Final Workshop

Passive Sampler Intercomparison Exercise

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Results for Metals

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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

Passive samplers and exposure durations

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

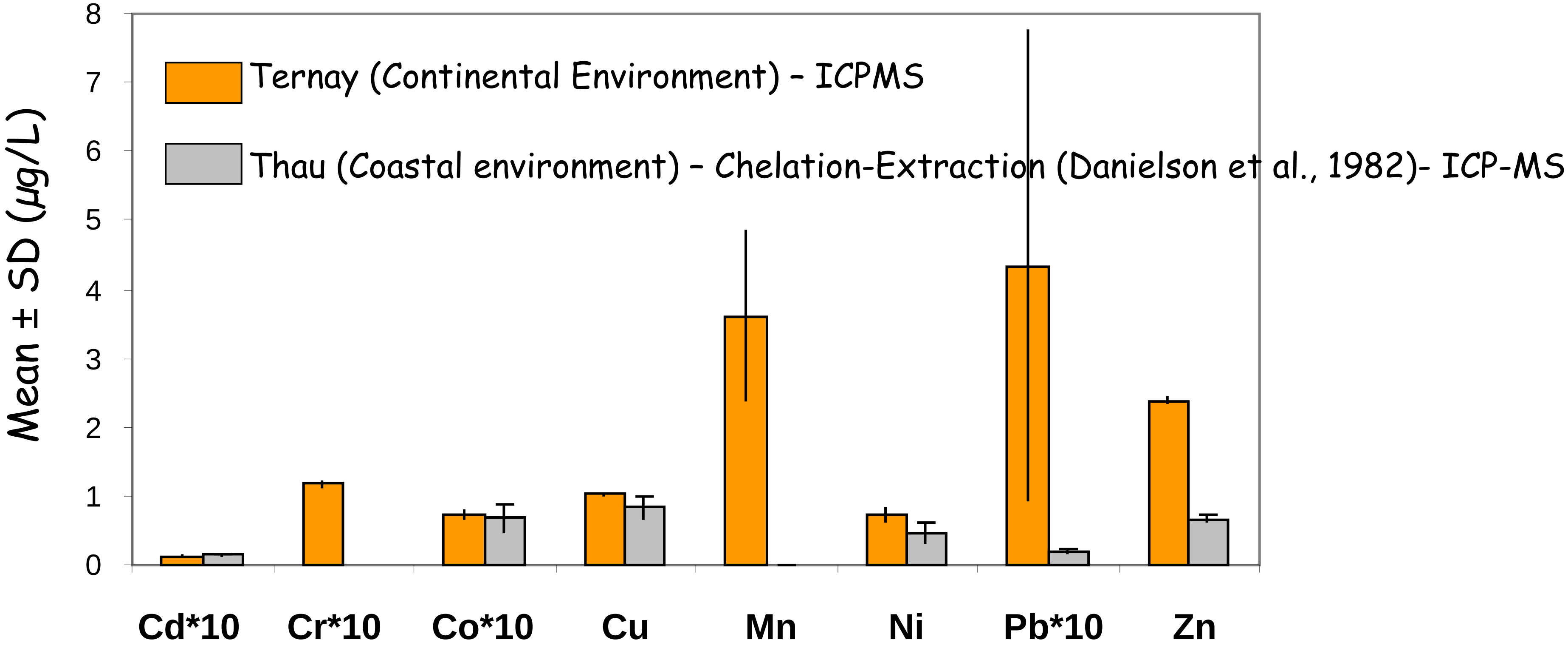
Sampling sites

- 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	 

Spot sampling concentrations

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



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	
Cd	12	7
Ni	13	7
Pb	12	6
Cu	13	7
Cr	11	7
Zn	10	5
Co	8	6
Mn	11	7

Nb results/ nb tools (%)	
Ternay	Thau
92	100
100	100
92	86
100	100
85	100
77	71
62	86
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%

Statistical data treatment and methodology

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

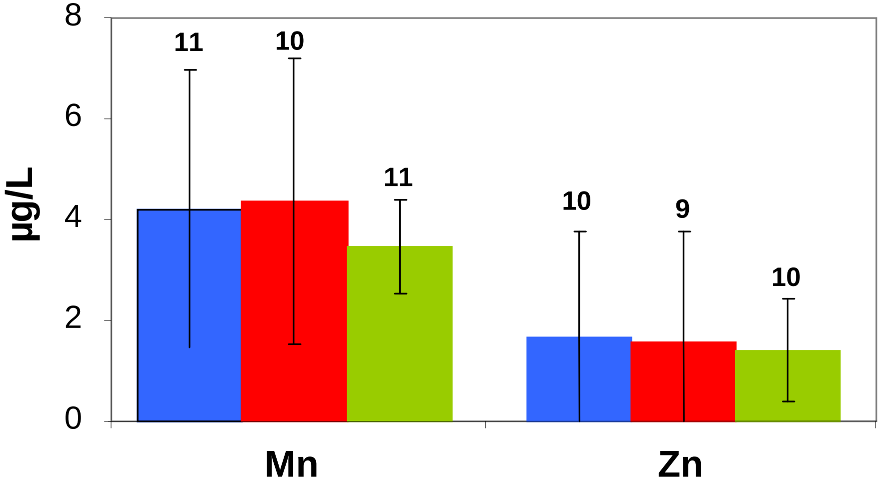
- Robust statistics: ISO 5725-5

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.

