Final Workshop

Passive Sampler Intercomparison Exercise

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B. Lepot: INERIS – Paris

C. Gonzalez: EMA - Ales

Results for Polycyclic Aromatic Hydrocarbons

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

18 EXPERT LABORATORIES

✓ 6 French laboratories and 12 foreign laboratories

(Czech Republic, Germany, Italy, Netherlands, Norway, Slovakia, Spain, Sweden, United Kingdom, USA)

✓ Various strategies

- Passive sampler
  - Standard **commercial or home-made** passive samplers *(SPMD, Chemcatcher, LDPE or silicone membranes, …)*
  - Standard commercial or home-made exposure system
- Analytical Procedure
  - **Purification** of the extracts
  - HPLC/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

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)*

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
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Benzo[*a*]anthracene	21	9 *(4)*	**84**	**69**	0.4	0.1 ± 0.0
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Benzo[*b*]fluoranthene	20 *(2)*	8	**80**	**62**	< 0.4	0.1 (SBFLs)
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

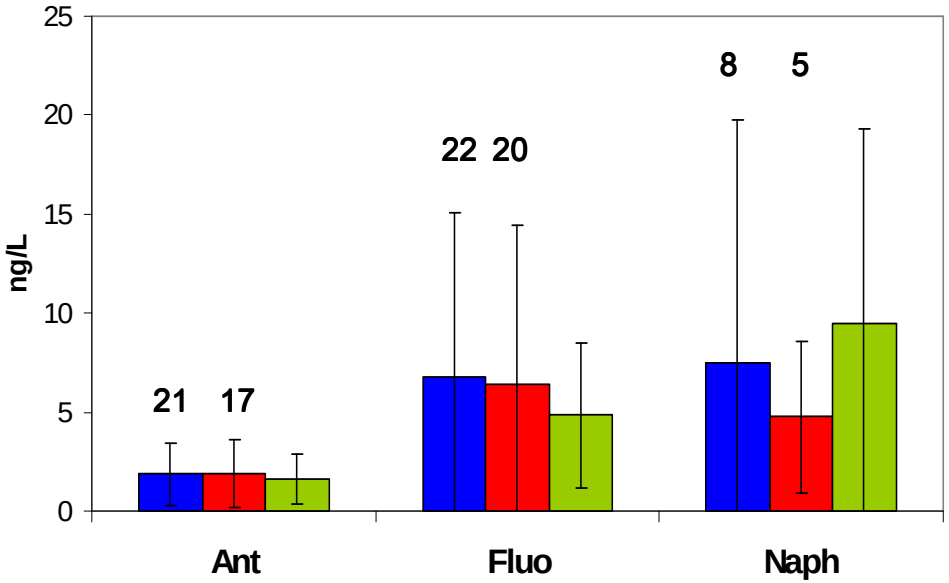
- ✓ More than 60 % of quantified results for 10 to 12 PAHs
- ✓ Thau: few data and some results close to field blank
- ✓ Lower LOQs with passive sampling / spot sampling

PAH WATER CONCENTRATION (TWAC, ng/L)

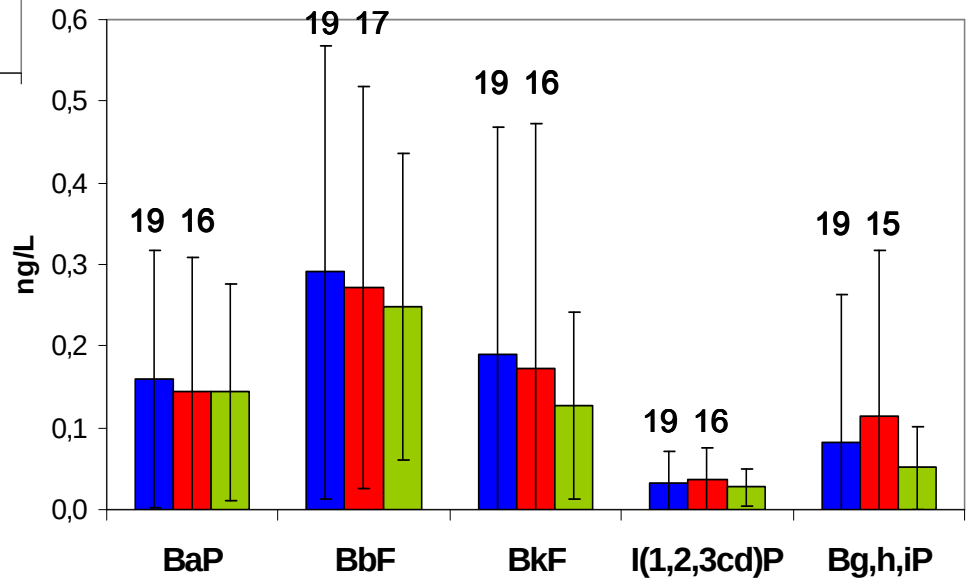
Means and sd (all participants)

