Assessing variability in the ratio of metal concentrations measured by DGT-type passive samplers and spot sampling in European seawaters

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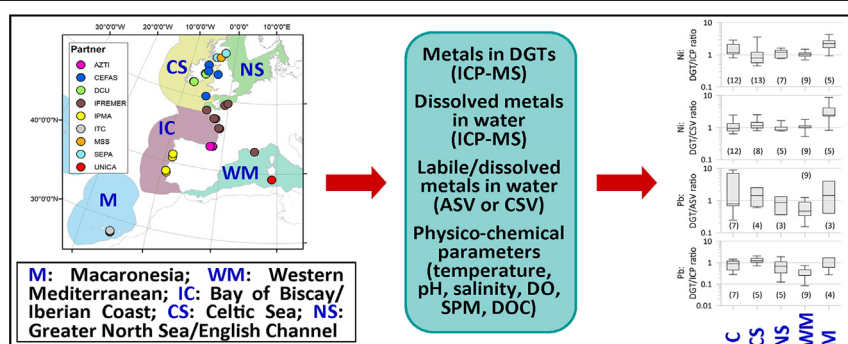[n] MSS, Marine Scotland Science, Marine Laboratory, 365 Victoria Road, Aberdeen AB11 9DB, United Kingdom
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HIGHLIGHTS

- Assessment of DGT *vs* spot sampling metal measurements in European seawaters
- A first broad geographical scale study for DGT technique in different marine areas
- Median DGT/spot sampling ratios were ≤1, except for Zn.
- DGT/spot sampling ratios were independent of environmental variables.
- DGT technique presents a major advantage in a regulatory context.

GRAPHICAL ABSTRACT

M: Macaronesia; WM: Western Mediterranean; IC: Bay of Biscay/Iberian Coast; CS: Celtic Sea; NS: Greater North Sea/English Channel

ARTICLE INFO

ABSTRACT

The current study evaluates the effect of seawater physico-chemical characteristics on the relationship between the concentration of metals measured by Diffusive Gradients in Thin films (DGT) passive samplers (*i.e.*, DGT-labile concentration) and the concentrations measured in discrete water samples. Accordingly, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure the total dissolved metal concentrations in

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the discrete water samples and the labile metal concentrations obtained by DGT samplers; additionally, lead and cadmium conditional labile fractions were determined by Anodic Stripping Voltammetry (ASV) and total dissolved nickel was measured by Cathodic Stripping Voltammetry (CSV). It can be concluded that, in general, the median ratios of DGT/ICP and DGT/ASV(CSV) were lower than 1, except for Ni (median ratio close to 1) and Zn (higher than 1). This indicates the importance of speciation and time-integrated concentrations measured using passive sampling techniques, which is in line with the WFD suggestions for improving the chemical assessment of waterbodies. It is the variability in metal content in waters rather than environmental conditions to which the variability of the ratios can be attributed. The ratios were not significantly affected by the temperature, salinity, pH, oxygen, DOC or SPM, giving a great confidence for all the techniques used. Within a regulatory context such as the EU Water Framework Directive this is a great advantage, since the simplicity of not needing to use corrections to minimize the effects of environmental variables could help in implementing DGTs within monitoring networks.

1. Introduction

The EU Water Framework Directive (WFD, 2000/60/EC) defines good chemical status of water bodies as being achieved when the concentrations of priority substances do not exceed the relevant Environmental Quality Standards (EQS) established by Directive 2008/105/EC (subsequently amended by Directive 2013/39/EU). With respect to metals (cadmium, nickel and lead), the EQS refers to the dissolved concentration, *i.e.* the metal concentrations measured in a water sample previously filtered through a 0.45 μm filter and acidified or subjected to any equivalent pre-treatment (CIS, 2009). In water, however, metals are present in different chemical forms; *i.e.*, free ions, complexes with inorganic and organic ligands and/or adsorbed on the surface of particles or colloids (Hirose, 2006; Tercier-Waeber et al., 2012). This implies that different methodologies may measure different fractions (or chemical forms) of the total metal content. The most common monitoring approach used for the purpose of WFD compliance assessments for metals relies on water samples obtained by spot sampling, followed by filtration (dissolved metal), preconcentration and instrumental analysis (CIS, 2009). The limitations of low-frequency spot sampling, such as the lack of representativeness in dynamic systems and the inability to account for bioavailability and potential toxicity of the contaminants, have been discussed elsewhere (*e.g.*, Allan et al., 2006; Brack et al., 2017). Thus, the inclusion of complementary methodologies, which integrate the environmental metal fluctuations and/or measure the metal speciation that can be more easily related to ecotoxicological effects, might improve the quality of the assessment (CIS, 2009).

Anodic Stripping Voltammetry (ASV) has been widely used for the measurement of labile metal species in water samples at natural pH (thereafter ASV-labile concentration) (see *e.g.*, Pesavento et al., 2009). Laboratory-based bioassays have demonstrated that ASV-labile concentrations correlated more closely with the observed toxicity than total dissolved metal concentrations (Sánchez-Marín, 2020). Thus, this labile concentration might be more useful to evaluate the metal exposure and potential toxicity for at least part of the biota (Illuminati et al., 2019). The determination of ASV-labile concentrations at natural pH must be performed within a reasonable time after sample collection to minimize loss of metal species due to adsorption on vessel walls. *In situ* filtration and acidification of the water samples can, however, give information about the labile fraction at a lower pH than the natural one, in the presence of a still inert fraction that may comprise metals strongly bound to natural organic molecules or bound to colloids. However, voltammetry is notably more time consuming than the determination of the total dissolved concentration by other techniques, complicating its inclusion for routine monitoring, even in the case of saline waters.

