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Metals concentrations in transitional and coastal waters by ICPMS and voltammetry analysis of spot samples and passive samplers (DGT)

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ABSTRACT

This study investigates the relationships among Ni, Cd and Pb's different chemical forms determined by different methodologies in coastal and transitional waters across a broad geographical scale. Concentrations were measured in spot samples and through passive sampling (DGT). High variability of metal concentrations was found among sampling sites and methodologies due to natural water fluctuations rather than to a given metal or method. Total dissolved metal concentrations in spot samples were lower than the EQS-WFD values. The labile fractions of Cd and Pb, measured in spot samples by Anodic Stripping Voltammetry and by DGT-ICPMS, were highly correlated. Similar labilities were found for Cd, while for Pb, the ASV labile fraction was ≈50% lower. These results reflect the pool of mobile and labile species available towards each technique kinetic window, and they seem not to be affected by discrete sampling flaws.

1. Introduction

Trace metals are ubiquitous in the environment. For example, copper (Cu), zinc (Zn) and nickel (Ni) are essential for the optimal growth and development of organisms. However, high concentrations can negatively impact the health of biota. Metals like lead (Pb) and mercury (Hg) have no known biological functions and can directly cause toxicity (Fraústo-da-Silva and Williams, 2001). To protect the health and biodiversity of aquatic ecosystems, environmental contaminants such as trace metals must be monitored and the impact of contamination events

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reduced. Cadmium (Cd), Pb and Ni were identified as priority metals of ecological concern under the European Union Water Framework Directive (WFD, 2000/60/EC and its subsequent amendment by Directive, 2013/39/EU). These directives define the good chemical status of water bodies as being achieved when the concentrations of priority substances, including trace elements, do not exceed the relevant Environmental Quality Standards (EQS). For Cd, Pb and Ni, the EQS are relative to dissolved concentrations which are operationally defined as the metal concentrations in a discrete water sample filtered through a 0.45 μm and acidified or subjected to any equivalent pre-treatment (CIS, 2009). However, each trace metal's toxicity depends on its total dissolved concentration and its chemical or physical form (speciation) present in the aquatic medium, which changes its mobility and bioavailability (Gao et al., 2019). Consequently, EQS required by WFD for appropriate monitoring of water quality should consider the chemical speciation of the element.

For the determination of labile metal ion concentrations (free ions, inorganic forms, and metals weakly bonded to organic ligands), Anodic Stripping Voltammetry (ASV) and Diffusive Gradients in Thin-films (DGT) with Inductively Coupled Plasma Mass Spectrometry (ICPMS) are two of the few analytical methods that can be used at ultra-trace level (Davison and Zhang, 1994, 2012; Unsworth et al., 2006; Gao et al., 2019). Both (ASV and DGT) are dynamic speciation techniques. The accumulation step depends on the diffusion of the metal species through an effective diffusion layer before being trapped either onto an electrode or onto an ion exchange resin. The amount of metal accumulated depends on the dynamic features of the complexes formed in the medium relative to the diffusion layer thickness and their mobility. Therefore, both ASV and DGT lability measurements are operationally defined by the characteristic kinetic window of the technique, longer in DGT than is ASV (Gao et al., 2019). The dynamic species measured by these methods are both labile and mobile, i.e., a size range of a few nanometers (van Leeuwen, 2000). However, methodologies differ. While ASV measurements are performed on discrete spot samples, DGT is a passive sampler. Thus, DGT sampling allows for the accumulation of an analyte over time, providing a time-weighted average of the analyte concentrations. Additionally, in situ sampling for the labile trace metals with DGT avoids the generation of analytical artefacts (from the contamination and perturbation effects on the distribution of labile and non-labile species), which are especially prone to occur when dealing with concentrations at the ultra-trace level. Conventional discrete sampling, which is relatively easy to perform, provides information on the localized metal concentration in water at the exact sampling moment. In highly dynamic systems like transitional and coastal waters, discrete sampling methods may suffer from a lack of representativeness (Rodríguez et al., 2021) as metal ion speciation can be controlled by the complexity of both organic and inorganic ligands present in colloidal forms. In respect of organic ligands, most are polyfunctional heterogeneous macromolecules, e.g., humic substances (HS), with different binding sites such as carboxylic and phenolic (hard complexing sites) and nitrogen and sulphur (soft complexing sites). As HS are common in coastal and estuarine waters, many metal ions can bind to these ligands. As a result, the complexes formed are characterized by a continuous distribution of thermodynamic stability constants and dissociation rate constants. They are functions of the relative affinities of the metal-to-ligand ratio coupled with the kinetic window of the analytical technique (Buffle, 1988). Consequently, previous works have shown that the degree of ligand heterogeneity in an aqueous medium is reflected in the measured concentrations by non-equilibrium techniques such as DGT and ASV (Town et al., 2009).

Widespread implementation of existing and future regulatory policies regarding the priority metals and other trace elements requires appropriate sampling in parallel with more advanced analytical techniques, which are often costly and, in some cases, are a barrier to compliance. There is a need to develop further and validate low-cost and easy-to-use sampling and analytical protocols for monitoring. In this sense, the Interreg MONITOOL project (EAPA 565/2016; https://www.monitoolproject.eu) was conceived based on the challenge of providing a robust database of total dissolved and labile metal concentrations in transitional and coastal waters based on concurrent spot water sampling and DGT deployments. In this study, the focus was the priority metals for which EQS were established under the WFD. Accordingly, the labile chemical forms of Cd and Pb in waters were measured by DGT-ICPMS and ASV, while ICPMS was determined the total dissolved metal concentrations. For Ni, the total dissolved concentrations were measured with two distinct methods, ICPMS and Cathodic Stripping Voltammetry (CSV) (van den Berg, 1986) and the labile fraction by DGT. The extent of relationships across a broad geographical scale covering various environmental conditions was evaluated.

2. Study area

The study was performed in the coastal and estuarine areas in the North-East Atlantic Area (from the Canary Islands to the North Sea) and the Western Mediterranean Sea (Sardinia). Sampling sites were selected to cover various anthropogenic influences from almost pristine environments to impacted areas. The sampling campaigns were carried out by nine research institutes (AZTI, CEFAS, DCU, IFREMER, IPMA, ITC, MSS, SEPA and UNICA) covering eight countries (Spain, England, Ireland, France, Portugal, Scotland, Northern Ireland and Italy) following the methodologies described in Bersuder et al. (2021). To minimize the operational variability, unified protocols were used for sampling, and the same laboratory performed each type of analysis. A short description of each coastal and estuarine sampling site is presented in Tables 1 and 2, respectively.

3. Materials and methods

3.1. Spot sampling

The sampling campaigns were carried out in 2018 and 2019, covering the dry (summer) and the wet (winter) seasons. A total of 28 sites from the Canary Islands to the North Sea, including the Western Mediterranean Sea, were surveyed (Table S1). For each partner, the same stations were sampled twice (wet and dry seasons). Sampling campaigns were completed in several ways (foot access, platforms, via boat) to access sites depending on accessibility and weather conditions. The sampling sites were chosen in such a way as to consider a wide range of concentrations for each metal. For the transition waters, sites with expected high contaminations were selected. Subsurface samples (≈0.5 m below the surface at the same depth as deployed DGTs) were collected independently for ICPMS and voltammetry with Niskin bottles or directly to collection flasks (polypropylene) with extendable poles avoiding direct contact to minimize contamination (Bersuder et al., 2021). In total, 712 spot water samples were collected during all survey campaigns. All sampling equipment used in the field was acid cleaned (10–20% v/v, pro-analysis grade) and rinsed thoroughly with ultra-pure water (conductivity 18.2 MΩ·cm, 25 °C). Field blanks were processed at all sites and by all teams concurrently to the collected water samples to evaluate the potential contamination during sampling.

3.2. Passive sampling

The passive samplers used were from DGT® Research Ltd. (Lancaster, UK), with the reference LSNM-NP open-pore Loaded DGT device for metals (A) in solution. All DGTs used were from the same production batch to minimize differences related to manufacturing. Three DGTs were loaded onto a plastic holder (polycarbonate) and, when necessary, protected with a nylon net (1 cm mesh size) to prevent damage from side impacts or aquatic organisms. DGT-holders were deployed at ≈0.5 m depth below the surface in the same sites and seasons of spot sampling. Holders were retrieved from the water between 2 and 7 days of

Table 1
Main geomorphological characteristics and pressures of sampled coastal sites (ES - Spain; PT - Portugal; FR - France; IE – Ireland; IT - Italy).

