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Metal measurement in aquatic environments by passive sampling methods: Lessons learning from an in situ intercomparison exercise

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Abstract :

Passive sampling devices (PS) are widely used for pollutant monitoring in water, but estimation of measurement uncertainties by PS has seldom been undertaken. The aim of this work was to identify key parameters governing PS measurements of metals and their dispersion. We report the results of an in situ intercomparison exercise on diffusive gradient in thin films (DGT) in surface waters. Interlaboratory uncertainties of time-weighted average (TWA) concentrations were satisfactory (from 28% to 112%) given the number of participating laboratories (10) and ultra-trace metal concentrations involved. Data dispersion of TWA concentrations was mainly explained by uncertainties generated during DGT handling and analytical procedure steps. We highlight that DGT handling is critical for metals such as Cd, Cr and Zn, implying that DGT assembly/dismantling should be performed in very clean conditions. Using a unique dataset, we demonstrated that DGT markedly lowered the LOQ in comparison to spot sampling and stressed the need for accurate data calculation.

Highlights

► Uncertainties on DGT results were assessed during an in-situ intercomparison exercise.► DGT handling and analytical procedure steps are responsible for the dispersion of data.► Data dispersion was similar between raw data and the TWA concentrations.

Keywords : DGT, Uncertainty, Blank, Continental waters, Coastal waters

1. Introduction

Reliable chemical monitoring of surface waters has become a crucial issue, especially in the context of the Water Framework Directive (WFD). In particular, there is an emerging need to find cheap and easy alternatives to spot sampling taking into account temporal variability (e.g. flood events, seasons). Several tools have been developed over the years to address this challenge, including bioassays/biosensors, biomonitors, chemical sensor probes and passive samplers (PS).

The last 20 years have seen a surge in the development of PS to enable measurements of a wide range of contaminants in surface waters (e.g. Vrana et al, 2014). PS tools carry many advantages, as they (i) provide an integrated measure of the contamination over the period of deployment, (ii) preconcentrate contaminants, which enables a lower limit of quantification (LOQ) than classical analysis in spot samples and (iii) simplify the matrix of the sample. Allan et al. (2006) showed that time-weighted average (TWA) concentrations estimated by PS could be used to monitor long-term trends, to screen contaminants at very low concentrations, and to identify sources of pollution. For metals, diffusive gradients in thin films (DGT) and Chemcatcher® are the main PS devices used for monitoring surface waters (Allan et al., 2008). The DGT device consists in a plastic piston loaded with a diffusive gel layer backed by an ion-exchange resin gel (Chelex-100). The diffusive gel of the DGT allows to measure metals in ionic form and weakly bound to small inorganic and organic complexes, which represent a fraction of the total metal dissolved concentration (<0.45 µm), commonly called the ―labile" fraction. Metal accumulation in the resin is governed by the concentration gradient established in the diffusive gel between the media and the resin. The TWA concentration of the metal present in water over the period of exposure may be estimated as follows:

$$TWAC = \frac{m \cdot \Delta g}{D \cdot t \cdot A} \qquad (1)$$

where m is the mass of metal accumulated in the receiving phase of the DGT (ng), Δg is the thickness of the diffusive gel/filter (cm), D is the diffusion coefficient of the ionic metal in the diffusive gel ($cm^2.s^{-1}$), t is the period of deployment (s), and A is the surface area (cm^2) of DGT. For this calculation, only m has to be determined by the analytical step, as Δg, D, t and A are generally known (DGT supplier and field data). The Chemcatcher® is constituted by a standardized body combining a cellulose acetate membrane with a 47 mm Empore™ chelating disk for metals measurement. The uptake rates needed to calculate TWA concentrations are less well known for Chemcatcher than the diffusive coefficient determined for DGT (DGT Lancaster), and require element-specific uptake rate estimations in field conditions (Neziri et al., 2011).

The DGT has a rapid response to fluctuating concentrations of Cd, Cu, Ni, Pb and Zn during the period of deployment (Allan et al., 2007). For Cu, Zn and Pb, TWA concentrations were in agreement with the filtered or ultrafiltered fractions obtained in spot samples and with predicted inorganic and inorganic-fulvic acid associated metal fraction according to the visual MINTEQ programme (Allan et al., 2007). Thus, DGT has been widely used as a speciation tool for metals in freshwaters (Roig et al., 2011), coastal waters (Schintu et al., 2008), and sediments (Dabrin et al., 2012). Several studies have focused on the applicability of DGT for monitoring metals in freshwaters. Montero et al. (2012) reported that DGT gave reproducible TWA concentrations for Cd, Cu, Ni and Zn in highly-fluctuating systems such as estuaries. However, Buzier et al. (2014) reported that DGT monitoring of Cu, Cd, Ni and As in surface waters requires stringent procedures to avoid DGT contamination and biases in the TWA concentration estimation. Allan et al. (2008) also assessed Chemcatcher performances for measuring Cd, Cu, Ni, Pb and Zn in surface waters. They reported that DGT and

Chemcatcher gave similar Cd and Zn concentrations to filtered samples, but both PS consistently underestimated Cu and Ni concentrations and carried high measurement uncertainty for Pb due to low sampler accumulation for this metal. Moreover, to improve validity of Chemcatcher TWA concentrations, a performance reference compounds procedure was needed to account for *in situ* turbulence, biofouling and temperature (Allan et al., 2008).

The upshot is that while both DGT and Chemcatcher are widely used for monitoring metals in waters, there has been little effort to assess the uncertainty of their measurements. To date, only one study has reported global results of an *in situ* intercomparison exercise on several PS for priority pollutants (polycyclic aromatic hydrocarbons, pesticides and metals) in surface waters (Miège et al. 2012). This first trial allowed to evaluate the representativeness of PS for *in situ* monitoring and showed that despite the very low concentration levels, the variety of tools and the different exposure and analytical strategies, global interlaboratory dispersion was relatively low (relative standard deviation, RSD<100%). Nevertheless, this work needed further investigations of results on metals measurements by DGT, particularly to scrutinize sources of TWA concentration uncertainties, such as analytical and data treatment steps.