As an alternative, passive samplers (PS) have been used for measuring labile metal concentrations in waters (Fernández-Gómez et al., 2012). The Diffusive Gradients in Thin films (DGT, Davison and Zhang, 1994) are the most extensively used samplers for *in situ* labile metal measurements (Menegário et al., 2017). DGT samplers accumulate metals continuously during the deployment time, usually ranging from several days to weeks. This provides time-weighted average metal concentrations and enables the achievement of lower limits of quantification compared with low-volume water samples (Dabrin et al., 2016). In addition, DGT samplers only accumulate free metal ions and easily dissociable metal complexes, operationally known as the DGT-labile concentration, which has been related to observed toxicity in different types of organisms (*e.g.*, Gao et al., 2020; Koppel et al., 2019; Strivens et al., 2019). These advantages might favour the inclusion of the DGT technique within monitoring programmes. However, their use in a regulatory context is limited by the incomplete understanding of the effect of physico-chemical parameters on the speciation of metals in the water column, and hence, their availability for uptake by DGT samplers (Mills et al., 2014).

Thus, the current study evaluates the effect of seawater physico-chemical characteristics on the relationship between the concentration of metals measured by DGT (*i.e.*, DGT-labile concentration) and concentrations measured in discrete water samples by complementary methodologies. Hence, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure the total dissolved metal concentrations in the discrete water samples and to quantify the amount of accumulated metals in the DGT samplers for obtaining labile metal concentrations; additionally, ASV was used for determining lead and cadmium labile fractions at pH 2 in the discrete water samples, while total dissolved nickel concentration was measured by Cathodic Stripping Voltammetry (CSV). Accordingly, in the framework of the Interreg MONITOOL project (EAPA 565/2016), DGT samplers were deployed, during different seasons, in estuaries and coasts of the Atlantic region (from the Canary Islands to Scotland) as well as in Sardinia coastal water in the Western Mediterranean. Discrete water samples were collected during the DGT deployment period. Previous studies comparing the metal concentrations measured by DGT samplers and spot sampling were performed at a local scale, with a limited number of samples (*e.g.*, Canovas et al., 2020a, 2020b; Cindrić et al., 2020; Egardt et al., 2018; Vannuci-Silva et al., 2017; Wallner-Kersanach et al., 2009). In this study the relationships between the different chemical forms of metals present in waters measured by three different techniques were investigated across a broad geographical scale, covering a variety of environmental conditions.

2. Material and methods

2.1. Study area

Sampling campaigns were carried out by nine research organizations (AZTI, CEFAS, DCU, IFREMER, IPMA, ITC, MSS, SEPA and UNICA) covering eight countries (England, France, Ireland, Italy, Northern Ireland, Portugal, Scotland and Spain) located in five sub-regions (Fig. 1). Sampling campaigns were carried out in 2018, consisting of the simultaneous deployment of DGT samplers, collection of discrete
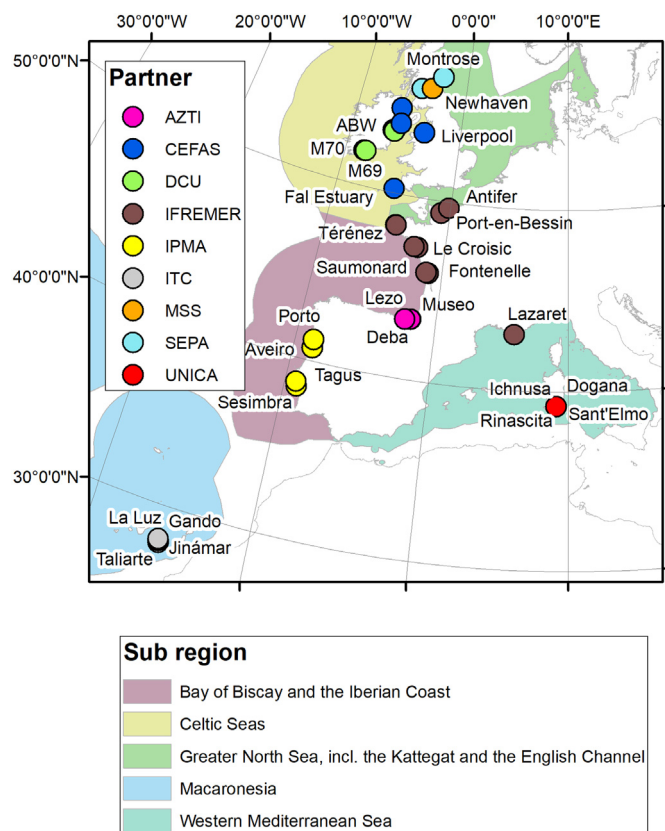
Fig. 1. Sampling sites. Labels indicate the partner (research centre) that carried out the sampling. Sub-regions according to the EU Marine Strategy Framework Directive (MSFD).

water samples and measurement of physico-chemical parameters: temperature, pH, salinity, dissolved oxygen (DO), suspended particulate matter (SPM) and dissolved organic carbon (DOC). A total of 36 sites were sampled and when possible, the same stations were sampled in different seasons (see Table S1, for more details).