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

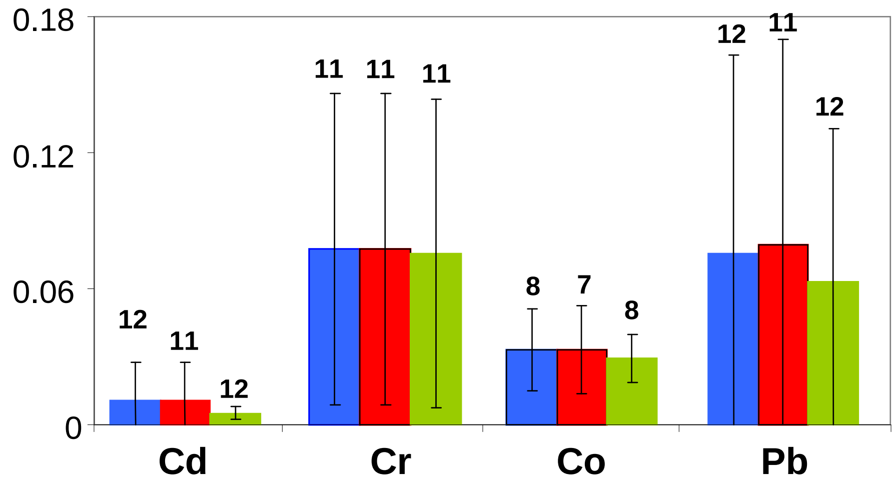
- Ternay site:

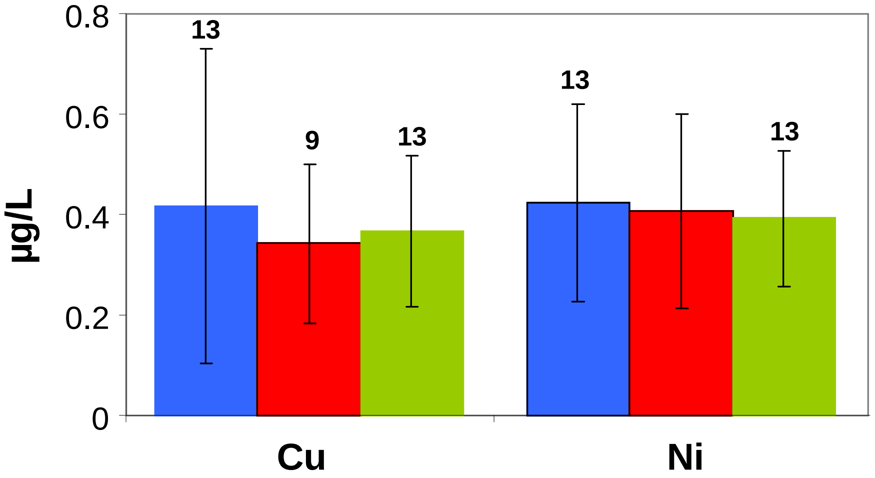


Means and standard deviations (all participants)

Means and standard deviations (without QC outliers)

Robust statistic (all participants)





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

Data dispersion of passive samplers

	Passive sampler data							SWIFT-WFD proficiency Testing Exercise (2006)		
	Ternay			Thau						
Metals	Robust mean x* ± SD (µg/L)	RSD %	n	Robust mean x* ± SD (µg/L)	RSD %	n	LQ Water µg/L	Robust mean x* ± 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

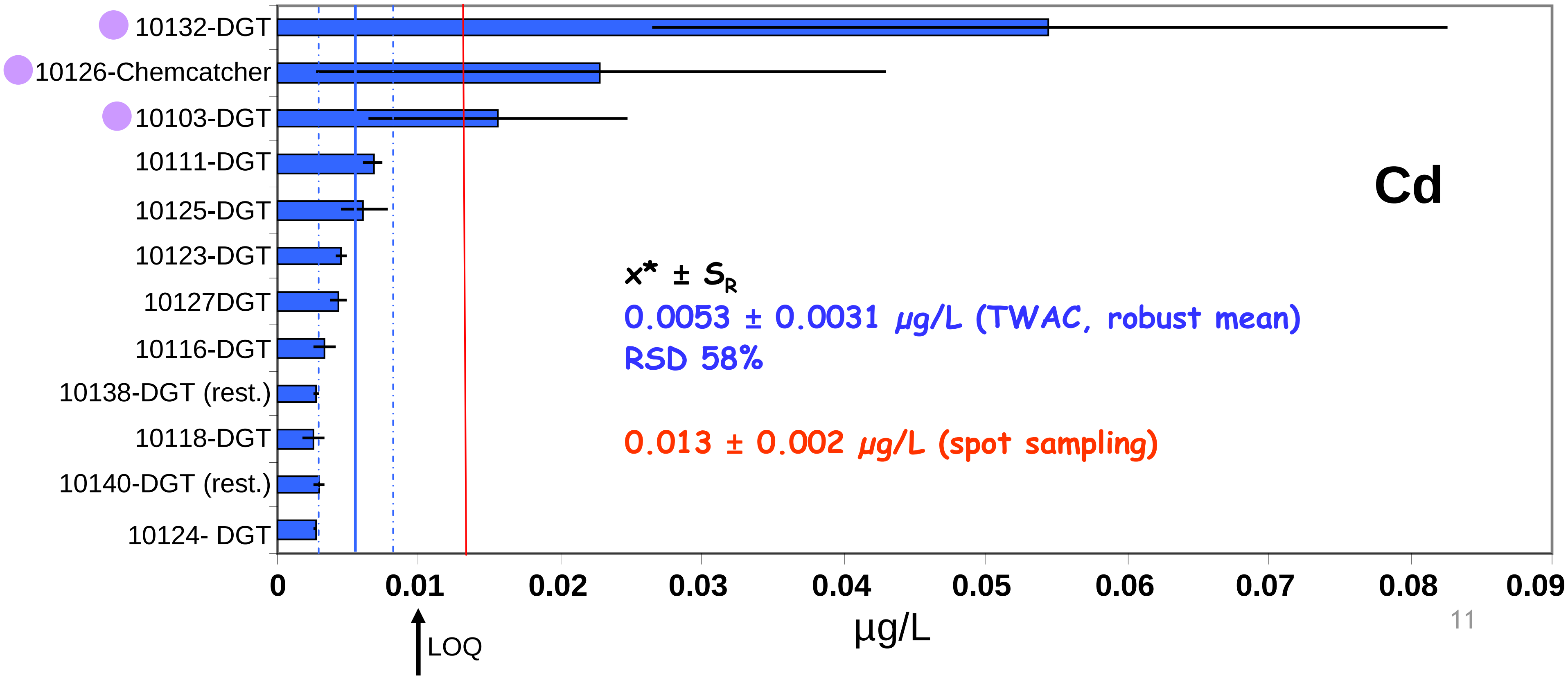
- However, much lower concentrations determined by passive samplers

