

# Metals concentrations in Transitional and Coastal Waters by ICPMS and Voltammetry analysis of spot samples and passive samplers (DGT)

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45 **Abstract**

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

57

58 **Keywords**

59 Priority metals, Broad geographical scale, European coastal and transitional waters, DGT,  
60 Voltammetry

61

62 **Highlights**

- 63 • Broad geographical study on priority metals by spot measurements and passive  
64 samplers
- 65 • Dissolved metal concentrations were below the EU WFD's guideline levels
- 66 • Similar Cd-labile concentration by ASV and DGT
- 67 • Different degrees of heterogeneity of Cd and Pb complexes in estuarine waters
- 68 • DGT is more suitable for monitoring marine systems with high variability

69

70 **1. Introduction**

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

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

89 For the determination of labile metal ion concentrations (free ions, inorganic forms, and metals  
90 weakly bonded to organic ligands), Anodic Stripping Voltammetry (ASV) and Diffusive Gradients  
91 in Thin-films (DGT) with Inductively Coupled Plasma Mass Spectrometry (ICPMS) are two of the  
92 few analytical methods that can be used at ultra-trace level (Davison and Zhang, 1994, 2012,  
93 Unsworth et al., 2006, Gao et al., 2019). Both (ASV and DGT) are dynamic speciation techniques.  
94 The accumulation step depends on the diffusion of the metal species through an effective  
95 diffusion layer before being trapped either onto an electrode or onto an ion exchange resin. The  
96 amount of metal accumulated depends on the dynamic features of the complexes formed in the  
97 medium relative to the diffusion layer thickness and their mobility. Therefore, both ASV and DGT  
98 lability measurements are operationally defined by the characteristic kinetic window of the  
99 technique, longer in DGT than is ASV (Gao et al., 2019). The dynamic species measured by these  
100 methods are both labile and mobile, i.e., a size range of a few nanometers (van Leeuwen et al.,  
101 2000). However, methodologies differ. While ASV measurements are performed on discrete  
102 spot samples, DGT is a passive sampler. Thus, DGT sampling allows for the accumulation of an  
103 analyte over time, providing a time-weighted average of the analyte concentrations.  
104 Additionally, *in situ* sampling for the labile trace metals with DGT avoids the generation of  
105 analytical artefacts (from the contamination and perturbation effects on the distribution of  
106 labile and non-labile species), which are especially prone to occur when dealing with  
107 concentrations at the ultra-trace level. Conventional discrete sampling, which is relatively easy  
108 to perform, provides information on the localized metal concentration in water at the exact  
109 sampling moment. In highly dynamic systems like transitional and coastal waters, discrete  
110 sampling methods may suffer from a lack of representativeness (Rodríguez et al., 2021) as metal  
111 ion speciation can be controlled by the complexity of both organic and inorganic ligands present

112 in colloidal forms. In respect of organic ligands, most are polyfunctional heterogeneous  
113 macromolecules, e.g., humic substances (HS), with different binding sites such as carboxylic and  
114 phenolic (hard complexing sites) and nitrogen and sulphur (soft complexing sites). As HS are  
115 common in coastal and estuarine waters, many metal ions can bind to these ligands. As a result,  
116 the complexes formed are characterized by a continuous distribution of thermodynamic stability  
117 constants and dissociation rate constants. They are functions of the relative affinities of the  
118 metal-to-ligand ratio coupled with the kinetic window of the analytical technique (Buffle, 1988).  
119 Consequently, previous works have shown that the degree of ligand heterogeneity in an  
120 aqueous medium is reflected in the measured concentrations by non-equilibrium techniques  
121 such as DGT and ASV (Town et al., 2009).

122 Widespread implementation of existing and future regulatory policies regarding the priority  
123 metals and other trace elements requires appropriate sampling in parallel with more advanced  
124 analytical techniques, which are often costly and, in some cases, are a barrier to compliance.  
125 There is a need to develop further and validate low-cost and easy-to-use sampling and analytical  
126 protocols for monitoring. In this sense, the Interreg MONITOOL project (EAPA 565/2016;  
127 <https://www.monitoolproject.eu>) was conceived based on the challenge of providing a robust  
128 database of total dissolved and labile metal concentrations in transitional and coastal waters  
129 based on concurrent spot water sampling and DGT deployments. In this study, the focus was the  
130 priority metals for which EQS were established under the WFD. Accordingly, the labile chemical  
131 forms of Cd and Pb in waters were measured by DGT-ICPMS and ASV, while ICPMS was  
132 determined the total dissolved metal concentrations. For Ni, the total dissolved concentrations  
133 were measured with two distinct methods, ICPMS and Cathodic Stripping Voltammetry (CSV)  
134 (van der Berg, 1991) and the labile fraction by DGT. The extent of relationships across a broad  
135 geographical scale covering various environmental conditions was evaluated.

136

## 137 **2. Study area**

138 The study was performed in the coastal and estuarine areas in the North-East Atlantic Area (from  
139 the Canary Islands to the North Sea) and the Western Mediterranean Sea (Sardinia). Sampling  
140 sites were selected to cover various anthropogenic influences from almost pristine  
141 environments to impacted areas. The sampling campaigns were carried out by nine research  
142 institutes (AZTI, CEFAS, DCU, IFREMER, IPMA, ITC, MSS, SEPA and UNICA) covering eight  
143 countries (Spain, England, Ireland, France, Portugal, Scotland, Northern Ireland and Italy)  
144 following the methodologies described in Bersuder et al. (2021). To minimize the operational

145 variability, unified protocols were used for sampling, and the same laboratory performed each  
146 type of analysis. A short description of each coastal and estuarine sampling site is presented in  
147 Tables 1 and 2, respectively.

148

### 149 **3. Materials and methods**

#### 150 *3.1. Spot sampling*

151 The sampling campaigns were carried out in 2018 and 2019, covering the dry (summer) and the  
152 wet (winter) seasons. A total of 28 sites from the Canary Islands to the North Sea, including the  
153 Western Mediterranean Sea, were surveyed (Table S1). For each partner, the same stations  
154 were sampled twice (wet and dry seasons). Sampling campaigns were completed in several ways  
155 (foot access, platforms, via boat) to access sites depending on accessibility and weather  
156 conditions. The sampling sites were chosen in such a way as to consider a wide range of  
157 concentrations for each metal. For the transition waters, sites with expected high  
158 contaminations were selected. Subsurface samples ( $\approx 0.5$  m below the surface at the same depth  
159 as deployed DGTs) were collected independently for ICPMS and voltammetry with Niskin bottles  
160 or directly to collection flasks (polypropylene) with extendable poles avoiding direct contact to  
161 minimize contamination (Bersuder et al., 2021). In total, 712 spot water samples were collected  
162 during all survey campaigns. All sampling equipment used in the field was acid cleaned (10-20%  
163 v/v, pro-analysis grade) and rinsed thoroughly with ultra-pure water (conductivity 18.2 M $\Omega$ .cm,  
164 25 °C). Field blanks were processed at all sites and by all teams concurrently to the collected  
165 water samples to evaluate the potential contamination during sampling.

166

#### 167 *3.2. Passive sampling*

168 The passive samplers used were from DGT<sup>®</sup> Research Ltd (Lancaster, UK), with the reference  
169 LSNM-NP open-pore Loaded DGT device for metals (A) in solution. All DGTs used were from the  
170 same production batch to minimize differences related to manufacturing. Three DGTs were  
171 loaded onto a plastic holder (polycarbonate) and, when necessary, protected with a nylon net  
172 (1 cm mesh size) to prevent damage from side impacts or aquatic organisms. DGT-holders were  
173 deployed at  $\approx 0.5$  m depth below the surface in the same sites and seasons of spot sampling.  
174 Holders were retrieved from the water between 2 to 7 days of deployment. Differences in  
175 deployment time were due to weather and logistical conditions at each site. Biofouling on DGT  
176 membranes was minimal, with a median surface cover of 3% (data not shown). Thus, effects

177 from biofouling on the accumulated metals were not expected, which agrees with observations  
178 on short-term deployment studies (Schintu et al., 2008, Baeyens et al., 2018). A total of 238 DGT  
179 devices were deployed and retrieved from the sampling sites (Table S1). Field DGT blanks (not  
180 immersed in water) were used at all sites and by all teams to evaluate the potential  
181 contamination derived from manufacturing and handling, respectively.

182

### 183 *3.3. Sample preparation*

184 Water and DGT samples were processed following the methodology described in Bersuder et al.  
185 (2021). Briefly, to minimize contamination, all the materials used were acid cleaned (20% v/v,  
186 pro-analysis grade), subsequently rinsed with ultra-pure water and dried in rooms with  
187 environmental conditions limiting sample contamination. Powder-free gloves were also used to  
188 minimise contamination. Spot samples for voltammetric analysis (hereafter referred to as  
189 “Volt”) were filtered and acidified in the field (when practical) or as soon as they were returned  
190 in the laboratory, while for ICPMS, the procedure was carried out in the laboratory. Spot samples  
191 where trace elements were subsequently measured using ICPMS are, hereafter, referred to as  
192 “ICPMS”. Additionally, care was taken to avoid possible contamination sources (e.g. fumes from  
193 engines deposition of atmospheric particles) in the field. In both situations, waters were filtered  
194 through 0.45 µm polycarbonate membranes and acidified to  $\text{pH} \leq 2$  with suprapure grade  $\text{HNO}_3$   
195 or bi-distillate and kept refrigerated (4-6 °C) until analysis. DGT units were removed from  
196 holders, opened using a plastic screwdriver, and the resin-gel layer was retrieved with plastic  
197 tweezers. Metals from the gel were back-extracted with a 1M  $\text{HNO}_3$  solution and measured by  
198 ICPMS. Passive samples are hereafter referred to as “DGT”. The final solution was kept  
199 refrigerated (4-6 °C) until analysis.

200

### 201 *3.4. Analytical methods*

202 Total dissolved metal concentrations in water samples were determined by an online pre-  
203 concentration SeaFast system (model picoSP4, Elemental Scientific Inc) coupled with an ICPMS  
204 (model NexION 2000, Perkin Elmer). The Seafast column (ethylenediaminetriacetic acid and  
205 iminodiacetic acid chelating groups immobilized on a hydrophilic methacrylate polymer) has a  
206 high affinity for a range of metal ions (Langerstrom et al., 2013). The complete column recovery  
207 of metals was optimized to occur at a pH between 5.5 and 7.0 (Langerstrom et al., 2013). The  
208 system was programmed with a cleaning process between samples to avoid memory effects.

