

# 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

- acetochlor
- alachlor \*
- atrazine \* + DEA / DIA
- diuron \*
- isoproturon \*
- metolachlor
- simazine \*

## Devices

- 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<sub>18</sub>)

← 14 days



\* *priority substances (WFD)*

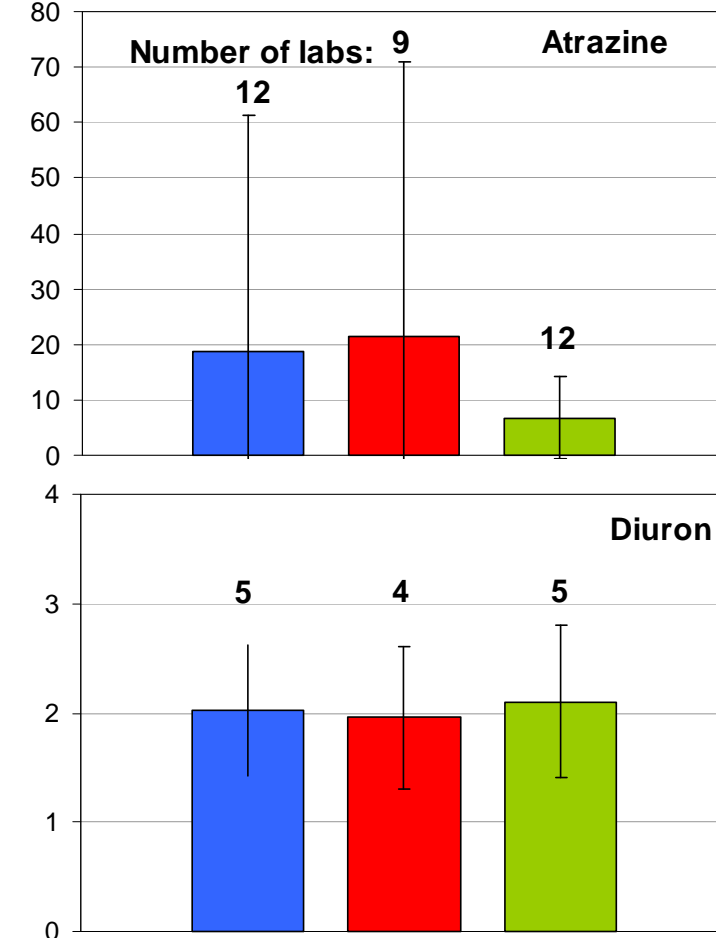
# Sampling sites and planning

<p><b>Coastal waters</b></p>	<p><b>Thau Lagoon (Hérault)</b> 27th April-18th May</p>	
<p><b>River waters</b></p>	<p><b>Beillant site (Charente maritime)</b> 27th May-10th June</p>	

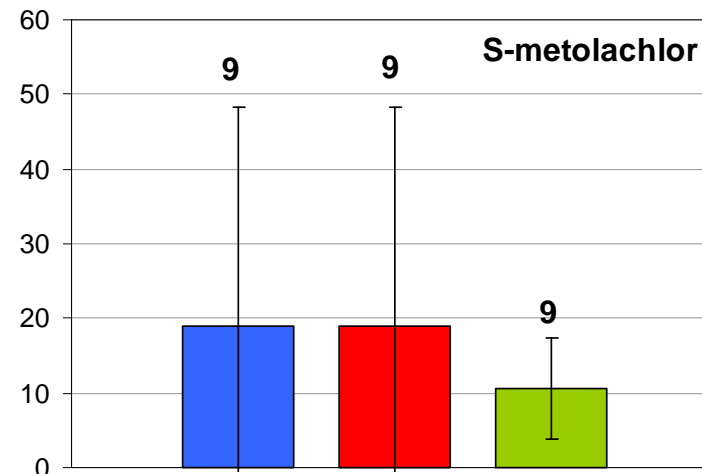
# Water concentration estimates (ng/L) and data treatment methodology

- For Beillant site:

ng/L



- 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.