Means and sd (without QC outliers)

Means and sd (Robust statistic, all participants)



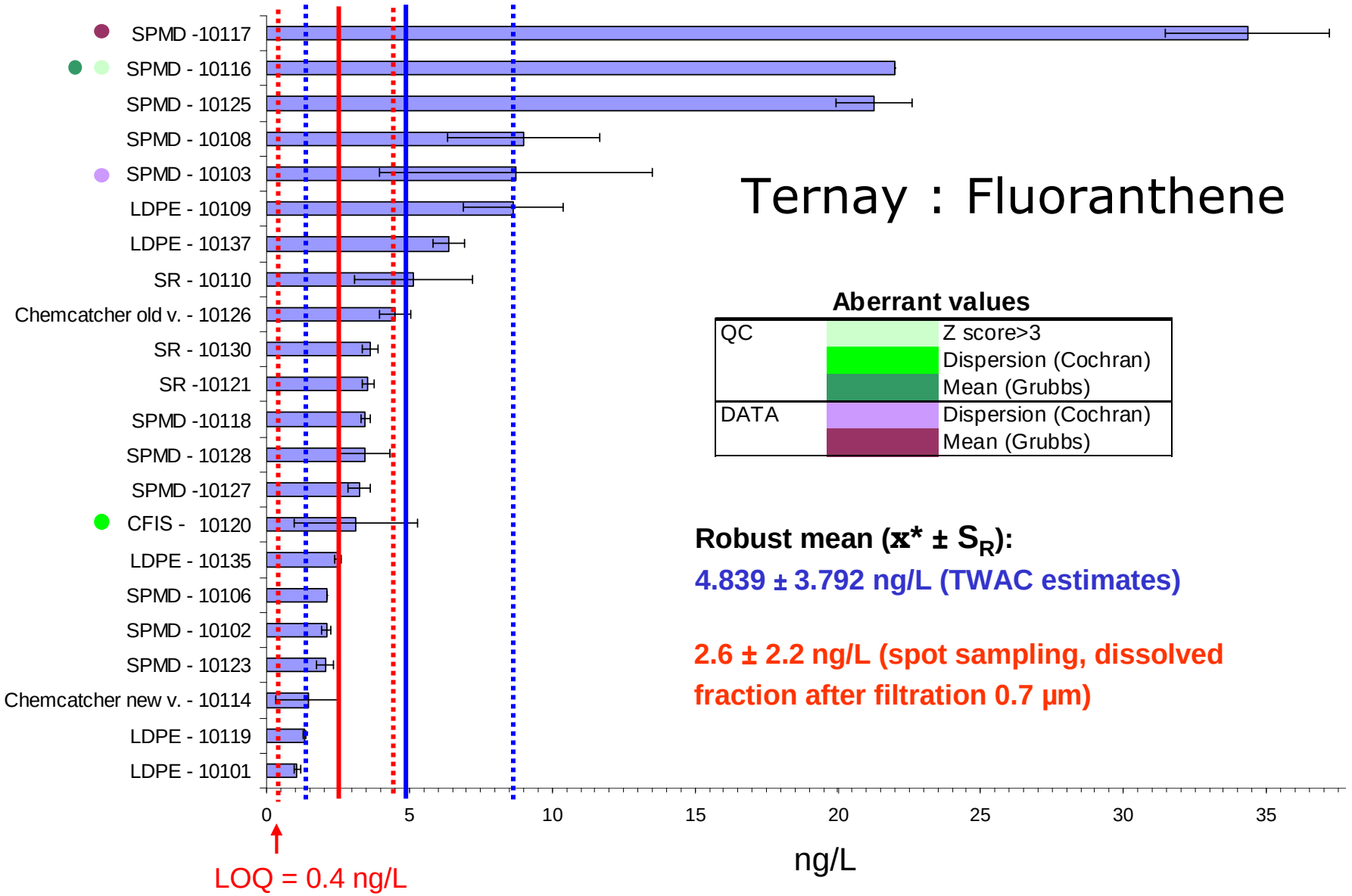
Ternay site



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

PAH WATER CONCENTRATION (ng/L)

