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A new approach to using Diffusive Gradient in Thin-films (DGT) labile concentration for Water Framework Directive chemical status assessment: adaptation of Environmental Quality Standard to DGT for cadmium, nickel and lead

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Abstract

Integrative passive samplers, such as DGT (Diffusive Gradients in Thin-films), are identified in European Technical Guidance Documents as promising tools to improve the quality of the assessment, in the context of the WFD (EU Water Framework Directive). However, DGT results cannot yet be used directly in a regulatory framework to assess the chemical status of water bodies, as DGT labile concentrations cannot be directly compared to the metal AA-EQS_{marine water} (Annual Average Environmental Quality Standard) established by the WFD, which are defined in the dissolved concentration. Therefore, prior to using DGT results in a regulatory context, for cadmium, nickel and lead, an adaptation of existing AA-EQS_{marine water} for DGTs should be pursued, ensuring at least the same level of protection. In this sense, in the framework of the MONITOOL project, a robust database of dissolved and labile metal concentrations in transitional and coastal waters, for adapting the existing AA-EQS_{marine water} for DGT technique, was obtained. Building on these results, this study proposes a methodology and provides values and equations for using DGT results for the chemical status assessment of marine waters, by adapting the EQS_{marine water} to adapted EQS_{DGT} or predicting dissolved concentrations from DGT results. Based on available dataset, a first simulation of “chemical status” assessment per MONITOOL sampling site using DGT measured labile concentrations was carried out and the results were compared to an assessment based on dissolved concentration to check their compliance. These results demonstrate that the use of DGT passive samplers is appropriate for the metal concentrations level encountered in the marine environment. Further work is recommended to test the effectiveness of the methodology proposed in this study under

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WFD conditions on more sites and to establish common strategy guidelines for the use of DGT passive samplers in monitoring.

Keywords Water Framework Directive (WFD), DGT (Diffusive Gradients in Thin-films), EQS_{marine water}, Chemical status assessment, Metal dissolved concentration, Metal labile concentration, Bioavailability, Cadmium, Nickel, Lead

Background

According to the European Water Framework Directive (WFD; Directive 2000/60/EC) [14], the chemical status of water bodies is established on the basis of the compliance for each priority substance, assessed by the comparison of measured concentrations with the Environmental Quality Standards (EQS). The WFD defines an EQS as the concentration of a particular substance or group of substances in water, sediment or biota that should not be exceeded to protect human health and freshwater and marine ecosystems from adverse effects. Regarding cadmium, nickel and lead in marine waters, the WFD requires the monthly collection of spot water samples (12 per year) per WFD cycle (every 6 years) and the comparison with the respective AA-EQS_{marine water} (Annual Average EQS). The latter refers to the dissolved concentration, defined as total metal concentration in filtered (0.45 µm filter or equivalent pre-treatment) discrete water samples. The toxicity of metals in aquatic system is a complex phenomenon involving interactions between the environment and the metal pollutants of concern [15], which complicates the derivation of EQS for metals. When evaluating toxicity data to derive QS for metals, it should be noted that total dissolved metal concentrations are not the best indicator of the potential ecotoxicological effects because many abiotic and biotic processes can modify the speciation of metals and thus their (bio)availability, affecting the uptake by organisms [10]. Therefore, when adequate understanding exists, it is strongly recommended to incorporate bioavailability in the derivation of QSs for metals [10]. However, current EQS_{marine water} fails to properly address this as (i) they were derived using the few available ecotoxicological data on marine species [10] and (ii) metal speciation (e.g. metals bound to organic ligands might present lower toxicity to marine organisms) was not considered for their derivation.

Since one of the primary objectives of the WFD is the assessment of the annual average concentrations of pollutants in water bodies, the determination of time-integrated concentrations using passive samplers (PS) is a promising approach, i.e. PS integrate contaminants fluctuations occurring during the deployment time, compared to the snapshot concentrations provided by grab sampling (i.e. discrete spot sampling), which is more prone to the over or underestimation of real concentrations.

The Diffusive Gradients in Thin films (DGT) technique, developed in the early 1990s at the University of Lancaster by Zhang and Davison [31] in collaboration with the UK Environment Agency, stands out as the most widely used passive sampler for metals [21]. DGT samplers provide the time-integrated concentration of metals, as a function of deployment time and temperature, represented by the "labile" forms (i.e. free ions and easily dissociable metal complexes), which is suggested as a good indicator of toxicity to the lower trophic level organisms of the food chain, i.e. to benthic invertebrates, bivalves, amphipods [2–4, 19, 28], plants [9]; crustaceans, fishes and molluscs in freshwater [25, 26]; microalgae and molluscs in marine water [18, 29]. Considering that the ultimate objective of the WFD is to prevent adverse effects, the metal forms measured by DGT technique may be presumably more relevant to the EQS, than total dissolved concentrations [22].