Country	Ecoregion	Site	Coastal typology	Geological remarks	Human pressures
ES	Canary Islands	La Luz	Sheltered	Artificial construction (marina)	Domestic effluents, yachting port
ES	Canary Islands	Jinámar	Sheltered)	Artificial construction	Domestic effluents, industrial activity, urban runoff
ES	Canary Islands	Taliarte	Sheltered	Basaltic lava, artificial construction	Fish port area, aquaculture (algae and fish) activities
ES	Canary Islands	Gando	Exposed	Sandy beach	Military airbase, airport runoff.
PT	Iberian Coast	Matosinhos	Exposed	Granitoids, schist, greywacke	Domestic effluents, harbour, oil refinery
PT	Iberian Coast	Oeiras	Moderately Exposed	Schist, greywacke, granitoid, sand, sandstones, carbonates	Agriculture, harbour, industrial activities, shipyard
PT	Iberian Coast	Sesimbra	Moderately Exposed	metavolcanic	Agriculture, mining activity, shipyard, domestic effluents
FR	Bay of Biscay and English Channel	Port-en-Bessin	Sheltered	Grey marl and limestone	Fish port area fairing area, domestic effluents
FR	Bay of Biscay and English Channel	Saint-Nazaire basin	Sheltered	Granites and gneisses	Harbour activities, shipyard
FR	Bay of Biscay and English Channel	Saumonard	Moderately Exposed	Sandstone and limestone	Agriculture, shellfish production area
IE	Irish Sea	Dublin Bay-2	Exposed	Limestone, shale, calcareous mudstone, granites	Shipping and transport activities, sediment disposal area
IE	Irish Sea	Dublin Bay-4	Exposed	Limestone, shale, calcareous mudstone, granites	Domestic effluents and recreational use
England	Irish Sea	Liverpool	Exposed	Offshore site	Nutrients rich bay
England	Celtic Sea	Buoy 38A	Exposed	Offshore site	"Pristine" site, 18 miles offshore
Scotland	North Sea	Newhaven	Sheltered	Gravely sand and mud	Artificial harbour; urban industrial activities, including petrochemical
IT	Western Mediterranean Sea	Molo Dogana	Sheltered	Slightly gravelly muddy sand	Firefighters station, leisure port
IT	Western Mediterranean Sea	Molo Ichnusa	Moderately exposed	Slightly gravelly muddy sand	Military ship docking area
IT	Western Mediterranean Sea	Molo Rinascita	Moderately exposed	Slightly gravelly muddy sand	Harbour
IT	Western Mediterranean Sea	Sant'Elmo Dock	Sheltered	Slightly gravelly muddy sand	Leisure port

Table 2
Main geomorphological characteristics and pressures of sampled estuarine sites (ES - Spain; PT - Portugal; FR - France; IE – Ireland).

Country	Ecoregion	River-estuarine system	Morphology	Tidal regime	Annual mean river flow (m^3s^{-1})	Estuarine area (km^2)	Human pressures
PT	Iberian coast	Ria of Aveiro	Bar-built estuary	Mesotidal	32	60	Urban and industrial discharges, dredging
ES	Iberian coast	Oiartzun	Drowned river valley	Mesotidal	4.8	0.9	Pollutants discharge, dredging
ES	Iberian coast	Deba	Drowned river valley	Mesotidal	14	0.6	Urban and industrial discharges
FR	Bay of Biscay	Charente estuary	Coastal plain estuary	Macrotidal	64	[a]	Agriculture, shellfish production area, urban effluents
FR	Bay of Biscay	Aulne Estuary	Coastal plain estuary	Macrotidal	25	443	Agriculture, urban effluents
IE	Irish Sea	Alexandra Basin - River Liffey	Artificial port	Mesotidal	18	4.8	Urban and industrial activity and discharges
IE	Celtic Sea	River Lee - Lough Mahon	Salt wedge	Mesotidal	40.4	1.31	Urban and industrial activity and discharges
IE	Celtic Sea	River Ballynacorra	Salt wedge	Mesotidal	[a]	0.34	Urban activity
England	Celtic Sea	Fal estuary	Drowned river valley	Macrotidal	[a]	24.8	Inputs from farming, sewage treatment discharges, shellfisheries, boating and historical mining catchment
Northern Ireland	Irish Sea	Belfast Lough	Artificial port in a coastal plain	Mesotidal	[a]	73.6	Nutrient-rich estuarine harbour, passing ships and ferry terminal

[a] Not available information.

deployment. Differences in deployment time were due to weather and logistical conditions at each site. Biofouling on DGT membranes was minimal, with a median surface cover of 3% (data not shown). Thus, effects from biofouling on the accumulated metals were not expected, which agrees with observations on short-term deployment studies (Schintu et al., 2008; Baeyens et al., 2018). A total of 238 DGT devices were deployed and retrieved from the sampling sites (Table S1). Field DGT blanks (not immersed in water) were used at all sites and by all teams to evaluate the potential contamination derived from manufacturing and handling, respectively.

3.3. Sample preparation

Water and DGT samples were processed following the methodology described in Bersuder et al. (2021). Briefly, to minimize contamination, all the materials used were acid cleaned (20% v/v, pro-analysis grade), subsequently rinsed with ultra-pure water and dried in rooms with environmental conditions limiting sample contamination. Powder-free gloves were also used to minimize contamination. Spot samples for voltammetric analysis (hereafter referred to as "Volt") were filtered and acidified in the field (when practical) or as soon as they were returned in the laboratory, while for ICPMS, the procedure was carried out in the laboratory. Spot samples where trace elements were subsequently measured using ICPMS are, hereafter, referred to as "ICPMS". Additionally, care was taken to avoid possible contamination sources (e.g. fumes from engines deposition of atmospheric particles) in the field. In both situations, waters were filtered through 0.45 μm polycarbonate membranes and acidified to $pH \leq 2$ with suprapure grade HNO_3 or bidistillate and kept refrigerated (4–6 °C) until analysis. DGT units were removed from holders, opened using a plastic screwdriver, and the resin-gel layer was retrieved with plastic tweezers. Metals from the gel were back-extracted with a 1 M HNO_3 solution and measured by ICPMS. Passive samples are hereafter referred to as "DGT". The final solution was kept refrigerated (4–6 °C) until analysis.

3.4. Analytical methods

Total dissolved metal concentrations in water samples were determined by an online pre-concentration SeaFast system (model picoSP4, Elemental Scientific Inc) coupled with an ICPMS (model NexION 2000, Perkin Elmer). The Seafast column (ethylenediaminetriacetic acid and iminodiacetic acid chelating groups immobilized on a hydrophilic methacrylate polymer) has a high affinity for a range of metal ions (Lagerström et al., 2013). The complete column recovery of metals was optimized to occur at a pH between 5.5 and 7.0 (Lagerström et al., 2013). The system was programmed with a cleaning process between samples to avoid memory effects. The ICPMS was equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer (Rodríguez et al., 2021). The equipment was set up by ensuring low variability of counts (RSD <1%). The isotope ^{115}In was used as an online internal standard. Calibration curves (7 points) were used in different dynamic ranges depending on the metal concentration in samples. For most of the Seafast preconcentrated samples, concentration intervals of calibration curves were 0.5–320 μg/L for Ni, 0.007–18 μg/L for Cd and 0.010–25 μg/L for Pb. The detection limits (LOD) were 2.1 ng/L for Ni, 0.50 ng/L for Cd and 4.0 ng/L for Pb. Field blanks for Cd were always below the LOD. For Ni and Pb, 6 and 13% of the blank samples were above the LOD but accounted for less than 5% element concentrations in the respective samples. Metal concentrations in DGT extracts were quantified by an ICPMS equipped with a collision cell with Helium (model iCAP-Q, Thermo Fisher). The isotope ^{115}In was used as an online internal standard. The equipment was set up by ensuring low variability of counts (RSD < 5% after ^{115}In standardization). Typically, 7-point standard calibration curves ranging from 0.1 to 100 μg/L for Ni and Pb and from 0.1 to 20 μg/L for Cd were used to quantify metals in extracts. The detection limit was 0.1 μg/L for Ni, Cd and Pb. The calculation of the DGT concentration was carried out following Zhang (2020) and using the diffusion coefficients provided by the supplier (DGT® Research Ltd., Lancaster, UK). Field blanks accounted for less than 10% of the concentrations on DGT extracts. Final DGT concentrations were corrected with respective blank values. The average concentration of DGT triplicates from each side were calculated and an RSD <30% was obtained after identifying outliers using the Dixon test.

The determination of conditional labile metal (Pb-ASV-labile and Cd-ASV-labile) concentrations, i. e. the concentration of the metal species in the acidified water samples (Rodríguez et al., 2021), was done directly by ASV (Florence and Batley, 1977). A conventional three-electrode configuration was used with an Ag/AgCl reference electrode, a glassy carbon rod as the counter electrode and a thin Mercury Film Electrode as a working electrode (Rocha et al., 2007). Deposition potential and deposition time were −0.9 V (vs Ag/AgCl) and 100–300 s respectively. In the stripping step, the square wave mode was used with an amplitude of 25 mV, step height of 5 mV, and a frequency range of 25 Hz. Total Ni dissolved concentrations were determined by CSV based on adsorption of the surface-active complex of Ni with dimethylglyoxime on the mercury after UV irradiation of water samples to guarantee the oxidation of organic matter (van den Berg, 1986). A three-electrode cell was also used with a static mercury drop as a working electrode. Deposition potential and deposition time were −0.8 V (vs Ag/AgCl) and 60–120 s, respectively, and in the stripping step, the same pulse variation as aforementioned was used. Voltammetric measurements, carried out in clean disposable polyethylene terephthalate (PET) vessels to minimize contamination between samples, were performed by a Potentiostat/Galvanostast (model μAutolab, Metrohm AG) connected to the VA stand (model 663, Methrom AG). Experimental parameters on the equipment and data acquisition were controlled with GPES v.4.9 software (Eco-Chemie). After purging the solutions with nitrogen ($N_2 > 99.999\%$) for 10–15 min, all determinations were made at least in duplicate using the standard addition method (4–5 additions). Variable volumes of standard solution were added to obtain a 30% to 100% increase of the analytical signal with a total volume variation ≤1%. The detection limits of ASV analysis obtained for the water samples using a deposition time of 300 s were 5 ng/L for Pb and 3 ng/L for Cd. For the CSV-Ni determinations, using 120 s deposition time, the 5 ng/L DL was obtained. Analytical variability was assessed as relative standard deviation (RSD) of duplicates, and values below 10%–15% were considered satisfactory. Most field blanks were below the LOD of Cd. For the Ni and Pb, the majority accounted for less than 10% of the concentrations on the samples. Otherwise, final concentrations were corrected with respective blank values.

In addition to metal determinations, dissolved organic carbon (DOC) was determined in spot water samples at some sampled sites. In most cases, DOC was measured as the difference between the total and inorganic carbon measured with automated carbon analysers (Standard Methods, 2017).