Various tools and laboratories



Ternay : Fluoranthene

Aberrant values

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

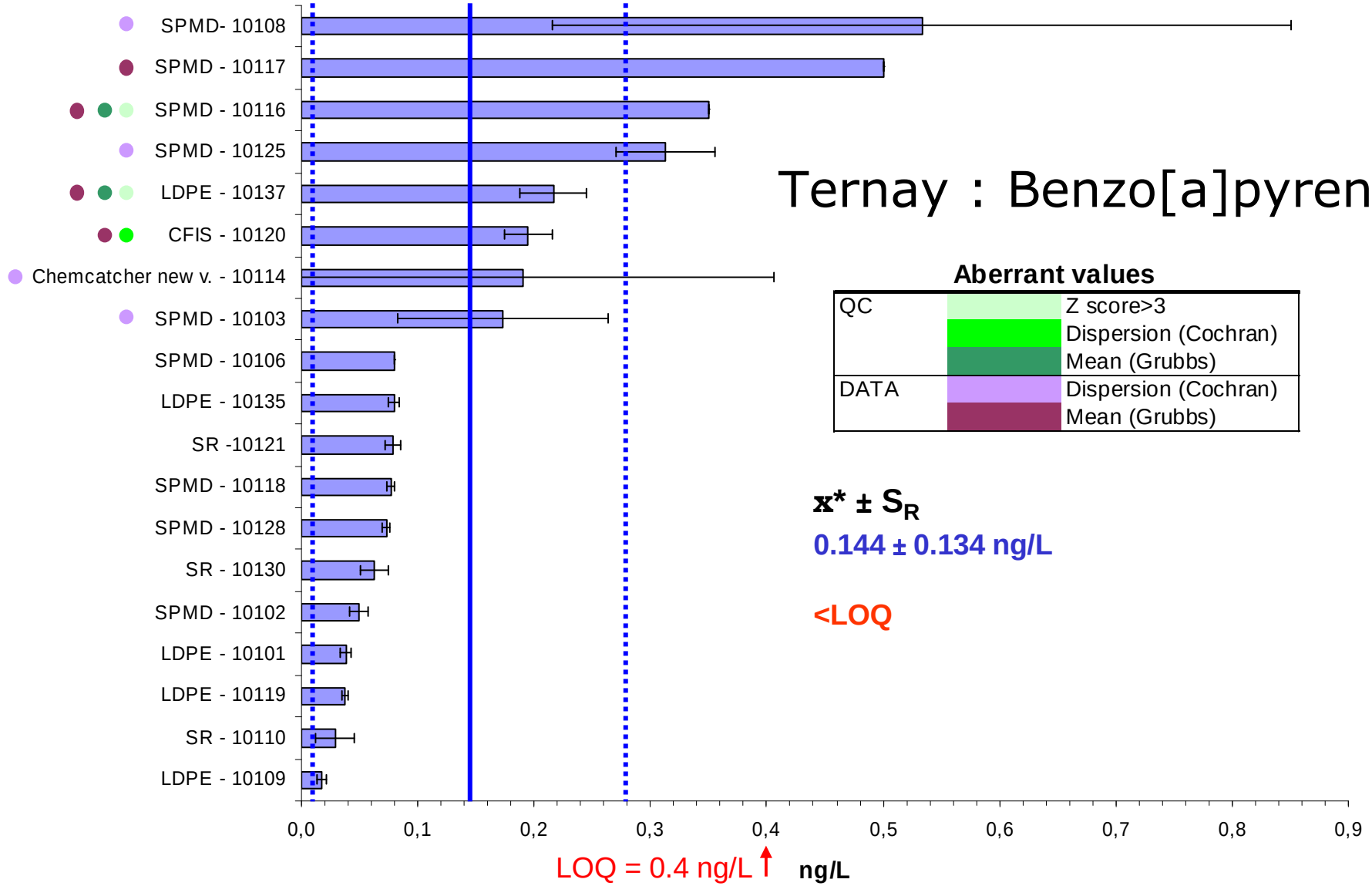
Robust mean ($x^* \pm S_R$):

4.839 ± 3.792 ng/L (TWAC estimates)

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

PAH WATER CONCENTRATION (ng/L)