2.2. Sampling procedures

All the material used in the laboratory and in the field were soaked in a 10% HNO₃ acid bath overnight and rinsed thoroughly with Milli-Q water before use. Detailed descriptions of the deployment, retrieval and processing of DGTs can be found elsewhere (*e.g.*, Marras et al., 2020). Briefly, triplicated DGT samplers were loaded onto a plastic holder and, if required, protected with a nylon net to prevent damage from side impacts or aquatic organisms present in the deployment zone. DGT samplers were deployed at each site at a depth of around 1–1.5 m from the surface. To minimize the operational variability, unified protocols were developed at the beginning of the project, consisting in using the same DGT supplier (DGT® Research Ltd., Lancaster, UK) and production batch (LSNM-NP open pore loaded DGT device for metals (A) in solution) and following the same sampling and metal analysis procedures. Median time of exposure of DGT samplers was 4 days, ranging from 2 to 15 days (Table S1). The variability in exposure time was mainly due to access limitations in port or navigation areas that required the use of boats. Laboratory and field DGT blanks were used for controlling the potential contamination of DGT samplers during transport, handling for deployment/retrieval and processing of the samplers.

During the DGT deployment time, subsurface water samples were collected with Niskin bottles or handheld water samplers at the same depth of the deployed DGT samplers. After retrieval, they were transported in coolers to the laboratory for the measurement of metal concentrations and physico-chemical parameters (*i.e.*, SPM and DOC).

Additionally, multiparameter probes (see Supplementary Material for detailed description) were used for the *in situ* measurement, at the same depth as DGT samplers, of physico-chemical parameters (temperature, pH, salinity and dissolved oxygen) at each water sampling time. The frequency for spot sampling of water was, when possible, twice a day (at high and low tide) at estuarine sites and at least every two days at coastal sites. The samples for voltammetric analysis were filtered and acidified on site (or as soon as possible) and kept refrigerated until analysis. The samples for ICP-MS analysis were sent frozen to a single laboratory where they were filtered and acidified. The operational variability was minimized by following unified protocols for the collection and processing of water samples and by ensuring that all the voltammetric and ICP-MS analyses were performed by the same reference laboratory. Blank samples for voltammetry and ICP-MS consisted of Milli-Q water treated similarly to the collected water samples.

2.3. Laboratory analyses

2.3.1. Pb, Cd and Ni concentrations in spot samples by ASV/CSV

The determination of conditional labile Pb and Cd concentrations in filtered and acidified water samples was done by ASV (Florence, 1972; Florence and Batley, 1977). For the determination of total Ni dissolved concentrations, CSV was carried out after UV irradiation of water samples to guarantee the oxidation of organic matter (Van Den Berg, 1986). For Cd and Pb determination the samples were not UV-irradiated before the analysis. Voltammetric measurements were performed using a μAutolab Potentiostat/Galvanostast (Metrohm AG) monitored by the control and data acquisition software GPES 4.9 (EchoChemie) connected to the VA stand model 663 (Metrohm). A conventional three-electrode configuration was used with an Ag/AgCl reference electrode and a glassy carbon rod as the counter electrode. As working electrodes, in ASV a thin Mercury Film Electrode (TMFE) was used (Rocha and Pinheiro, 2007) while in CSV a Static Mercury Drop Electrode (SMDE) was used. High-grade purity chemicals and ultra-pure water (18.2 MΩ·cm) were used and the analysis was carried out in clean disposable PET vessels to minimize contamination between samples. After purging the solutions with U-Type nitrogen, all concentration determinations were made at least in duplicate using the standard addition method. Throughout the entire procedure, blank reagents, quality control standards and certified reference materials (CASS-6 and SLWE from the National Research Council of Canada) were used (see Table S2).

It should be noted that (ASV) is typically used for the measurement of labile metal species in water samples at natural pH, instead of acidified water samples. Because the determination of ASV-labile concentrations at natural pH must be performed within a reasonable time after sample collection to minimize loss of metal species due to adsorption on vessel walls, samples were acidified on site in this study. Immediate acidification of the water samples once filtered can, however, give information about the labile fraction at a lower pH than the natural one, in the presence of a still inert fraction that may comprise metals strongly bound to natural organic molecules or bound to colloids. To distinguish our ASV measurement from the *in situ* labile species at natural pH, we name it "conditional labile concentration".

2.3.2. Trace elements in spot samples by ICP-MS

The total dissolved concentrations of trace metals Cd, Cu, Ni, Pb and Zn in filtered and acidified water samples were determined by an online pre-concentration seaFAST system (Elemental Scientific, Nebraska, USA) coupled with an ICP-MS. All the chemicals used were of high-grade purity (suprapure or distilled) and the water was ultra-pure (18.2 MΩ·cm). The ICP-MS was equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. The equipment was set up by ensuring low variability of counts (RSD <1%). The isotope ¹¹⁵In was used as online internal standard. Typically, 7-point calibration curves were used in different dynamic ranges depending on the metal

concentration in samples. The precision and accuracy of the analytical procedures were controlled through repeated metal analysis in certified reference materials (CASS-6 from the National Research Council of Canada, Table S3). Each batch of 20 samples included a blank, a certified reference material and a QC solution. Less than 10% of blanks were above the detection limit of the method for quantification.

