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

AQUAREF

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

ONEMA

AQUAREF

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

Cemagref LNE INERIS Ifremer brgm

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)

N°4

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

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

N°3

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

How to design the intercomparison exercise ? (1)

1/ PS not used in France by routine lab. for monitoring programs, (especially for continental waters)

☞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)

☞necessity to find foreign lab.

N°5

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

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, ...)

☞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

☞ 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

N°6

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

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

N°7

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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), •Cemagref (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), •ALS Scandinavia AB (SW), LEESU (FR), •LPTC Bordeaux (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)

N°8

Various tools and exposure systems

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

Substances	Tools and main characteristics
Metals	* DGT: binding agent (Chelex-100) with open pore or restrictive diffusive gels (thickness: 0.8 mm) * Chemcatcher (metals)
PAHs	* SPMD: standard, 460 cm2 * LDPE: from 390 to 490 cm2 * Chemcatcher (apolar), C18 : 15,9 and 17,4 cm2 * SR : 5, 160 et 600 cm2 * MESCO : LDPE membrane, silicone phase * CFIS (PDMS)
Pesticides	* POCIS: 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

N°9

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

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

N°10

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

Target substances

- Metals (8) : Cd*‡, Ni*, Pb*‡, Zn⁋, Cu⁋, Mn, Co, Cr⁋

- PAHs (16 EPA): naphthalene*, acenaphtylene, acenaphthene, fluorene, phenanthrene‡, anthracene*‡, fluoranthene*‡, pyrene‡, benzo(a)anthracene‡, chrysene‡, benzo(b)fluoranthene*, benzo(a)pyrene*‡, benzo(k)fluoranthene*, benzo(ghi)perylene*‡, dibenzo(ah)anthracene, indeno(1,2,3-c,d)pyrene*‡

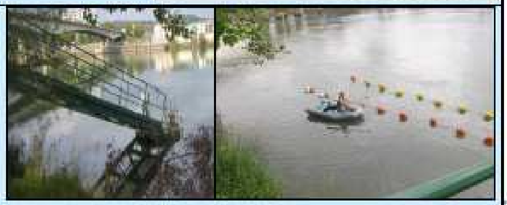
- Pesticides (9) : acetochlor, alachlor*, atrazine* and metabolites (DEA / DIA), diuron*, isoproturon*, simazine*, S-metolachlor

Priority molecules : WFD* OSPAR ‡ Good ecological status ⁋

Exposure durations

Pesticides	PAHs	Metals
• POCIS	• SPMD	• DGT
• SBSE	• LDPE	• Chemcatcher
• Chemcatcher	• Chemcatcher	
• SR	• SR (PDMS sheet)	
• MESCO	• MESCO	
	• CFIS	
☛ 14 days	☛ 21 days	☛ 7 days

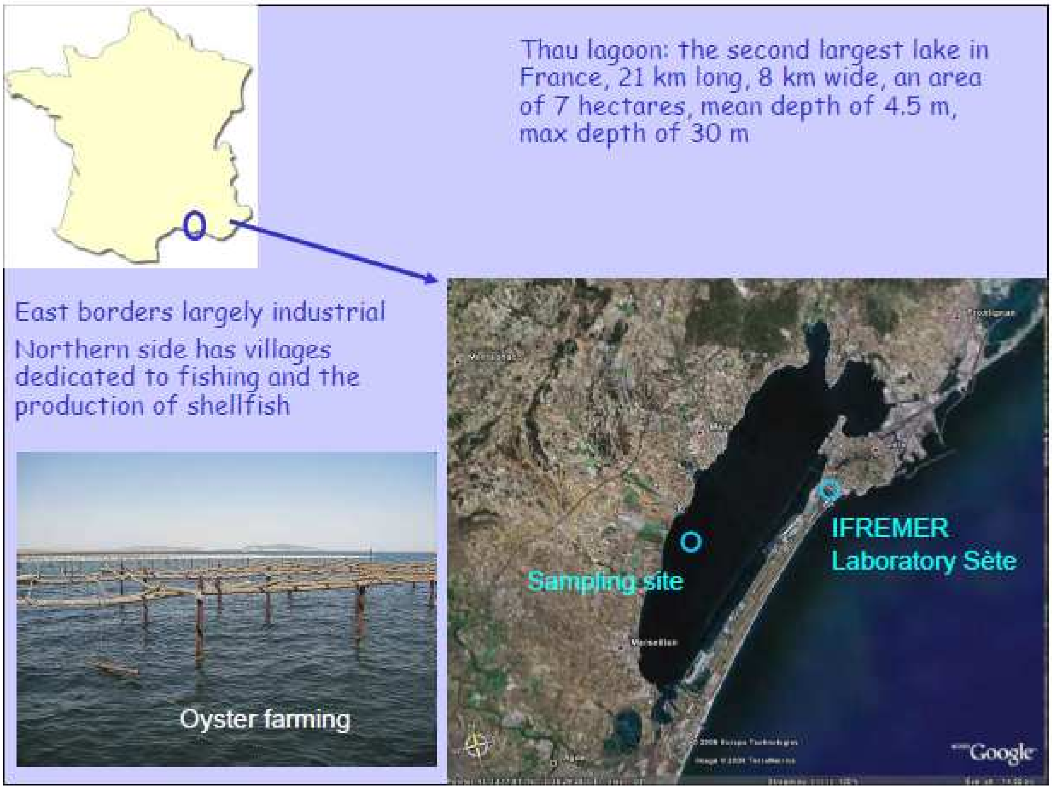
3 sampling sites

Coastal waters	**Thau** (Hérault) 27th April-18th May 2010 Pesticides, PAHs and metals	
River waters	**Beillant** (Charente maritime) 27th May-10th June 2010 Pesticides	
	Ternay (Rhône) 17th June-8th July 2010 PAHs and metals	

Thau site

(Hérault, France)

☞ PAH, Pesticides, Metals

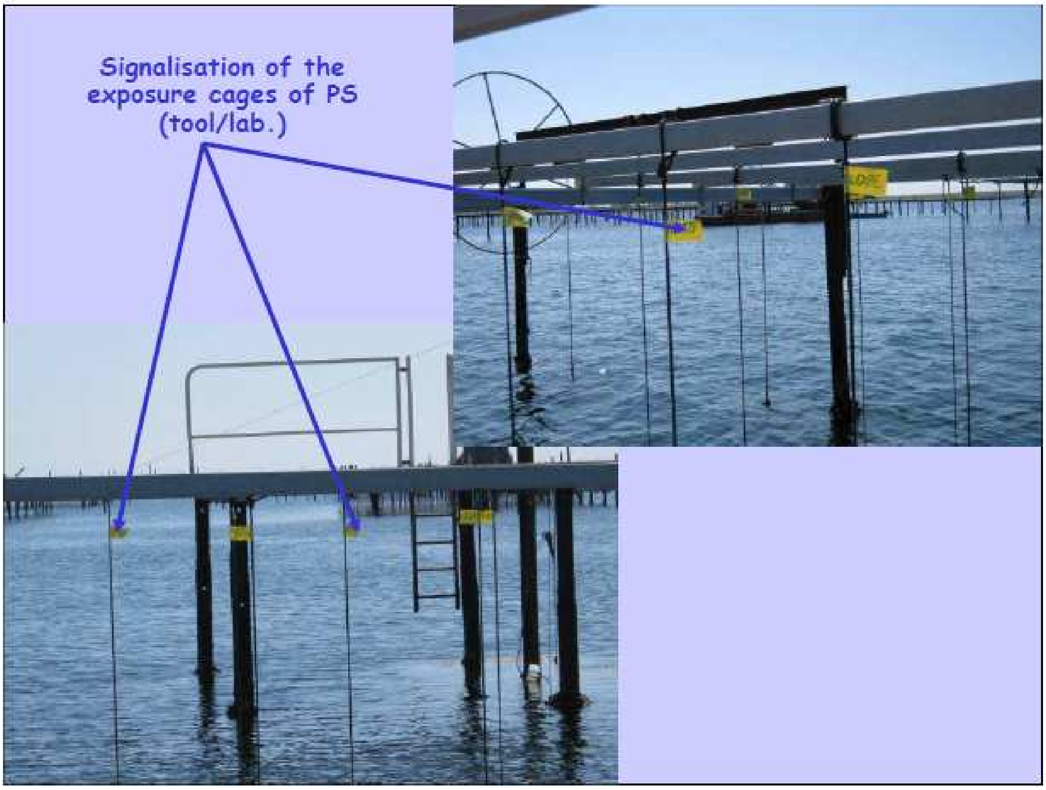


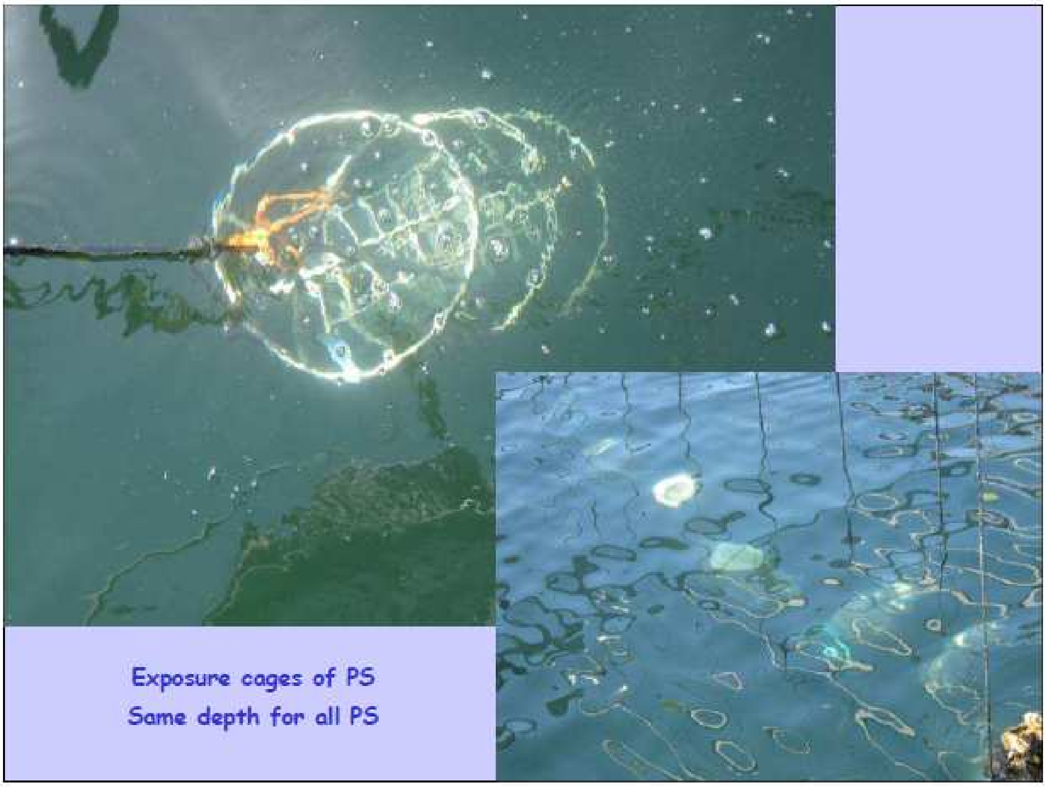
Thau site

- Lagoon waters : mean during exercice (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 shelf 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

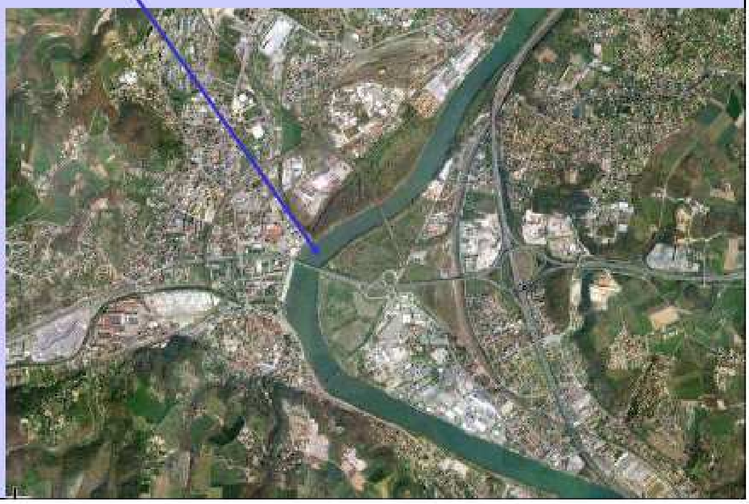

Preparation of the PS for exposure in laboratory
(at 5.5 miles from the exposure site, by boat)

Ternay site
(south of Lyon, Rhône, France)

☞PAH and Metals

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

Sampling site



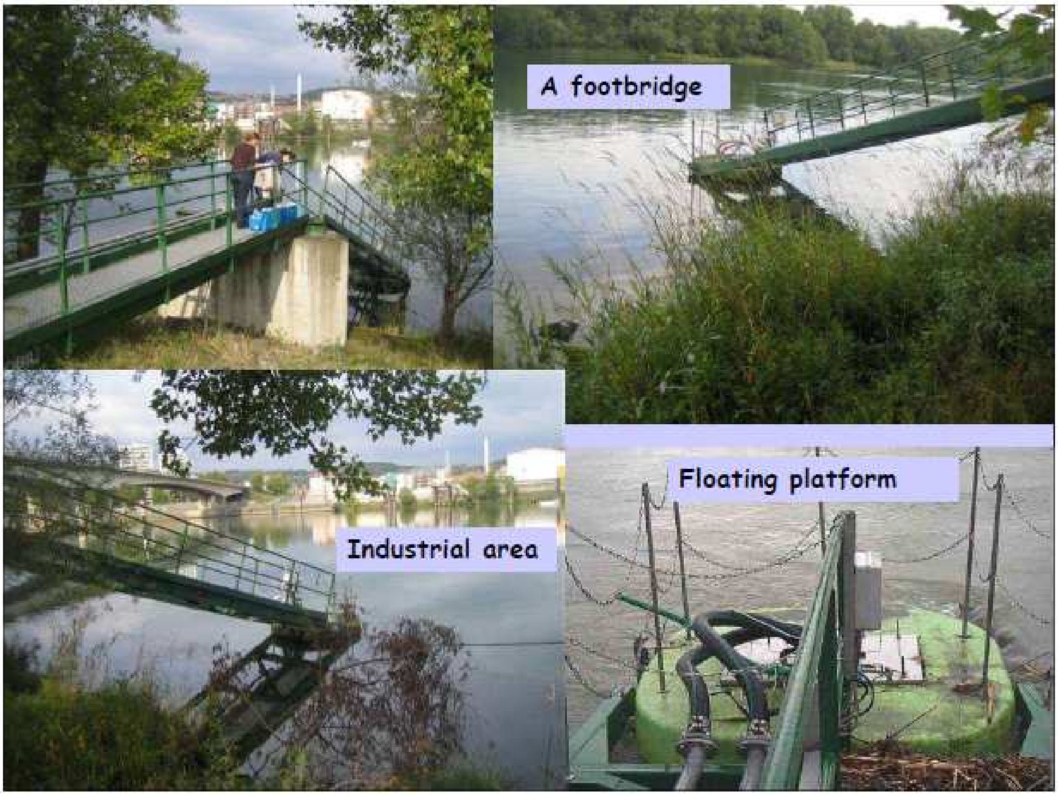
Ternay site

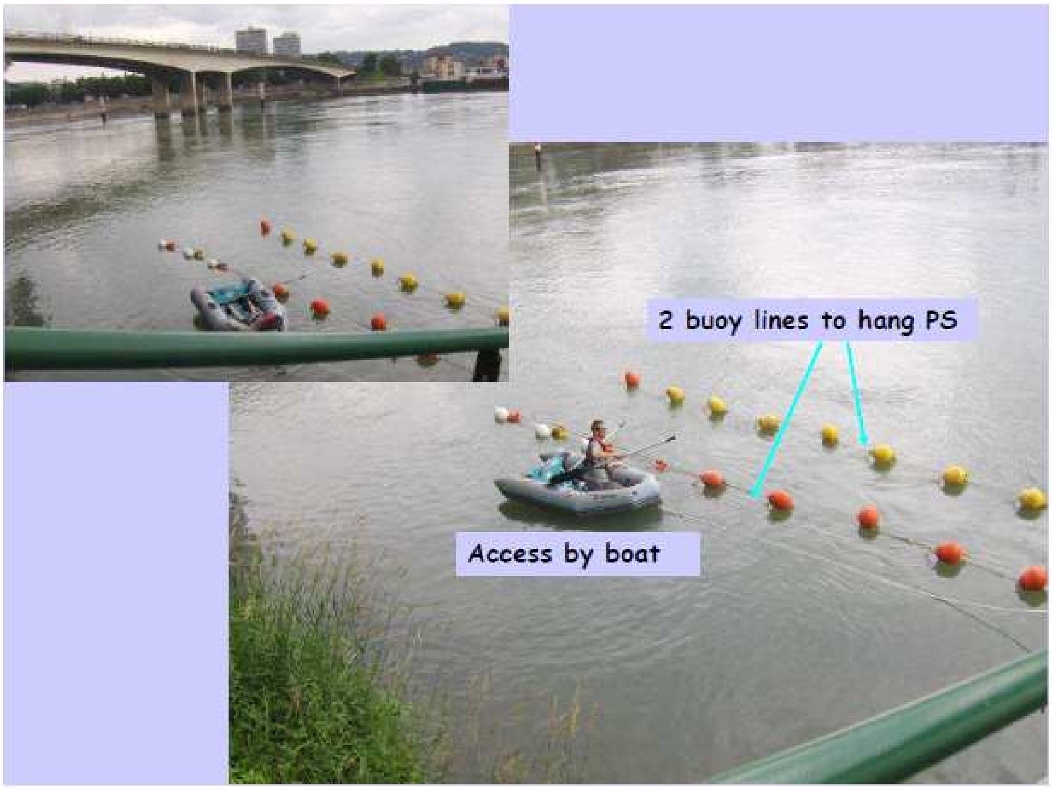
- Rhone river waters (mean ± sd on the 3 weeks campaign)
  - Suspended solids: 14,0 ± 12,1 mg/L (> Beillant > Thau)
  - Temperature: 19,8 ± 2,7 °C
  - Flow velocity: 0,217 ± 0,078 m/s (> Thau and Beillant)
  - Conductivity: 389 ± 28 µSm/cm
  - Micropollutants mean concentrations in dissolved phase: (Metals: 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. The great 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

N°25


A footbridge
Industrial area
Floating platform


2 buoy lines to hang PS
Access by boat


The exposure cages hanged to the buoy lines
Folding tables covered with aluminim foils


Exp. syst. for SR


After exposure...