Various tools and laboratories



Ternay : Benzo[a]pyrene

Aberrant values

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

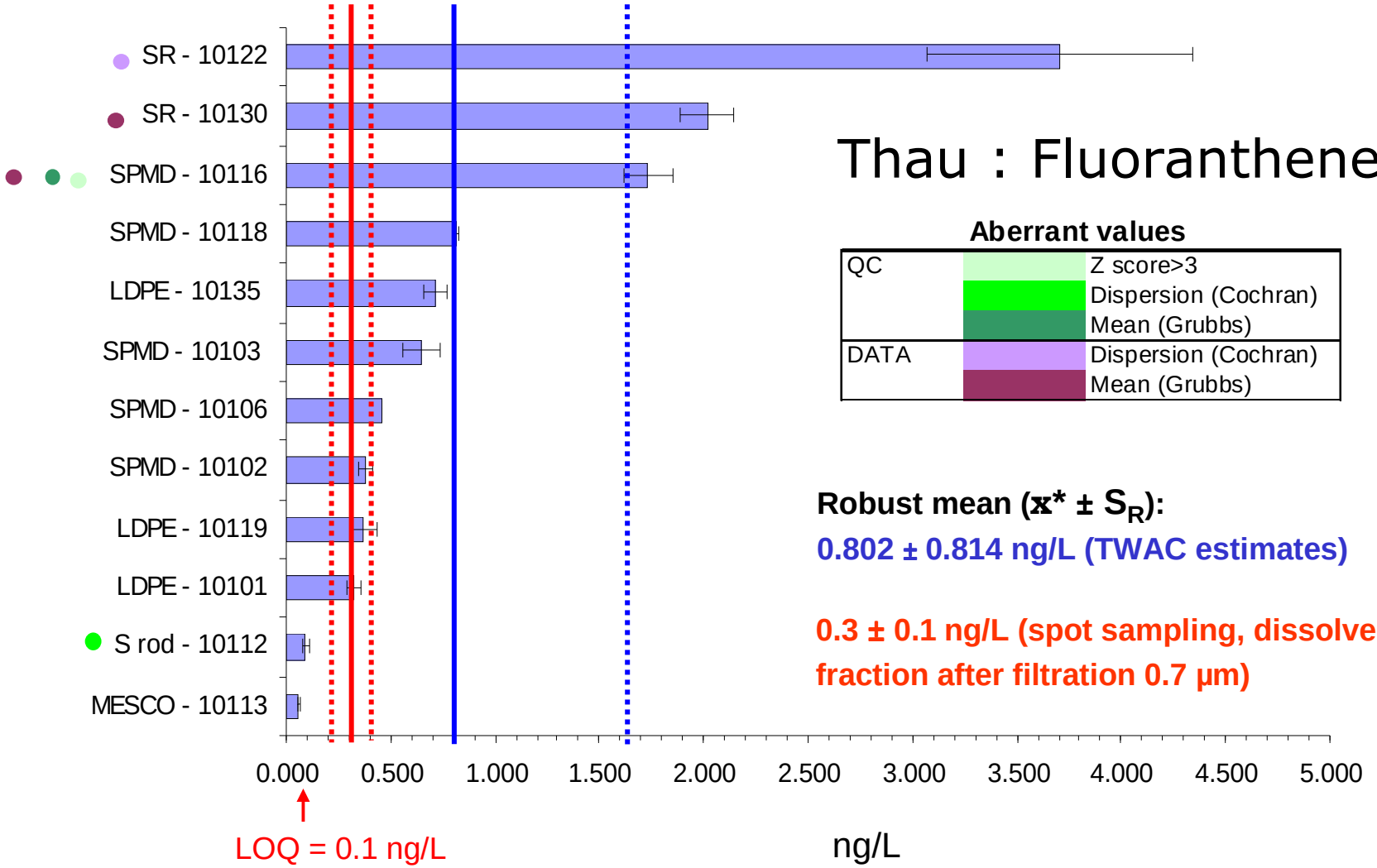
$x^* \pm S_R$

0.144 ± 0.134 ng/L

<LOQ

PAH WATER CONCENTRATION (ng/L)

