Monitoring of metals in surface waters: an in situ intercomparison exercise on passive samplers

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A. Dabrin[1*], J-L. Gonzalez[2], J-P. Ghestem[3], E. Uher[4], C. Miège[1], M. Coquery[1]
I.J Allan[5], M. Schintu[6], J. Balaam[7], E. Peinerud[8], N Montero[9], N. Chhim[10]

[1*]**IRSTEA**, UR MALY, 5 rue de la Doua, CS700077, F-69626 Villeurbanne Cedex, France, [2] **Ifremer**, F- 83507,La Seyne/Mer, France, [3]**BRGM**, F-45060, Orléans, France, [4]**Irstea**, UR HBAN, F-92163, Antony, France.
[5]NIVA, Oslo, Norway, [6]Università degli Studi di Cagliari, Italy, [7]Cefas, Centre for the Environment Fisheries and Aquaculture Science, Lowestoft, United Kingdom, [8]ALS Scandinavia, Sweden, [9]AZTi-Tecnalia, Marine Research Division, 20110 Pasaia, Spain, [10]EDF R&D, LNHE, Moret-sur-Loing, France
*: corresponding author (aymeric.dabrin@irstea.fr)

1 Objective of the AQUAREF intercomparison passive sampling exercise

● **Context**: In the context of the Marine Strategy Framework Directive (MSFD) and the Water Framework Directive (WFD), monitoring of marine waters and freshwaters quality became a crucial point. Thus, there is a need to apply innovative sampling tools in surface waters such as passive samplers, taking into account temporal and spatial aspects, with a limited cost and easy to use by non-expert routine laboratories.

● **Aim** : To assess the relevance of passive samplers for the monitoring of metals in surface freshwaters and coastal waters, an in-situ intercomparison passive sampling exercise was realised in 2010. The aim of this study was to assess interlaboratory variability, at each step of the exercise leading to a "dissolved-labile" metal Time Weighted Average Concentration (TWAC).

2 Description of the trials

● 2 sampling sites

Coastal waters

Thau Lagoon (Hérault)

River Waters

Rhône River: Ternay site

● Common constraints

- Exposure of passive samplers

Exposure in triplicate (7 days)
Field blank

- Analytical control (QC)

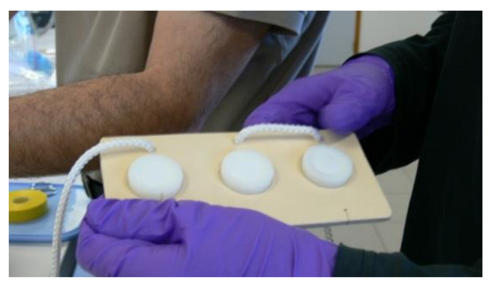
Analysis of a reference solution (8 metals at 1 µg/L)

- Target metals

Priority substances (WFD): **Cd, Pb and Ni**
Other metals (including 3 of the good ecological status): **Cr, Zn, Cu, Mn and Co**

● 10 European expert laboratories

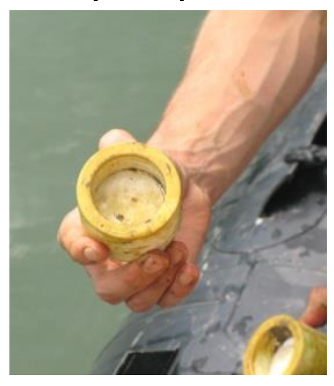
5 FR, ES, UK, SWE, NO, IT
(10 at Ternay site, 6 at Thau site)



● Lab usual tools & protocols

- 3 types of passive samplers

DGT OP: Diffusive Gradient in Thin films (Chelex-100, « open pores » gel
DGT RP: Chelex-100, « restrictive pores » gel
Chemcatcher® (Empore chelating disc)