2.3.3. Trace elements in DGTs by ICP-MS

After DGT retrieval and transport to the laboratory, the binding resin gel was removed from the sampler and eluted in 1.22 mL of 1 M HNO_3 acid solution (ultrapure grade nitric acid 60%, Merck Millipore, Germany) for at least 24 h. The resulting acid extracts were analysed by ICP-MS for the determination of trace elements Cd, Cu, Ni, Pb and Zn after dilution 5 times with ultrapure water (Milli-Q, Millipore). All reagents, standards, samples and blanks were prepared using Suprapure acid (HNO_3) and previously cleaned LDPE or Teflon flasks. The calculation of the DGT measured *in situ* labile concentration was carried out following Zhang (2020) and using the diffusion coefficients provided by the DGT supplier (DGT® Research Ltd., Lancaster, UK).

For each metal, those replicated samples whose mean concentration in their eluate was less than three times the mean of all laboratory blanks, were discarded. After that, the ratio of average (*i.e.*, among replicates) concentration in eluates of laboratory blanks to samples were 0.33–0.006 for Cd, 0.33–0.017 for Cu, 0.33–0.047 for Ni, 0.33–0.008 for Pb and 0.33–0.04 for Zn.

2.3.4. Determination of [DGT metal]/[spot sample metal] concentration ratios

After validation of the individual analytical results, and for each period of exposure of DGT samplers, the DGT/ICP ratio for each metal was calculated. This was determined as the ratio of the *in situ* labile metal concentration obtained by DGT samplers (deployment time integrated concentrations; in triplicate) to the total dissolved concentration measured in spot samples by ICP-MS (average of the results from several discrete water samples collected during the DGT deployment time). Similarly, DGT/ASV(CSV) ratio was calculated as the ratio of the time-integrated *in situ* labile metal concentration obtained *via* DGT to the mean conditional labile concentration measured by ASV (or total dissolved by CSV) in spot samples. The ratio was not calculated when metal concentrations were below the limit of quantification (LOQ).

2.3.5. Total suspended particulate material (SPM)

Total suspended particulate material was determined by the gravimetric method, consisting in filtering a known volume of water through GF/C 1.2 μm glass microfiber filters, drying at 103–105 °C (2−3 h) and weighing the filters using an analytical balance (0.1 mg precision) after desiccation.

2.3.6. Dissolved organic carbon (DOC)

Different methods were used by each research organization for the determination of dissolved organic carbon (DOC). In most cases, DOC was measured as the difference of the total carbon and the inorganic carbon measured with automated carbon analysers.

2.4. Statistical analyses

2.4.1. Outlier exploration of mean concentration values

Outliers were identified using linear modelling of the data. The objective was to identify outliers samples whose standardized residuals from the linear model were greater than 3 (rejection of values above 99.73% of the total values, assuming that their distribution follows a normal distribution). A detailed procedure is given in the Supplementary material (Fig. S1). Values identified as outliers were excluded.

2.4.2. Exploration of ratios between methods and environmental variables

Differences, among sub-regions, of median values of environmental variables (except pH) and of the ratio of the mean concentrations

measured with different methods were tested with the non-parametric Kruskal-Wallis test (alpha: 0.05). Moreover, the Spearman's correlation coefficient was calculated as a measure of the strength of the monotonic relationships between the ratio of the mean concentrations measured with different methods and the mean values of environmental variables; alpha value (0.05) was adjusted with the Bonferroni correction method (Legendre and Legendre, 1998). It should be noted that Cd, Ni and Pb concentrations obtained by ICP-MS could be complemented with the voltammetry results.

3. Results

3.1. Physicochemical characteristics of seawater

The ranges of measured mean values of salinity, temperature, oxygen content, pH, DOC and SPM were 0.2–38.1, 5.7–26.3 °C, 5.42–11.85 mg/L, 7.3–8.8, 583–4490 μg/L and 0.45–262 mg/L, respectively. Significant differences in the median values of salinity, temperature, oxygen content and SPM were found among the five sampled sub-regions (p < 0.05), whereas none were found in the median values of DOC (Fig. 2).

3.2. DGT/spot sampling ratios

The boxplots presenting the ratio of Cd concentration measured in DGTs (*in situ* labile Cd concentration) to that measured in discrete water samples by ICP (total dissolved Cd; Cd: DGT/ICP ratio) and by ASV (conditional labile Cd concentration; Cd: DGT/ASV ratio), at the five sampled sub-regions, can be found in Fig. 3. The median values of Cd: DGT/ICP and Cd: DGT/ASV ratios were 0.91 and 0.78, respectively. No significant differences were found in both ratios among the median values of the five sampled sub-regions (most of the Cd: ASV data at the Macaronesia and Mediterranean sub-regions were below LOQ, *i.e.*, <10 ng/L).

The boxplots presenting the ratio of Ni concentration measured in DGTs (*in situ* labile Ni concentration) to that measured in discrete water samples (total dissolved Ni concentration) by ICP (Ni: DGT/ICP ratio) and by CSV (Ni: DGT/CSV ratio), at the five sampled sub-regions, are represented in Fig. 3. The median values of Ni: DGT/ICP and Ni: DGT/ASV ratios were 1.14 and 1.04, respectively. No significant differences were found in either ratios among the median values of the five sampled sub-regions.

The median values of Pb: DGT/ICP and Pb: DGT/ASV ratios were 0.65 and 0.78, respectively (Fig. 3), significantly lower than 1, indicating an important speciation effect. No significant differences were found among the median ratios calculated for the five sampled sub-regions.