Various tools and laboratories

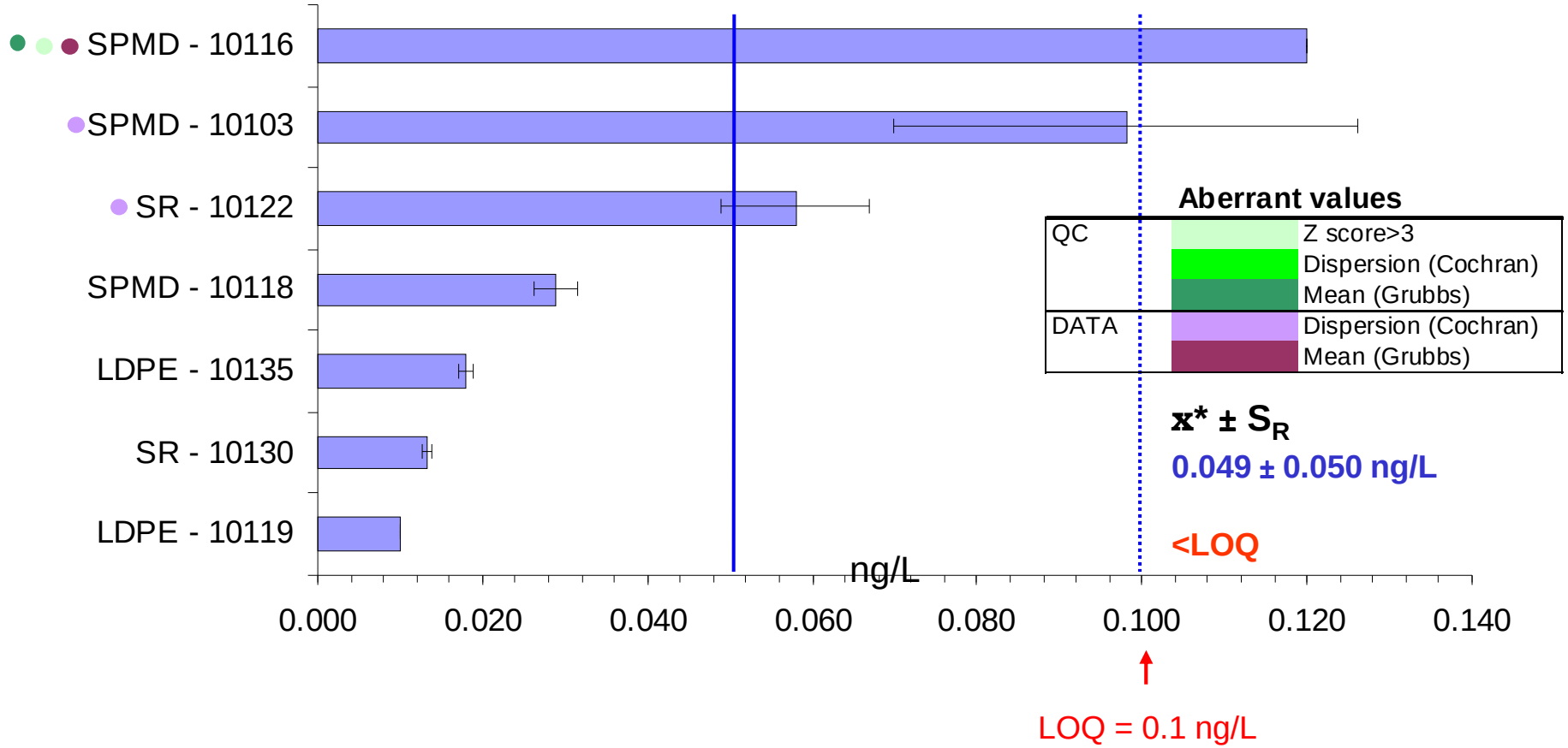


PAH WATER CONCENTRATION (ng/L)

Various tools and laboratories

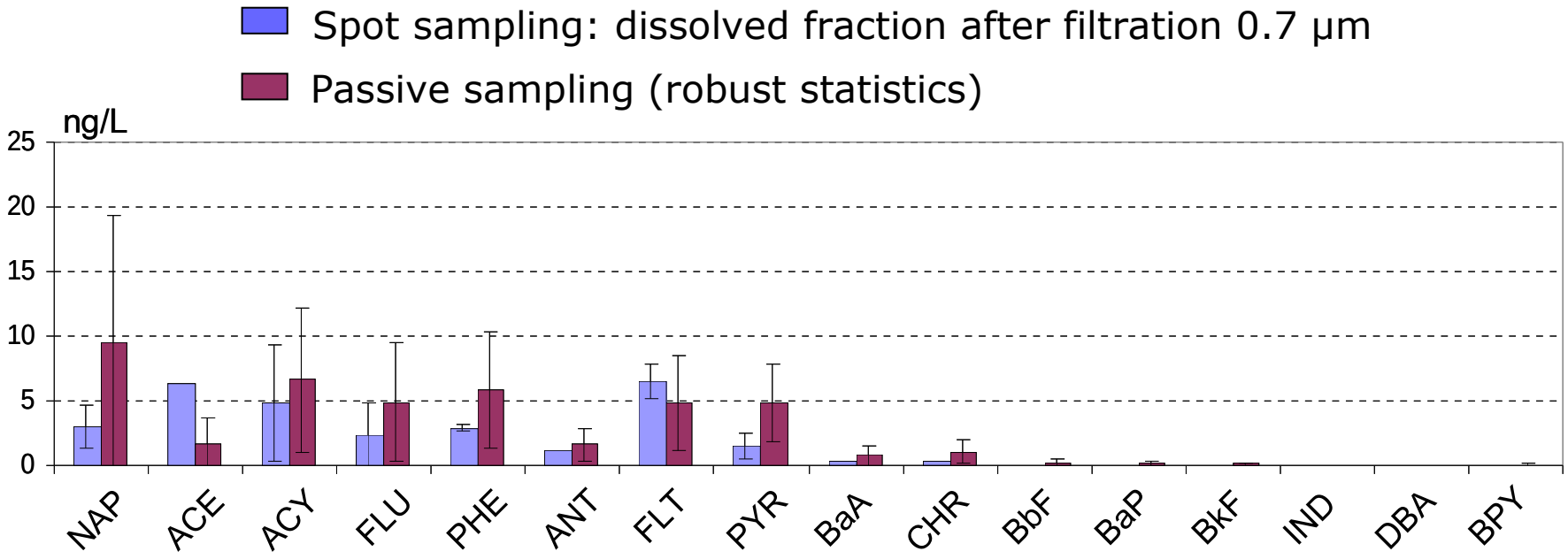
AQUAREF
Consortium scientifique et technique
BRGM, Cemagref, IFREMER, INERIS et LNE