209 The ICPMS was equipped with a Peltier Impact bead spray chamber and a concentric Meinhard  
210 nebulizer (Rodriguez et al., 2021). The equipment was set up by ensuring low variability of counts  
211 (RSD <1%). The isotope <sup>115</sup>In was used as an online internal standard. Calibration curves (7  
212 points) were used in different dynamic ranges depending on the metal concentration in samples.  
213 For most of the Seafast pre-concentrated samples, concentration intervals of calibration curves  
214 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  
215 (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  
216 below the LOD. For Ni and Pb, 6 and 13 % of the blank samples were above the LOD but  
217 accounted for less than 5% element concentrations in the respective samples. Metal  
218 concentrations in DGT extracts were quantified by an ICPMS equipped with a collision cell with  
219 Helium (model iCAP-Q, Thermo Fisher). The isotope <sup>115</sup>In was used as an online internal  
220 standard. The equipment was set up by ensuring low variability of counts (RSD < 5% after <sup>115</sup>In  
221 standardization). Typically, 7-point standard calibration curves ranging from 0.1 to 100 µg/L for  
222 Ni and Pb and from 0.1 to 20 µg/L for Cd were used to quantify metals in extracts. The detection  
223 limit was 0.1 µg/L for Ni, Cd and Pb. The calculation of the DGT concentration was carried out  
224 following Zhang (2020) and using the diffusion coefficients provided by the supplier (DGT®  
225 Research Ltd, Lancaster, UK). Field blanks accounted for less than 10% of the concentrations on  
226 DGT extracts. Final DGT concentrations were corrected with respective blank values. The  
227 average concentration of DGT triplicates from each side were calculated and an RSD <30% was  
228 obtained after identifying outliers using the Dixon test.

229 The determination of conditional labile metal (Pb-ASV-labile and Cd-ASV-labile) concentrations,  
230 i. e. the concentration of the metal species in the acidified water samples (Rodriguez et al.,  
231 2021), was done directly by ASV (Florence and Batley, 1977). A conventional three-electrode  
232 configuration was used with an Ag/AgCl reference electrode, a glassy carbon rod as the counter  
233 electrode and a thin Mercury Film Electrode as a working electrode (Rocha et al., 2007).  
234 Deposition potential and deposition time were -0.9 V (vs Ag/AgCl) and 100-300 s respectively.  
235 In the stripping step, the square wave mode was used with an amplitude of 25 mV, step height  
236 of 5 mV, and a frequency range of 25 Hz. Total Ni dissolved concentrations were determined by  
237 CSV based on adsorption of the surface-active complex of Ni with dimethylglyoxime on the  
238 mercury after UV irradiation of water samples to guarantee the oxidation of organic matter (Van  
239 Den Berg, 1986). A three-electrode cell was also used with a static mercury drop as a working  
240 electrode. Deposition potential and deposition time were -0.8 V (vs Ag/AgCl) and 60-120 s,  
241 respectively, and in the stripping step, the same pulse variation as aforementioned was used.  
242 Voltammetric measurements, carried out in clean disposable polyethylene terephthalate (PET)

243 vessels to minimize contamination between samples, were performed by a  
244 Potentiostat/Galvanostat (model  $\mu$ Autolab, Metrohm AG) connected to the VA stand (model  
245 663, Metrohm AG). Experimental parameters on the equipment and data acquisition were  
246 controlled with GPES v.4.9 software (EcoChemie). After purging the solutions with nitrogen  
247 ( $N_2 > 99.999\%$ ) for 10-15 minutes, all determinations were made at least in duplicate using the  
248 standard addition method (4-5 additions). Variable volumes of standard solution were added to  
249 obtain a 30% to 100 % increase of the analytical signal with a total volume variation  $\leq 1\%$ . The  
250 detection limits of ASV analysis obtained for the water samples using a deposition time of 300 s  
251 were 5 ng/L for Pb and 3 ng/L for Cd. For the CSV-Ni determinations, using 120 s deposition time,  
252 the 5 ng/L DL was obtained. Analytical variability was assessed as relative standard deviation  
253 (RSD) of duplicates, and values below 10%-15% were considered satisfactory. Most field blanks  
254 were below the LOD of Cd. For the Ni and Pb, the majority accounted for less than 10% of the  
255 concentrations on the samples. Otherwise, final concentrations were corrected with respective  
256 blank values.

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

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

268

### 269 *3.5. Statistics*

270 The non-parametric (median, 10<sup>th</sup> and 90<sup>th</sup> percentiles) statistics were calculated. The dissolved  
271 and labile metal results obtained with the three applied methodologies were compared by box  
272 plots using STATISTICA™ 6 software (Statsoft). When the metal concentrations of a given sample  
273 are below the limit of detection, the result of the measurement was considered half the value  
274 of the limit, for statistical calculations. Before the statistical analyses, metal concentrations were  
275 tested for normality and equality of variances. Non-compliance with parametric ANOVA



276 assumptions led to the employment of the Kruskal-Wallis H (KW-H) and Mann-Whitney (U) non-  
277 parametric tests to evaluate the existing differences between methodologies in the different  
278 studied areas. For linear comparison of variables, after log transformation, Pearson correlations  
279 ( $r$ ) were used. The minimum level of confidence used was 95 %.

280

## 281 **4. RESULTS**

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

### 284 *4.1. Coastal waters*

#### 285 *4.1.1. Metal and DOC concentration variability per region*

286 The median, 10<sup>th</sup> and 90<sup>th</sup> percentiles of Ni, Cd, Pb and DOC concentrations in the dissolved  
287 fraction of coastal waters from the Canary Islands to the North Sea, including the Western  
288 Mediterranean Sea, are presented in Figure 1. Higher Ni concentrations were found at the Bay  
289 of Biscay including the English Channel (hereafter referred to as “Bay of Biscay”) and Celtic/Irish  
290 Seas, reaching 2474 ng/L (DGT), and the lowest levels were recorded at the Canary Islands (70  
291 ng/L, ICPMS). For most regions, the median concentrations for the three methodologies were  
292 comparable, but increased variability was found for DGT data from the Bay of Biscay (272-2007  
293 ng/L). For Cd, values were found to differ among regions and methodologies. At the Iberian  
294 Coast and Bay of Biscay stations, all determinations showed higher concentrations and  
295 variability (ICPMS: 5-40 ng/L; Volt: 3-63 ng/L; DGT: 9-24 ng/L) than in the North Sea, Western  
296 Mediterranean and Canary Islands (ICPMS: 3-36 ng/L; Volt: 2-14 ng/L; DGT: 1-22 ng/L). The  
297 lowest median values found for voltammetric data arise from the samples with concentrations  
298 below the LOD of the technique (LOD<sub>Cd</sub>, 3 ng/L). Similar to those found for Ni, the lowest  
299 concentrations of Cd were found at the Canary Islands (ICPMS: 3-10 ng/L; Volt: 3 ng/L; DGT: 1-  
300 11 ng/L). Lead concentrations showed a different distribution pattern since some samples  
301 showed increased concentrations (Figure 1). Despite that, the higher values were found in the  
302 Western Mediterranean stations (ICPMS: 70-1938 ng/L; Volt: 80-550 ng/L; DGT: 38-319 ng/L).  
303 The median DOC content was comparable among Canary Island (1250 µg/L), Bay Biscay (1745  
304 µg/L) and Western Mediterranean Sea (1420 µg/L). At Celtic/Irish seas, higher median DOC  
305 (3330 µg/L) was found and a broader variability (270-5150 µg/L).

306

307

308 4.1.2. *Metal concentration in each region*

309 4.1.2.1. *Canary Islands*

310 The variability of Ni concentrations in the four stations from the Canary Islands (Gando, Jinámar,  
311 La Luz and Taliarte) is presented in Figure 2. Broader range of values was found for DGT at all  
312 sites (161-928 ng/L at Gando; 181-932 ng/L at La Luz; 145-1169 ng/L at Taliarte) except Jinámar  
313 (128-168 ng/L). This station's Ni median concentration was comparable among the three  
314 methodologies (ICPMS: 154 ng/L; Volt: 170 ng/L; DGT: 141 ng/L). Concentrations of Cd were low  
315 at all sites being below LOD in most voltammetric determinations. This element's median values,  
316 measured by ICPMS (Gando: 4.4 ng/L; Jinámar: 4.7 ng/L; La Luz: 8.7 ng/L; Taliarte: 5.6 ng/L),  
317 were higher than those measured by voltammetry and DGT (1.3-5.9 ng/L). Otherwise, Pb  
318 concentrations were more variable amongst sites and between methodologies. Except for  
319 Taliarte, lower median values were detected by voltammetry (2.5-43 ng/L), although at La Luz,  
320 a broader variability was found (50-220 ng/L). Higher variability of DOC content was found at  
321 Gando (900-7900 µg/L) and Jinámar (900-4900 µg/L), although their median values (Gando:  
322 1100 µg/L; Jinámar: 1000 µg/L) were in the same order of magnitude as the other sites (La Luz:  
323 1500 µg/L; Taliarte: 1600 µg/L).

324

325 4.1.2.2. *Iberian Coast, the Bay of Biscay and the Celtic/Irish Seas*

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

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338

339

340 *4.1.2.3. The North Sea*

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

348

349 *4.1.2.4. Western Mediterranean Sea*

350 The median, 10<sup>th</sup> and 90<sup>th</sup> percentiles of Ni, Cd and Pb concentrations in the West Mediterranean  
351 Sea stations are presented in Figure 4. Concentrations of Ni varied within similar intervals among  
352 the four sites, although lower values were found for voltammetry (ICPMS: 217-813 ng/L; Volt:  
353 90-660 ng/L; DGT: 242-663 ng/L). This pattern was even more evident for Cd, where most  
354 voltammetric data was below LOD. Furthermore, Cd-DGT concentrations were lower (6-14 ng/L)  
355 than ICPMS (11-22 ng/L) at all sites, except Dogana, where the variability was similar (DGT: 13  
356 ng/L; ICPMS: 13-15 ng/L). Lead concentrations measured by ICPMS were higher at Rinascita  
357 (982-1938 ng/L) than at the other sites (38-806 ng/L). A similar pattern for this metal was  
358 observed at all sites with higher ICPMS concentrations than values measured with the other  
359 methodologies.

360

361 *4.2. Transitional waters*

362 *4.2.1. Metal concentration variability per sub-region*

363 The median, 10<sup>th</sup> and 90<sup>th</sup> percentiles of Ni, Cd and Pb concentrations in the different estuaries  
364 in the Iberian Coast, Bay of Biscay and Celtic/Irish seas are presented in Figure 5. The Ni  
365 concentrations using the three methodologies varied within the same range in the Celtic/Irish  
366 seas estuaries (Liffey, Ballynacorra, Lee, Fal and Belfast Lough), although the DGT presented the  
367 lower median values. Higher median concentrations of this element measured by voltammetry  
368 were found at Ria of Aveiro in the Iberian coast (970 ng/L), Aulne estuary at Bay of Biscay (515  
369 ng/L) and Belfast Lough at the Irish Sea (640 ng/L). Estuaries located in the Northern Iberian  
370 coast (Oiartzun and Deba) presented the highest Ni values for the three techniques, reaching  
371 2600 ng/L by ICPMS. This pattern was also found for Cd, where values determined in these

372 transitional waters were up to 9 times higher than at the other stations. In most locations, the  
373 voltammetric Cd median concentration was lower than those determined using the different  
374 methodologies. The Pb concentrations measured at Ria of Aveiro (Iberian coast), Charente and  
375 Aulne estuaries (Bay of Biscay) and Fal estuary and Belfast Lough (Celtic/Irish seas) showed a  
376 broad variability ranging from 2 to 282 ng/L. Higher concentrations were found in Ballynacorra  
377 and Lee river-estuary systems reaching 1960 ng/L. Noteworthy, elevated Pb levels were  
378 recorded at Oiartzun and Deba estuaries (3-6319 ng/L; Iberian coast) and at river Liffey (177-  
379 6687 ng/L, Irish seas). Despite the broad variability of Pb concentration at all studied Celtic/Irish  
380 estuaries (59-72 ng/L), the median value was comparable to that found for the Bay of Biscay  
381 estuaries (55-188 ng/L). The content of DOC was only measured in the Northern Iberian coast  
382 (median 1273 µg/L) and Bay of Biscay (median 1550 µg/L) estuaries, where concentrations  
383 varied in a broader range.