- 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

Comparison of passive sampling results from various tool and lab

- 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



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	●	(Grubbs test) between-laboratory variability
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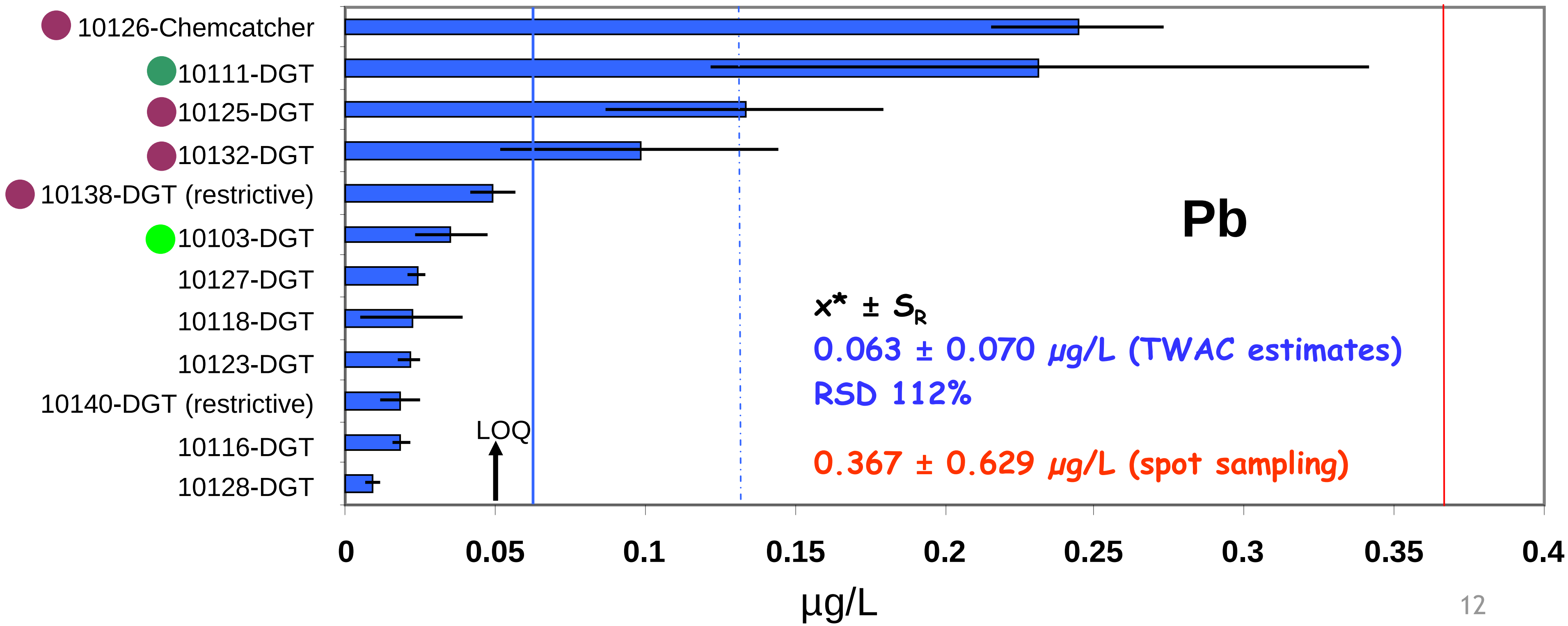
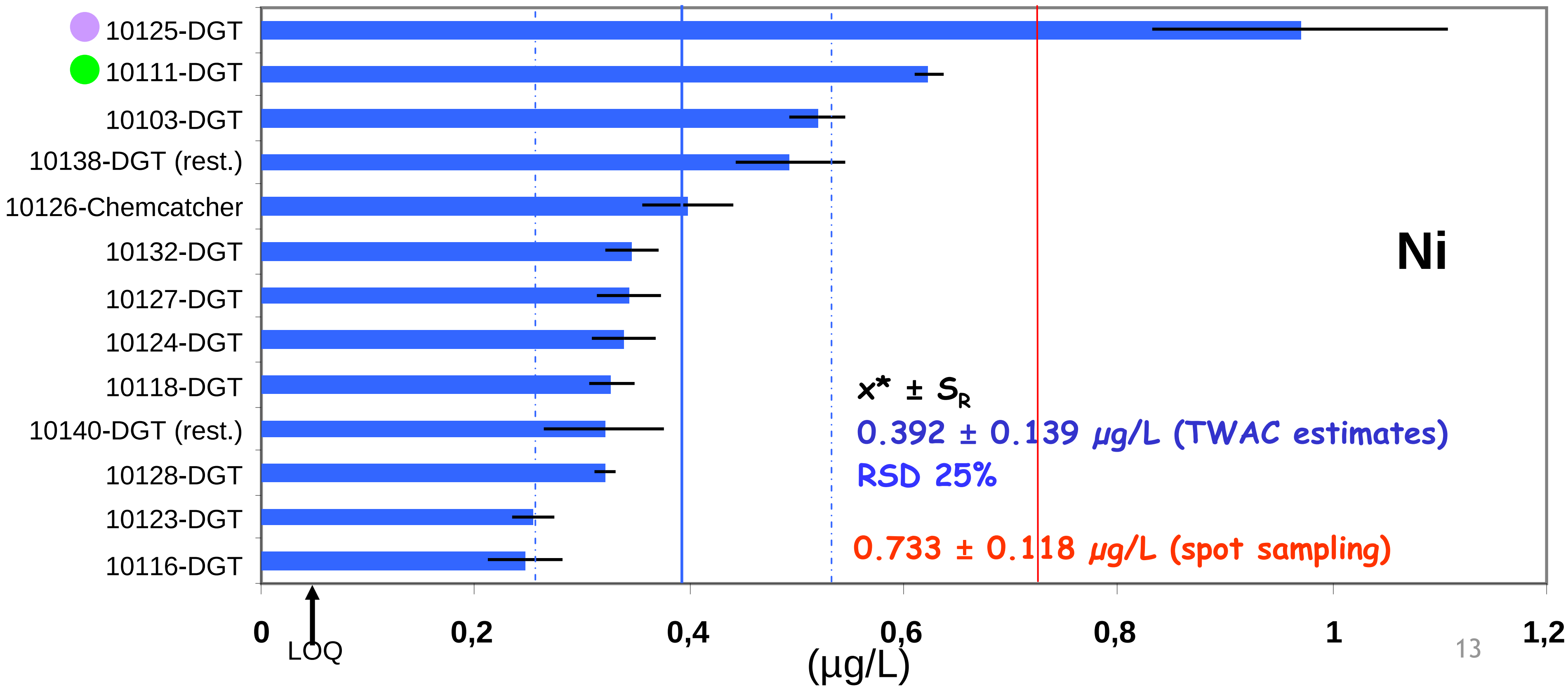


