Final Workshop

Passive Sampler Intercomparison Exercise

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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

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

Sampling sites and planning

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

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 trueness 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).

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)

Various tools and exposure systems

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

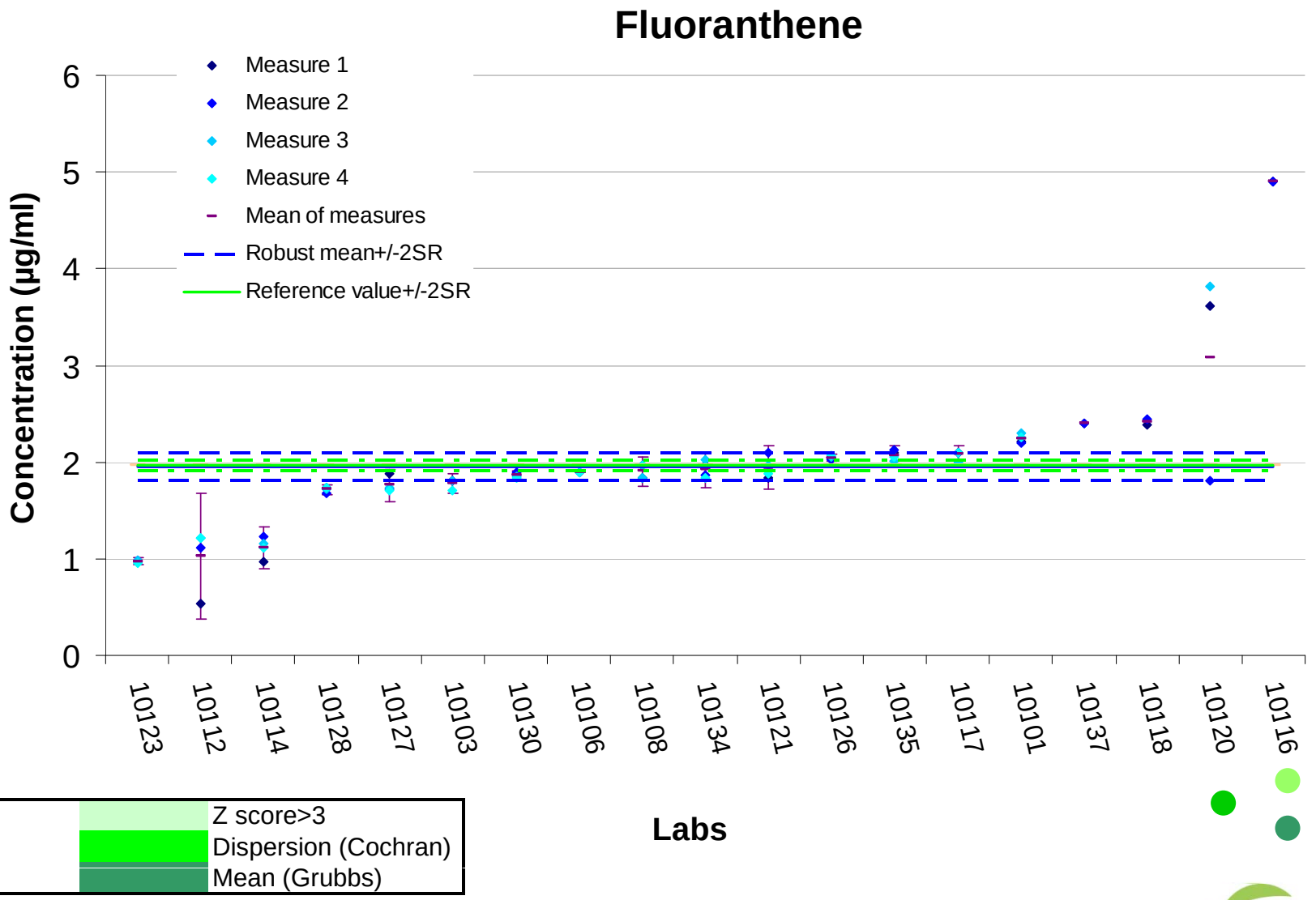
Substances	Tools and main characteristics
Metals	* DGT: binding agent (Chelex-100) with open pore or restrictive diffusive gels (thickness: 0.8 mm) * Chemcatcher (metals)
PAHs	* SPMD: standard, 460 cm2 * LDPE: from 390 to 490 cm2 * Chemcatcher (apolar), C18 : 15,9 and 17,4 cm2 * SR : 5, 160 et 600 cm2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

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

QC and standard solutions



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

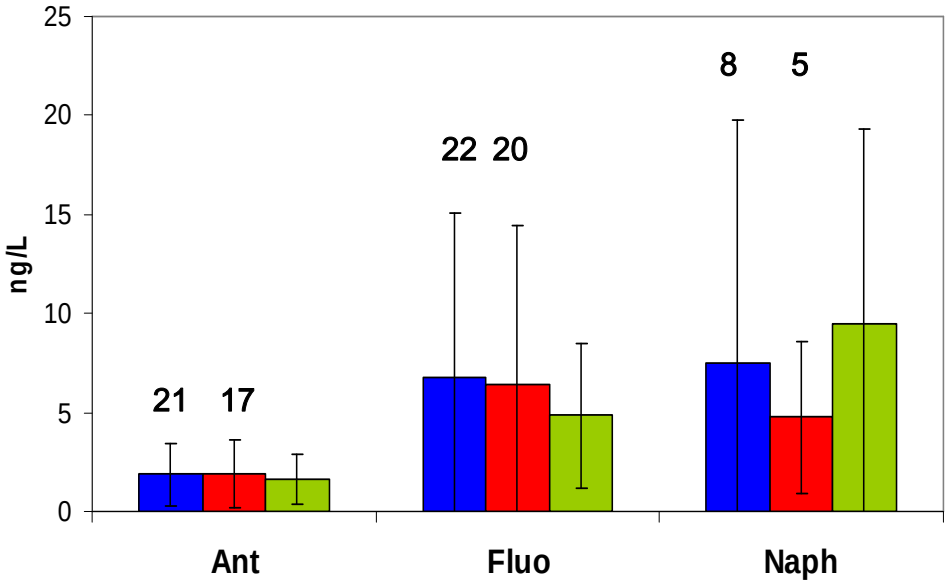
- Comparison on:
  - Arithmetic means and S_R with data of all lab.
  - Arithmetic means and S_R after elimination of QC outliers
  - Robust means (x*) and S_R with data of all lab.

PAH WATER CONCENTRATION (TWAC, ng/L)

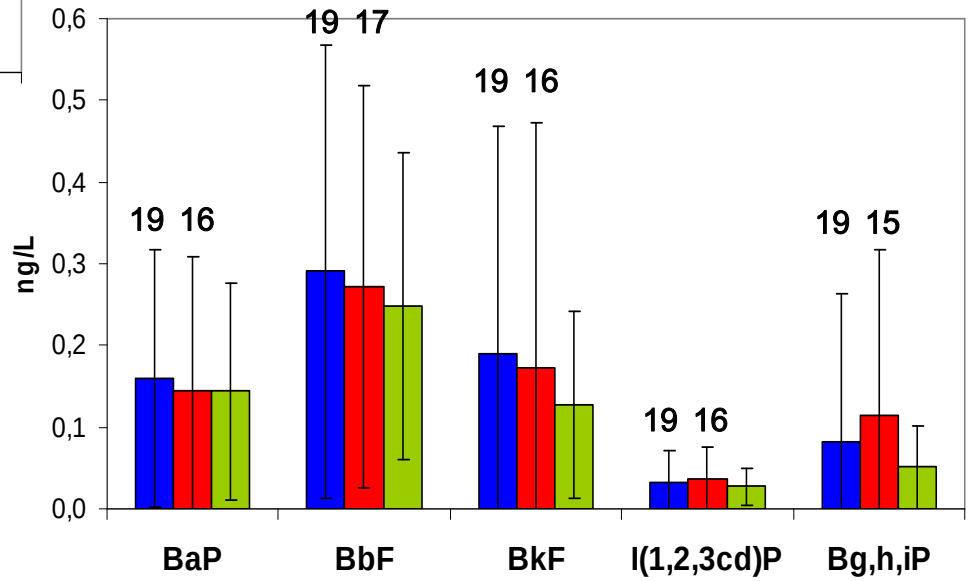
Means and sd (all participants)