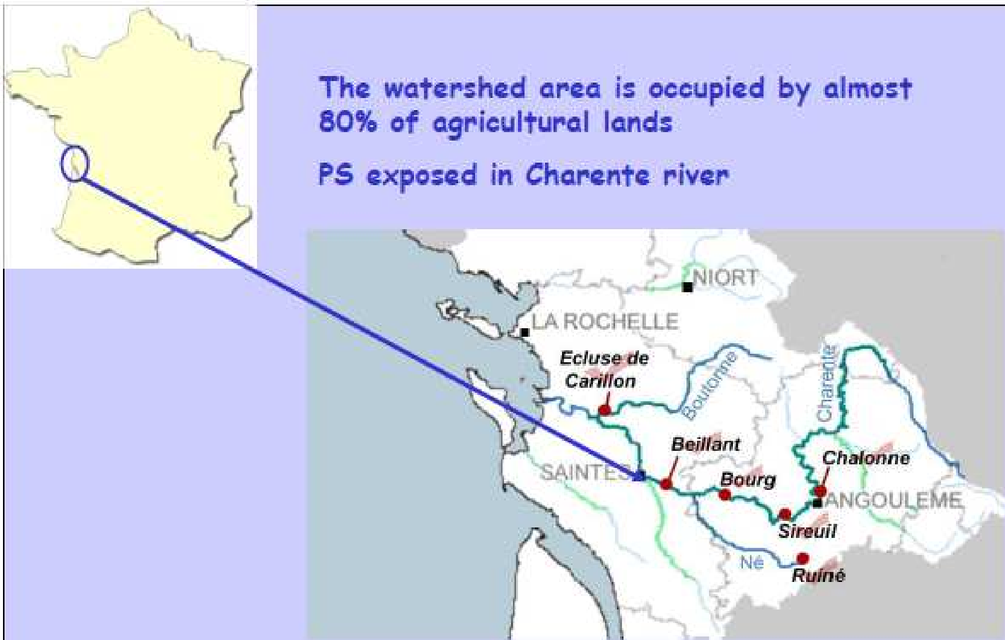

After exposure...
CFIS

Beillant site
(Charente maritime, France)

☞ Pesticides

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

PS exposed in Charente river



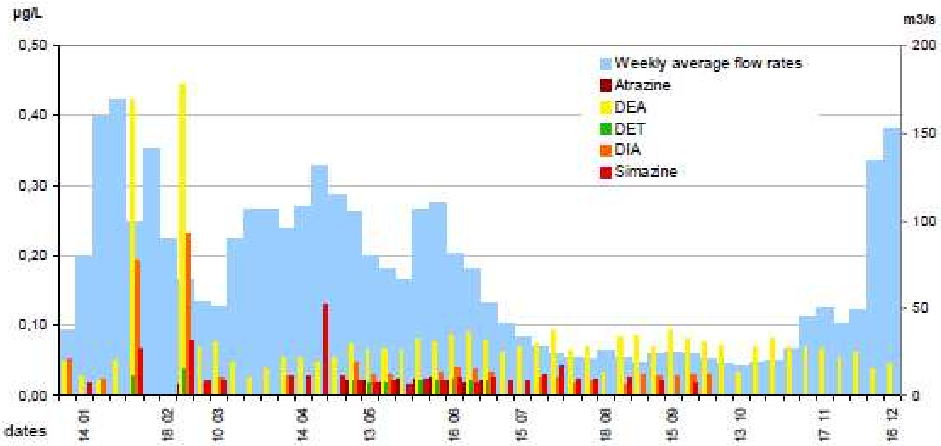
376 km long, watershed of about 10 050 km^2

Mean annual flow of 68 $m^3.s^{-1}$ (at Beillant, 2008)

Beillant site

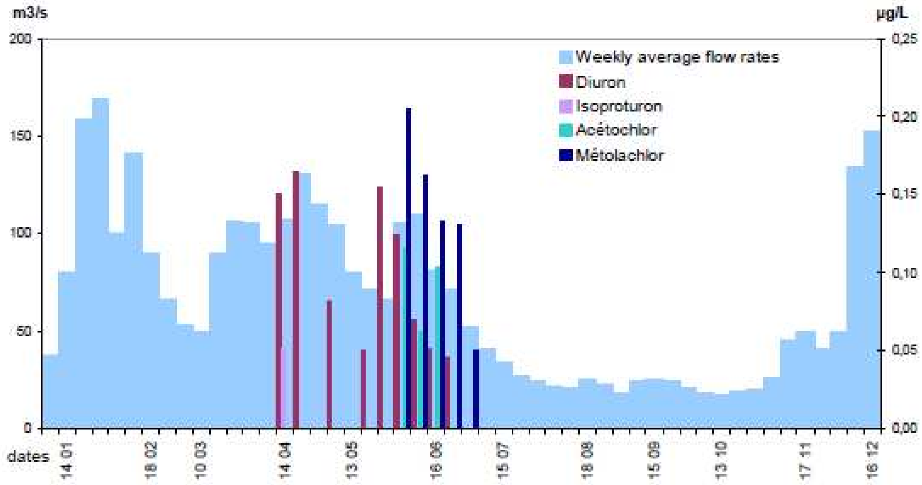
- Charente river waters (mean ± sd on the 2 weeks campaign) :
  - Suspended solids: 7 ± 0.7 mg/L
  - Temperature: 19.4 ± 1.1°C
  - Flow velocity: 0.01-0.02 m/s
  - Conductivity: 539.8 ± 10.8 µSm/cm
  - Pesticide mean concentrations in dissolved phase: 10 to 50 ng/L for DIA, MET, DEA, < LQ for others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

Triazine concentrations (2008)



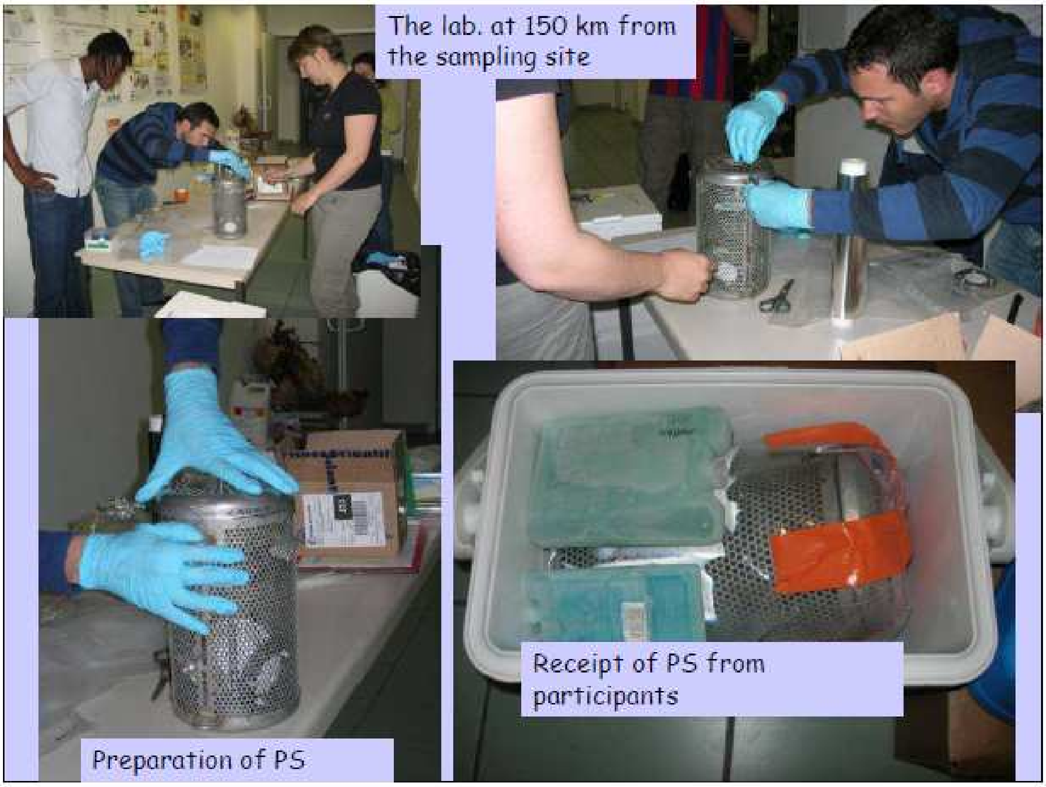
Background levels and low fluctuations of concentrations
Metabolites (DEA and DIA) are generally more abundant than parent compounds

Phenylurea and chloroacetanilide concentrations (2008)



Applications and detection typically during the spring

The Charente river at Beillant



Access by boat…


Access by boat...


1 buoy line to hang PS
Home made
exp. syst. for
Chemcatcher

Other aspects:

- A web site
- Water monitoring
- Quality assurance

A web site

- To register
- To collect results and information (sampling and anaytical 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),
- EPOC-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).

N°45

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):

	Beillant	Ternay	Thau
Metals	/	50 mL Direct analysis by ICP-MS LQ from 0.01 for Cd to 0.5 for Zn	500 mL Danielson method (1982) ICP-MS LQ from 0.1 ng/L for Cd to 10 for Cu and Zn
PAHs	/	5L samples LLE (dichloromethane) HPLC-Fluo LQ: 0.4 ng/L except ACE and PHE at 2 ng/L	2 L SPE (C18) GC-MS LQ: 0.1 ng/L
Pesticides	50 mL samples SPE (Oasis HLB) HPLC-MS-MS LQ from 10 to 20 ng/L	/	2L SPE (Oasis HLB) HPLC-MS-MS LQ from 10 to 20 ng/L

Quality controls and Quality assurance

- Each sampler exposed in triplicate
- 1 field blank per sampler and per site, participant are free to substract 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

N°49

Thank you for your attention !!

N°50

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QA/QC in the AQUAREF inter comparison exercise

S. Lardy-Fontan [7], B. Lepot [8], N. Mazzella [1], D. Munaron [2], C. Miège [3], S. Schiavone [3], C. Berho [4], J-P. Ghestem [4], C. Gonzalez [5], J-L Gonzalez [6], B. Lalere [7], C. Tixier [9], A. Togola [4], M. Coquery [3]

[1] Cemagref, UR REBX, [2] Ifremer, LERLR, [3] Cemagref, UR MALY, 3 [4] BRGM, MMA, [5] Ecole des Mines d'Alès, [6] Ifremer, BE, [7] LNE, DMSI, [8] INERIS, [9] Ifremer, RBE-BE-LBCO

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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

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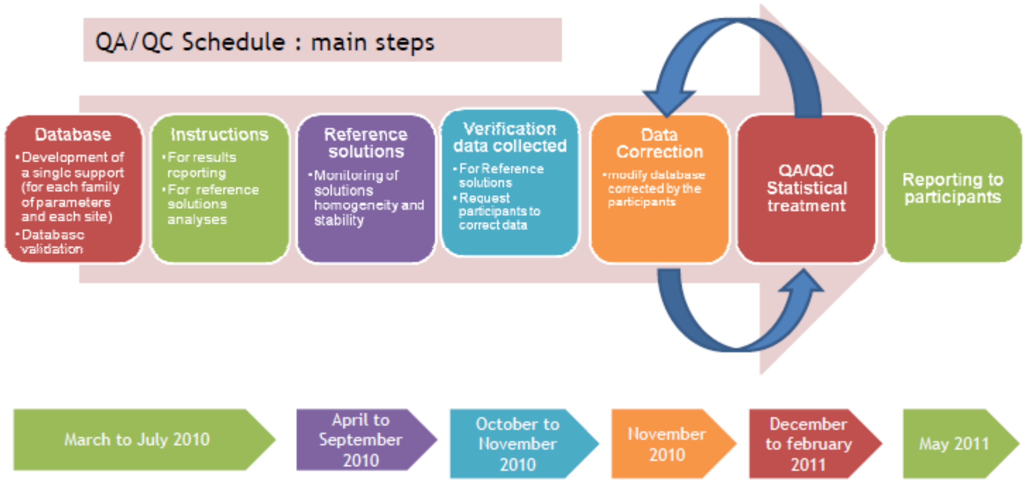
QA/QC
in the AQUAREF
inter comparison exercise

Schedule
From database conception to participant reporting

General organization of the collaborative trial

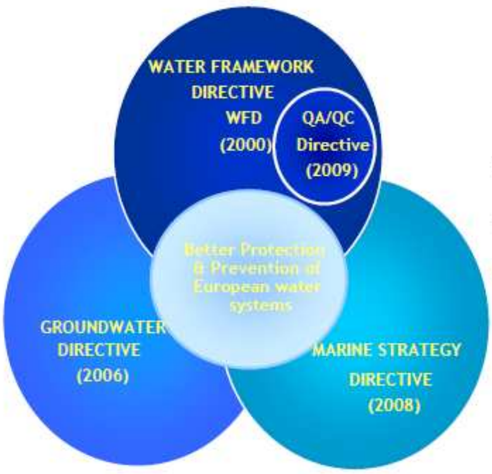
⚠ It is not a proficiency test



QA/QC
in the AQUAREF
inter comparison exercise

From basic concepts to the final implemented strategy

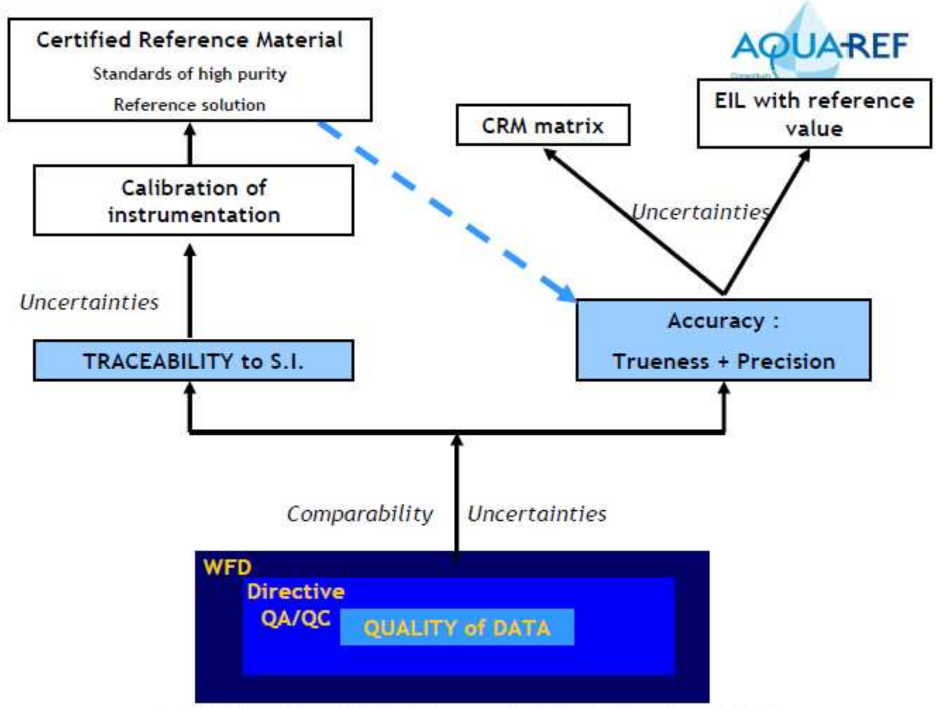
From basic concepts... (1)



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

METROLOGIC INFRASCTUCTURE → ***QA/QC***

From basic concepts… (2)



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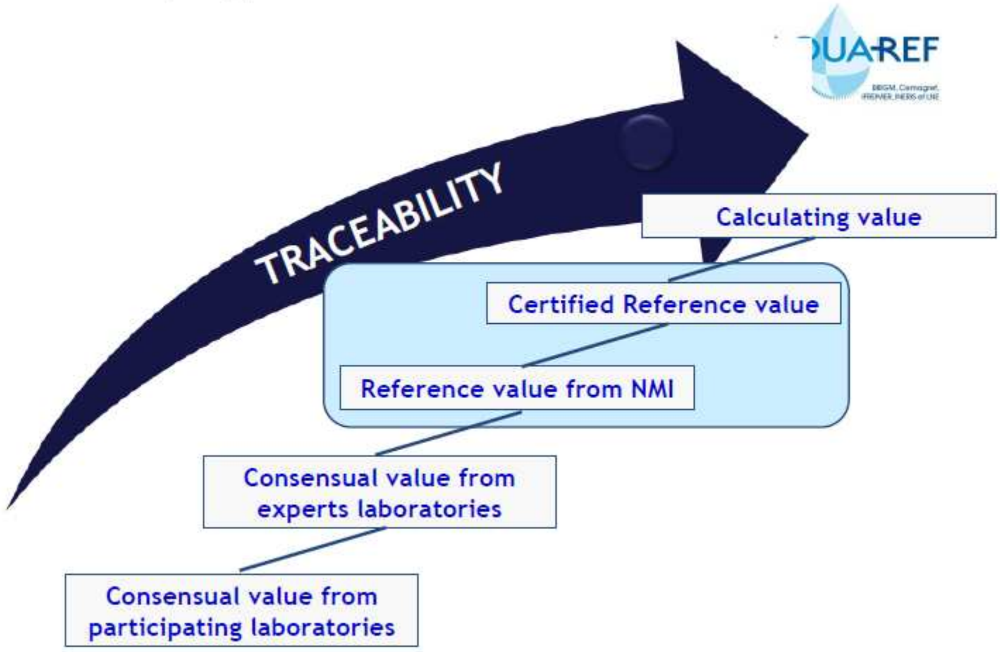
From basic concepts… (3)



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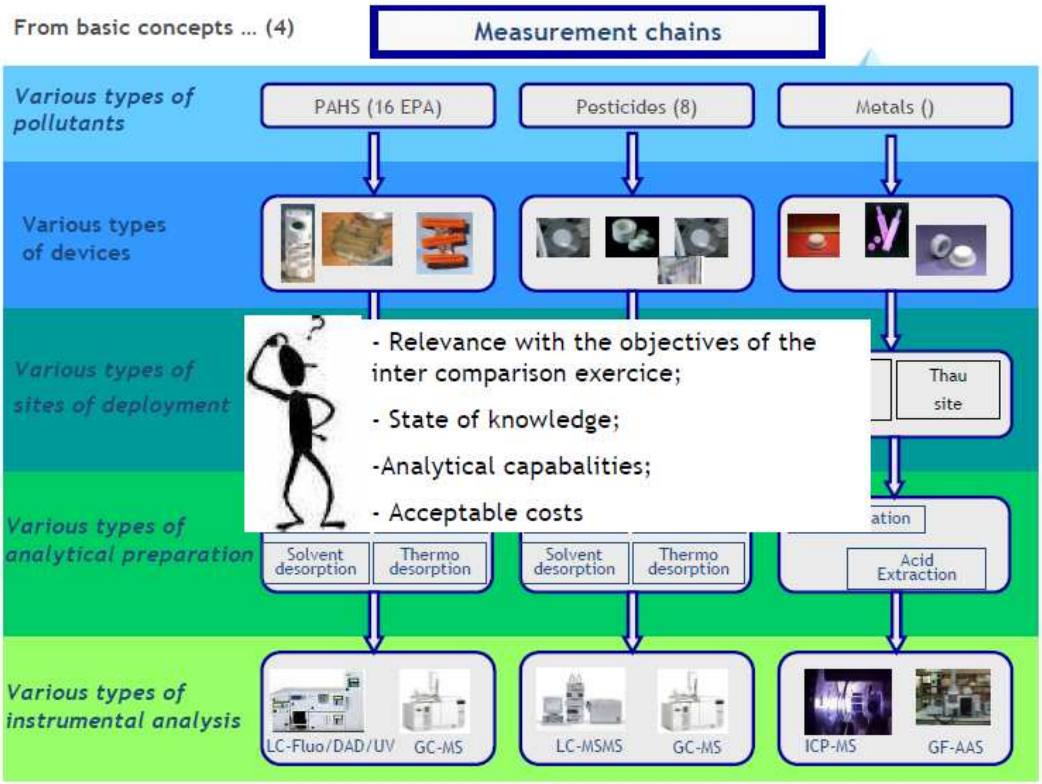
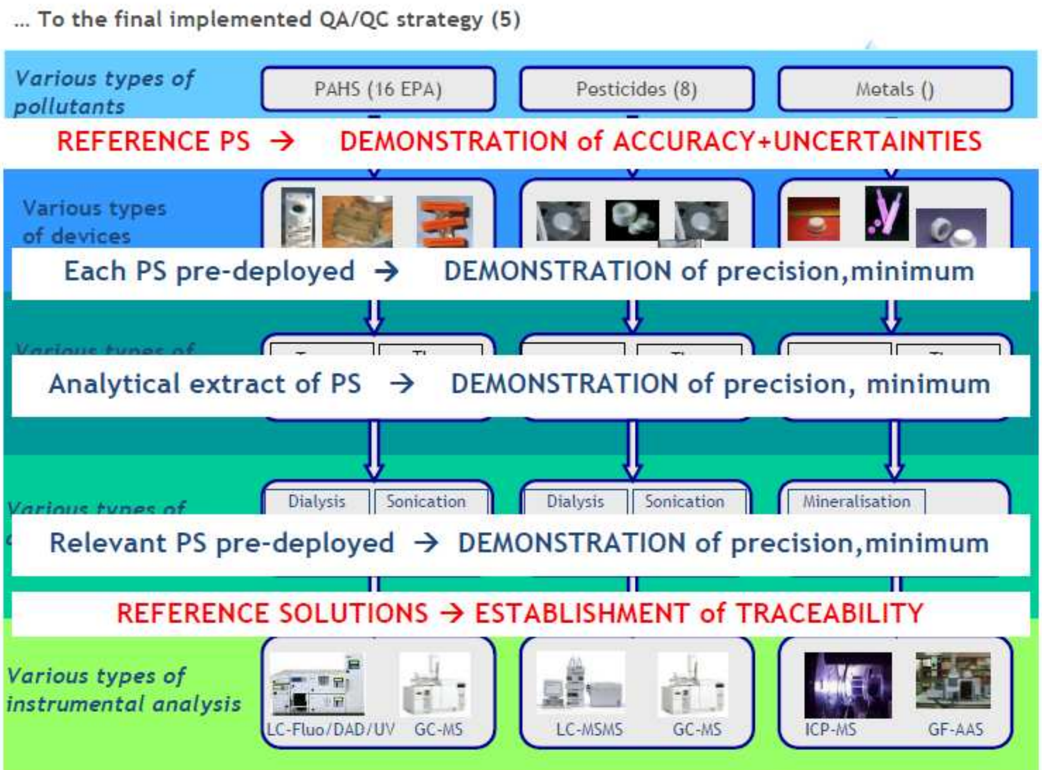
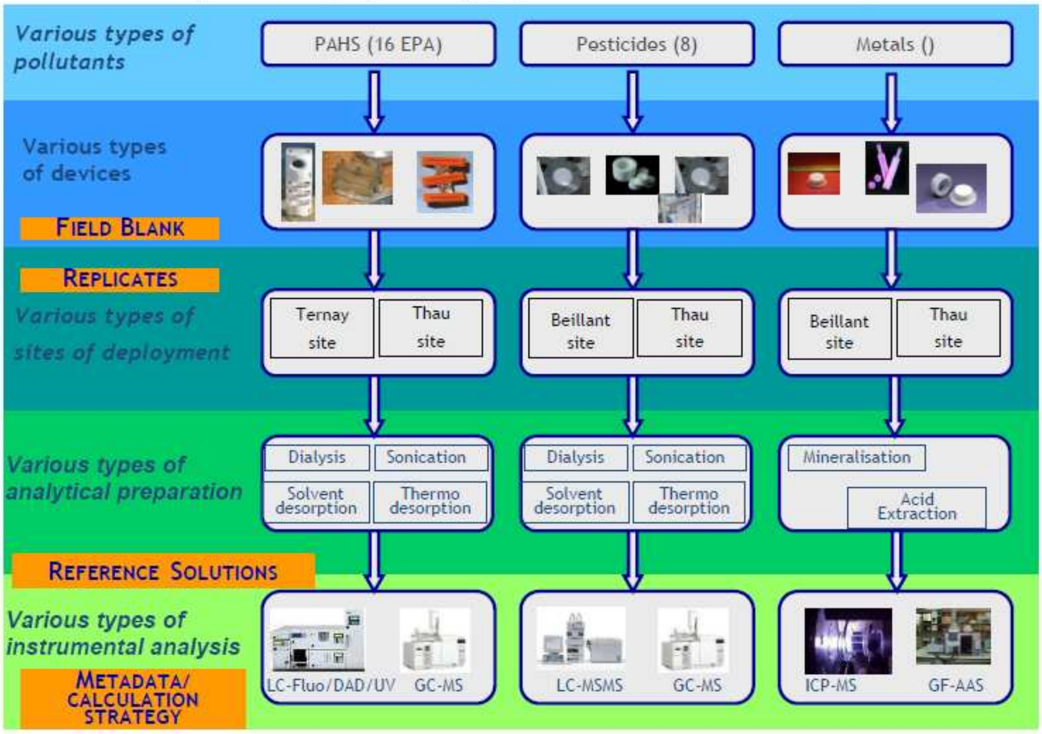