Comparison of passive sampling results from various tool and lab

- For Ternay site:

Aberrant values

QC	● (green)	(Cochran test) within-laboratory variability
	● (dark green)	(Grubbs test) between-laboratory variability
PSs DATA	● (lilac)	(Cochran test) within-laboratory variability
	● (purple)	(Grubbs test) between-laboratory variability



Comparison of passive sampling results from various tool and lab

- For Thau site:

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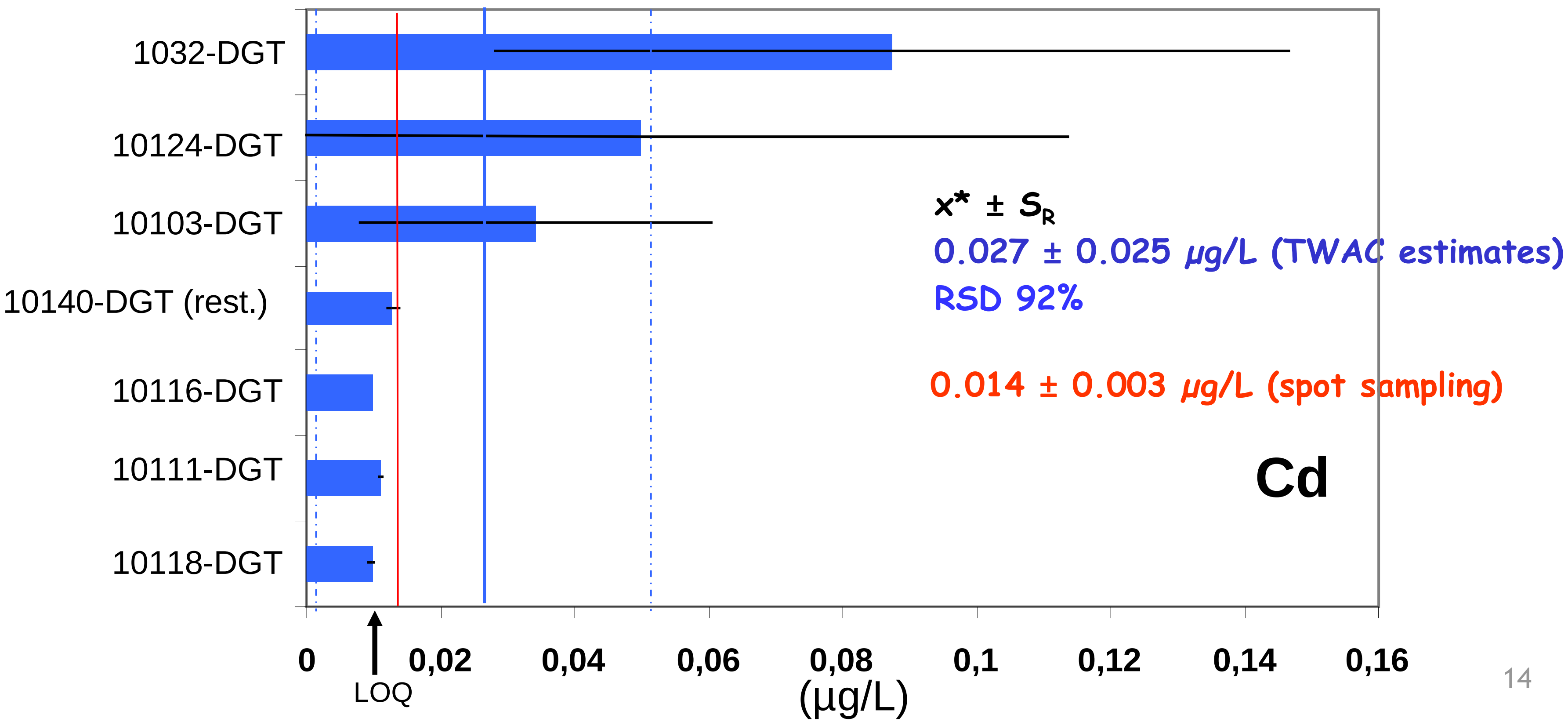