The median value of all the calculated Cu: DGT/ICP ratios was 0.81 (Fig. 3), significantly lower than 1, indicating an important speciation effect. No significant differences were found among the median Cu: DGT/ICP values measured at the five sampled sub-regions.

The median value of the Zn: DGT/ICP ratio presented in Fig. 3 was 1.74 and no significant differences were found among the five sampled sub-regions.

3.3. Correlation analysis of all parameters

There was a significant inverse correlation between the Cd: DGT/ICP ratio and the measured pH (Table 1, Fig. S2), while a direct correlation was found between Cd: DGT/ICP ratio and the Cd concentration measured by DGTs (Table 1, Figs. S10 and S11). On the other hand, there were no significant correlations between the Cd: DGT/ASV ratio and the environmental variables (Table 1, Fig. S2), but there was a significant inverse monotonic relationship between the Cd: DGT/ASV ratio and the Cd concentration measured with the ASV technique (Table 1, Figs. S10 and S11). These results indicate higher *in situ* DGT-labile than ASV conditional labile values at low Cd concentrations.

The Ni: DGT/CSV ratio was significantly correlated with the temperature (monotonic direct relationship, Table 2, Fig. S5), while the Ni:
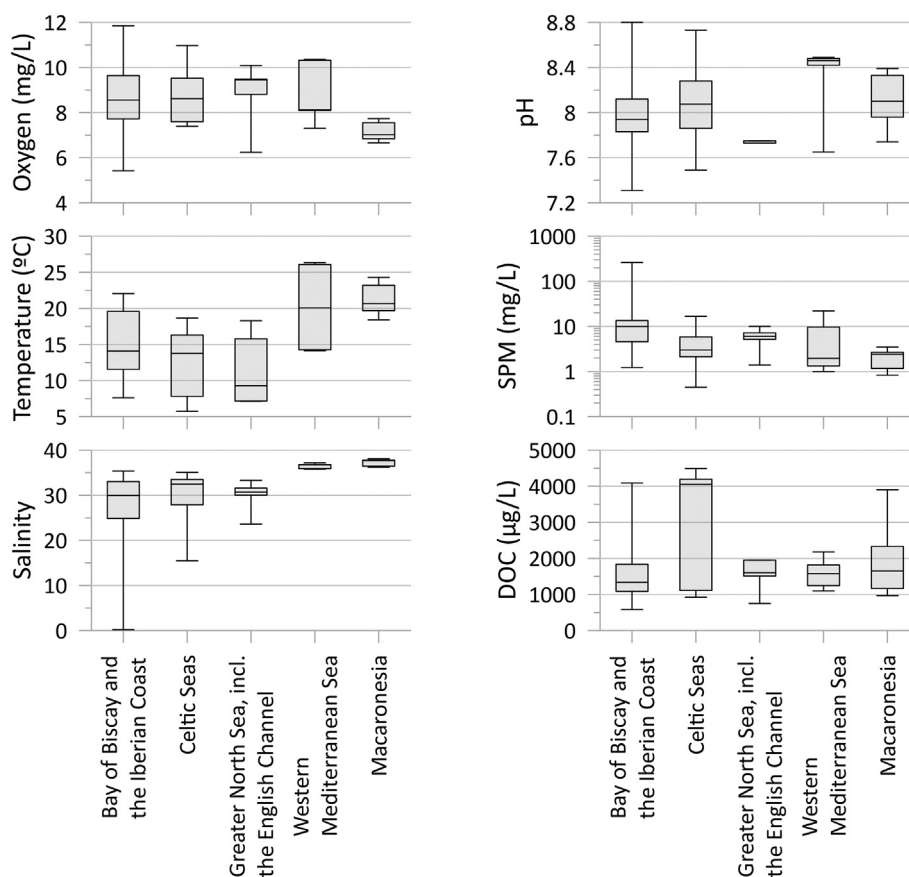
Fig. 2. Box-plots of mean salinity, temperature, oxygen, pH, total suspended particulate material (SPM) and dissolved organic carbon (DOC) in seawater.

DGT/ICP ratio was significantly correlated with the oxygen concentration (monotonic inverse relationship, Table 2, Fig. S4). Moreover, the Ni: DGT/ICP ratio was significantly correlated to the Ni concentration measured with ICP (monotonic inverse relationship), for Ni concentration less than 400 ng/L, and the Ni: DGT/CSV ratio with the Ni concentration measured with CSV (monotonic inverse relationship) (Table 1, Figs. S12 and S13).

The Pb: DGT/ICP and Pb: DGT/ASV ratios were not significantly correlated with any of the environmental variables (Table 1, Figs. S6 and S7). Conversely, the Pb: DGT/ICP ratio was significantly correlated to the Pb concentration measured with ICP (monotonic inverse relationship), and the Pb: DGT/ASV ratio with the Pb concentration measured by ASV (monotonic inverse relationship), at concentrations lower than 100 ng/L (Table 1, Figs. S14 and S15).

The Cu: DGT/ICP ratio was not significantly correlated with any of the environmental variables (Table 1, Fig. S8), nor to the concentration of Cu measured by ICP or DGT (Table 1, Fig. S16).