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

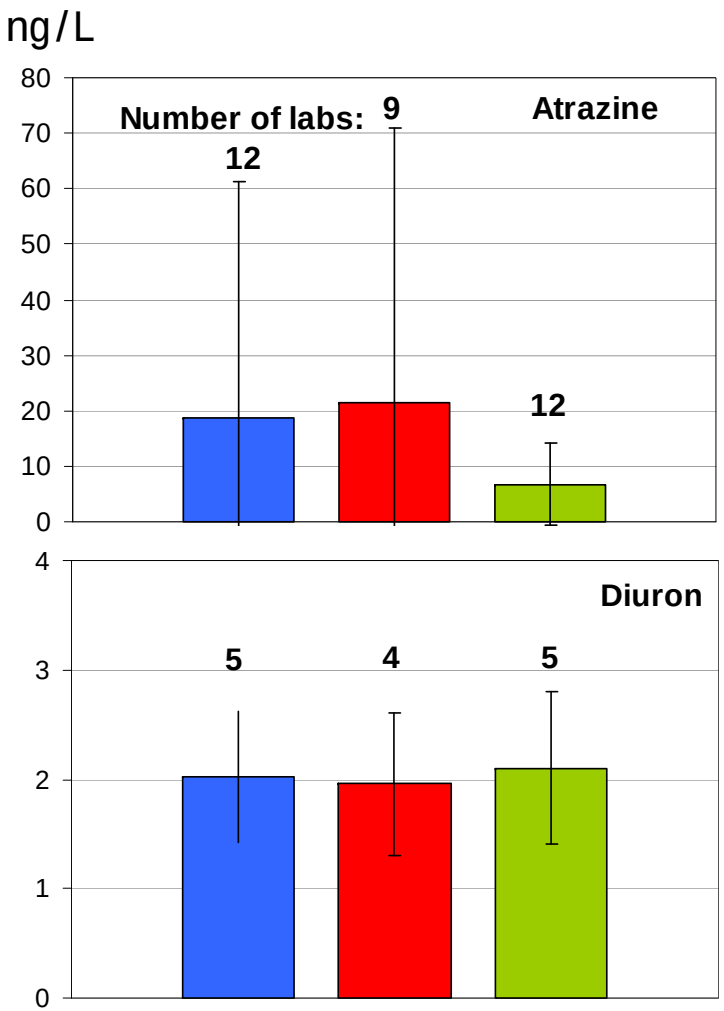
Pesticide WATER CONCENTRATION (TWAC, ng/L)

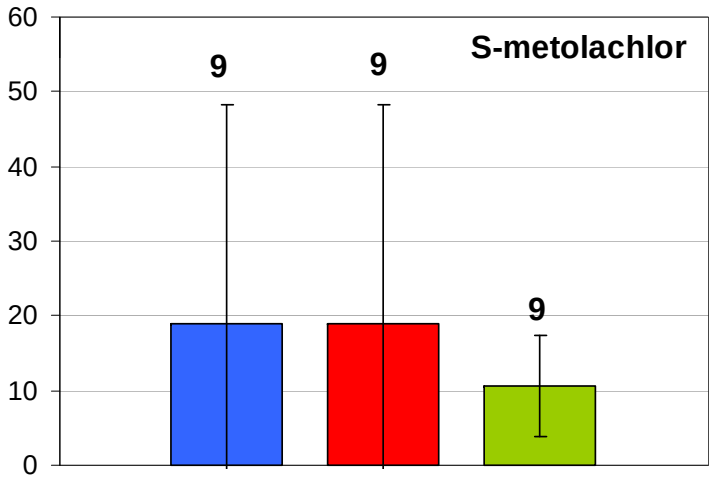
- For Beillant site:

Means and standard deviations (all participants)

Means and standard deviations (without QC outliers)

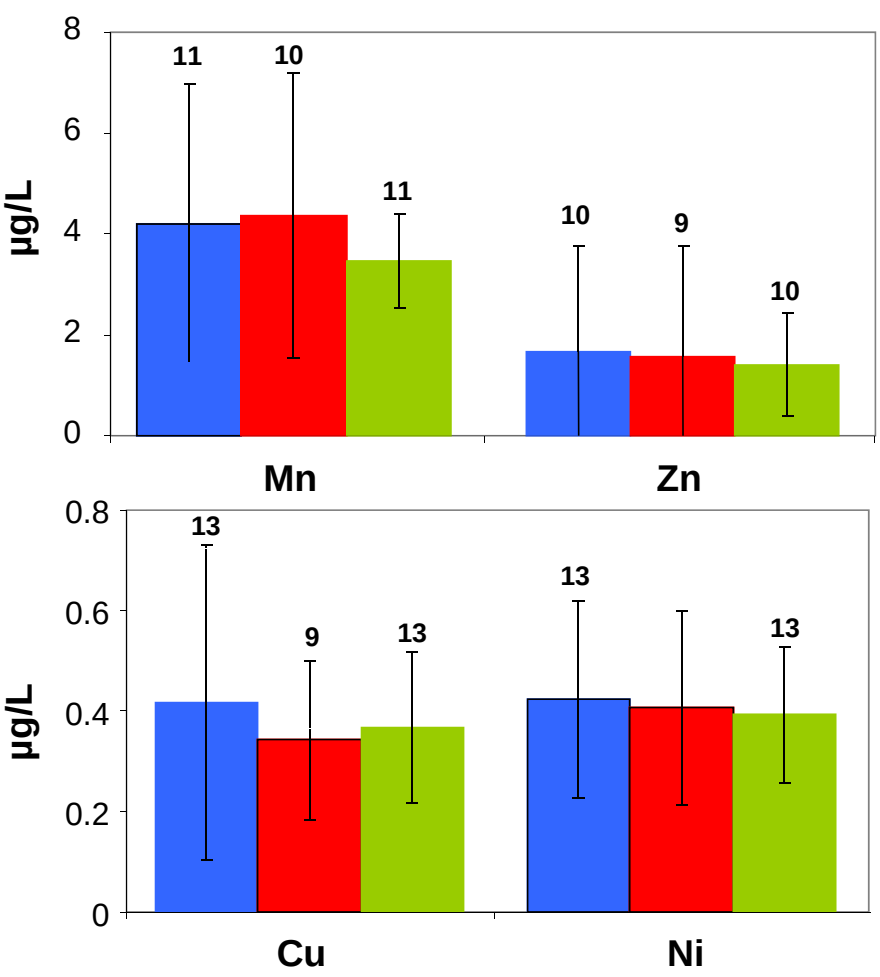
Robust statistic (all participants)

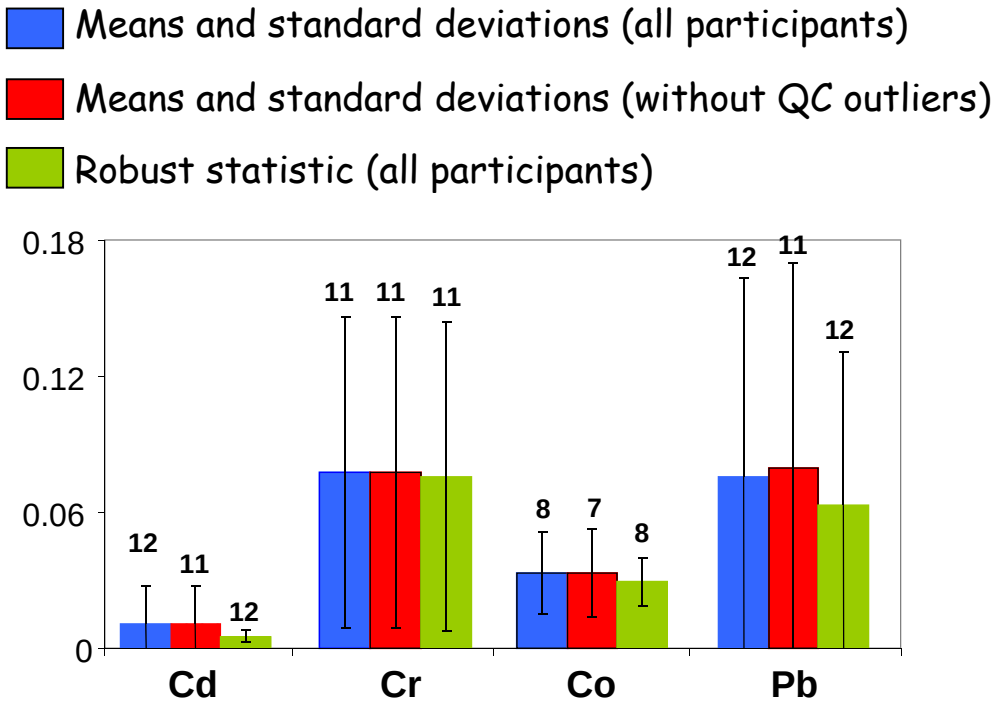




Metal WATER CONCENTRATION (TWAC, ng/L)