From basic concepts ... (4)
Measurement chains
Various types of pollutants
PAHS (16 EPA)
Pesticides (8)
Metals ()
Various types of devices
Various types of sites of deployment
- Relevance with the objectives of the inter comparison exercice;
- State of knowledge;
-Analytical capabalities;
- Acceptable costs
Thau site
Various types of analytical preparation
Solvent desorption
Thermo desorption
Solvent desorption
Thermo desorption
Acid Extraction
Various types of instrumental analysis
LC-Fluo/DAD/UV
GC-MS
LC-MSMS
GC-MS
ICP-MS
GF-AAS


... To the final implemented QA/QC strategy (5)
Various types of pollutants
PAHS (16 EPA)
Pesticides (8)
Metals ()
REFERENCE PS → DEMONSTRATION of ACCURACY+UNCERTAINTIES
Various types of devices
Each PS pre-deployed → DEMONSTRATION of precision,minimum
Analytical extract of PS → DEMONSTRATION of precision, minimum
Dialysis
Sonication
Dialysis
Sonication
Mineralisation
Relevant PS pre-deployed → DEMONSTRATION of precision,minimum
REFERENCE SOLUTIONS → ESTABLISHMENT of TRACEABILITY
Various types of instrumental analysis
LC-Fluo/DAD/UV
GC-MS
LC-MSMS
GC-MS
ICP-MS
GF-AAS

... To the final implemented QA/QC strategy (7)



QA/QC
in the AQUAREF
inter comparison exercise

Data base overview

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Data base Overview (1)

Personal login and password

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Data base Overview (2)

Transmission and validation Results

Personal login and password

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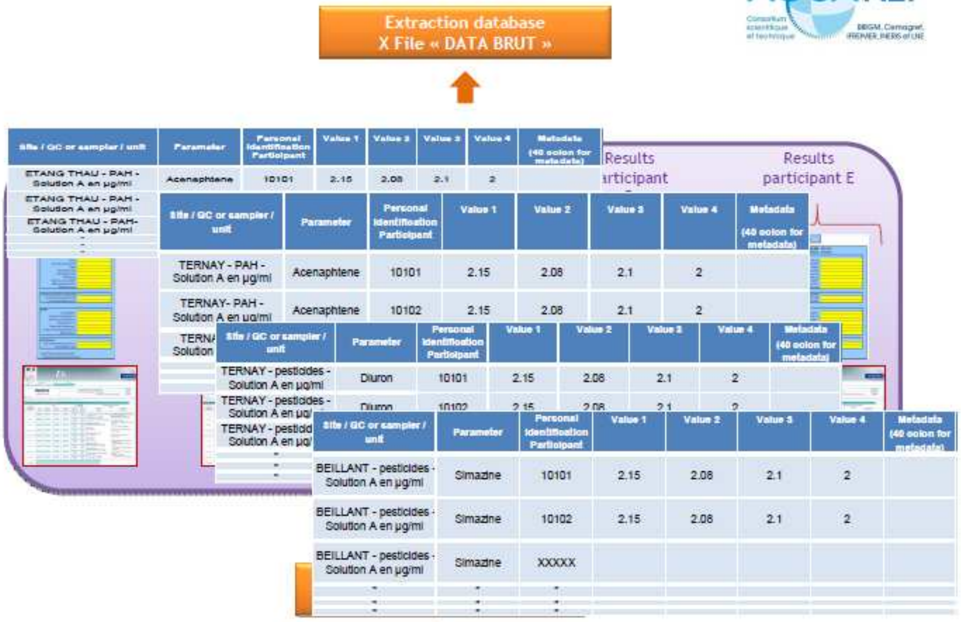
Data base Overview (3)

AQUAREF
Consortium scientifique et technique
BRGM, Cemagref, IFREMER, INERIS et LNE



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Data base Overview (4)

AQUAREF
Consortium scientifique et technique
BRGM, Cemagref, IFREMER, INERIS et LNE

Assigned value of solution A Robust Approach

Parameter en µg/mL	robust mean	robust standard deviation	Incertainty assigned value	Standard deviation within laboratory	Standard deviation between laboratory	Repeatability en %	Reproductibility en %
Benzo_a_pyrène	2.364	0.906	0.303	0.113	0.906	4.0%	39.9%
Benzo_b_fluoranthène	2.270	0.722	0.250	0.126	0.719	5.3%	32.2%
Benzo_k_fluoranthène	2.254	0.613	0.205	0.107	0.610	6.2%	27.5%
Indeno_1,2,3c,d_pyrène	2.236	1.190	0.372	0.067	1.189	4.6%	53.3%
Acénaphtène	2.006	0.441	0.134	0.048	0.441	2.4%	22.1%
Anthracène	1.954	0.413	0.122	0.058	0.411	2.5%	21.3%
Benzo_g,h,i_perylène	2.297	1.233	0.374	0.112	1.232	5.6%	53.8%
Fluoranthène	2.002	0.390	0.115	0.069	0.388	4.5%	19.7%
Fluorène	2.004	0.462	0.136	0.072	0.461	3.2%	23.3%
Naphtalène	2.113	0.520	0.196	0.061	0.519	2.8%	24.7%

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QA/QC in the AQUAREF inter comparison exercise

Statistical treatment

Statistical treatment of QC A (1)

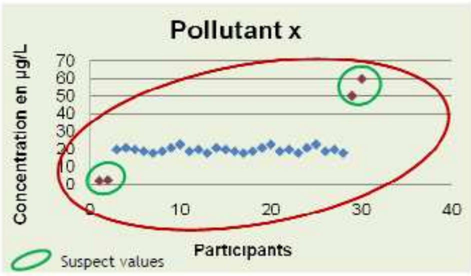
- According to the standards and guidelines
  - ISO 13528 (2005) « Statistical methods for use in proficiency testing by interlaboratory comparisons »
  - ISO 5725-5 (1998) « Accuracy (trueness and precision) of measurement methods and results – Part 5 : Alternative methods for the determination of the 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

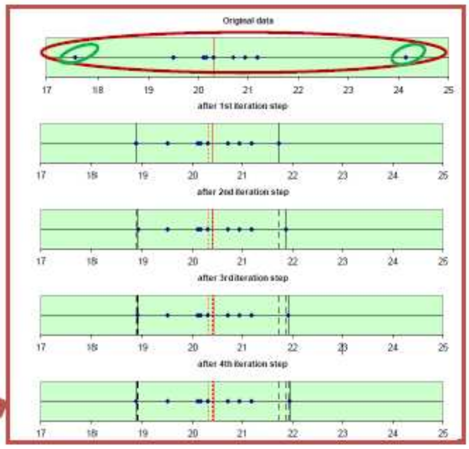
With this approach, the assigned value is the robust average of the results reported by all the participants: No exclusion of participants

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.

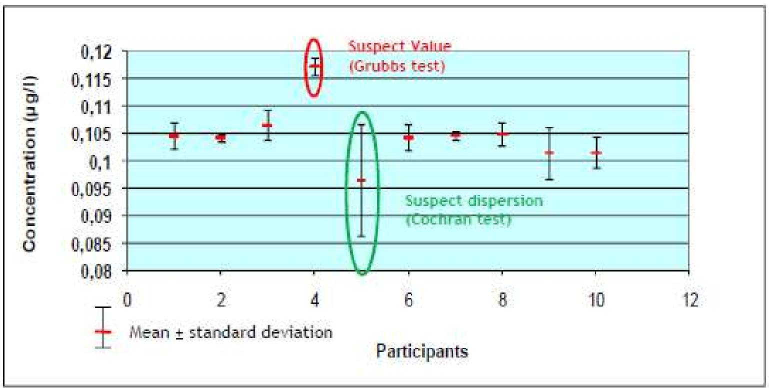




After x iteration
For each parameter :
✓robust mean
✓robust standard deviation

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

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Statistical treatment of QC A (4)

•Comparison of the assigned value between :

Robust method	Based on consensus values from participants	Robust mean and Robust standard deviation
Reference value	Based on reference solution A	Reference value and uncertainty (k=2)

•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/EtangThau
✓Pesticides/Beillant
✓Pesticides/Ternay
✓Metals/Ternay
✓Metals/Etang Thau

Total for QC A
9 statistical treatments were performed

✓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

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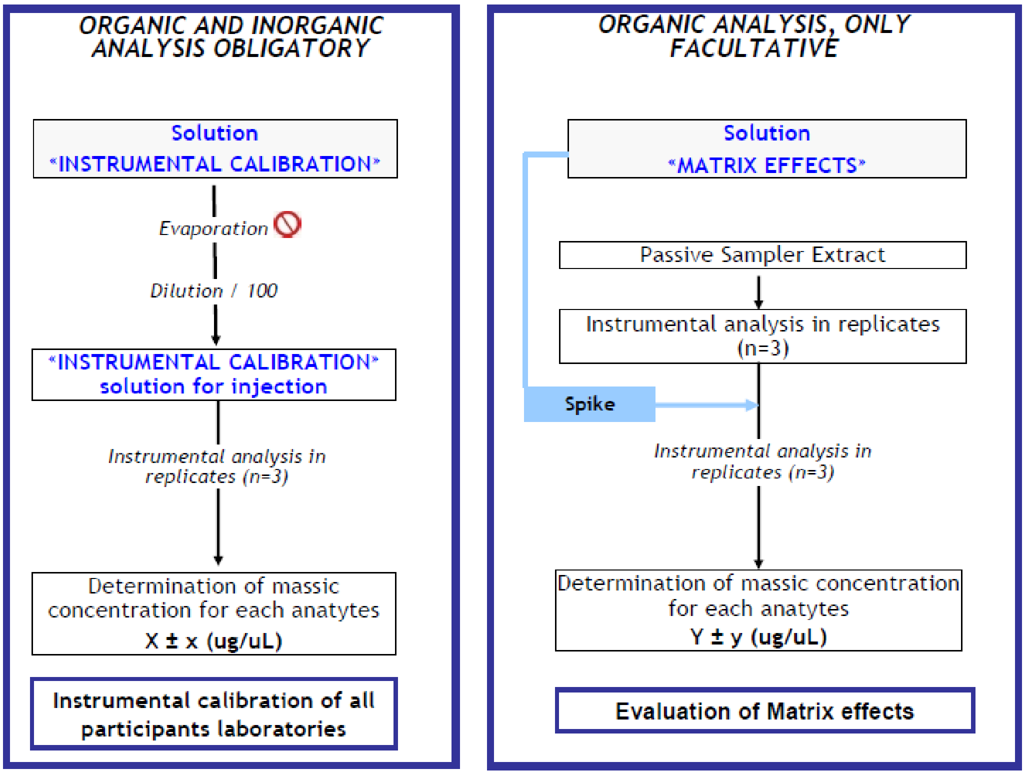
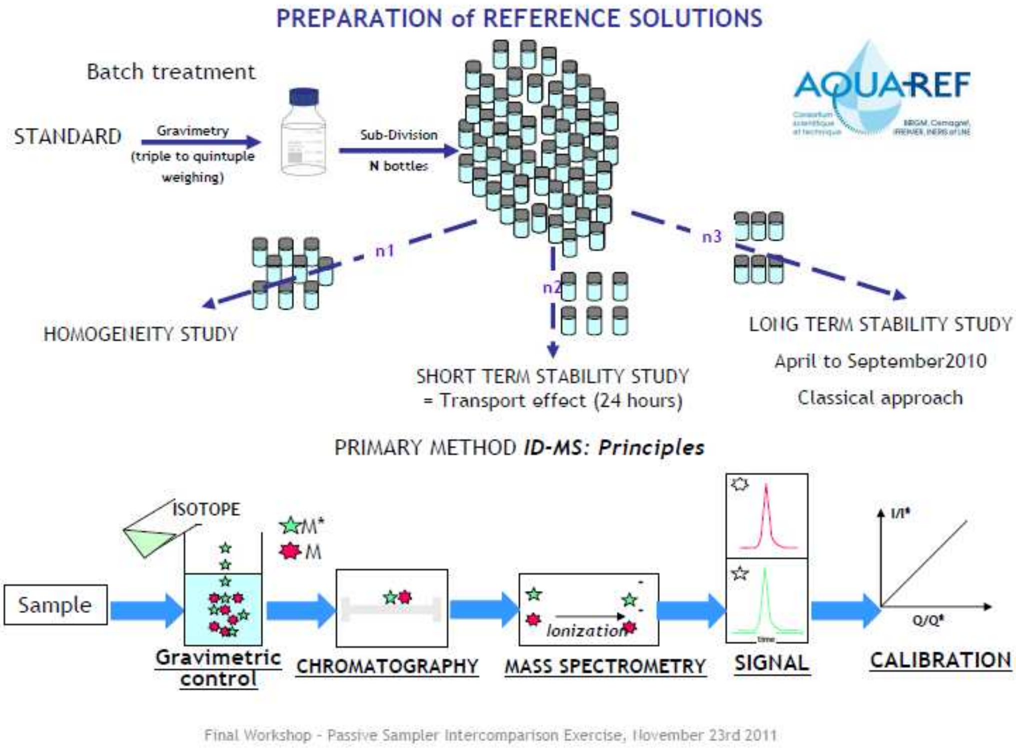
Reference solutions: Summary

TARGETS EIL	PAHS (16 EPA)	Pesticides (8)	Metals (8)
TARGETS REFERENCE SOLUTION	✓ Benzo (a) Pyrene ✓ Benzo (b) Fluoranthene ✓ Benzo (g, h, i) Perylene ✓ Benzo (k) Fluoranthene ✓ Indeno (1,2,3-cd) Pyrene ✓ Naphtalene ✓ Fluoranthene ✓ Anthracene ✓ Fluorene ✓ Acenaphtene	✓ Atrazine ✓ Simazine ✓ DEA ✓ DIA ✓ Diuron ✓ Isoproturon ✓ Alachlore ✓ Acetochlore ✓ Metolachlore	✓ Cadmium ✓ Nickel ✓ Lead ✓ Zinc ✓ Copper ✓ Manganese ✓ Cobalt ✓ Chromium
SOLVENT	Acetone	Acetone	Nitric Acid (2 %)
MASSIC CONC.	≈ 2 µg / ml ind.	≈ 2 µg / ml ind.	≈ 1 µg / l ind.
VOLUME	≈ 1 ml	≈ 1 ml	≈ 100 ml

WFD (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 (ug/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 (ug/uL)
Evaluation of Matrix effects


PREPARATION of REFERENCE SOLUTIONS
Batch treatment
STANDARD
Gravimetry
(triple to quintuple weighing)
Sub-Division
N bottles
AQUAREF
n1
n2
n3
HOMOGENEITY STUDY
SHORT TERM STABILITY STUDY
= Transport effect (24 hours)
LONG TERM STABILITY STUDY
April to September2010
Classical approach
PRIMARY METHOD ID-MS: Principles
ISOTOPE
M*
M
Sample
Gravimetric control
CHROMATOGRAPHY
Ionization
MASS SPECTROMETRY
SIGNAL
CALIBRATION
Final Workshop - Passive Sampler Intercomparison Exercise, November 23rd 2011

METALS

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

The study demonstrates :

- No inhomogeneity
- No instability

Attribution of reference value with U < 10%

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PESTICIDES

	Reference Value Massic concentration ± U (U expanded, k=2)
Alachlore	2.05 ± 0.09 µg/ml
Acétochlore	1.97 ± 0.12 µg/ml
DEA	1.89 ± 0.14 µg/ml
DIA	2.04 ± 0.12 µg/ml
Atrazine	1.99 ± 0.04 µg/ml
Isoproturon	2.02 ± 0.08 µg/ml
Diuron	2.03 ± 0.18 µg/ml
Simazine	2.23 ± 0.1 µg/ml
Métolachlore	2.12 ± 0.14 µg/ml

The study demonstrates :

- No inhomogeneity
- No instability

Attribution of reference value with U < 10%

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PAHs

	Reference Value Massic concentration ± U (U expanded, k=2)
Naphtalene	1.96 ± 0.12 µg/ml
Fluoranthene	1.97 ± 0.12 µg/ml
Benzo (b) Fluoranthene	1.99 ± 0.12 µg/ml
Benzo (k) Fluoranthene	1.93 ± 0.16 µg/ml
Benzo (a) Pyrene	1.87 ± 0.12 µg/ml
Indeno (1,2,3-cd) Pyrene	1.73 ± 0.36 µg/ml
Benzo (g, h, i) Perylene	1.88 ± 0.32 µg/ml
Acenaphtene	1.94 ± 0.12 µg/ml
Anthracene	1.93 ± 0.48 µg/ml
Fluorene	1.93 ± 0.08 µg/ml