The Zn: DGT/ICP ratio was significantly correlated with SPM (monotonic inverse relationship, Table 1, Fig. S9). Moreover, it was significantly correlated to the Zn concentration measured in discrete water samples by ICP (monotonic inverse relationship) and to the Zn concentration measured by DGTs (monotonic direct relationship) (Table 1, Fig. S17).

4. Discussion

In general, the median DGT/spot sampling ratios were lower than 1, except for Ni (median ratio close to 1) and Zn (1.74). The results for Cd, Pb and Cu suggest that only fractions of the dissolved metals are labile and available for uptake by DGT. The results for Ni and Zn indicate that they were mostly labile and available for their uptake by DGT. These observations are consistent with the results described in previous

studies (Caro et al., 2015; Cindrić et al., 2020; Kim et al., 2016; Munksgaard and Parry, 2003; Roig et al., 2007; Umbría-Salinas et al., 2021; Wang et al., 2017). The metals Cu and Pb presented the lowest DGT/ICP ratios, 0.81 and 0.65, as their speciation in seawater is more influenced by organic complexation and association to colloids than the rest of the studied metals (Cindrić et al., 2020; Illuminati et al., 2019; Markich et al., 2001). For some DGT/spot sampling ratios, a large number of observations with values above 1 were found. This might be explained by the high environmental variability in metal concentrations, which was not fully integrated by the applied spot sampling design and the calculated mean concentrations (representing all the DGT deployment-time). In some cases, the collection of discrete water samples might have coincided with the lowest metal concentrations, missing the highest levels. On the other hand, DGTs being deployed the entire time, also integrated events with higher metal concentrations, which implies higher DGT/spot sampling ratios (see Fig. 4, case 'A' vs Case 'B'). This may also partially explain the high variability in the observed ranges.

Although there was a high variability in the environmental variables (temperature, salinity, pH, oxygen, DOC and SPM) measured in the five sub-regions (Fig. 2), these parameters had a limited effect on the DGT/spot sampling ratios, as concluded by the near absence of significant correlations (Table 1). In fact, the significant relationships found between some DGT/spot sampling ratios and water characteristics (i.e., Cd: DGT/ICP ratio vs pH, Ni: DGT/ICP ratio vs oxygen concentration, Ni: DGT/CSV ratio vs temperature, and Zn: DGT/ICP ratio vs SPM), are very weak trends, as it can be observed in the highly scattered graphs (Figs. S2, S4, S5 and S9). As previously mentioned, the inclusion of DGT samplers for the regulatory monitoring of metals is predicated on an understanding of the metal forms accumulated by DGT and the effect of physico-chemical variables in the uptake. Based on these preliminary results, covering a high regional scale and environmental conditions, it
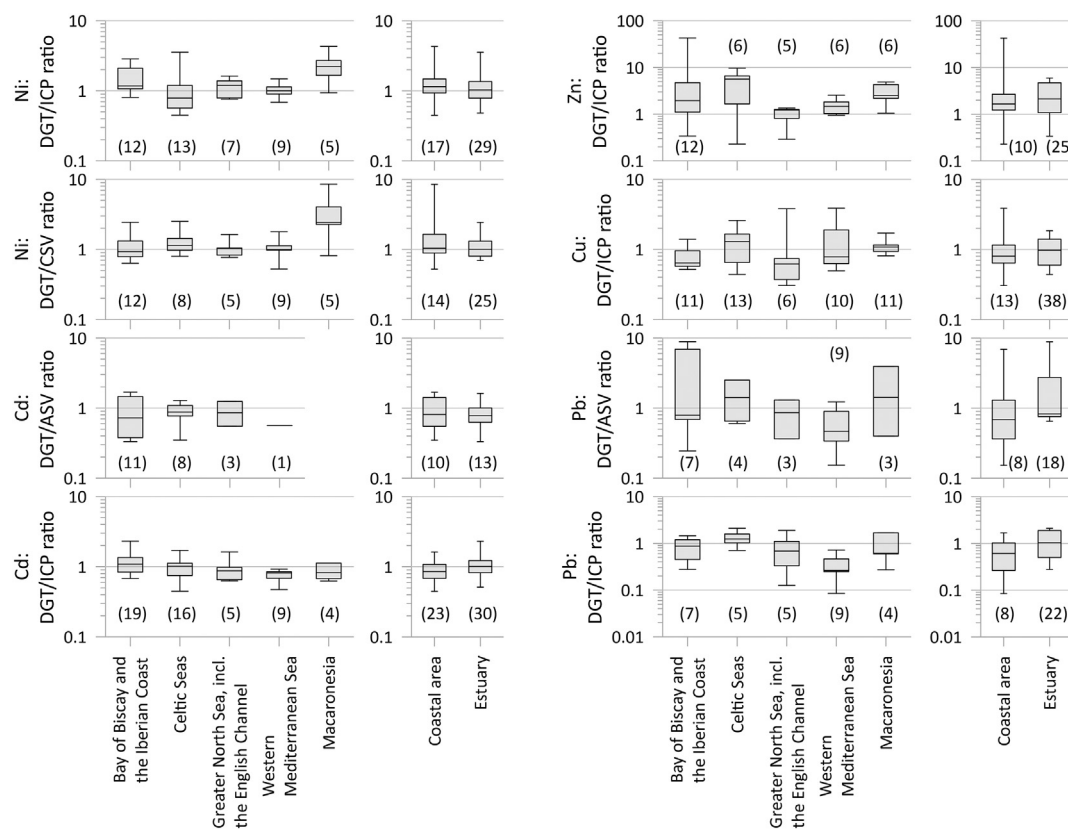
Fig. 3. Box-plots of ratios of metal concentration measured with different methods. Number of data is indicated in brackets. Key: DGT – concentration of a metal measured by DGT passive sampler, ICP – mean metal concentration measured in filtered spot water samples using ICP-MS, ASV (CSV) – mean metal concentration measured in filtered spot water samples using anodic stripping voltammetry (or cathodic stripping voltammetry). Whiskers indicate maximum and minimum values. Note: at Macaronesia the concentration of Cd measured by ASV was lower than LOQ therefore no data of Cd: DGT/ASV ratio is available.