Instrumental and procedural blanks were run during each analysis session and between samples for all the methodologies. Blanks are critical because of the high sensitivity of the methods. These blanks always accounted for less than 1% of element concentrations in the samples. Quality control solutions and certified reference materials (CRM) were also used to monitor the precision and accuracy of the methodologies. The CRM used, CASS-6 and SLEW-3, were from the National Research Council of Canada, and the recoveries of the analysed elements (Table S2) were consistent with the certified values ($p < 0.05$).

3.5. Statistics

The non-parametric (median, 10th and 90th percentiles) statistics were calculated. The dissolved and labile metal results obtained with the three applied methodologies were compared by box plots using STATISTICA™ 6 software (Statsoft). When the metal concentrations of a given sample are below the limit of detection, the result of the measurement was considered half the value of the limit, for statistical calculations. Before the statistical analyses, metal concentrations were tested for normality and equality of variances. Non-compliance with parametric ANOVA assumptions led to the employment of the Kruskal-Wallis H (KW-H) and Mann-Whitney (U) non-parametric tests to evaluate the existing differences between methodologies in the different studied areas. For linear comparison of variables, after log transformation, Pearson correlations (*r*) were used. The minimum level of confidence used was 95%.

4. Results

Metal concentrations were measured by different methodologies, ICPMS, Voltammetry (Volt), and DGT (Supplementary Information).

4.1. Coastal waters

4.1.1. Metal and DOC concentration variability per region

The median, 10th and 90th percentiles of Ni, Cd, Pb and DOC concentrations in the dissolved fraction of coastal waters from the Canary Islands to the North Sea, including the Western Mediterranean Sea, are presented in Fig. 1. Higher Ni concentrations were found at the Bay of Biscay including the English Channel (hereafter referred to as "Bay of Biscay") and Celtic/Irish Seas, reaching 2474 ng/L (DGT), and the lowest levels were recorded at the Canary Islands (70 ng/L, ICPMS). For most regions, the median concentrations for the three methodologies were comparable, but increased variability was found for DGT data from the Bay of Biscay (272–2007 ng/L). For Cd, values were found to differ among regions and methodologies. At the Iberian Coast and Bay of Biscay stations, all determinations showed higher concentrations and variability (ICPMS: 5–40 ng/L; Volt: 3–63 ng/L; DGT: 9–24 ng/L) than in the North Sea, Western Mediterranean and Canary Islands (ICPMS: 3–36 ng/L; Volt: 2–14 ng/L; DGT: 1–22 ng/L). The lowest median values found for voltammetric data arise from the samples with concentrations below the LOD of the technique (LOD_{Cd}, 3 ng/L). Similar to those found for Ni, the lowest concentrations of Cd were found at the Canary Islands (ICPMS: 3–10 ng/L; Volt: 3 ng/L; DGT: 1–11 ng/L). Lead concentrations showed a different distribution pattern since some samples showed increased concentrations (Fig. 1). Despite that, the higher values were found in the Western Mediterranean stations (ICPMS: 70–1938 ng/L; Volt: 80–550 ng/L; DGT: 38–319 ng/L). The median DOC content was comparable among Canary Island (1250 μg/L), Bay Biscay (1745 μg/L) and Western Mediterranean Sea (1420 μg/L). At Celtic/Irish seas, higher median DOC (3330 μg/L) was found and a broader variability (270–5150 μg/L).

4.1.2. Metal concentration in each region

4.1.2.1. Canary Islands. The variability of Ni concentrations in the four stations from the Canary Islands (Gando, Jinámar, La Luz and Taliarte) is presented in Fig. 2. Broader range of values was found for DGT at all sites (161–928 ng/L at Gando; 181–932 ng/L at La Luz; 145–1169 ng/L at Taliarte) except Jinámar (128–168 ng/L). This station's Ni median concentration was comparable among the three methodologies (ICPMS: 154 ng/L; Volt: 170 ng/L; DGT: 141 ng/L). Concentrations of Cd were low at all sites being below LOD in most voltammetric determinations. This element's median values, measured by ICPMS (Gando: 4.4 ng/L; Jinámar: 4.7 ng/L; La Luz: 8.7 ng/L; Taliarte: 5.6 ng/L), were higher than those measured by voltammetry and DGT (1.3–5.9 ng/L). Otherwise, Pb concentrations were more variable among sites and between methodologies. Except for Taliarte, lower median values were detected by voltammetry (2.5–43 ng/L), although at La Luz, a broader variability was found (50–220 ng/L). Higher variability of DOC content was found at Gando (900–7900 μg/L) and Jinámar (900–4900 μg/L), although their median values (Gando: 1100 μg/L; Jinámar: 1000 μg/L) were in the same order of magnitude as the other sites (La Luz: 1500 μg/L; Taliarte: 1600 μg/L).

4.1.2.2. Iberian Coast, the Bay of Biscay and the Celtic/Irish Seas. Stations from this large geographical region were distributed among the Iberian Coast, the Bay of Biscay, the Celtic Sea and the Irish Sea. The lowest Ni concentrations were found in the Iberian Coast (ICPMS: 109–485 ng/L; Volt: 190–610 ng/L; DGT: 167–513 ng/L), and the median values in the three methodologies were comparable (Fig. 3). Increased concentrations and variability were found in the Bay of Biscay and Celtic/Irish seas. Unlike Ni, Cd showed similar median values among sites and techniques (ICPMS: 13–20 ng/L; Volt: 9.0–24 ng/L; DGT: 17–26 ng/L). Although low median values were found, a broader variability was obtained at the Bay of Biscay and Celtic/Irish seas, where concentrations reached 66 ng/L. At the Iberian Coast and Bay of Biscay, the median levels of Pb quantified by voltammetry (18–30 ng/L) were lower than those determined by the other methodologies (ICPMS 39–48 ng/L; DGT 46–77 ng/L). Higher median concentrations were found at Celtic/Irish Seas (ICPMS: 95 ng/L; Volt: 74 ng/L; DGT: 67 ng/L).

4.1.2.3. The North Sea. The Ni concentrations at the North Sea station (Newhaven) showed higher median values for DGT (465 ng/L) in comparison with ICPMS (336 ng/L) and voltammetry (360 ng/L). This pattern was also found for Pb where DGT concentrations (77–93 ng/L), despite being higher than the other methodologies, also varied in a narrower interval (ICPMS: 58–102 ng/L; Volt: 46–150 ng/L). For Cd, the median concentration values measured by voltammetry are influenced by several determinations below LOD. This metal's concentration using DGT was lower and varied in a narrower range (15–18 ng/L) than levels measured by ICPMS (20–36 ng/L).

4.1.2.4. Western Mediterranean Sea. The median, 10th and 90th percentiles of Ni, Cd and Pb concentrations in the West Mediterranean Sea stations are presented in Fig. 4. Concentrations of Ni varied within similar intervals among the four sites, although lower values were found for voltammetry (ICPMS: 217–813 ng/L; Volt: 90–660 ng/L; DGT: 242–663 ng/L). This pattern was even more evident for Cd, where most voltammetric data was below LOD. Furthermore, Cd-DGT concentrations were lower (6–14 ng/L) than ICPMS (11–22 ng/L) at all sites, except Dogana, where the variability was similar (DGT: 13 ng/L; ICPMS: 13–15 ng/L). Lead concentrations measured by ICPMS were higher at Rinascita (982–1938 ng/L) than at the other sites (38–806 ng/L). A similar pattern for this metal was observed at all sites with higher ICPMS concentrations than values measured with the other methodologies.

4.2. Transitional waters

4.2.1. Metal concentration variability per sub-region

The median, 10th and 90th percentiles of Ni, Cd and Pb concentrations in the different estuaries in the Iberian Coast, Bay of Biscay and Celtic/Irish seas are presented in Fig. 5. The Ni concentrations using the three methodologies varied within the same range in the Celtic/Irish seas estuaries (Liffey, Ballynacorra, Lee, Fal and Belfast Lough), although the DGT presented the lower median values. Higher median concentrations of this element measured by voltammetry were found at Ria of Aveiro in the Iberian coast (970 ng/L), Aulne estuary at Bay of Biscay (515 ng/L) and Belfast Lough at the Irish Sea (640 ng/L). Estuaries located in the Northern Iberian coast (Oiartzun and Deba) presented the highest Ni values for the three techniques, reaching 2600 ng/L by ICPMS. This pattern was also found for Cd, where values determined in these transitional waters were up to 9 times higher than at the other stations. In most locations, the voltammetric Cd median concentration was lower than those determined using the different methodologies. The Pb concentrations measured at Ria of Aveiro (Iberian coast), Charente and Aulne estuaries (Bay of Biscay) and Fal estuary and Belfast Lough (Celtic/Irish seas) showed a broad variability ranging from 2 to 282 ng/L. Higher concentrations were found in Ballynacorra and Lee river-estuary systems reaching 1960 ng/L. Noteworthy, elevated Pb levels were recorded at Oiartzun and Deba estuaries (3–6319 ng/L; Iberian coast) and at river Liffey (177–6687 ng/L, Irish seas). Despite the broad variability of Pb concentration at all studied Celtic/Irish estuaries (59–72 ng/L), the median value was comparable to that found for the Bay of Biscay estuaries (55–188 ng/L). The content of DOC was only measured in the Northern Iberian coast (median 1273 μg/L) and Bay of Biscay (median 1550 μg/L) estuaries, where concentrations varied in a broader range.

