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

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

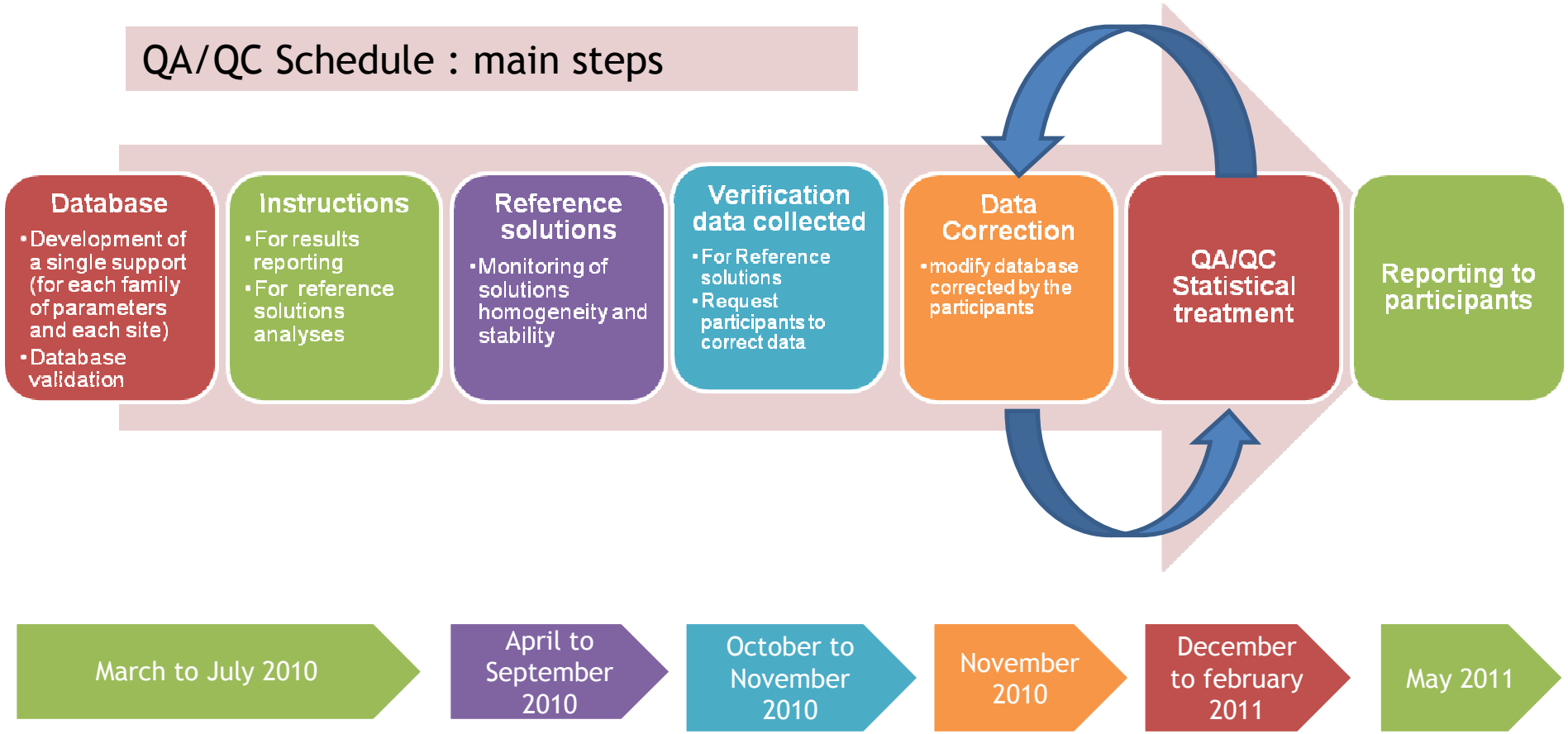
QA/QC
in the AQUAREF
inter comparison exercise

Schedule
From database conception to participant reporting

General organization of the collaborative trial

It is not a proficiency test

QA/QC Schedule : main steps



QA/QC
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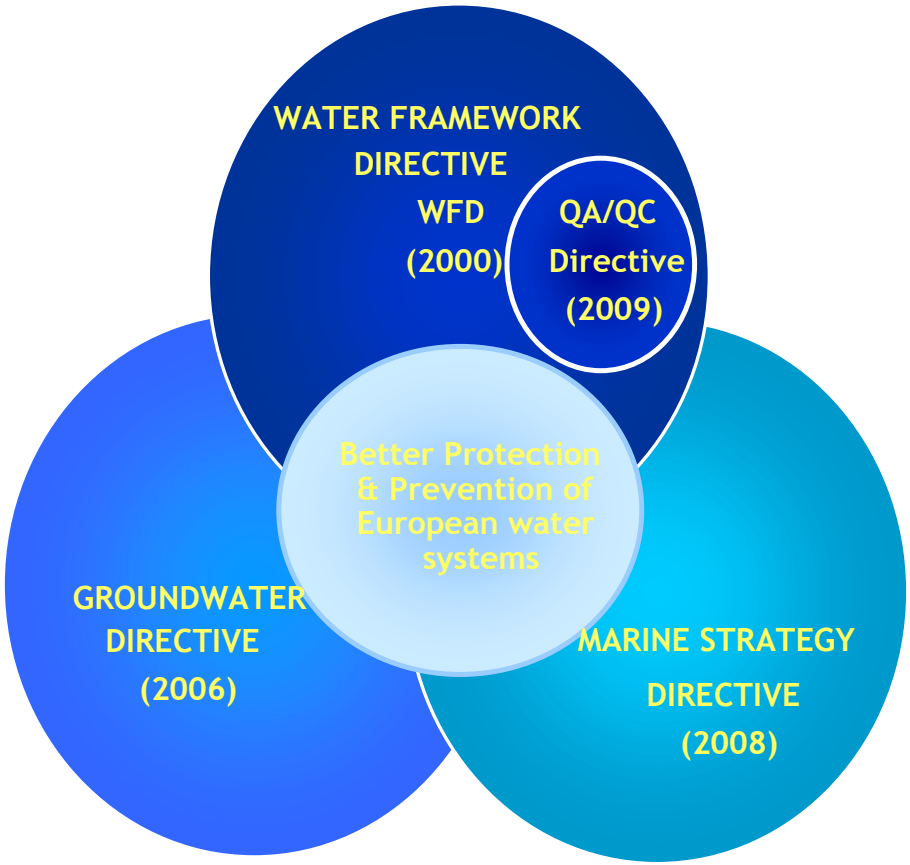
From basic concepts to the final implemented strategy

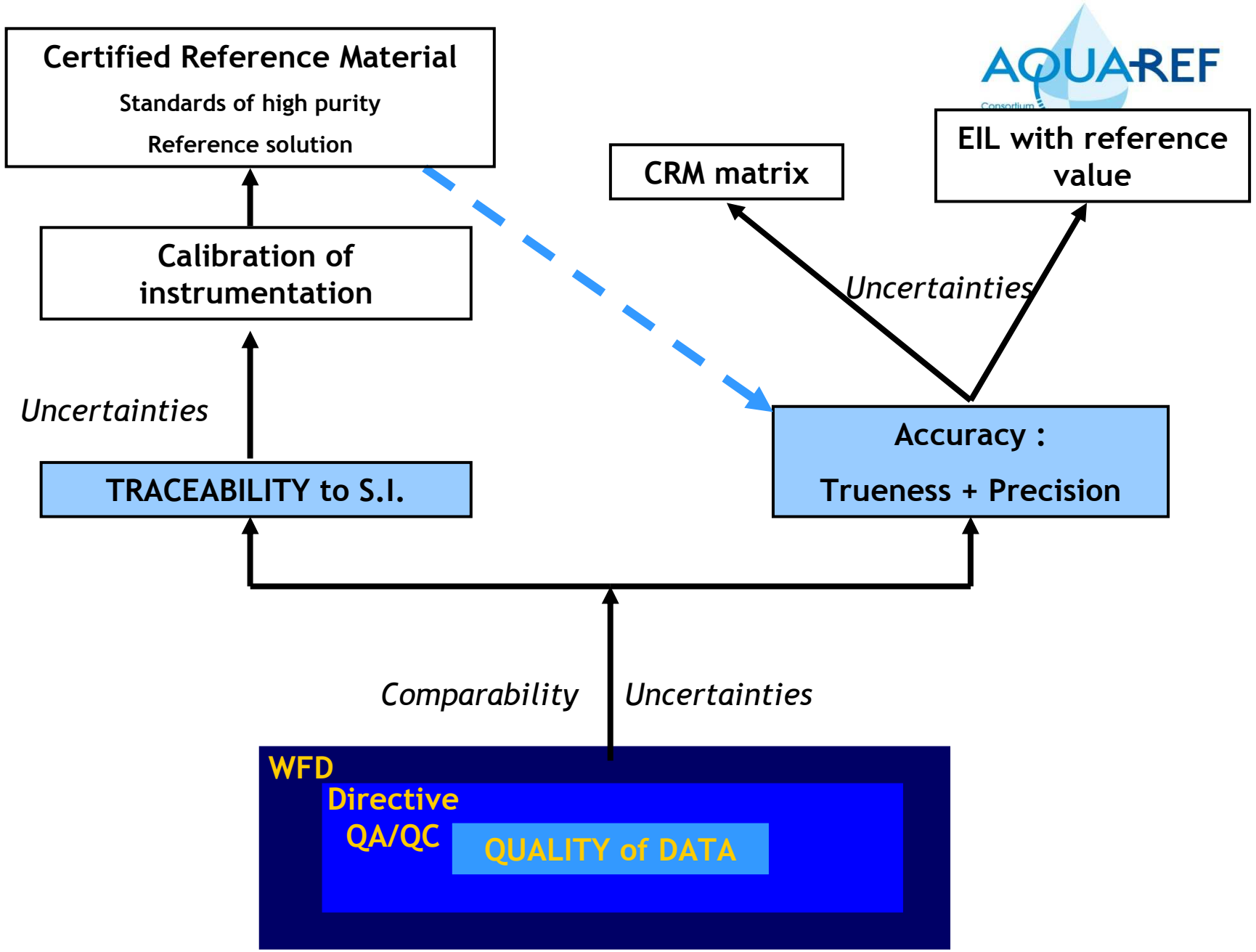
From basic concepts… (1)



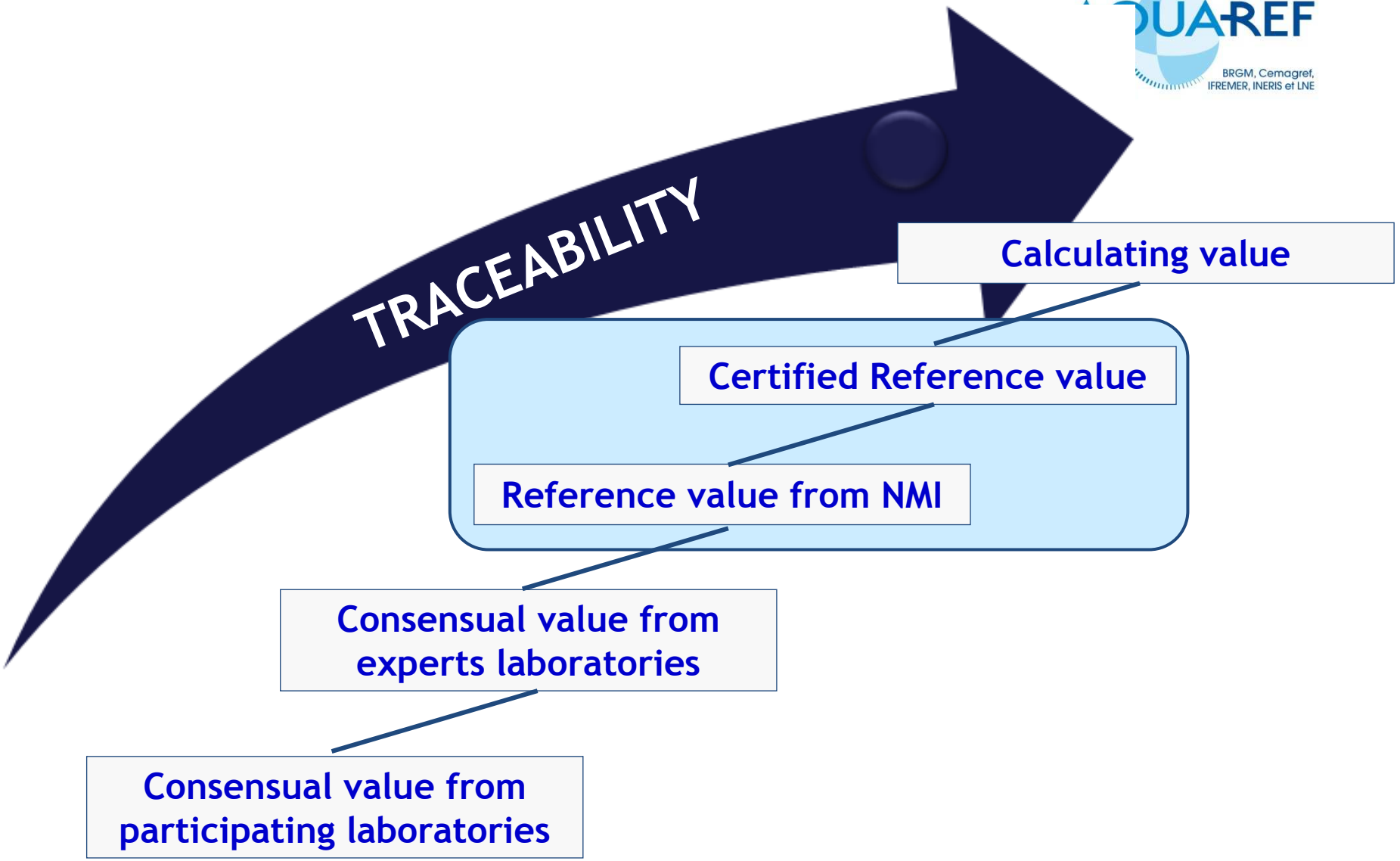
- ✓ Quality and comparability of data;
- ✓ Representativity of data;
- ✓ Rationalization of costs of monitoring;
- ✓ Evaluation of capabilities and competencies;