384

## 385 **5. DISCUSSION**

386 The results presented in Figures 1-5 show in some situations high variability of metal  
387 concentrations both among sampling sites and between methodologies that cannot be  
388 attributed to a given metal and/or methodology. Therefore, it can be concluded that these  
389 results are indeed due to fluctuations in metal concentrations in waters analysed. Additionally,  
390 in some cases, the applied spot sampling design did not fully integrate the high environmental  
391 variability in metal concentrations (Rodríguez et al., 2021). It should be noticed that sampling  
392 sites were selected to fulfil the research goals of the Monitool project ranging from almost  
393 pristine to anthropogenically impacted areas. Therefore, obtained results may not fully  
394 represent metals concentrations from wider sea areas where broader spatially representative  
395 (legislative) national monitoring would be applied.

396

### 397 *5.1. Comparison of environmental metal level*

398 Concentrations of Ni, Cd and Pb measured by ICPMS in coastal stations from the Canary Islands  
399 to the North Sea and in the Western Mediterranean Sea were, in general, comparable to  
400 previous works performed in the NE Atlantic waters. Furthermore, all total dissolved metal  
401 concentrations measured by Seafast-ICPMS were lower than the EQS values for Ni (8.6 µg/L), Cd  
402 (0.2 µg/L) and Pb (1.3 µg/L) (Directive 2013/39/EU). Concentrations of Cd in the Canary Islands  
403 varied within the range of values reported in open-waters of this Atlantic Area (Landing et al.,

404 1995; Saager et al., 1997; Cotté-Krief et al., 2002). Increased concentrations of Ni and Pb found in  
405 these stations suggest anthropogenic contributions from urban and industrial activities at the  
406 east coast of Gran Canaria Island, where the largest population and economic activity are  
407 concentrated. A similar pattern was found at the Celtic/Irish seas, although the median values  
408 were comparable to the concentrations published in other works (Kremling and Hydes, 1988;  
409 Laslett, 1995; Atcherberg and van den Berg, 1996). Higher concentrations of Ni and Pb were  
410 found at Dublin Bay, presumably due to metal remobilization associated with the site's proximity  
411 to historic industrial and ore shipping and transport activities. Concentrations of Ni and Cd found  
412 in the Iberian Coast and the North Sea were similar to those found in previous works (Laslett,  
413 1995; Fileman et al., 1991; Santos-Echeandia et al., 2012). For Pb, higher concentrations were  
414 found in both coastal areas reflecting several inputs from rivers and anthropogenic activities in  
415 the vicinity of the sampling sites. In the Western Mediterranean Sea, Ni, Cd, and Pb  
416 concentrations were above reported values (Yoon et al., 1999; Morley et al., 1997; Saager et al.,  
417 1993; Schlitzer et al., 2017). Additionally, measured median DGT values obtained in this study  
418 were higher than those reported by Schintu et al. (2008) and Marras et al. (2020) in the Gulf of  
419 Cagliari (Ni: 33-246 ng/L; Cd: 5-17 ng/L; Pb: 4-45 ng/L). The increased metal concentrations point  
420 to anthropogenic inputs related to the harbour and urban activities. This finding is in line with  
421 the conclusions of Schintu et al. (2016) in a study with sediments and benthic foraminifera from  
422 a wider area of the Cagliari harbour.

423 Metal concentrations in estuaries were in general higher than values found in coastal waters,  
424 reflecting inputs from anthropogenic or natural sources. Nevertheless, total dissolved metal  
425 concentrations (ICPMS) were systematically lower than the EQS values for Ni, Cd and Pb  
426 (Directive 2013/39/EU). Concentrations of Cd and Pb at Ria of Aveiro, a coastal lagoon located  
427 in the West Iberian coast (Portugal), were respectively up to 10 and 60 times lower than results  
428 obtained a couple of decades ago (Pereira et al., 2009). The deindustrialization in the margins of  
429 the lagoon that had chemical industries in the past is presumably the main reason for such a  
430 decrease in Cd concentrations. This argument, coupled with the phasing out of leaded gasoline  
431 in Europe around 2000 (Mil-Homens et al., 2013), also explains the decrease of Pb  
432 concentrations. Both estuarine systems in the north coast of the Iberian coast (Deba and  
433 Oiartzun) have been historically highly impacted by human activities (Tueros et al., 2008).  
434 Reported concentrations of Ni, Cd and Pb (total dissolved concentrations) from the 90's decade  
435 were up to 2 orders of magnitude higher (Belzunce et al., 2004) than values obtained in this  
436 study. This difference resulted from implemented management actions to reduce the pressures  
437 leading to successful water quality improvement for several priority contaminants (Borja et al.,

438 2016). At the end of the 20<sup>th</sup> Century, the industrial recession with the closure of highly polluting  
439 industries (mining, steel factories) reduced the contaminant loads to the estuaries also played a  
440 significant role in the improvement. Similar Cd and Ni DGT-labile concentrations were reported  
441 by Montero et al. (2012). The lower Cd values in both studies, separated by a decade, indicate  
442 that this element kept a low bioavailable dissolved fraction in the two estuaries (Deba and  
443 Oiartzun). Otherwise, the high total and DGT-Ni labile concentrations found in the last ten years  
444 at Deba estuary resulted from their anthropogenic origin, since substantial input of these metals  
445 derives from the surrounding industry of electrolytic and chemical surface treatment and iron  
446 and steel-related metallurgy (Belzunce et al., 2004; Tueros et al., 2009). The main anthropogenic  
447 inputs to the Charente estuary located in the Bay of Biscay (France) are agriculture and urban  
448 activities (Dabrin, 2009). Concentrations of total dissolved Cd varied in a narrow range and were  
449 lower than previously reported values (Boutier et al., 2000; Dabrin, 2009; Guesdon et al., 2016).  
450 This difference may result from freshwater inputs, which induce large variability of this metal  
451 concentration in the estuarine waters (Dabrin, 2009). According to Boutier et al. (2009), the  
452 intrusion of the Gironde water plume into the Antioche Straits led to the increase of Cd in the  
453 coastal water. Thus, Charente estuarine water has been diluted with an endmember with  
454 increased values of this element. Nickel concentrations were comparable with values reported  
455 by Guesdon et al. (2016) but lower than those obtained by Dabrin (2009). This trend was also  
456 found for Pb concentrations, where this study evidenced a decrease of up to 5 times the  
457 concentrations found by that author. Scarce information exists on metal contamination in  
458 waters of the Aulne estuary (France). The estuary flows to a wider Brest harbour area with  
459 several anthropogenic activities (COMENRADE project, 2020). The Aulne river basin crosses two  
460 abandoned mining areas (Huelgat and Poullaouen) in its upstream section rich in Pb-Zn ores  
461 (Lemièrre et al., 2002), which may explain the increase in the metal load in the estuary area.  
462 Similarly, little information exists on metal concentrations in the Irish estuaries. Data from the  
463 national monitoring programs from 2018 and 2020 showed that the total dissolved Ni, Cd and  
464 Pb concentrations varied within the range of values measured by ICPMS (Brendan McHugh,  
465 personal communication). Conversely, increased ICPMS concentrations of Pb and Ni in  
466 Alexandra Basin – River Liffey compared with those from the monitoring programs suggests the  
467 presence of point sources. During the sampling period, the navigation channels from the  
468 Alexandra Basin were dredged, which induced metal remobilization from the particulate fraction  
469 to the dissolved. Caetano et al. (2003) showed that the resuspension of anoxic sediment  
470 remobilizes metals from their reactive phases concerning changes in redox conditions. Metals  
471 are transferred to the dissolved fraction being subsequently scavenged by newly formed solid  
472 phases or remain in solution as stable complexes.

473 *5.2. Comparison of CSV and ICP-MS dissolved Ni concentrations*

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

478 Significant linear correlations exist between dissolved Ni concentrations determined by CSV and  
479 ICPMS for coastal and estuarine sample ( $r= 0.797$ ,  $p<0.0001$ ,  $n= 53$  and  $r=0.833$ ,  $p<0.0001$ ,  $n=$   
480  $32$  respectively), and the values are close to the 1:1 line. These results confirm that both  
481 methodologies are suitable for determining Ni dissolved concentrations in coastal and  
482 transitional waters through proper control of the precision and accuracy of the analytical  
483 procedures. This was expected since the determination of Ni by CSV in filtered and acidified  
484 water after UV-radiation guarantees the oxidation of organic matter, providing a quantification  
485 of the total dissolved content comparable to SeaFast-ICPMS. In the case of Ni, information about  
486 its speciation cannot be attained by ASV due to the non-reversibility of the Ni reduction on the  
487 electrode (Mota et al., 1995). Both techniques rely on discrete sampling that requires some pre-  
488 treatment before analysis, leading to possible contamination and perturbation of the samples.  
489 While the samples for ICPMS analysis were filtered and acidified at the laboratory, for CSV  
490 analysis, this procedure was done in the field and kept refrigerated until analysis. In the case of  
491 ICPMS, a pre-concentration of the metal ions and removal of the salt matrix is required.  
492 However, CSV requires complexing reagents to convert Ni into an absorbable complex prior to  
493 the analysis. Yet, the data obtained by both techniques were close to the 1:1 line, indicating that  
494 the different treatments of the samples did not substantially affect the measured total dissolved  
495 Ni concentration.

496

497 *5.3. Comparison of ASV-labile and DGT-labile Cd and Pb*

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

502 Despite the variability and differences in concentrations among regions and methodologies,  
503 both in coastal and estuarine sampling sites, significant linear correlations were found between  
504 Cd ASV-labile and Cd DGT-labile concentrations ( $r=0.780$ ,  $p<0.0001$ ,  $n=49$ , for coastal and  
505  $r=0.687$ ,  $p<0.0001$ ,  $n=31$ , for estuarine). As shown in Figure 7, the measured data points are

506 closer to the 1:1 lines. Both regressions show that similar labile concentrations are being  
507 measured using both techniques, despite the shorter time scale of ASV, imposed by the smaller  
508 diffusion layer thickness around the electrode when compared to the time scale associated with  
509 the 0.8 mm diffusive gel used in DGT, and the acidification of the water samples for ASV. This  
510 means that Cd speciation in solution is controlled by mobile and very labile species that rapidly  
511 dissociate even when traversing the small diffusion layer around the electrode in ASV. This is  
512 also in agreement with Cd speciation in seawater that might be controlled by the inorganic  
513 chloro-complexes and/or labile organic complexes (Simões et al., 1981). The immediate  
514 acidification of the water samples once filtered can, however, give information about the labile  
515 fraction at a lower pH than the natural one, in the presence of a still inert fraction that may  
516 comprise metals strongly bound to natural organic molecules or bound to colloids (Rodríguez et  
517 al., 2021).