- Analytical procedures

Elution (HNO_3 1M), ICP-MS or GF/AAS

- Data treatment

Diffusion coefficients from literature

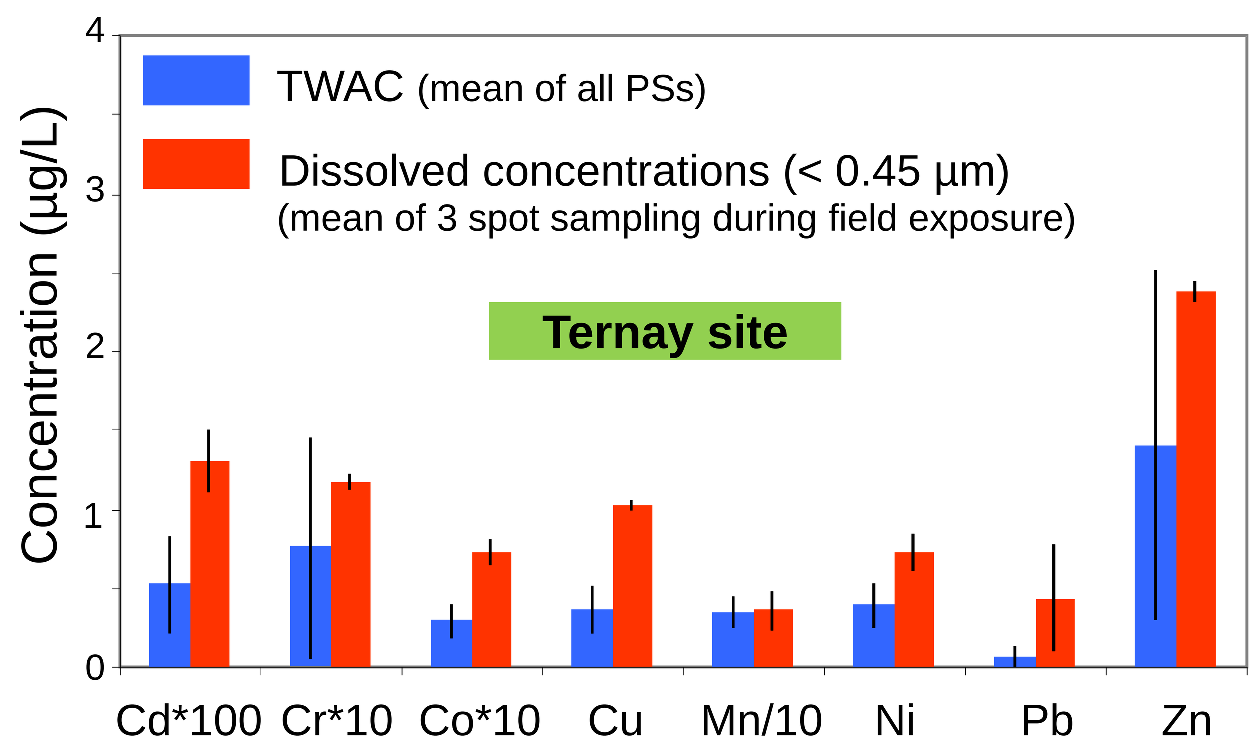
3 Significant Results

● Data dispersion of passive samplers

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

● PSs allow to decrease limit of quantification (LQ).
● Comparison with a classical proficiency testing exercise, only taking into account analytical procedure, show a **similar dispersion for Cd, Cr and Cu,** a **lower dispersion for Ni,** and a **higher dispersion of PSs data for Pb and Zn**.
● The reproducibility is very satisfying considering the different tools and analytical procedures. Since analytical variability was low in this exercise (from 8 to 25%), the dispersion was mainly due to PS deployment step.