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

From basic concepts… (2)



From basic concepts… (3)



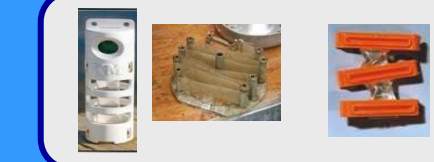
From basic concepts … (4)

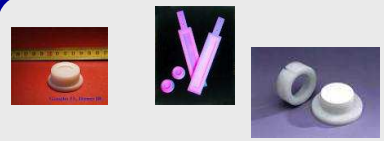
Measurement chains

Various types of pollutants

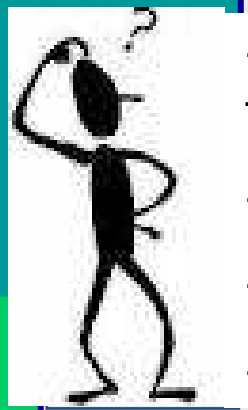
PAHS (16 EPA) | Pesticides (8) | Metals ()

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

ation

Acid Extraction

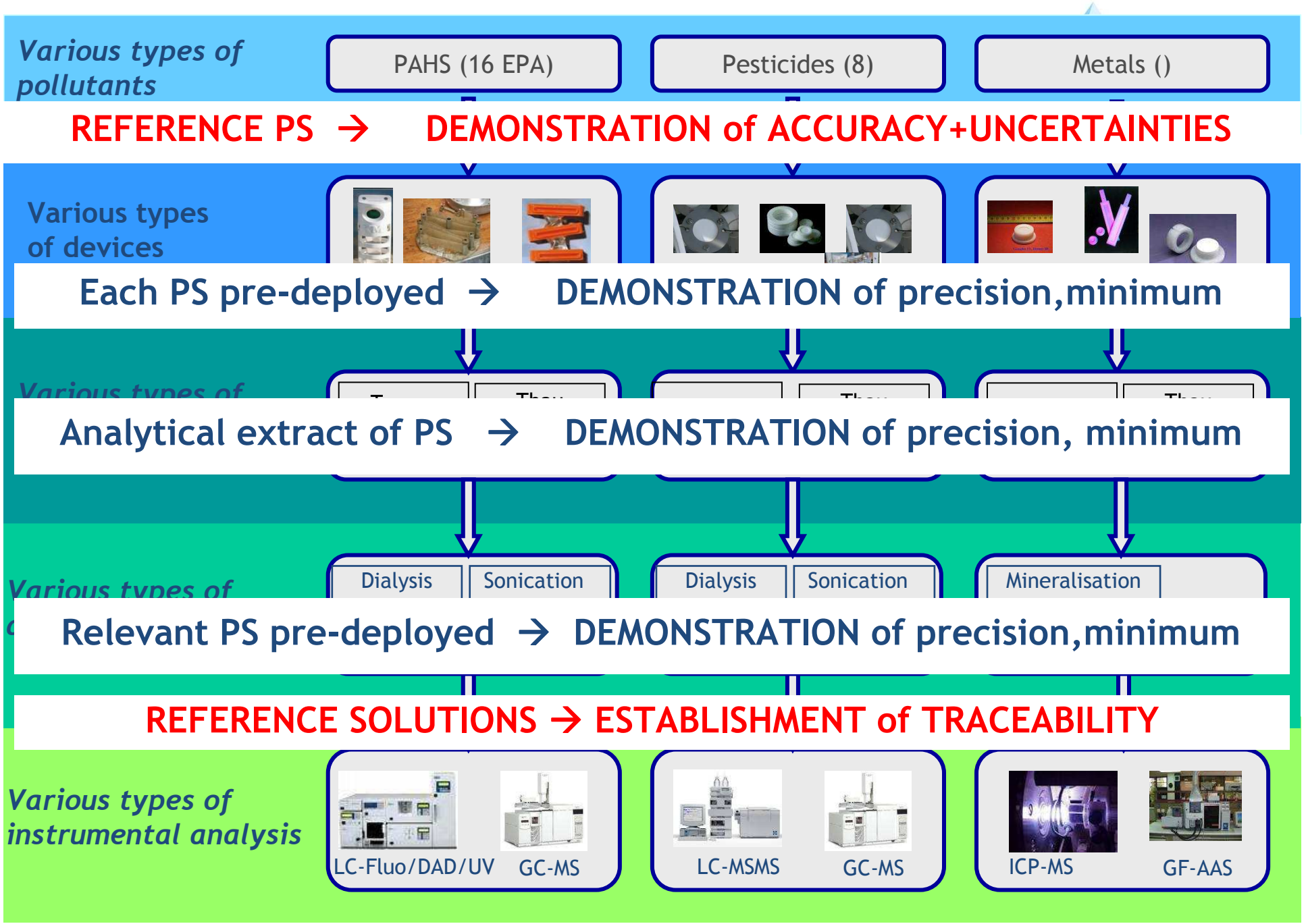
Various types of instrumental analysis


LC-Fluo/DAD/UV | GC-MS

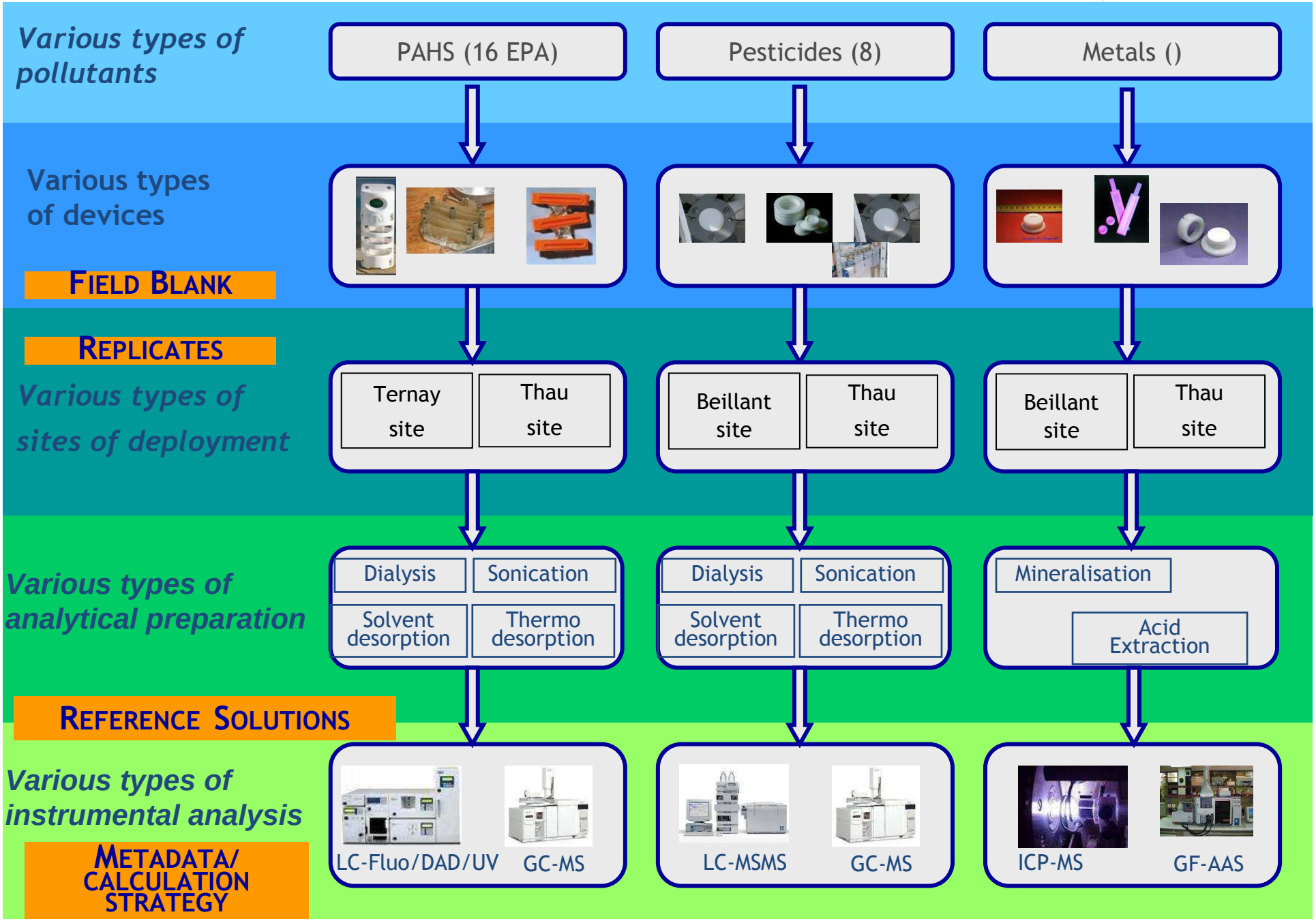

LC-MSMS | GC-MS


ICP-MS | GF-AAS

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



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



QA/QC
in the AQUAREF
inter comparison exercise

Data base overview

Data base Overview (1)

Personal login and password

Data base Overview (2)

Transmission and validation
Results

Personal login and password

Data base Overview (3)

Extraction database
X File « DATA BRUT »

Site / QC or sampler / unit	Parameter	Personal Identification Participant	Value 1	Value 2	Value 3	Value 4	Metadata (40 colon for metadata)
ETANG THAU - PAH - Solution A en µg/ml	Acenaphtene	10101	2.15	2.08	2.1	2	
ETANG THAU - PAH - Solution A en µg/ml							
ETANG THAU - PAH- Solution A en µg/ml							
"							
"							
"							

Results participant

Results participant E

Site / QC or sampler / unit	Parameter	Personal Identification Participant	Value 1	Value 2	Value 3	Value 4	Metadata (40 colon for metadata)
TERNAY - PAH - Solution A en µg/ml	Acenaphtene	10101	2.15	2.08	2.1	2	
TERNAY- PAH - Solution A en µg/ml	Acenaphtene	10102	2.15	2.08	2.1	2	
TERNA Solution							

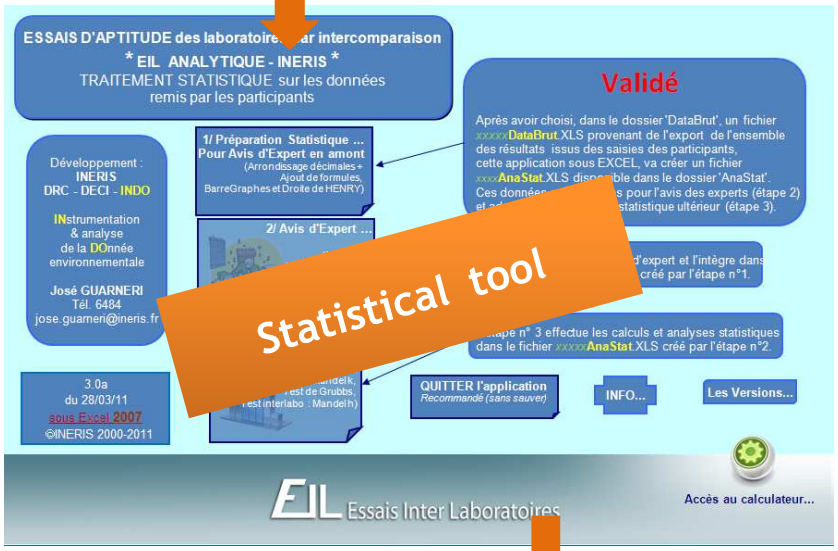
Site / QC or sampler / unit	Parameter	Personal Identification Participant	Value 1	Value 2	Value 3	Value 4	Metadata (40 colon for metadata)
TERNAY - pesticides - Solution A en µg/ml	Diuron	10101	2.15	2.08	2.1	2	
TERNAY - pesticides - Solution A en µg/ml	Diuron	10102	2.15	2.08	2.1	2	
TERNAY - pesticid Solution A en µg/ml							
"							
"							
"							