Thau : Benzo[a]pyrene



PAH WATER CONCENTRATION (ng/L)

Passive sampling – Spot sampling



✓ 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

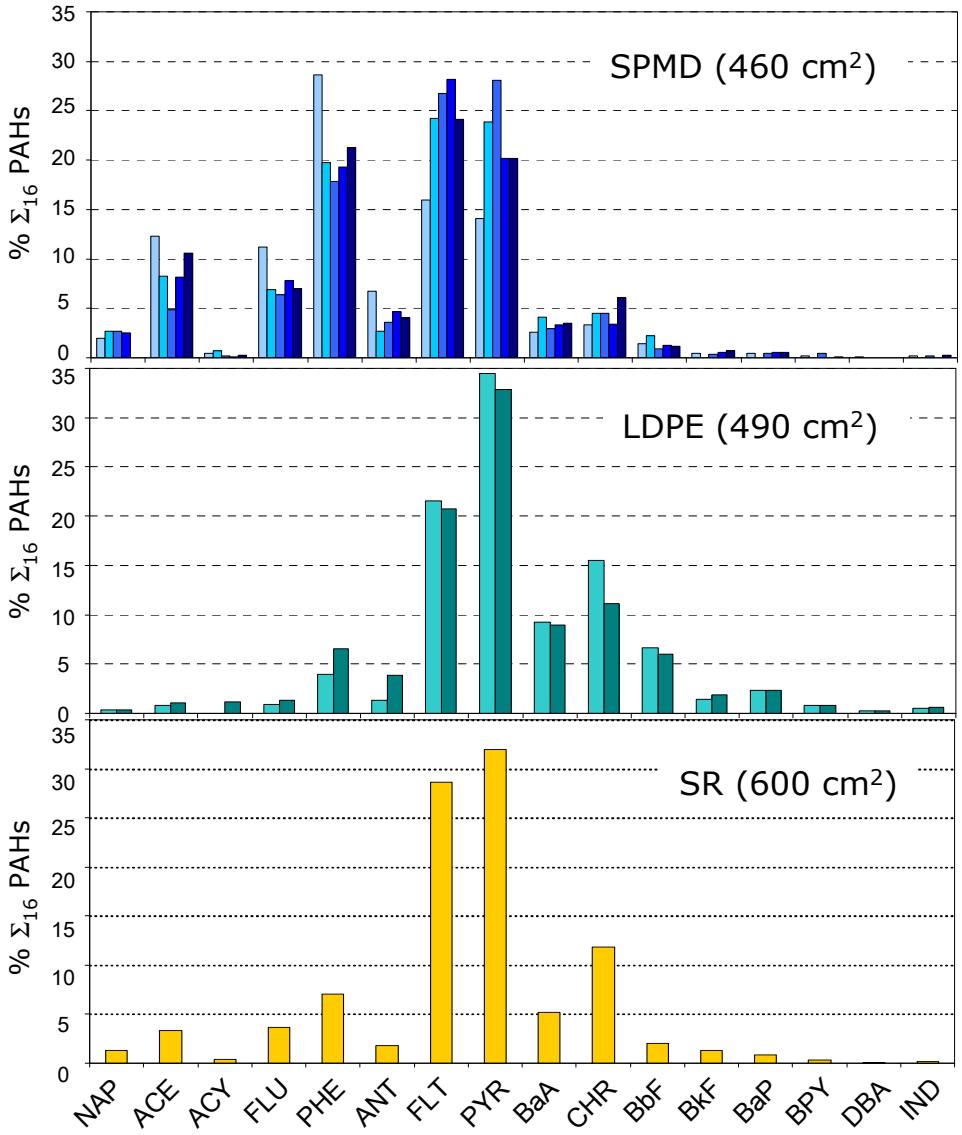
REPRODUCIBILITY
Passive sampling – Spot sampling