2. Strategy of the intercomparison exercise

Ten laboratories with previous expertise in PS deployment participated in this intercomparison exercise, i.e. ALS Scandinavia (SW), AZTI (SP), BRGM (FR), Cefas (UK), Irstea Paris (FR), Irstea Lyon (FR), EDF R&D/LNHE (FR), IFREMER Toulon (FR), NIVA (NO) and University of Cagliari (IT). Ten and 6 laboratories participated in the exercise for metals at Ternay (France) and Thau (France), respectively. Each laboratory was asked to provide its own samplers and apply its own methodology and strategy for PS assembly/deployment, PS analytical treatment and TWA concentration calculation.

Field campaigns were led on two contrasted environments: one continental (Rhône River, Ternay, France) and one coastal (Thau Lagoon, Hérault, France). All PS were deployed 7 days at Ternay (17–24 June 2010) and 9 days at Thau (27 April–5 May 2010). Details of the exercise strategy are available in Miege et al. (2012).

Since some laboratories (3 at Ternay and 1 at Thau) exposed two types of PS for metals, each laboratory code corresponds to the association of one laboratory and one tool. The exposed PS were represented by DGT with open pores (OP) or restrictive pores (RP), while only one Chemcatcher® was deployed at the Ternay site (Table 1). For each laboratory, PS were exposed in triplicate together with one field blank (i.e. brought to the field but not exposed in waters). Results from PS blanks (DGT/Chemcatcher laboratory blank) and from the acid used for resin elution (acid blank) were also provided by each participant. Each laboratory was asked to analyze 8 metals, i.e. Cd, Pb and Ni (priority substances of the WFD; EC, 2013), Cr, Cu and Zn (substances on the French ecological status list; MEEDDM, 2010), Mn and Co; and to provide information related to analytical performances (Table 2), diffusion coefficients used (Table 3), resin elution, analytical procedure and calculation steps (Table 3).

In order to evaluate the accuracy and uncertainty of the analytical step, all participants were provided with a reference solution (QC solution) that had to be analyzed in triplicate (n=3) at the same time as PS eluate. The reference values for the QC solution were obtained by isotope dilution coupled with inductively-coupled plasma mass spectrometry (ICP-MS). Since Mn and Co have only one isotope, a standard addition method was used.

In order to compare TWA concentrations against total dissolved metal concentrations, surface water samples were collected at the start, during and at the end of PS deployment. Samples were collected in polypropylene bottles, immediately kept at 4°C, then filtered with polyvinylidene difluoride (PVDF) filters (0.45 µm) previously cleaned in HNO_3 10% (v/v). At the Ternay site, filtrates were acidified with ultra-pure HNO_3 (0.5% v/v). At the Thau site, due to the saline matrix, samples were preconcentrated by liquid-liquid extraction prior to analysis (Danielsson et al., 1982). All samples were then analyzed by ICP-MS (Thermo X7, Series ^{II}).

A robust mean value and associated uncertainty was calculated for the QC solution and the field-exposed PS according to ISO standard method 5725-5 (1994); Miège et al., (2012).

3. Results and discussion

3.1. The analytical step: the need for a clean room to avoid contaminations

In order to identify which step(s) could affect the dispersion of TWA concentrations obtained by PS, a thorough evaluation of the analytical step was performed. Figure 1 displays results of QC data from each laboratory with robust means and reference values of the QC solution. The ratio between robust mean and reference value (expressed in percentage) varied from 91% for Ni to 123% for Zn. Clearly, there was a lack of accuracy for Zn, since there was no overlap between the reference value ± uncertainty of the QC solution (1.030 ± 0.036 µg/L) and the robust mean (1.263 ± 0.130 µg/L). This is not surprising, since Zn is known to be one of the most critical metals to analyze at low levels due to sample contamination at low level. Since the QC solution had to be directly analyzed without pretreatment, this suggests that sample and calibration solutions have to be handled in very clean conditions (clean room and/or under a laminar flow hood) to minimize contamination. A recent intercomparison exercise on surface water analysis at low-level concentrations (Zn=1 µg/L) involving 24 routine laboratories in France also showed a tendency to overestimate Zn concentrations (139%) (Ghestem et al., 2012). Hence, these results confirm that laboratories liable to run PS measurements must first learn to master contamination during the analytical step, especially for Zn.

3.2. The choice of instrumental method for metal analyses: a crucial point to reduce uncertainties

Zn, Cr, and Ni showed the highest analytical-step dispersion, at 24%, 22% and 16%, respectively (Fig. 1). Our results are in accordance with the intercomparison exercise from Ghestem et al. (2012) on water analysis, which also showed that at similar concentrations (Zn: 1 µg/L, Cr: 1.5 µg/L and Ni: 0.5 µg/L), RSDs were 23%, 13% and 17%, respectively. Here, two laboratories *(#E and #K*) reported concentrations that were systematically far from the reference values for Zn, Cr and Ni. In some cases, concentrations were also far from the reference values for Cd, Co, Mn, Pb or Cu, for which one or both laboratories reported results with poor accuracy or poor analytical repeatability. Table 2 details the analytical technique and LOQ reported by each laboratory. Most laboratories used ICP-MS, whereas laboratories *#E* and #K used graphite furnace atomic absorption spectrophotometry (GF/AAS). As expected, LOQ was one order of magnitude lower for ICP-MS than for GF/AAS (Table 2), which could explain the poor repeatability and/or accuracy for GF/AAS results at the µg/L level. Therefore, laboratories need to analyze PS extracts with analytical instrumentation combining high precision and sensitivity to ensure valid data for low-level metal concentrations in environmental waters.

