternative methods for the determination of the precision of the standard measurement method »

- Different approaches to determine the assigned value
  - Known values from formulation
  - Certified reference values
  - Reference values
  - Consensus values from expert laboratories
  - Consensus values from participants

With this approach, the assigned value is the robust average of the results reported by all the participants: No exclusion of participants
Statistical treatment of QC A (2)

- Consensus values from participants
  - Method implemented: Robust method

  Calculate the assigned value and other statistical parameters from all data including those that might be deemed suspicious by an expert or a test for outliers. Data is processed to minimize the weight of suspect values, so that these do not significantly impact the result.

  After x iteration
  For each parameter:
  ✓ robust mean
  ✓ robust standard deviation

Statistical treatment of QC A (3)

- Research statistically different values
  - Cochran test: is a test of the within-laboratory variability
  - Grubbs test: is a test of between-laboratory variability

  • Suspect values are studied to find correlation with
    ✓ the implemented analytical strategies (metadata provided during the reporting)
    ✓ the results of passive samplers measurements
**Statistical treatment of QC A (4)**

- Comparison of the assigned value between:
  - **Robust method**
    - Based on consensus values from participants
  - **Reference value**
    - Based on reference solution A
  - Robust mean and Robust standard deviation

- **In order to identify:**
  - ✓ a good agreement whatever the approach adopted
  - ✓ Otherwise identify the possible reasons for non-agreement
  - ✓ a common bias in the results of the laboratories,
  - ✓ biased participant method(s) or several biased laboratories

---

**Statistical treatment of QC A (5)**

- This statistical treatment chosen for this trial was implemented:

- ✓ Class of parameters and site
  - PAH/Ternay
  - PAH/etang Thau
  - Pesticides/Beillant
  - Pesticides/Ternay
  - Metals/Ternay
  - Metals/Etang Thau

- ✓ Class of parameters and all sites
  - PAH/Ternay + Etang Thau
  - Pesticides/Beillant + Ternay
  - Metals/Ternay + Etang Thau

Last option was made possible because reference solution (sol A) was the same regardless of the site.
QA/QC in the AQUAREF inter comparison exercise

Reference solutions: From conception to the assignation of the final value

Reference solutions: Summary

<table>
<thead>
<tr>
<th>TARGETS EIL</th>
<th>PAHS (16 EPA)</th>
<th>Pesticides (8)</th>
<th>Metals (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Benz(e) Pyrene</td>
<td>✓ Atrazine</td>
<td>✓ Cadmium</td>
<td>✓ Nickel</td>
</tr>
<tr>
<td>✓ Benz(b) Fluoranthene</td>
<td>✓ Simazine</td>
<td>✓ Nickel</td>
<td>✓ Lead</td>
</tr>
<tr>
<td>✓ Benz(a, h, i) Perylene</td>
<td>✓ DEA</td>
<td>✓ Lead</td>
<td>✓ Zinc</td>
</tr>
<tr>
<td>✓ Benz(k) Fluoranthene</td>
<td>✓ DIA</td>
<td>✓ Copper</td>
<td>✓ Copper</td>
</tr>
<tr>
<td>✓ Indeno (1,2,3-cd) Pyrene</td>
<td>✓ Dieldrin</td>
<td>✓ Manganese</td>
<td>✓ Manganese</td>
</tr>
<tr>
<td>✓ Naphthalene</td>
<td>✓ Isoproturon</td>
<td>✓ Cobalt</td>
<td>✓ Cobalt</td>
</tr>
<tr>
<td>✓ Fluoranthene</td>
<td>✓ Alachlor</td>
<td>✓ Chromium</td>
<td>✓ Chromium</td>
</tr>
<tr>
<td>✓ Anthracene</td>
<td>✓ Acetochlor</td>
<td>✓ Chromium</td>
<td>✓ Chromium</td>
</tr>
<tr>
<td>✓ Fluorene</td>
<td>✓ Alachlor</td>
<td>✓ Chromium</td>
<td>✓ Chromium</td>
</tr>
<tr>
<td>✓ Acenaphthene</td>
<td>✓ Alachlor</td>
<td>✓ Chromium</td>
<td>✓ Chromium</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>Acetone</th>
<th>Acetone</th>
<th>Nitric Acid (2 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MASSIC CONC.</td>
<td>= 2 µg / ml Ind.</td>
<td>= 2 µg / ml Ind.</td>
<td>= 1 µg / 1 Ind.</td>
</tr>
<tr>
<td>VOLUME</td>
<td>= 1 ml</td>
<td>= 1 ml</td>
<td>= 100 ml</td>
</tr>
</tbody>
</table>