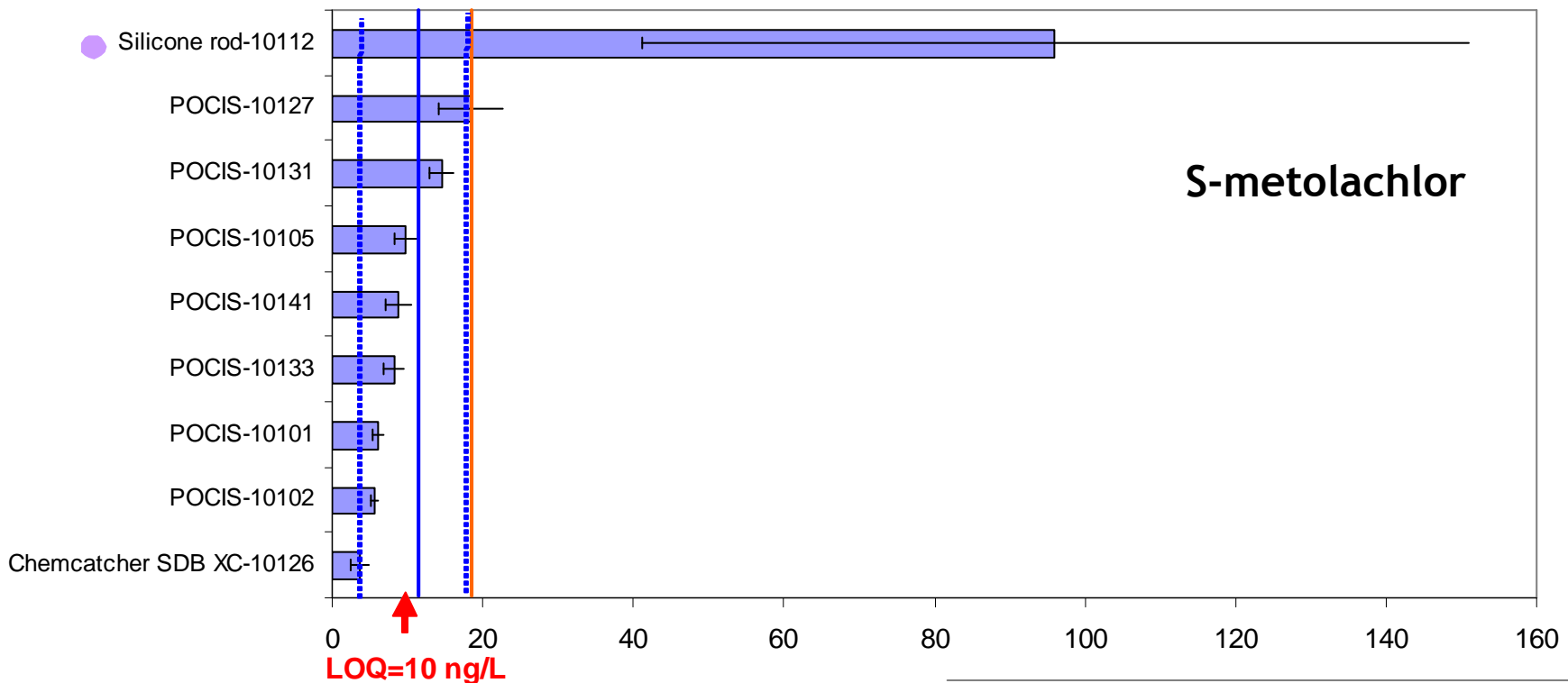
- For Beillant site:

$$\bar{x}^* \pm S_R$$

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)





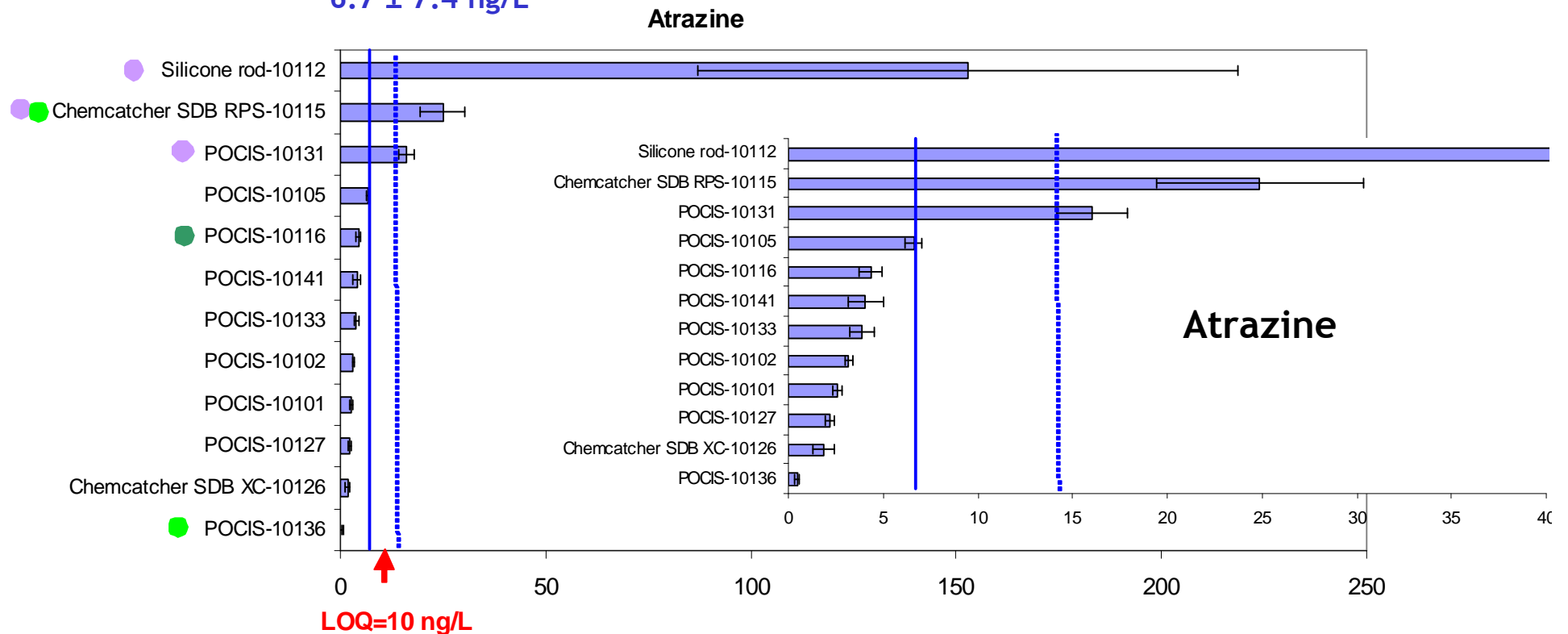
# Comparison of pesticides water concentration (ng/L) from various tools and lab.