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

522

523 Consequently, Figure 8 (A and B) indicates that the labile Pb concentrations measured by ASV  
524 are lower than those determined using DGT. Although Pb concentrations were variable amongst  
525 sites and between methodologies, these relationships were more evident at the Iberian Coast,  
526 Bay of Biscay and some sites at the Canary Islands. This pattern may be due to non-labile  
527 complexes in terms of the time scale of the voltammetric measurement and/or non-mobile  
528 species, namely colloidal species (van Leeuwen et al., 2005; Sigg et al., 2006). As to the former  
529 hypothesis, several Pb complexation studies with naturally occurring organic ligands (e.g. humic  
530 substances) in aquatic media by ASV indicate that the complexes formed are labile within the  
531 time scale of the technique even at a higher pH (Pinheiro et al., 1994; Mota et al., 2005)  
532 therefore also labile for DGT conditions. On the other hand, Pb is present in the dissolved phase  
533 in colloidal forms that may not be mobile enough to be detected by ASV but can diffuse through  
534 the diffusive gel layer as previously described for colloidal Fe and Al (Sherwood et al., 2009).  
535 However, it should also be taken into account that ASV measurements refer to spot water  
536 samples, while DGTs provide a time-averaged concentration that integrates the environmental  
537 metal fluctuations, which could partly explain the observed differences.

538



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

550

#### 551 *5.4. Heterogeneity of the binding ligands*

552 The degree of ligand heterogeneity of a system is reflected in the measured concentrations by  
553 non-equilibrium techniques such as DGT and ASV (Town et al., 2009, (Buffle, 1988). It can be  
554 expressed by a heterogeneity parameter ( $\Gamma$ ) that is a measure of the variation of binding sites  
555 affinities for a given ion. This can be computed with the logarithm of DGT (or ASV)  
556 concentrations (converted to mol/L) as a function of the fraction of occupied sites calculated as  
557 the logarithm of dissolved metal concentrations normalized to DOC (converted to mg/L). If an  
558 excess of binding sites exists, the graph should display a linear relationship with a slope equal to  
559  $1/\Gamma$  (Town et al., 2009) with  $\Gamma=1$  for a single ligand, while  $\Gamma$  decreases as the heterogeneity of  
560 the ligands increase (Buffle, 1988).

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

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

581

582 In the case of Cd and Pb, operational labile concentrations were determined by DGT and ASV.  
583 The relationship between labile concentrations measured by DGT or ASV and the metal to ligand  
584 ratio for Cd in estuarine sites (with available DOC), sampled along the Northern Iberian Coast  
585 (Oiartzun and Deba), Bay of Biscay (Charente and Aulne) and Irish Sea (Belfast Lough and Fal)  
586 are shown in Figure 10. Significant linear correlations are observed ( $r=0.748$ ,  $p < 0.001$ ,  $n=22$  and  
587  $r=0.682$ ,  $p=0.001$ ,  $n=19$  for the ASV and DGT data, respectively) and the  $\Gamma$  values computed  
588 using either the DGT or ASV data are within the experimental error close to one.

589

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

593

594 The heterogeneity should be discussed considering several factors, such as the nature of the  
595 DOC and the pH dependence due to the different types of acidic groups from carboxylic to amino  
596 and sulfhydryl present in HS. Additionally, the apparent lability of the formed complexes  
597 depends on the metal ion, the technique's kinetic window, and the time scales of ASV and DGT.  
598 Nonetheless, in this work, the same degree of heterogeneity was found across the estuarine  
599 sampling sites at the Iberian coast, the Bay of Biscay and Celtic Seas for the Ni, Cd and Pb metal  
600 ions (see Figure 9 for Ni). This may result from a stable complexation at the trace level and the  
601 non-significantly dependence of the DGT/spot sampling ratios on the physical-chemical  
602 parameters such as temperature, salinity, pH, oxygen, DOC or SPM as previously reported  
603 (Rodríguez et al., 2021). No differences were found for Cd between the values determined using  
604 the ASV or the DGT data, confirming that equivalent operational labilities were measured by  
605 both techniques (Figure 7). The differences of  $\Gamma$  in Pb (Table 3) suggest some heterogeneity of

606 the ligands or less dynamic complexes (Filela and Town, 2001), while for Ni and Cd, the ligands  
607 act as homogeneous. The complexes are labile, similar to the findings of Town (2009) using a  
608 compilation of data of various origins (Town et al., 2009) and Cindric (2020) for a highly stratified  
609 estuary.

610

## 611 **6. CONCLUSIONS**

612 This study has the unique characteristic of using a large number of spot samples and DGTs in a  
613 broad geographical area to tackle labile and total dissolved concentrations of priority metals.  
614 The singularity of being a coordinated multi-country assessment highlights this approach's  
615 advantages, allowing the comparison of locations and evaluation of analytical variability, which  
616 is impossible to do when looking at individual studies from different batches. Overall, the  
617 relationships among the different chemical forms of Ni, Cd and Pb were investigated in coastal  
618 and transitional waters, measured by three different methodologies, and covering a variety of  
619 environmental conditions. Despite the high variability, the dissolved concentrations found for  
620 the priority metal ions were, in almost all locations, below the EU WFD's guideline levels for non-  
621 inland water bodies. In the case of Ni, these results were corroborated by two distinct  
622 techniques, ICPMS and CSV, that had discrete sampling in common. As to the labile fractions,  
623 ASV and DGT were shown to be well suited for the simultaneous determination of Cd and Pb  
624 dynamic speciation in the marine environment. Either in coastal or transitional waters, similar  
625 labilities were measured for Cd, while for Pb, the ASV labile fraction was lower than the one  
626 determined by DGT. The heterogeneity of the binding ligands in estuarine waters was observed  
627 for Ni using DGT labile concentrations. Additionally, both dynamic techniques provided  
628 comparable information about the heterogeneity of the binding ligands towards Cd and Pb.  
629 These results reflect the pool of mobile and labile species available towards the kinetic windows  
630 of each technique. They seem not to be affected by the flaws traditionally associated with  
631 discrete sampling. In other aquatic systems with higher variability of dissolved metal  
632 concentrations, the results could differ. Additionally, DGT can measure the potentially  
633 bioavailable concentrations of far more metal ions existing in the aquatic environments and is,  
634 therefore, more suitable for a good design of surveillance monitoring programs under the WFD.

635

## 636 **7. DECLARATION OF COMPETING INTEREST**

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

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657

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661

## 662 **9. REFERENCES**

- 663 Achterberg, E.P., van den Berg, C.M., 1994. In line ultraviolet-digestion of natural water samples  
664 for trace metal determination using an automated voltammetric system. Anal. Chim.  
665 Acta. 291:213-232
- 666 Baeyens, W., Gao, Y., Davison, W., Galceran, J., Leermakers, M., Puy, J., Superville, P.J., Begery,  
667 L., 2018. In situ measurements of micronutrient dynamics in open seawater show that  
668 complex dissociation rates may limit diatom growth. Sci. Rep. 8:16125
- 669 Belzunce, M.J., Solaun, O., González-Oreja, J.A., Millán, E., Pérez, V., 2004. Contaminants in  
670 sediments. In: Borja, A., Collins, M. (Eds.), Oceanography and Marine Environment of  
671 the Basque Country, vol. 70. Elsevier Oceanography Series, pp. 283–315.
- 672 Bersuder, P., Amouroux, I., Belzunce-Segarra, M.J., Bolam, T., Caetano, M., Carvalho, I., Correia-  
673 dos-Santos, M., Fones, G., et al. 2021. Concurrent sampling of transitional and coastal

674 waters by Diffusive Gradient in Thin-films (DGT) and spot sampling for trace metals  
675 analysis. *MethodX* 8:101462

676 Boutier, B., Chiffolleau, J.F., Gonzalez, J.L., Lazure, P., Auger, D., Truquet, I., 2000. Influence of  
677 the Gironde estuary outputs on cadmium concentrations in the coastal waters:  
678 consequences on the Marennes-Oléron bay (France). *Oceanol. Acta* 23:745-757.

679 Borja, A., Chust, G., Rodríguez, J.G., Bald, J., Belzunce-Segarra, M.J., Franco, J., Garmendia, J.,  
680 Larreta, J., Menchaca, I., Muxika, I., Solaun, O., Revilla, M., Uriarte, A., Valencia, V.,  
681 Zorita, I., 2016. 'The past is the future of the present': Learning from long-time series of  
682 marine monitoring, *Sci. Total Environ.* 566–567:698–711

683 Buffle, J., 1988. *Complexation Reactions in Aquatic Systems: an Analytical Approach*, Ellis  
684 Horwood, Chichester

685 Brown, J.W. 1987. Studies of humic and fulvic acid dynamics in coastal marine waters of South  
686 Florida *Mar. Environ. Res.* 21:163-174

687 Caetano, M., Madureira, M., Vale, C., 2003. Metal remobilisation during resuspension of anoxic  
688 contaminated sediment – short-term laboratory study. *Water, Air and Soil Poll.* 143:23-  
689 40

690 Chakraborty, P., Fasfous, I.I., Murimboh, J., Chakarabarti, C.L. 2007. Simultaneous determination  
691 of speciation parameters of Cu, Pb, Cd and Zn in model solutions of Suwannee River  
692 fulvic acid by pseudopolarography. *Anal. Bioanal. Chem.* 388:463

693 Cindric, A.M., Marcinek, S., Garnier, C., Salaünc, P., Cukrova, N., Oursel, B., Lenoble, V.,  
694 Omanović, D., 2020. Evaluation of diffusive gradients in thin films (DGT) technique for  
695 speciation of trace metals in estuarine waters – A multimethodological approach. *Sci.*  
696 *Total Environ.* 721:137784

697 CIS, 2009. *Common Implementation Strategy for the Water Framework Directive (2000/60/EC).*  
698 *Guidance document n° 19 Guidance on surface water chemical monitoring under the*  
699 *water framework directive. Technical report. European Communities*

700 COMENRADE Project 2021. <https://wwz.ifremer.fr/pollution/Projets/COMENRADE-2020-2021>

701 Cottè-Krief, M.H., Thomas, A.J., Martin, J.M., 2002. Trace metal (Cd, Cu, Ni and Pb) cycling in the  
702 upper water column near the shelf edge of the European continental margin (Celtic Sea).  
703 *Mar. Chem.* 79:1–26

704 Dabrin, A., 2009. *Mécanismes de transfert des éléments traces métalliques (ETM) et réactivité*  
705 *estuarienne – Cas des systèmes Gironde, Charente, Seudre et Baie de Marennes Oléron.*  
706 *Université de Bordeaux. Ph.D. Thesis. 363 pp.*

707 Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural  
708 waters using thin-film gels. *Nature* 367:546-548

709 Davison, W., Zhang, H., 2012. Progress in understanding the use of diffusive gradients in thin  
710 films (DGT) – back to basics. *Environ. Chem.* 9:1-13

711 Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013  
712 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the  
713 field of water policy.