The study demonstrates :

- No inhomogeneity
- No instability

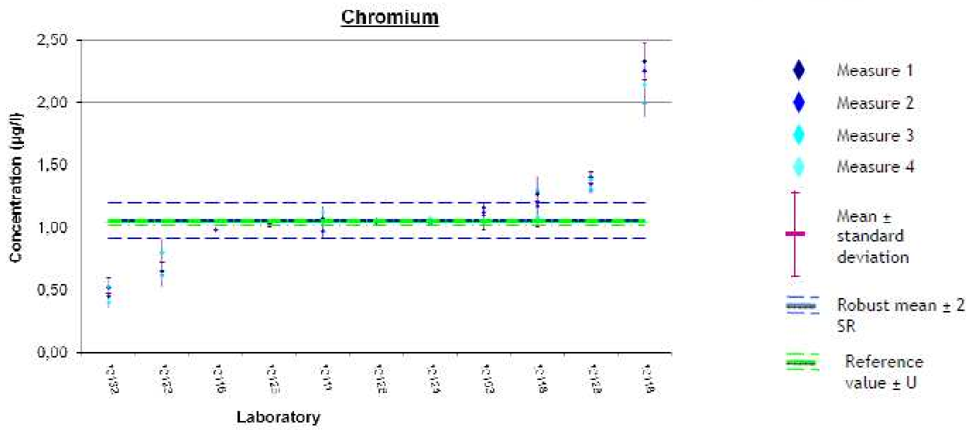
→ Attribution of reference value with U < 10%, except for Anthracene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene

QA/QC in the AQUAREF inter comparison exercise

Presentation of results, discussions

LABORATORY QUALITY CONTROL : REFERENCE SOLUTIONS FOR VERIFICATION OF INSTRUMENT CALIBRATION (1)

METALS

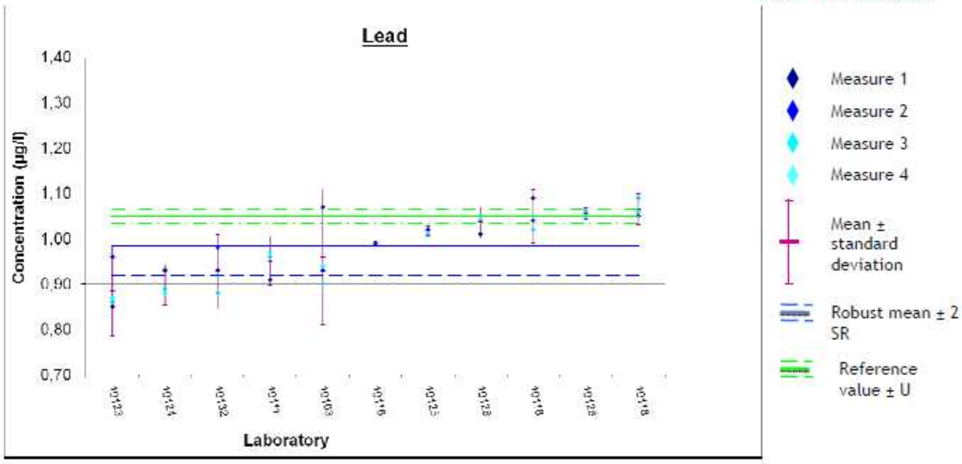


- Robust mean ≈ reference value
- Accuracy : precision + trueness of measurements the general population

→ Mastery of participants

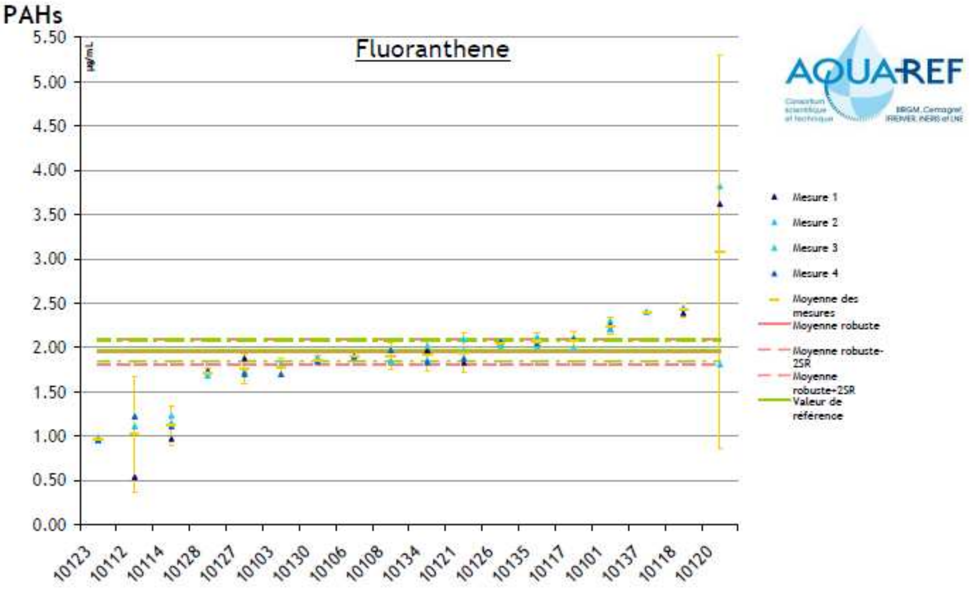
LABORATORY QUALITY CONTROL : REFERENCE SOLUTIONS FOR VERIFICATION OF INSTRUMENT CALIBRATION (2)

METALS



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

PAHs



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

→ Mastery of participants

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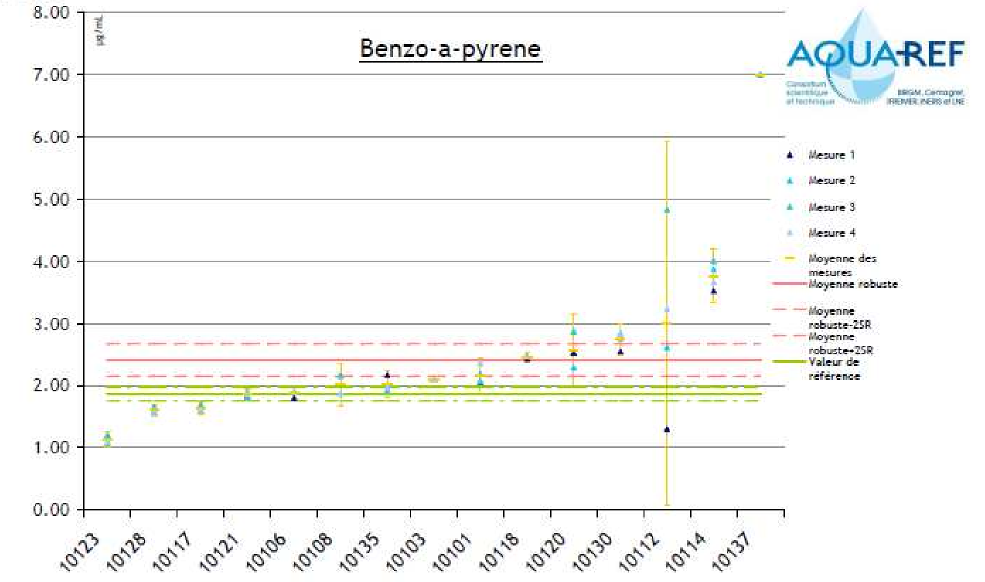
PAHs



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

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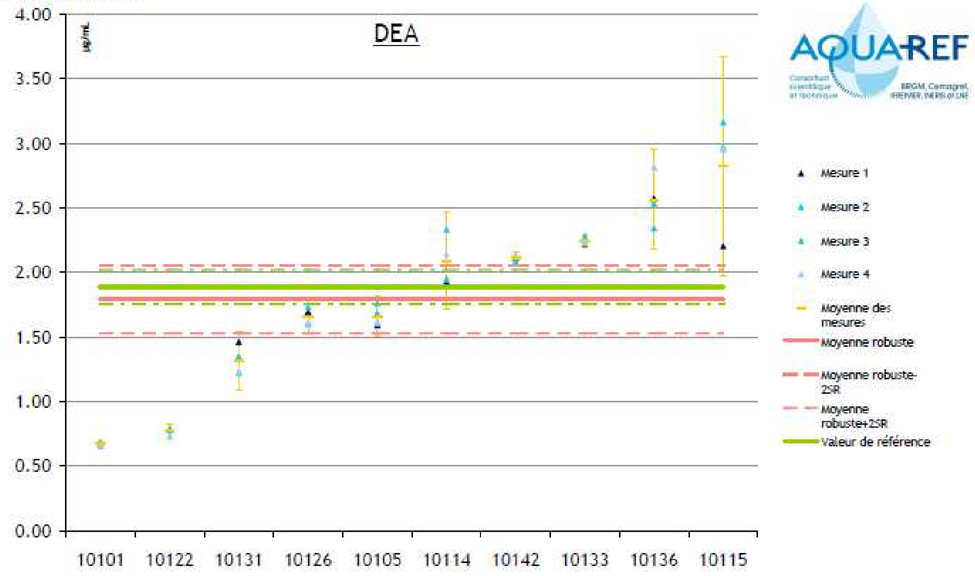
PESTICIDES



- ➢ Robust mean ≈ reference value
- ➢ Accuracy : precision + trueness of measurements the general population → Mastery of participants

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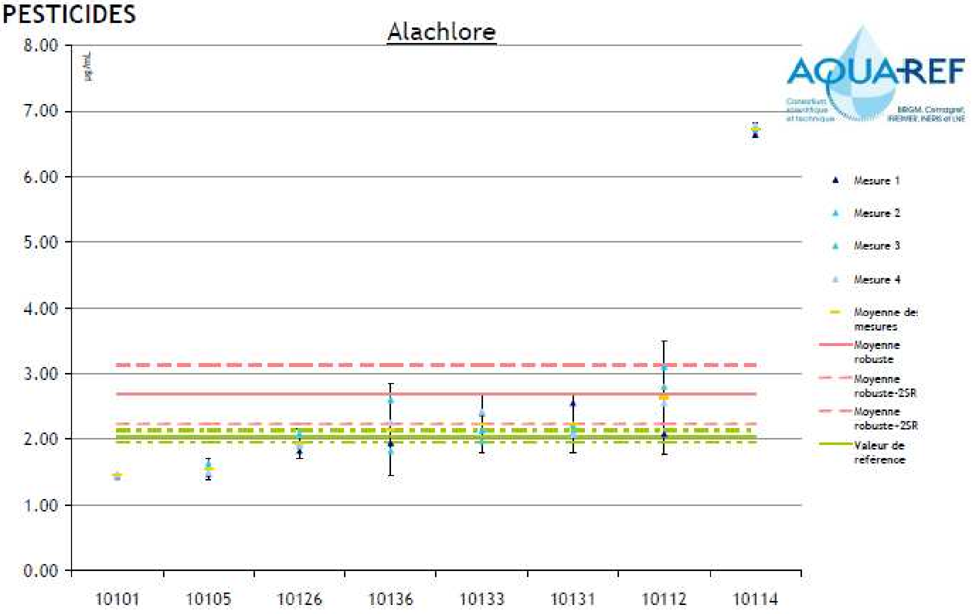
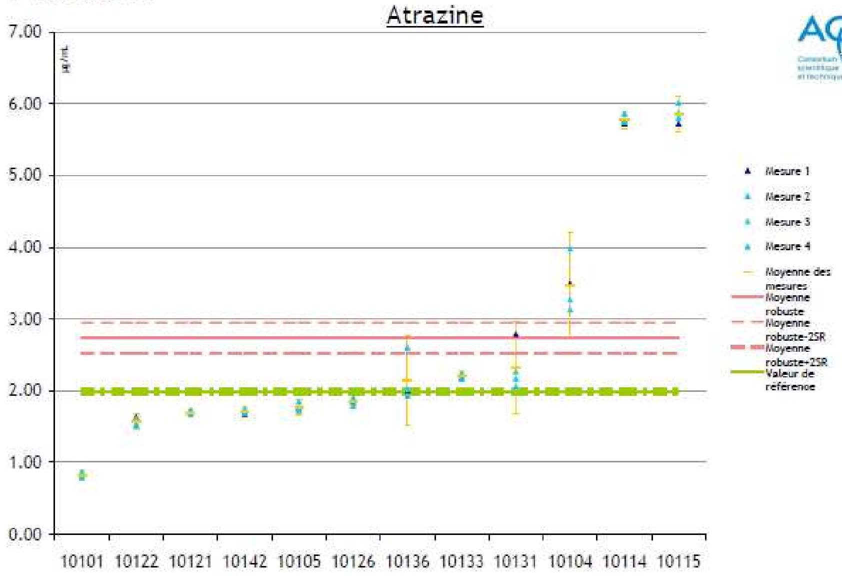
PESTICIDES



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

PESTICIDES



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

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (1/8)

METALS:

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

TERNAY participants		Field BlanK	
Parameter ng/sampler	Mean	Min	Max
Cadmium	1.86	0.02	20.80
Chromium	3.62	0.80	9.10
Cobalt	0.92	0.02	6.34
Copper	6.31	1.06	26.00
Manganese	3.94	0.09	8.80
Nickel	9.42	0.51	65.00
Lead	3.63	0.05	33.97
Zinc	271.40	27.37	1300.00

THAU participants		Field BlanK	
Parameter ng/sampler	Mean	Min	Max
Cadmium	0.76	0.03	3.35
Chromium	3.94	0.14	18.70
Cobalt	0.28	0.02	0.06
Copper	4.86	1.06	7.76
Manganese	2.67	0.95	4.56
Nickel	6.23	0.82	26.00
Lead	1.72	0.03	4.17
Zinc	788.49	18.00	3400.00

→ Discussed in the dedicated session p.m

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (2/8)

PESTICIDES:

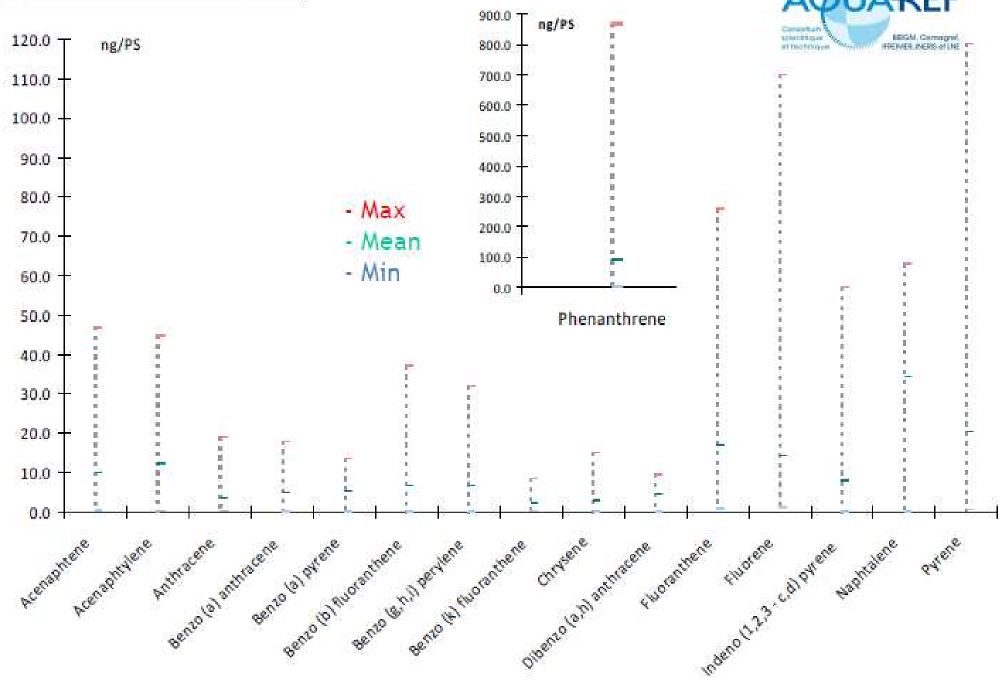
-No field blanks positive except for one compound in one PS and in one site

→ Consistent with the physico-chemical properties of the selected molecules

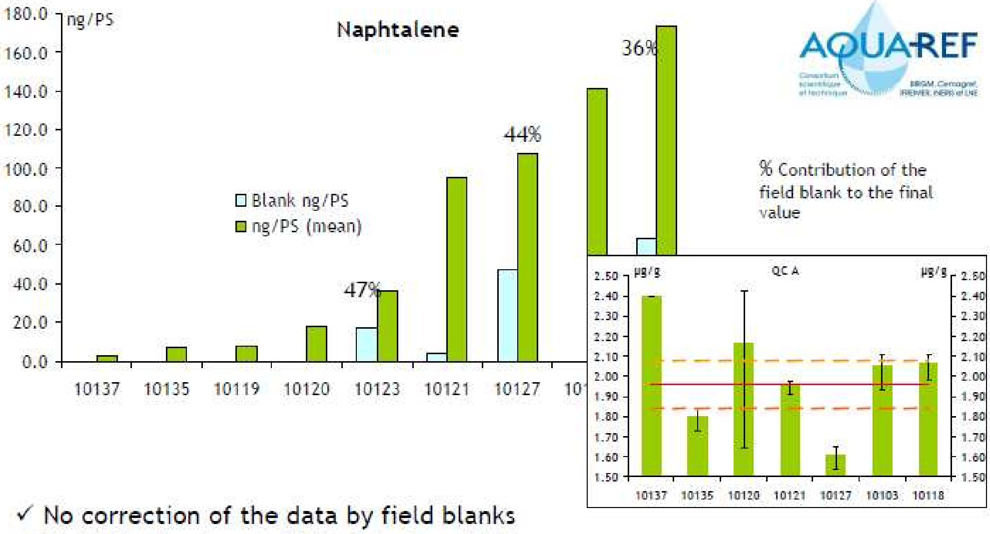
Focus on PAHs

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (3/8)

Case study1: PAH Ternay



FIELD QUALITY CONTROL : BLANK MEASUREMENTS (4/8)

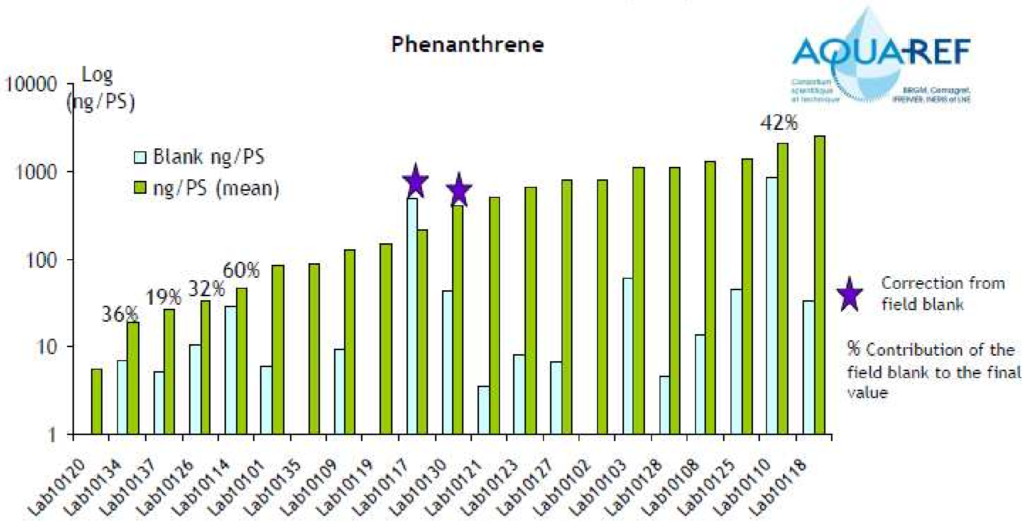


- ✓ No correction of the data by field blanks
- ✓ Field blanks close to 50% of deployed PS