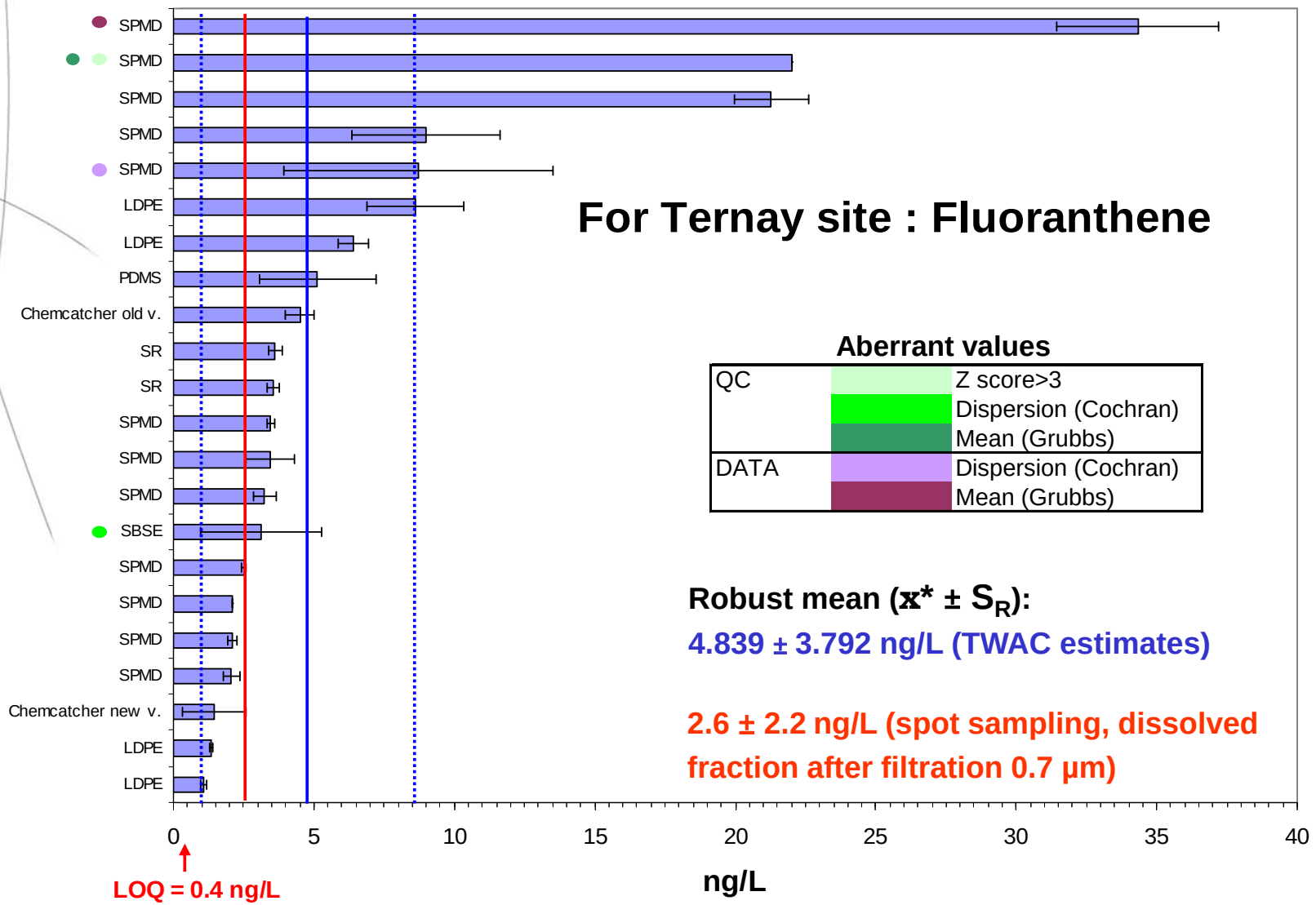
- Ternay site:





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

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



For Ternay site : Fluoranthene

Aberrant values

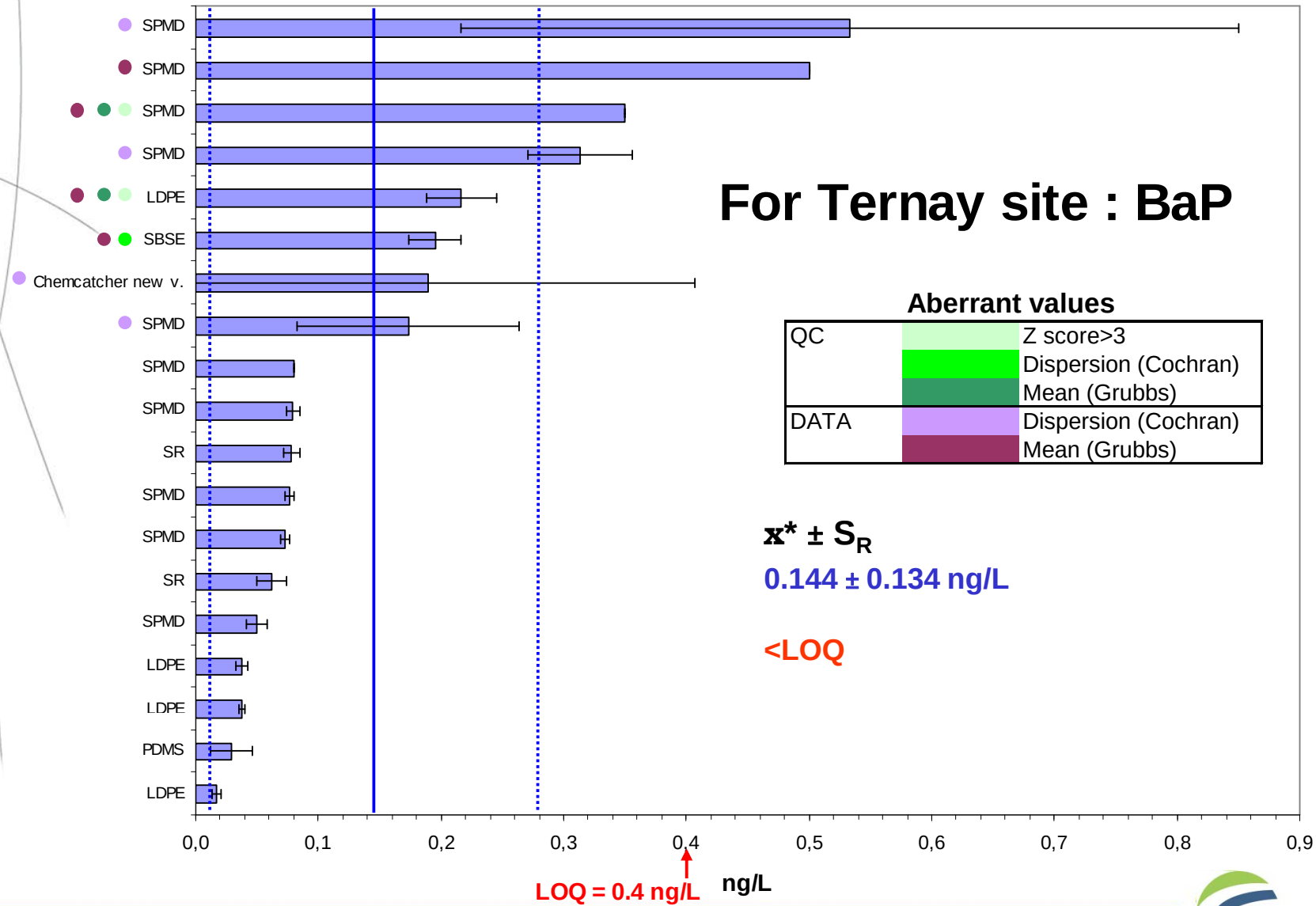
QC		Z score>3
		Dispersion (Cochran)
		Mean (Grubbs)
DATA		Dispersion (Cochran)
		Mean (Grubbs)

Robust mean ($x^* \pm S_R$):

4.839 ± 3.792 ng/L (TWAC estimates)

2.6 ± 2.2 ng/L (spot sampling, dissolved fraction after filtration 0.7 µm)