5. Discussion

The results presented in Figs. 1–5 show in some situations high

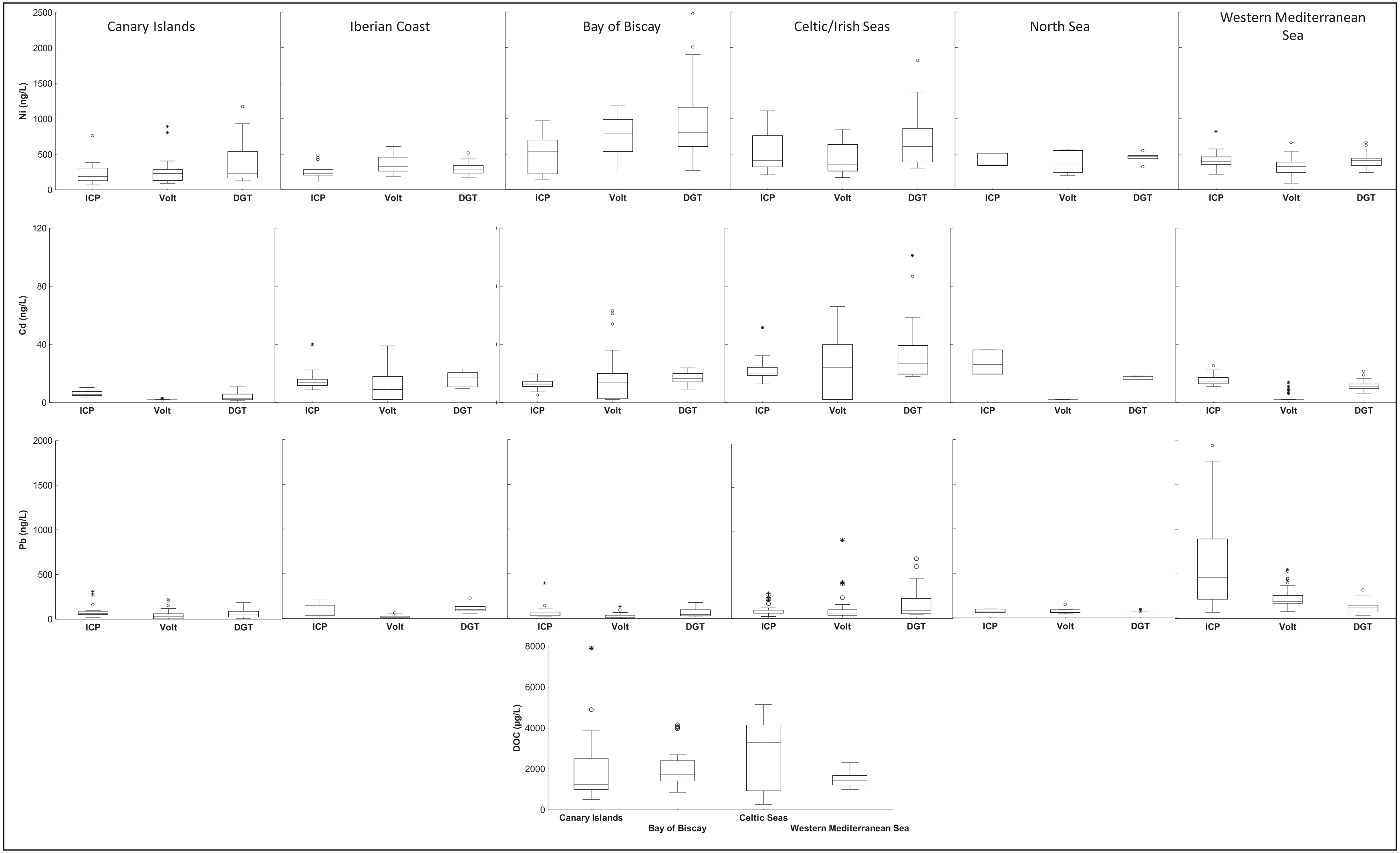

Fig. 1. Box and whisker plots of Ni, Cd, Pb (ng/L) and DOC (μg/L) in water from the Canary Islands (n = 30–42 samples), Iberian Coast (n = 17–34 samples), Bay of Biscay (n = 23–36 samples), Celtic/Irish Seas (n = 19–36 samples), North Sea (n = 3–6 samples) and Western Mediterranean Sea (n = 24–40 samples). Metal concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS. Horizontal lines correspond to the median, the edges of the box for the 10th and 90th percentiles and minimum and maximum concentrations (whiskers).

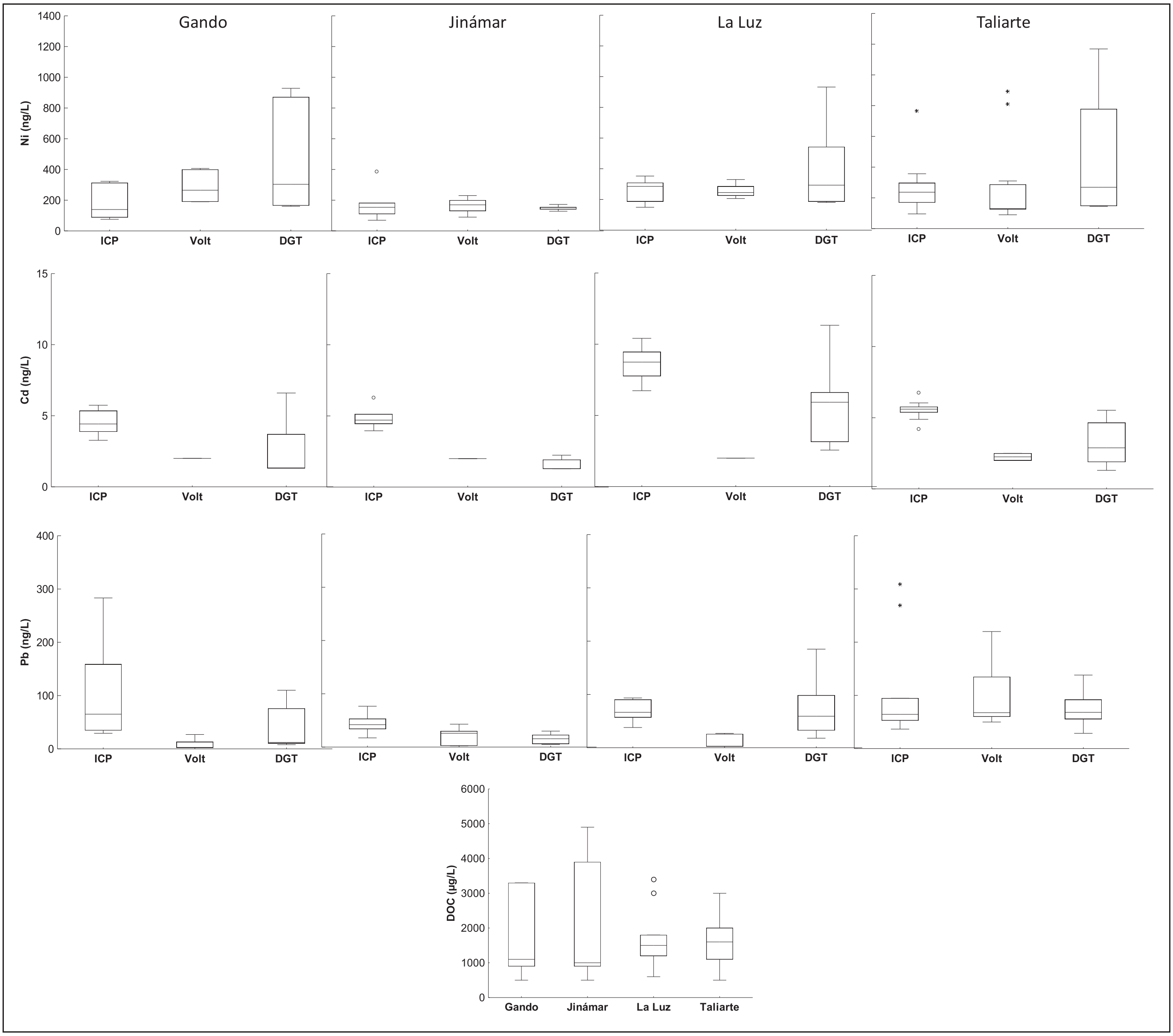

Fig. 2. Box and whisker plots of Ni, Cd, Pb (ng/L) and DOC (μg/L) in water from Gando (n = 6 samples), Jinámar (n = 5–6 samples), La Luz (n = 9–18 samples) and Taliarte (n = 9–12 samples) stations (Canary Islands). Metal concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS. Horizontal lines correspond to the median, the edges of the box for the 10th and 90th percentiles and minimum and maximum concentrations (whiskers).

variability of metal concentrations both among sampling sites and between methodologies that cannot be attributed to a given metal and/or methodology. Therefore, it can be concluded that these results are indeed due to fluctuations in metal concentrations in waters analysed. Additionally, in some cases, the applied spot sampling design did not fully integrate the high environmental variability in metal concentrations (Rodríguez et al., 2021). It should be noticed that sampling sites were selected to fulfil the research goals of the Monitool project ranging from almost pristine to anthropogenically impacted areas. Therefore, obtained results may not fully represent metals concentrations from wider sea areas where broader spatially representative (legislative) national monitoring would be applied.