3.3. Blank control

Figure 2 reports the results for acid blanks, DGT laboratory blanks and Ternay-site DGT field blanks as the mass of analyte in the eluates. For Mn, the mass in field blanks (mean of 3.6 ng) was about 1% of the mass in Ternay-exposed DGT (mean: 306 ng) after the 7-day deployment. For Co, Ni, Cu and Pb, the mean contribution of mass of metal in DGT field blanks to the mass of metal in exposed DGT was 11%, 12%, 12% and 21%, respectively (excluding laboratory *#J* for Co and Pb, which reported higher values). For Zn, Cd and Cr, DGT field blank levels were high compared to the mass accumulated in DGTs exposed for 7 days in the river, representing mean contribution of 83%, 72% and 65%, respectively. In most cases, the mass of metal in DGT field blanks could be explained by a contamination already present in DGT laboratory blanks. Since the mass of metal was negligible in acid blanks (Fig. 2), this suggests that observed contaminations were mainly due to contamination of the resin itself (during its preparation) and/or to the pre-elution resin handling step. These results clearly show that the determination of TWA concentrations for trace metals such as Zn, Cd or Cr is a delicate issue. For Zn, high blank levels in DGT were also reported by Munksgaard et al. (2003). However, Sigg et al. (2006) also reported blank values in commercially available DGT for Zn which were lower (32±55 ng) than those obtained during this intercomparison exercise (137±242 ng). It is possible to subtract DGT laboratory blank from results obtained for exposed DGT, but only if the results for DGT laboratory blanks are sufficiently reproducible. To overcome this problem, a deployment over several weeks could enable to trap a significantly higher mass of Zn, Cd and Cr than the mass initially present in DGT laboratory blanks. Alternatively, Buzier et al. (2014) proposed to determine a LOQ-DGT value representing the lowest mass of metal that could be quantified without a significant blank contribution. This LOQ-DGT value was determined as the mean of DGT field blanks (n=44) and 10-fold the standard deviation (mean ± 10×SD). In our case study, this approach could have been an interesting alternative but it would have required each laboratory to determine its own LOQ-DGT by analyzing several DGT laboratory blanks.

Clearly, there is a need to improve the DGT measurement protocol in terms of blanks and risk of contamination. Improvement hinges on clean conditions (e.g. cleanroom, laminar flow hood), precise estimation of global contamination, and a methodology for factoring these blanks into the final result. In our opinion, the estimation of LOQ-DGT appears to be the best way forward on this issue.

3.4. Effect of LOQ decrease

One asset offered by PS is the possibility to decrease LOQ by preconcentrating the metal on the receiving phase, which this intercomparison exercise has demonstrated as a powerful advantage of PS devices. For Cd, for example, analytical LOQ averaged 32 ng.L^{-1} in spot samples (Table 2); but, when DGT was applied with the average elution volume (4.05 mL), average dilution factor (6.4), average diffusion coefficient of Cd at 20°C (5.3. 10^{-6} cm².s^{-1}), average diffusive gel thickness (0.94 mm) and a period of deployment of 7 days (604 800 s), the LOQ for Cd was reduced to 0.80 ng/L. This means that DGT could decrease LOQ by a factor ~40. Another asset of PS is related to its application in coastal or marine environments. Indeed, the PS devices investigated allowed to directly measure metals at ultra-trace levels in coastal waters and, contrary to spot water samples direct analysis, which requires an extraction step for eliminating the saline matrix that potentially induces analytical interferences (i.e. Danielsson et al., 1982).

3.5. Exploration of usual practices

3.5.1. The PS extract dilution factor before analysis

Table 1 shows the volume of elution and the dilution factor applied by each laboratory to prepare the PS extract. These parameters ranged from 1 to 10 mL (elution volume) and from 1 to 10 (dilution factor). For example, if each laboratory was handed the same PS with an amount of 1 ng of metal for analysis, the actual combination of volumes of elution and dilutions factor used by laboratories would have given a metal concentration in the eluate ranging from 0.020 to 1 µg/L, which underlines the huge variation in laboratory practices. These different practices mainly reflect laboratory habits and are also justified according to their analytical LOQ, and to the percentage of nitric acid concentration required in the final eluent solution. Thus, applying a small volume of eluent and minimizing the dilution factor before analysis could drastically concentrate metals before analysis. The choice of the these two steps also highly depends on the compromise which was chosen by each laboratory: (i) obtain a more diluted sample in a large volume, which leaves the possibility to perform several replicates of analysis or (ii) obtain a more concentrated sample but in a small volume; thus, leaving no second chance to perform replicate analysis. These are the two crucial steps in DGT extract preparation for which good practice could radically reduce problems linked to contamination and decrease analytical uncertainty. These different analytical protocol-related practices can lead to very different (up to a factor of 50) measured final concentrations and to variation in the defined LOQ for PS.

3.5.2. Correction of the PS extraction yield

In order to evaluate the mass of metal on the resin, most laboratories applied a correction factor called “elution factor” to take into account partial extraction from the resin. As presented in Table 1, most laboratoriess applied an elution factor of 0.8, as provided by the DGT manufacturer. However, two laboratories (*#C and #D*) did not correct DGT data by an elution factor, and one laboratory (*#K*) did not correct DGT data for Cd, yet applied an elution factor of 0.7 for Pb. In fact, the two laboratories that used an elution factor of 1 were those that also used the highest volume of elution (10 mL). Unfortunately, this elution factor of 0.8 provided by the DGT supplier was mainly applied by laboratories that used the most disparate conditions. Given the broad differences in elution practice, this “common” empirical extraction yield emerges as a key factor of dispersion in DGT measurement (RSD of 20% with or without correction, as observed in this study); which suggests the need for either intra-laboratory estimation of extraction yield or the development of an elution protocol leading to “total extraction” of metals from the resin.

3.5.3. Influence of PS model constants: diffusion coefficient, gel thickness, DGT surface area

The diffusion coefficients (D) applied by each laboratory to calculate TWA concentrations (Eq.1) from DGT results are reported in Table 3. Even though the trial organizer provided the mean temperature of the exposure period at both sites (19.8°C at Ternay site; 17.9°C at

Thau site) to all laboratories, the diffusion coefficients used by each laboratory were quite variable. For example, at Ternay site for Pb and for DGT-OP, laboratory #B applied a diffusion coefficient of 6.29 . 10^{-6} cm²/s whereas laboratory #D used a value of 10.0 .10^{-6} cm²/s. In fact, for both the Ternay and Thau sites, the ratio between the minimum and maximum value of diffusion coefficients applied for a same metal ranged from 1.3 for Cd to 1.6 for Pb. This large variation in diffusion coefficients is explained by the fact that some laboratories (i.e. laboratory #E) had prepared their own diffusive gels and characterized metal diffusion coefficients for their own gel. DGT-RP was deployed by two laboratories who applied a diffusion coefficient that represents 70% of the diffusion coefficients used for DGT-OP (Scally et al., 2003).