✓ 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

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (5/8)

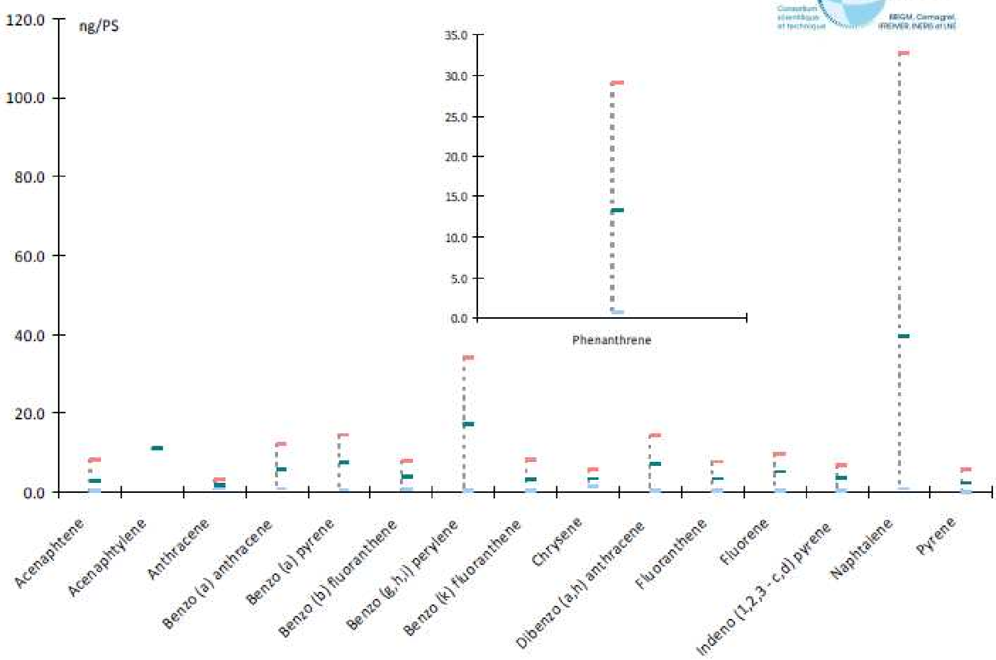


- ✓ No correction of the data by field blanks, except 2 labs.
- ✓ Field blanks close to 60% of deployed PS

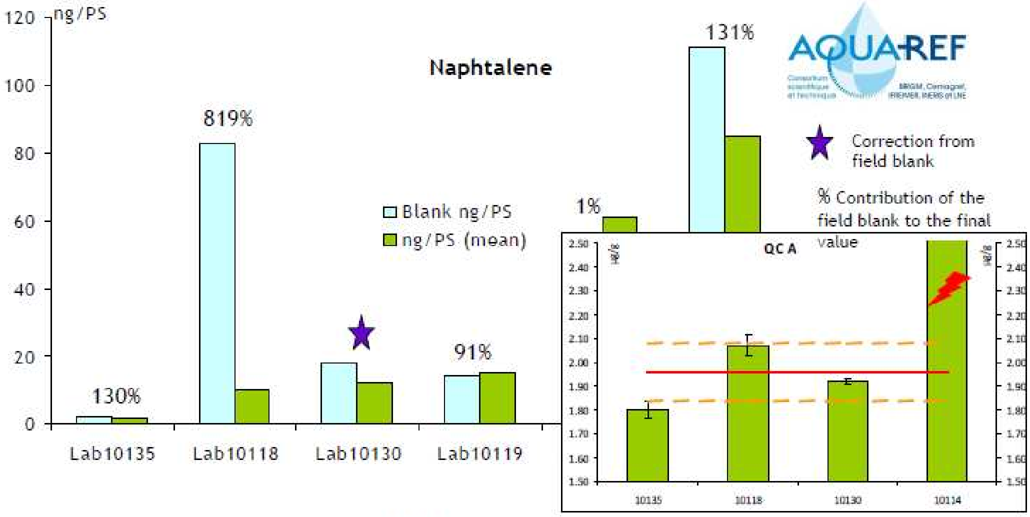
✓ No correlation with the type of PS, the type of extraction technique nor type of instrumental analysis, the quantification approach

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (6/8)

Case study 2: PAH Thau

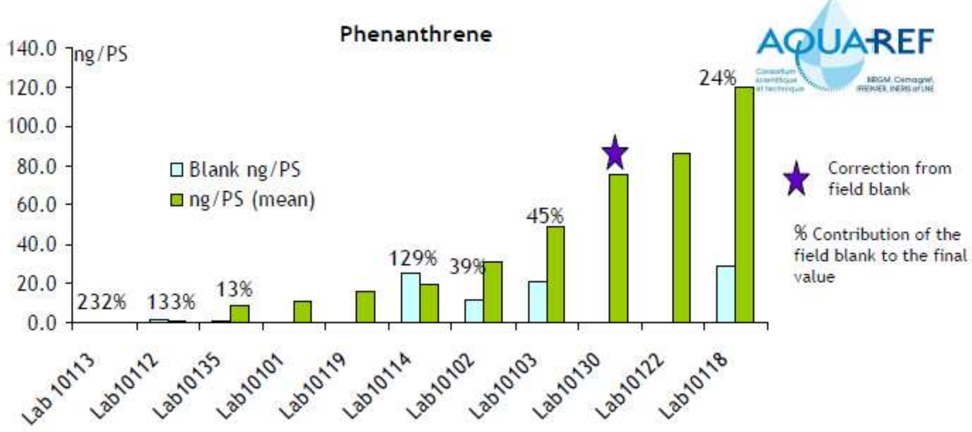


FIELD QUALITY CONTROL : BLANK MEASUREMENTS (7/8)



- ✓ 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

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (8/8)



- ✓ 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)

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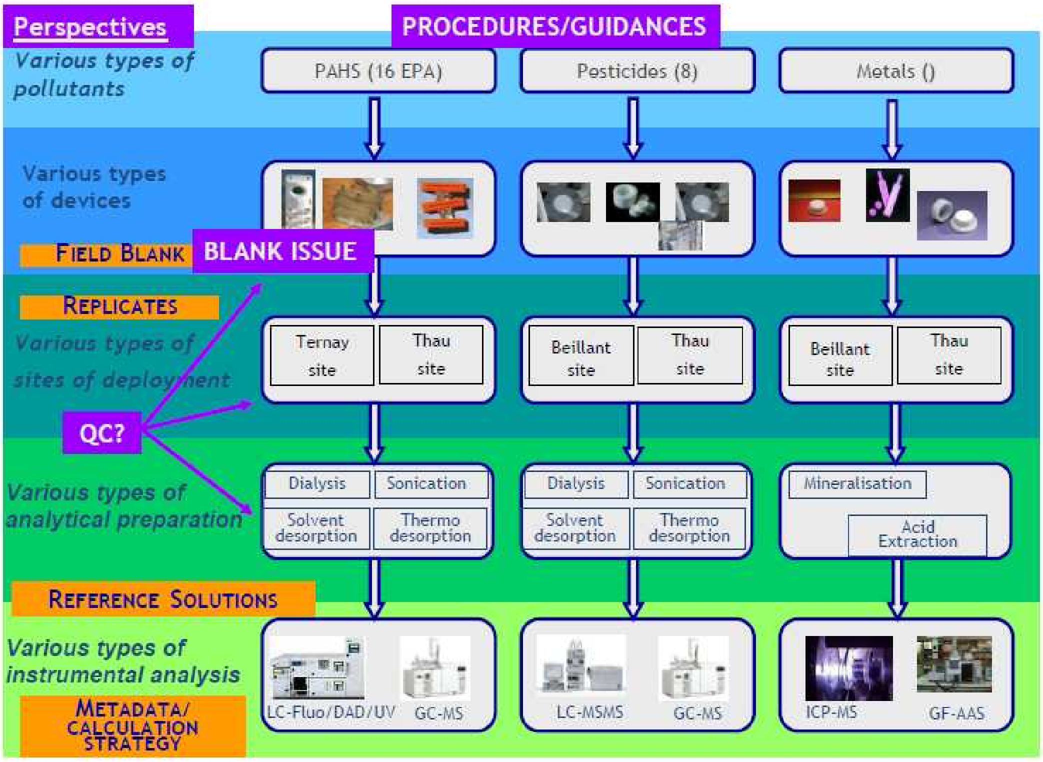
- ✓ Importance of :
  - ➢ QA / QC (field and laboratory) with reference value
  - ➢ Replicat during deployment
  - ➢ Procedure (deployment and analysis)

- ✓ 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



Perspectives
PROCEDURES/GUIDANCES
Various types of pollutants
PAHS (16 EPA)
Pesticides (8)
Metals ()
Various types of devices
FIELD BLANK
BLANK ISSUE
REPLICATES
Various types of sites of deployment
QC?
Ternay site
Thau site
Beillant site
Thau site
Beillant site
Thau site
Various types of analytical preparation
Dialysis
Sonication
Solvent desorption
Thermo desorption
Dialysis
Sonication
Solvent desorption
Thermo desorption
Mineralisation
Acid Extraction
REFERENCE SOLUTIONS
Various types of instrumental analysis
METADATA/ CALCULATION STRATEGY
LC-Fluo/DAD/UV
GC-MS
LC-MSMS
GC-MS
ICP-MS
GF-AAS

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

1

Results for Metals

A. Dabrin, J-P. Ghestem, J-L. Gonzalez, M. Coquery

2

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

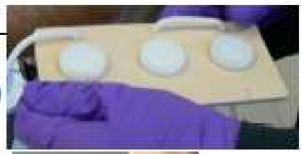
  - Analytical treatment

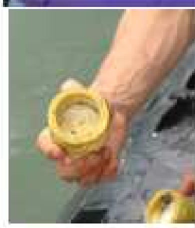
  - Using diffusion coefficients/uptake rates from literature

3

Passive samplers and exposure durations

8 metals	devices
• Cadmium* • Chromium* • Lead* • Nickel* • Manganese • Zinc* • Copper* • Cobalt	• DGT (Diffusive Gradient in Thin films) Open pores Restrictive pores Chelex-100 • Chemcatcher Empore chelating disk ☛ 7 days





Priority substances (WFD)

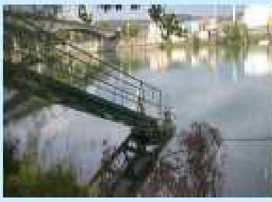
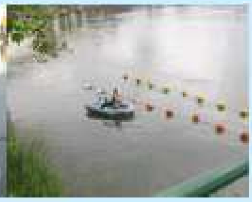
***Substances of the ecological status**

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

4

Sampling sites

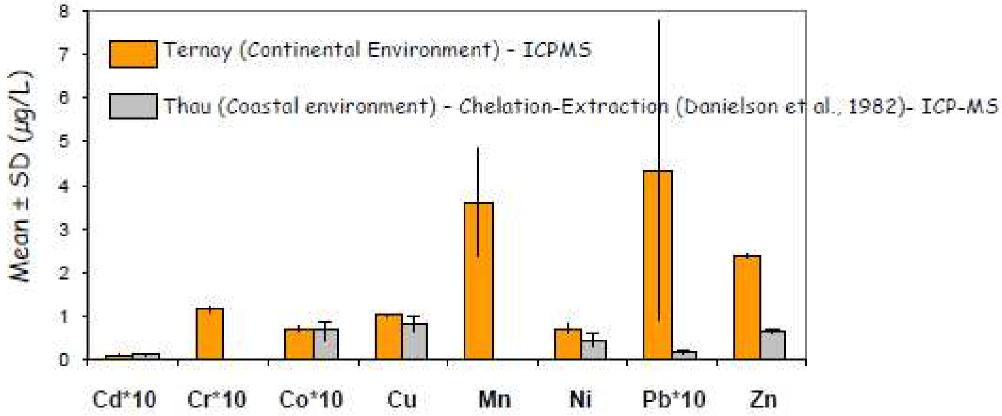
- 2 contrasted environments

Coastal environment	Thau Lagoon (Hérault) 27 April-5 May 2010	 Former site of oyster farming
Continental environment	Rhône River Ternay site 17-24 June 2010	 

5

Spot sampling concentrations

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



6

Comparison of passive sampling concentrations from various tools and laboratories

	Ternay	Thau
Number of participants	10	6
Number of Tools	13	7

Metals	Number of results Ternay	Number of results Thau	Nb results/ nb tools (%) Ternay	Nb results/ nb tools (%) Thau
Cd	12	7	92	100
Ni	13	7	100	100
Pb	12	6	92	86
Cu	13	7	100	100
Cr	11	7	85	100
Zn	10	5	77	71
Co	8	6	62	86
Mn	11	7	85	100

- 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%

7

Statistical data treatment and methodology

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

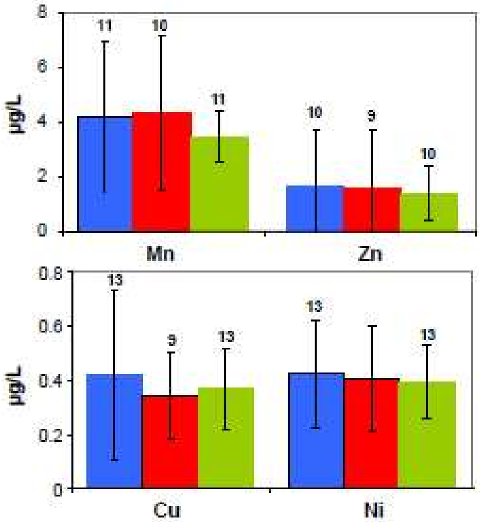
- Robust statistics: ISO 5725-5
No exclusion from laboratories with outliers results
Data was processed to minimize the weight of suspect values

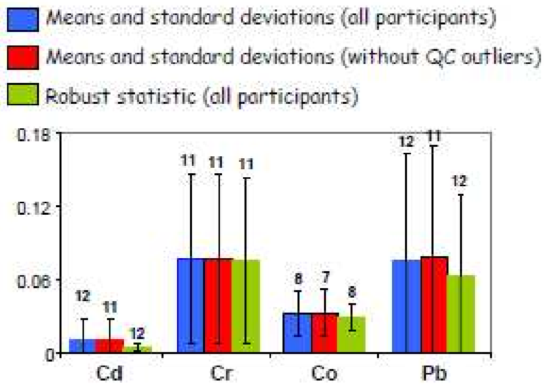
- Comparison of:
  - Arithmetic means and S_R with data of all lab.
  - Arithmetic means and S_R after elimination of QC outliers
  - Robust means (x*) and S_R with data of all lab.

8

Water concentrations (µg/L) for metals – passive samplers

- Ternay site:





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

9

Data dispersion of passive samplers

Metals	Passive sampler data: Ternay Robust mean $x^* \pm SD$ (µg/L)	RSD %	n	Thau Robust mean $x^* \pm SD$ (µg/L)	RSD %	n	LQ Water µg/L	SWIFT-WFD proficiency Testing Exercise (2006): Robust mean $x^* \pm SD$ (µg/L)	RSD %	n
Cd	0.005 ± 0.003	58	12	0.027 ± 0.025	92	7	0.010	0.09 ± 0.08	89	27
Cr	0.076 ± 0.070	93	11	0.036 ± 0.029	80	7	0.050	1.73 ± 1.57	91	36
Cu	0.367 ± 0.153	42	13	0.233 ± 0.1089	47	7	0.050	4.15 ± 1.66	40	42
Mn	3.47 ± 0.99	28	11	7.48 ± 2.646	35	7	0.100	154 ± 17	11	47
Ni	0.392 ± 0.139	35	13	0.261 ± 0.1265	48	7	0.050	1.85 ± 1.40	75	32
Pb	0.063 ± 0.070	112	12	0.021 ± 0.012	58	6	0.010	1.20 ± 0.83	69	31
Zn	1.40 ± 1.10	79	10	3.15 ± 3.13	99	5	0.500	12.3 ± 2.8	23	39

- 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

10

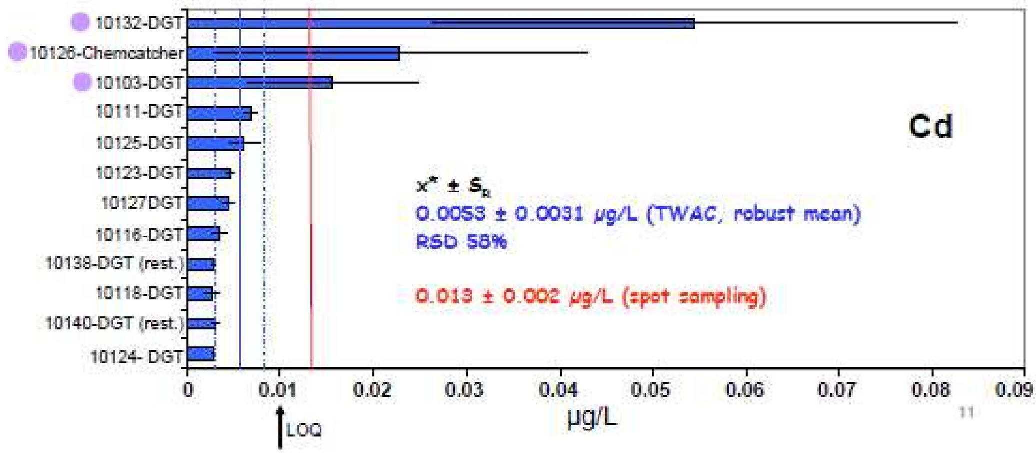
Comparison of passive sampling results from various tool and lab

AQUAREF

- 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



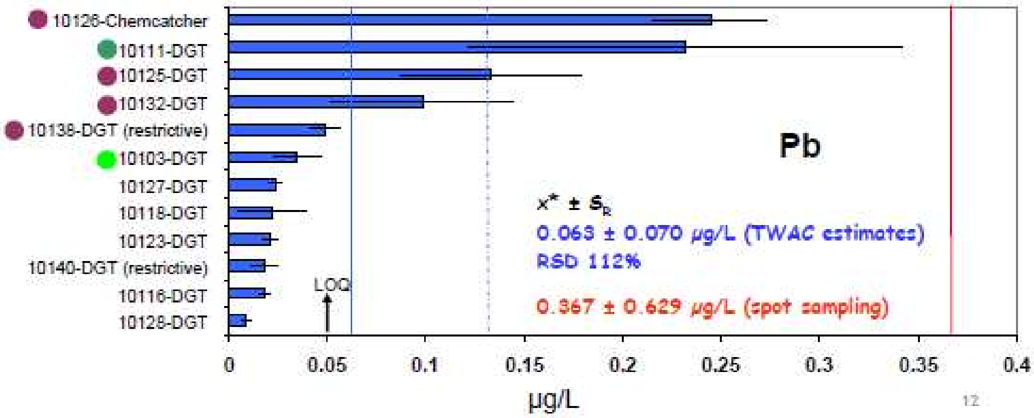
Comparison of passive sampling results from various tool and lab