714 Filella, M., Buffle, J., van Leeuwen, H.P., 1990. Effect of physico-chemical heterogeneity of  
715 natural complexants: Part I. Voltammetry of labile metal—fulvic complexes. *Anal. Chim.*  
716 *Acta* 232:209-223

717 Filella, M., Town, R.M. 2001. Heterogeneity and lability of Pb(II) complexation by humic  
718 substances: practical interpretation tools. *Fresenius J. Anal. Chem.* 370:413

719 Fileman, C.F., Althaus, M., Law, R.J., 1991. Dissolved and particulate trace metals in surface  
720 waters over the Dogger Bank, Central North Sea. *Mar. Poll. Bull.* 22:241-244

- 721 Florence, T.M., Batley, G.E., 1977. Determination of the chemical forms of trace metals in natural  
722 waters, with special reference to copper, lead, cadmium and zinc. *Talanta*, 24:151-158
- 723 Fraústo-da-Silva, J., Williams, R. 2001. *The Biological Chemistry of the Elements: The Inorganic*  
724 *Chemistry of Life*, 2<sup>nd</sup> edition, Oxford Press, 600 pp.
- 725 Gao, Y., Zhou, C., Gaulier, C., Bratkic, A., Galceran, J., Puy, J., Zhang, H., Leermakers, M., Baeyens,  
726 W. 2019. Labile trace metal concentration measurements in marine environments: From  
727 coastal to open ocean areas. *Trends in Anal. Chem.* 116:92-101
- 728 Guesdon, S., Stachowski-Haberkorn, S., Lambert, C., Beker, B., Brach-Papa, C., Auger, D.,  
729 Béchemin, C., 2016. Effect of local hydroclimate on phytoplankton groups in the  
730 Charente estuary. *Est. Coast Shelf Sci.* 181:325-337
- 731 Kremling, K., Hydes, D., 1988. Summer distributions of dissolved Al, Cd, Co, Cu, Mn and Ni in  
732 surface waters around the British Isles. *Cont. Shelf Res.* 8:89-105
- 733 Lagerström, M.P. Field, M. Séguret, L. Fischer, S. Hann, R.M. Sherrell, 2013. Automated on-line  
734 flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open  
735 ocean seawater: Application to the GEOTRACES program. *Mar. Chem.* 155:71–80
- 736 Landing, W.M., Cutter, G.A., Dalziel, J.A., Flegal, A.R., Powell, R.T., Schmidt, D., Shiller, A.,  
737 Statham, P., Westerlund, S., Resing, J., 1995. Analytical intercomparison results from the  
738 1990 intergovernmental oceanographic commission open ocean baseline survey for  
739 trace metals: Atlantic Ocean. *Mar. Chem.* 49:253–265
- 740 Laslett, R.E., 1995. Concentrations of dissolved and suspended particulate Cd, Cu, Mn, Ni, Pb and  
741 Zn in surface waters around the coasts of England and Wales and in adjacent seas. *Est.*  
742 *Coast Shelf Sci.* 40:67-85
- 743 Lemière, B., Clozel, B., Charbonnier, P., avec la collaboration de J-P. Jégou-BRGM, 2002. Etude  
744 de l'origine des pollutions métalliques naturelles du bassin versant de la Rade de Brest -  
745 Nouvelles données disponibles pour l'interprétation géochimique des eaux de surface  
746 (Bassins versants de l'Aulne et de la Douffine) (phase 2) - rapport BRGM/RP-51566-FR,  
747 28 p.
- 748 Mil-Homens, M., Caetano, M., Costa, A.M., Lebreiro, S., Richter, T., de Stigter, H., Trancoso, M.A.,  
749 Brito, P. 2013. Temporal evolution of lead isotope ratios in sediments of the Central  
750 Portuguese Margin: A fingerprint of human activities. *Mar. Poll. Bull.* 74:274-284
- 751 Marras, B., Montero, N., Marrucci, A., Bettoschi, A., Atzori, M., Schintu, M. 2020. Operational  
752 DGT threshold values for metals in seawater from protected coastal areas in Sardinia  
753 (Western Mediterranean). *Mar. Poll. Bull.* 150:110692
- 754 Montero, N., Belzunce-Segarra, M.J., Gonzalez, J.L., Larreta, J., Franco, J. 2012. Evaluation of  
755 diffusive gradients in thin-films (DGTs) as a monitoring tool for the assessment of the  
756 chemical status of transitional waters within the Water Framework Directive, *Mar. Poll.*  
757 *Bull.* 64:31–39
- 758 Morley, N.H., Burton, J.D., Tankere, S.P., Martin, J.M. 1997. Distribution and behaviour of some  
759 dissolved trace metals in the western Mediterranean Sea. *Deep sea Res. II* 44:675-691.
- 760 Mota, A.M., Correia-dos-Santos, M.M. 1995. Trace Metal Speciation of Labile Chemical Species  
761 in Natural Waters: Electrochemical Methods" In: "Metal Speciation and Bioavailability,  
762 in Aquatic Systems", A. Tessier, D.R. Turner, Eds, John Wiley and Sons, Chichester,  
763 Chapter 5, p. 205-259
- 764 Mota A.M., Cruz P., Vilhena C., Gonçalves M.L., 2005. Influence of the sediment on lead  
765 speciation in the Tagus estuary. *Water Res.* 39:1451–1460
- 766 Pereira, E., Otero, M., Monterroso, P., Vale, C., Duarte, A.C., 2009. Transport of trace metals (Cd,  
767 Pb and Cu) in a coastal temperate lagoon. *Fresenius Environ. Bull.* 18:70-81

768 Pinheiro J.P., Mota A.M., Gonçalves M.L., 1994 Complexation study of humic acids with  
769 Cadmium(II) and Lead(II). *Anal. Chim. Acta* 284:525–537

770 Rocha, L.S., Pinheiro, J.P., Carapuça, H.M. 2007. Evaluation of nanometer thick mercury film  
771 electrodes for stripping chronopotentiometry. *J. Electroanal. Chem.* 610:37-45

772 Rodríguez, J., Amouroux, I., Belzunce-Segarra, M., Bersuder, P., Bolam, T., Caetano, M., Carvalho,  
773 I., Correia-dos-Santos, M.M., Fones, G.R., Gonzalez, J.L., Guesdon, S., Larreta, J., Marras,  
774 B., McHugh, B., Menet-Nédélec, F., Menchaca, I., Millán-Gabet, V., Montero, N., Nolan,  
775 M., Regan, F., Robinson, C., Rosa, N., Rodrigo-Sanz, M., Schintu, M., White, B., Zhang, H.,  
776 2021. Assessing variability in the ratio of metal concentrations measured by Diffusive  
777 Gradients in Thin-films (DGT) passive samplers and by spot sampling in European  
778 seawaters. *Sci. Total Environ.* 783:147001

779 Saager, P.M., deBaar, H.J., deJong, J.T., Nolting, R.F., Schijf, J., 1997. Hydrography and local  
780 sources of dissolved trace metals Mn, Ni, Cu, and Cd in the northeast Atlantic Ocean.  
781 *Mar. Chem.* 57:195–216

782 Saager, P., Schijf, J., de Barr, H. 1993. Trace-metal distributions in seawater and anoxic brines in  
783 the eastern Mediterranean Sea. *Geochim. Cosm. Acta* 57:1419-1432

784 Santos-Echeandía, J., Caetano, M., Brito, P., Canário, J., Vale, C. 2012. Regional variation of trace-  
785 element baseline concentrations in the Portuguese coastal waters (SW Europe). *Mar.*  
786 *Environ. Res.* 79:86-99

787 Schintu, M., Durante, L., Maccioni, A., Meloni, P., Degetto, S., Contu, A., 2008. Measurement of  
788 environmental trace-metal levels in Mediterranean coastal areas with transplanted  
789 mussels and DGT techniques. *Mar. Pollut. Bull.* 57:832–837

790 Schintu, M., Marrucci, A., Marras, B., Galgani, F., Buosi, C., Ibba, A., Cherchi, A. 2016. Heavy  
791 metal accumulation in surface sediments at the port of Cagliari (Sardinia, Western  
792 Mediterranean): Environmental assessment using sequential extractions and benthic  
793 foraminifera. *Mar. Pollut. Bull.* 111:45-56

794 Schlitzer, R., Anderson, R., Dodas, E., Lohan, M., Geibert, W., Tagliabue, A., Bowie, A., et al. 2018.  
795 The GEOTRACES Intermediate Data Product 2017. *Chem. Geol.* 493:210-223

796 Sherwood, J., Barnett, D., Dover, K., Howitt, J., Li, H., Kew, P., Mondon, J. 2009. Deployment of  
797 DGT units in marine waters to assess the environmental risk from a deep sea tailings  
798 outfall. *Anal. Chim. Acta* 652:215-223

799 Sigg, L., Black, F., Buffle, J., Cao, J., Cleven, R., Davison, W., Galceran, J., Gunkel, P., Kalis, E.,  
800 Kistler, D., Martin, M., Noël, S. 2006. Comparison of analytical techniques for dynamic  
801 trace metal speciation in natural freshwaters. *Environ. Sci. Technol.* 40:1934

802 Simões, M.L., Vaz, M.C., Fraústo-da-Silva, J. 1981. Stability constants of chloro-complexes of  
803 cadmium(ii) in sea-water medium. *Talanta* 28:237-240

804 Standard Method's for the examination of Water and Wastewater, 2017. American Public Health  
805 Association, AWWA (American Water Work's Association), Water Environment  
806 Federation, E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri (Eds), 23<sup>rd</sup> edition.

807 Town, R.M., Chakraborty, P., van Leeuwen, H.P., 2009. Dynamic DGT speciation analysis and  
808 applicability to natural heterogeneous complexes. *Environ. Chem.* 6:170-177

809 Town, R.M., Filella, M., 2002. Crucial role of the detection window in metal ion speciation  
810 analysis in aquatic systems: the interplay of thermodynamic and kinetic factors as  
811 exemplified by nickel and cobalt. *Anal. Chim. Acta* 466:285

812 Tueros, I., Borja, A., Larreta, J., Rodríguez, J.G., Valencia, V., Millán, E., 2009. Integrating long-  
813 term water and sediment pollution data, in assessing chemical status within the  
814 European Water Framework Directive. *Mar. Pollut. Bull.* 58:1389–1400

- 815 Tueros, I., Rodríguez, J.G., Borja, A., Solaun, O., Valencia, V., Millán, E. 2008. Dissolved metal  
816 background levels in marine waters, for the assessment of the physico-chemical status,  
817 within the European Water Framework Directive. *Sci. Total Environ.* 40:40–52
- 818 Unsworth, E.R., Warnken, K.W., Zhang, H. Davison, W., Black, F., Buffle, J., Cao, J., Cleven, R.,  
819 Galceran, J., Gunkel, P., Kalis, E., Kistler, D. 2006. Model predictions of metal speciation  
820 in freshwaters compared to measurements by in situ techniques. *Environ. Sci. Technol.*  
821 40:1942
- 822 van den Berg, C., 1986. The determination of trace metals in sea-water using cathodic stripping  
823 voltammetry. *Sci. Total Environ.* 49:89-99
- 824 van Leeuwen, H.P., 2000. Dynamic aspects of in situ speciation processes and techniques. In: *In*  
825 *Situ Monitoring of Aquatic Systems. Chemical Analysis and Speciation.* J. Buffle, G.  
826 Horvai (Eds), Wiley: Chichester p. 253
- 827 van Leeuwen, H.P., Town, R.M., Buffle, J., Cleven, R.F., Davison, W., Puy, J., van Riemsdijk, W.H.,  
828 Sigg, L. 2005. Dynamic speciation analysis and bioavailability of metals in aquatic  
829 systems. *Environ. Sci. Technol.* 39:8545-8556
- 830 Yoon, Y., Martin, J.M., Cotté, M. 1999. Dissolved trace metals in the Western Mediterranean  
831 Sea: total concentration and fraction isolated by C18 Sep-Pak technique. *Mar. Chem.*  
832 66:129-148
- 833 Zhang, H., 2020. *General Guide for Using DGT Passive Samplers in Waters.* DGT Research Ltd,  
834 Lancaster, UK.