[33 Priority substances] [Substances of the ecological status]
ORGANIC AND INORGANIC ANALYSIS OBLIGATORY

Solution
"INSTRUMENTAL CALIBRATION"
Evaporation
Dilution / 100
"INSTRUMENTAL CALIBRATION" solution for injection
Instrumental analysis in replicates (n=3)

Determination of massic concentration for each analytes
X ± x (μg/UL)

Instrumental calibration of all participants laboratories

ORGANIC ANALYSIS, ONLY FACULTATIVE

Solution
"MATRIX EFFECTS"
Passive Sampler Extract
Instrumental analysis in replicates (n=3)

Spike
Instrumental analysis in replicates (n=3)

Determination of massic concentration for each analytes
Y ± y (μg/UL)

Evaluation of Matrix effects

PREPARATION of REFERENCE SOLUTIONS

Batch treatment
STANDARD
Gravimetry
(liquid to quintuple weighing)
Sub-Division
N bottle

HOMOGEDITY STUDY

SHORT TERM STABILITY STUDY
- Transport effect (24 hours)

LONG TERM STABILITY STUDY
April to September 2010
Classical approach

PRIMARY METHOD ID-MS: Principles

Sample
Gravimetric control
CHROMATOGRAPHY
MASS SPECTROMETRY
SIGNAL
CALIBRATION

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METALS

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference Value Massic concentration ± U (U expanded, k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>1.042 ± 0.012 µg/l</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1.005 ± 0.003 µg/l</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.040 ± 0.020 µg/l</td>
</tr>
<tr>
<td>Copper</td>
<td>1.099 ± 0.044 µg/l</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.002 ± 0.080 µg/l</td>
</tr>
<tr>
<td>Nickel</td>
<td>1.035 ± 0.023 µg/l</td>
</tr>
<tr>
<td>Lead</td>
<td>1.049 ± 0.015 µg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.025 ± 0.071 µg/l</td>
</tr>
</tbody>
</table>

The study demonstrates:

- No inhomogeneity
- No instability

---

ATTRIBUTION OF REFERENCE VALUE WITH U < 10%

Final Workshop - Passive Sampler Intercomparison Exercise, November 23rd 2011

PESTICIDES

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Reference Value Massic concentration ± U (U expanded, k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachloro</td>
<td>2.05 ± 0.09 µg/ml</td>
</tr>
<tr>
<td>Atrazetine</td>
<td>1.97 ± 0.12 µg/ml</td>
</tr>
<tr>
<td>DEA</td>
<td>1.89 ± 0.14 µg/ml</td>
</tr>
<tr>
<td>DIA</td>
<td>2.04 ± 0.12 µg/ml</td>
</tr>
<tr>
<td>Atrazine</td>
<td>1.99 ± 0.04 µg/ml</td>
</tr>
<tr>
<td>Boproturon</td>
<td>2.07 ± 0.08 µg/ml</td>
</tr>
<tr>
<td>Dicloron</td>
<td>2.03 ± 0.18 µg/ml</td>
</tr>
<tr>
<td>Simazine</td>
<td>2.23 ± 0.1 µg/ml</td>
</tr>
<tr>
<td>Metolachloride</td>
<td>2.12 ± 0.14 µg/ml</td>
</tr>
</tbody>
</table>

The study demonstrates:

- No inhomogeneity
- No instability

---

ATTRIBUTION OF REFERENCE VALUE WITH U < 10%

Final Workshop - Passive Sampler Intercomparison Exercise, November 23rd 2011
The study demonstrates:

- No inhomogeneity
- No instability

Attribution of reference value with U < 10%, except for Anthracene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene

QA/QC in the AQUAREF inter comparison exercise

Presentation of results, discussions
LABORATORY QUALITY CONTROL : REFERENCE SOLUTIONS FOR VERIFICATION OF INSTRUMENT CALIBRATION (1)

METALS

Chromium

- Robust mean = reference value
- Accuracy: precision + trueness of measurements the general population

Final Workshop - Passive Sampler Intercomparison Exercise, November 23rd 2011

LABORATORY QUALITY CONTROL : REFERENCE SOLUTIONS FOR VERIFICATION OF INSTRUMENT CALIBRATION (2)

METALS

Lead

- No overlap between robust mean and reference value
- Lack of accuracy especially trueness: reference value needed in this case

Final Workshop - Passive Sampler Intercomparison Exercise, November 23rd 2011
PAHs

Fluoranthene

Robust mean = reference value

Accuracy: precision + trueness of measurements the general population

Mastery of participants

Benzo-a-pyrene

No overlap between robust mean and reference value

Lack of accuracy especially trueness: interest of reference value in such exercise
PESTICIDES

Robust mean = reference value
Accuracy: precision + trueness of measurements in the general population

Mastery of participants

PESTICIDES

Alachlore

No overlap between robust mean and reference value
Lack of accuracy: interest of reference value in such exercise
No overlap between robust mean and reference value
Lack of accuracy especially trueness: interest of reference value in such exercise

Final Workshop - Passive Sampler Intercomparision Exercise, November 23rd 2011

FIELD QUALITY CONTROL: BLANK MEASUREMENTS (1/8)

METALS:

-Field blanks for metals display significant contamination depending on the element:

<table>
<thead>
<tr>
<th>Parameter/Element</th>
<th>TERNAY participants</th>
<th>Field Blank</th>
<th>THAU participants</th>
<th>Field Blank</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Min</td>
<td>Max</td>
<td>Mean</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.86</td>
<td>0.82</td>
<td>20.80</td>
<td>0.76</td>
</tr>
<tr>
<td>Cobalt</td>
<td>3.62</td>
<td>3.80</td>
<td>9.30</td>
<td>3.94</td>
</tr>
<tr>
<td>Copper</td>
<td>6.31</td>
<td>1.96</td>
<td>26.00</td>
<td>2.86</td>
</tr>
<tr>
<td>Manganese</td>
<td>3.04</td>
<td>0.09</td>
<td>8.30</td>
<td>2.67</td>
</tr>
<tr>
<td>Nickel</td>
<td>5.42</td>
<td>0.51</td>
<td>65.00</td>
<td>6.23</td>
</tr>
<tr>
<td>Lead</td>
<td>3.03</td>
<td>0.95</td>
<td>33.07</td>
<td>2.72</td>
</tr>
<tr>
<td>Zinc</td>
<td>271.40</td>
<td>27.37</td>
<td>1300.00</td>
<td>768.45</td>
</tr>
</tbody>
</table>

Discussed in the dedicated session p.m
FIELD QUALITY CONTROL : BLANK MEASUREMENTS (2/8)

PESTICIDES:

-No field blanks positive except for one compound in one PS and in one site

Consistent with the physico-chemical properties of the selected molecules

Focus on PAHs

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (3/8)

Case study 1: PAH Ternay

![Graph showing PAH concentrations](image-url)
FIELD QUALITY CONTROL: BLANK MEASUREMENTS (4/8)

- No correction of the data by field blanks
- Field blanks close to 50% of deployed PS
- No correlation with the type of PS, the type of extraction technique nor type of instrumental analysis, the quantification approach
- No clear correlation with the QC A results

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FIELD QUALITY CONTROL: BLANK MEASUREMENTS (5/8)

- No correction of the data by field blanks, except 2 labs.
- Field blanks close to 60% of deployed PS
- No correlation with the type of PS, the type of extraction technique nor type of instrumental analysis, the quantification approach

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FIELD QUALITY CONTROL : BLANK MEASUREMENTS (6/8)

Case study 2: PAH Thau

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (7/8)