Concerning the other coefficients of the equation (Eq.1), gel thickness (Δg) values applied by each laboratory were fairly similar, ranging from 0.76 mm to 0.94 mm and varying according to the different DGTs used. Also, surface area of DGT (A) was similar (3.14 cm²) for all DGTs purchased from DGT Research Limited, Lancaster (Table 1). However, some laboratories applied different surface areas to calculate TWA concentrations for DGT-OP and DGT-RP (#L and #G: 3.80 cm²; #*D* 4.91 cm²). The 3.80 cm² area represents the effective sampling area provided by Warnken et al. (2006) when a diffusive boundary layer (DBL) is taken into account; while the value of 4.91 cm² used by one laboratory (#D) is a wrong value, since its represents the total surface area of the filter. In this case, the total diffusion layer comprises the filter and the gel layer (Δg) plus the DBL thickness δ (0.2 mm in well-stirred cases). Even if the surface area applied by laboratory #D was 56% higher than by the other laboratories, the TWA concentrations calculated were not identified as outlier (Fig. 4 and 5), suggesting that this term of the equation had no impact on the final result of this laboratory.

For example, we applied different combinations of data in the model calculation from raw data obtained by laboratory #F for Cu at Ternay site. By applying a thickness of 0.91 mm (gel + filter), a surface area of 3.14 cm² and by neglecting the DBL, this laboratory obtained a TWA concentration of 0.305 µg/L. If the thickness of the filter was neglected, result should have been 16% lower (0.254 µg/L). By applying a DBL of 0.2 mm and an adapted surface area of 3.8 cm², TWA concentration should have been equal to 0.307 µg/L, which is close to the initial result. In an another case, if a DBL was added (0.2 mm) to the model calculation without changing the surface area, TWA concentration should have been equal to 0.372 µg/L which is 22% higher than initial result. These simulations of various combinations of data inputs lead to TWA concentrations ranging from 0.254 to 0.372 µg/L , which correspond to the range of data obtained at Ternay site for laboratories (Figure 4) which did not exhibit outliers' for TWA data.

3.6. Dispersion of PS measurements

3.6.1. Comparison between concentrations in ng/tool and TWA concentrations

Figure 3 gives the RSD (%) of Ternay-site and Thau-site data expressed in ng/tool and for TWA (µg/L). Considering all the sampling and analytical steps, the dispersion of data in ng/tool was very satisfactory for Mn, Ni and Cu, with a RSD lower than 18% and 35% at Ternay and Thau, respectively. For Co, the dispersion of data in ng/tool at Thau site was also very satisfactory (14%) but climbed to an unsatisfactory 64% at Ternay. For Mn, Cu and Co, good reproducibility and accuracy was reported for the QC solution (Cf. 3.1, 3.2). Moreover, we observed little contamination of DGT blanks (Figure 2) for these metals, thus resulting in little dispersion of TWA data. In contrast, for Pb, the RSD in ng/tool was higher, reaching 31% and 48% at Ternay and Thau, respectively. Also, data dispersion was higher for Zn, Cd and Cr, ranging from 40% to 88% at Ternay and from 69% to 111% at Thau. The high dispersions in the mass of metals in ng/tool for Zn, Cd and Cr suggest that contamination issues, as previously discussed, were the main sources of dispersion in TWA concentrations.

TWA concentration (Figure 3) followed similar data dispersion patterns as ng/tool. At Ternay for example, RSD for Cu was 18% in ng/tool while RSD of TWA concentration was 15%. At Thau, the dispersion of Cd in ng/tool (111%) was close to that of TWA concentration (101%). Also, data dispersion was reduced, by 21% for Co at Ternay site and by 27% for Cr at Thau site, suggesting that dispersion in ng/tool could be reduced by data used as model inputs. Since data dispersion was similar between data in ng/tool and in TWA concentration, this suggests that whatever the data used as model inputs by laboratories, calculation was proportional, dispersion of data being mainly driven by DGT handling and analytical steps. Although laboratories used different values for certain parameters like diffusion coefficient, gel thickness or surface area (Table 1 and 3), the calculation step did not lead to any greater dispersion of the data. This suggests that the different coefficients needed to calculate TWA concentration did not add significant dispersion over that calculated for DGT accumulated mass. Thus, even if diffusive coefficient values could vary (Table 3) since they are specific to the gel used by each participant, they allowed leading to a similar TWA concentration.

3.6.2. Dispersion of TWA concentrations compared to single analyses

The dispersion of the TWA concentrations obtained during this intercomparison exercise was compared against that obtained in one international proficiency test on freshwaters spiked with selected metals (Table 4; Brunori et al., 2007). The comparison showed higher RSDs for Zn (79-99%), Pb (58-112%) and Mn (28-35) measured by DGT. For Zn and Pb, these higher RSDs could be explained by biases induced by the PS itself, during field deployment (e.g. contamination of PS) and by the low level of concentrations in these two environments (spot sampling: from 0.67 to 1.80 µg/L for Zn and from 0.02 to 0.37 µg/L for Pb). For Mn, the RSD was lower for the proficiency testing (11%) than for this *in situ* PS exercise (28%), probably since proficiency testing was led with 44-fold higher water concentrations than our TWA concentrations. For Cu, Cr and Cd, PS gave similar dispersion as the RSD of the proficiency testing dataset; whereas for Ni, PS gave lower dispersion (41%) compared to proficiency testing (75%). To conclude, the data dispersion on TWA concentration obtained during this PS intercomparison proved very satisfactory given the different laboratories, different tools, *in situ* deployment and ultra-trace concentrations of metals in these two environments (e.g. Cd ~12 ng.L^{-1}).