5.1. *Comparison of environmental metal level*

Concentrations of Ni, Cd and Pb measured by ICPMS in coastal stations from the Canary Islands to the North Sea and in the Western Mediterranean Sea were, in general, comparable to previous works performed in the NE Atlantic waters. Furthermore, all total dissolved metal concentrations measured by Seafast-ICPMS were lower than the EQS values for Ni (8.6 μg/L), Cd (0.2 μg/L) and Pb (1.3 μg/L) (Directive, 2013/39/EU). Concentrations of Cd in the Canary Islands varied within the range of values reported in open-waters of this Atlantic Area (Landing et al., 1995; Saager et al., 1997; Cotté-Krief et al., 2002). Increased concentrations of Ni and Pb found in these stations suggest anthropogenic contributions from urban and industrial activities at the east coast of Gran Canaria Island, where the largest population and economic activity are concentrated. A similar pattern was found at the Celtic/Irish seas, although the median values were comparable to the concentrations published in other works (Kremling and Hydes, 1988; Laslett, 1995; Achterberg and van den Berg, 1994). Higher concentrations of Ni and Pb were found at Dublin Bay, presumably due to metal remobilization associated with the site's proximity to historic industrial and ore shipping and transport activities. Concentrations of Ni and Cd

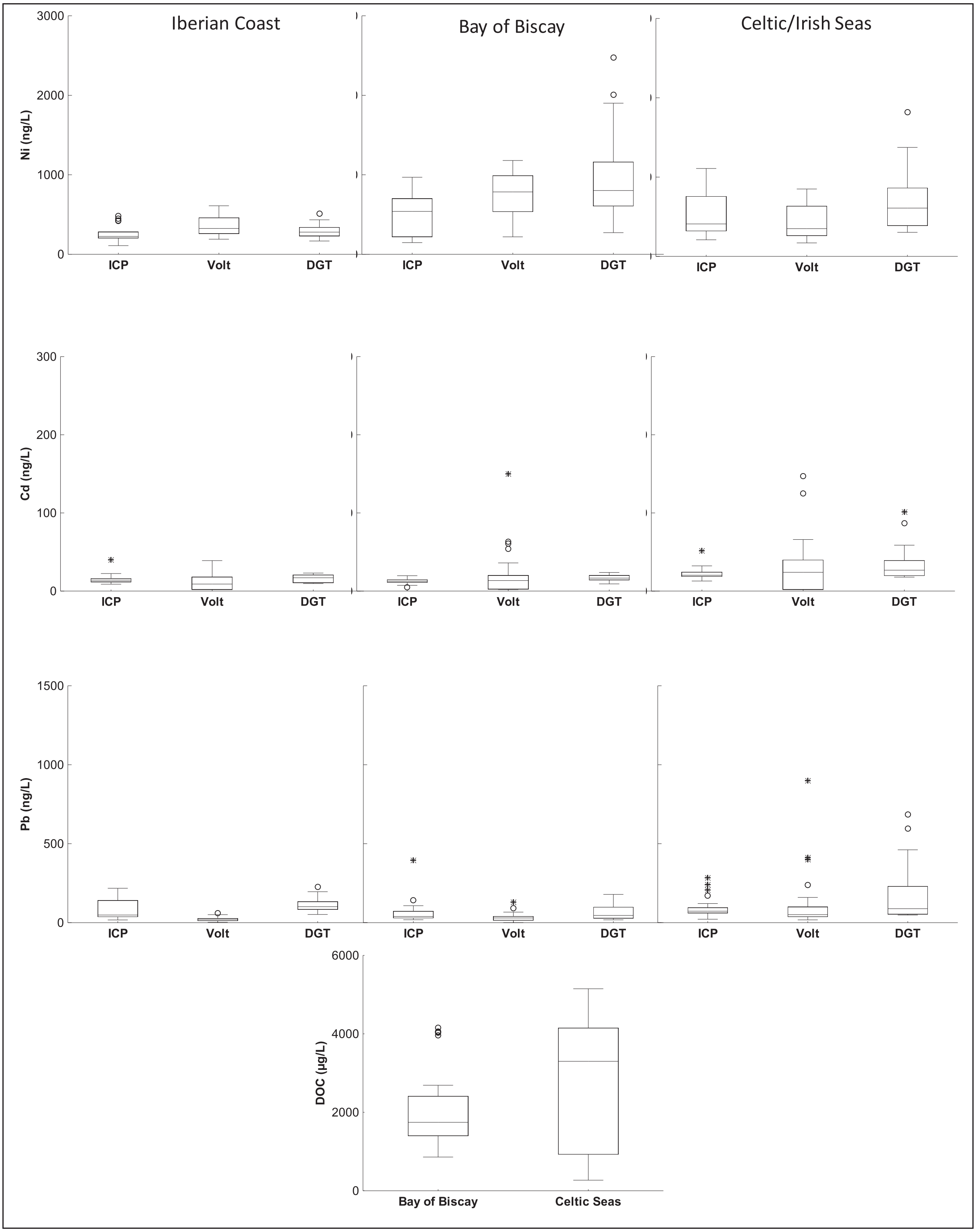

Fig. 3. Box and whisker plots of Ni, Cd and Pb (ng/L) in water from the Iberian Coast (Matosinhos, Oeiras, Sesimbra; n = 17–34 samples), Bay of Biscay (Port-en-Bessin, Saumonard, Nazaire; n = 23–36 samples) and Celtic/Irish seas (Dublin Bay, Liverpool, Buoy 38A; n = 19–36 samples). Metal concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS. Horizontal lines correspond to the median, the edges of the box for the 10th and 90th percentiles and minimum and maximum concentrations (whiskers).

found in the Iberian Coast and the North Sea were similar to those found in previous works (Laslett, 1995; Fileman et al., 1991; Santos-Echeandía et al., 2012). For Pb, higher concentrations were found in both coastal areas reflecting several inputs from rivers and anthropogenic activities in the vicinity of the sampling sites. In the Western Mediterranean Sea, Ni, Cd, and Pb concentrations were above reported values (Yoon et al., 1999; Morley et al., 1997; Saager et al., 1993; Schlitzer et al., 2018). Additionally, measured median DGT values obtained in this study were higher than those reported by Schintu et al. (2008) and Marras et al. (2020) in the Gulf of Cagliari (Ni: 33–246 ng/L; Cd: 5–17 ng/L; Pb: 4–45

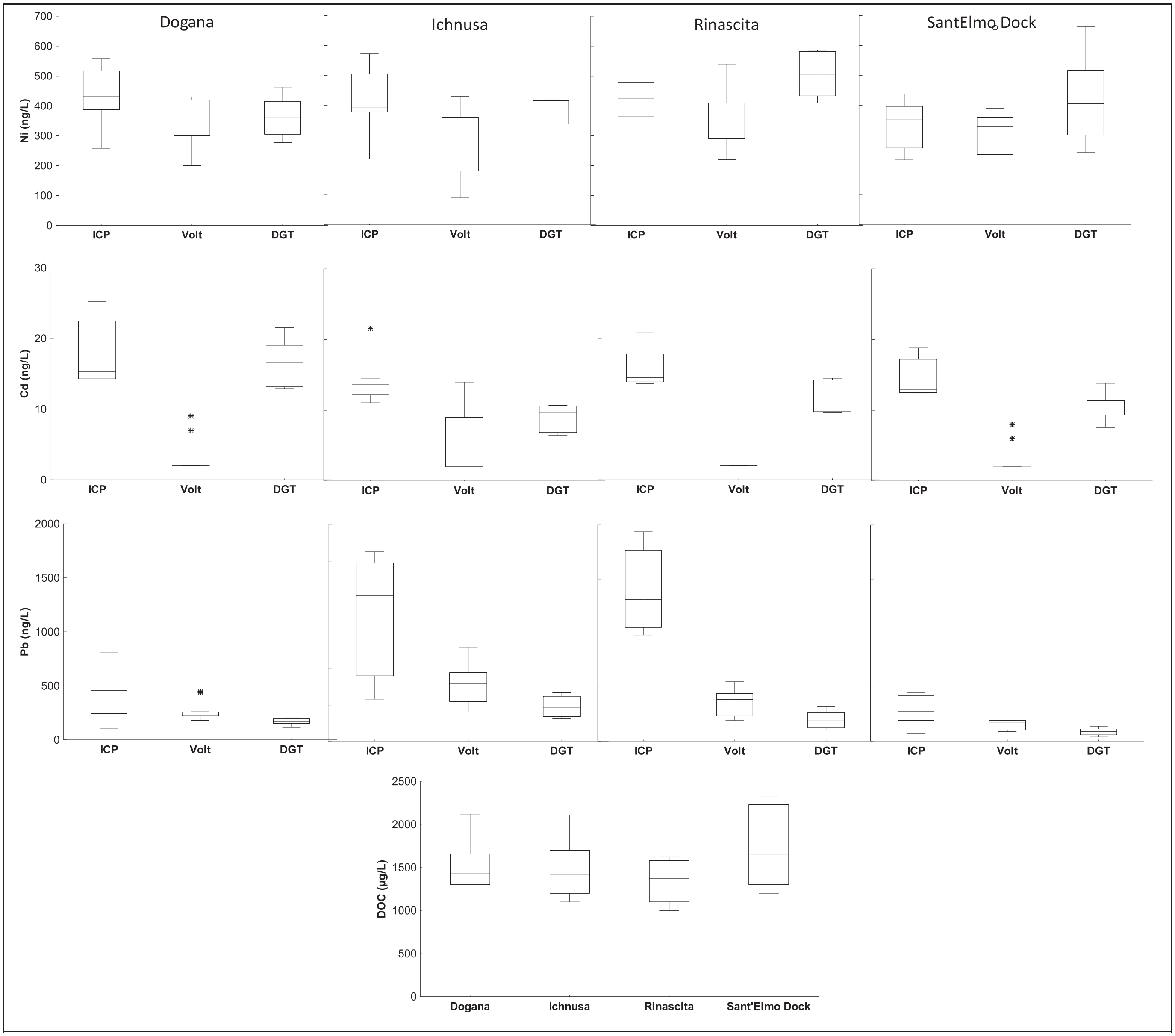

Fig. 4. Box and whisker plots of Ni, Cd and Pb (ng/L) in water from stations Dogna (n = 6–10 samples), Ichusa (n = 6–10 samples), Rinascita (n = 6–10 samples) and Sant'Elmo Dock (n = 6–12 samples) (Western Mediterranean Sea). Metal concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS. Horizontal lines correspond to the median, the edges of the box for the 10th and 90th percentiles and minimum and maximum concentrations.

ng/L). The increased metal concentrations point to anthropogenic inputs related to the harbour and urban activities. This finding is in line with the conclusions of Schintu et al. (2016) in a study with sediments and benthic foraminifera from a wider area of the Caligari harbour.