seems that the physico-chemical parameters did not significantly affect the DGT/spot sampling ratios. However, the influence of environmental variables at a more local scale cannot be discarded, as has been previously observed by other authors (Cindrić et al., 2020; Mangal et al., 2016). Therefore, the results of this research should be interpreted with caution and highlight the necessity of considering site and metal specific conditions when investigating the relationship between labile metal speciation and water characteristics.

In contrast to that observed for environmental variables, there were significant relationships between the DGT/spot sampling ratios and the concentrations obtained by means of spot sampling and/or DGTs, for most of the studied metals (Table 1). It was observed that there were monotonic inverse relationships between the DGT/spot sampling ratio

and the concentrations obtained by spot sampling for Cd, Ni, Pb and Zn, while between the DGT/spot sampling ratios and the concentration obtained by means of DGT there were monotonic direct relationships, as observed for Cd and Zn. Those relationships were mainly demonstrated in the low concentration samples. The presence of these inverse relationships could be linked to the non-linear accumulation of some metals due to the competition for the binding sites with other components in solution (Jiménez-Piedrahita et al., 2017). However, competitive effects that might affect the measurements of DGTs are only expected when approaching the maximum capacity of the binding resin (Davison and Zhang, 2012). Considering that DGTs were only deployed for a median time of exposure of 4 days, the observed inverse relationships between the DGT/spot sampling ratio and the concentrations measured by spot

Table 1

Spearman correlations between the ratios of metal concentration measured by different methods and the environmental variables and concentration of metals measured by different techniques. Number of data is indicated in brackets. Key: DGT – concentration of a metal measured by means of DGT, ASV – mean metal concentration measured in filtered spot water samples using anodic stripping voltammetry, CSV – mean metal concentration measured in filtered spot water samples using cathodic stripping voltammetry, ICP – mean metal concentration measured in filtered spot water samples using ICP-MS, SPM - suspended particulate material in seawater, DOC - dissolved organic carbon, * - significant (alpha value: 0.05, adjusted with Bonferroni correction method), N/a – not available.

| Metal	Cd	Cd	Ni	Ni	Pb	Pb	Cu	Zn
	DGT/ICP ratio	DGT/ASV ratio	DGT/ICP ratio	DGT/CSV ratio	DGT/ICP ratio	DGT/ASV ratio	DGT/ICP ratio	DGT/ICP ratio
Temperature	−0.3 (52)	−0.09 (23)	0.26 (44)	0.45 (39)*	−0.19 (28)	−0.46 (26)	−0.05 (49)	−0.09 (33)
Salinity	−0.38 (52)	0.06 (23)	0.21 (44)	0.42 (39)	−0.39 (28)	−0.21 (26)	0.25 (49)	0.16 (33)
Oxygen	0.1 (51)	0.09 (22)	−0.44 (43)*	−0.42 (38)	−0.21 (27)	0.42 (25)	−0.06 (48)	−0.21 (32)
pH	−0.46 (46)*	−0.03 (19)	0.39 (37)	0.36 (32)	−0.44 (21)	−0.31 (19)	0.43 (42)	0.23 (28)
SPM	0.12 (51)	0.09 (23)	0.09 (43)	−0.19 (39)	−0.03 (27)	0.44 (21)	−0.31 (48)	−0.53 (32)*
DOC	0.21 (34)	0.01 (15)	−0.22 (34)	0.1 (34)	0.56 (22)	0.2 (26)	−0.06 (40)	0.41 (26)
[metal] ASV	0.27 (32)	−0.79 (23)*	N/a	N/a	−0.22 (26)	−0.73 (26)*	N/a	N/a
[metal] CSV	N/a	N/a	−0.12 (39)	−0.56 (39)*	N/a	N/a	N/a	N/a
[metal] ICP	−0.21 (53)	0.04 (23)	−0.64 (46)*	−0.29 (39)	−0.85 (30)*	−0.22 (25)	−0.3 (51)	−0.63 (35)*
[metal] DGT	0.51 (53)*	0.05 (23)	0.36 (46)	0.33 (39)	0.16 (30)	0.43 (26)	0.37 (51)	0.67 (35)*
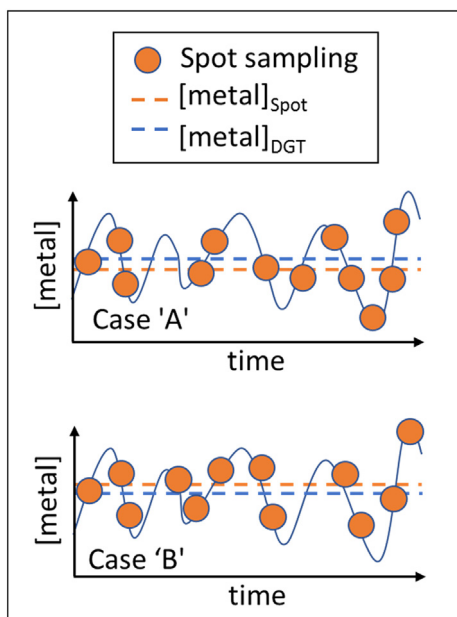
Fig. 4. Sampling scenarios. In case 'A' the average concentration resulting from spot sampling is lower than the concentration measured with DGT and *vice versa* (case 'B'). Key: [metal]$_{Spot}$ – mean metal concentration measured in discrete water samples collected during DGT deployment time; [metal]$_{DGT}$ – time-weighted average metal concentration measured with DGTs.