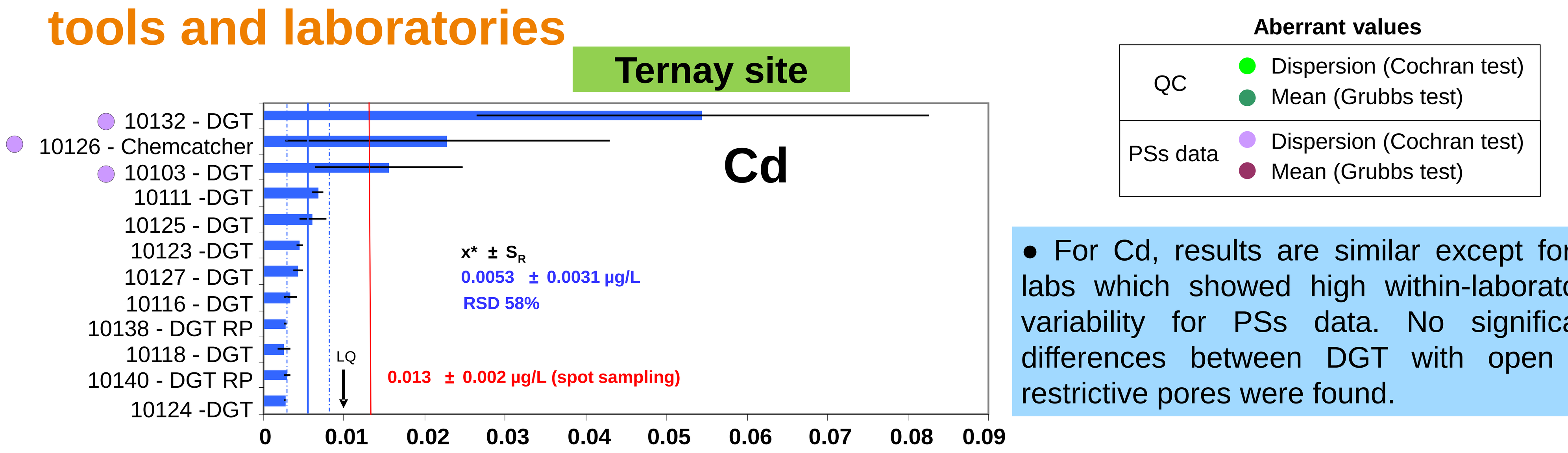
● Comparison of TWAC *vs* Spot sampling



● TWAC were systematically lower or similar to total dissolved concentrations obtained after spot sampling
● For example, dissolved Mn was totally sampled, while only 35% of dissolved Cu was sampled by PSs.

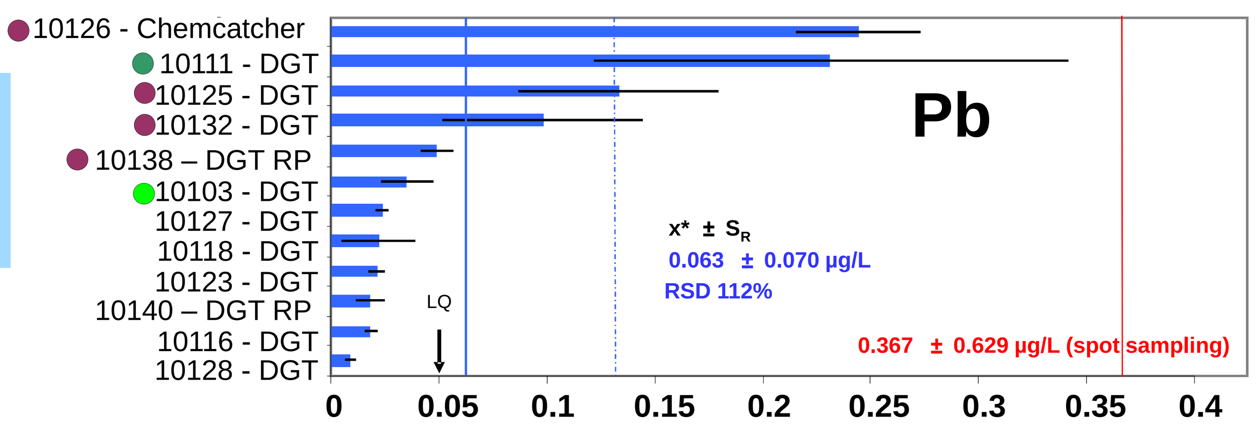
● Comparison of passive sampling results from various tools and laboratories