Site / QC or sampler / unit	Parameter	Personal Identification Participant	Value 1	Value 2	Value 3	Value 4	Metadata (40 colon for metadata)
BEILLANT - pesticides - Solution A en µg/ml	Simazine	10101	2.15	2.08	2.1	2	
BEILLANT - pesticides - Solution A en µg/ml	Simazine	10102	2.15	2.08	2.1	2	
BEILLANT - pesticides - Solution A en µg/ml	Simazine	XXXXX					
"	"	"					
"	"	"					
"	"	"					

Data base Overview (4)

Site / QC or sampler / unit	Parameter	Personal Identification Participant	Value 1	Value 2	Value 3	Value 4	Metadata (40 colon for metadata)
TERNAY - PAH - Solution A en µg/ml	Acenaphtene	10101	2.15		1	2	
TERNAY- PAH - Solution A en µg/ml	Acenaphtene	10102				2	
TERNAY - PAH- Solution A en µg/ml	Acenaphtene	XXXXX					
"	"	"					
"	"	"					
"	"	"					

Each File. XLS « DATA BRUT »



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	Repetability en %	Reproductibility en %
Benzo_a_pyrène	2.364	0.938	0.303	0.113	0.936	4.0%	39.9%
Benzo_b_fluoranthène	2.270	0.722	0.250	0.128	0.719	5.3%	32.2%
Benzo_k_fluoranthène	2.254	0.613	0.205	0.107	0.610	6.2%	27.5%
Indéno_1,2,3c,d_pyrène	2.236	1.190	0.372	0.087	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_pérylène	2.297	1.233	0.374	0.112	1.232	5.8%	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%

QA/QC
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inter comparison exercise

Statistical treatment

Statistical treatment of QC A (1)

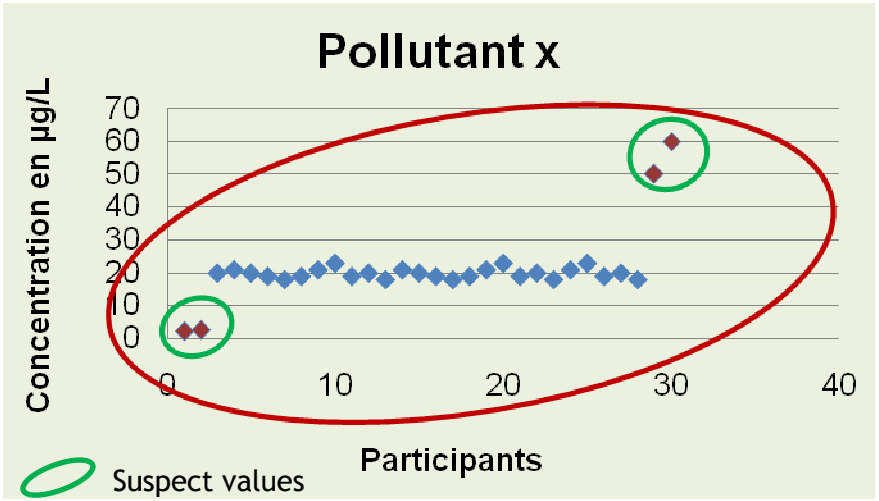
- According to the standards and guidelines
  - ISO 13528 (2005) « Statistical methods for use in proficiency testing by interlaboratory comparisons »
  - ISO 5725-5 (1998) « Accuracy (trueness and precision) of measurement methods and results – Part 5 : Alternative methods for the determination of the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

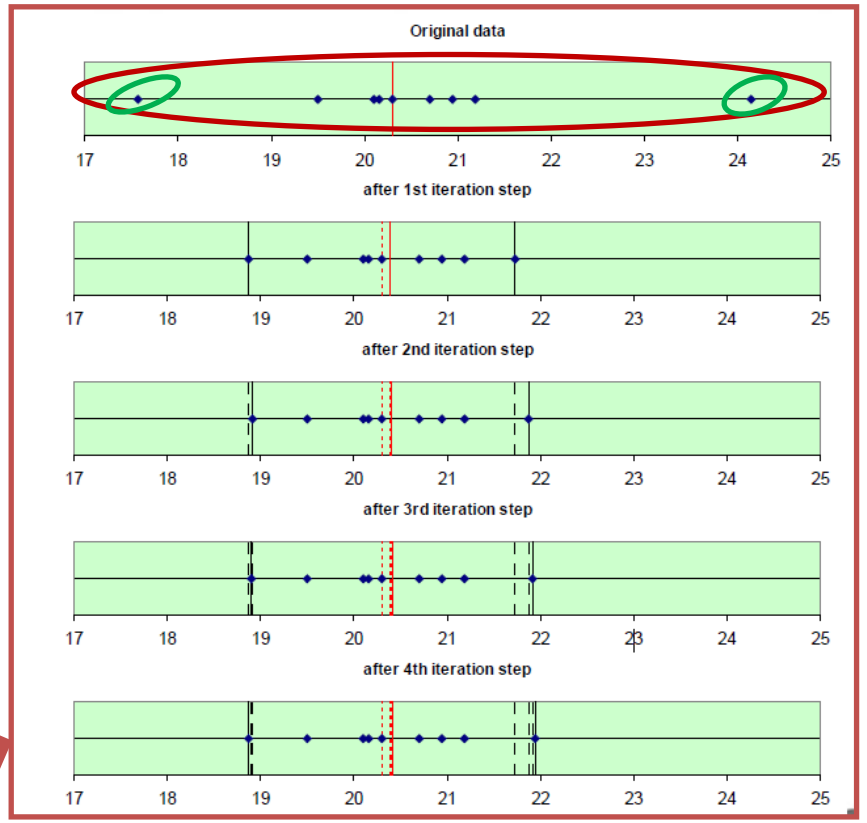
With this approach, the assigned value is the robust average of the results reported by all the participants: No exclusion of participants

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.





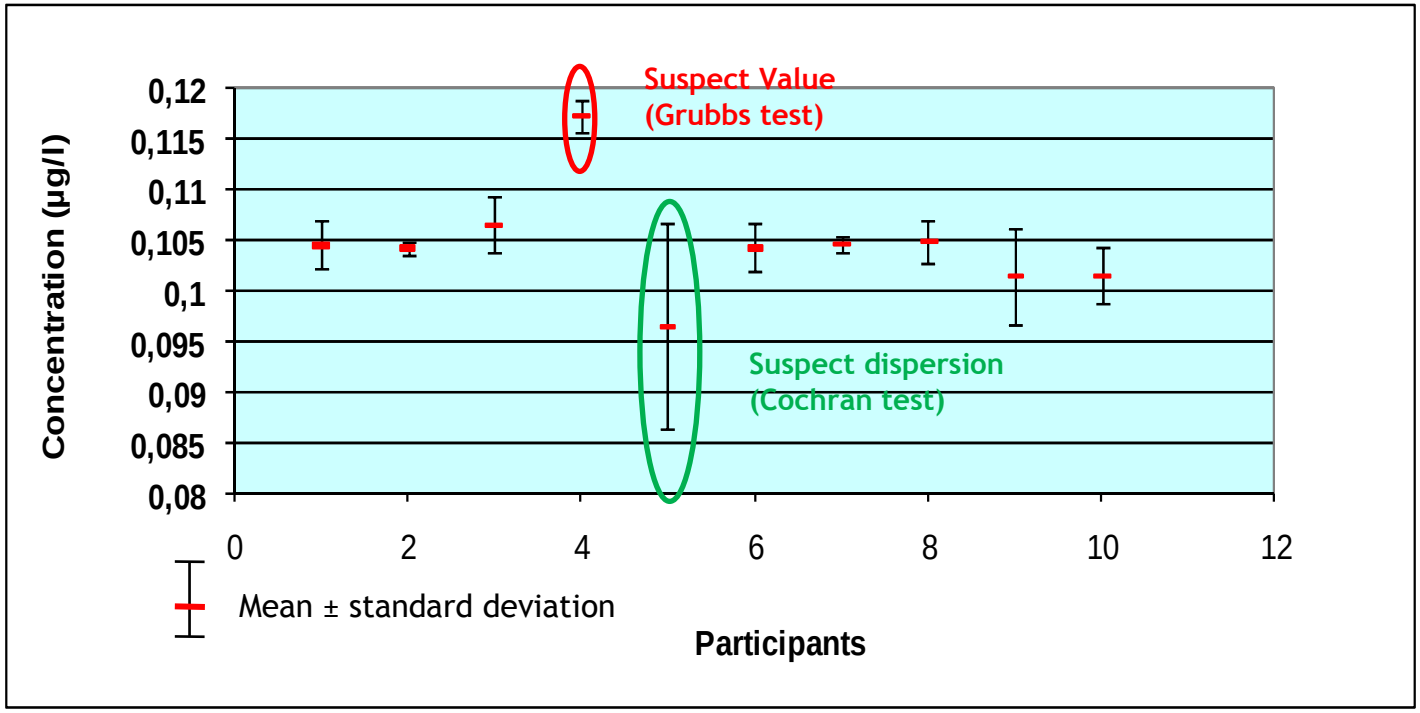
After x iteration

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

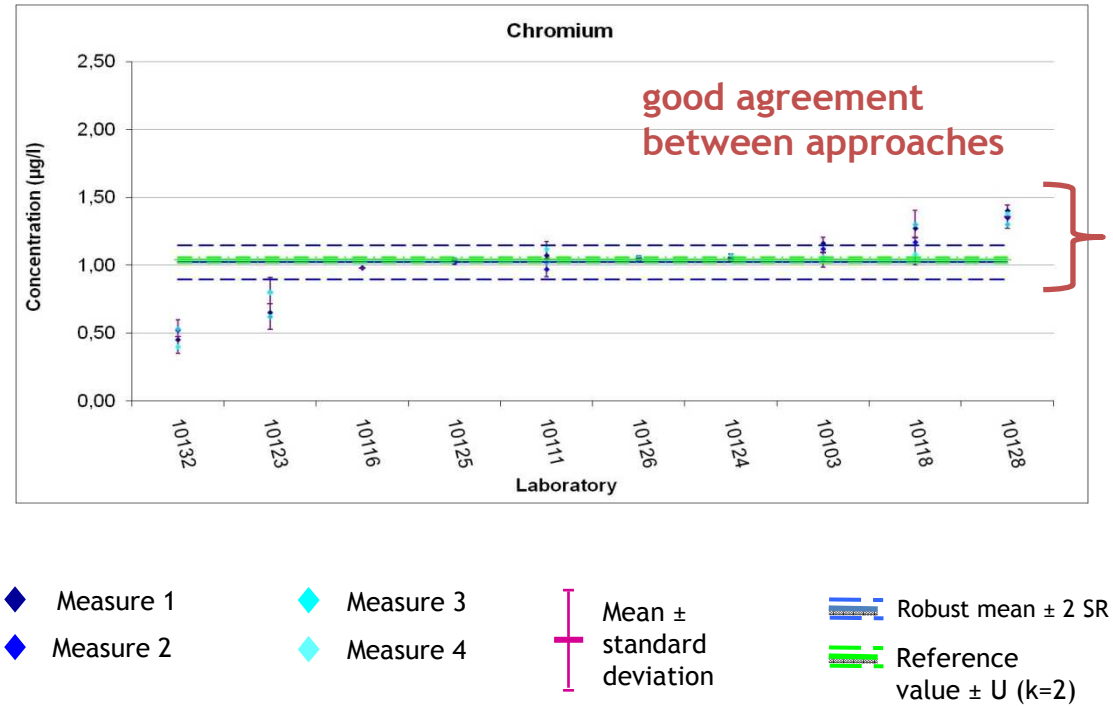
Statistical treatment of QC A (4)