Passive sampling techniques are mentioned in the Directive 2013/39/EU as novel monitoring methods showing promise for future application and in the Technical Guidance Documents (TGD; "Surface water chemical monitoring" [13], "Chemical monitoring of sediment and biota" [12] and "Biota monitoring" [11]), as methods under development and evaluation that are desirable to be introduced, as they become available, for improving the quality of the assessment. This presents the opportunity for their use in future directives if sufficient scientific evidence demonstrates their reliability in establishing the chemical status of water bodies. However, metal concentration measurements carried out using DGT samplers cannot be directly compared to existing EQS_{marine water}. In this sense, as regards the requirements of the WFD, there are two major differences between DGT and spot water sampling results, which need to be considered: (i) results represent different sampling time scales, that is, a time-integrated measurement of several days in the case of DGT sampling versus an average of punctual concentrations from spot water sampling, and (ii) DGT labile concentrations (free ions and metals dissociating sufficiently fast from inorganic and organic complexes) will usually be lower than total dissolved concentrations (0.45 µm-filtered), as the latter also accounts for metals associated to strong organic complexes, colloidal forms and small particles, and thus the comparison of DGT results with EQS_{marine water} would not be considered to

be as protective as with dissolved concentrations. Therefore, prior to using DGT results in a regulatory context, for the chemical status assessment of water bodies, an adaptation of existing AA-EQS_{marine water} for DGTs should be pursued, ensuring at least the same level of protection. Nowadays, no specific TGD provides indications for converting QS_{marine water} or EQS_{marine water} to EQS-Passive sampler. However, the TGD for the derivation of EQS [10] indicates that the conversion of biota standards into other matrices (from QS_{biota} to QS_{water}) or species (from QS_{biota, fish} to QS_{biota, monitored species}) can be performed by dividing the biota standards by appropriate conversion factors (Bioaccumulation factor—BAF, Bioconcentration factor—BCF, trophic magnification factor—TMF). Therefore, this approach could be potentially used for converting EQS_{marine water} into adapted EQS_{DGT} (abbreviation (A)-EQS_{DGT}) if an appropriate concentration factor for DGT results is determined. This requires determining the relationships between total dissolved and DGT labile concentrations and understanding the effects of environmental parameters on these relationships (see [7, 27]). This term « (A)-EQS_{DGT} » is used to highlight the fact that this is not an EQS_{DGT} derived from ecotoxicological results, but an adaptation of the existing EQS_{marine water}. This is the ultimate objective of the MONITOOL project (EAPA 565/2016; <https://www.monitoolproject.eu>), where a robust database of total dissolved and labile metal concentrations in transitional and coastal waters, based on concurrent spot water sampling and DGT deployments, has been obtained, aiming at adapting existing EQS_{marine water} to DGT ((A)-EQS_{DGT}) for the three priority metals of interest (Cd, Ni and Pb).

This study proposes a methodology for using DGT results in a regulatory context for the assessment of chemical status in marine waters, by comparing DGT results to existing EQS_{marine water}. The compliance of the application of this methodology with that expected in the regulation is also tested.

Methods

Working methodology and analytical techniques

Although the relationship between the labile and dissolved content of a metal has been found to be influenced by physicochemical characteristics in some reports [8, 20], our previous statistical treatment of this large dataset found no significant relationships (within the experimental error) in this regard for Cd, Ni and Pb [27]. It was observed that the ratios between the mean concentrations measured by DGT and by spot sampling were not significantly affected by temperature, salinity, pH, oxygen, dissolved organic carbon or suspended particulate matter. Therefore, statistical analyses were performed without taking into account physicochemical variables.

Methodology for comparison of DGT results to existing

EQS_{marine water}

Pending the derivation of EQS_{bioavailable} for marine water, there are two approaches for using DGT results in relation to existing EQS_{marine water}, that is, (i) comparing DGT labile concentrations to an (A)-EQS_{DGT} or (ii) estimating dissolved concentrations from DGT results and comparing them to existing EQS_{marine water}.

The first approach consists in using a conversion factor, as it is done for biota, where the BCF or BAF (i.e. the ratio of the concentration of the substance in the organism and marine water, in steady state) concept enables the determination of QS_{biota} by multiplying the QS_{marine water} by the BCF or BAF. Similarly, a DGT-conversion factor (CF_{DGT}) could be calculated by using the geometric mean of the ratio between measured DGT labile and dissolved metal concentrations, and an (A)-EQS_{DGT} could be determined by multiplying the EQS_{marine water} by the CF_{DGT}, or more effectively by establishing robust relationships (i.e. linear regression) between the total dissolved metal concentrations ([M]) measured in spot water samples and the DGT labile concentrations. The relationship would be described by Eq. (1) (Fig. 1A):

$$[M]_{DGT} = \text{slope} \times [M]_{\text{Dissolved concentration}} + \text{intercept}. \quad (1)$$

From Eq. (1), the (A)-EQS_{DGT} corresponding to the EQS_{marine water} value is obtained directly, which could be used for comparison with DGT labile metal concentrations measured in marine water bodies and for establishing their chemical status.

The second approach consists in directly comparing DGT results to existing EQS_{marine water}. It requires the establishment of valid relationships between the DGT labile metal concentrations measured by DGTs and the dissolved concentrations measured in spot water samples, which allows the back-calculation of the dissolved concentrations from the measured DGT labile concentrations. The relationship would be described by Eq. (2) (Fig. 1B):

$$[M]_{\text{Dissolved concentration}} = \text{slope} \times [M]_{DGT} + \text{intercept}. \quad (2)$$

DGT labile concentration results obtained in water quality monitoring campaigns could thus be used to predict the total dissolved concentrations, using Eq. (2), that can be compared to the EQS_{marine water} for the chemical status assessment of water bodies.