3.6.3. Comparison of dispersion in TWA concentrations according to laboratory and type of PS

Figures 4 and 5 plot TWA concentrations obtained by each laboratory and tool at the Ternay and Thau sites, respectively. Robust means of TWA concentrations obtained for all laboratories are also displayed. At Ternay, only one Chemcatcher was deployed during the intercomparison exercise and results were only reported for Cd, Cu, Ni, Pb and Zn. Despite satisfactory QC results, TWA concentrations obtained with Chemcatcher nevertheless included some outliers (Cochran test), notably for Cd, Pb and Zn. Unfortunately, with only one dataset, the lack of comparison rules out any definitive conclusions on interlaboratory dispersion for Chemcatcher.

Theoretically, DGT-RP allows the diffusion of free ions and small organic complexes, while DGT-OP also allows the diffusion of metals associated with large organic ligands. In fact, Allan et al. (2007) demonstrated that combining DGT-RP with DGT-OP allows to assess the metal fraction linked to large organic ligands. Nonetheless, results obtained for DGT-OP and DGT-RP by the same laboratory (*#F and #M*) at Ternay were not significantly different for any of the selected metals (Figure 4). It is difficult to reach a conclusion for the other laboratories *(#G* and *#L*), since in most cases (Cr, Co, Cu, Mn, Ni and Pb) TWA concentrations from DGT-RP and/or DGT-OP showed high dispersion according to Cochran and/or Grubbs tests. For Cd and Zn, we found no significant differences between DGT-OP and DGT-RP. These results suggest that, in this specific context, it was difficult to discriminate labile metals (free ions and small inorganic complexes) from metals associated with large organic ligands, even when the analyses were performed by the same laboratory.

4. Conclusion

This in-situ intercomparison exercise on PS for metal analysis in surface waters provided, to our knowledge, a first attempt to identify key parameters controlling TWA metal concentrations estimation and to quantify uncertainties and evaluate their main sources/origin. We clearly demonstrated that DGT handling and analytical procedure steps are responsible for the dispersion of data. Thus, it is necessary that laboratories using such passive samplers for trace metal analysis master contamination by using a clean room (Class 100) for all analytical steps, from the assembly of the DGT tool, their dismantling and elution, to the analysis of eluates. Moreover, laboratories must analyze PS extracts with analytical instrumentation combining high precision and sensitivity to ensure valid data, allowing applying large combination of elution volume and dilution before analysis. For natural marine and fresh waters, the use of ICP-MS is highly recommended. Finally, we showed that whatever the data inputs (i.e., diffusive coefficient, elution factor from bibliography for purchased DGT, or determined in laboratory for home made DGT) which were used by laboratories in model calculation, data dispersion was similar between raw data obtained in ng/tool and the TWA concentrations.

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Tables

Table 1: Type and characteristics of passive sampler and extraction steps before analysis used by each laboratory at the two deployment sites.

(1) DGTOP: DGT with a diffusive gel with open pores (~ 5 nm), DGT-RP: DGT with a diffusive gel with restrictive pores (~ 1 nm)

nd : not determined

Laboratories were identified (by *, # and □) when they deployed two types of tools.

Lab code	PS tool	Ternay Site	Thau Site	Binding agent	Gel thickness (mm)	Surface area (cm²)	Volume elution (ml)	Volume resin (ml)	Dilution before analysis	Elution factor	Analysis
A	DGT-OP	●	●	Chelex-100	0.94	3.14	1.0	0.15	10	0.8	ICP/MS
B	DGT-OP	●	●	Chelex-100	0.80	3.14	1.8	0.16	10	0.8	ICP/MS
C	DGT-OP	●	●	Chelex-100	0.80	3.14	10	0	5.0	1.0	ICP/MS
D	DGT-OP	●	●	Chelex-100	0.78	4.91	10	0.20	nd	1.0	ICP/MS
E	DGT-OP	●		Chelex-100	0.76	3.14	1.0	0.16	nd	0.8	GF/AAS
F*	DGT-OP	●	●	Chelex-100	0.78	3.14	2.5	0.15	3.5	0.8	ICP/MS
G$^{\#}$	DGT-OP	●		Chelex-100	0.78	3.80	1.0	0.16	3.0	0.8	ICP/MS
H$^{\square}$	Chemcatcher	●		Empore chelating disk	nd	nd	nd	nd	10	nd	ICP/MS
I$^{\square}$	DGT-OP	●		Chelex-100	0.90	3.14	1.0	0.16	10	0.8	ICP/MS
J	DGT-OP	●		Chelex-100	0.76	3.14	10	0.15	nd	0.8	ICP/MS
K	DGT-OP	●	●	Chelex-100	0.76	3.14	4.5	0.15	nd	0.8 (Cd: 1, Pb: 0.7)	GF/AAS
L$^{\#}$	DGT-RP	●		Chelex-100	0.78	3.80	1.0	0.16	3.0	0.8	ICP/MS
M*	DGT-RP	●	●	Chelex-100	0.78	3.14	2.5	0.15	3.5	0.8	ICP/MS

Table 2: Analytical technique and limit of quantification (LOQ) of each laboratory. Laboratories were identified (by *, # and □) when they deployed two types of tools.
LOQ were determined according to NF T90-210 (AFNOR, 2009) or were equal to $\mathrm{Mean}_{\mathrm{blank}}$ + $10^{*}\mathrm{SD}_{\mathrm{blank}}$.