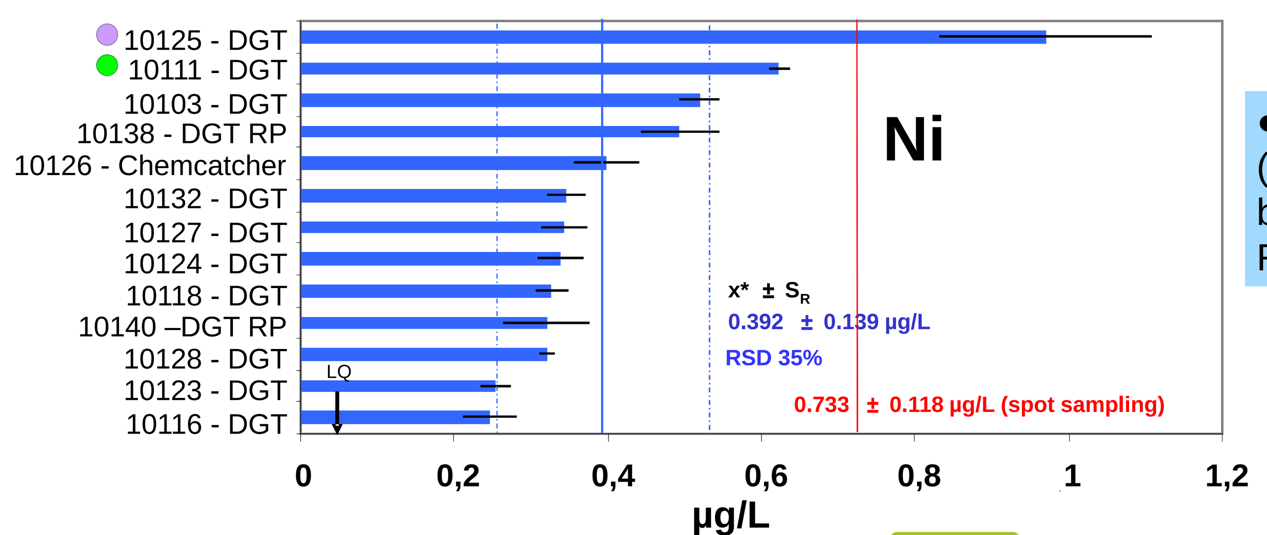
Ternay site



● For Cd, results are similar except for 3 labs which showed high within-laboratory variability for PSs data. No significant differences between DGT with open or restrictive pores were found.

● Pb presents high variability with 6 labs out of 10 in where aberrant values for CQ or PSs were obtained.