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



For Ternay site : BaP

Aberrant values

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

$x^* \pm S_R$

0.144 ± 0.134 ng/L

<LOQ

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

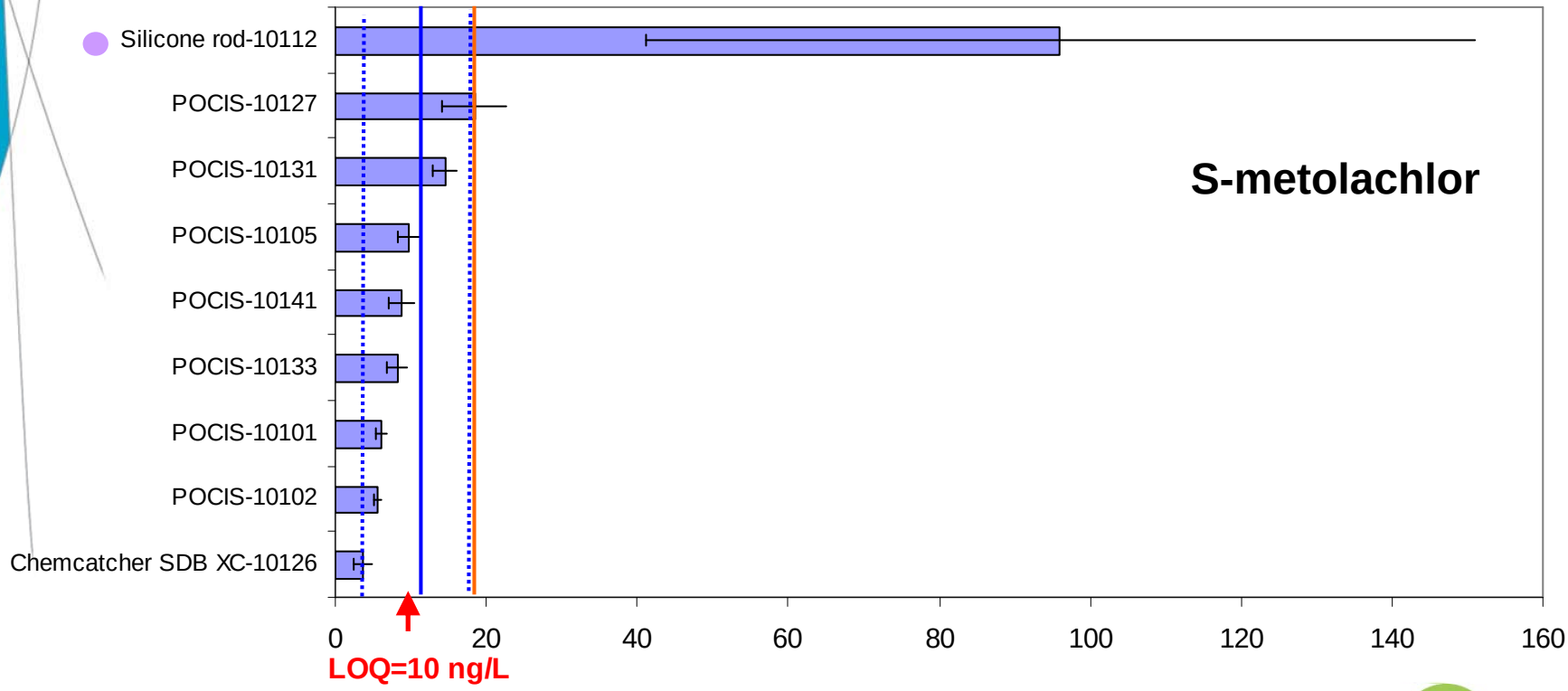
- For Beillant site:

$x^* \pm S_R$

10.6 ± 6.7 ng/L (TWAC estimates)

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

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



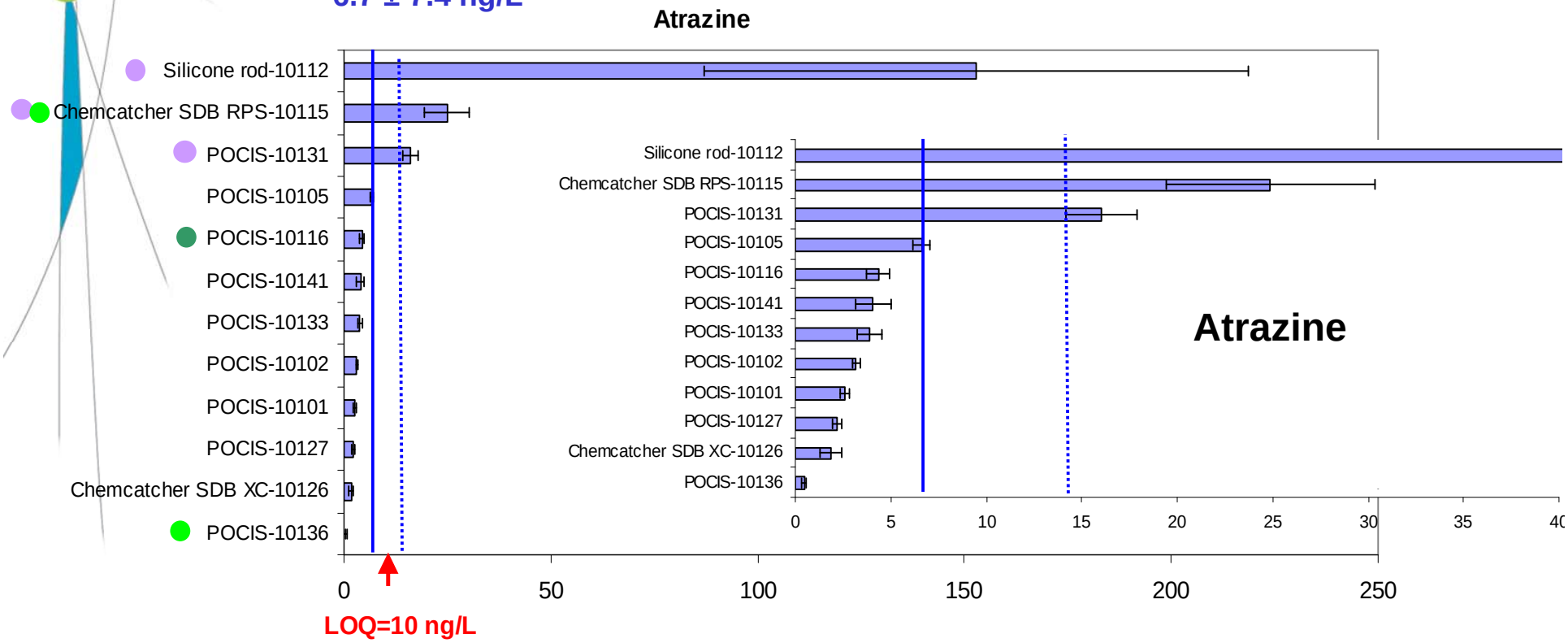
Comparison of pesticides water concentration (ng/L) from various tools and lab.

- For Beillant site:

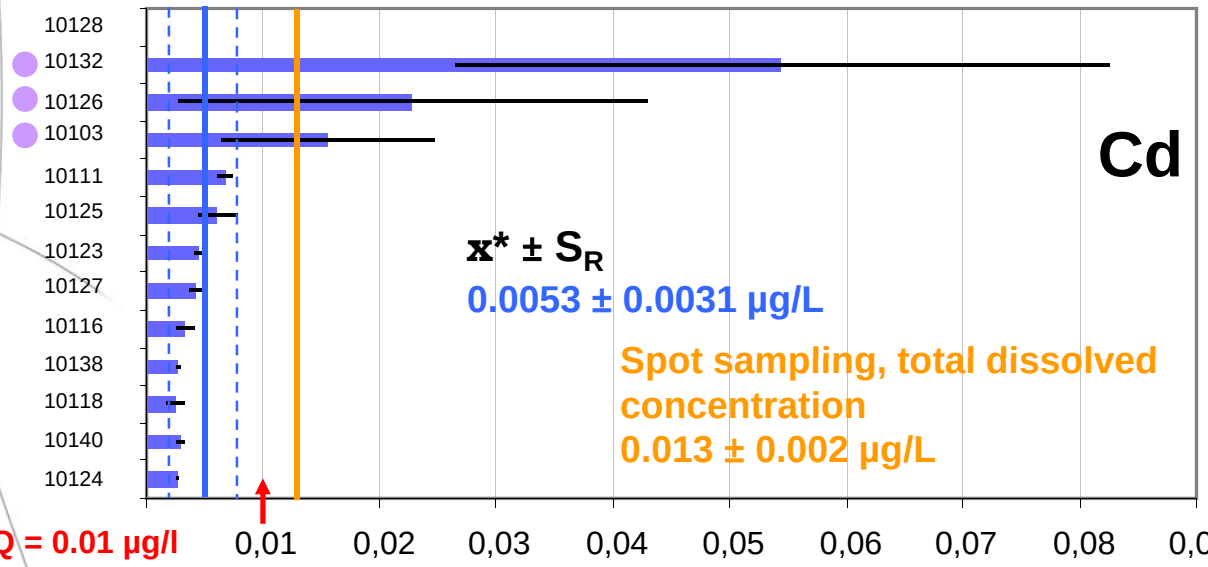
Aberrant values		
QC		Z score>3
		Dispersion (Cochran)
		Mean (Grubbs)
DATA		Dispersion (Cochran)
		Mean (Grubbs)

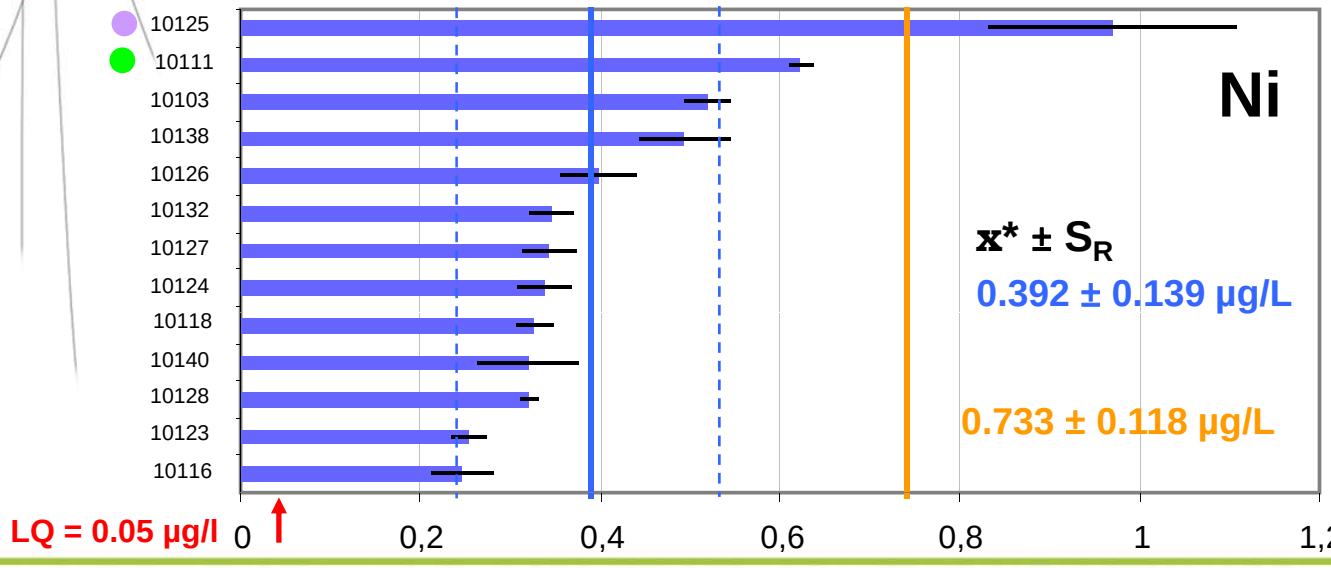
$x^* \pm S_R$

6.7 ± 7.4 ng/L



Comparison of metal water concentration (µg/L) from various lab.