Metal concentrations in estuaries were in general higher than values found in coastal waters, reflecting inputs from anthropogenic or natural sources. Nevertheless, total dissolved metal concentrations (ICPMS) were systematically lower than the EQS values for Ni, Cd and Pb (Directive, 2013/39/EU). Concentrations of Cd and Pb at Ria of Aveiro, a coastal lagoon located in the West Iberian coast (Portugal), were respectively up to 10 and 60 times lower than results obtained a couple of decades ago (Pereira et al., 2009). The deindustrialization in the margins of the lagoon that had chemical industries in the past is presumably the main reason for such a decrease in Cd concentrations. This argument, coupled with the phasing out of leaded gasoline in Europe around 2000 (Mil-Homens et al., 2013), also explains the decrease of Pb concentrations. Both estuarine systems in the north coast of the Iberian coast (Deba and Oiartzun) have been historically highly impacted by human activities (Tueros et al., 2008). Reported concentrations of Ni, Cd and Pb (total dissolved concentrations) from the 90's decade were up to 2 orders of magnitude higher (Belzunce et al., 2004) than values obtained in this study. This difference resulted from implemented management actions to reduce the pressures leading to successful water quality improvement for several priority contaminants (Borja et al., 2016). At the end of the 20th Century, the industrial recession with the closure of highly polluting industries (mining, steel factories) reduced the contaminant loads to the estuaries also played a significant role in the improvement. Similar Cd and Ni DGT-labile concentrations were reported by Montero et al. (2012). The lower Cd values in both studies, separated by a decade, indicate that this element kept a low bioavailable dissolved fraction in the two estuaries (Deba and Oiartzun). Otherwise, the high total and DGT-Ni labile concentrations found in the last ten years at Deba estuary resulted from their anthropogenic origin, since substantial input of these metals derives from the surrounding industry of electrolytic and chemical surface treatment and iron and steel-related metallurgy (Belzunce et al., 2004; Tueros et al., 2009). The main

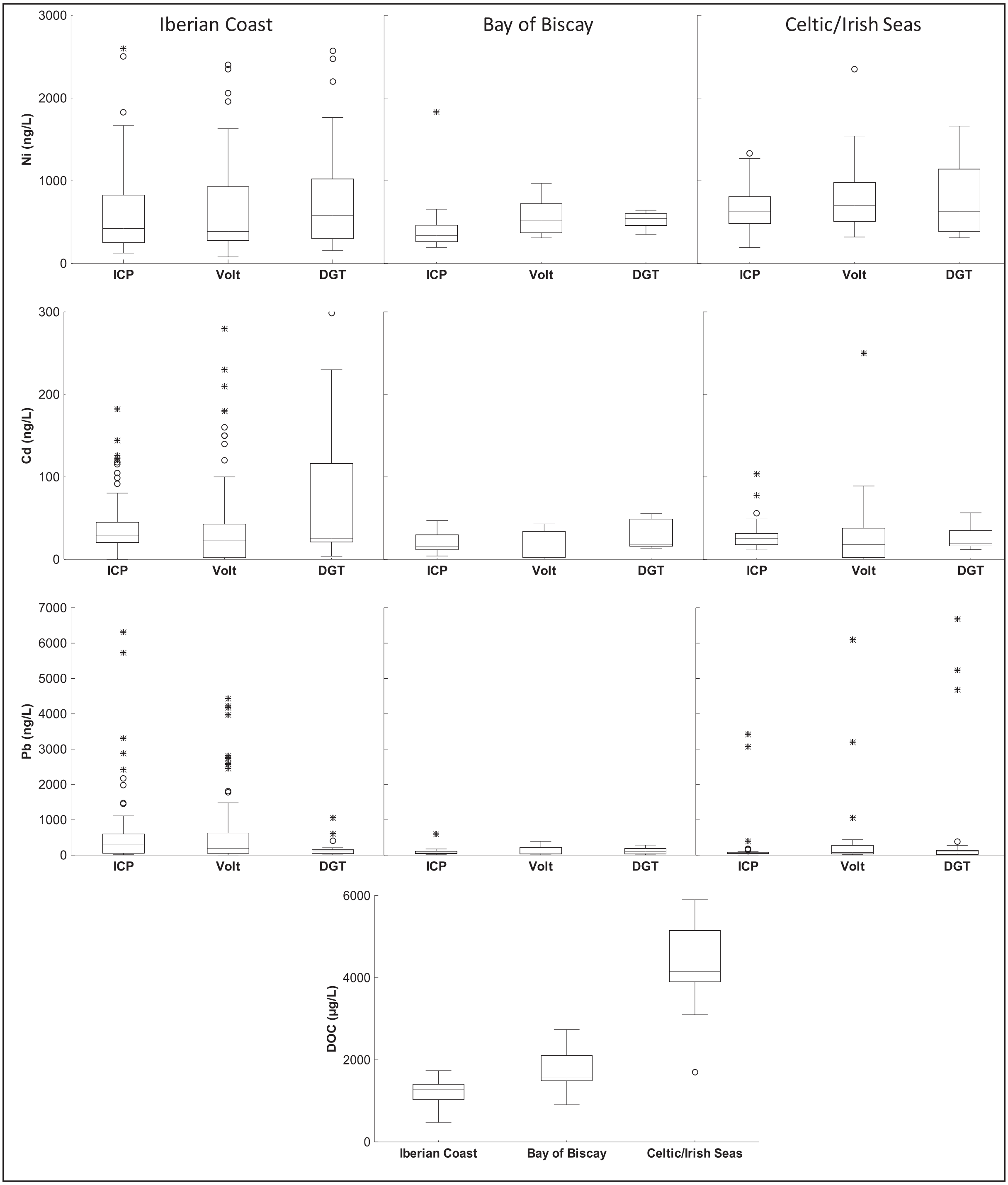

Fig. 5. Box and whisker plots of Ni, Cd, Pb (ng/L) and DOC (μg/L) in water from Ria of Aveiro, Oiartzun, Deba (Iberian Coast; n = 102–119 samples), Charente, Aulne (Bay of Biscay; n = 9–32 samples), Liffey, Ballynacorra, Lee, Fal and Belfast Lough (Celtic/Irish Sea; n = 36–60 samples). Metal concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS. Horizontal lines correspond to the median, the edges of the box for the 10th and 90th percentiles and minimum and maximum concentrations.

anthropogenic inputs to the Charente estuary located in the Bay of Biscay (France) are agriculture and urban activities (Dabrin, 2009). Concentrations of total dissolved Cd varied in a narrow range and were lower than previously reported values (Boutier et al., 2000; Dabrin, 2009; Guesdon et al., 2016). This difference may result from freshwater inputs, which induce large variability of this metal concentration in the estuarine waters (Dabrin, 2009). According to Boutier et al. (2000), the intrusion of the Gironde water plume into the Antioche Straits led to the increase of Cd in the coastal water. Thus, Charente estuarine water has been diluted with an endmember with increased values of this element. Nickel concentrations were comparable with values reported by Guesdon et al. (2016) but lower than those obtained by Dabrin (2009). This trend was also found for Pb concentrations, where this study evidenced a decrease of up to 5 times the concentrations found by that author. Scarce information exists on metal contamination in waters of the Aulne estuary (France). The estuary flows to a wider Brest harbour area with several anthropogenic activities (COMENRADE Project, 2021). The Aulne river basin crosses two abandoned mining areas (Huelgat and

Poullaouen) in its upstream section rich in Pb-Zn ores (Lemière et al., 2002), which may explain the increase in the metal load in the estuary area. Similarly, little information exists on metal concentrations in the Irish estuaries. Data from the national monitoring programs from 2018 and 2020 showed that the total dissolved Ni, Cd and Pb concentrations varied within the range of values measured by ICPMS (Brendan McHugh, personal communication). Conversely, increased ICPMS concentrations of Pb and Ni in Alexandra Basin – River Liffey compared with those from the monitoring programs suggests the presence of point sources. During the sampling period, the navigation channels from the Alexandra Basin were dredged, which induced metal remobilization from the particulate fraction to the dissolved. Caetano et al. (2003) showed that the resuspension of anoxic sediment remobilizes metals from their reactive phases concerning changes in redox conditions. Metals are transferred to the dissolved fraction being subsequently scavenged by newly formed solid phases or remain in solution as stables complexes.

5.2. Comparison of CSV and ICP-MS dissolved Ni concentrations

The relationship between CSV and ICPMS dissolved mean concentrations of Ni measured in discrete water samples in coastal sites located in the North-East Atlantic Area (from the Canary Islands to the North Sea and in the Western Mediterranean Sea) and in estuarine sites at the Iberian Coast, the Bay of Biscay and Celtic Seas is shown in Fig. 6, A and B, respectively.

Significant linear correlations exist between dissolved Ni concentrations determined by CSV and ICPMS for coastal and estuarine sample ($r = 0.797$, $p < 0.0001$, $n = 53$ and $r = 0.833$, $p < 0.0001$, $n = 32$ respectively), and the values are close to the 1:1 line. These results confirm that both methodologies are suitable for determining Ni dissolved concentrations in coastal and transitional waters through proper control of the precision and accuracy of the analytical procedures. This was expected since the determination of Ni by CSV in filtered and acidified water after UV-radiation guarantees the oxidation of organic matter, providing a quantification of the total dissolved content comparable to SeaFast-ICPMS. In the case of Ni, information about its speciation cannot be attained by ASV due to the non-reversibility of the Ni reduction on the electrode (Mota and Correia-dos-Santos, 1995). Both techniques rely on discrete sampling that requires some pre-treatment before analysis, leading to possible contamination and perturbation of the samples. While the samples for ICPMS analysis were filtered and acidified at the laboratory, for CSV analysis, this procedure was done in the field and kept refrigerated until analysis. In the case of ICPMS, a pre-concentration of the metal ions and removal of the salt matrix is required. However, CSV requires complexing reagents to convert Ni into an absorbable complex prior to the analysis. Yet, the data obtained by both techniques were close to the 1:1 line, indicating that the different treatments of the samples did not substantially affect the measured total dissolved Ni concentration.