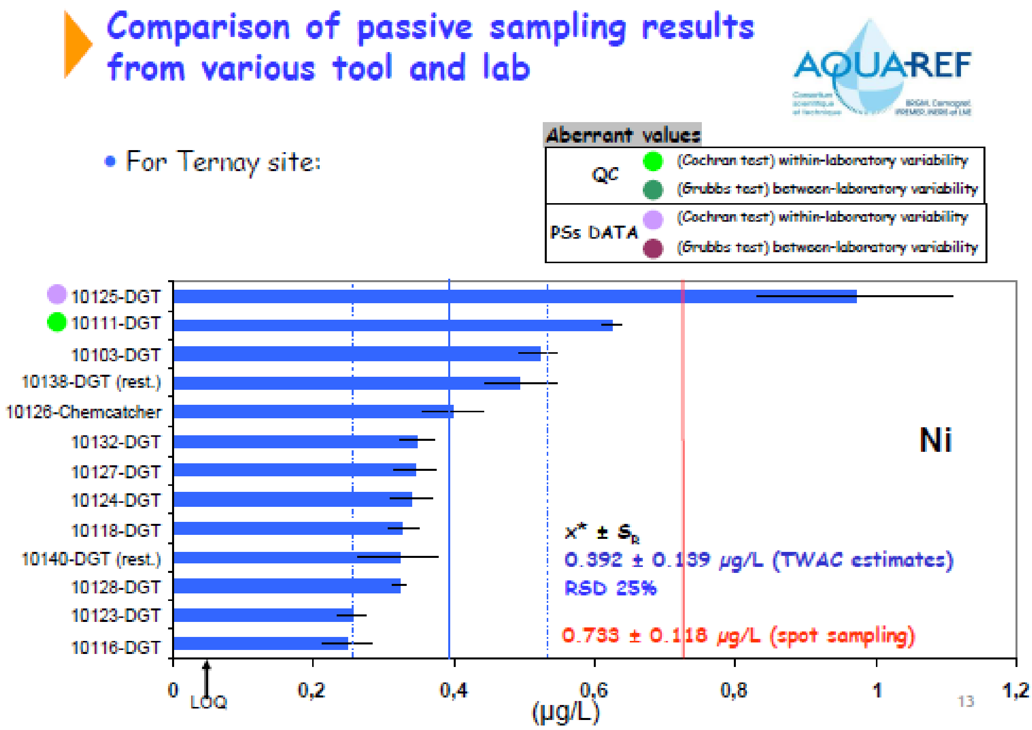
AQUAREF

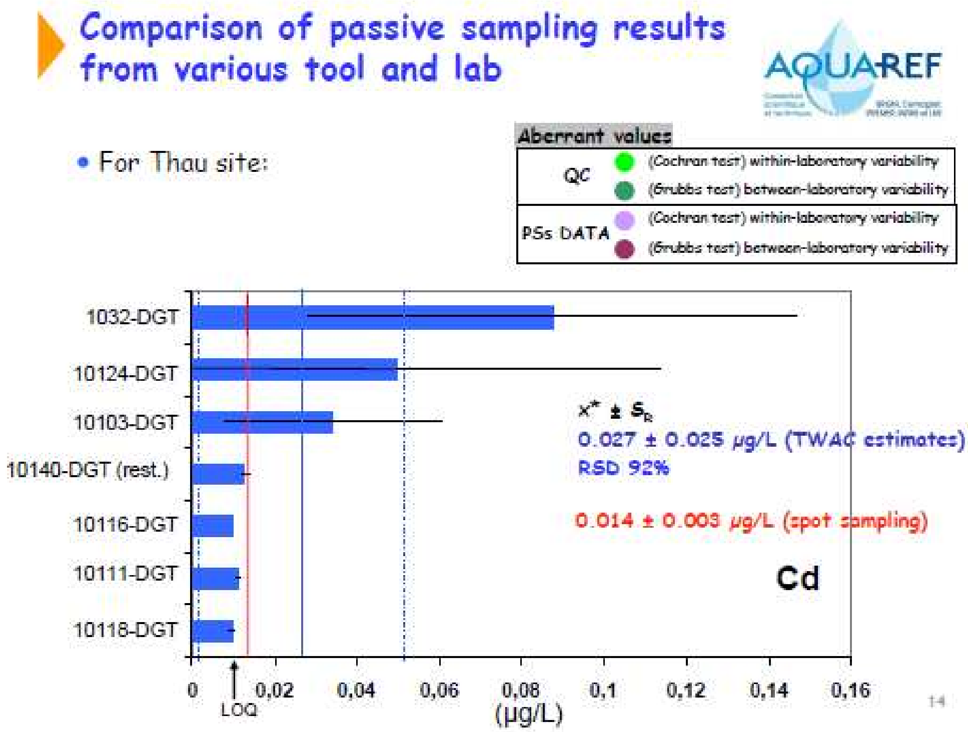
- For Ternay site:

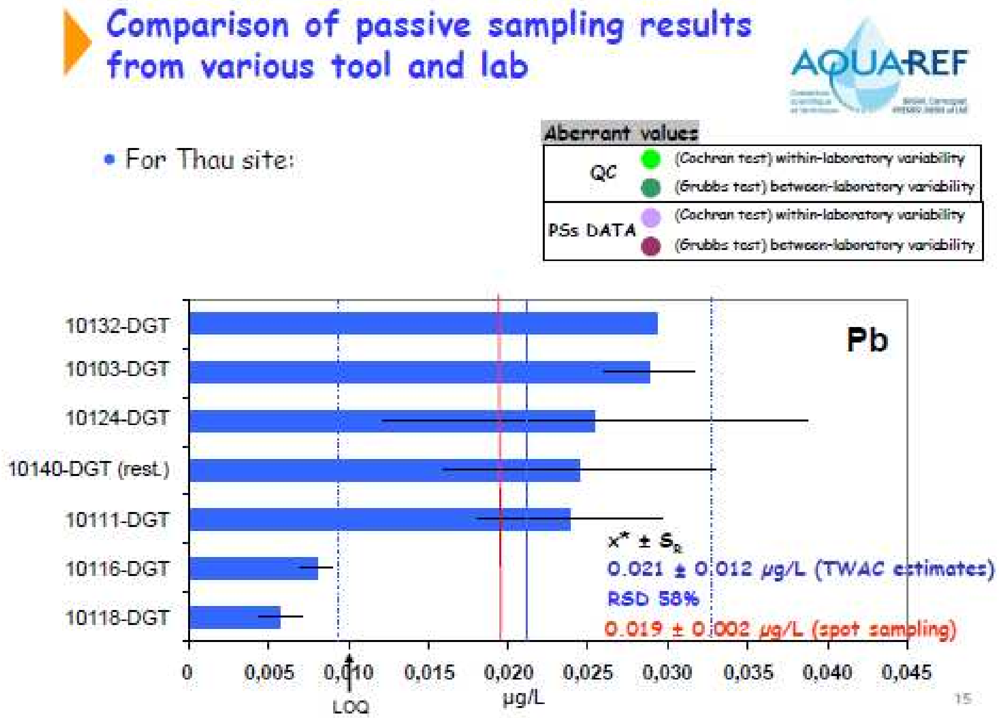
Aberrant values

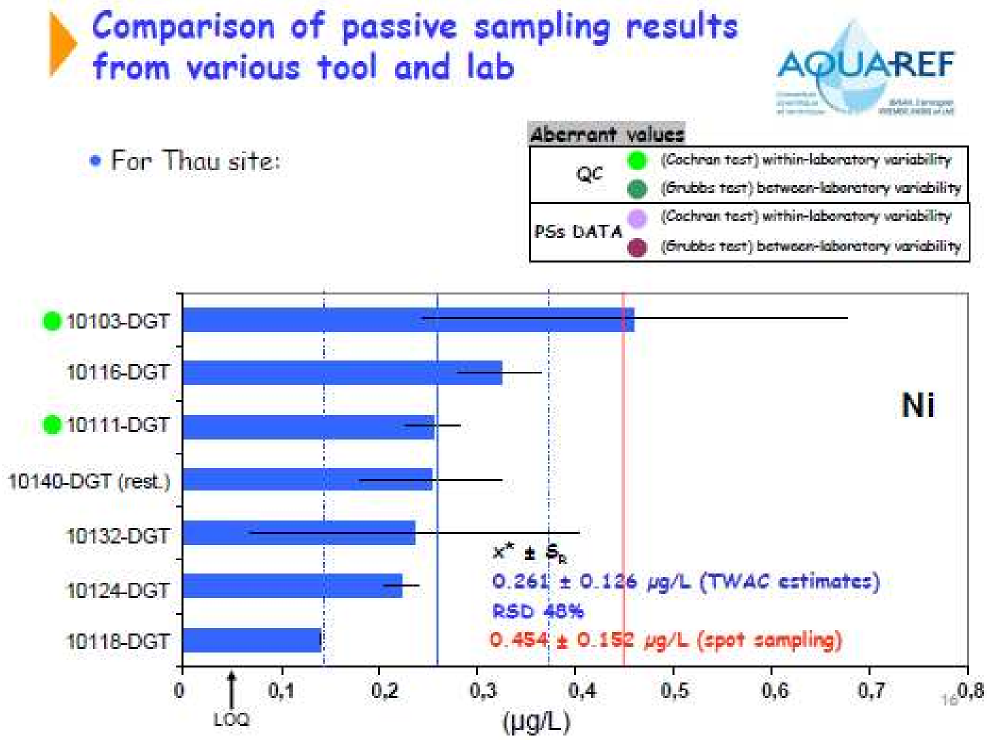
QC	●	(Cochran test) within-laboratory variability
	●	(Grubbs test) between-laboratory variability
PSs DATA	●	(Cochran test) within-laboratory variability
	●	(Grubbs test) between-laboratory variability



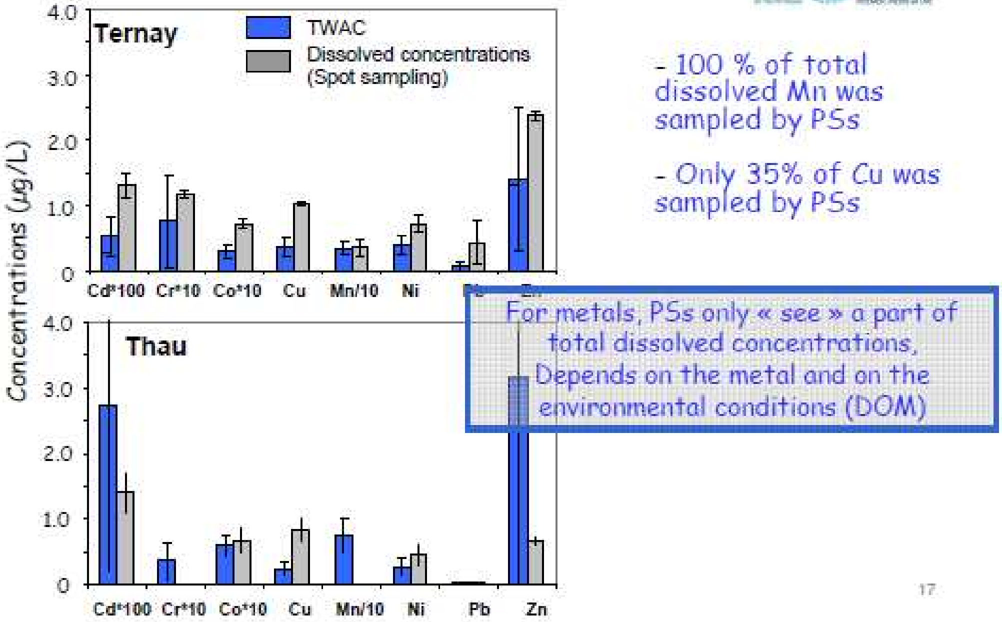

Comparison of passive sampling results from various tool and lab
AQUAREF
• For Ternay site:
Aberrant values
QC (Cochran test) within-laboratory variability
(Grubbs test) between-laboratory variability
PSs DATA (Cochran test) within-laboratory variability
(Grubbs test) between-laboratory variability
10125-DGT
10111-DGT
10103-DGT
10138-DGT (rest.)
10126-Chemcatcher
10132-DGT
10127-DGT
10124-DGT
10118-DGT
10140-DGT (rest.)
10128-DGT
10123-DGT
10116-DGT
Ni
x* ± S_R
0.392 ± 0.139 µg/L (TWAC estimates)
RSD 25%
0.733 ± 0.118 µg/L (spot sampling)
0
LOQ
0,2
0,4
0,6
0,8
1
1,2
(µg/L)
13


Comparison of passive sampling results from various tool and lab
AQUAREF
• 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
1032-DGT
10124-DGT
10103-DGT
10140-DGT (rest.)
10116-DGT
10111-DGT
10118-DGT
x* ± S_R
0.027 ± 0.025 µg/L (TWAC estimates)
RSD 92%
0.014 ± 0.003 µg/L (spot sampling)
Cd
0
LOQ
0,02
0,04
0,06
0,08
0,1
0,12
0,14
0,16
(µg/L)
14


Comparison of passive sampling results from various tool and lab
AQUAREF
• 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
10132-DGT
10103-DGT
10124-DGT
10140-DGT (rest.)
10111-DGT
10116-DGT
10118-DGT
x* ± S_R
0.021 ± 0.012 µg/L (TWAC estimates)
RSD 58%
0.019 ± 0.002 µg/L (spot sampling)
0
0,005
0,010
0,015
0,020
0,025
0,030
0,035
0,040
0,045
µg/L
LOQ
15


Comparison of passive sampling results from various tool and lab
AQUAREF
• 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
Ni
10103-DGT
10116-DGT
10111-DGT
10140-DGT (rest.)
10132-DGT
10124-DGT
10118-DGT
x* ± S_R
0.261 ± 0.126 µg/L (TWAC estimates)
RSD 48%
0.454 ± 0.152 µg/L (spot sampling)
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
(µg/L)
LOQ
16

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

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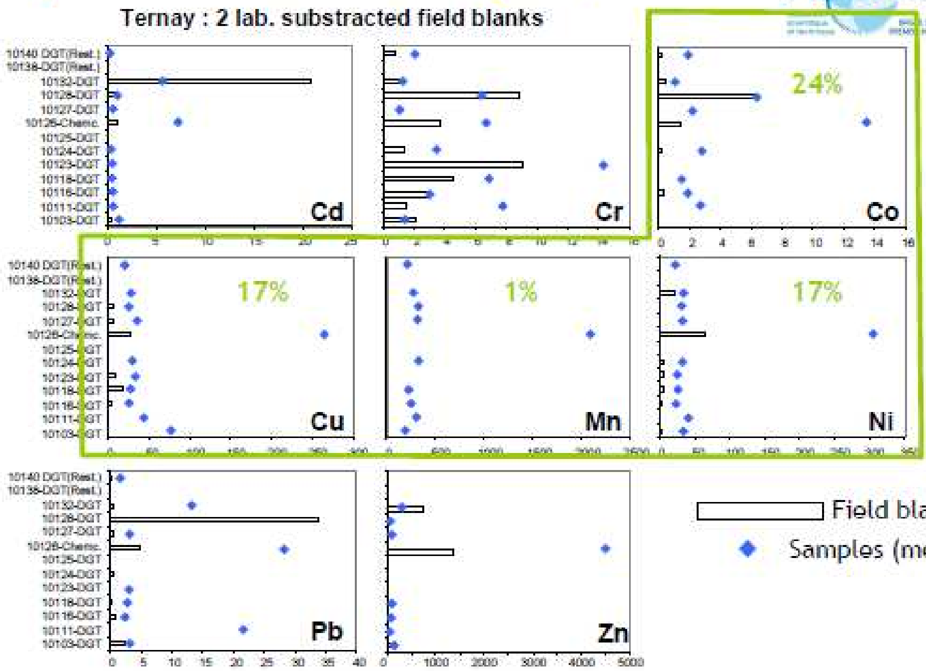
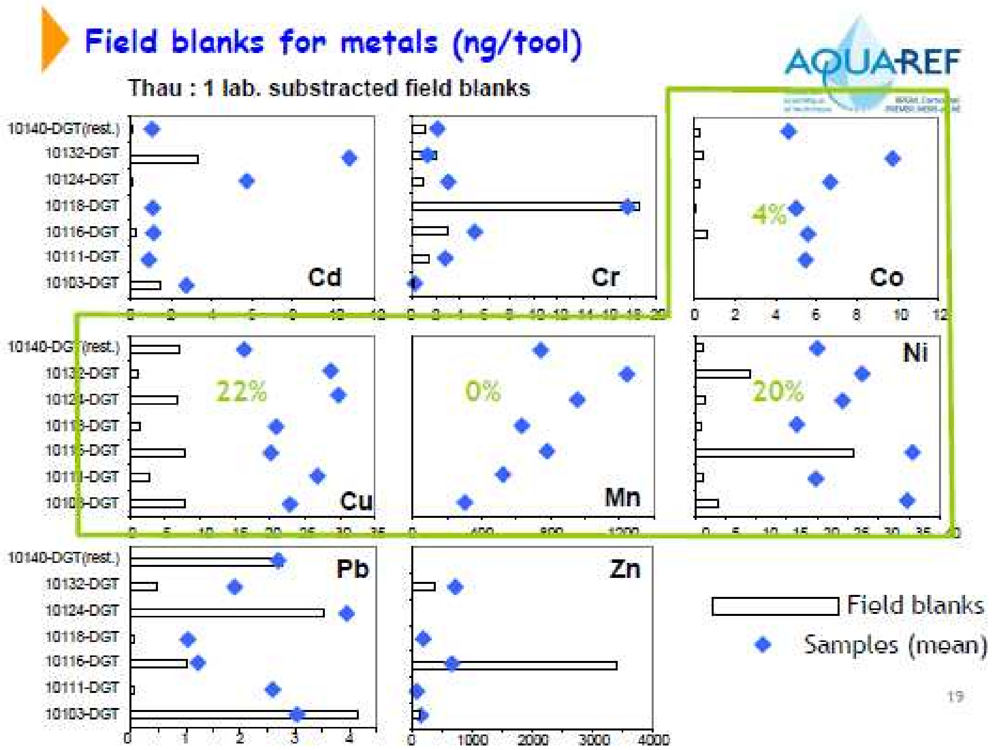
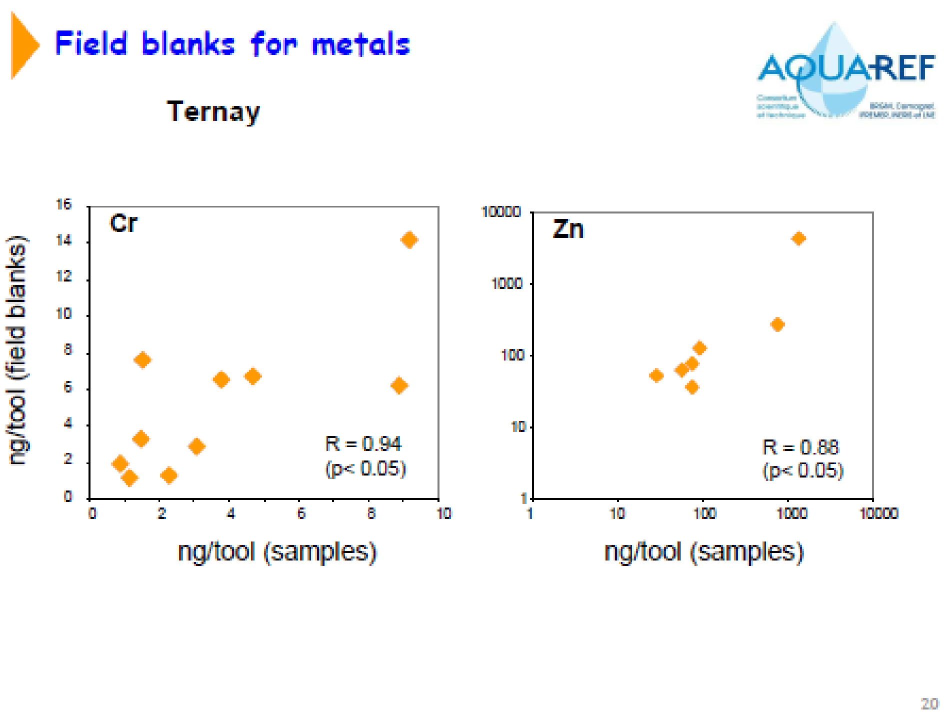
Field blanks for metals (ng/tool)