- For Beillant site:

$\bar{x}^* \pm S_R$   
6.7 ± 7.4 ng/L

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



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

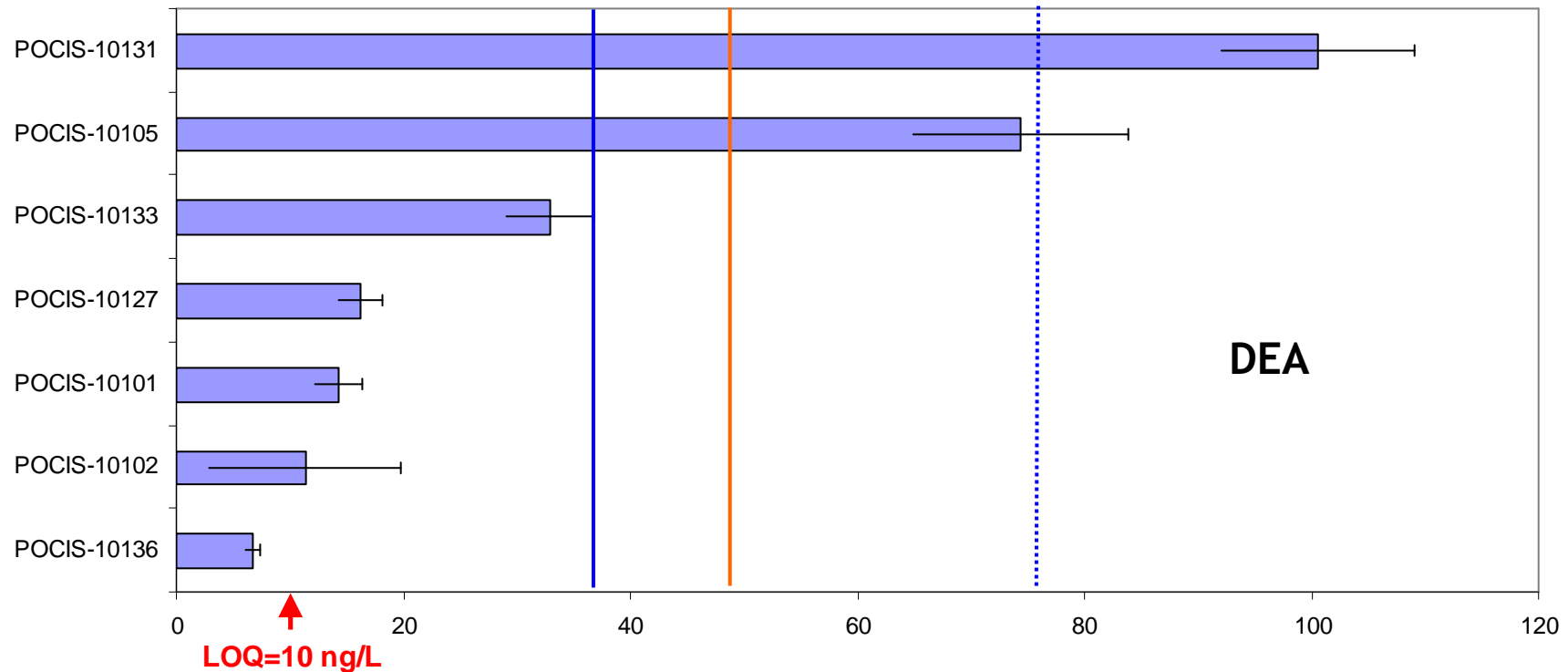


- For Beillant site:

$\bar{x}^* \pm S_R$   
 35.9 ± 39.6 ng/L (TWAC estimates)

49.2 ± 18.7 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.