835 Figure and Table captions

836

837 **Figure 1** – Box and whisker plots of Ni, Cd, Pb (ng/L) and DOC ( $\mu\text{g/L}$ ) in water from the Canary Islands (n=30-42 samples),  
838 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  
839 samples) and Western Mediterranean Sea (n=24-40 samples). Metal concentrations were analysed by ICPMS, voltammetry  
840 and using DGT-ICPMS. Horizontal lines correspond to the median, the edges of the box for the 10<sup>th</sup> and 90<sup>th</sup> percentiles and  
841 minimum and maximum concentrations (whiskers).

842

843 **Figure 2** – Box and whisker plots of Ni, Cd, Pb (ng/L) and DOC ( $\mu\text{g/L}$ ) in water from Gando (n=6 samples), Jinámar (n=5-6  
844 samples), La Luz (n=9-18 samples) and Taliarte (n=9-12 samples) stations (Canary Islands). Metal concentrations were  
845 analysed by ICPMS, voltammetry and using DGT-ICPMS. Horizontal lines correspond to the median, the edges of the box for  
846 the 10<sup>th</sup> and 90<sup>th</sup> percentiles and minimum and maximum concentrations (whiskers).

847

848 **Figure 3** – Box and whisker plots of Ni, Cd and Pb (ng/L) in water from the Iberian Coast (Matosinhos, Oeiras, Sesimbra; n=17-  
849 34 samples), Bay of Biscay (Port-en-Bessin, Saumonard, Nazaire; n=23-36 samples) and Celtic/Irish seas (Dublin Bay,  
850 Liverpool, Buoy 38A; n=19-36 samples). Metal concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS.  
851 Horizontal lines correspond to the median, the edges of the box for the 10<sup>th</sup> and 90<sup>th</sup> percentiles and minimum and maximum  
852 concentrations (whiskers).

853

854 **Figure 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  
855 samples), Rinascita (n=6-10 samples) and Sant’Elmo Dock (n=6-12 samples) (Western Mediterranean Sea). Metal  
856 concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS. Horizontal lines correspond to the median, the  
857 edges of the box for the 10<sup>th</sup> and 90<sup>th</sup> percentiles and minimum and maximum concentrations.

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859 **Figure 5** – Box and whisker plots of Ni, Cd, Pb (ng/L) and DOC ( $\mu\text{g/L}$ ) in water from Ria of Aveiro, Oiartzun, Deba (Iberian  
860 Coast; n=102-119 samples), Charente, Aulne (Bay of Biscay; n=9-32 samples), Liffey, Ballynacorra, Lee, Fal and Belfast Lough  
861 (Celtic/Irish Sea; n=36-60 samples). Metal concentrations were analysed by ICPMS, voltammetry and using DGT-ICPMS.  
862 Horizontal lines correspond to the median, the edges of the box for the 10<sup>th</sup> and 90<sup>th</sup> percentiles and minimum and maximum  
863 concentrations.

864

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

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871 **Figure 7** - Relationship between Cd ASV and Cd DGT for coastal sampling sites (A) at the Canary Islands, Iberian coast, Bay of  
872 Biscay, Celtic Seas, North Sea and Western Mediterranean Sea and for estuarine sampling sites (B) at the Iberian Coast, the  
873 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  
874 data. Key: ASV – mean concentration of metal measured by spot sampling using anodic stripping voltammetry on filtered  
875 seawater; DGT – concentration of metal measured using DGT passive sampler.

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877 **Figure 8** - Relationship between Pb-ASV and Pb-DGT coastal sampling sites (A) at the Canary Islands, Iberian coast, Bay of  
878 Biscay, Celtic/Irish Seas, North Sea and Western Mediterranean Sea and for estuarine sampling sites (B) Ria of Aveiro,  
879 Oiartzun, Deba (Iberian Coast), Charente, Aulne (Bay of Biscay), Liffey, Ballynacorra, Lee, Fal and Belfast Lough (Celtic/Irish  
880 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  
881 concentration of metal measured by spot sampling using anodic stripping voltammetry on filtered seawater; DGT –  
882 concentration of metal measured using DGT passive sampler.

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

889

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

896

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

899

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

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903 **Table 3** - Heterogeneity parameter  $\Gamma$  for estuarine waters.

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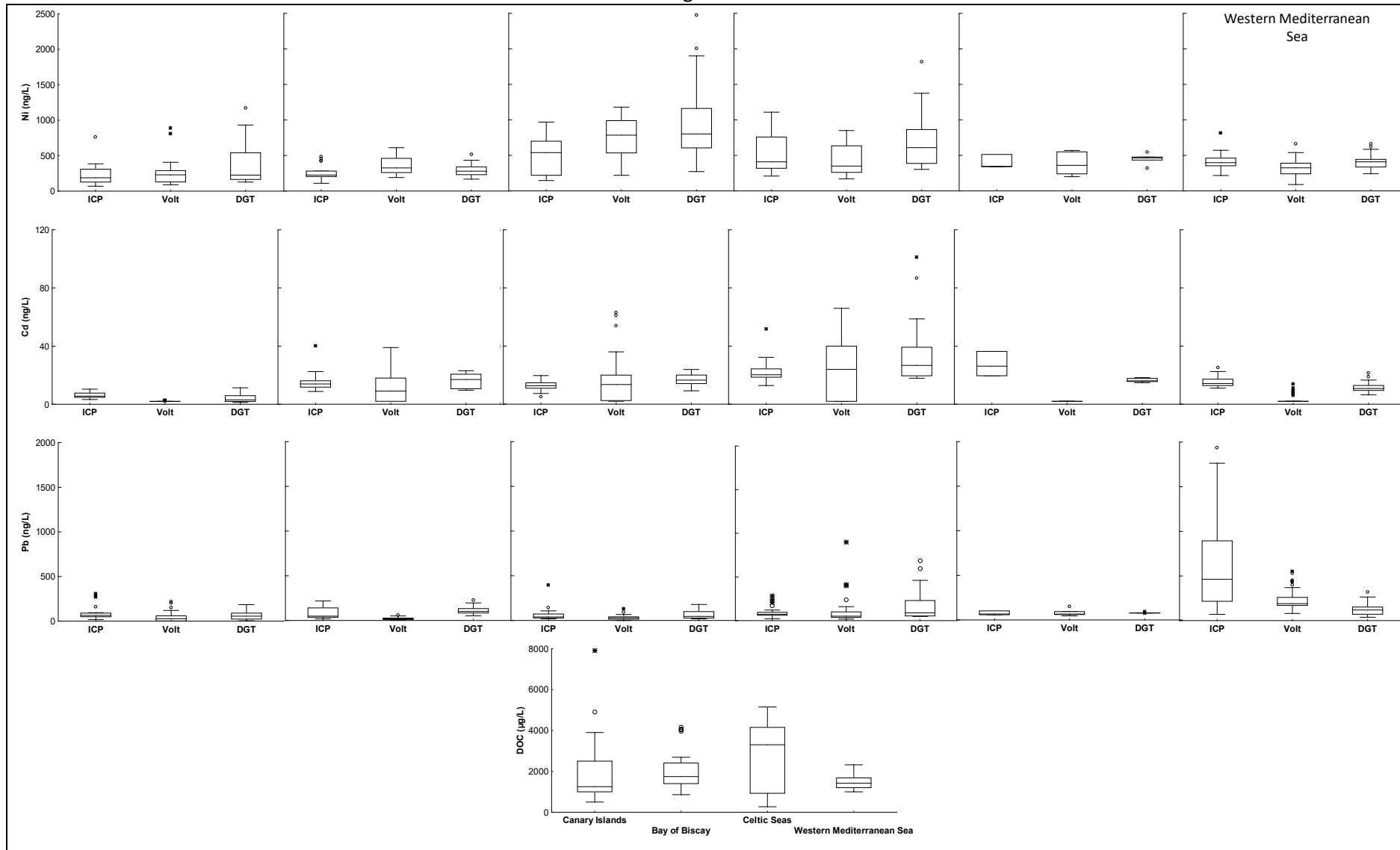
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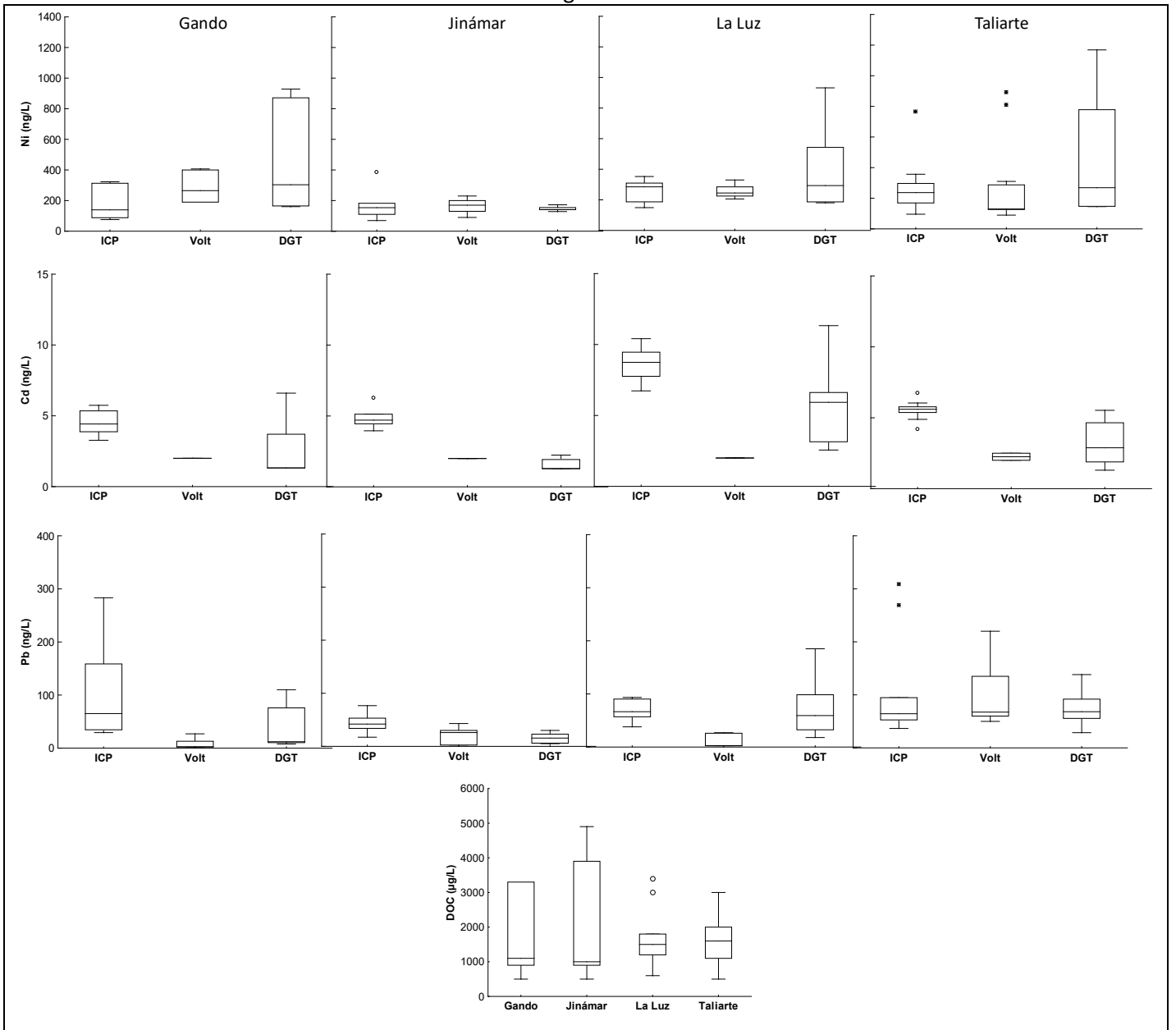
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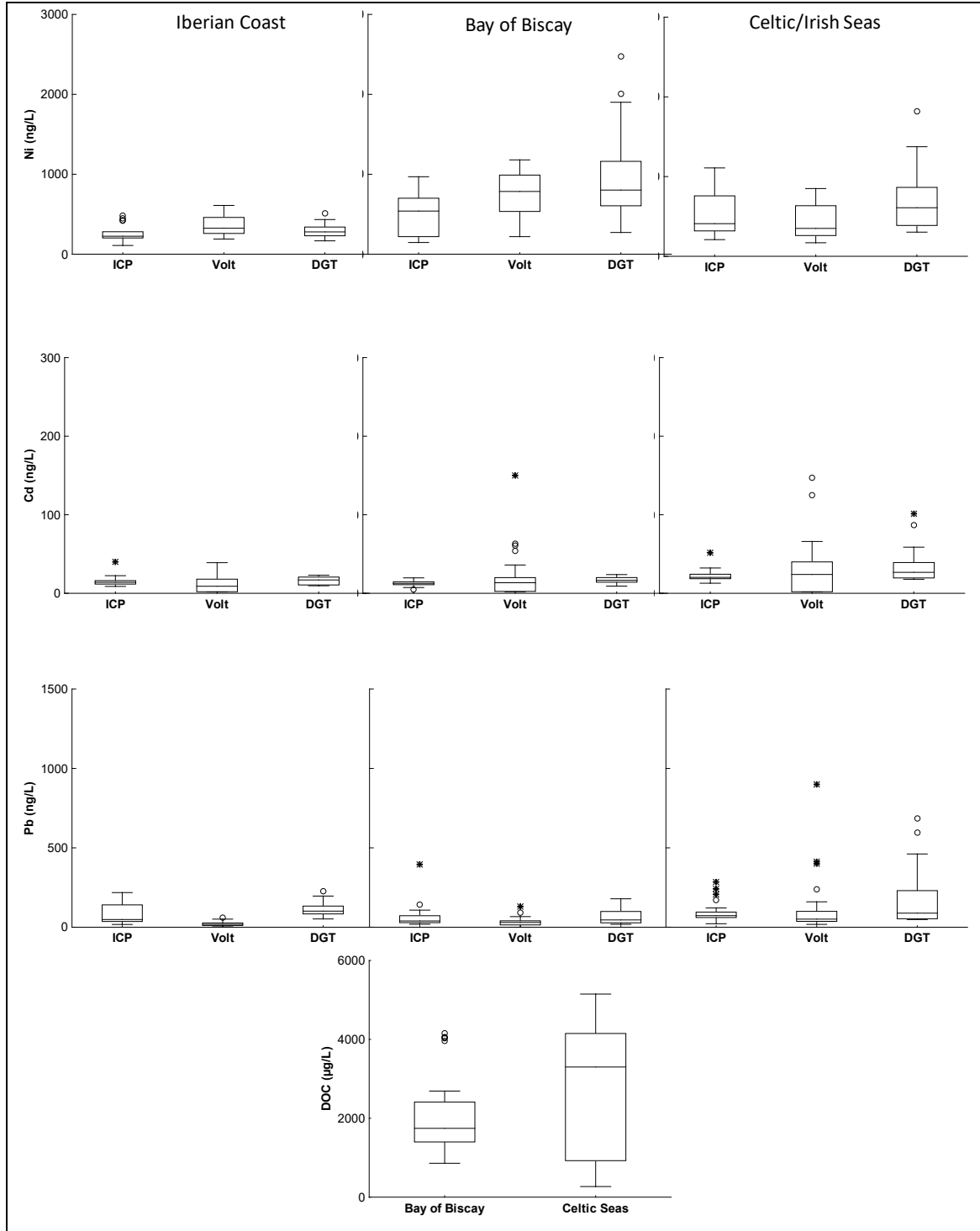