•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

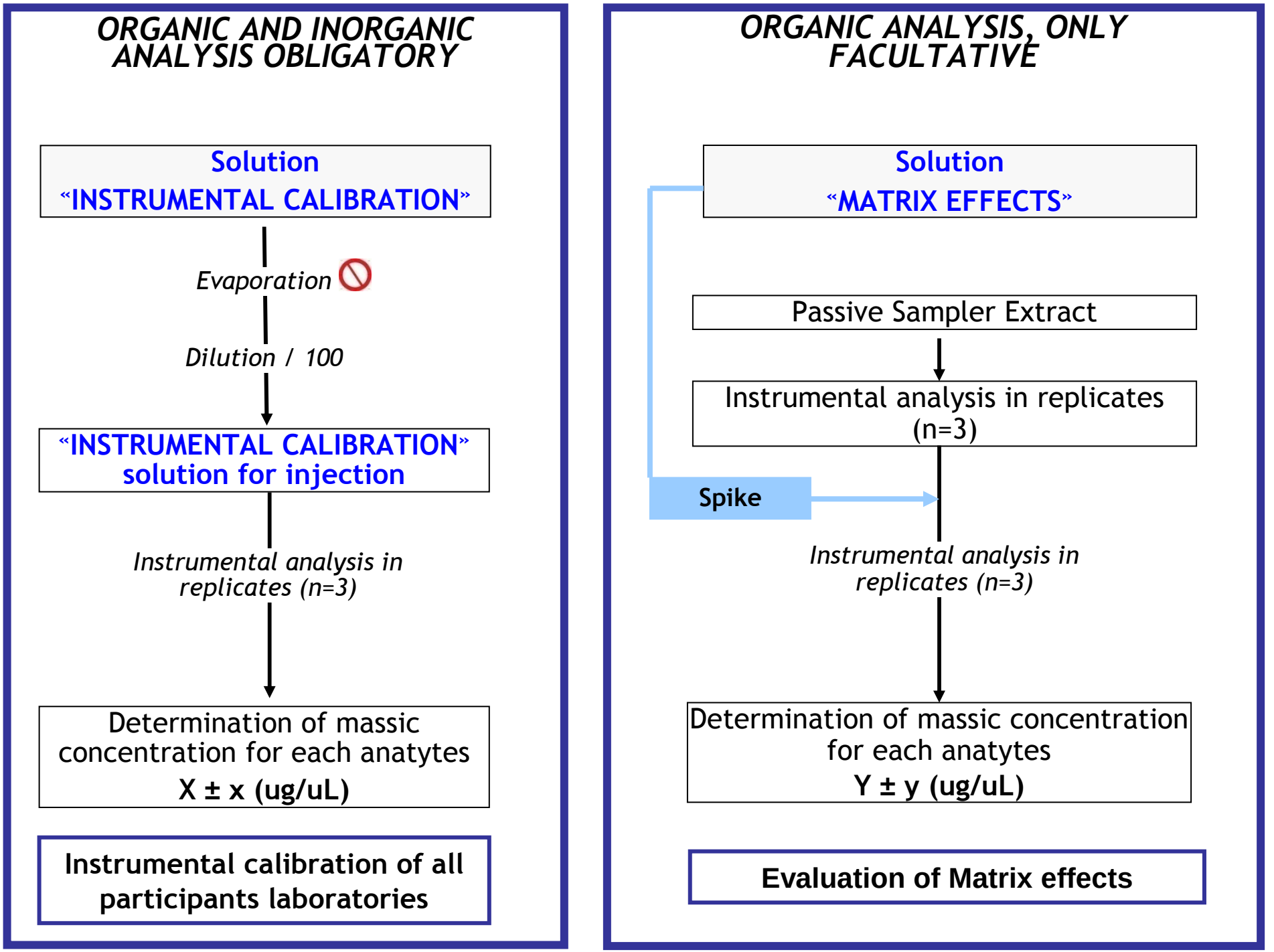
QA/QC
in the AQUAREF
inter comparison exercise

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

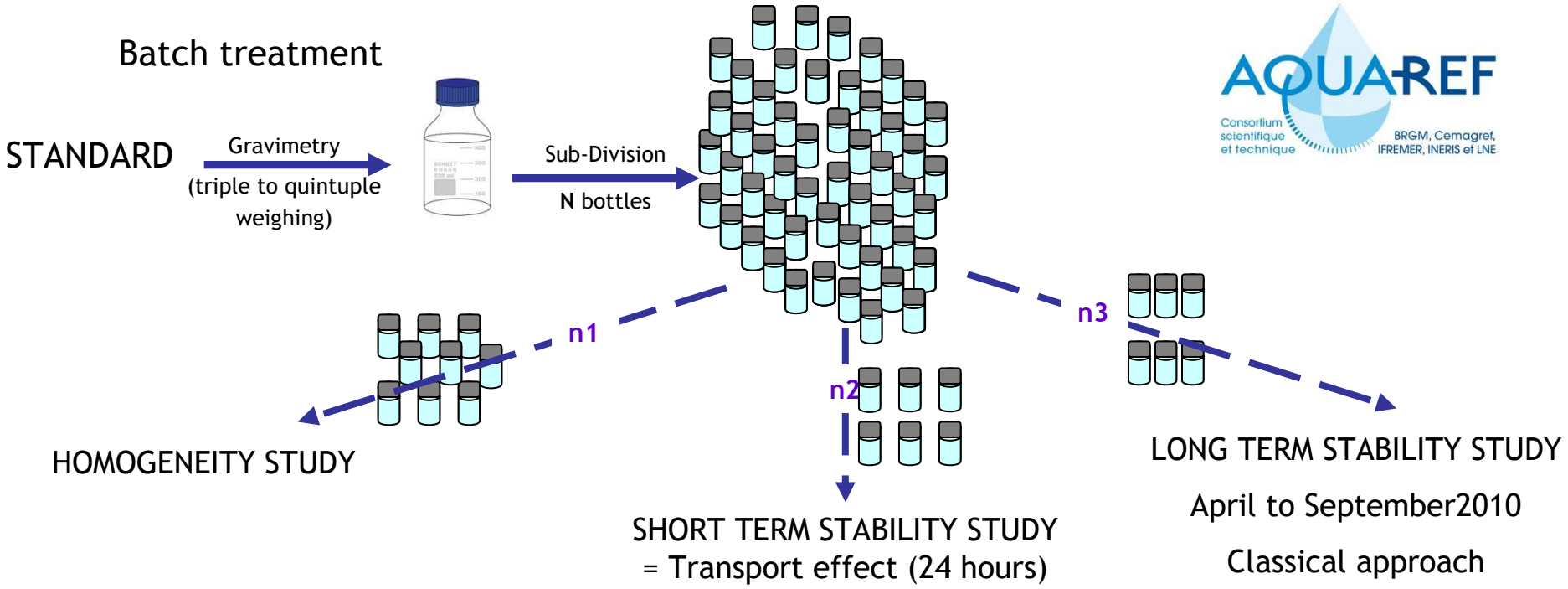
Reference solutions: Summary

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

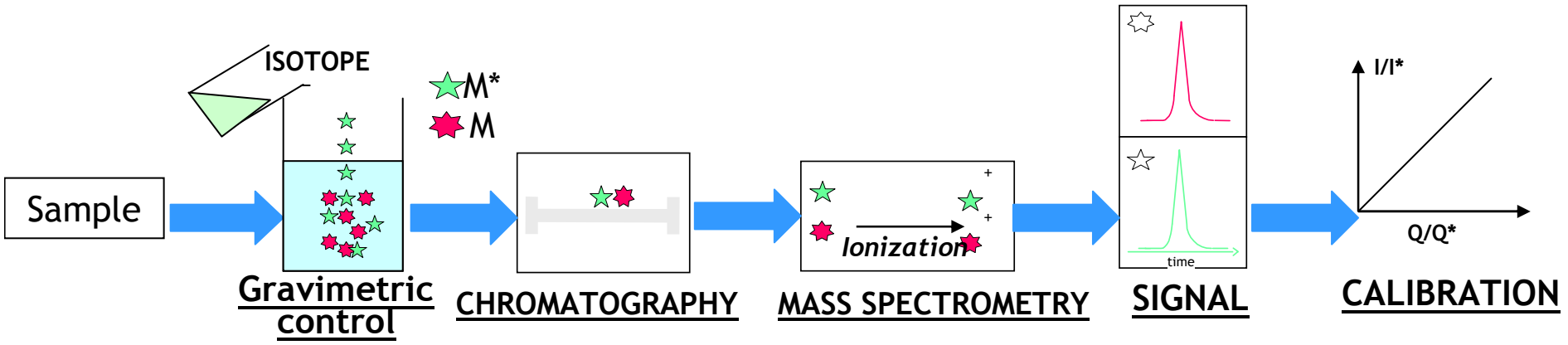
WFD (33 Priority substances) Substances of the ecological status


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 anatytes
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 anatytes
Y ± y (ug/uL)
Evaluation of Matrix effects

PREPARATION of REFERENCE SOLUTIONS



PRIMARY METHOD *ID-MS: Principles*



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%

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%

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

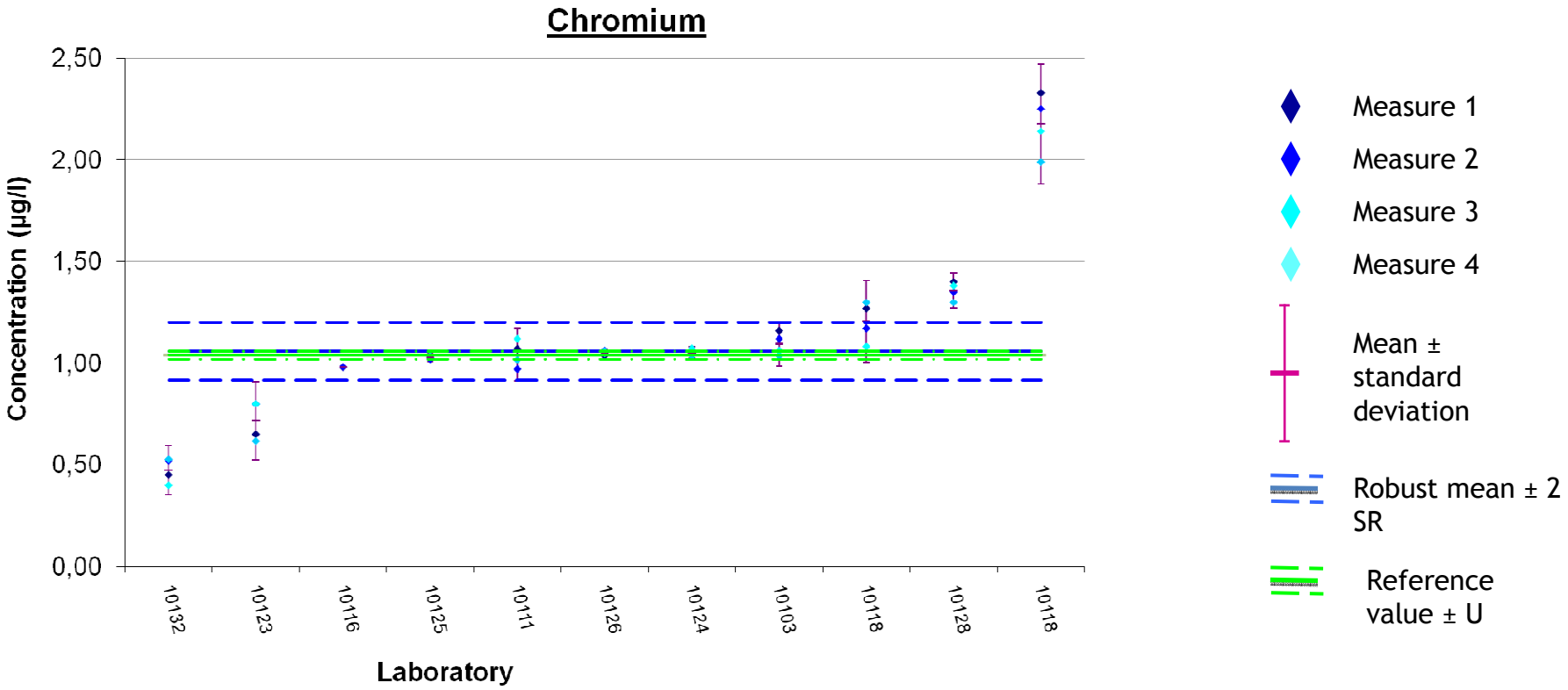
→ Attribution of reference value with U < 10%, except for Anthracene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene

QA/QC
in the AQUAREF
inter comparison exercise

Presentation of results, discussions

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

METALS

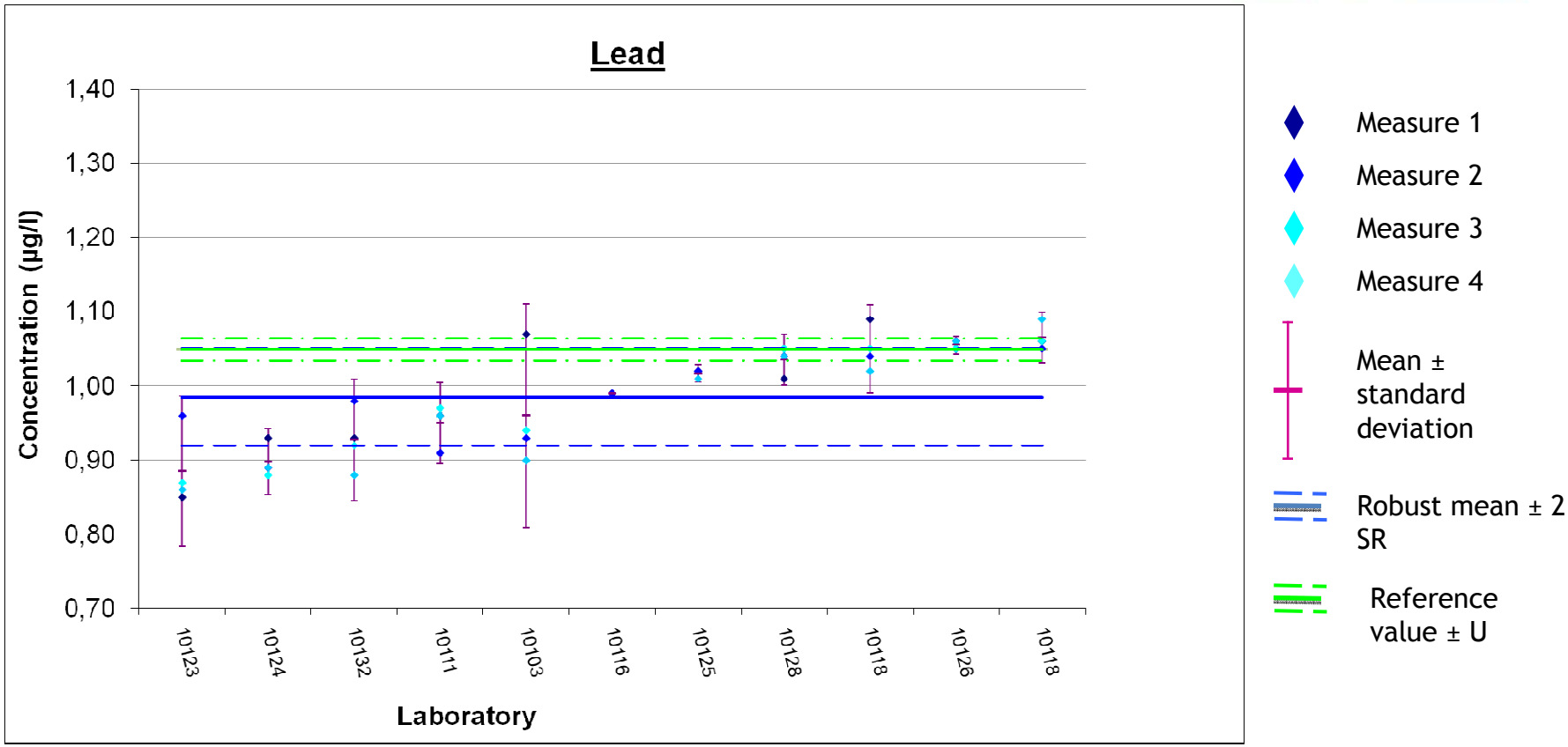


- Robust mean ≈ reference value
- Accuracy : precision + trueness of measurements the general population

→ Mastery of participants

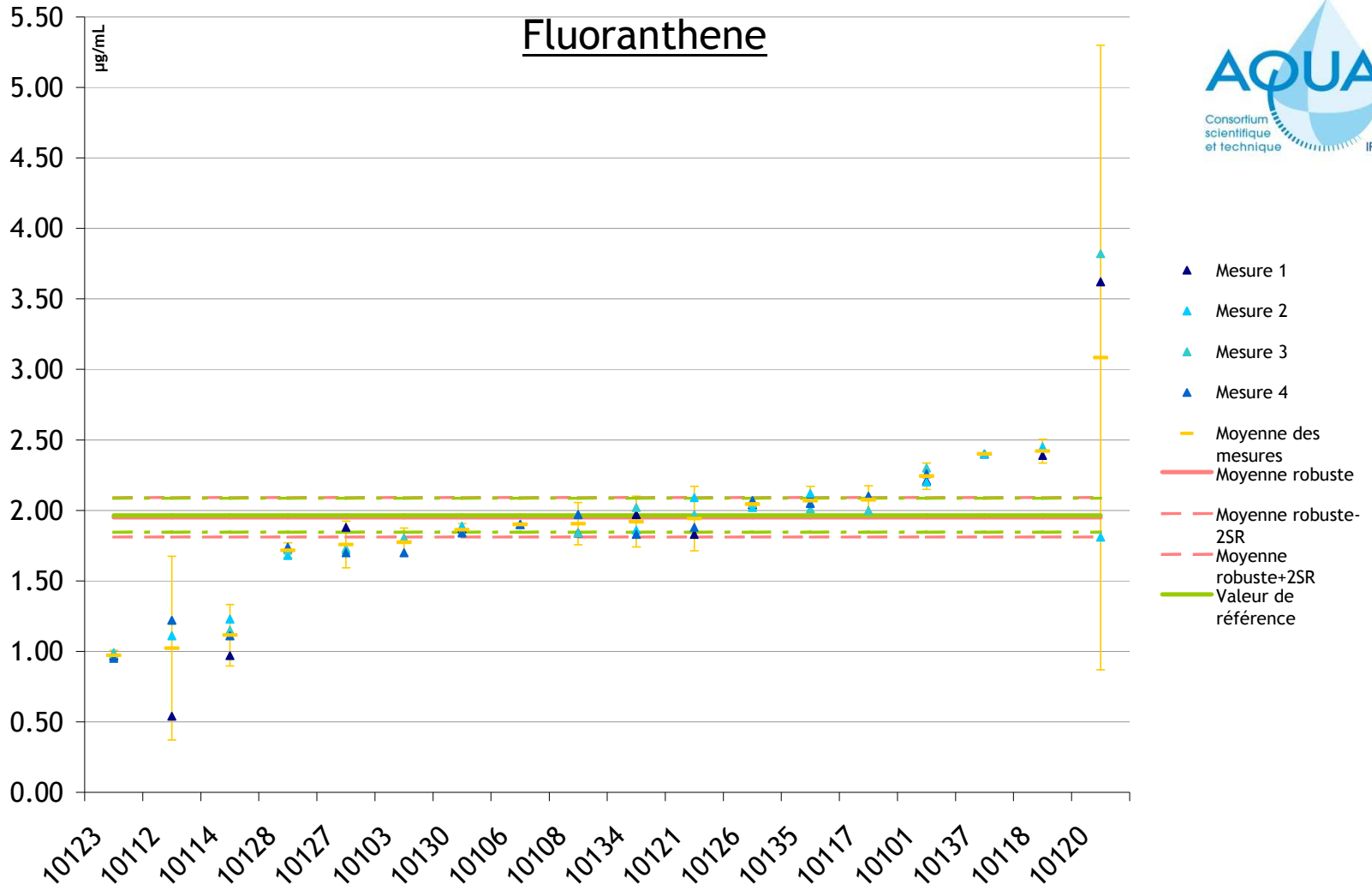
LABORATORY QUALITY CONTROL : REFERENCE SOLUTIONS FOR VERIFICATION OF INSTRUMENT CALIBRATION (2)