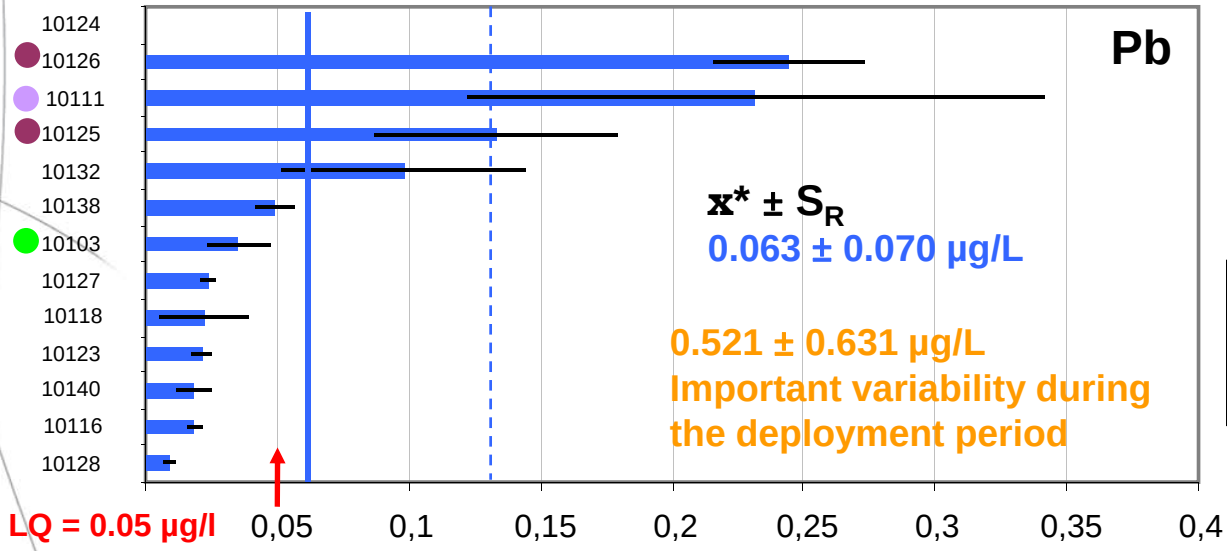


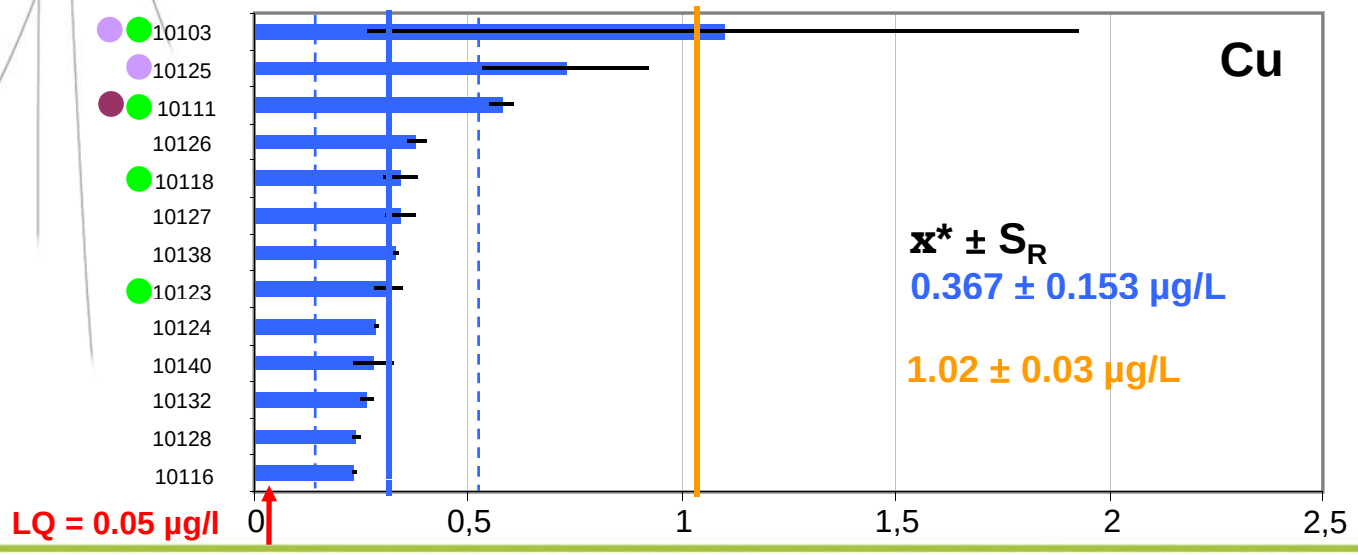
- For Ternay site:

Aberrant values

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

Comparison of metal water concentration (µg/L) from various lab.





- For Ternay site:

Aberrant values

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

Mean TWAC and its variability

Parameters	*Population mean*	*Population standard deviation*	*Robust mean (x*)*	*Robust reproductibility standard deviation (SR)*	*Robust reproductibility relative standard deviation (SR)*	*n*
Units	*ng/L for organics, µg/L for metals*				*%*	
			All passive samplers			
benzo(a)anthracene	0.812	0.805	0.806	0.758	94	21
benzo(a) pyrene	0.160	0.157	0.144	0.134	93	19
benzo(b) fluoranthene	0.291	0.278	0.248	0.190	77	20
benzo(k) fluoranthene	0.191	0.277	0.127	0.115	91	19
dibenzo(a,h)anthracene	0.021	0.050	0.008	0.007	88	11
indeno(1,2,3cd)pyrene	0.032	0.039	0.027	0.023	85	14
phenanthrene	7.924	9.436	5.757	4.612	80	22
acenaphtene	8.295	8.033	6.606	5.580	84	18
acenaphtylene	8.849	24.661	1.603	2.085	130	14
anthracene	1.883	1.573	1.594	1.287	81	21
benzo(g,h,i)perylene	0.083	0.180	0.051	0.051	100	15
chrysene	1.079	0.976	1.069	0.940	88	21
fluoranthene	6.758	8.349	4.839	3.792	78	22
fluorene	5.373	5.207	4.913	4.590	93	21
naphtalene	7.535	12.230	9.495	9.847	104	8
pyrene	5.213	4.548	4.797	3.041	63	22
			All passive samplers			
acetochlor	4.064	3.423	3.843	3.932	102	5
alachlor	2.036	1.262	1.858	1.558	84	2
atrazine	18.571	42.858	6.735	7.455	111	12
deethylatrazine	36.639	36.439	35.890	39.977	111	7
deisopropylatrazine	9.148	7.733	7.520	4.525	60	7
diuron	2.028	0.601	2.103	0.763	36	5
isoproturon	0.413	0.121	0.413	0.148	36	3
metalochlor	19.014	29.257	10.647	7.023	66	9
simazine	21.860	3.936	6.613	5.753	87	8
			All passive samplers			
cadmium	0.0107	0.0151	0.0053	0.0031	59	12
chrome	0.0773	0.0599	0.0756	0.0705	93	11
cobalt	0.0332	0.0177	0.0292	0.0111	38	9
cuivre	0.4168	0.2488	0.3672	0.1533	42	13
manganese	4.2124	2.7857	3.4760	0.9902	28	11
nickel	0.4231	0.1965	0.3920	0.1390	35	13
plomb	0.0755	0.0843	0.0630	0.0705	112	12
zinc	1.6674	1.5392	1.4050	1.1034	79	10

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

- For Thau Lagoon site:

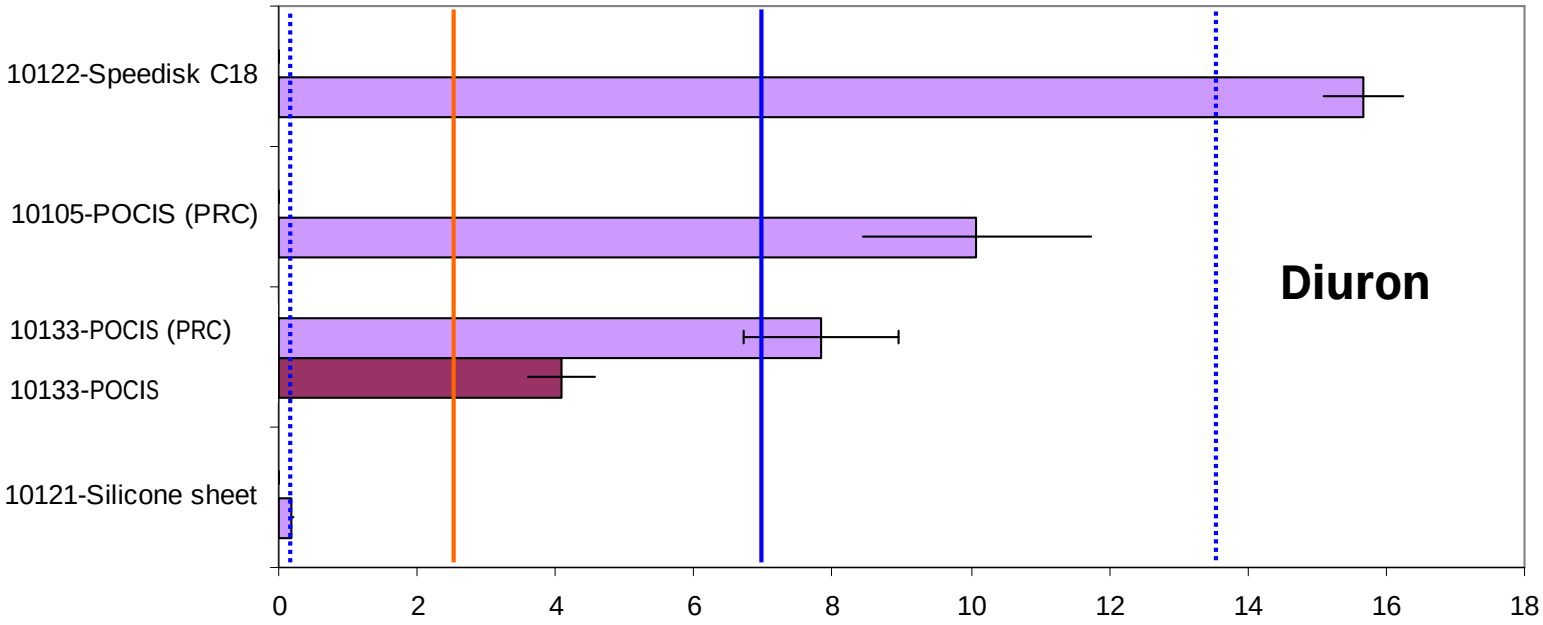
Aberrant values

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

$x^* \pm S_R$

7.5 ± 6.8 ng/L

2.4 ± 0.3 ng/L (spot sampling, filtered water)

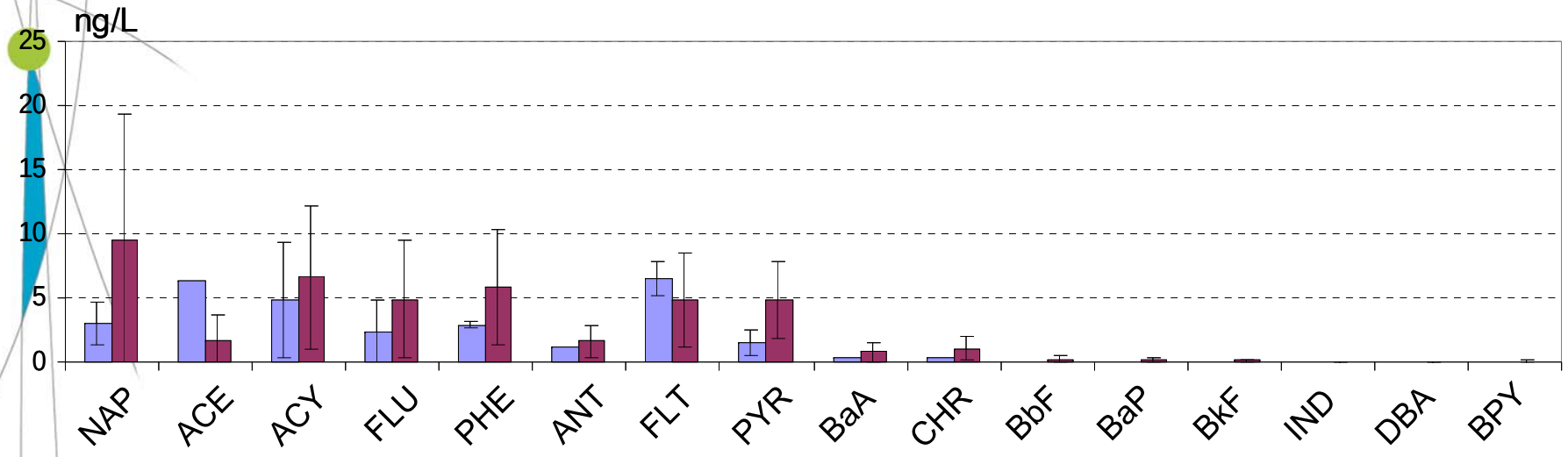


☛ Very few data… but two labs used the same PRC (DIA-*d*5)

PAH WATER CONCENTRATION (ng/L)
Passive sampling – Spot sampling

Spot sampling: dissolved fraction after filtration 0.7 µm

Passive sampling (robust statistics)



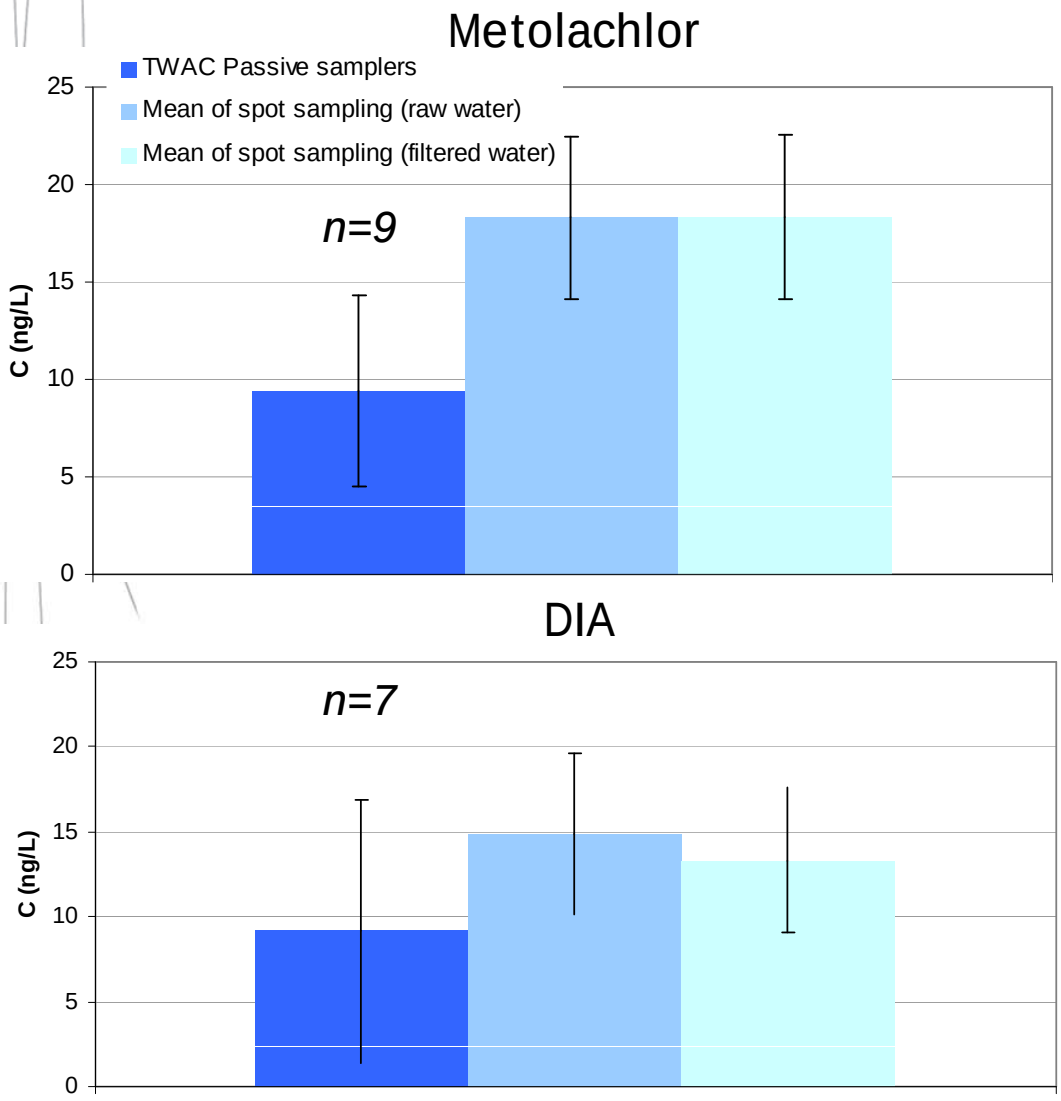
✓ Same range of concentration levels

✓ Higher concentration levels with passive sampling

✓ Different time scale: spot sampling / integrative sampling

Different fractions: need for a better characterization of the fraction sampled by passive sampling