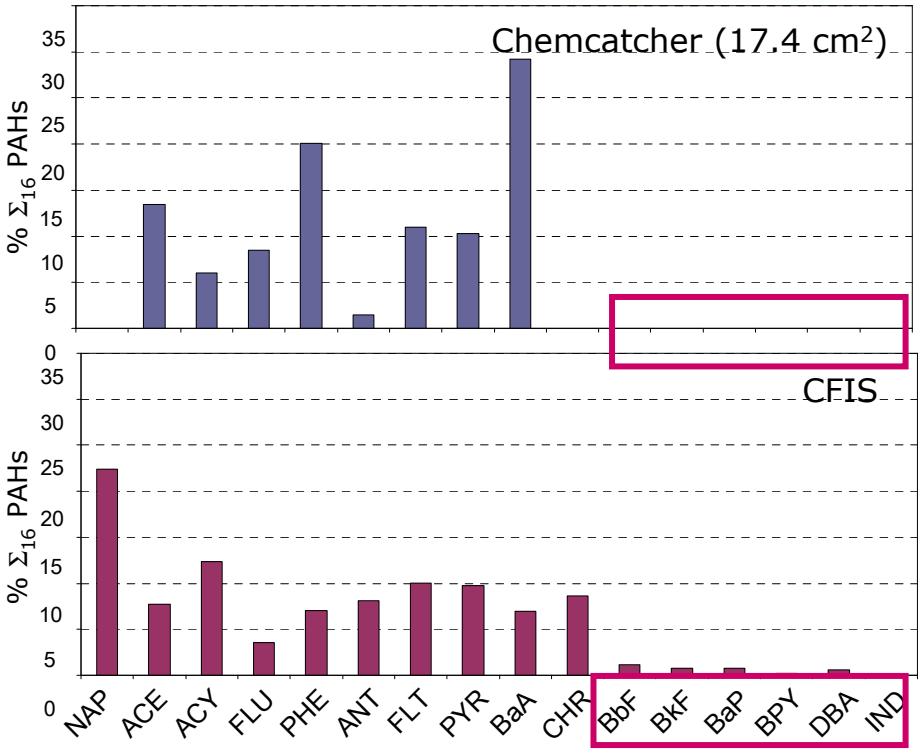
	Ternay passive sampler data		AGLAE Proficiency Testing Exercise (Spiked surface water, 20-40 ng/L)
	Robust mean X* ± sd (ng/L)	Robust reproducibility (RSD %)	Robust reproducibility (RSD %)
Naphthalene	9.49 ± 9.84	**81**	**26**
Acenaphthylene	1.60 ± 2.07	**130**	**-**
Acenaphthene	6.61 ± 5.54	**84**	**18**
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



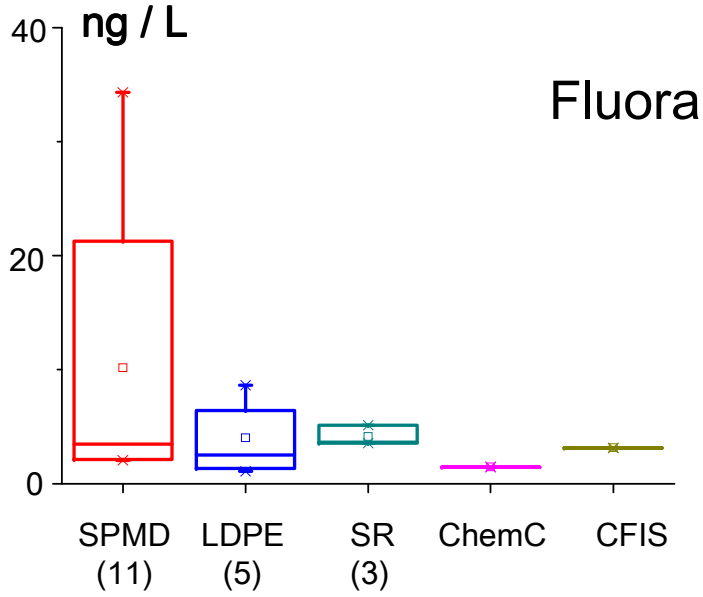


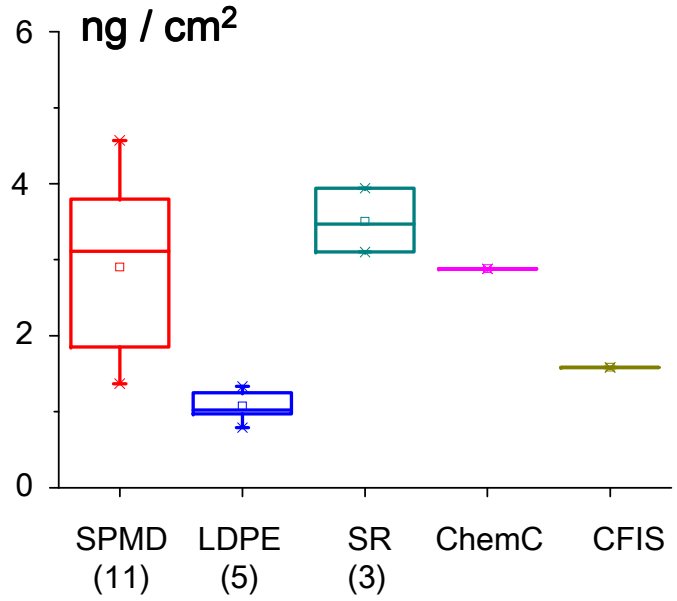
✓ LDPE, SR: similar accumulation patterns