METALS



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

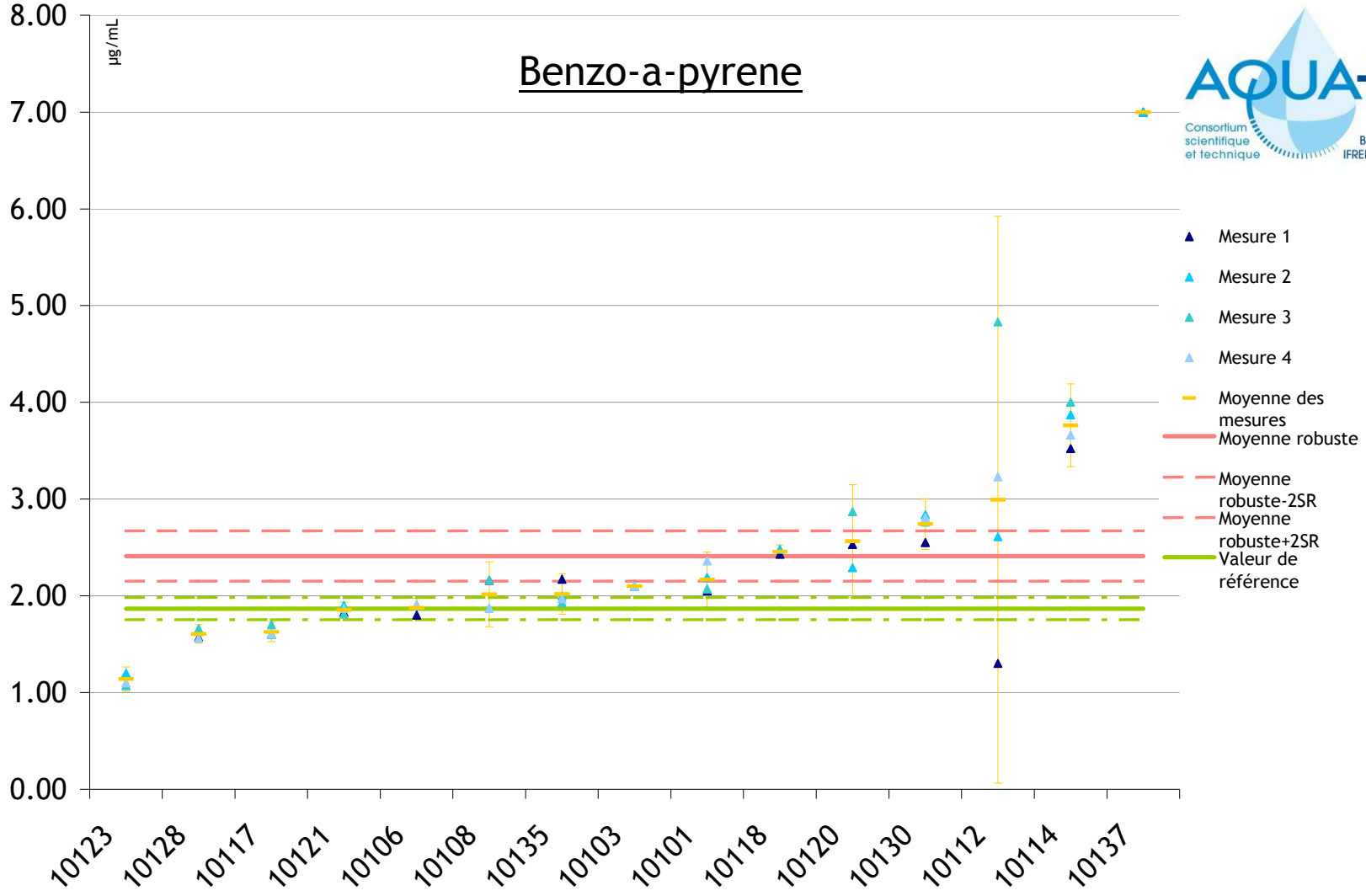
PAHs



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

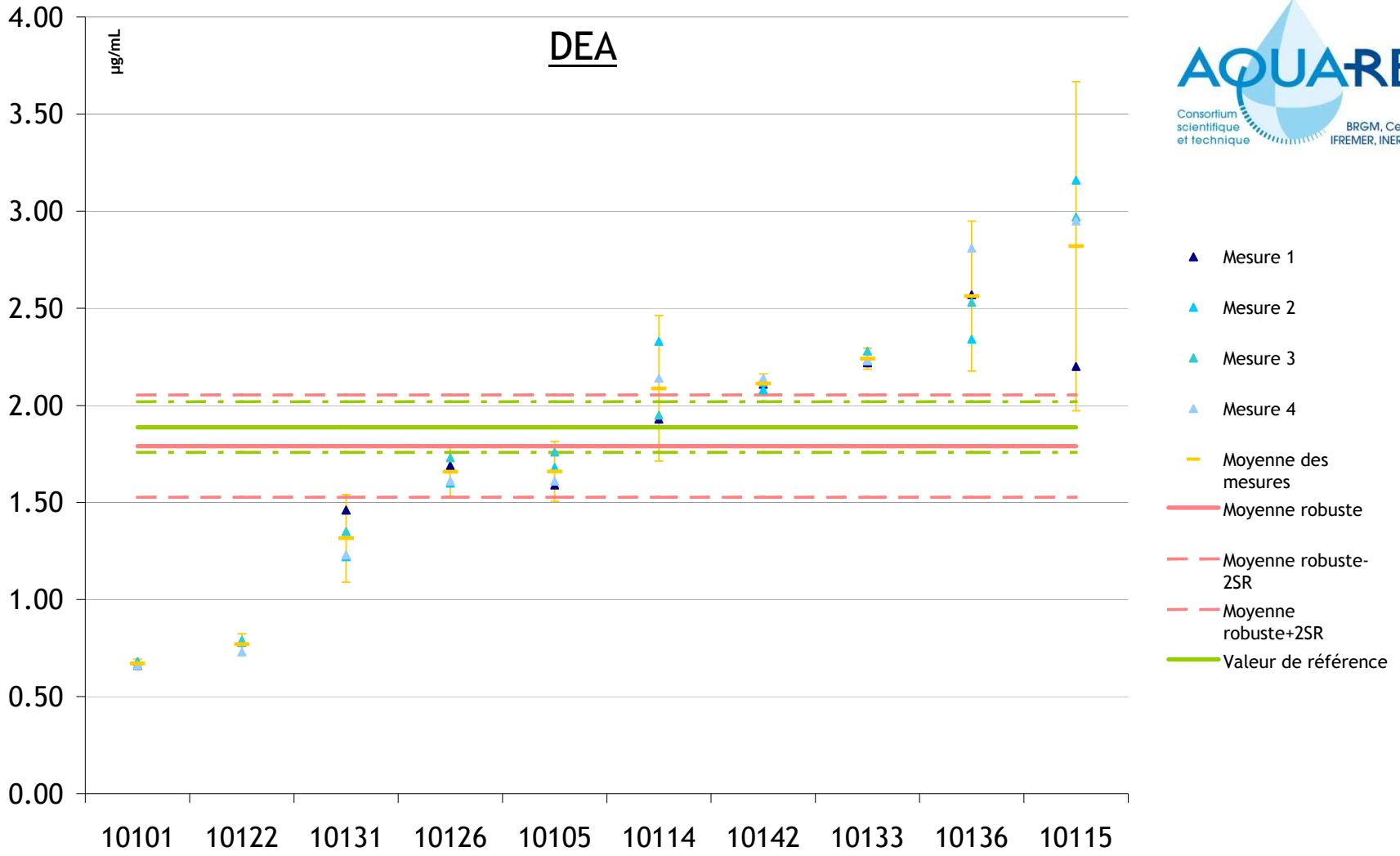
→ Mastery of participants

PAHs



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

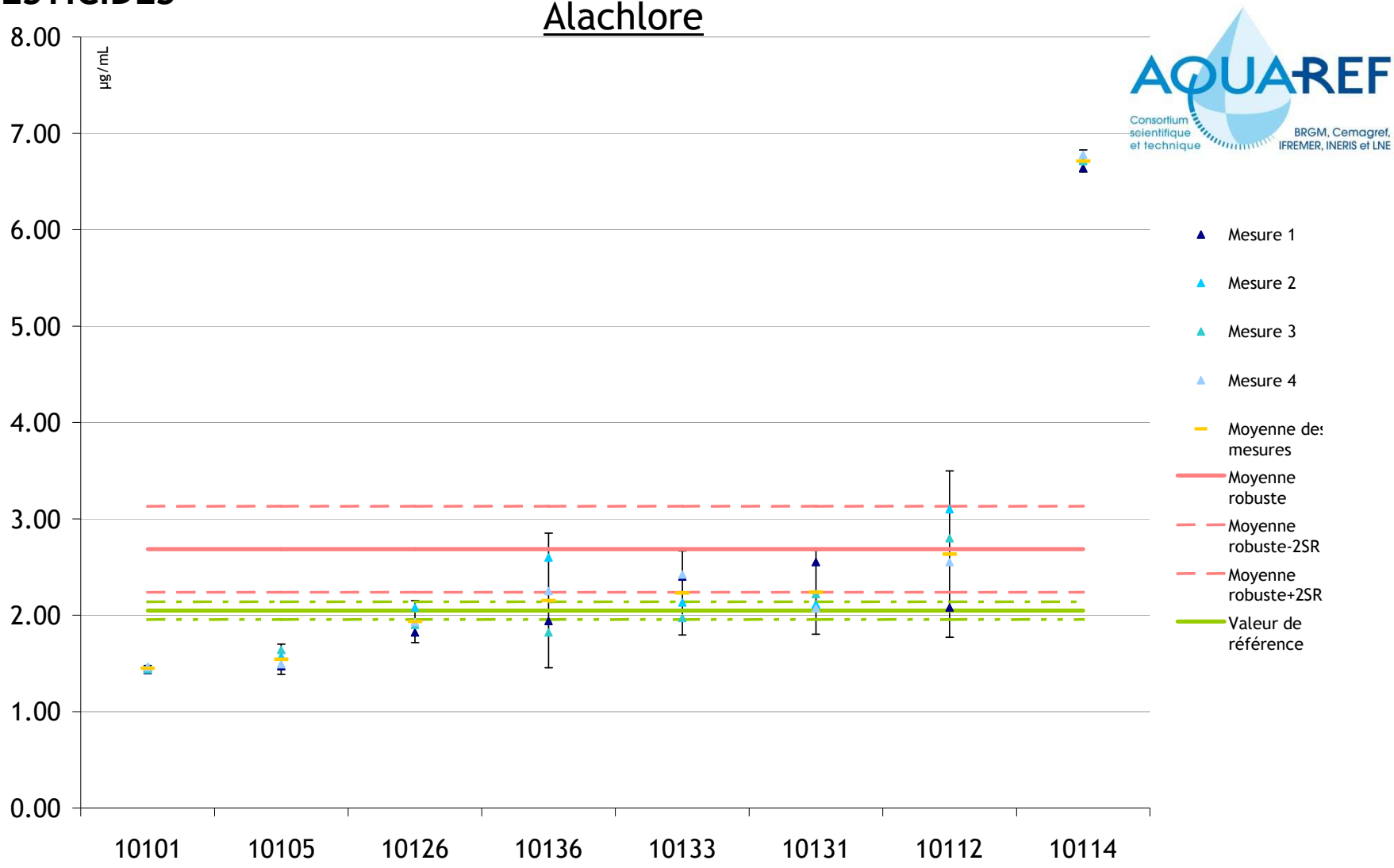
PESTICIDES



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

→ Mastery of participants

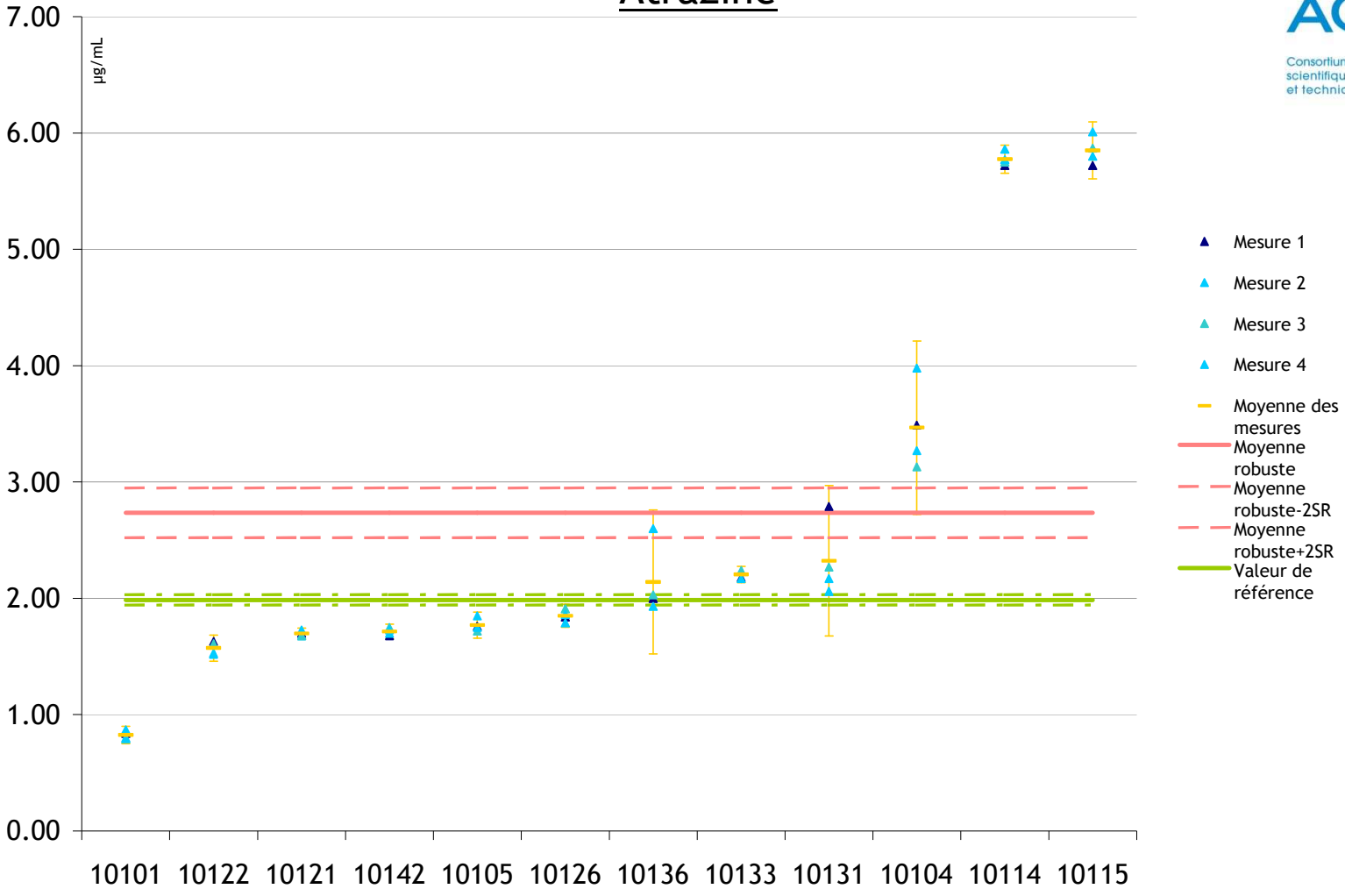
PESTICIDES



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

PESTICIDES

Atrazine



- 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:

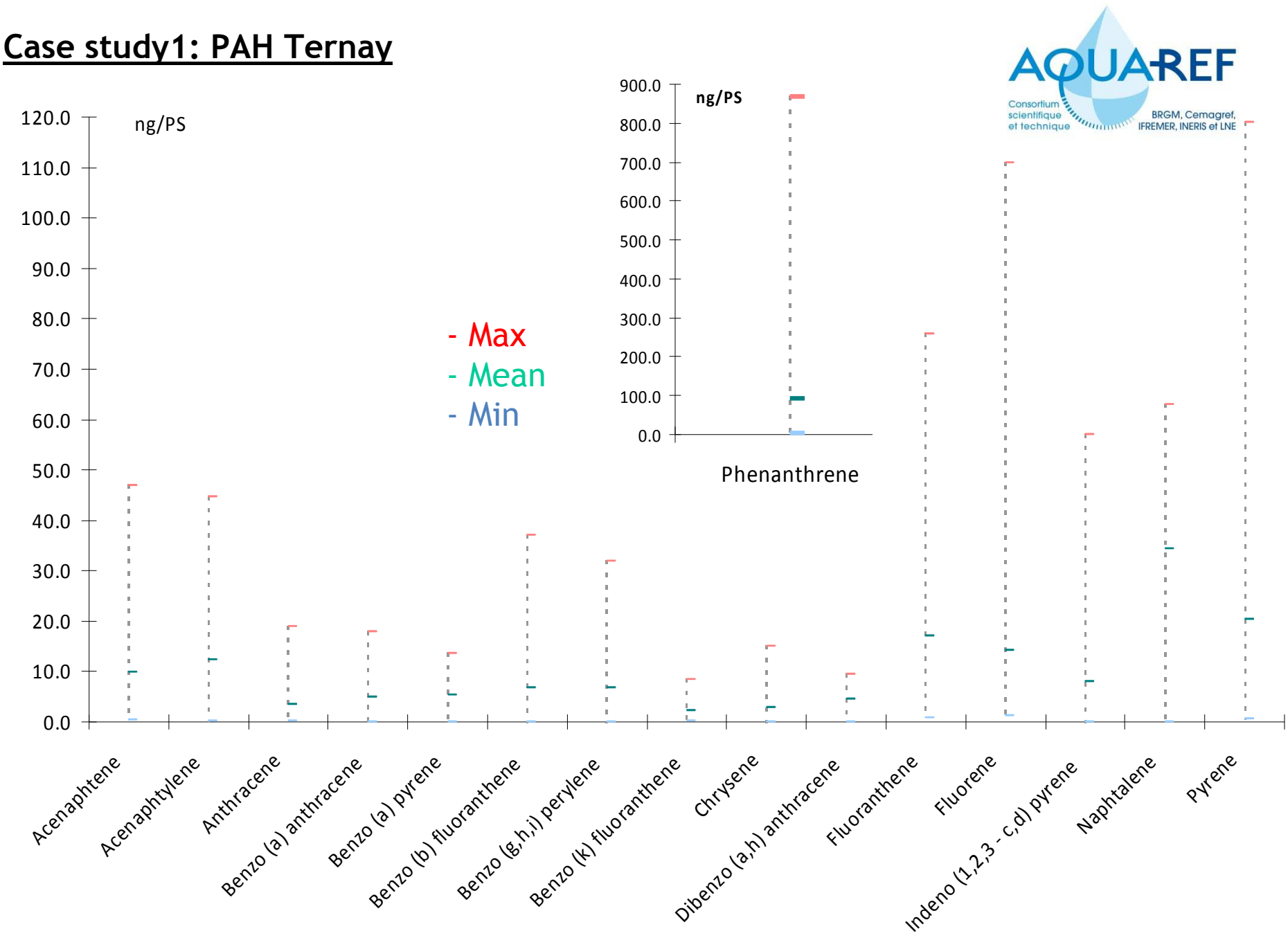
-No field blanks positive except for one compound in one PS and in one site