5.3. Comparison of ASV-labile and DGT-labile Cd and Pb

The relationships between conditional labile forms of Cd measure by ASV and Cd using DGT for coastal stations located in the Canary Islands, Iberian coast, Bay of Biscay, Celtic/Irish Seas, North Sea and Western Mediterranean Sea, and estuaries stations located in the Iberian Coast, the Bay of Biscay and Celtic/Irish Seas are displayed in Fig. 7, A and B, respectively.

Despite the variability and differences in concentrations among regions and methodologies, both in coastal and estuarine sampling sites, significant linear correlations were found between Cd ASV-labile and Cd DGT-labile concentrations ($r = 0.780$, $p < 0.0001$, $n = 49$, for coastal and $r = 0.687$, $p < 0.0001$, $n = 31$, for estuarine). As shown in Fig. 7, the measured data points are closer to the 1:1 lines. Both regressions show that similar labile concentrations are being measured using both techniques, despite the shorter time scale of ASV, imposed by the smaller diffusion layer thickness around the electrode when compared to the time scale associated with the 0.8 mm diffusive gel used in DGT, and the acidification of the water samples for ASV. This means that Cd speciation in solution is controlled by mobile and very labile species that rapidly dissociate even when traversing the small diffusion layer around the electrode in ASV. This is also in agreement with Cd speciation in seawater that might be controlled by the inorganic chloro-complexes and/or labile organic complexes (Simões et al., 1981). The 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 (Rodríguez et al., 2021).

In the case of Pb significant, but poorer linear correlations were also found between the ASV labile fraction and the DGT labile concentrations measured in all coastal ($r = 0.356$, $p = 0.008$, $n = 55$) (Fig. 8A) and estuarine samples ($r = 0.554$, $p = 0.001$, $n = 32$) (Fig. 8B) with slopes close to 0.5.

Consequently, Fig. 8 (A and B) indicates that the labile Pb concentrations measured by ASV are lower than those determined using DGT. Although Pb concentrations were variable among sites and between methodologies, these relationships were more evident at the Iberian Coast, Bay of Biscay and some sites at the Canary Islands. This pattern may be due to non-labile complexes in terms of the time scale of the voltammetric measurement and/or non-mobile species, namely colloidal species (van Leeuwen et al., 2005; Sigg et al., 2006). As to the former hypothesis, several Pb complexation studies with naturally occurring organic ligands (e.g. humic substances) in aquatic media by ASV indicate that the complexes formed are labile within the time scale of the technique even at a higher pH (Pinheiro et al., 1994; Mota et al., 2005) therefore also labile for DGT conditions. On the other hand, Pb is

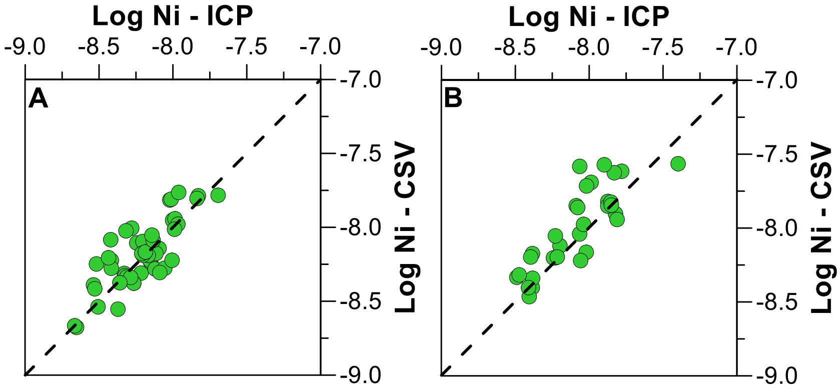

Fig. 6. Relationship between CSV and ICP dissolved Ni for coastal sampling sites (A) at the Canary Islands, Iberian coast, Bay of Biscay, Celtic Seas, North Sea and Western Mediterranean Sea and in estuarine sampling sites (B) located in the Iberian Coast, the Bay of Biscay and Celtic Seas. The dashed line corresponds to the 1:1 line. Key: CSV – mean concentration of metal measured by spot sampling using cathodic stripping voltammetry on filtered seawater; ICP – mean concentration of metal measured by spot sampling using ICP-MS on filtered seawater.

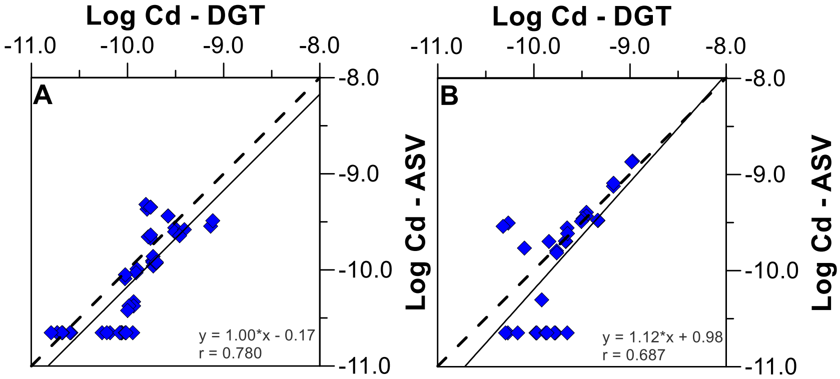

Fig. 7. Relationship between Cd ASV and Cd DGT for coastal sampling sites (A) at the Canary Islands, Iberian coast, Bay of Biscay, Celtic Seas, North Sea and Western Mediterranean Sea and for estuarine sampling sites (B) at the Iberian Coast, the Bay of Biscay, Celtic and Irish Seas. The dashed corresponds to the 1:1 line and the solid line to the linear regression fit of the data. Key: ASV – mean concentration of metal measured by spot sampling using anodic stripping voltammetry on filtered seawater; DGT – concentration of metal measured using DGT passive sampler.

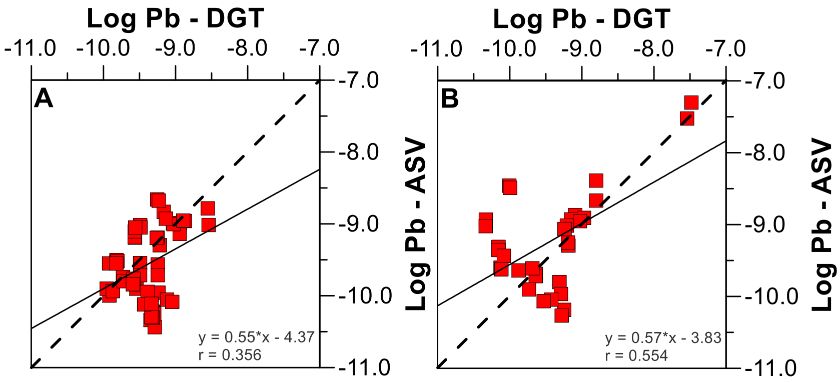

Fig. 8. Relationship between Pb-ASV and Pb-DGT coastal sampling sites (A) at the Canary Islands, Iberian coast, Bay of Biscay, Celtic/Irish Seas, North Sea and Western Mediterranean Sea and for estuarine sampling sites (B) Ria of Aveiro, Oiartzun, Deba (Iberian Coast), Charente, Aulne (Bay of Biscay), Liffey, Ballynacorra, Lee, Fal and Belfast Lough (Celtic/Irish Seas). The dashed line corresponds to the 1:1 line and the solid line to the linear regression fit of the data. Key: ASV – mean concentration of metal measured by spot sampling using anodic stripping voltammetry on filtered seawater; DGT – concentration of metal measured using DGT passive sampler.

present in the dissolved phase in colloidal forms that may not be mobile enough to be detected by ASV but can diffuse through the diffusive gel layer as previously described for colloidal Fe and Al (Sherwood et al., 2009). However, it should also be taken into account that ASV measurements refer to spot water samples, while DGTs provide a time-averaged concentration that integrates the environmental metal fluctuations, which could partly explain the observed differences.

As previously acknowledged and further supported by the results discussed here, for Cd and Pb, both the ASV technique and DGT passive sampler can provide information about labile metal concentrations. Both labilities are operationally defined, and therefore, the labile fraction determined by the different techniques may be distinct. Due to the different kinetic window, i.e. on the order of minutes for a diffusive gel with 0.8 mm thickness and tenths of seconds in ASV (Gao et al., 2019), usually the DGT labile fraction is higher than the ASV due to the kinetic effects associated with the dissociation of the complexes formed. In the case of non-mobile ASV species (diffusion coefficients 10^{-9}–10^{-8} cm^2/s; van Leeuwen, 2000), some diffusion might occur through the diffusive gel layer of the DGT, thus enhancing the labile fraction measured by DGT. Similarly, Cindric et al. (2020) report the suitability of both ASV and DGT for Cu speciation in an estuarine environment.

5.4. Heterogeneity of the binding ligands

The degree of ligand heterogeneity of a system is reflected in the measured concentrations by non-equilibrium techniques such as DGT and ASV (Town et al., 2009, (Buffle, 1988). It can be expressed by a heterogeneity parameter (Γ) that is a measure of the variation of binding sites affinities for a given ion. This can be computed with the logarithm of DGT (or ASV) concentrations (converted to mol/L) as a function of the fraction of occupied sites calculated as the logarithm of dissolved metal concentrations normalized to DOC (converted to mg/L). If an excess of binding sites exists, the graph should display a linear relationship with a slope equal to $1/\Gamma$ (Town et al., 2009) with $\Gamma = 1$ for a single ligand, while Γ decreases as the heterogeneity of the ligands increase (Buffle, 1988).