Regardless of the approach selected, the reliability of the obtained results will depend on the quality of the data. Thus, concurrent Cd, Ni and Pb dissolved concentrations in spot samples and DGT labile metal concentrations

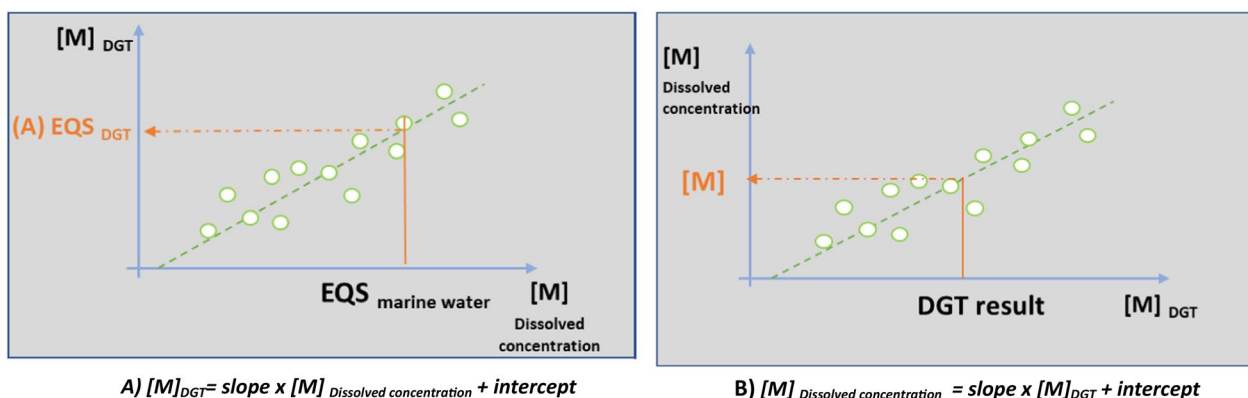


Fig. 1 Example of the generic relationships: **A** Metal concentration ($[M]_{DGT}$), representing the labile concentration for DGTs and dissolved concentration for spot samples, $[M]_{\text{Dissolved concentration}}$, and determination of (A)- EQS_{DGT} ; **B** $[M]_{\text{Dissolved concentration}}$ and $[M]_{DGT}$ and prediction of dissolved metal concentrations ($[M]$; orange) from DGT results

should be obtained, covering a wide range of concentrations (from slightly contaminated to highly contaminated sites) and, if possible, reaching concentrations close to or higher than the $EQS_{\text{marine water}}$. Additionally, these data must be reliable, use standard analytical protocols, and have low analytical uncertainty at the required low metal concentrations.

Study area, sampling and analysis strategy

In the framework of the MONITOOL project, nine institutes (AZTI, CEFAS, DCU, Ifremer, IPMA, ITC, MSS, SEPA and UNICA) performed two sampling campaigns, in wet (February–March 2018) and dry (July–September 2018) seasons, covering 31 sites in transitional and coastal areas, in 7 European countries (Fig. 2; Additional file 1: Annex 1). In order to find high Cd, Ni and Pb concentrations, several stations were located within harbours, some of which classified as heavily modified water bodies (Saint-Nazaire, Oiartzun estuary, Dublin Bay). In addition to the MONITOOL stations, Ifremer sampled five additional sites in French coastal areas or estuaries as part of a DGT-based Interlaboratory exercise [16] and the “VGE mollusques” project (2015–2020—Ifremer OFB-<https://ccem.ifremer.fr/en/News/Projects/VGE-Mollusques-2015-2020>), focused on the BAF determination between marine water (including DGT) and molluscs.

All the materials used in the laboratory and the field were soaked in a 10% HNO_3 acid bath overnight and rinsed thoroughly with ultrapure water (conductivity 18.2 $M\Omega \cdot cm$, 25 °C) before use. Spot water samples were collected using precleaned 500 mL HDPE bottles and were subsequently filtered, using 0.4 μm polycarbonate filters, and acidified (100 mL sample and 0.070 mL of HNO_3). The type of DGT selected was the open pore loaded DGT device for metals in solution (product code LSNM-NP;

DGT[®] Research Ltd., Lancaster, UK), consisting of a standard DGT plastic holder with a polyethersulphone (PES) 0.45 μm pore size filter membrane, 0.8 mm agarose cross-linked polyacrylamide (APA) diffusive gel, and Chelex-100 binding gel layer. The resin gel elution was done by adding 1 mL of nitric acid (1 M HNO_3 , 69%, ultrapure grade). Detailed descriptions of the deployment, retrieval, sample processing and analysis are described elsewhere [6, 7]. Briefly, triplicate DGT samplers were deployed at most sites for 5–7 days (depending on weather and field access conditions), and in several sites additional DGT samplers were deployed only for the first two days, as part of a biofouling study (Nolan et al., in prep.). Spot water samples were collected during the DGT deployment time: at least three times in coastal sites (start, middle, end) and twice a day for estuarine sites (at low and high tide). At each water sampling time, environmental parameters (temperature, salinity, pH and dissolved oxygen) together with suspended particulate matter (SPM) and dissolved organic carbon (DOC) were measured. All the DGT samples were analysed by a single laboratory, namely Ifremer, using an ICP-MS (inductively coupled plasma mass spectrometry), while the total dissolved metal concentrations in all the filtered and acidified water samples were determined by IPMA using an online pre-concentration seaFAST system (Elemental Scientific, Nebraska, USA) coupled with an ICP-MS. The variability among Partners was minimized by developing common sampling protocols and using the same DGT production batch.). In total, 235 DGT devices and 321 filtered water samples were analysed. After an exhaustive validation process performed by expert laboratories (see [23]), the resulting valid dataset, consisting of Cd, Ni and Pb DGT labile and total dissolved concentrations in spot samples, was used for data processing.



Fig. 2 MONITOOL sampling sites

Statistical process

For each sampling site and season (wet season and dry season), coupled DGT labile concentration (average of triplicates) and total dissolved concentration (average of the discrete marine water samples collected during the DGT deployment time) results were obtained for each of the metals of interest (Cd, Ni and Pb), finally obtaining 84 couples of data (DGT and spot sampling). In cases where the concentration value was lower than the limit of quantification, this was replaced by 50% of the limit of quantification.