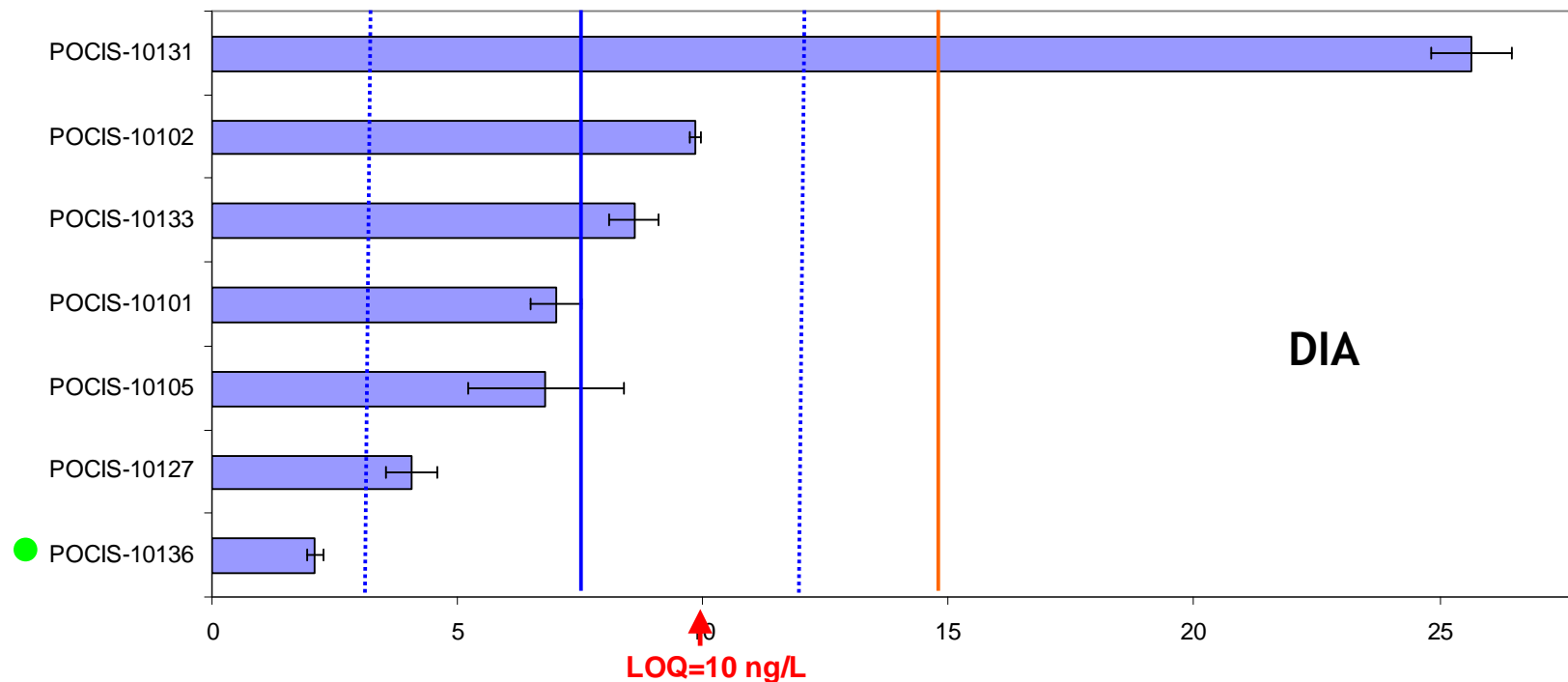


- For Beillant site:

$$\bar{x}^* \pm S_R$$

7.5 ± 4.5 ng/L (TWAC estimates)    14.8 ± 4.7 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.

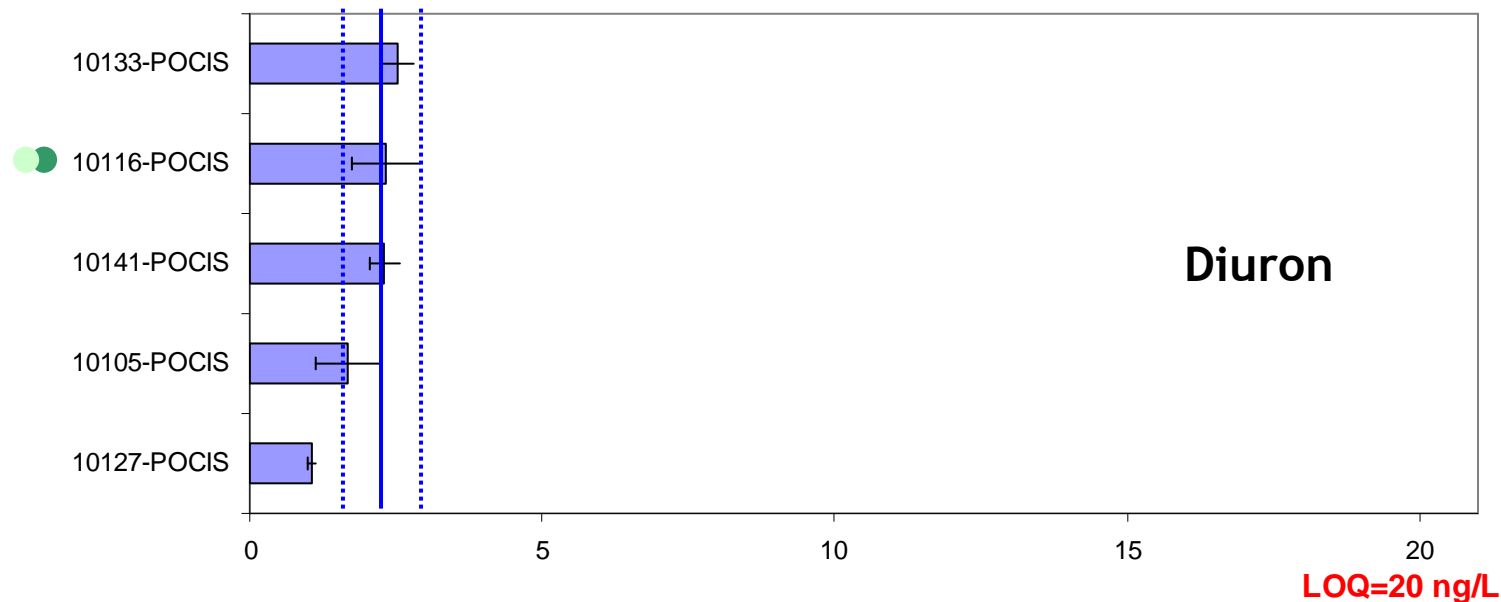


- For Beillant site:

$$\bar{x}^* \pm S_R$$

2.1 ± 0.7 ng/L (TWAC estimates)

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



- 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.