Ternay : 2 lab. substracted field blanks

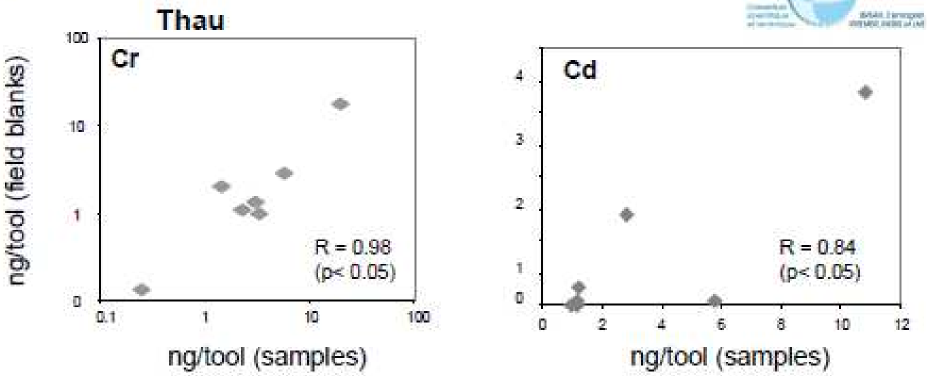


18


Field blanks for metals (ng/tool)
AQUAREF
Thau : 1 lab. substracted field blanks
Cd
Cr
Co
4%
Cu
22%
Mn
0%
Ni
20%
Pb
Zn
Field blanks
Samples (mean)
19


Field blanks for metals
AQUAREF
Ternay
Cr
R = 0.94
(p< 0.05)
Zn
R = 0.88
(p< 0.05)
ng/tool (field blanks)
ng/tool (samples)
ng/tool (samples)
20

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

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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 exercice, 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**

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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

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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)**

24

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

25

Thank you for your attention

26

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

9 Pesticides/metabolites	Devices
• acetochlor • alachlor * • atrazine * + DEA / DIA • diuron * • isoproturon * • metolachlor • simazine *	• 9 POCIS (DIA-*d5* as PRC for 2 participants only, mainly HLB receiving phase) • 4 SBSE, Silicone rod/sheet and MESCO • 5 Chemcatchers (SDB and C_{18}) ➼ 14 days

** priority substances (WFD)*

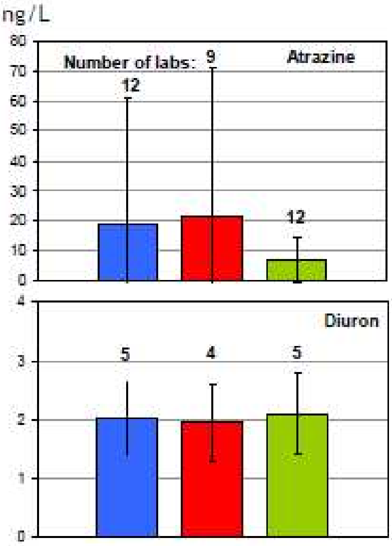
Sampling sites and planning

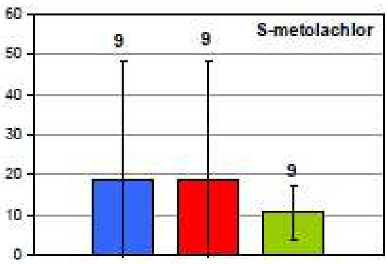
Coastal waters	**Thau Lagoon** (Hérault) 27th April-18th May	
River waters	**Beillant site** (Charente maritime) 27th May- 10th June	

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

- For Beillant site:

Means and standard deviations (all participants)
Means and standard deviations (without QC outliers)
Robust statistic (all participants)





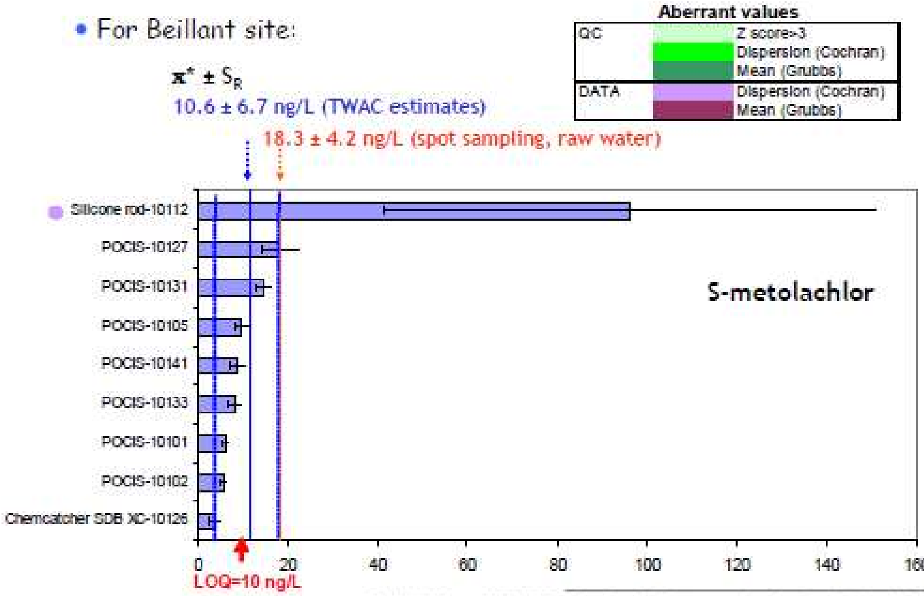
Comparison of pesticides water concentration (ng/L) from various tools and lab.

Compounds	Number of quantified results		Results/Participants ratio	
	Beillant	Thau	Beillant	Thau
Acetochlor	5	1	28%	8%
Alachlor	2	1	11%	8%
Atrazine	12	4	67%	33%
Deethylatrazine	7	2	39%	17%
Deisopropylatrazine	7	1	39%	8%
Diuron	5	5	28%	42%
Isoproturon	3	2	17%	17%
Metalochlor	9	3	50%	25%
Simazine	7	3	39%	25%

- 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:



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

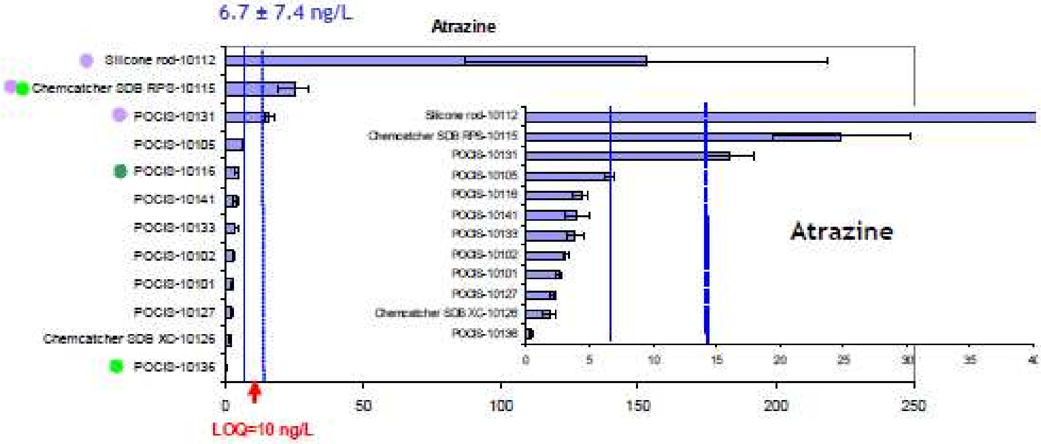
- For Beillant site:

Aberrant values

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

$x^* \pm S_R$

6.7 ± 7.4 ng/L



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

- For Beillant site:

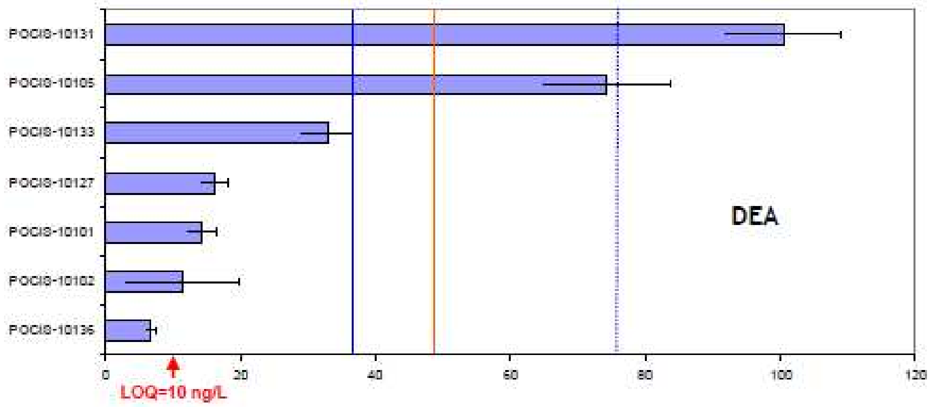
Aberrant values

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

$x^* \pm S_R$

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.

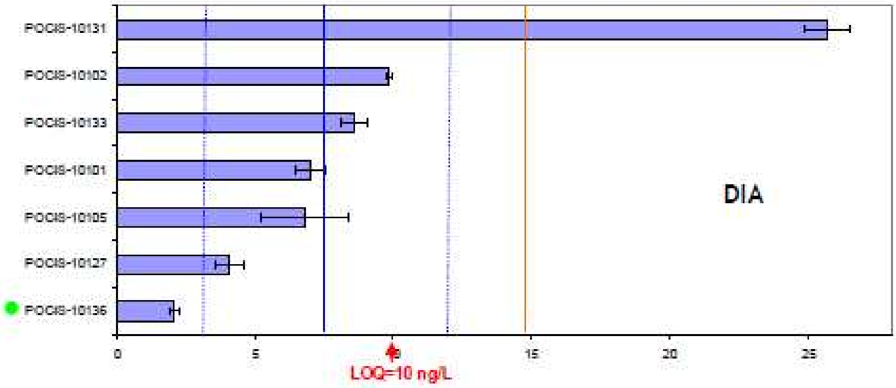
- For Beillant site:

Aberrant values

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

$x^* \pm S_R$

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.

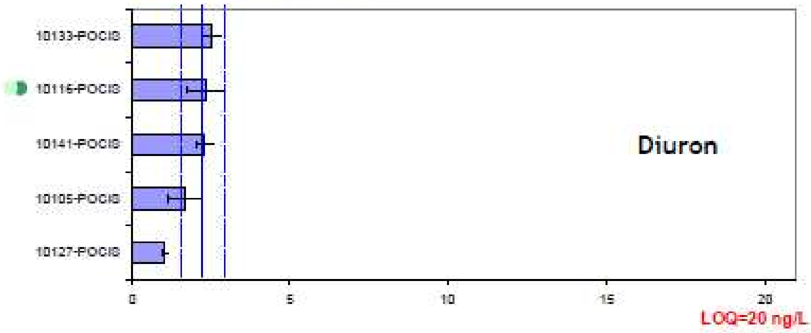
- For Beillant site:

Aberrant values

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

$x^* \pm S_R$

2.1 ± 0.7 ng/L (TWAC estimates)



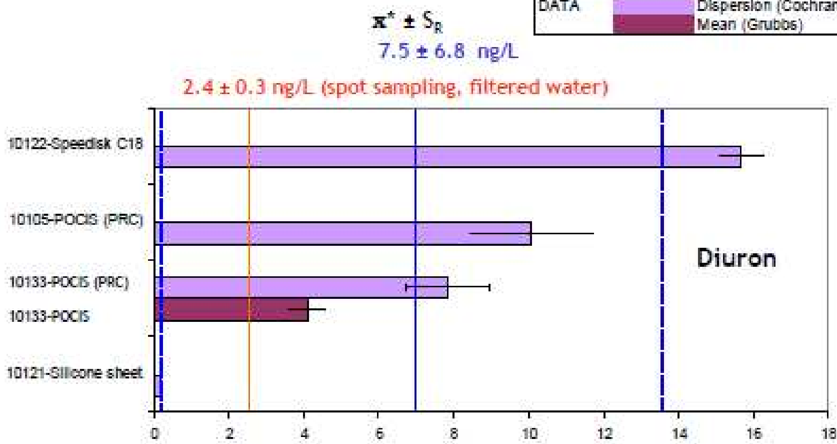
- Less results, but lower data dispersion
- Quite low concentrations, especially regarding to « spot sampling » LOQs

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

- For Thau Lagoon site:

Aberrant values

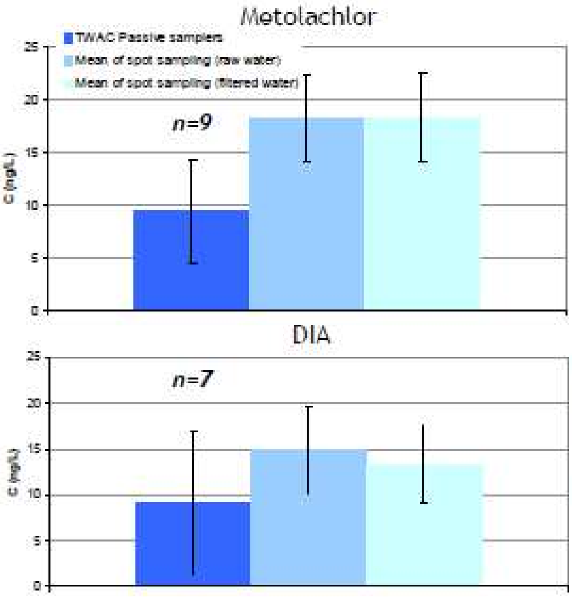
QC		Z score>3
		Dispersion (Cochran)
		Mean (Grubbs)
DATA		Dispersion (Cochran)
		Mean (Grubbs)



➨ Very few data... but two labs used the same PRC (DIA-d5)

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

- *For Beillant site*



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*

Parameters	Passive sampler data: Robust mean x* ± 1 SD (ng/L)	Passive sampler data: Robust reproducibility (% RSD)	SWIFT-WFD Proficiency Testing Exercise (natural water): Robust mean x* ± 1 SD (ng/L)	SWIFT-WFD Proficiency Testing Exercise (natural water): Robust reproducibility (% RSD)
Alachlor	1.8 ± 1.6	84	144 ± 52	36
Atrazine	6.7 ± 7.5	111	131 ± 32	24
Diuron	2.1 ± 0.8	36	152 ± 72	47
Isoproturon	0.4 ± 0.1	36	133 ± 44	33
Simazine	6.6 ± 5.7	87	136 ± 33	24

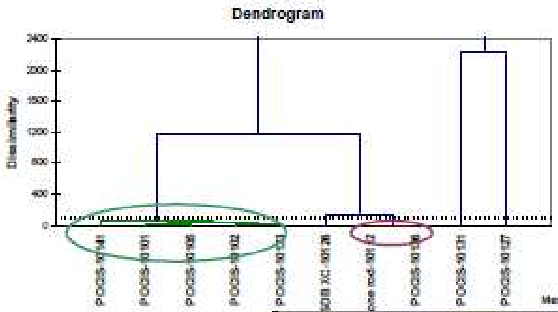
➜ Comparison with a classical proficiency testing: higher dispersion of PS data for some analytes

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

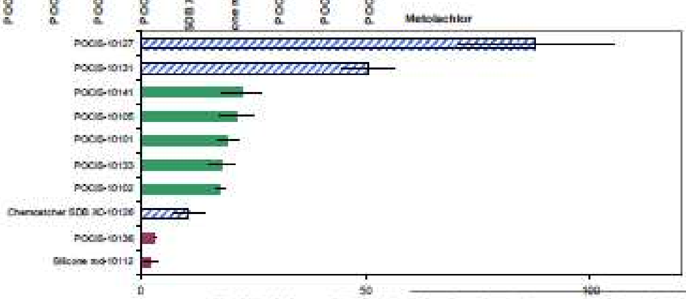
Comparison of data in ng/tool and ng/L

- *For Beillant site*



Metolachor (ng/tool)

50 % of populations in the same group



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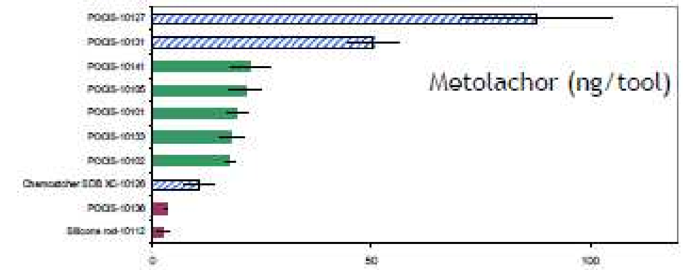
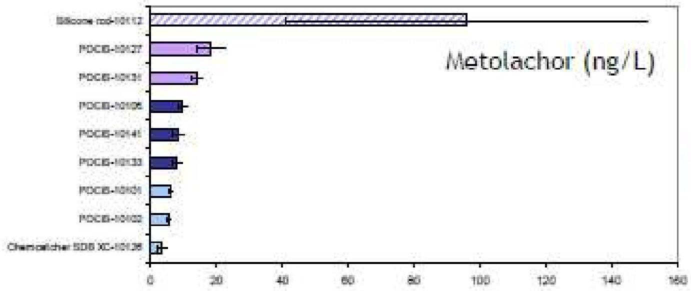
Comparison of data in ng/tool and ng/L

- *For Beillant site*





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

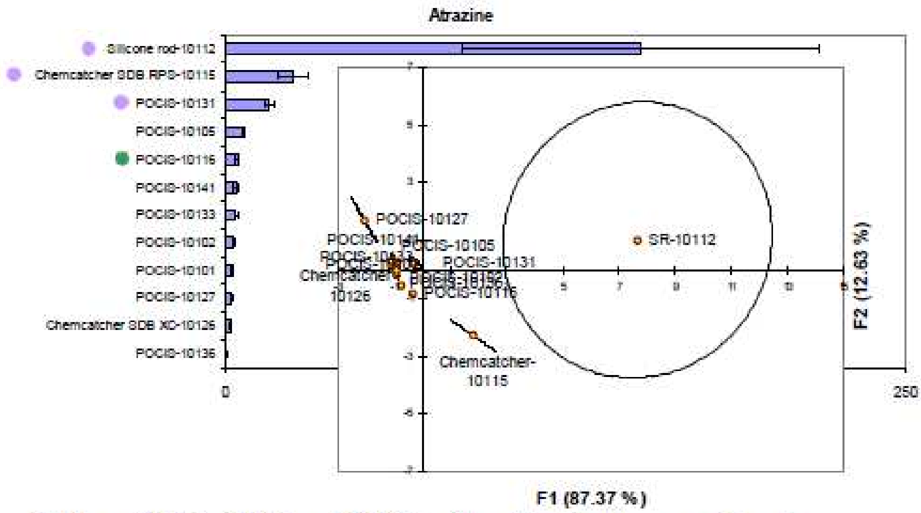
No direct correspondance between data

➨ **Higher dispersion?**

Comparison of data in ng/tool and ng/L

- *For Beillant site*

Factorial Discriminant Analysis (atrazine and S-metolachlor)



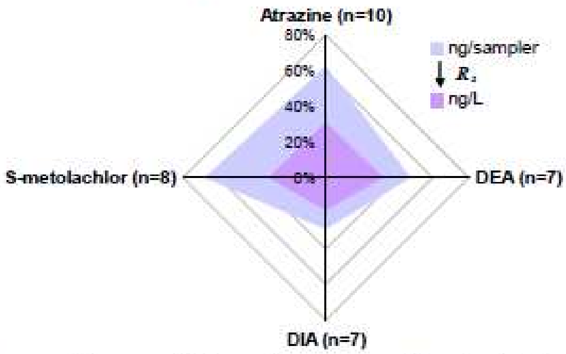
Outliers (10112, 10115 and 10131) will not be further considered...

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)



- Comparable populations decrease with calculations of TWACs…
- Need of harmonization of R_s for a same type of device?

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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*

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

Thanks to the participant lab.