✓ No correction of the data by field blanks, except 1 lab.
✓ Field blanks close to 50% of deployed PS
✓ No correlation with the type of PS, the type of extraction technique nor type of instrumental analysis, the quantification approach
✓ No clear correlation with the QC A results

Final Workshop – Passive Sampler Intercomparison Exercise, November 23rd 2011
☑ No correction of the data by field blanks
☑ Field blanks > deployed PS
☑ No correlation with the type of PS, the type of extraction technique nor type of instrumental analysis or the quantification approach

QA/QC in the AQUAREF inter comparison exercise

Conclusion and Perspectives
**Laboratory QC**

- Results on reference solution (sol A) in accordance (in term of dispersion) with results of analytical intercomparison exercise in routine laboratories
- Systematic integration of control solution in analytical intercomparison exercise led to better evaluation of participants on results of these QC
- Interest of the reference value by comparison to the consensual value

**Field QC**

- Have to be taken into consideration
- Many issues not yet answered

- Importance of:
  - QA / QC (field and laboratory) with reference value
  - Replicat during deployment
  - Procedure (deployment and analysis)

✓ ISO 5667- Part 23: “Guidance on passive sampling in surface waters”
  - Published in February 2011
  - Some aspects are to be completed light of these results
  - A procedure (deployment and analysis) for each type of passive sampler
Final Workshop
Passive Sampler Intercomparison Exercise

C. Miége, N. Mazzella, S. Schiavone, A. Dabrin, M. Coquery: Cemagref - Lyon, Bordeaux
C. Berho, J-P Ghestem: BRGM - Orléans
J-L Gonzalez, D Munaron, C. Tixier: Ifremer - La Seyne/Mer, Sète, Nanterre
B. Lalere, S. Lardy-Fontan: LNE - Paris
B. Lepot: INERIS - Paris
C. Gonzalez: EMA - Ales

Results for Metals

A. Dabrin, J-P. Ghestem, J-L. Gonzalez, M. Coquery
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>Coastal environment</th>
<th>Thou Lagoon (Hérault)</th>
<th>27 April-5 May 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image1" alt="Former site of oyster farming" /></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Continental environment</th>
<th>Rhône River Ternay site</th>
<th>17-24 June 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image2" alt="Rhône River Ternay site" /></td>
<td></td>
</tr>
</tbody>
</table>

Spot sampling concentrations

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

![Graph showing mean ± SD (µg/L) for different elements](image3)
Comparison of passive sampling concentrations from various tools and laboratories

<table>
<thead>
<tr>
<th></th>
<th>Ternay</th>
<th>Thou</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of participants</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Number of Tools</td>
<td>13</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metals</th>
<th>Ternay</th>
<th>Thou</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>Ni</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>Pb</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Cu</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>Cr</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Mn</td>
<td>11</td>
<td>7</td>
</tr>
</tbody>
</table>

- Two times more results were obtained for the exercise at Ternay site than Thou.
- 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 %
  - Thou: 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 ($\bar{x}^*$) and $S_R$ with data of all lab.
**Water concentrations (µg/L) for metals - passive samplers**

- Ternary site:

![Graph showing water concentrations for Mn, Zn, Cu, Ni, Cd, Cr, Co, Pb](image)

- Robust approach allows to decrease the means and the standard deviations

**Data dispersion of passive samplers**

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Sw</td>
</tr>
<tr>
<td>X̄ ± SD (µg/L)</td>
<td>RSD</td>
</tr>
<tr>
<td>Cd</td>
<td>0.005 ± 0.003</td>
</tr>
<tr>
<td>Cr</td>
<td>0.076 ± 0.070</td>
</tr>
<tr>
<td>Cu</td>
<td>0.367 ± 0.153</td>
</tr>
<tr>
<td>Mn</td>
<td>3.47 ± 0.99</td>
</tr>
<tr>
<td>Ni</td>
<td>0.92 ± 0.139</td>
</tr>
<tr>
<td>Pb</td>
<td>0.063 ± 0.070</td>
</tr>
<tr>
<td>Zn</td>
<td>1.40 ± 1.10</td>
</tr>
</tbody>
</table>

- 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:

Cd

\[ x^* \pm s_b \]