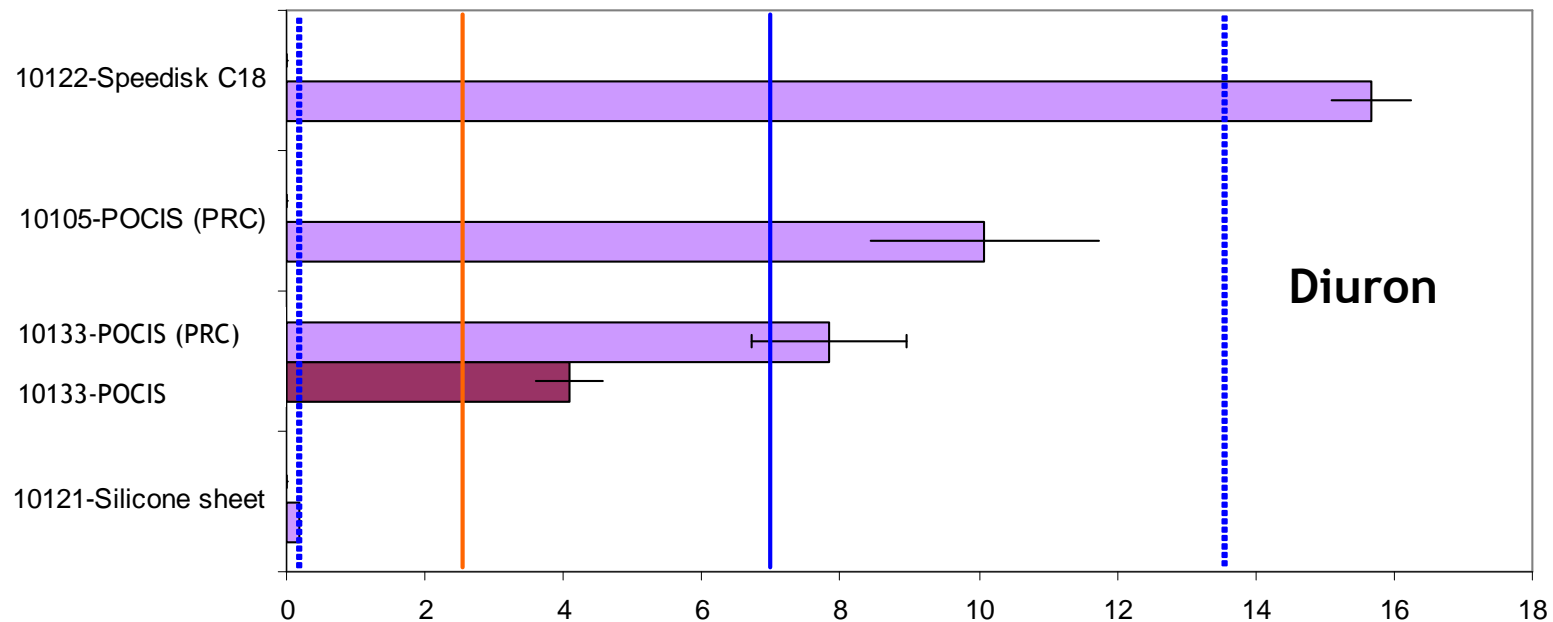
- For Thau Lagoon site:

$$\bar{x}^* \pm S_R$$

$$7.5 \pm 6.8 \text{ ng/L}$$

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

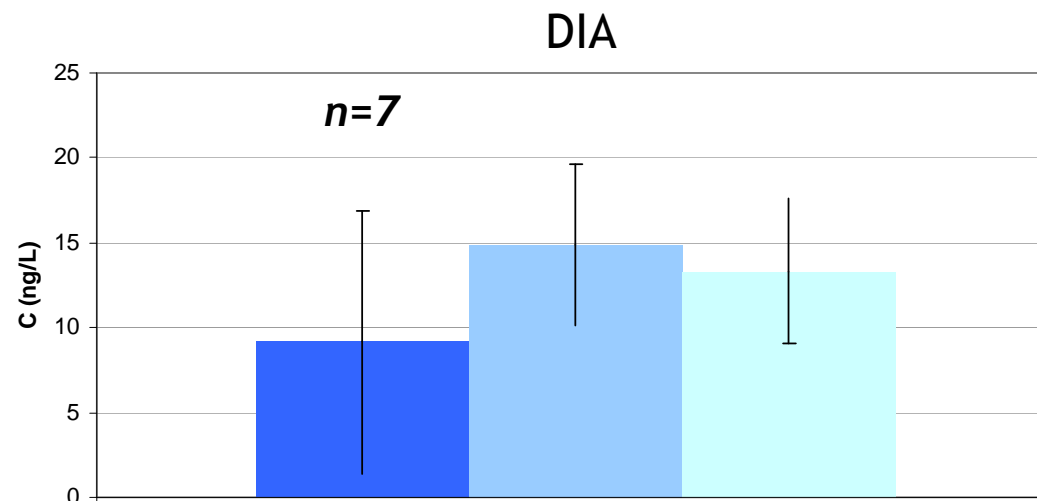
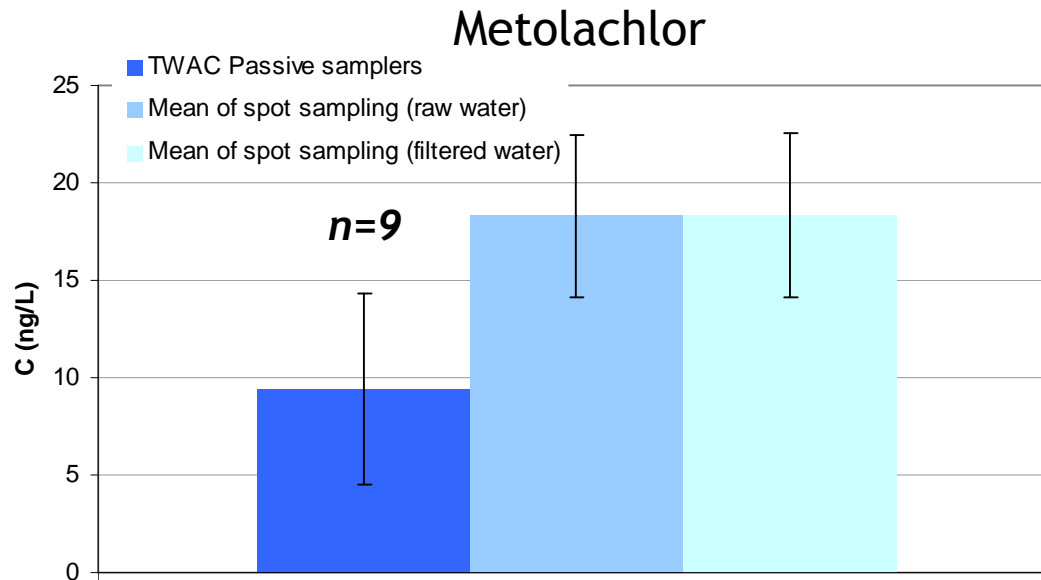
2.4 ± 0.3 ng/L (spot sampling, filtered water)