The detailed explanation of the statistical processing is shown in the supplementary information (Additional file 1: Annex 2). Briefly, outliers were identified based on the results of linear models (i.e. standardized residuals > 3) and, once removed, new linear models were executed until all the outliers were removed. The last model without outliers was then kept and diagnosed. The

validity of the final model for each metal was evaluated first based on its p -value (valid if < 0.05) and secondly on the normality (the Shapiro–Wilk and Lilliefors (Kolmogorov–Smirnov) tests, in addition to QQ-plot) and homoscedasticity (the Breusch Pagan and Goldfeld–Quandt tests) of the residues (valid if p -value of test > 0.05), to get a clearer picture (each test having its limits/gaps). The validation of the model was accepted if one of the two tests for each criterion was valid. When a model is valid, its use is reliable within its validity range.

Results and discussion

Determination of (A)-EQS_{DGT} for cadmium, nickel and lead

The graphical representations of the linear regression models between dissolved and labile concentrations for Cd, Ni and Pb (Eq. 1) are presented in Fig. 3. Prior to studying the validation of the models, it should be pointed out that MONITOOL results for Cd, Ni, and Pb

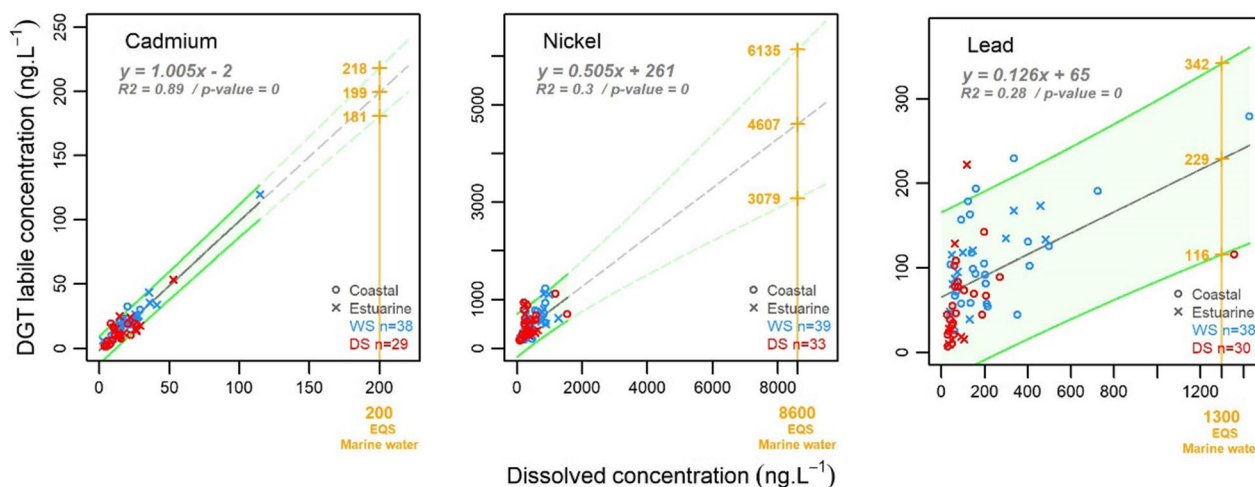


Fig. 3 Linear regression models between dissolved and DGT labile concentrations for the determination of (A)-EQS_{DGT}: (a) cadmium, (b) nickel and (c) lead. The regression line (black line) and its corresponding prediction interval ($\pm 95\%$; green lines and shaded green area) are shown. The shaded area corresponds to the range of validity of the model, defined on the horizontal axis, indicating that for a measured dissolved concentration value within the range of validity of the model, 95% of the DGT results will be between these 2 lines. WS wet season, DS dry season

were below the EQS_{marine water} values, except for Pb at one site, in both wet and dry seasons. The highest dissolved concentrations of the model were 0.11 $\mu\text{g}\cdot\text{L}^{-1}$ for Cd, 1.5 $\mu\text{g}\cdot\text{L}^{-1}$ for Ni and 1.4 $\mu\text{g}\cdot\text{L}^{-1}$ for Pb, while the corresponding EQS_{marine water} for those metals are 0.2 $\mu\text{g}\cdot\text{L}^{-1}$, 8.6 $\mu\text{g}\cdot\text{L}^{-1}$ and 1.3 $\mu\text{g}\cdot\text{L}^{-1}$, respectively.

The results of the statistical tests are presented in Table 1, and further details are presented in the supplementary information (Additional file 1: Annexes 3 and 4). The model validation assumptions were fulfilled for Cd and Pb (i.e. model p -value was <0.05 , and the normality and homoscedasticity of the residues p -value were >0.05). For Ni, they were partially satisfied, but the relationship was significant. The model validation criteria were met (p -values, homoscedasticity) except for residue normality, which does not imply the outright invalidation of the model. The relationship between DGT labile and spot sampling dissolved concentration was significant for Cd, Ni and Pb. For Cd, a strong relationship with a slope of 1 was found, pointing to a direct relationship between total dissolved and DGT labile Cd concentrations. This confirms that Cd is mainly in a labile form [7, 27],

presumably as chloride complexes [24]. Otherwise, for Ni and Pb, although significant, a higher data dispersion was found. In both cases, the slopes were below 1 (0.51 for Ni and 0.13 for Pb), suggesting that a high proportion of these metals were non-DGT labile, presumably as they were present forming organic complexes or in colloidal forms [7, 27] with slow dissociation and diffusion rates through the diffusive layer of the DGT [1]. Ideally, the (A)-EQS_{DGT} value should be determined in the model's validity range. However, as it has been observed in the current study, especially for Ni and Cd, it is difficult to find metal concentrations close to the EQS_{marine water} in the marine environment, even at sites located in environments affected by different contaminant sources (e.g. harbours). Therefore, for these metals, the (A)-EQS_{DGT} values were determined by extrapolation of the regression line, which may bring uncertainty outside the validity range of the model. This was acknowledged not only by determining the (A)-EQS_{DGT}, based on extrapolating the projection of the EQS_{marine water} value ((A)-EQS_{DGT} no. 1) of the regression line, but also by using the Lowest 95% prediction interval (LPI 95%) ((A)-EQS_{DGT} no. 2)