0.0053 ± 0.0031 μg/L (TWAC, robust mean)
RSD 55%

0.013 ± 0.002 μg/L (spot sampling)

Pb

\[ x^* \pm s_b \]

0.060 ± 0.070 μg/L (TWAC estimates)
RSD 112%

0.367 ± 0.629 μg/L (spot sampling)
Comparison of passive sampling results from various tool and lab

For Ternay site:

Comparison of passive sampling results from various tool and lab

For Thau site:
Comparison of passive sampling results from various tool and lab

For Thou site:

**Pb**

- QC: 0.021 ± 0.012 µg/L (TWAC estimates)
- RSD: 56%
- PSr DATA: 0.015 ± 0.005 µg/L (spot sampling)

**Ni**

- QC: 0.261 ± 0.126 µg/L (TWAC estimates)
- RSD: 48%
- PSr DATA: 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. subtracted field blanks

Field blanks

Samples (mean)
Field blanks for metals (ng/tool)

Thau : I ab. substracted field blanks

Field blanks for metals

Ternay
Field blanks for metals

- Field blanks are partly responsible for PSs TWAC variability in these exercises:
  - Cr, Zn : Ternay
  - Cr, Cd : 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 chemocycler 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
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. Laloro, S. Lardy-Fontan: LNE - Paris
B. Lepeil: INERIS - Paris
C. Gonzalez: EMA - Alex

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>Pesticides/metabolites</th>
<th>Devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetochlor</td>
<td>9 POCIS (DIA-dB as PRC for 2 participants only, mainly HLB receiving phase)</td>
</tr>
<tr>
<td>clachlor</td>
<td>4 SBSE, Silicone rod/sheet and MESCO</td>
</tr>
<tr>
<td>atrazine * + DEA / DIA</td>
<td>5 Chemcatchers (SDB and Csb)</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

Coastal waters
Thau Lagoon (Hérault)
27th April-18th May

River waters
Beillant site (Charente maritime)
27th May-10th June

Water concentration estimates (ng/L) and data treatment methodology

For Beillant site:

- Number of labs: 9
- Parazine
  - Means and standard deviations (all participants)
  - Means and standard deviations (without QC outliers)
  - Robust statistic (all participants)

- Diuron
  - Means and standard deviations (all participants)
  - Robust statistic (all participants)
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>Atraclophor</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>Diethylstilbestrol</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Diclorpropatrazine</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Diuron</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Metabolololololololololo</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:
  \[ X^2 \pm S_x \]
  \[ 10.6 \pm 6.7 \text{ ng/L (TWAC estimates)} \]

- Aberrant values
  - C6: Z-score=3
  - C7: Dispersion (Cochran) Mean (Gibbons)

- S-metolachlor

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

For Beillant site:

\[ x' \pm S_R \]

6.7 ± 7.4 ng/L

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:

\[ 7.5 \pm 4.5 \text{ ng/L (TWAC estimates)} \]

\[ 14.8 \pm 4.7 \text{ ng/L (spot sampling, raw water)} \]

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

- For Beillant site:

\[ 2.1 \pm 0.7 \text{ ng/L (TWAC estimates)} \]

- 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:

\[ x' = S_x = 7.5 \pm 6.8 \text{ ng/L} \]

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

- For Beillant site

\[ \text{Motolachlor} \]

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>SWFT-WFD Proficiency Testing Exercise (natural water)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Robust mean</td>
<td>Robust reproducibility (% RSD)</td>
</tr>
<tr>
<td>Alachlor</td>
<td>1.5 ± 1.6</td>
<td>34</td>
</tr>
<tr>
<td>Atrazine</td>
<td>1.7 ± 0.5</td>
<td>38</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>Dinobenzine</td>
<td>0.5 ± 0.7</td>
<td>37</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 alachlor) 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

Metolachor (ng/tool)

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

For Beillant site

Motolachor (ng/tool)

Motolachor (ng/L)

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

No direct correspondence 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...

Final Workshop – AQUAREF Passive Sampler Intercomparison Exercise, Rantes, 23rd November
Comparison of data in ng/tool and ng/L

- For Brilliant 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 comparison of data in ng/tool and ng/L](image)

- Comparable populations decrease with calculations of TWACs...
- Need of harmonization of $R_2$ 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 $R_2$ 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

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Thanks to the participant lab.