- ALS Scandinavia AB (SW),
- AZTI-Foundation (ES),
- BRGM (FR),
- Cefas (UK),
- Cemagref (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),
- LPTC Bordeaux (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 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 – 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 Polycyclic Aromatic Hydrocarbons

C. Tixier, C. Miège, S. Schiavone, C Berho

18 EXPERT LABORATORIES

AQUAREF

✓ 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/fluo, 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

AQUAREF

Coastal waters	**Thau** (Hérault) 27th April 18th May	
River waters	**Ternay** (Rhône) 17th June 8th July	

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
- Dibenz[*a,h*]anthracene
- *‡ Indeno[*1,2,3-cd*]pyrene

* *Priority substances (WFD)*

‡ *Priority substances (OSPAR)*

AQUAREF

PS Devices	Ternay	Thau
SPMD	11	5
LDPE sheets	5	3
Silicone R sheets	3	2
Chemcatchers *(2 versions)*	3	1
MESCO	1	1
Silicone rod	1*(lost)*	1
CFIS (SBSE)	1	0

21 exposure days

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

	Nb of quantified results		Results/Participants (%)		Spot sampling (ng/L)	
	Ternay	Thau	Ternay	Thau	Ternay	Thau
Naphthalene	8	2	**32**	**15**	3.0 ± 1.7	1.3 ± 0.6
Acenaphthylene	14	5	**56**	**38**	6.3	0.4 ± 0.2
Acenaphthene	18	6	**72**	**46**	4.8 ± 4.5	0.1 ± 0.0
Fluorene	21	8	**84**	**62**	2.3 ± 2.6	0.2 ± 0.1
Phenanthrene	22	10	**88**	**77**	2.9 ± 0.2	0.7 ± 0.1
Anthracene	21	8	**84**	**62**	1.2	-
Fluoranthene	22	12	**88**	**92**	6.5 ±1.4	0.3 ±0.1
Pyrene	22	11	**88**	**85**	1.5 ±1.0	0.2 ±0.0
Benz[*a*]anthracene	21	9	**84**	**69**	0.4	0.1 ± 0.0
Chrysene	21	10	**84**	**77**	0.4	0.2 ± 0.0
Benzo[*b*]fluoranthene	20	8	**80**	**62**	< 0.4	0.1 (SBFLs)
Benzo[*a*]pyrene	19	7	**76**	**54**	< 0.4	< 0.1
Benzo[*k*]fluoranthene	19	8	**76**	**62**	< 0.4	-
Indeno[1,2,3-cd]pyrene	14	7	**58**	**54**	< 0.4	< 0.1
Dibenz[*a,h*]anthracene	11	3	**44**	**23**	< 0.4	< 0.1
Benzo[*g,h,i*]perylene	15	6	**60**	**46**	< 0.4	< 0.1

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

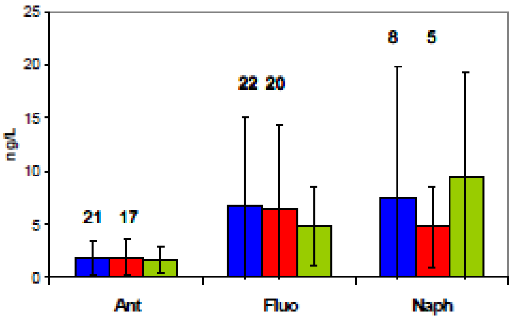
PAH WATER CONCENTRATION (ng/L)
Various tools and laboratories

	Nb of quantified results		Results/Participants (%)		Spot sampling (ng/L)	
	Ternay	Thau	Ternay	Thau	Ternay	Thau
Naphthalene	8 *(3)*	2	**32**	**15**	3.0 ± 1.7	1.3 ± 0.6
Acenaphthylene	14 *(2)*	5 *(2)*	**56**	**38**	6.3	0.4 ± 0.2
Acenaphthene	18 *(1)*	6 *(1)*	**72**	**46**	4.8 ± 4.5	0.1 ± 0.0
Fluorene	21 *(2)*	8 *(3)*	**84**	**62**	2.3 ± 2.6	0.2 ± 0.1
Phenanthrene	22 *(3)*	10 *(4)*	**88**	**77**	2.9 ± 0.2	0.7 ± 0.1
Anthracene	21	8 *(4)*	**84**	**62**	1.2	-
Fluoranthene	22	12 *(2)*	**88**	**92**	6.5 ±1.4	0.3 ±0.1
Pyrene	22	11 *(1)*	**88**	**85**	1.5 ±1.0	0.2 ±0.0
Benzo[*a*]anthracene	21	9 *(4)*	**84**	**69**	0.4	0.1 ± 0.0
Chrysene	21	10 *(5)*	**84**	**77**	0.4	0.2 ± 0.0
Benzo[*b*]fluoranthene	20 *(2)*	8	**80**	**62**	< 0.4	0.1 (SBRLs)
Benzo[*a*]pyrene	19 *(1)*	7 *(1)*	**76**	**54**	< 0.4	< 0.1
Benzo[*k*]fluoranthene	19	8 *(2)*	**76**	**62**	< 0.4	-
Indeno[1,2,3-cd]pyrene	14 *(2)*	7 *(2)*	**58**	**54**	< 0.4	< 0.1
Dibenz[*a,h*]anthracene	11 *(3)*	3 *(1)*	**44**	**23**	< 0.4	< 0.1
Benzo[*g,h,i*]perylene	15 *(5)*	6 *(2)*	**60**	**46**	< 0.4	< 0.1

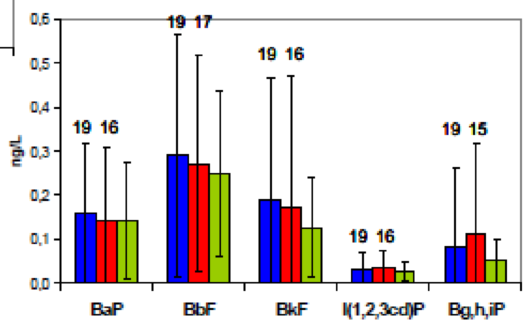
- ✓ More than 60 % of quantified results for 10 to 12 PAHs
- ✓ Thau: few data and some results close to field blank
- ✓ Lower LOQs with passive sampling / spot sampling

PAH WATER CONCENTRATION (TWAC, ng/L)

Means and sd (all participants)
Means and sd (without QC outliers)
Means and sd (Robust statistic, all participants)



Ternay site



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

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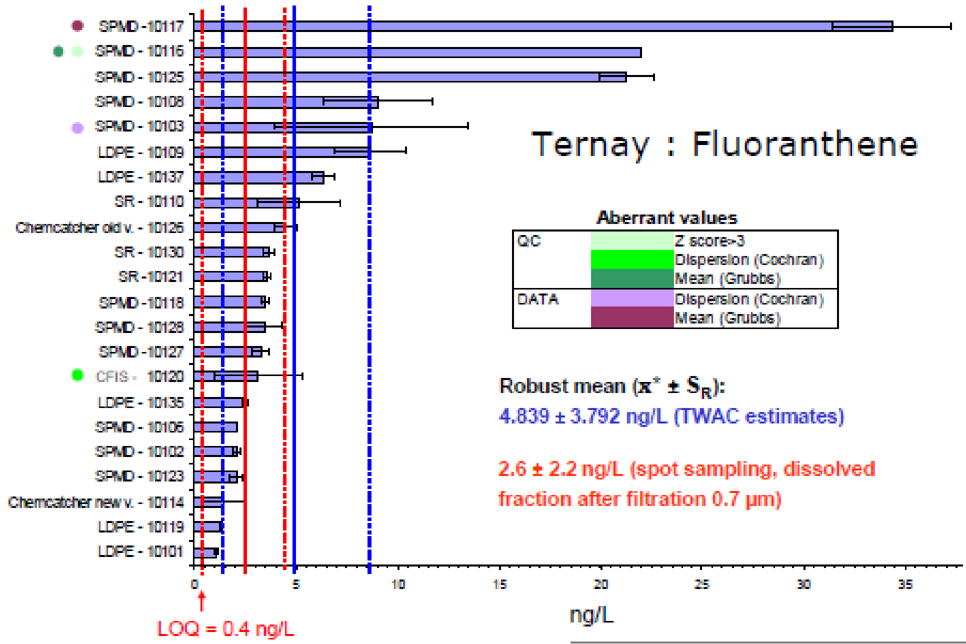
PAH WATER CONCENTRATION (ng/L)
Various tools and laboratories



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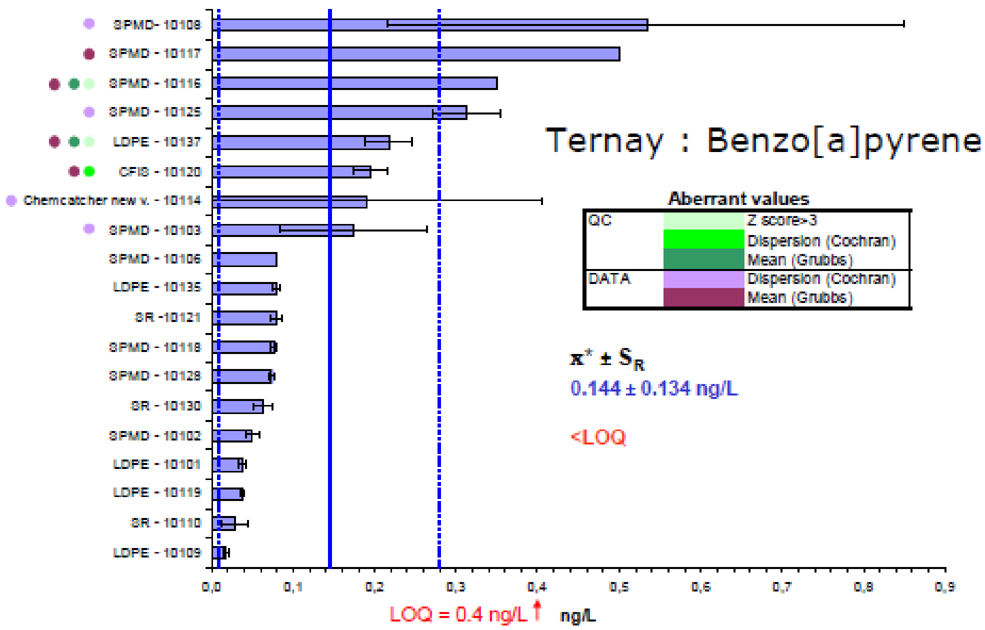
PAH WATER CONCENTRATION (ng/L)
Various tools and laboratories



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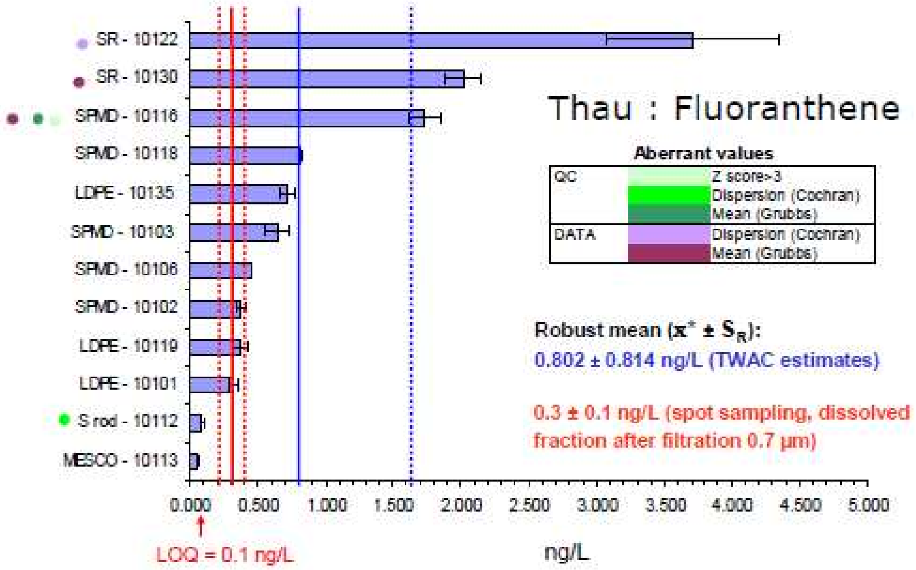
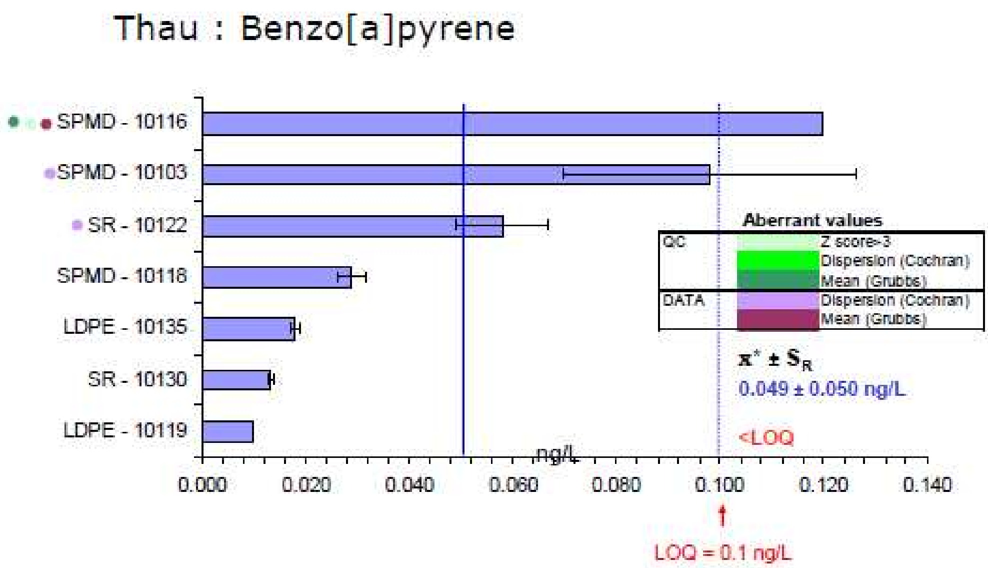
PAH WATER CONCENTRATION (ng/L)
Various tools and laboratories



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



REPRODUCIBILITY
Passive sampling – Spot sampling

	Ternay passive sampler data		AGLAE Proficiency Testing Exercise (Spiked surface water, 20-40 ng/L)
	Robust mean X* ± sd (ng/L)	Robust reproducibility (RSD %)	Robust reproducibility (RSD %)
Naphthalene	9.49 ± 9.84	**81**	**26**
Acenaphthylene	1.60 ± 2.07	**130**	-
Acenaphthene	6.61 ± 5.54	**84**	**18**
Fluorene	4.91 ± 4.52	**93**	**15**
Phenanthrene	5.76 ± 4.50	**80**	**14**
Anthracene	1.59 ± 1.27	**81**	**16**
Fluoranthene	4.84 ± 3.65	**78**	**14**
Pyrene	4.80 ± 2.96	**63**	**12**
Benz[*a*]anthracene	0.81 ± 0.73	**94**	**11**
Chrysene	1.07 ± 0.93	**88**	**11**
Benzo[*b*]fluoranthene	0.25 ± 0.19	**77**	**13**
Benzo[*a*]pyrene	0.14 ± 0.13	**93**	**16**
Benzo[*k*]fluoranthene	0.13 ± 0.11	**91**	**10**
Indenopyrene	0.03 ± 0.02	**85**	**18**
Dibenz[*a*,*h*]anthracene	0.01 ± 0.01	**88**	**16**
Benzo[*g*,*h*,*i*]perylene	0.05 ± 0.05	**100**	**22**

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

PAH ACCUMULATION - VARIOUS TOOLS

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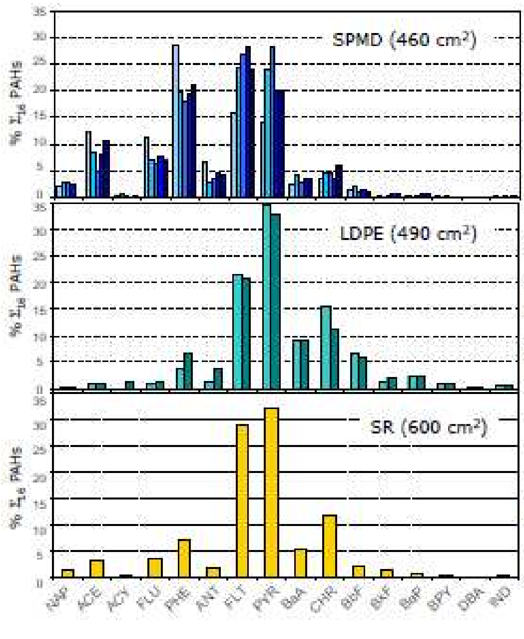
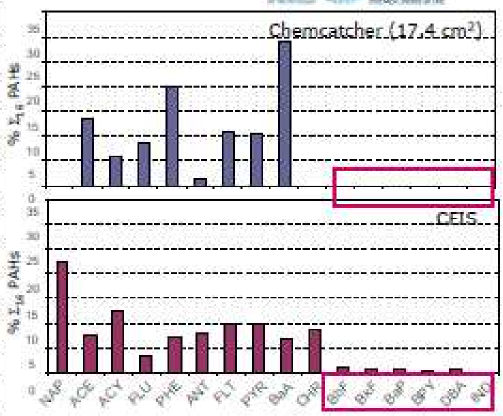
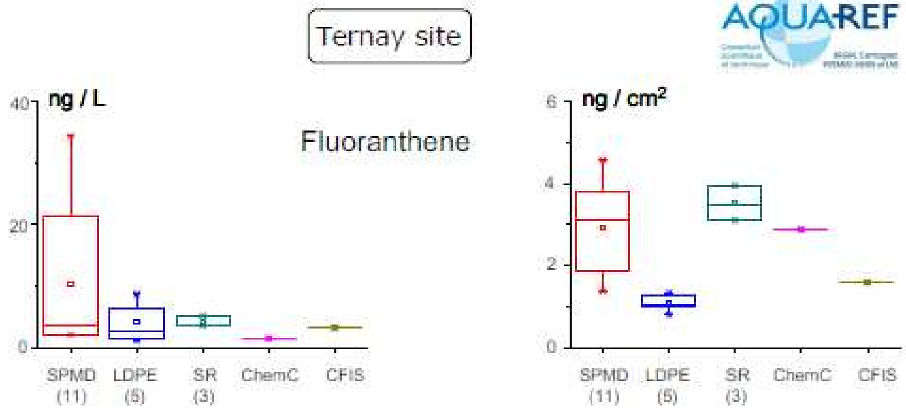




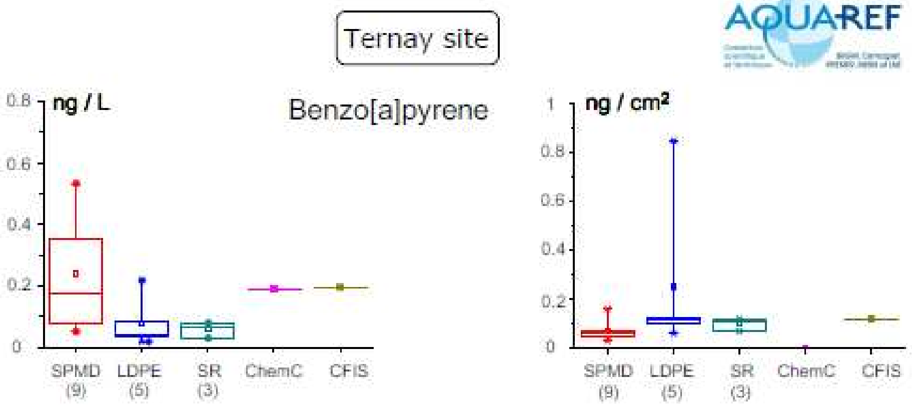
✓ LDPE, SR: similar accumulation patterns

✓ Chemcatcher: no accumulation of high molecular weight PAHs

PAH CONCENTRATION in ng/L and ng/cm²



PAH CONCENTRATION in ng/L and ng/cm²



✓ 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

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✓ 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

AQUAREF

- **ALS Scandinavia AB (SW),**
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- **Deltares/TNO (NL),**
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- **EDF R&D/LNHE (FR),**
- **Environment Agency, National Laboratory Service (UK),**
- **IFREMER (FR),**
- **Labaqua (ES),**
- **LEESU (FR),**
- **Marine Scotland - Science (UK),**
- **NIVA (NO),**
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- **Water Research Institute (SK)**

Thanks to the central laboratories for water analyses

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- 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 !

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