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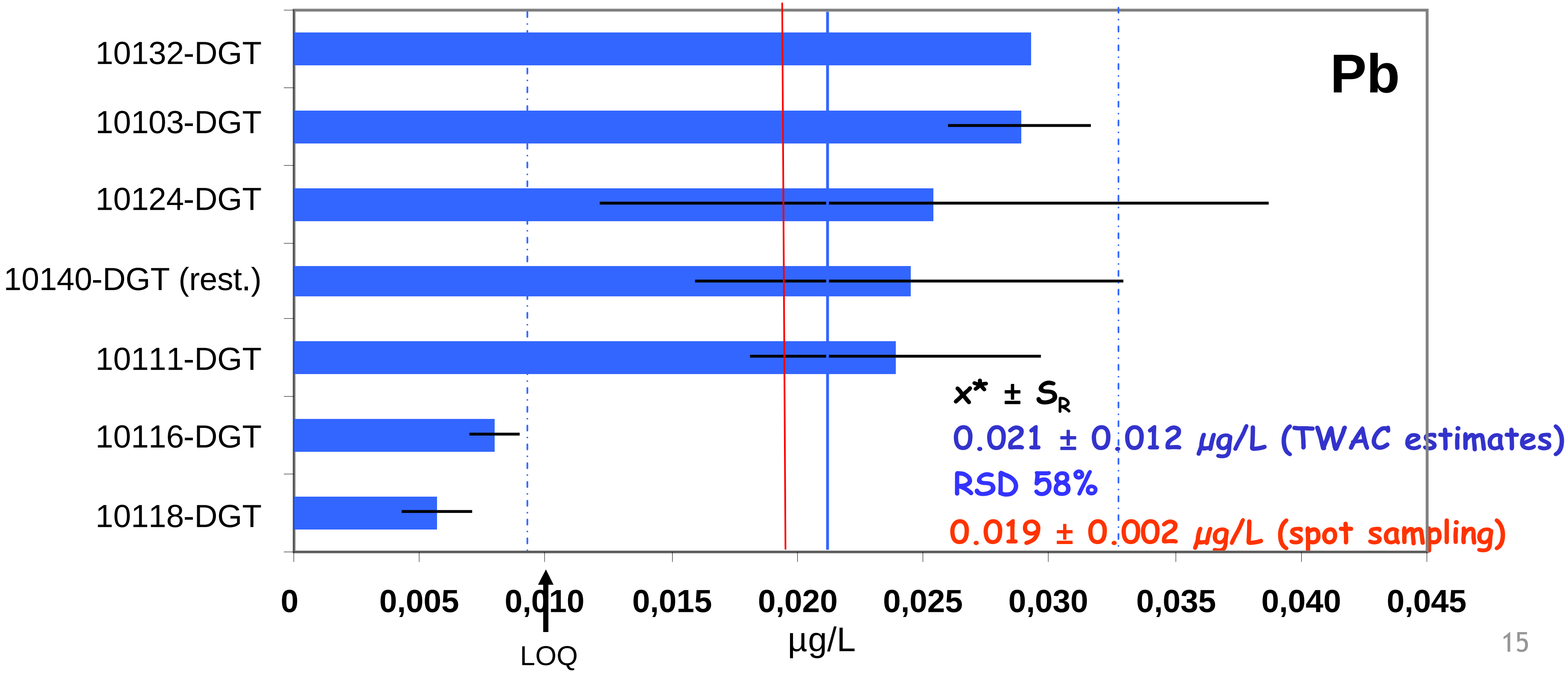

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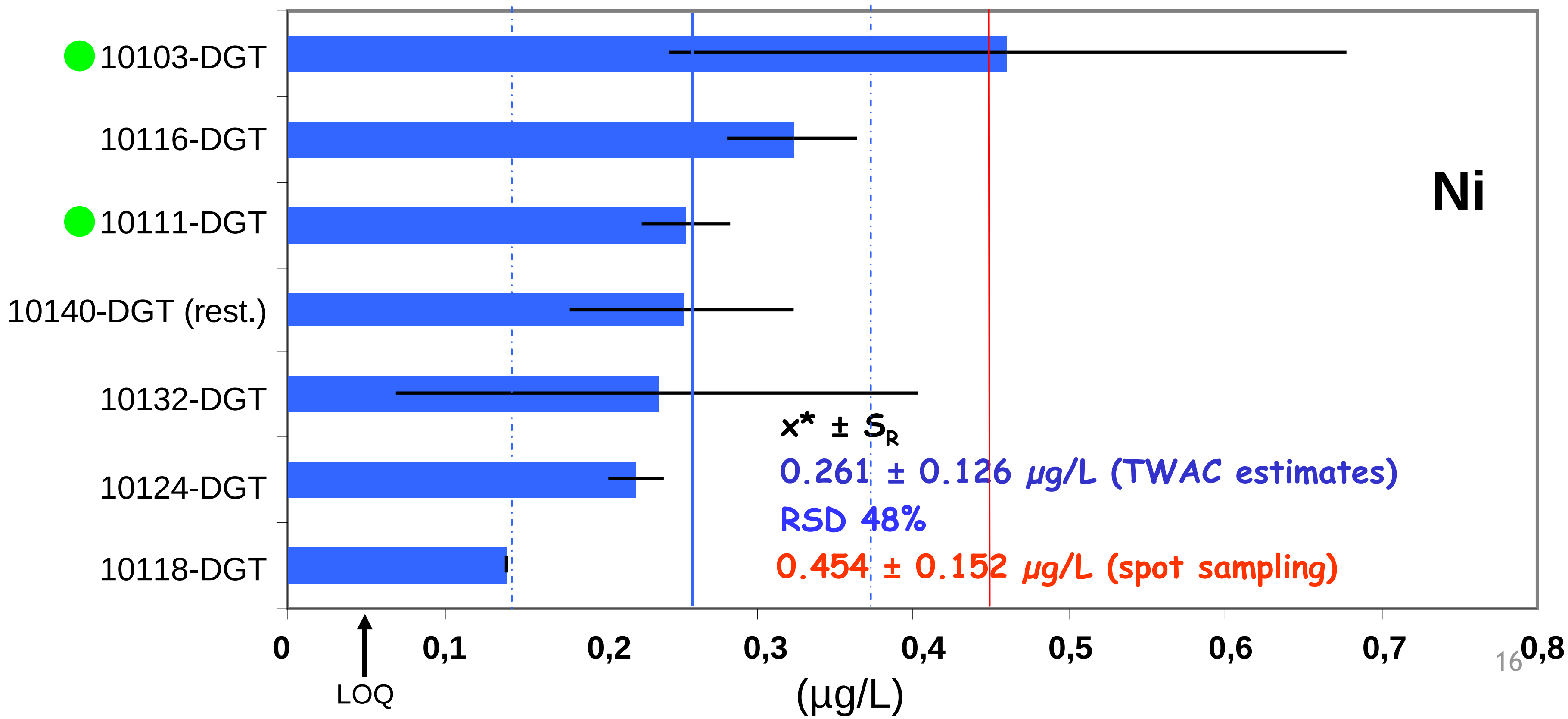
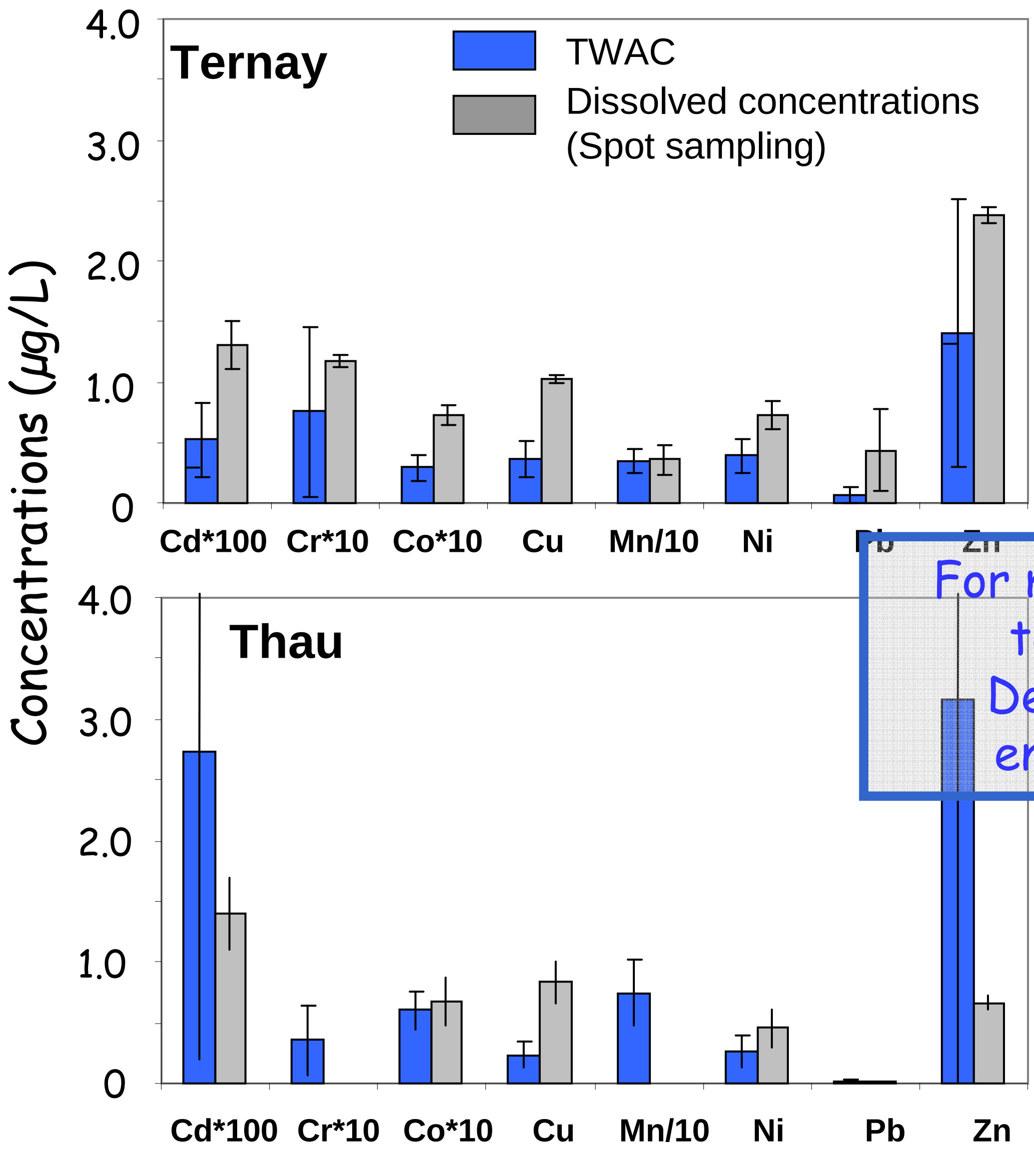