Table 1 Validity test results of the linear regression models between the dissolved concentration of metals (as dependent variable) and the DGT labile concentrations (as independent variable), Eq. (1) shown in Fig. 3

	Normality Shapiro	Normality Lilliefors	Homoscedasticity Breusch-Pagan	Homoscedasticity Goldfeld-Quandt	p -value	R^2	N
Cd	1.99 $\times 10^{-1}$	3.89 $\times 10^{-1}$	2.51 $\times 10^{-1}$	9.81 $\times 10^{-1}$	0.000	0.89	67
Ni	1.00 $\times 10^{-4}$	4.39 $\times 10^{-5}$	1.35 $\times 10^{-1}$	8.48 $\times 10^{-1}$	4.00 $\times 10^{-7}$	0.30	72
Pb	8.51 $\times 10^{-2}$	4.05 $\times 10^{-1}$	8.07 $\times 10^{-2}$	8.00 $\times 10^{-1}$	1.90 $\times 10^{-6}$	0.28	68

Significant results are indicated in bold text.

(Fig. 3), to ensure that the level of protection of the (A)-EQS_{DGT} is greater, as suggested by Babut et al. [5] for the TMF determination. Eq. (1) for Cd, Ni and Pb and the validity range of the model is detailed in Table 2. The (A)-EQS_{DGT} for Cd, Ni and Pb determined (Eq. 1) using this model, (A)-EQS_{DGT} no. 1 and (A)-EQS_{DGT} no. 2, are presented in Table 3.

Dissolved concentration estimation from DGT results

The relationships between Cd, Ni, and Pb DGT labile and dissolved concentrations are represented in Fig. 4. The regression line and the corresponding prediction interval

(PI 95%) have been represented. The results of the statistical tests are provided in Table 4.

The model validation assumptions were satisfied for Cd and Ni, and the relationships between dissolved concentrations and DGT labile concentrations were significant. For Pb, the model validation assumptions were partially satisfied, but the relationship was significant. The model validation criteria were met (*p*-values, homoscedasticity) except for residue normality, which does not imply the outright invalidation of the model, as linear models are very robust to violations of the normality assumption [17] (see details in Additional file 1: Annex 2).

Table 2 Application of Eq. (1) for predicting Cd, Ni and Pb DGT labile concentrations from dissolved concentrations

	Mean predicted [M] _{DGT} (ng L ⁻¹)	Lowest predicted [M] _{DGT} (ng L ⁻¹) (LPI 95%)	Validity range (ng L ⁻¹)
Cadmium	[Cd] _{DGT} = 1.01 [Cd] _{Dissolved concentration} - 2	[Cd] _{DGT} = 0.98 [Cd] _{Dissolved concentration} - 12	[Cd] _{Dissolved concentration} [$<LQ; 114$]
Nickel	[Ni] _{DGT} = 0.51 [Ni] _{Dissolved concentration} + 261	[Ni] _{DGT} = 0.48 [Ni] _{Dissolved concentration} - 166	[Ni] _{Dissolved concentration} [$<LQ; 1544$]
Lead	[Pb] _{DGT} = 0.13 [Pb] _{Dissolved concentration} + 65	[Pb] _{DGT} = 0.11 [Pb] _{Dissolved concentration} - 31	[Pb] _{Dissolved concentration} [$<LQ; 1428$]

The mean and lowest predicted concentrations and the validity range are shown

Table 3 AA-EQS_{marine water} expressed in µg L⁻¹ [30] and (A)-EQS_{DGT} for Cd, Pb and Ni

CAS number	Substance	AA-EQS _{marine water} (µg L ⁻¹)	(A)-EQS _{DGT} no. 1 Linear regression model (µg L ⁻¹)	(A)-EQS _{DGT} no. 2 Linear Regression Model minus lower Prediction interval (- PI _{95%}) (µg L ⁻¹)
7440-43-9	Cadmium	0.2	0.20	0.18
7440-02-0	Nickel	8.6	4.60	3.08
7439-92-1	Lead	1.3	0.23	0.12