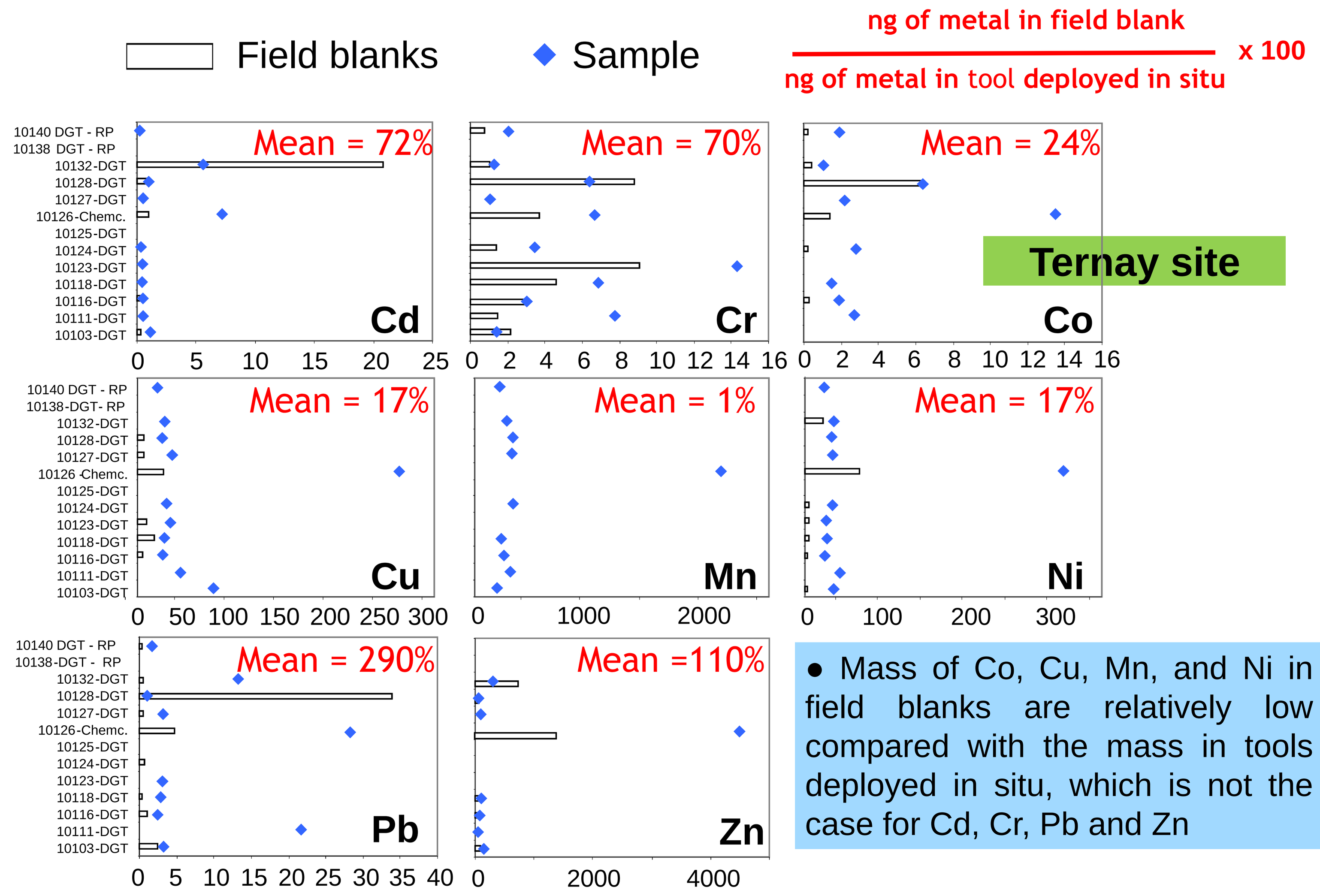




● For Ni, results of PSs are homogeneous (except one outlier) and no differences between Chemcatcher, DGT OP and DGT RP results were found.

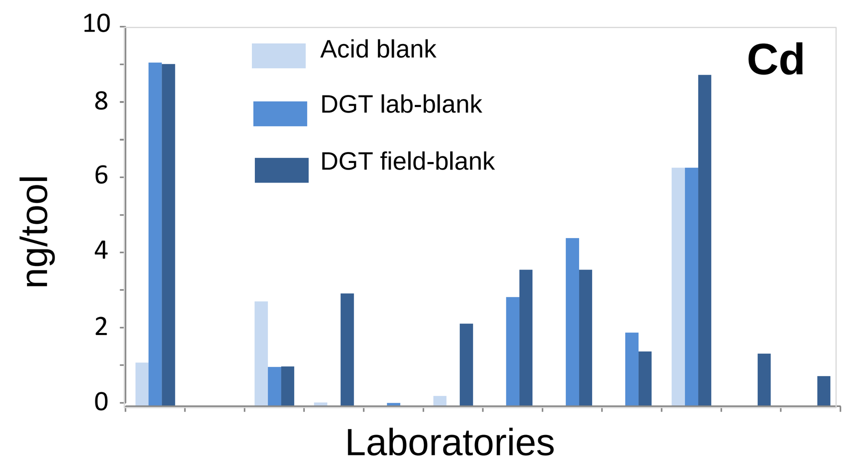
● Field and lab blanks

$$\frac{\text{ng of metal in field blank}}{\text{ng of metal in tool deployed in situ}} \times 100$$



● Mass of Co, Cu, Mn, and Ni in field blanks are relatively low compared with the mass in tools deployed in situ, which is not the case for Cd, Cr, Pb and Zn

● For example, high Cd contents in DGT field blanks seem related to a contamination from the DGT resin (DGT lab-blank)



For more information: Miège et al, Trends Anal. Chem., 2012,36, 128-143
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