Comparison of TWAC and spot sampling (Dissolved concentrations)



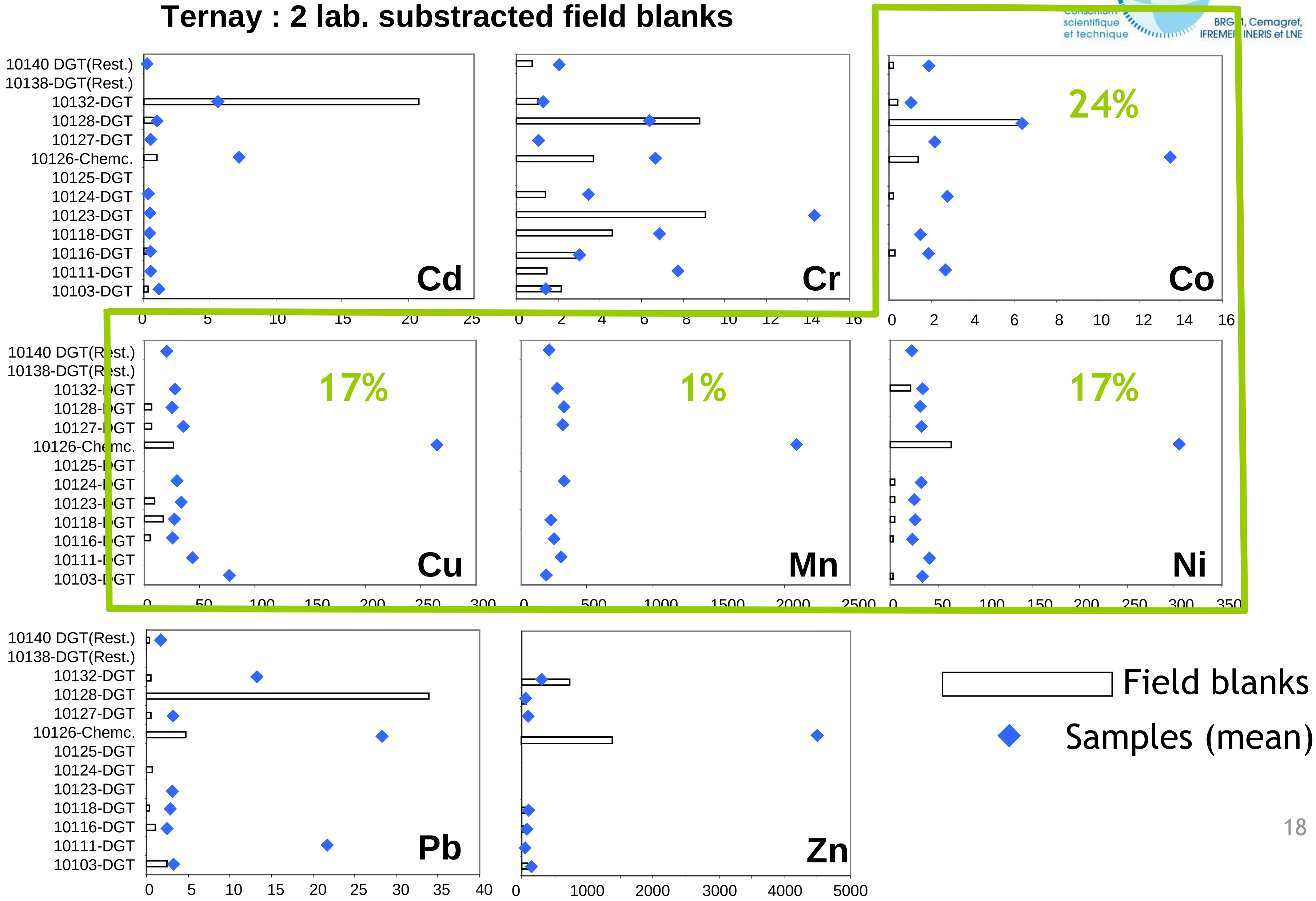
- 100 % of total dissolved Mn was sampled by PSs