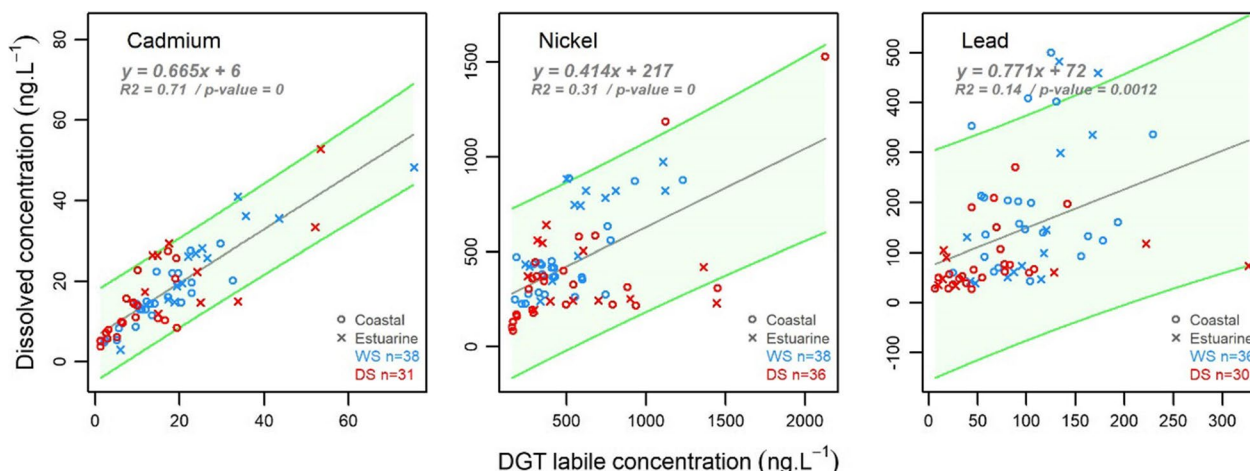


Fig. 4 Linear regression models between DGT labile and dissolved concentrations for the determination of dissolved metal concentrations from DGT measurements: (a) cadmium, (b) nickel and (c) lead. The regression line and its corresponding prediction intervals (PI 95%; green dashed lines and light green area) are shown. WS wet season, DS dry season

Table 4 Validity test results of the linear regression models between the dissolved concentration of metal (as dependent variable) and the DGT labile concentration (as independent variable), Eq. (2) shown in Fig. 4

	Normality Shapiro	Normality Lilliefors	Homoscedasticity Breusch-Pagan	Homoscedasticity Goldfeld-Quandt	p-value	R2	N
Cd	1.94 × 10⁻¹	8.76 × 10⁻²	6.64 × 10 ⁻⁴	1.000	0.000	0.71	69
Ni	7.54 × 10⁻¹	7.09 × 10⁻¹	0.000	0.999	1.00 × 10⁻⁷	0.31	74
Pb	4.80 × 10 ⁻⁶	2.40 × 10 ⁻⁶	1.58 × 10 ⁻³	0.832	1.25 × 10⁻³	0.14	66

Significant results are indicated in bold text

The equations of these relationships (including or not the PI 95%) and the validity range of the model are detailed in Table 5.

“Chemical status” simulation based on DGT results

Based on available data, simulations of the “chemical status” assessment were performed at each of the MONITOOL sampling sites for Cd, Ni and Pb. This exercise intended to check the conformity of the assessment when using the DGT results to the one based on the dissolved concentrations, and in case of mismatch, to check if the use of DGT results is at least as protective as the current assessment for the directive. The simulations were performed using the results obtained in the MONITOOL project, which focused on obtaining parallel DGT and spot sampling data in very diverse marine waters, in terms of geographical location and environmental variables. Data were not obtained on monthly basis for a year and there are not always 12 dissolved concentration results per sampling site (i.e. 6 data for coastal site, and more than 12 for estuarine sites) as demanded by the WFD for regulatory purposes. However, data were treated as close as possible as demanded by the Directive, by calculating annual average concentrations (using only those stations with wet and dry season results).

For each MONITOOL site, the following simulations were performed (Fig. 5):

- Simulation 1: Annual average dissolved concentrations of spot sampling results were compared to the AA-EQS_{marine water}

- Simulation 2: Annual mean DGT results were compared to (A)-EQS_{DGT} no. 1 and no. 2 (Table 3).
- Simulation 3: Predicted dissolved concentrations from DGT results (mean and highest predicted concentrations) (Table 5) were compared to EQS_{marine water}.

Of the 36 MONITOOL sampling sites, assessment on an annual basis could be performed at 21 sites for Cd, 23 for Ni and 19 for Pb, as the remaining sampling sites did not have results, of either dissolved or labile concentrations, for both periods.

It was observed that even including sites suspected to be highly contaminated (harbours, estuaries), dissolved average concentrations for Cd, Ni and Pb were far below the AA-EQS_{marine water} (simulation 1), excepting one site for Pb (site no. 22—Molo Rinascita).

Regarding the (A)-EQS_{DGT} (simulation 2), all the values were below the threshold for Cd and Ni. For Pb, differences were observed depending on the (A)-EQS_{DGT} applied. While one site (site no. 9—Dublin Bay Boy 4) was above the (A)-EQS_{DGT} no. 1, four sites (sites no. 9 Dublin Bay Boy 4, no. 11 North Chanel Great Island (M70), no. 20 Molo Dogana, no. 22 Molo Rinascita) were above the more conservative (A)-EQS_{DGT} no. 2.

The acceptance of (A)-EQS_{DGT} is conditional on these values being as protective as currently available EQS_{marine water}. In all the dataset, only one site (Molo Rinascita) presented dissolved Pb concentrations above the EQS_{marine water}, which was in accordance with the results obtained when applying the (A)-EQS_{DGT} no. 2. Thus, selecting the (A)-EQS_{DGT} no. 2 ensured at least the same protection

Table 5 Application of Eq. (2) for predicting Cd, Ni and Pb dissolved concentrations from DGT results

	Mean predicted [M] _{dissolved concentration} (ng L ⁻¹)	Highest predicted [M] _{dissolved concentration} (HPI 95%) (ng L ⁻¹)	Validity range (ng L ⁻¹)
Cadmium	[Cd] _{Dissolved concentration} = 0.67 [Cd] _{DGT} + 6	[Cd] _{Dissolved concentration} = 0.68 [Cd] _{DGT} + 17	[Cd] _{DGT} : [$< LQ, 75$]
Nickel	[Ni] _{Dissolved concentration} = 0.41 [Ni] _{DGT} + 217	[Ni] _{Dissolved concentration} = 0.44 [Ni] _{DGT} + 645	[Ni] _{DGT} : [$< LQ, 2128$]
Lead	[Pb] _{Dissolved concentration} = 0.77 [Pb] _{DGT} + 72	[Pb] _{Dissolved concentration} = 0.84 [Pb] _{DGT} + 292	[Pb] _{DGT} : [$< LQ, 327$]