		Analytical LOQ (µg/L)							
Lab code	Analysis	Cd	Cr	Co	Cu	Mn	Ni	Pb	Zn
A	ICP/MS	0.058	0.160	-	0.066	0.210	0.086	0.044	0.80
B	ICP/MS	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
C	ICP/MS	0.002	0.010	0.005	0.10	0.030	0.050	0.010	0.20
D	ICP/MS	0.020	0.300	0.020	0.03	0.200	0.200	0.020	0.20
E	GF/AAS	0.010	0.200	-	0.20	-	0.400	0.120	-
F*	ICP/MS	0.010	0.050	0.020	0.05	0.050	0.050	0.020	0.50
G#	ICP/MS	0.010	0.200	0.005	0.05	0.500	0.010	0.060	0.50
H□	ICP/MS	0.010	0.100	0.050	0.10	0.100	0.100	0.050	0.50
I□	ICP/MS	0.010	0.100	0.050	0.10	0.100	0.100	0.050	0.50
J	ICP/MS	0.100	0.500	0.500	0.50	0.500	0.500	0.100	1.00
K	GF/AAS	0.160	0.110	0.440	1.06	0.090	0.610	0.480	6.70
L#	ICP/MS	0.010	0.200	0.005	0.05	0.500	0.010	0.060	0.50
M*	ICP/MS	0.010	0.050	0.020	0.05	0.050	0.050	0.020	0.50

Table 3: Diffusion coefficient used by each laboratory to calculate time weighted average concentration (TWA). Laboratories were identified (by *, # and □) when they deployed two types of tools.

		Diffusion coefficients (10^{-6} cm²/s)															
Lab code	Tool	Cd		Cr		Co		Cu		Mn		Ni		Pb		Zn	
		Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau
A	DGT-OP	4.88	4.99	4.04	4.13	-	-	4.98	5.09	4.67	4.77	4.61	4.71	6.43	6.58	4.87	4.98
B	DGT-OP	4.77	4.82	3.95	3.99	4.65	4.7	4.88	4.92	4.58	4.62	4.52	4.56	6.29	6.35	4.76	4.8
C	DGT-OP	6.09	6.09	5.05	5.05	5.94	5.94	6.23	6.23	5.85	5.85	5.77	5.77	8.03	8.03	6.08	6.08
D	DGT-OP	6.10	6.10	5.10	5.10	6.14	6.14	6.20	6.20	6.02	6.02	6.37	6.37	10.0	10.0	6.10	6.10
E	DGT-OP	4.86	-	4.03	-	-	-	4.97	-	-	-	4.60	-	6.40	-	-	-
F*	DGT-OP	4.88	5.12	4.05	4.25	4.76	5.00	4.99	5.24	4.68	4.92	4.62	4.85	6.43	6.75	4.87	5.11
G#	DGT-OP	6.09	-	5.05	-	5.94	-	6.23	-	5.85	-	5.77	-	8.03	-	6.08	-
I□	DGT-OP	4.86	-	4.03	-	4.74	-	4.97	-	4.66	-	4.60	-	6.40	-	4.85	-
J	DGT-OP	4.86	-	4.03	-	4.74	-	4.97	-	4.66	-	4.60	-	6.40	-	4.85	-
K	DGT-OP	4.88	5.12	4.045	4.25	4.76	5.00	4.99	5.24	4.68	4.92	4.62	4.85	6.43	6.75	4.87	5.11
L#	DGT-RP	4.08		3.38		3.98		4.17		3.92		3.87		5.38		4.07	
M*	DGT-RP	3.41	3.60	2.83	2.98	3.32	3.49	3.49	3.67	3.27	3.44	3.23	3.39	4.49	4.72	3.40	3.58

Table 4: Comparison of relative standard deviation (RSD) for metal concentrations between this PS intercomparison exercise at Ternay/Thau sites and the SWIFT-WFD proficiency testing exercise on natural waters (Brunori et al., 2007).
x*: robust mean, SD: standard deviation of the robust mean, RSD: relative standard deviation.

	In situ passive sampler data (2010)							**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
Co	0.029 ± 0.011	38	9	0.060 ± 0.015	25		0.010	-	-	-
Cu	0.367 ± 0.153	42	13	0.233 ± 0.109	47	7	0.050	4.15 ± 1.66	40	42
Mn	3.47 ± 0.99	28	11	7.48 ± 2.65	35	7	0.100	154 ± 17	11	47
Ni	0.392 ± 0.139	35	13	0.261 ± 0.126	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

Figures

Figure 1: Metal concentration (mean ± SD, n = 3) measured by each laboratory, with interlaboratory robust mean (dotted line) and reference concentration (solid line) for the quality control (QC) solution.