✓ Chemcatcher: no accumulation of high molecular weight PAHs

PAH CONCENTRATION in ng/L and ng/cm²

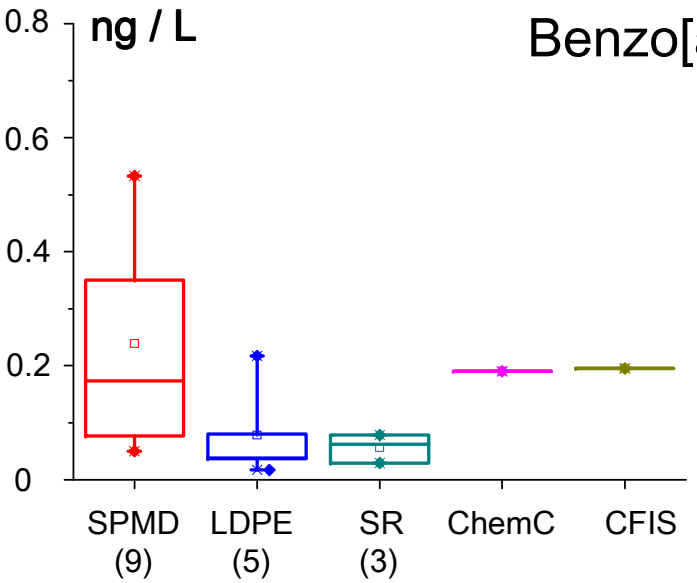
Ternay site

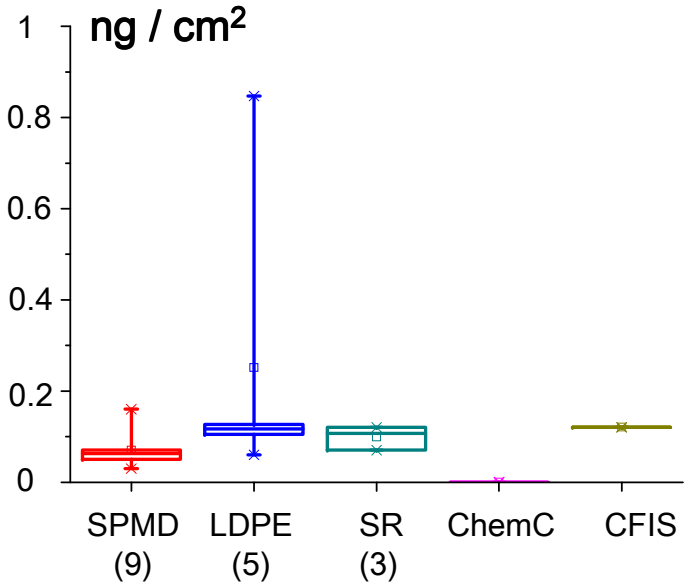




PAH CONCENTRATION in ng/L and ng/cm²

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

✓ Satisfying variability in the determination of PAH water concentrations by passive sampling (and expert lab.)

- Various lab., strategies and tools
- variability: Sampling + Analytical procedure + Calculation method

✓ Sampling:
- Various tools: various sampled fractions?

⟹ Need to better characterize these fractions

- Lower LOQs by using SPMD, LDPE or SR membranes

✓ Analytical variability: to be improved

PAH QC reference solution: reproducibility RDS = 20-54%

✓ Need for harmonized calculation methods:

- Field blank (correction or not)
- PRCs data
- Calculation models and parameters used for Rs and TWAC determination

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

Thanks to the participant laboratories

- **ALS Scandinavia AB (SW),**
- **BRGM (FR),**
- **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),**
- **Marine Scotland - Science (UK),**
- **NIVA (NO),**
- **T. G. Masaryk Water Research Institute, Public Research Institution (CZ),**
- **UFZ - Department of Ecological Chemistry, Helmholtz Centre for Environmental Research (DE),**
- **Universita di Cagliari (IT),**
- **University of Rhode Island (USA),**
- **Water Research Institute (SK)**

Thanks to the central laboratories for water analyses

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

Thank you for your attention !