• 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		SWIFT-WFD Proficiency Testing Exercise (natural water)	
	Robust mean $x^* \pm 1$ SD (ng/L)	Robust reproducibility (% RSD)	Robust mean $x^* \pm 1$ SD (ng/L)	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

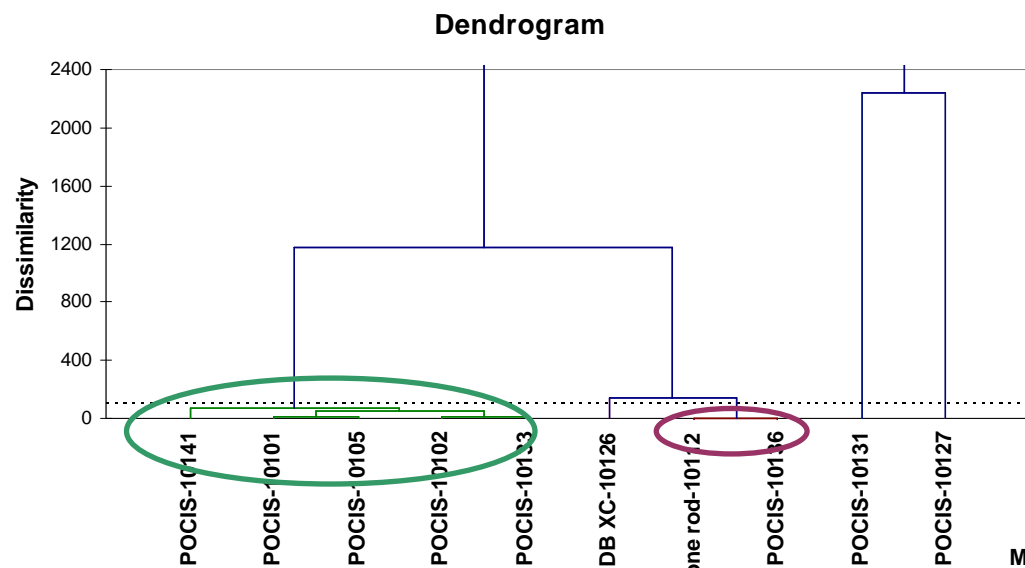
• Comparison with a classical proficiency testing: higher dispersion of PS data for some analytes

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

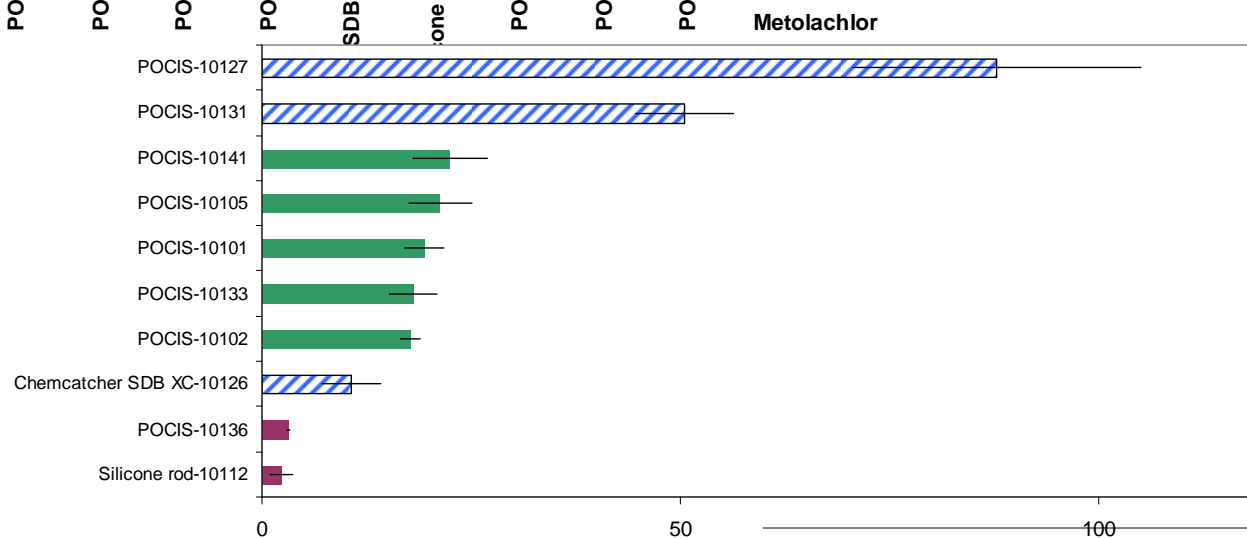
# Comparison of data in ng/tool and ng/L