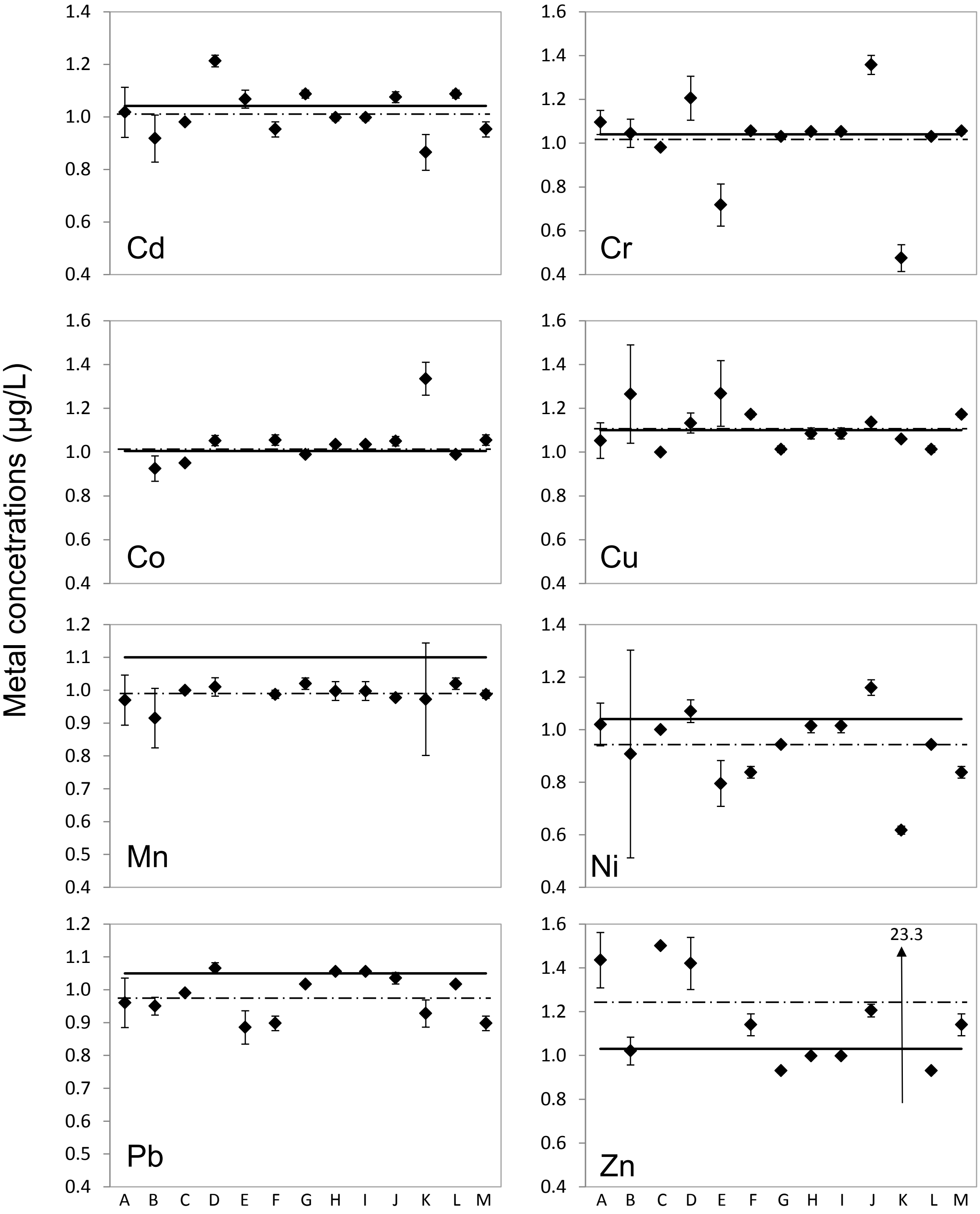

Figure 2: Amount of metal in acid blank, DGT lab blank, DGT field blank and DGT exposed in situ at Ternay site after 7 days of exposure for each laboratory.

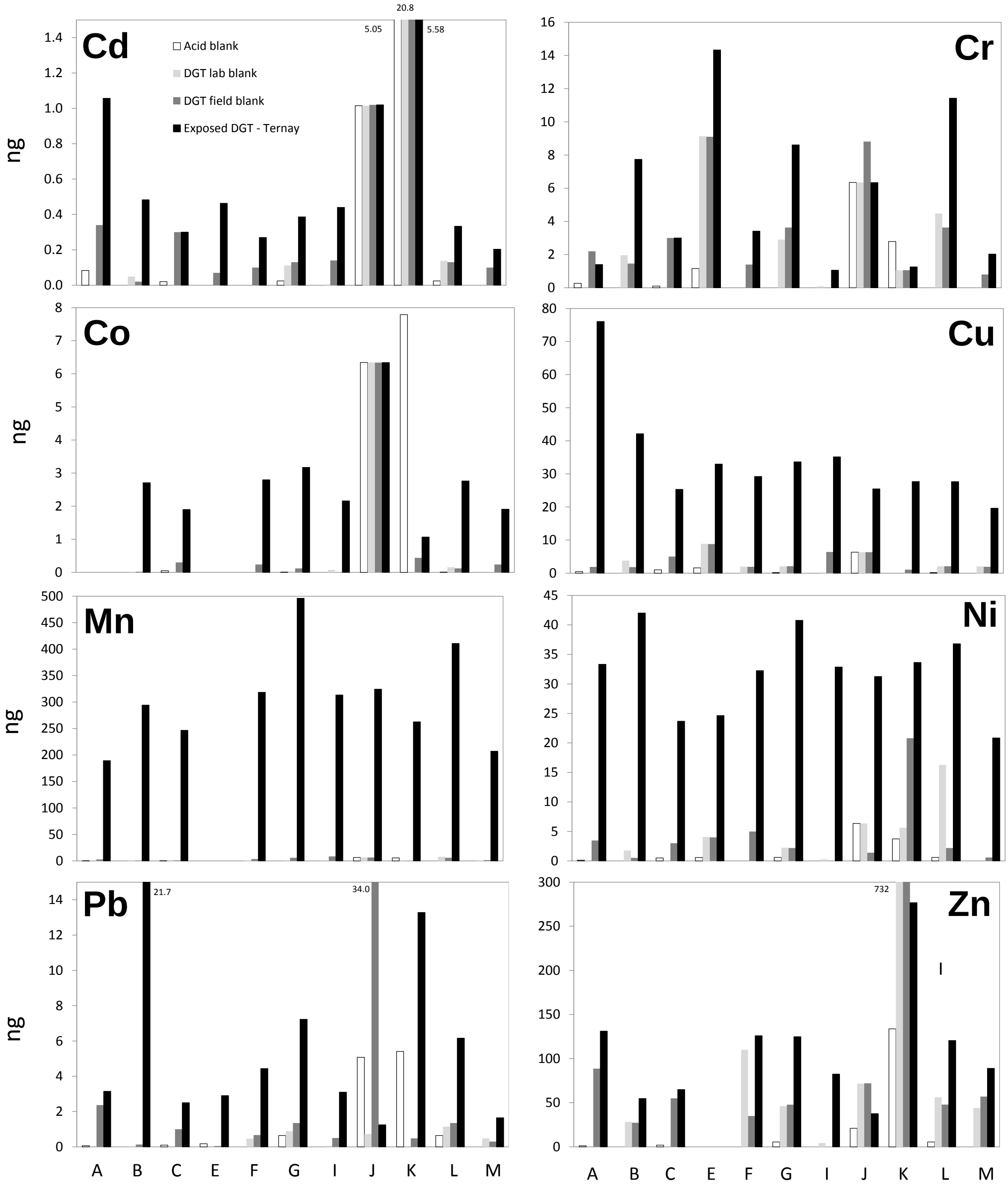

Figure 3: Relative standard deviations (in %) of DGT data (without QC outliers) in ng/tool (solid line) and for TWA concentration in µg/L (grey area), for Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn at Ternay (A) and Thau (B) sites.