- ALS Scandinavia AB (SW),
- AZTI-Foundation (ES),
- BRGM (FR),
- Cefas (UK),
- Cemagref (FR),
- Deltas/TNO (NL),
- Ecole des Mines d’Alès (FR),
- EDF R&D/LNH (FR),
- Environment Agency, National Laboratory Service (UK),
- IFREMER (FR),
- Labqua (ES),
- LECSU (FR),
- LPTC Bordeaux (FR),
- Marine Scotland - Science (UK),
- NIVA (NO),
- T. S. Masaryk Water Research Institute, Public Research Institution (CZ),
- UFZ - Department of Ecological Chemistry, Helmholtz Centre for Environmental Research (DE),
- Universita di Cagliari (IT),
- University of Rhode Island (USA),
- Water Research Institute (SK)

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 !!
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 - Orléans
J-L Gonzalez, D Munaron, C. Tixier: Ifremer - La Seyne/Mer, Sète, Nantes
B. Lalero, S. Lardy-Fontan: LNE - Paris
B. Lepot: INERIS - Paris
C. Gonzalez: EMA - Ales

Results for Polycyclic Aromatic Hydrocarbons

C. Tixier, C. Miège, S. Schiavone, C Berho
18 EXPERT LABORATORIES

- 6 French laboratories and 12 foreign laboratories
  (Czech Republic, Germany, Italy, Netherlands, Norway, Slovakia, Spain, Sweden, United Kingdom, USA)

Various strategies
- Passive sampler
  - Standard *commercial* or *home-made* passive samplers
    (SPMD, Chemcatcher, LDPE or silicone membranes, ...)
  - Standard commercial or home-made exposure system

Analytical Procedure
- Purification of the extracts
- HPLC/fluor, GC/MS or GC/MS/MS

Data treatment
- Correction for field blank or not
- Use of PRCs or not
- Use of Rs values from literature or calibrated
- Use of various calculation models for TWAC

SAMPLING SITES and PLANNING

<table>
<thead>
<tr>
<th>Coastal waters</th>
<th>Thau (Hérault)</th>
<th>27th April 18th May</th>
</tr>
</thead>
<tbody>
<tr>
<td>River waters</td>
<td>Ternay (Rhône)</td>
<td>17th June 8th July</td>
</tr>
</tbody>
</table>

Final Workshop – AQUAREF Passive Sampler Intercomparision Exercises, Nantes, 23rd November
**PAHs and PASSIVE SAMplers**

16 PAHs
- Naphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene
- Pyrene
- Benz[a]anthracene
- Chrysene
- Benzo[b]fluoranthene
- Benzo[a]pyrene
- Benzo[k]fluoranthene
- Benzo[g,h,i]perylene
- Dibenzo[a,h]anthracene
- Indeno[1,2,3-cd]pyrene

* Priority substances (WFD)
† Priority substances (OSPAR)

### PS Devices

<table>
<thead>
<tr>
<th>Device</th>
<th>Ternay</th>
<th>Thau</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPMD</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>LDPE sheets</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Silicone R sheets</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Chemcatchers (2 versions)</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>MESCO</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Silicone rod</td>
<td>1 (lost)</td>
<td>1</td>
</tr>
<tr>
<td>CFIS (SBSE)</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