- For Beillant site



Metolachlor (ng/tool)

50 % of populations in the same group

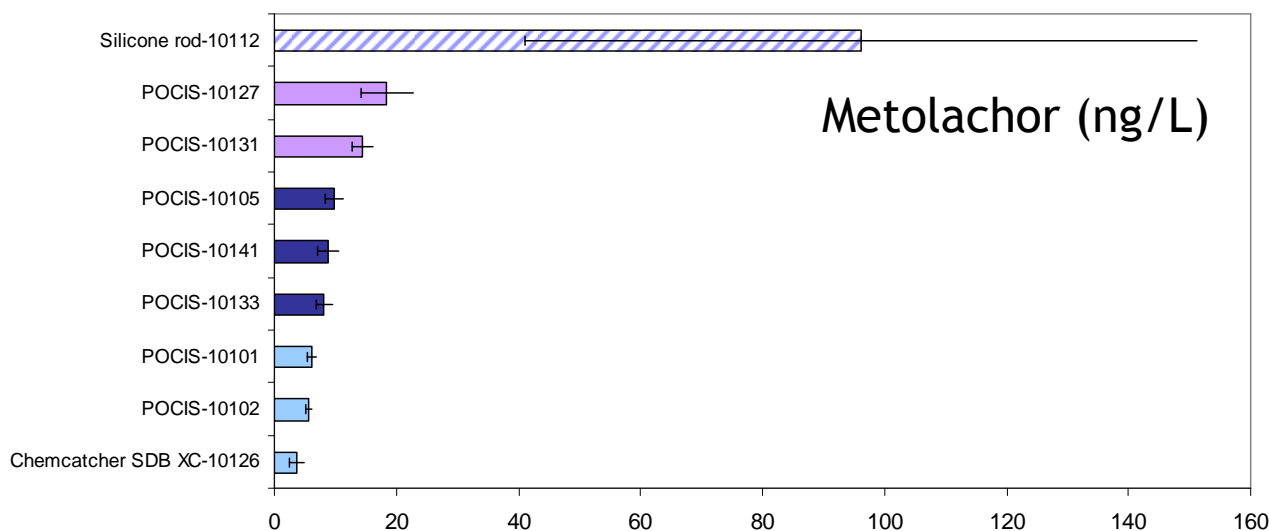
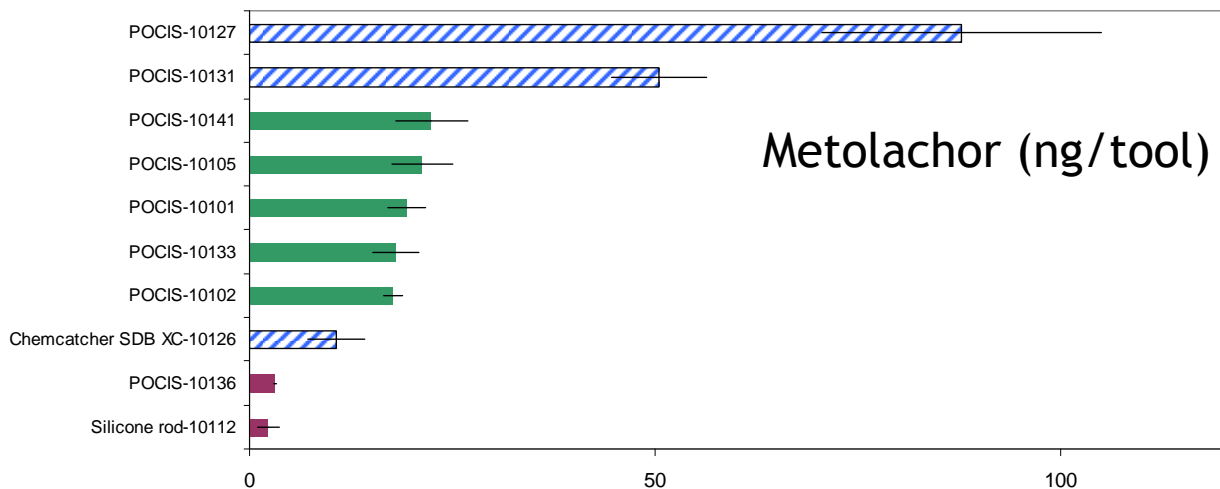