The mean and highest predicted concentrations and the validity range are shown

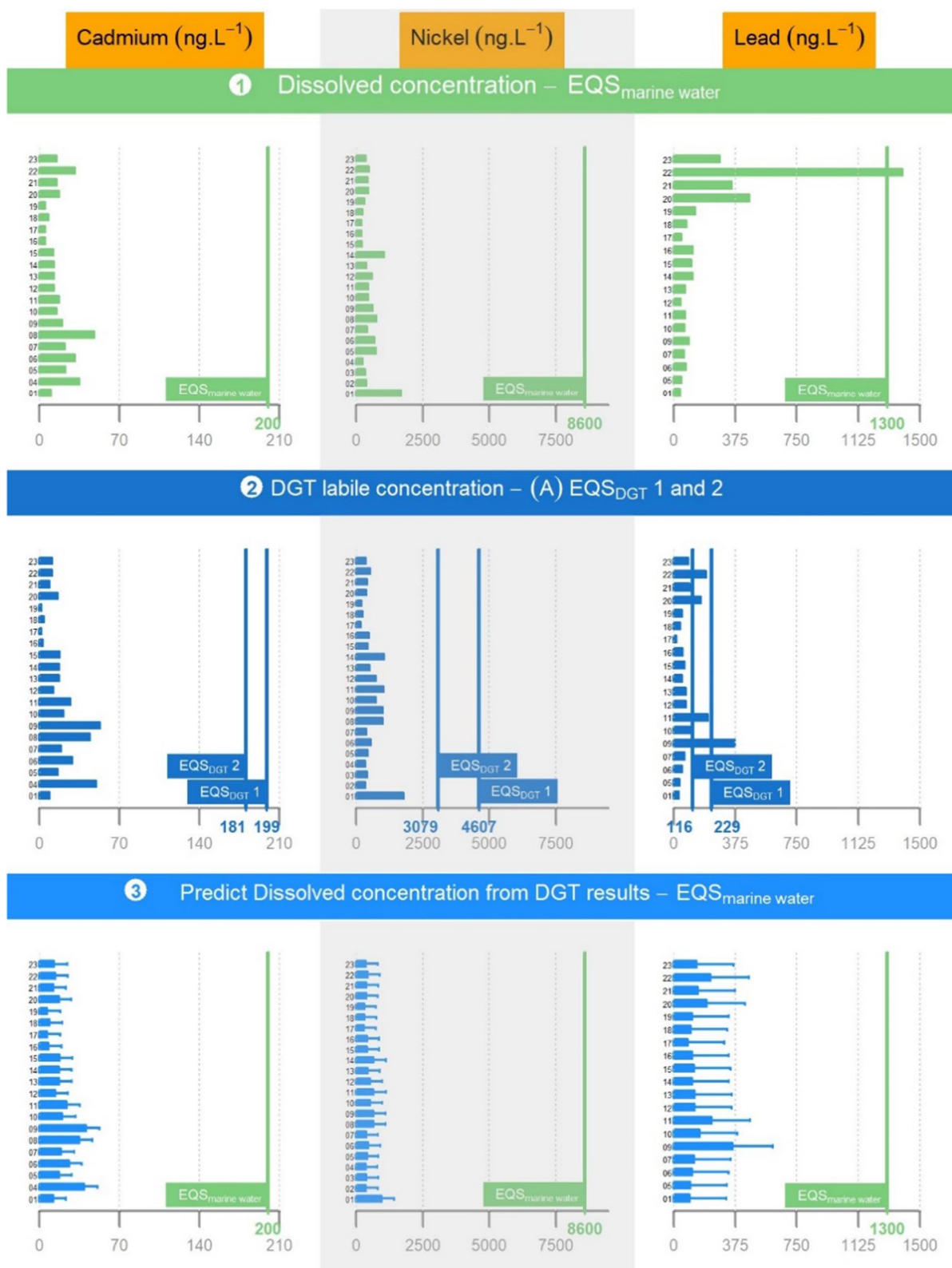


Fig. 5 Simulation of “chemical status” assessment per MONITOOL site for cadmium, nickel and lead: **1** Annual mean dissolved concentration (in green) and indication of EQS_{marine water}; **2** Annual mean labile DGT concentration (ng.L⁻¹) (in blue) and indication of (A)-EQS_{DGT} nos. 1 and 2; **3** Predict dissolved concentration from DGT results (Eq. 2) and indication of EQS_{marine water}

level than the use of $EQS_{\text{marine water}}$. Moreover, other 3 sites (Dublin Bay Boy 4, North Chanel Great Island (M70), Molo Dogana) presented Pb concentrations above the (A)- EQS_{DGT} no. 2 threshold, two of them corresponding to sites located in port areas.

When dissolved concentrations were predicted from DGT results (simulation 3) and compared to the existing AA- $EQS_{\text{marine water}}$, all the values were below the AA- $EQS_{\text{marine water}}$. Using the highest predicted concentration (HPI 95%—Eq. 2) is preferred to the use of the mean predicted concentration in order to avoid underestimating the predicted dissolved concentration that will be compared to the $EQS_{\text{marine water}}$. For each metal Cd, Ni and Pb, and for each site (respectively 21, 23 and 19 sites), these highest predicted dissolved concentrations were always higher than the measured dissolved concentrations, except for one site for Ni (Deba—site no. 1—1420 vs 1661 ng L⁻¹) and two sites for Pb (Molo Dogana—site no. 20—432 vs 461 ng L⁻¹—and Molo Rinascita—site no. 22—458 vs 1393 ng L⁻¹).