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

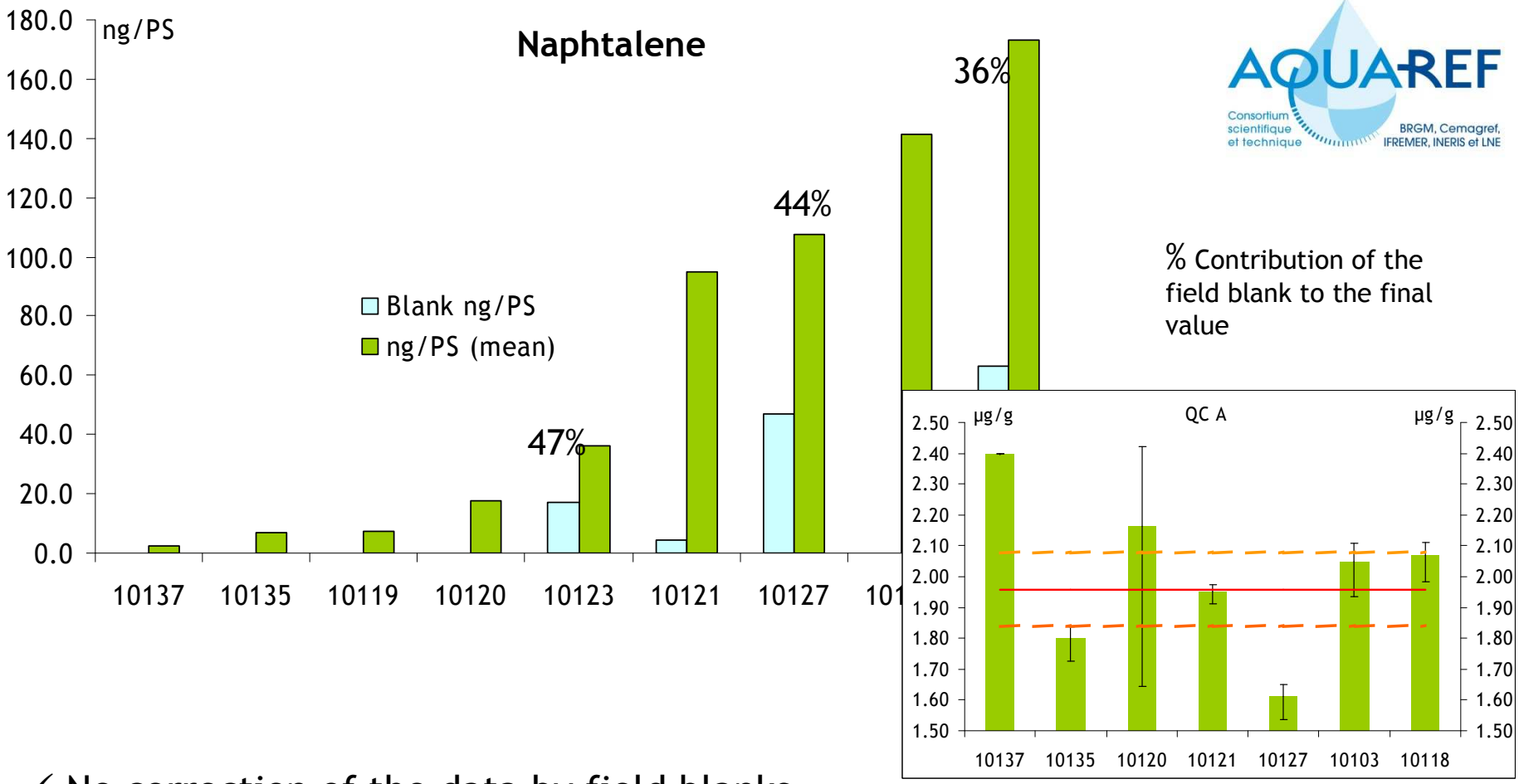
↻ ***Focus on PAHs***

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (3/8)

Case study1: PAH Ternay



FIELD QUALITY CONTROL : BLANK MEASUREMENTS (4/8)



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

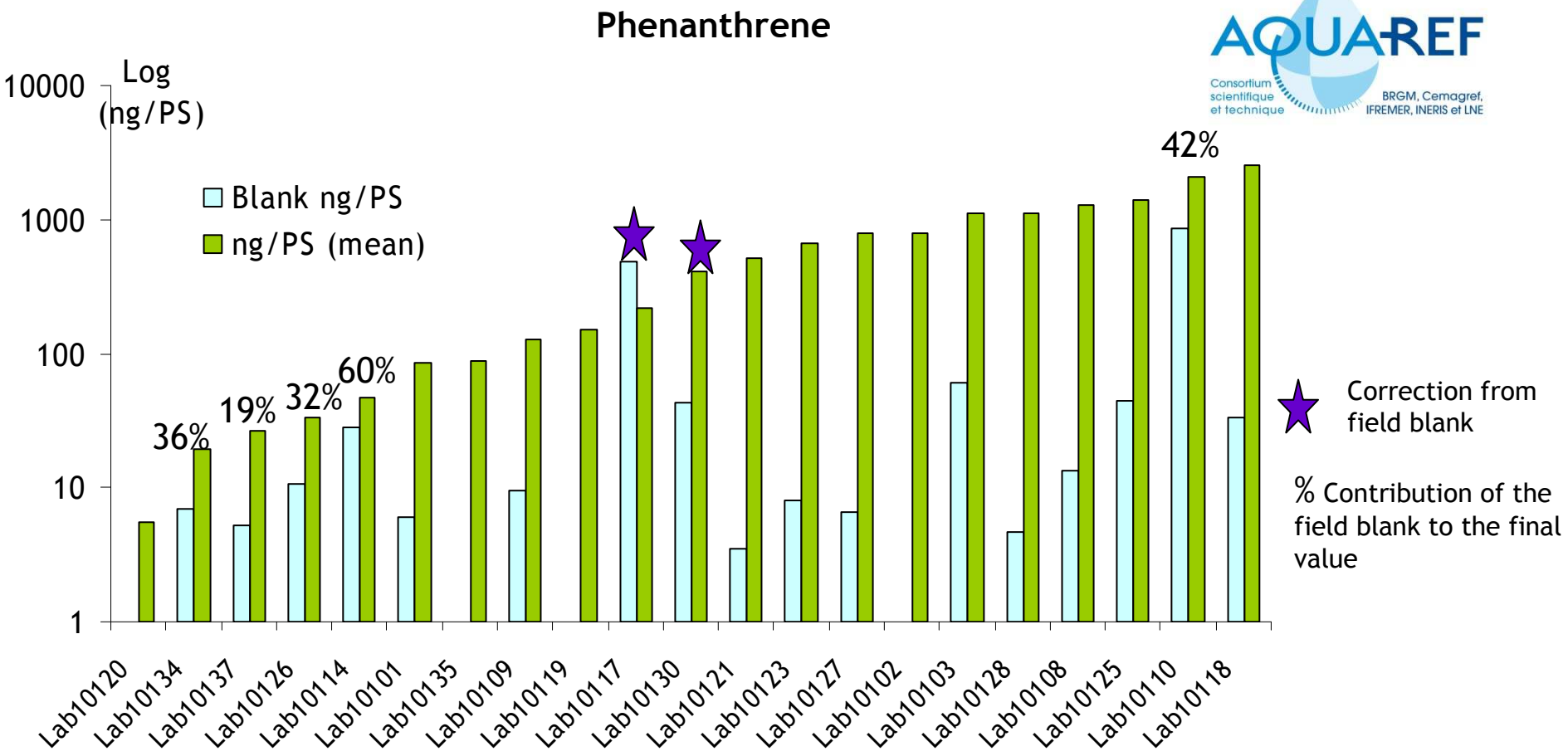
% Contribution of the field blank to the final value

✓ 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)

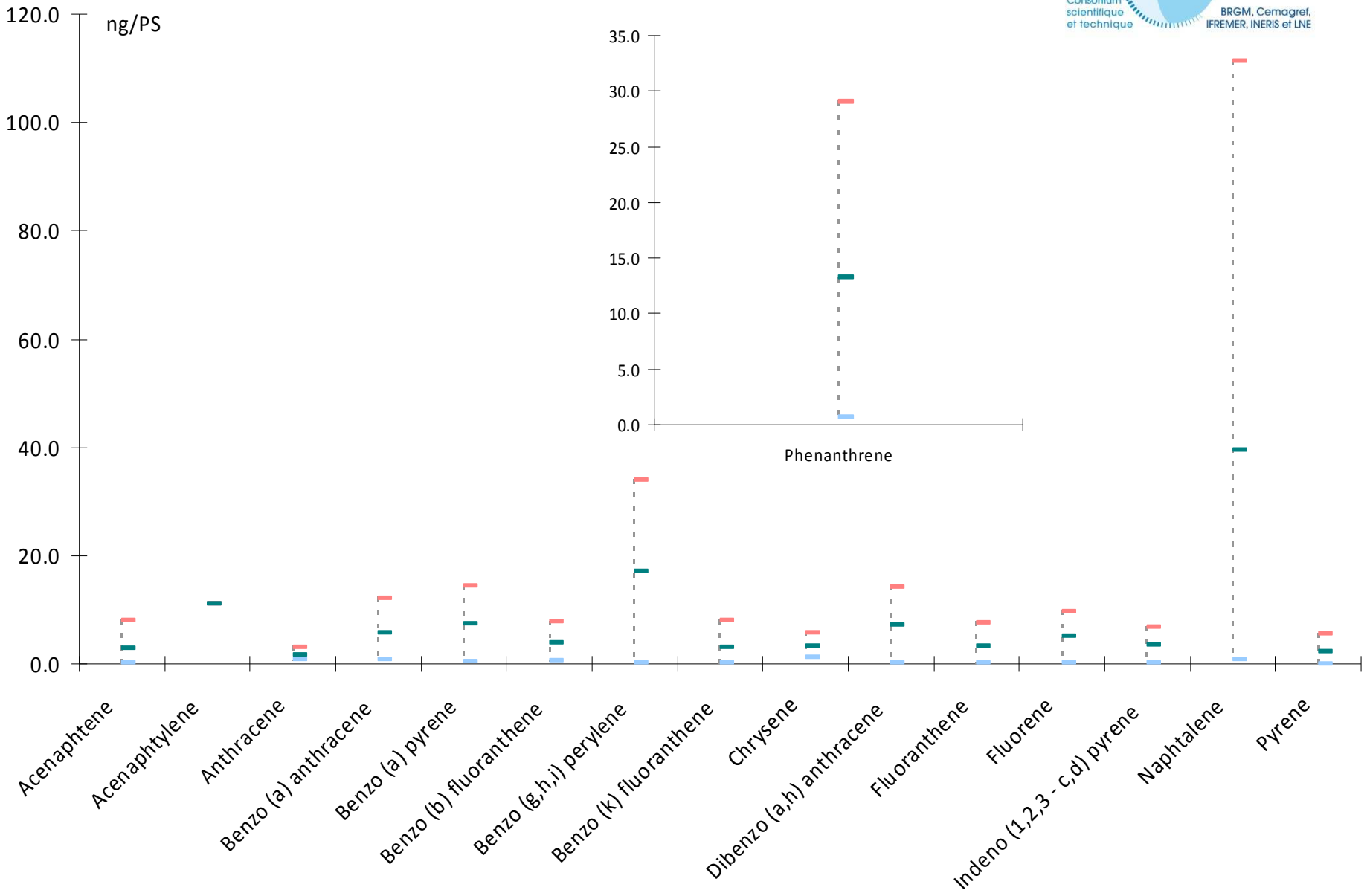


✓ No correction of the data by field blanks, except 2 labs.
✓ Field blanks close to 60% of deployed PS