# Comparison of data in ng/tool and ng/L



- For Beillant site



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

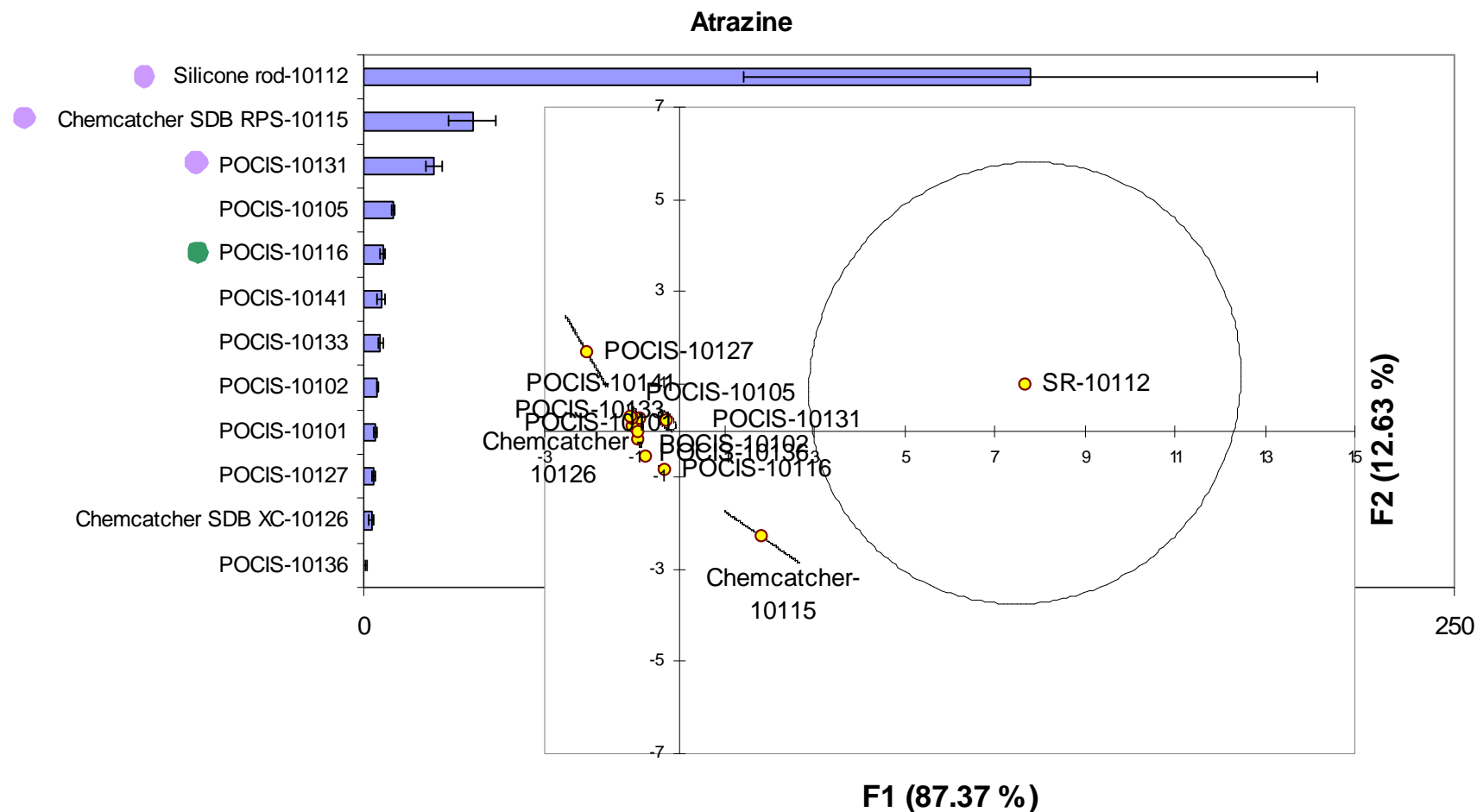
No direct correspondance between data

• Higher dispersion?

# Comparison of data in ng/tool and ng/L

- For Beillant site

## Factorial Discriminant Analysis (atrazine and S-metolachlor)



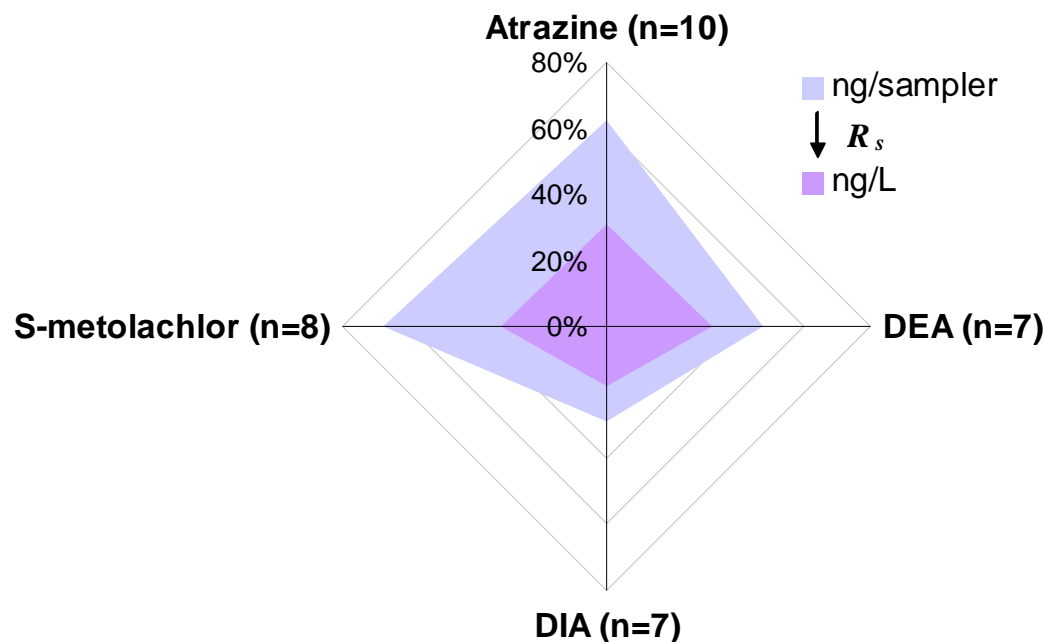
Outliers (10112, 10115 and 10131) will not be further considered...

# 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?

# 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***

## ***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 !!*