**21 exposure days**

---

**PAH WATER CONCENTRATION (ng/L)**

Various tools and laboratories

<table>
<thead>
<tr>
<th>Substance</th>
<th>Nb of quantified results</th>
<th>Results/Participants (%)</th>
<th>Spot sampling (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ternay</td>
<td>Thau</td>
<td>Ternay</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>8</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>14</td>
<td>5</td>
<td>56</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>10</td>
<td>6</td>
<td>72</td>
</tr>
<tr>
<td>Fluorene</td>
<td>21</td>
<td>8</td>
<td>84</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>22</td>
<td>10</td>
<td>66</td>
</tr>
<tr>
<td>Anthracene</td>
<td>21</td>
<td>8</td>
<td>64</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>22</td>
<td>12</td>
<td>88</td>
</tr>
<tr>
<td>Pyrene</td>
<td>22</td>
<td>11</td>
<td>68</td>
</tr>
<tr>
<td>Benz[a]anthracene</td>
<td>21</td>
<td>9</td>
<td>64</td>
</tr>
<tr>
<td>Chrysene</td>
<td>21</td>
<td>10</td>
<td>64</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>20</td>
<td>8</td>
<td>60</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>19</td>
<td>7</td>
<td>76</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>19</td>
<td>8</td>
<td>70</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>14</td>
<td>7</td>
<td>59</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>11</td>
<td>3</td>
<td>44</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>15</td>
<td>6</td>
<td>60</td>
</tr>
</tbody>
</table>

✓ More than 60% of quantified results for 10 to 12 PAHs

---

*Final Workshop – AQUAREF Passive Sampler Intercomparison Exercise, Nantes, 23rd November*
## PAH WATER CONCENTRATION (ng/L)

### Various tools and laboratories

<table>
<thead>
<tr>
<th>PAH</th>
<th>Nb of quantified results</th>
<th>Results/Participants (%)</th>
<th>Spot sampling (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ternay</td>
<td>Thau</td>
<td>Ternay</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>8 (2)</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>14 (2)</td>
<td>5 (2)</td>
<td>56</td>
</tr>
<tr>
<td>Acenaphthenne</td>
<td>18 (1)</td>
<td>6 (1)</td>
<td>72</td>
</tr>
<tr>
<td>Fluorinene</td>
<td>21 (2)</td>
<td>8 (2)</td>
<td>84</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>22 (3)</td>
<td>10 (4)</td>
<td>88</td>
</tr>
<tr>
<td>Anthracene</td>
<td>21</td>
<td>8 (4)</td>
<td>84</td>
</tr>
<tr>
<td>Fluoranthenne</td>
<td>22</td>
<td>12 (2)</td>
<td>88</td>
</tr>
<tr>
<td>Pyrene</td>
<td>22</td>
<td>11 (1)</td>
<td>88</td>
</tr>
<tr>
<td>Benzo[e]anthracene</td>
<td>21</td>
<td>0 (4)</td>
<td>84</td>
</tr>
<tr>
<td>Chrysene</td>
<td>21</td>
<td>10 (5)</td>
<td>84</td>
</tr>
</tbody>
</table>

- More than 60% of quantified results for 10 to 12 PAHs
- Thau: Few data and some results close to field blank
- Lower LOQs with passive sampling / spot sampling

---

## PAH WATER CONCENTRATION (TWAC, ng/L)

- Low influence of QC outliers
- Lower dispersion with robust statistics
- Same conclusions for Thau site

---

*Final Workshop – AQUAREP Passive Sampler Intercomparison Exercise, Rantes, 13th November*
PAH WATER CONCENTRATION (ng/L)
Various tools and laboratories

Ternay: Fluoranthene

Robust mean ($x^* \pm S_R$):
4.839 ± 3.752 ng/L (TWAC estimates)
2.6 ± 2.2 ng/L (spot sampling, dissolved fraction after filtration 0.7 μm)

LOQ = 0.4 ng/L

PAH WATER CONCENTRATION (ng/L)
Various tools and laboratories

Ternay: Benzo[a]pyrene

$x^* \pm S_R$
0.144 ± 0.134 ng/L
<LOQ

LOQ = 0.4 ng/L

Final Workshop – AQUARE Passive Sampler Intercomparison Exercise, Nantes, 23rd November
**PAH WATER CONCENTRATION (ng/L)**
Various tools and laboratories

**Thau : Fluoranthene**

- Robust mean ($\bar{x} \pm S_R$):
  - $0.002 \pm 0.014$ ng/L (TWAC estimates)
  - $0.3 \pm 0.1$ ng/L (spot sampling, dissolved fraction after filtration 0.7 μm)