The mismatch between the results obtained with simulation 1 ($EQS_{\text{marine water}}$) and 2 ((A)- EQS_{DGT} no. 2) might be explained by the reduced number of data, with a limited temporal coverage, which do not represent the 12 monthly samples demanded by the directive.

In order to check the conformity of the chemical status assessment based on DGTs (simulations 2 and 3) to the one based on dissolved concentrations (simulation 1), it is necessary to confirm the suitability of the two proposed approaches in real case scenarios (i.e. sampling sites monitored within WFD). Thus, the next step will involve setting up a pilot study at several sites, consisting of monthly parallel monitoring by DGTs and collection of filtered water samples for one year, in order to assess the comparability of the proposed approaches under WFD conditions. Additionally, including sites suspected of presenting a bad chemical status for lead, cadmium or nickel will allow the dataset to be completed with samples presenting higher concentrations, up to the $EQS_{\text{marine water}}$ level.

Conclusion

MONITOOL data were used for establishing robust relationships between DGT labile and dissolved concentrations, allowing not only the determination of (A)- EQS_{DGT} for Cd, Ni and Pb but also the possibility of predicting dissolved metal concentrations from DGT results for these metals.

A first simulation of using DGT results for the “chemical status” assessment of marine waters was done in order to test the applicability of both approaches (i.e. use of (A)- EQS_{DGT} no. 1 or no. 2, or use of predicted dissolved concentrations from DGT results). Although the

MONITOOL data do not fulfil the WFD requirements in terms of temporal representativity (i.e. annual average concentrations represented by 12 monthly water samples), the results presented here should be seen as a first step towards the inclusion of PS for the chemical status assessment of marine waters.

The current study, performed in different geographical locations characterized by different environmental conditions, enabled to rise three important points. Firstly, that average dissolved concentrations at all sites were far below the $EQS_{\text{marine water}}$ for Cd, Ni and Pb (except one for lead), even targeting suspected high contaminated sites. Accordingly, the range of dissolved concentrations measured within MONITOOL is very similar to the range of concentrations measured in Europe within WFD monitoring programmes (see the Data portal on Marine Environment; <https://www.ices.dk/data/data-portals/Pages/DOME.aspx>). Although the determination of the (A)- EQS_{DGT} is consistent, and in line, with the methodology used to adapt the thresholds from one matrix to another (BAF, BCF), as laid down in the TGD EQS [10], from a mathematical point of view, it would be important to complete the dataset in order to consolidate the model for the higher concentrations (to reach or even exceed the $EQS_{\text{marine water}}$ value). This could be done by carrying out additional sampling campaigns targeting highly contaminated sites and/or performing experimental laboratory studies including spiked samples for Cd, Ni and Pb.

Secondly, in addition to this EQS adaptation process, it would be necessary to establish a standard guideline for using DGTs in a regulatory context at European level (e.g. to set up frequency and period of deployment for DGTs). Besides, the approach presented in the current study should be tested under WFD conditions, by setting up a pilot study aligned with the European Directives requirements.

Finally, to complete the process of improving the chemical status assessment, and ideally moving towards an $EQS_{\text{bioavailable}}$ derivation, the existing EQS datasheets for Cd, Ni and Pb should be updated, since they are old (2005–2011, depending on the metal considered) and based only on few ecotoxicity results on marine species.

Abbreviation

AA-EQS	Annual Average Environmental Quality Standard
(A)- EQS_{DGT}	Adapted Environmental Quality Standard referred to the labile concentration of a metal in marine water measured with DGT technique, derived from the $EQS_{\text{marine water}}$
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
CF_{DGT}	Conversion Factor from metal labile concentration in marine water, measured with DGT technique, to metal dissolved concentration in marine water
CI	Confidence interval
DGT	Diffusive Gradients in Thin-films

DOC	Dissolved organic carbon
DS	Dry season
EQS	Environmental Quality Standard
HDPE	High-density polyethylene
ICP-MS	Inductively coupled plasma mass spectrometry
LQ	Limit of quantification
PI 95%	Prediction interval (within a regression model, estimation of the expected range of a single future observation, for a confidence level of 95%)
QQ-plot	Scatterplot plotting two sets of quantiles against one another
QS	Quality standard
SPM	Suspended particulate matter
TGD	Technical guidance document
WFD	EU Water Framework Directive, 2000/60/EC
WS	Wet season

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s12302-023-00733-4>.

Additional file 1: Annex 1: MONITOOL sampling sites. **Annex 2:** Statistical process and results. **Annex 3:** Statistical process results. **Annex 4:** Results of the three statistical methods used as a first approach in the data processing to determine the-EQSDGT.

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Author contributions

IA contributed to writing—original draft preparation, investigation, data curation, visualization, project administration for Ifremer and funding acquisition. MJB-S contributed to investigation, writing—review and editing, project administration and funding acquisition. PB, JL, IM and JGR contributed to investigation and writing—review and editing. LL and OP-D performed Investigation. MCS was involved in investigation, writing—review and editing, and project administration. BM, OP and HZ were involved in writing—review and editing. SG performed data curation, data processing, formal analysis, visualization, investigation and writing—review and editing. JLG and FM-N were involved in investigation and writing—review and editing. BM, NM and MRS contributed to investigation, writing—review and editing, and funding acquisition. VMG, TB, MC, FR, MS and BW were involved in investigation, data curation, writing—review and editing, project administration and funding acquisition. All the authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on request.

Declarations

Ethics approval and consent to participate

The corresponding author has read the Springer journal policies on author responsibilities and submits this manuscript in accordance with those policies.

Consent for publication

By submitting my article I agree to pay the APC in full if my article is accepted for publication.

Competing interests

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.

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