- Only 35% of Cu was sampled by PSs

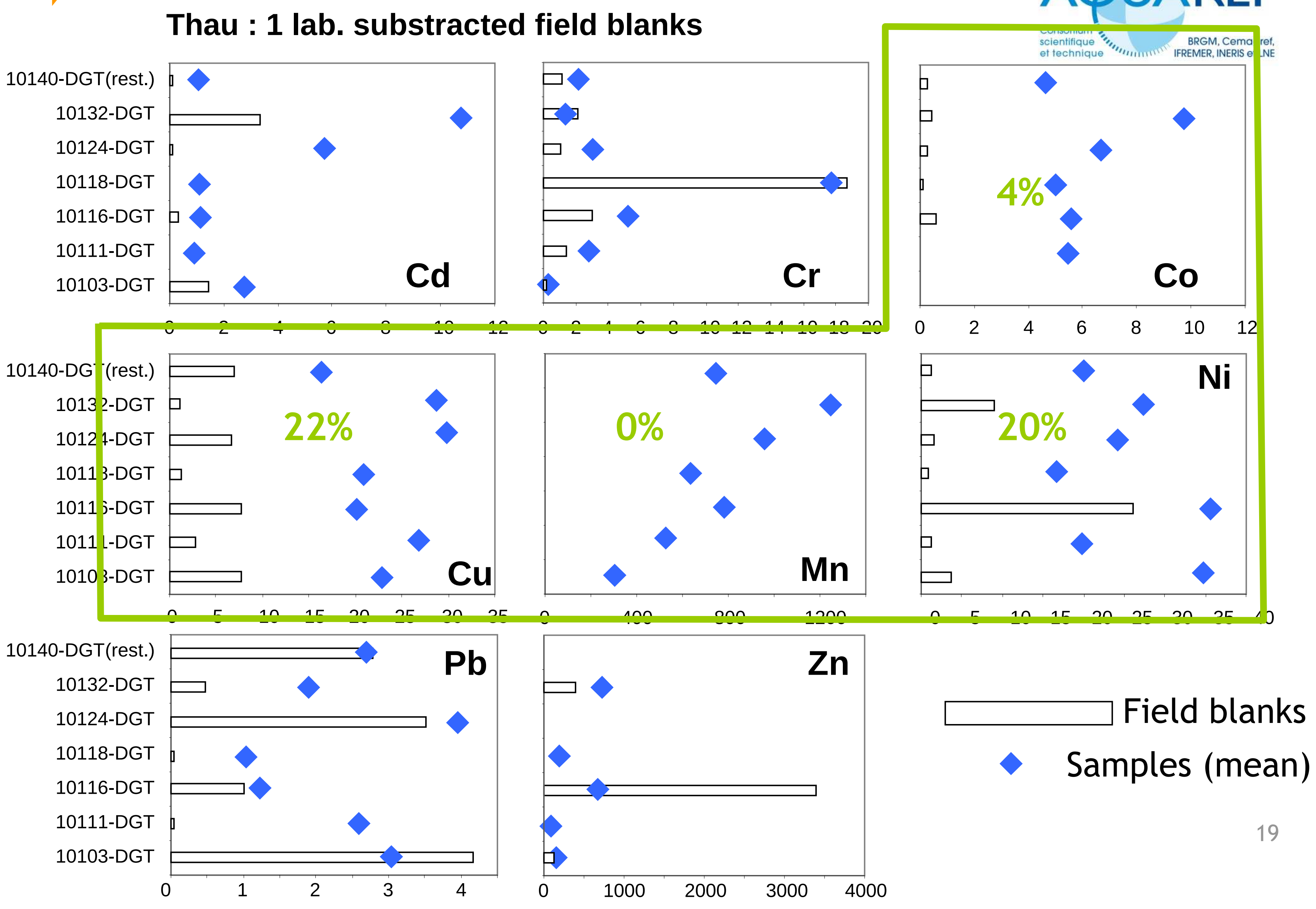
For metals, PSs only « see » a part of total dissolved concentrations,
Depends on the metal and on the environmental conditions (DOM)

Field blanks for metals (ng/tool)