- LOQ = 0.1 ng/L

**PAH WATER CONCENTRATION (ng/L)**
Various tools and laboratories

**Thau : Benzo[a]pyrene**

- Robust mean ($\bar{x} \pm S_R$):
  - $0.049 \pm 0.050$ ng/L

- LOQ = 0.1 ng/L
REPRODUCIBILITY
Passive sampling – Spot sampling

<table>
<thead>
<tr>
<th>Ternary passive sampler data</th>
<th>AGLAE Proficiency Testing Exercise (Spiked surface waters 20-40 ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Robust mean ( \bar{x} )</td>
<td>Robust reproducibility (RSD %)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>9.49 ± 0.64</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>1.00 ± 0.27</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>6.61 ± 5.54</td>
</tr>
<tr>
<td>Fluorene</td>
<td>4.01 ± 4.82</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>5.76 ± 4.50</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.59 ± 1.27</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.84 ± 0.65</td>
</tr>
<tr>
<td>Pyrene</td>
<td>4.00 ± 2.95</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>0.01 ± 0.73</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.07 ± 0.63</td>
</tr>
<tr>
<td>Benzo[a]fluoranthene</td>
<td>0.25 ± 0.59</td>
</tr>
<tr>
<td>Benzo[b]pyrene</td>
<td>0.14 ± 0.13</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>0.13 ± 0.11</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>0.03 ± 0.02</td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>0.05 ± 0.05</td>
</tr>
</tbody>
</table>

✓ Lower reproducibility with passive sampling:
  - Much lower concentration levels
  - Sampling and Analytical steps + Calculations

Final Workshop – AQUIFER Passive Sampler Intercomparison Exercise, Nantes, 23rd November

PAH ACCUMULATION - VARIOUS TOOLS

✓ LDPE, SR: similar accumulation patterns
✓ Chemcatcher: no accumulation of high molecular weight PAHS

Final Workshop – AQUIFER Passive Sampler Intercomparison Exercise, Nantes, 23rd November
PAH CONCENTRATION in ng/L and ng/cm²

Ternay site

Fluoranthene

NG / L

SPMD
LDPE
SR
ChemC
CFIS

Daily (11)
Daily (5)
Daily (3)

NG / cm²

SPMD
LDPE
SR
ChemC
CFIS

Daily (11)
Daily (5)
Daily (3)

✓ Lower dispersion of the data expressed in ng/cm² for each sampler
✓ Dispersion of the data expressed in ng/L mainly due to the use of various calculation models
CONCLUSIONS

✓ Satisfying variability in the determination of PAH water concentrations by passive sampling (and expert lab.)
  • Various lab., strategies and tools
  • Variability: Sampling + Analytical procedure + Calculation method

✓ Sampling:
  • Various tools: various sampled fractions?
    ⇒ Need to better characterize these fractions
  • Lower LOQs by using SPMD, LDPE or SR membranes

✓ Analytical variability: to be improved
  PAH QC reference solution: reproducibility RDS = 20-54%

✓ Need for harmonized calculation methods:
  • Field blank (correction or not)
  • PRCs data
  • Calculation models and parameters used for Rs and TWAC determination

Dispersion of the data expressed in ng/L mainly due to the use of various calculation models.

Thanks to the participant laboratories

- ALS Scandinavia AB (SW),
- BRGM (FR),
- Cofas (UK),
- Comagrof (FR),
- Deltares/TNO (NL),
- Ecole des Mines d’Alès (FR),
- EDF R&D/LNHE (FR),
- Environment Agency, National Laboratory Service (UK),
- IFREMER (FR),
- Labaqua (ES),
- LEESU (FR),
- Marine Scotland - Science (UK),
- NIVA (NO),
- T. G. Masaryk Water Research Institute, Public Research Institution (CZ),
- UFZ - Department of Ecological Chemistry, Helmholtz Centre for Environmental Research (DE),
- Universita di Cagliari (IT),
- University of Rhode Island (USA),
- Water Research Institute (SK)
Thanks to the central laboratories for water analyses

- Cemagref of Lyon (Ternay site: physico-chemical parameters)
- ISM-LPTC of Bordeaux (Thau site: PAHs)
- BRGM (Ternay site: PAHs)
- IFREMER of Sète (Thau site: physico-chemical parameters)
- Ineris for data treatment

Thank you for your attention!