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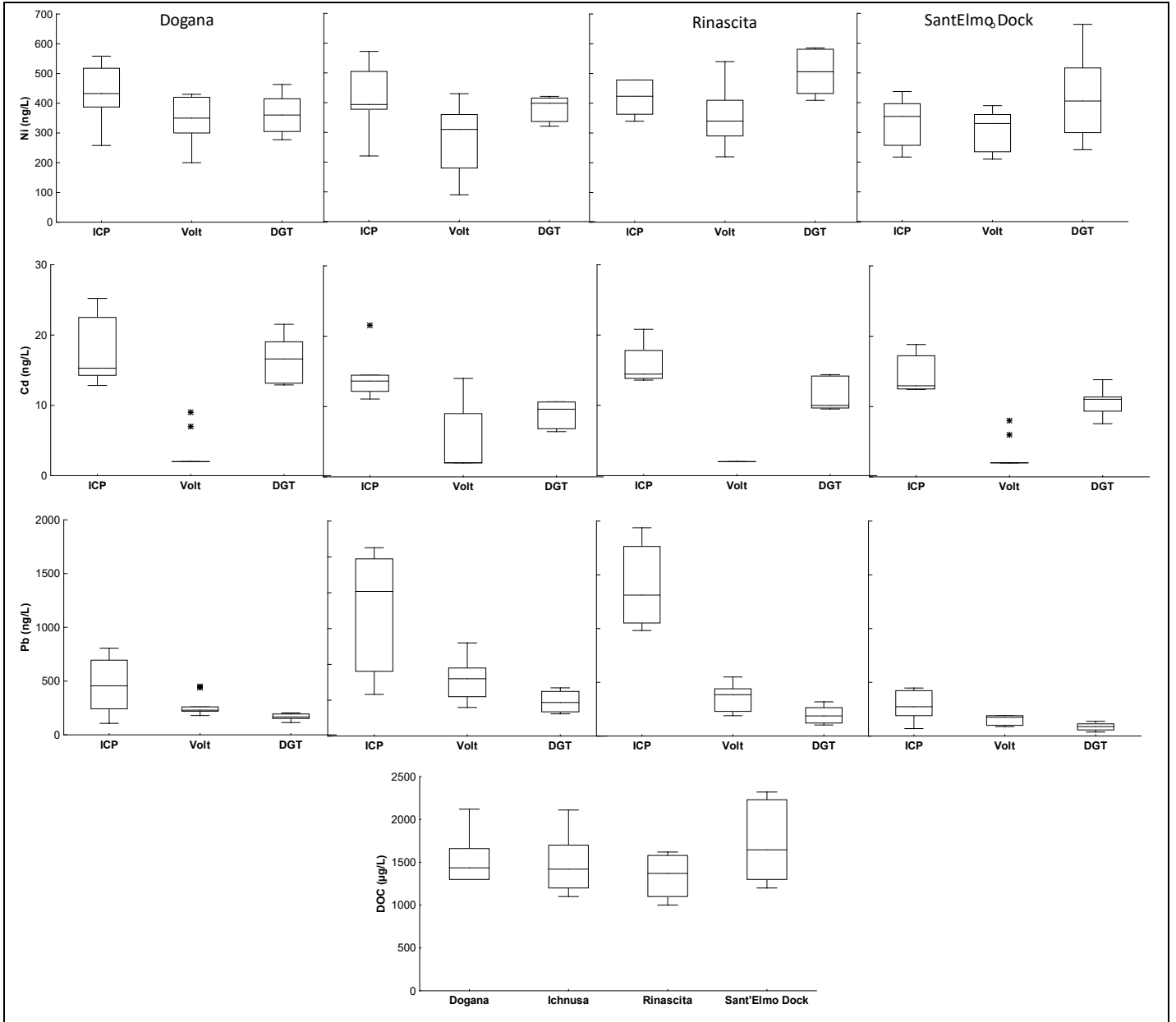
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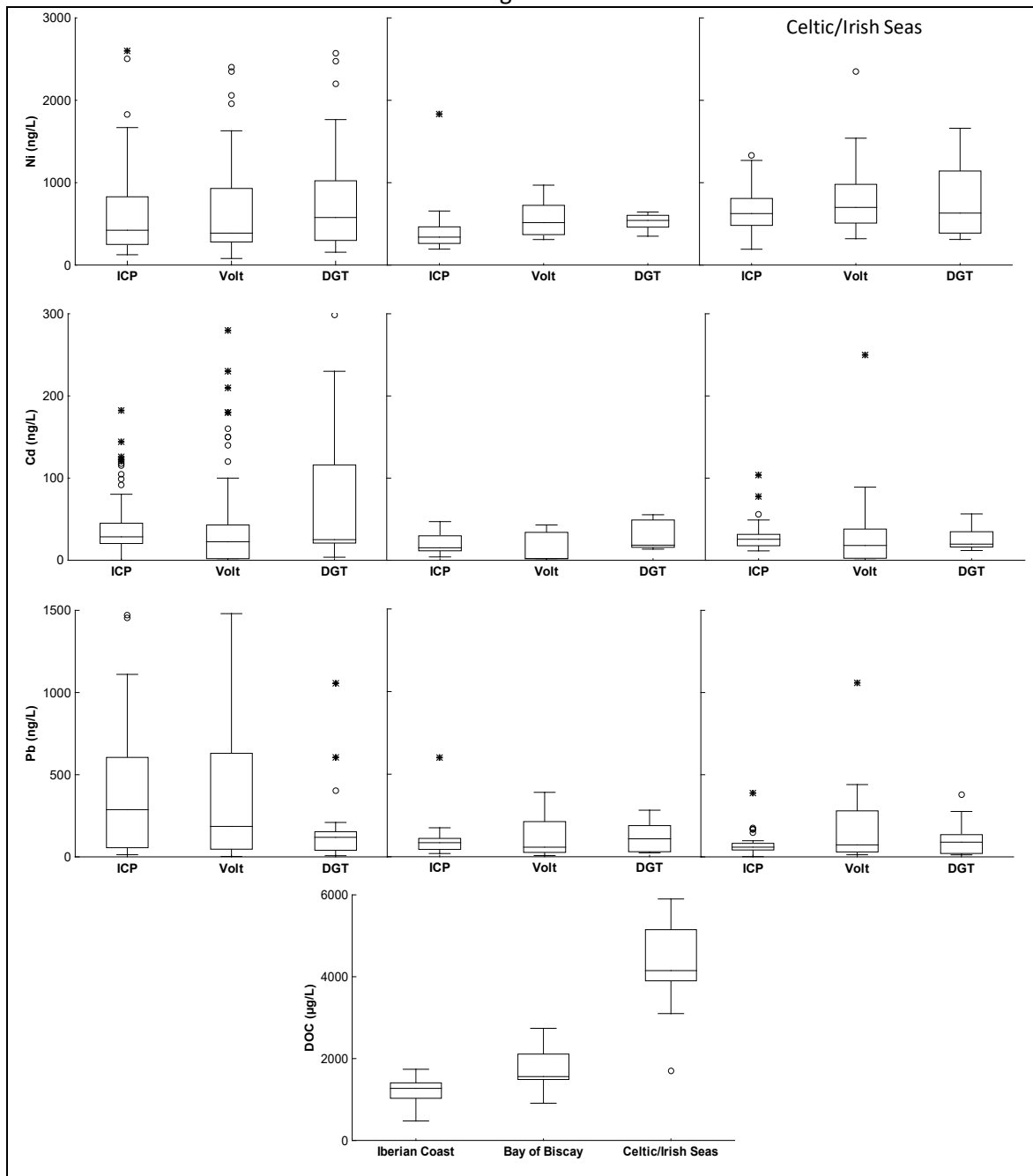
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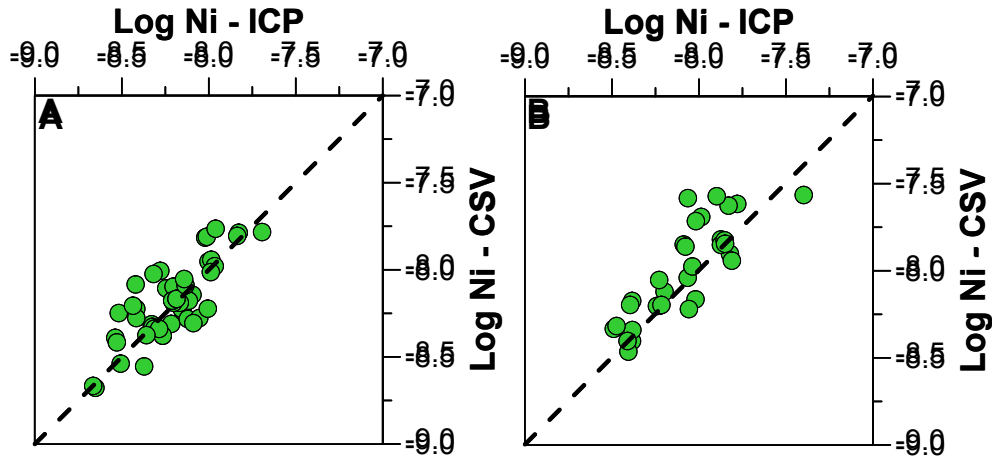
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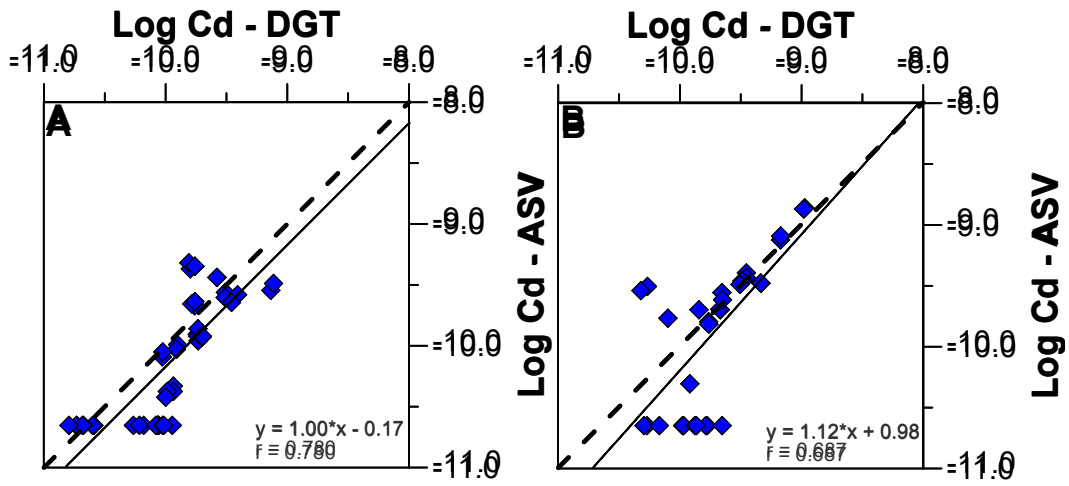
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Figure 6