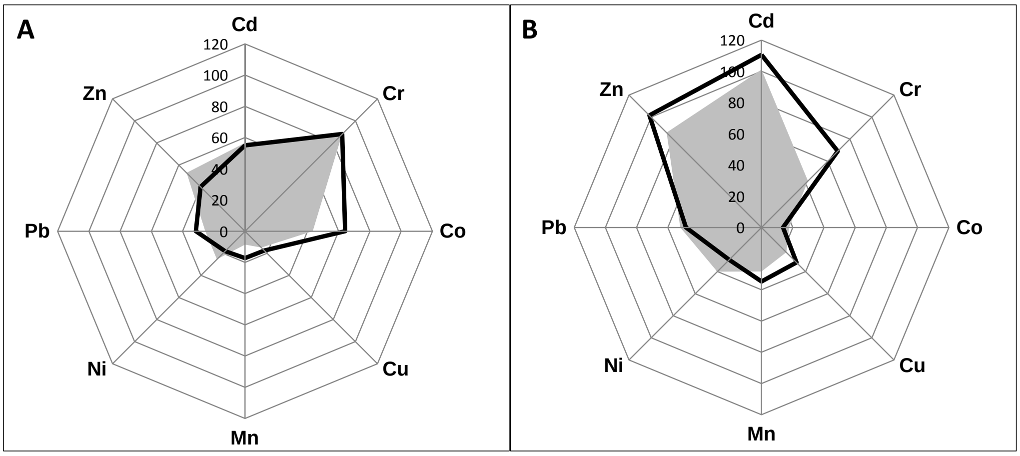

Figure 4: TWA concentration of each laboratory, robust mean (dotted lines) and spot sampling mean concentration (solid line) for Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn at Ternay site. Laboratories were marked when outliers were identified by Cochran (within laboratory variability) and Grubbs tests (between laboratory variability) for QC and TWA data; QC data: ○ Cochran test, ● Grubbs test - TWA data: □ Cochran test, ■ Grubbs test.

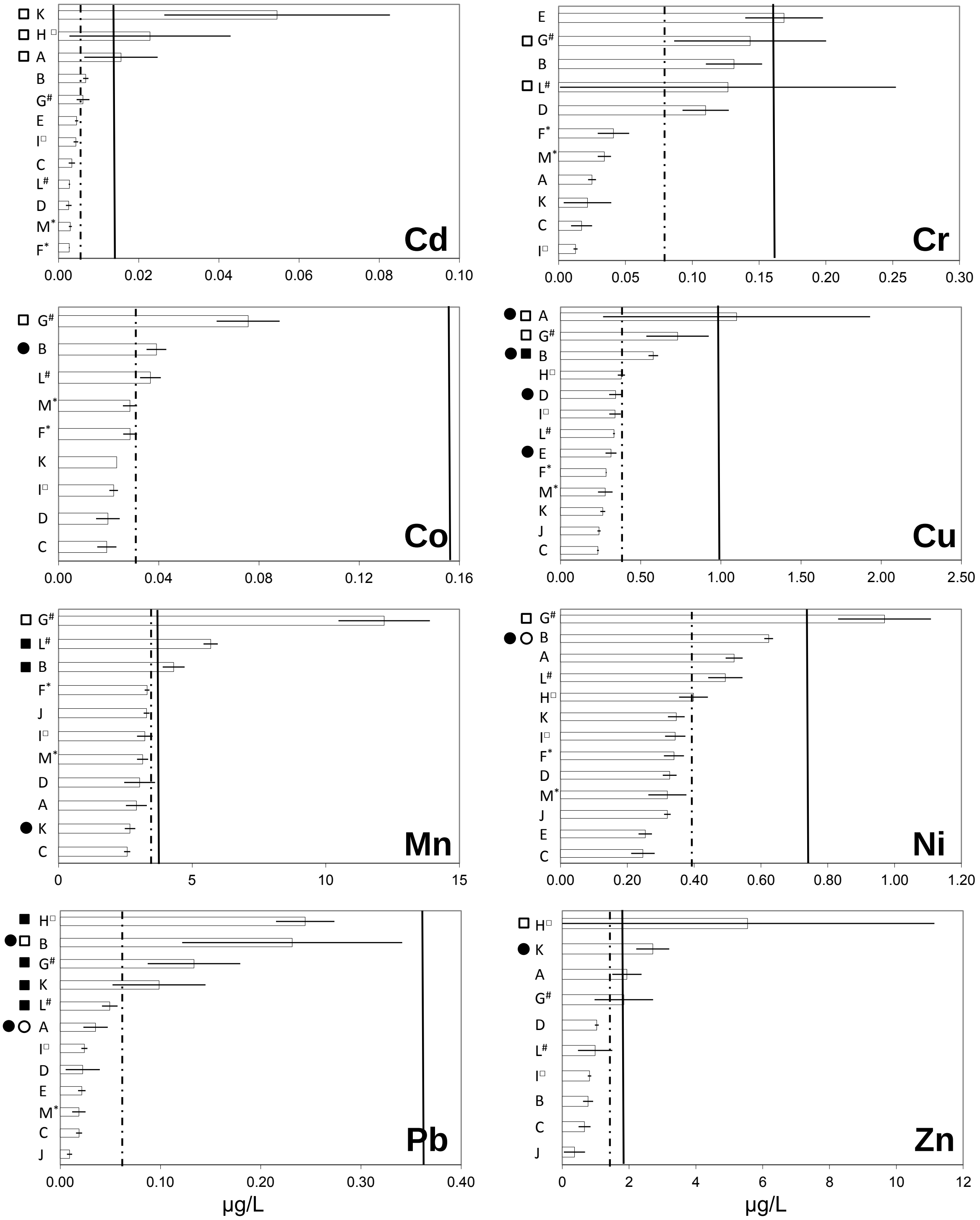

Figure 5: TWA concentration of each laboratory, robust mean (dotted lines) and spot sampling mean concentration (solid line) for Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn at Thau site. Laboratories were marked when outliers were identified by Cochran (within laboratory variability) and Grubbs test (between laboratory variability) for QC and TWA data; QC data: ○ Cochran test, ● Grubbs test - TWA data: □ Cochran test, ■ Grubbs test.