sampling might be better explained by a more pronounced complexation of these metals with organic ligands, as observed by Cindrić et al. (2020) for Cd and Co in a Croatian estuary. In any case, these results should be considered as preliminary and further research on the DGT/spot sampling ratio in low concentration areas should be pursued.

Within a regulatory context, such as the EU WFD, the absence of strong relationships between DGT/spot sampling ratios and physico-chemical parameters is a great advantage. It affords the simplicity of not needing to use corrections to minimize the effects of environmental variables, which could help in implementing DGTs within monitoring networks. This is in contrast to the case where corrections or adjustments would be necessary, as for the EQS of Cd as a function of water hardness in inland surface waters in the EU WFD.

Within the WFD there are three types of monitoring: (i) surveillance monitoring, (ii) operational monitoring and (iii) investigative monitoring (see *e.g.*, Ferreira et al. (2007) for details). The *in situ* continuous sampling based on passive samplers can be applied within these three types of monitoring, but some considerations should be taken into account. One of them is the cost of implementation where no generalisation can be made (see *e.g.*, Audet et al. (2014) for nutrient monitoring in streams), though Rougerie et al. (2021) found that measurement networks in continental waterbodies cost 2 to 3 times more when monitored by DGTs compared to standard grab monitoring. Therefore, the sampling effort with DGTs should focus on those cases and types of monitoring where it is more relevant in terms of the quality of the information required. Another aspect is related to the operational issues, *e.g.*, in inland and coastal waters several authors have found a potential risk of DGT contamination depending on the working environment (Dabrin et al., 2016; Miège et al., 2012), which requires experience and training in its use (for a more detailed discussion see Rougerie et al., 2021). Another operational issue is related to the time of exposure, that is a compromise between three main considerations: i) the concentration in the water (the lower the concentration of the analyte, the longer the optimal exposure time), ii) the temporal scale of the process that is being monitored or the time period that we want to integrate, and iii) specific logistical problems, such as access to the sampling locations, weather forecast, vandalism, or the need to avoid the use of ships.

Finally, it is also important to consider the difficulty and cost of deploying DGT samplers at great depths in estuaries or coastal areas, which may require the use of diving or complex facilities. In these considerations, however, it is also important to remember the limitations of low-frequency spot sampling. There is a lack of representativeness of such spot sampling in dynamic systems and an inability to account for bioavailability and potential toxicity of the contaminants. Therefore, complementary methodologies are highly desirable, especially those that integrate environmental metal fluctuations and/or account for metal speciation, which can be more easily related to ecotoxicological effects. Thus, evaluations should consider not only the cost but also the quality of the obtained information. In this sense, including DGT samplers in routine monitoring networks might initially result in higher expenses, but the importance of the reliability of the overall assessment, for reducing the costs associated to unnecessary measures (*e.g.*, implementation of emission control measures or establishment of additional investigative monitoring campaigns), should also be borne in mind.

The current study is the first of several studies developed in the framework of the Interreg MONITOOL project, aiming to assess the suitability of DGTs as a monitoring methodology for establishing the chemical status of transitional and coastal waters.

5. Conclusions

It can be concluded that in most cases, the median ratios of DGT/ICP and DGT/ASV(CSV) were lower than 1, except for Ni (median ratio close to 1) and Zn (1.7). The ratios lower than 1 indicated the importance of speciation and time-integrated concentrations measured using passive sampling techniques, which is in line with the WFD suggestions for improving the chemical assessment of waterbodies. The variability of the ratios can be better explained by the fluctuations in metal concentration in waters rather than the effect of environmental conditions. The ratios were not significantly affected by temperature, salinity, pH, oxygen, DOC or SPM. Within a regulatory context such as the EU Water Framework Directive, this is a great advantage since the simplicity of not needing to use corrections to minimize the effects of environmental variables could help in implementing the DGT technique within monitoring networks.

CRediT authorship contribution statement

I. Amouroux; Investigation, Writing - Review & Editing, Project administration for Ifremer, Funding acquisition.

M.J. Belzunce-Segarra: Writing- Original draft preparation, Investigation, Project administration, Funding acquisition.

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M. Correia dos Santos: Investigation, Writing - Review & Editing, Project administration.

G. Fones, B. McHugh, H. Zhang: Writing - Review & Editing.

S. Guesdon: Data Curation, Data Processing, Formal Analysis, Investigation, Writing - Review & Editing.

J.L. Gonzalez, F. Menet-Nédélec: Investigation, Writing - Review & Editing.

J. Larreta, I. Menchaca, J.G. Rodríguez: Writing- Original draft preparation, Investigation, Visualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.147001.

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