Pesticide WATER CONCENTRATION (ng/L)
Passive sampling – Spot sampling

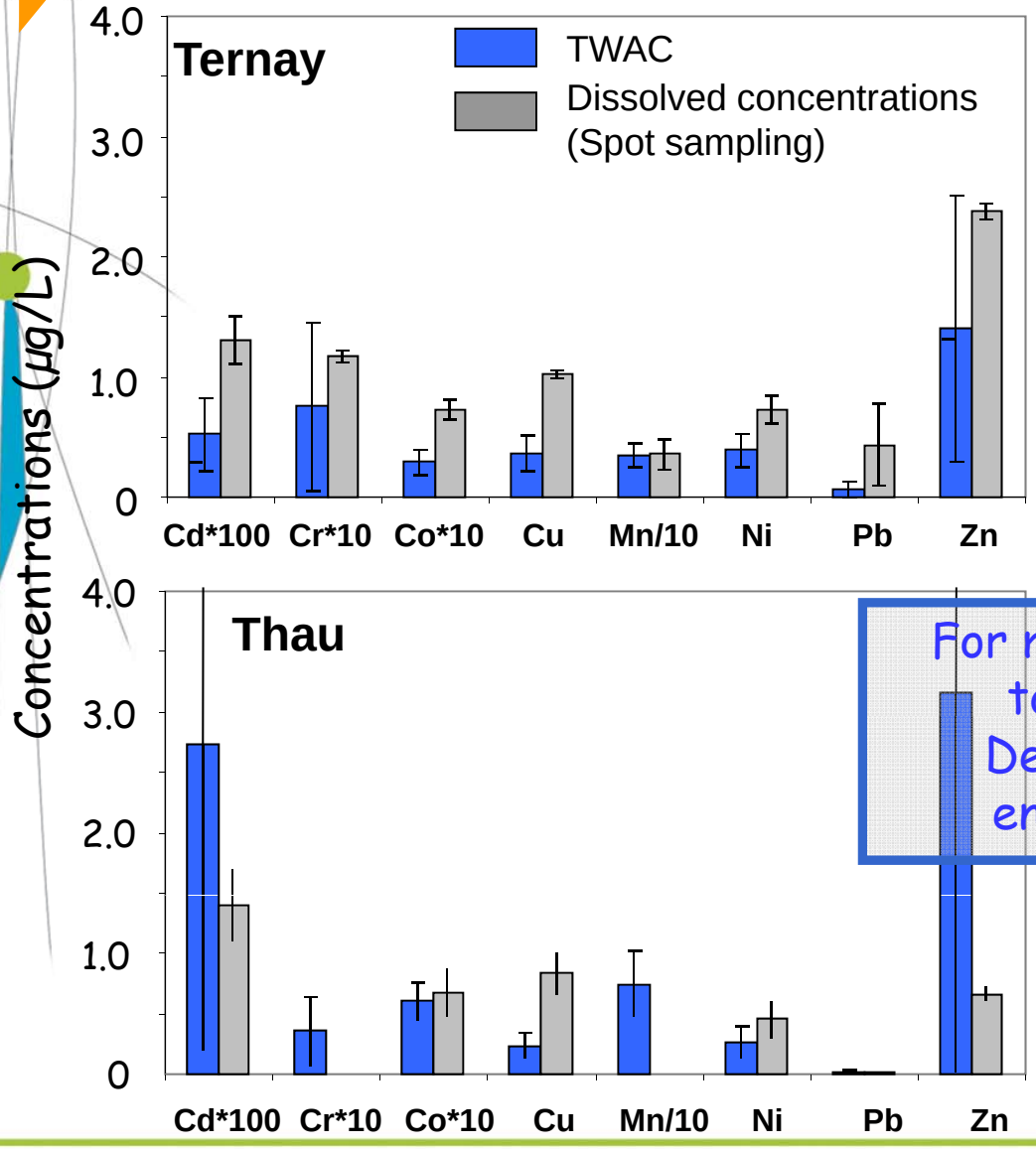


- *For Beillant site*

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

However, relatively higher data dispersion (e.g. DIA)