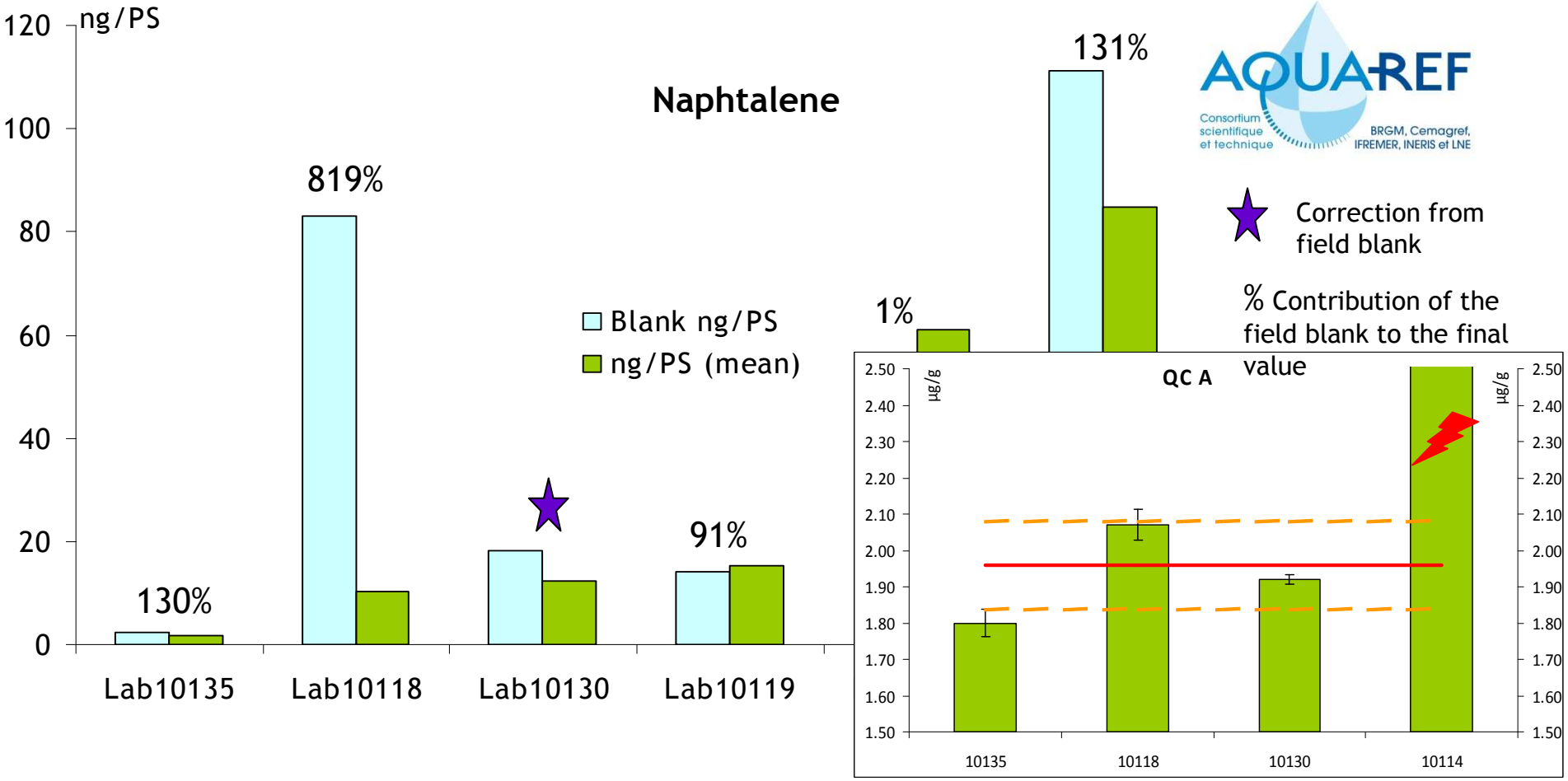
✓ No correlation with the type of PS, the type of extraction technique nor type of instrumental analysis, the quantification approach

FIELD QUALITY CONTROL : BLANK MEASUREMENTS (6/8)

Case study 2: PAH Thau



FIELD QUALITY CONTROL : BLANK MEASUREMENTS (7/8)

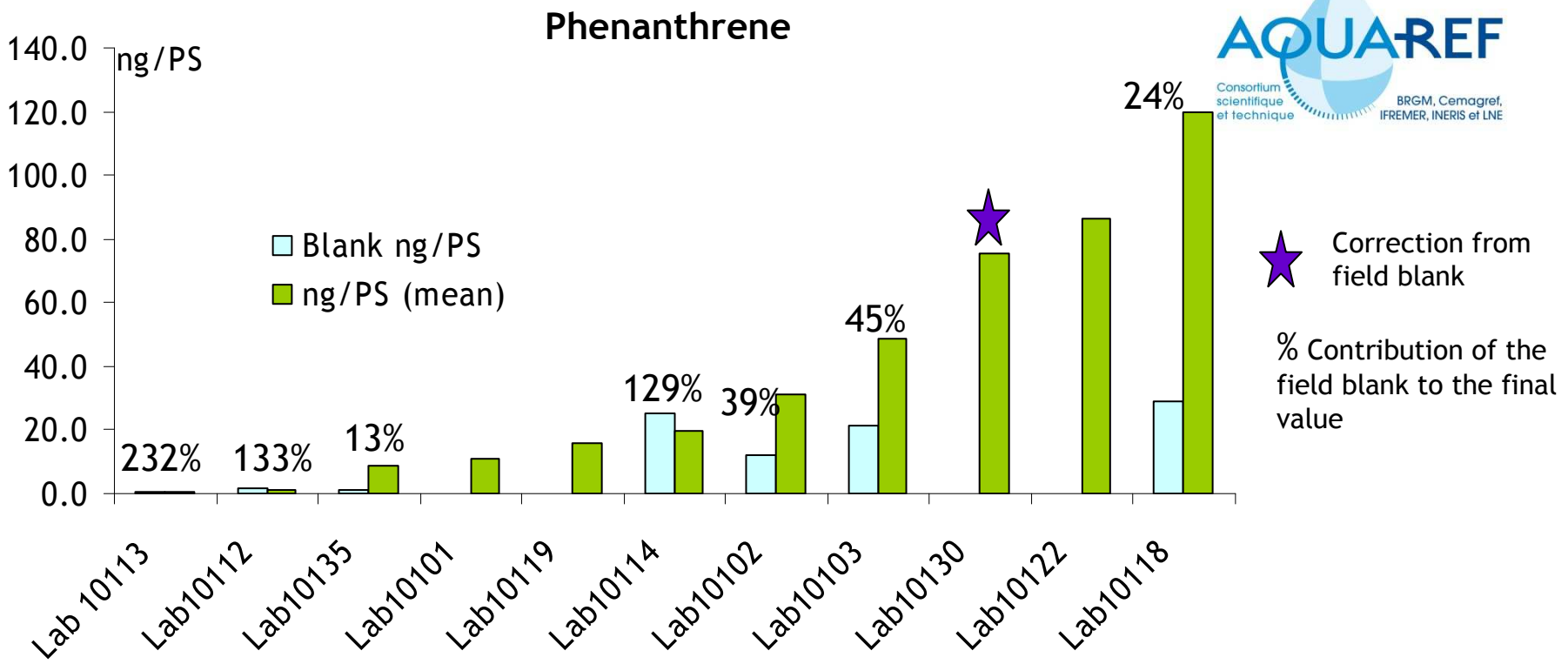


✓ No correction of the data by field blanks, except 1 lab.
✓ Field blanks close to 50% of deployed PS

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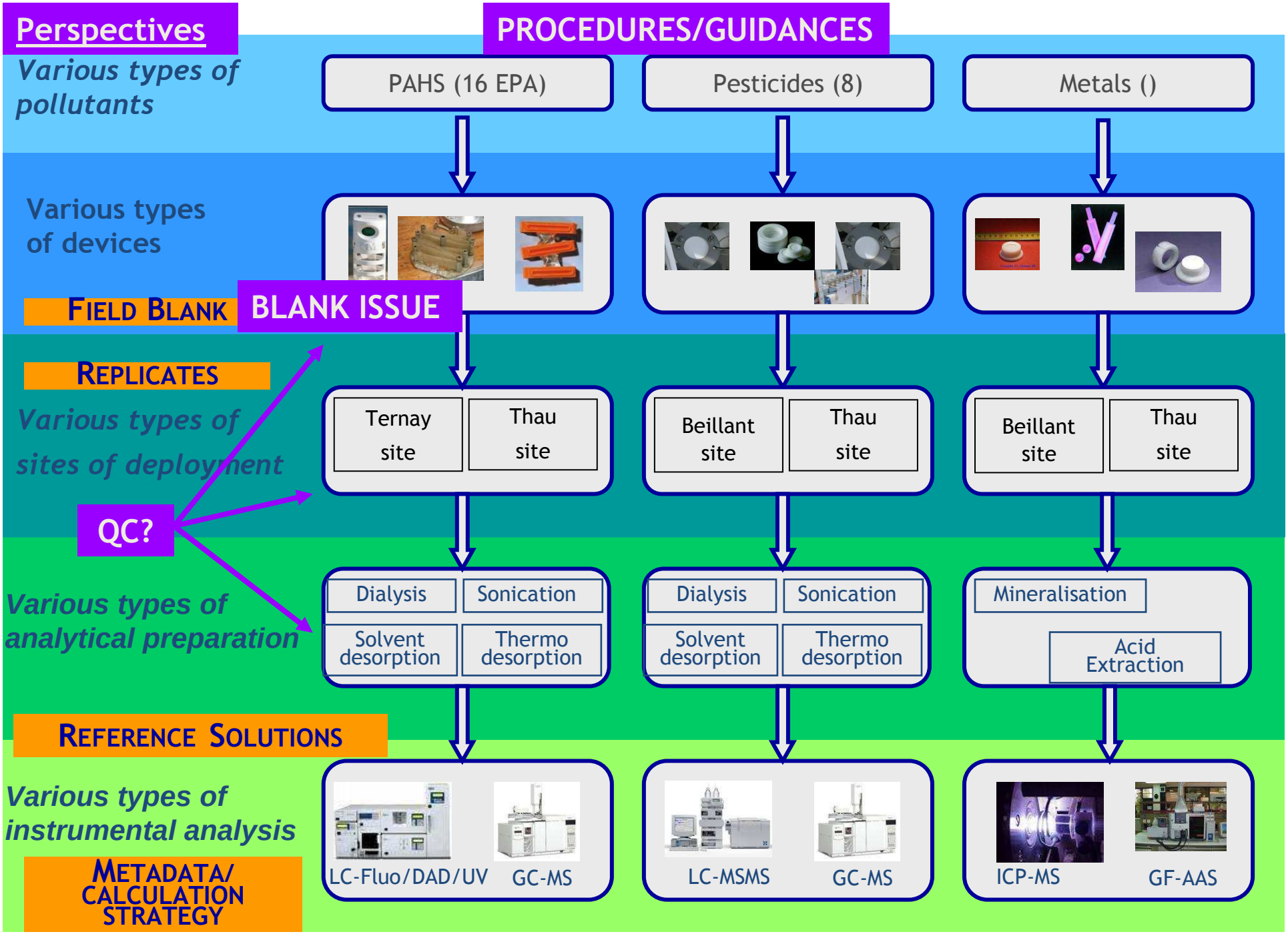
  - ➢ QA / QC (field and laboratory) with reference value
  - ➢ Replicat during deployment
  - ➢ Procedure (deployment and analysis)

- ✓ 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
Ternay site
Thau site
Beillant site
Thau site
Beillant site
Thau site
QC?
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
LC-Fluo/DAD/UV
GC-MS
LC-MSMS
GC-MS
ICP-MS
GF-AAS
METADATA/ CALCULATION STRATEGY