Considering the mean dissolved Ni, Cd and Pb concentrations (Ni: 460 ng/L, Cd: 21 ng/L, Pb: 514 ng/L) and DOC content ranging between 5 and 12 mg/L (Rodríguez et al., 2021), a large excess of binding sites over metal exists, and consequently, for those trace metals at the pH $\sim$ 8, is reasonable to assume that concentration of metal-complexes equals the metal dissolved concentrations (Town et al., 2009). No reliable values were obtained for the heterogeneity parameter (Γ) for Ni, Cd and Pb in coastal samples with available DOC. This pattern cannot be attributed to different metal ion loading in coastal waters compared to the values found in estuarine waters, but rather to fluctuations in HS's quantity and the DOC chemical nature more prone to occur in coastal environments (Brown, 1987). Another cause is the variability of metal concentrations, which was not fully integrated by the applied spot sampling design (Rodríguez et al., 2021).

Conversely, information about the heterogeneity of the ligands in estuarine waters samples could be obtained. Fig. 9 shows the DGT measured labile Ni concentrations related to the total dissolved concentrations normalized to DOC (metal to ligand ratio), obtained for Oiartzun and Deba estuaries in the Northern Iberian Coast and those of Belfast Lough and Fal located at the Irish Sea. Because total dissolved concentrations of Ni were measured by ICPMS and CSV, both sets of experimental points are displayed. Significant strong linear relationships ($r = 0.904$, $p < 0.001$, $n = 16$ and $r = 0.749$, $p < 0.001$, $n = 13$) were observed among all values and from the slopes of the linear regressions, $\Gamma \sim 0.80$ was computed for the Iberian Coast (Oiartzun, Deba) and Irish Sea (Belfast Lough and Fal).

In the case of Cd and Pb, operational labile concentrations were determined by DGT and ASV. The relationship between labile concentrations measured by DGT or ASV and the metal to ligand ratio for Cd in estuarine sites (with available DOC), sampled along the Northern

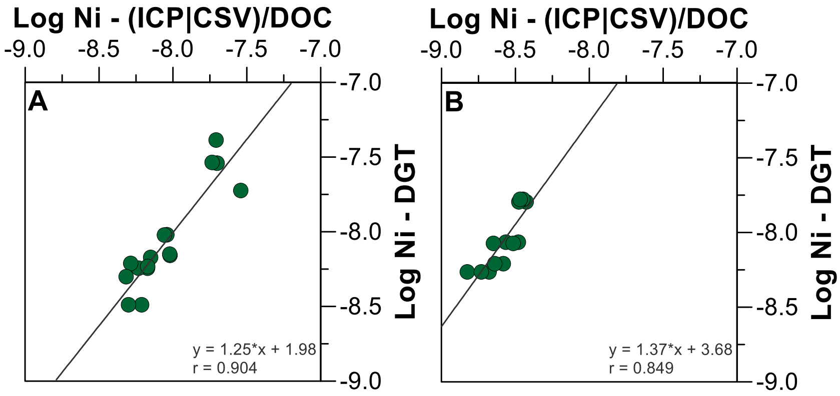

Fig. 9. Ni DGT as a function of metal to ligand ratio (dissolved metal concentrations measured by ICP or CSV normalized to DOC) for estuarine sampling site at (A) Oiartzun, Deba (Iberian coast) and at (B) Belfast Lough and Fal (Irish Sea). The solid line corresponds to the linear regression fit of the data. Key: DGT – concentration of metal measured using a DGT passive sampler; ICP – mean concentration of metal measured by spot sampling using ICP-MS on filtered seawater; CSV – mean concentration of metal measured by spot sampling using cathodic stripping voltammetry on filtered seawater.

Iberian Coast (Oiartzun and Deba), Bay of Biscay (Charente and Aulne) and Irish Sea (Belfast Lough and Fal) are shown in Fig. 10. Significant linear correlations are observed ($r = 0.748$, $p < 0.001$, $n = 22$ and $r = 0.682$, $p = 0.001$, $n = 19$ for the ASV and DGT data, respectively) and the Γ values computed using either the DGT or ASV data are within the experimental error close to one.

For Pb, only some data points could be used to estimate Γ, but values obtained using either the DGT or ASV were lower than 1 and comparable to the experimental errors. A summary of obtained and selected Γ values from literature is presented in Table 3.

The heterogeneity should be discussed considering several factors, such as the nature of the DOC and the pH dependence due to the different types of acidic groups from carboxylic to amino and sulfhydryl present in HS. Additionally, the apparent lability of the formed complexes depends on the metal ion, the technique's kinetic window, and the time scales of ASV and DGT. Nonetheless, in this work, the same degree of heterogeneity was found across the estuarine sampling sites at the Iberian coast, the Bay of Biscay and Celtic Seas for the Ni, Cd and Pb metal ions (see Fig. 9 for Ni). This may result from a stable complexation at the trace level and the non-significantly dependence of the DGT/spot sampling ratios on the physical-chemical parameters such as temperature, salinity, pH, oxygen, DOC or SPM as previously reported (Rodríguez et al., 2021). No differences were found for Cd between the values determined using the ASV or the DGT data, confirming that equivalent operational labilities were measured by both techniques (Fig. 7). The differences of Γ in Pb (Table 3) suggest some heterogeneity of the ligands or less dynamic complexes (Filella and Town, 2001), while for Ni and Cd, the ligands act as homogeneous. The complexes are labile, similar to the findings of Town et al. (2009) using a compilation of data of various origins (Town et al., 2009) and Cindric et al. (2020) for a highly stratified estuary.

Table 3
Heterogeneity parameter Γ for estuarine waters.

Nickel	Cadmium	Lead	Copper	Reference
0.8	1	0.6	–	This work
1	1	0.8	0.7	Town et al. (2009)
–	0.94	0.91	0.60	Cindric et al. (2020)
–	0.94	0.7	0.52	Chakraborty et al. (2007)
0.6	–	–	–	Town and Filella (2002)

6. Conclusions

This study has the unique characteristic of using a large number of spot samples and DGTs in a broad geographical area to tackle labile and total dissolved concentrations of priority metals. The singularity of being a coordinated multi-country assessment highlights this approach's advantages, allowing the comparison of locations and evaluation of analytical variability, which is impossible to do when looking at individual studies from different batches. Overall, the relationships among the different chemical forms of Ni, Cd and Pb were investigated in coastal and transitional waters, measured by three different methodologies, and covering a variety of environmental conditions. Despite the high variability, the dissolved concentrations found for the priority metal ions were, in almost all locations, below the EU WFD's guideline levels for non-inland water bodies. In the case of Ni, these results were corroborated by two distinct techniques, ICPMS and CSV, that had discrete sampling in common. As to the labile fractions, ASV and DGT were shown to be well suited for the simultaneous determination of Cd and Pb dynamic speciation in the marine environment. Either in coastal or transitional waters, similar labilities were measured for Cd, while for Pb, the ASV labile fraction was lower than the one determined by DGT. The heterogeneity of the binding ligands in estuarine waters was observed for Ni using DGT labile concentrations. Additionally, both dynamic techniques provided comparable information about the

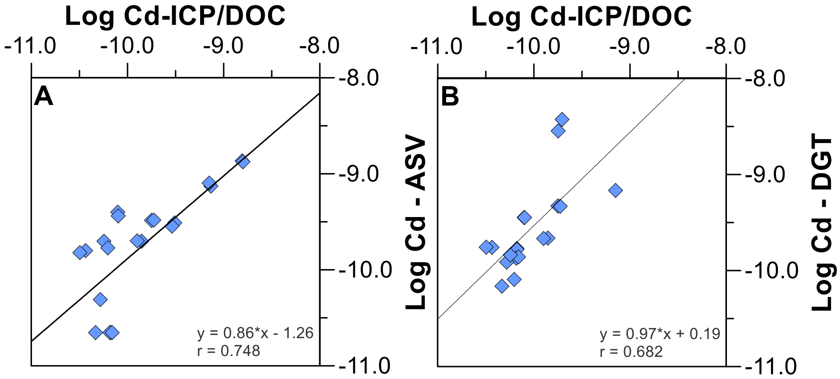

Fig. 10. Cd-ASV and Cd-DGT as a function of metal to ligand ratio (dissolved metal concentrations measured by ICP normalized by DOC) for estuarine sampling sites at (A) Oiartzun and Deba (Iberian Coast), Charente and Aulne (Bay of Biscay) and (B) Belfast Lough and Fal (Celtic Seas). The solid line corresponds to the linear regression fit of the data. Key: ASV – mean concentration of metal measured by spot sampling using anodic stripping voltammetry on filtered seawater; DGT – concentration of metal measured using DGT passive sampler; ICP – mean concentration of metal measured by spot sampling using ICP-MS on filtered seawater.

heterogeneity of the binding ligands towards Cd and Pb. These results reflect the pool of mobile and labile species available towards the kinetic windows of each technique. They seem not to be affected by the flaws traditionally associated with discrete sampling. In other aquatic systems with higher variability of dissolved metal concentrations, the results could differ. Additionally, DGT can measure the potentially bioavailable concentrations of far more metal ions existing in the aquatic environments and is, therefore, more suitable for a good design of surveillance monitoring programs under the WFD.

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CRediT authorship contribution statement

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I. Amouroux, M.J. Belzunce-Segarra: Investigation, Writing - Review & Editing, Project administration, Funding acquisition.

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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.

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Appendix A. Supplementary data

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