Ternay : 2 lab. substracted field blanks

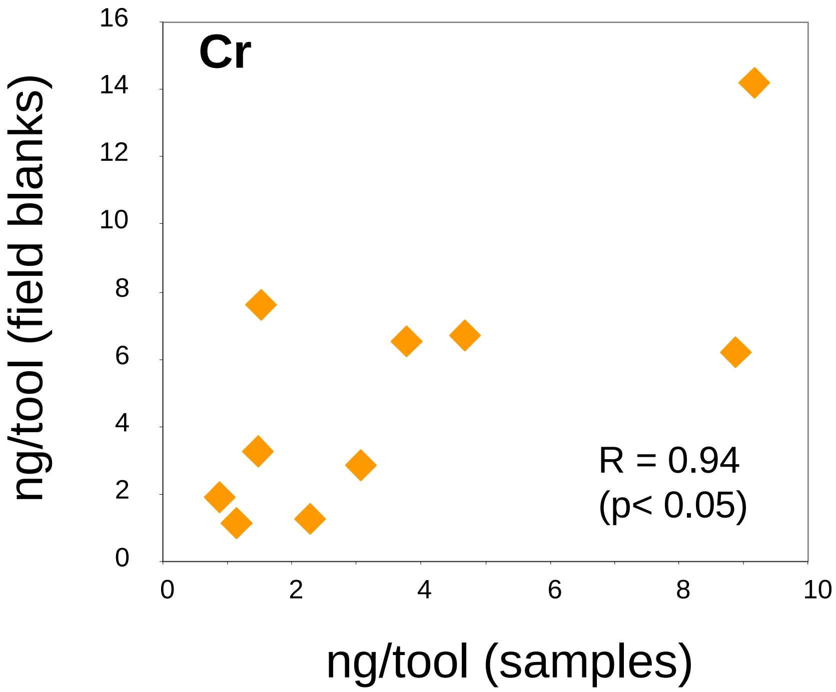


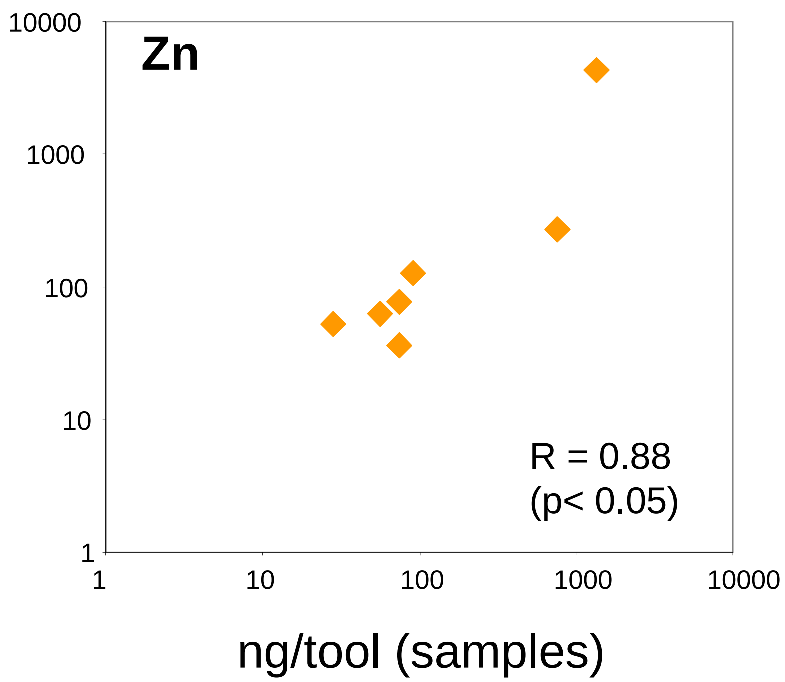
Field blanks for metals (ng/tool)



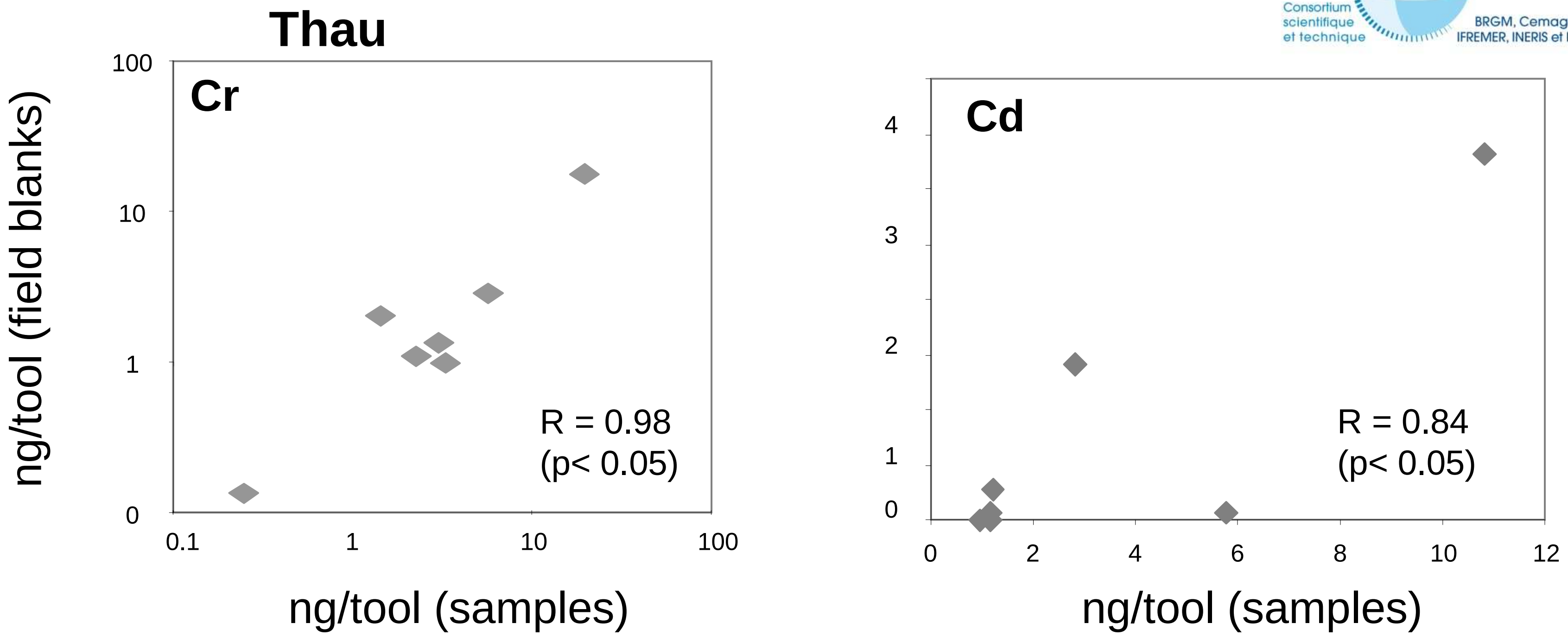
Field blanks for metals

Ternay





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

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**

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

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)

Thanks to central lab for water analysis

AQUAREF

Consortium scientifique et technique

BRGM, Cemagref, IFREMER, INERIS et LNE

- **IFREMER (metals and physico-chemical parameters in Thau site)**
- **Cemagref of Lyon (metals and physicochemical parameters at Ternay site)**
- **Ineris for data treatment**

Thank you for your attention