Metal WATER CONCENTRATION (µg/L)
Passive sampling – Spot sampling

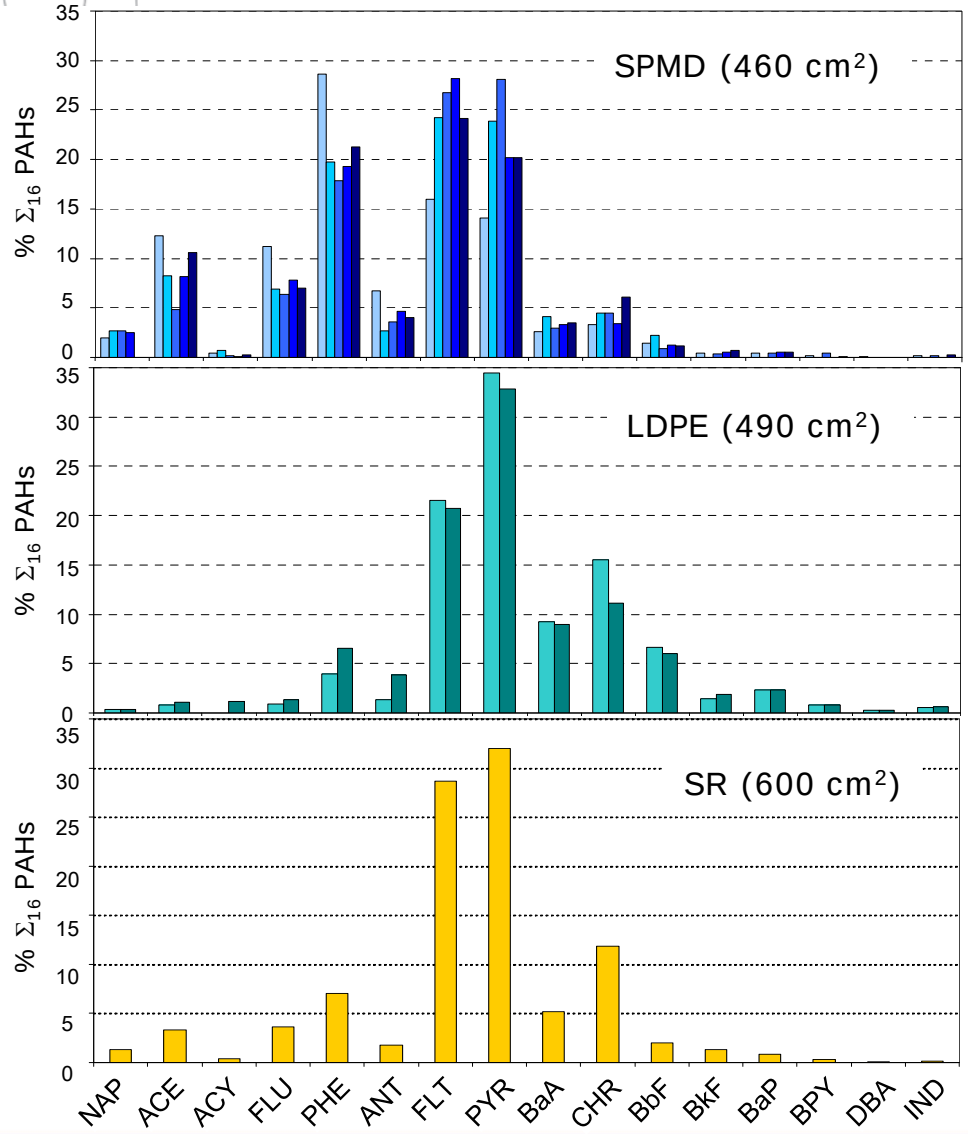


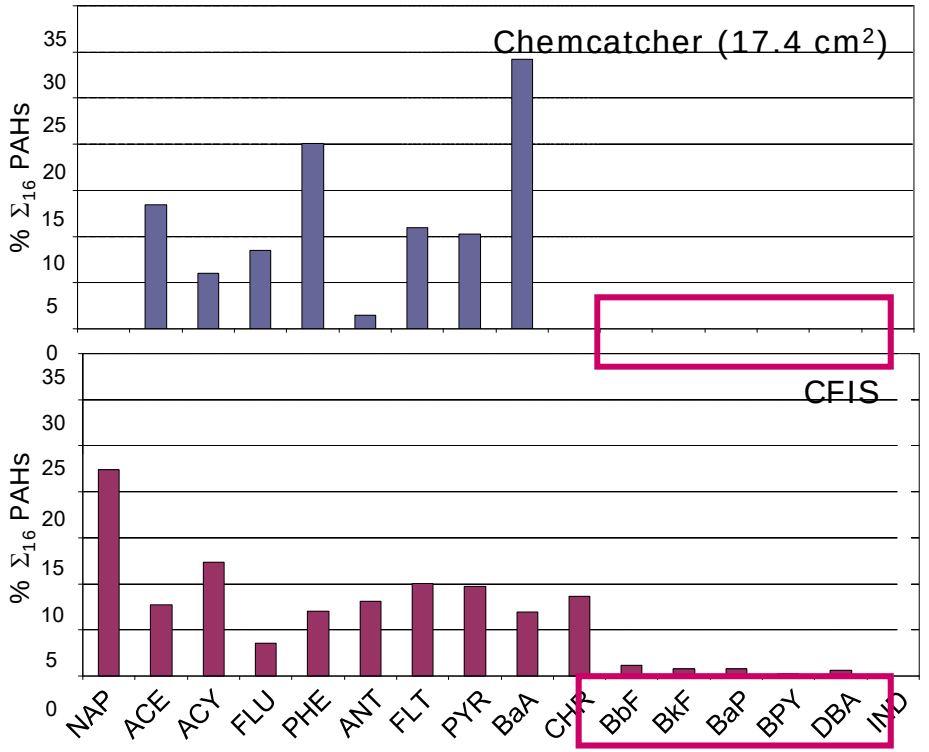
- 100 % of total dissolved Mn was sampled by PSs

- Only 35% of Cu was sampled by PSs

For metals, PSs only « see » a part of total dissolved concentrations, Depends on the metal and on the environmental conditions (DOM)

PAH ACCUMULATION - VARIOUS TOOLS

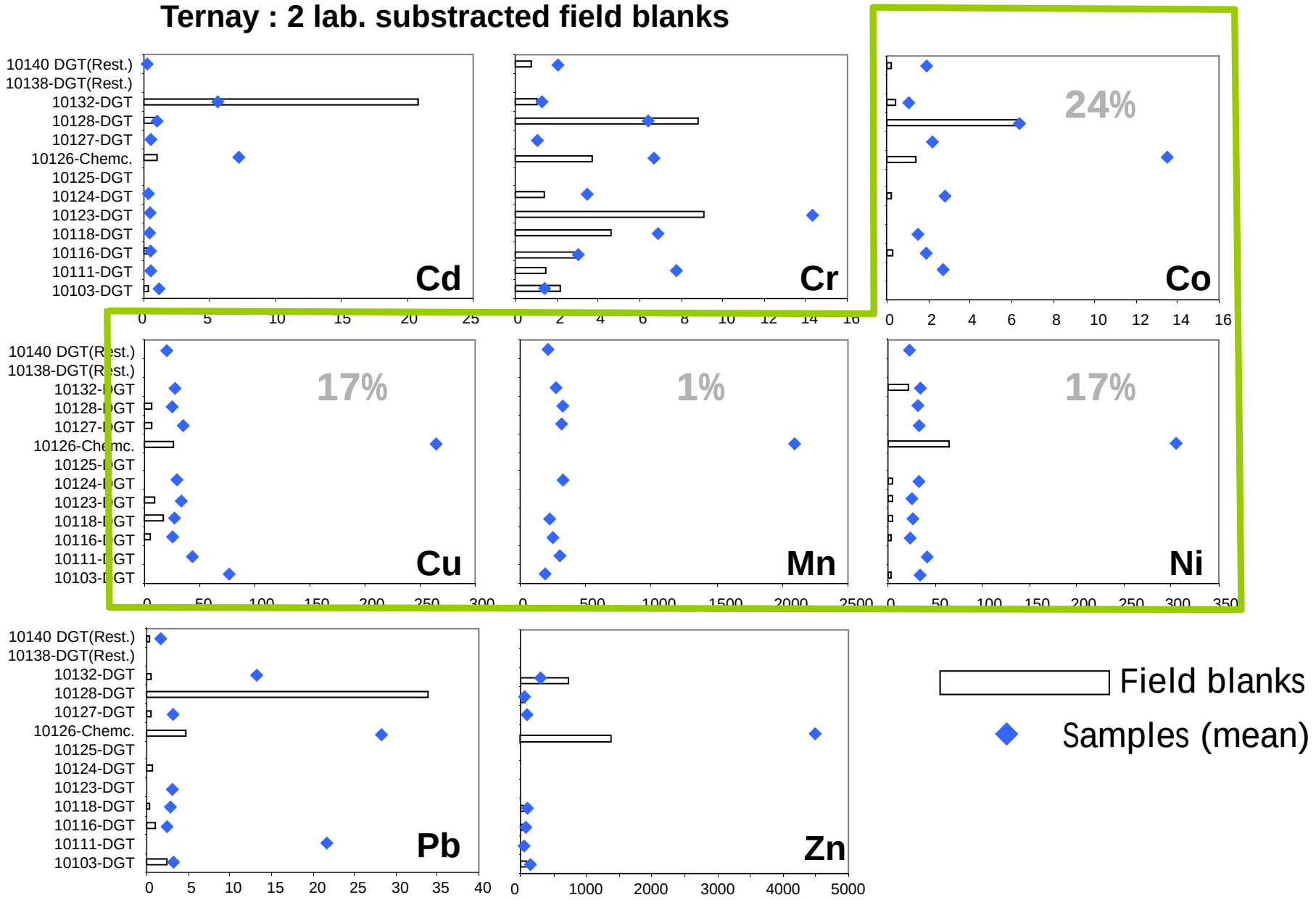




✓ LDPE, SR: similar accumulation patterns

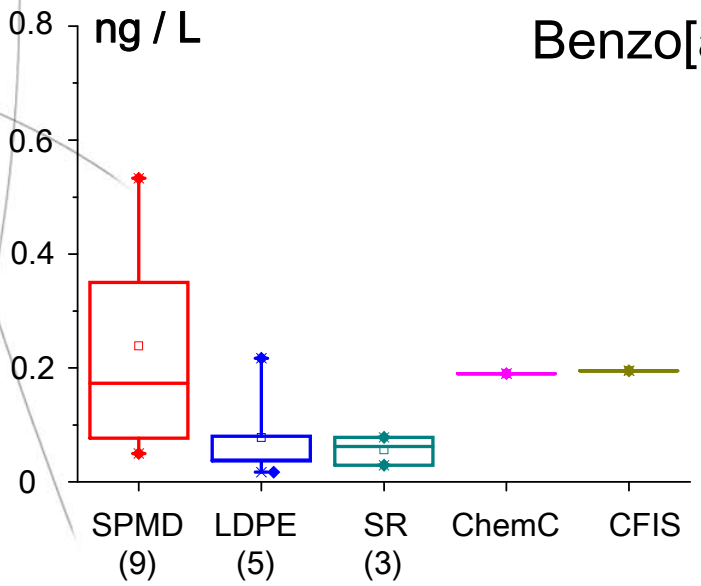
✓ Chemcatcher: no accumulation of high molecular weight PAHs

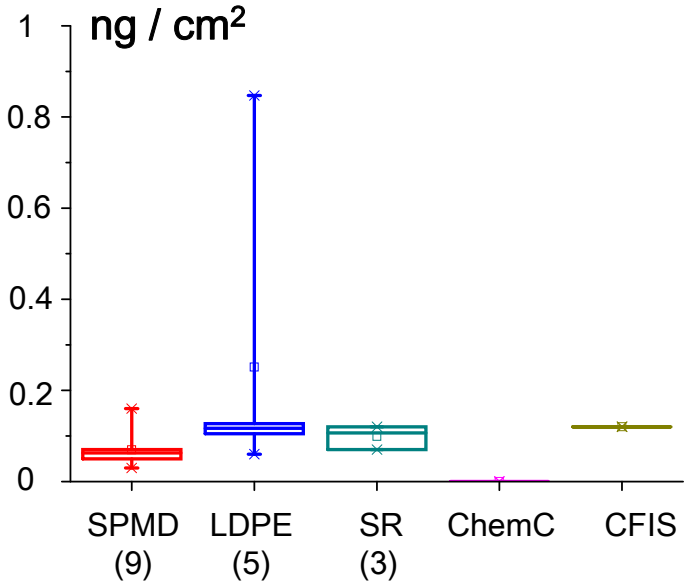
Field blanks for metals (ng/tool)



PAH CONCENTRATION in ng/L and ng/cm²

Ternay site





✓ 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

- Estimation of water concentrations by passive sampling (and expert lab.)
  ☛ low and satisfying variability, considering various lab, strategies and tools!
- Data dispersion may be reduced with harmonization of calculation method
- Contamination of field blanks (for Cd, Zn in particular) is partly responsible for DGT TWA concentrations variability
- Some tools not adapted? i.e. giving significant higher water conc. (SR for polar pesticides, …)

- Considering WFD:
  - A need of QC taking into account the sampling step (e.g. matrix effects)
  - A need of detailed protocols for non expert lab. with description of blanks, PRCs, R_s and equations to use, …
  - A need to clarify the fraction to be analyzed (dissolved *vs.* raw water)

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

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

- ***Thank you for your attention !!***