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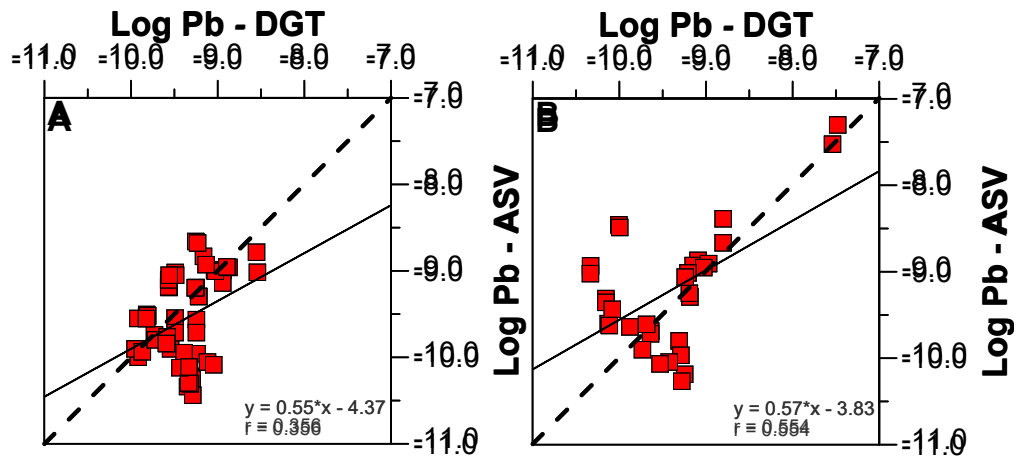


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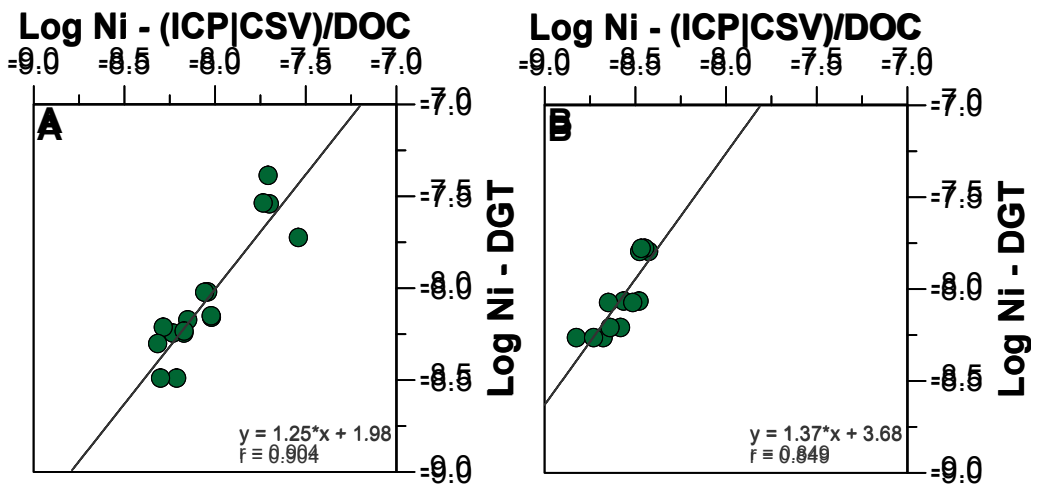
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Figure 8



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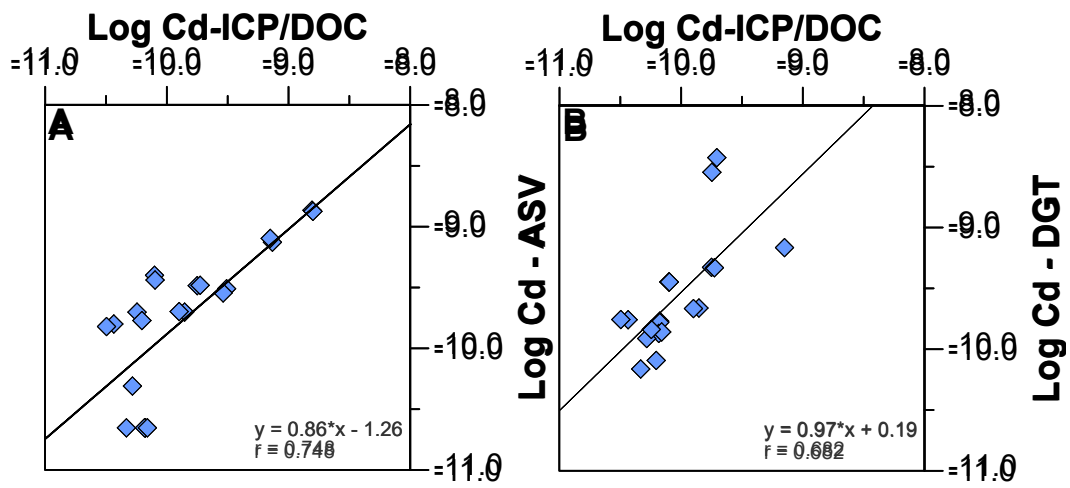
Figure 9



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Figure 10



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70 TABLES -

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Table 1

Country	Ecoregion	Site	Coastal Typology	Geological remarks	Human pressures
ES	Canary Islands	La Luz	Sheltered (wave exposure)	Artificial construction (marina)	Domestic effluents, yachting port
ES	Canary Islands	Jinámar	Sheltered (wave exposure)	Artificial construction	Domestic effluents, Industrial activity, urban runoff
ES	Canary Islands	Taliarte	Sheltered (wave exposure)	Basaltic lava, artificial construction	Fish port area, aquaculture (algae and fish) activities
PT	Iberian Coast	Matosinhos	Exposed	Granitoids, schist, greywacke	Domestic effluents, harbour, oil refinery
PT	Iberian Coast	Oeiras	Moderately Exposed	Schist, greywacke, granitoids, sand, sandstones, carbonates	Agriculture, harbour, industrial activities, shipyard
PT	Iberian Coast	Sesimbra	Moderately Exposed	Schist, greywacke, sandstone, gabbros, metavolcanics	Agriculture, mining activity, shipyard, domestic effluents
FR	Bay of Biscay	Port-en-Bessin	Sheltered	Grey marl and limestone	Fish port area
FR	Bay of Biscay	Saint-Nazaire basin	Sheltered	Granites and gneisses	Harbour - Sampling site located in a basin of the port area. Shipyard, harbour activities
FR	Bay of Biscay	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	Gravelly 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

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Table 2

Country	Ecoregion	River-Estuarine system	Morphology	Tidal regime	Annual mean river flow (m <sup>3</sup> s <sup>-1</sup> )	Estuarine area (km <sup>2</sup> )	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	Morphology, pollutants, 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	*	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	Man-made 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	*	0.34	Urban activity
England	Celtic Sea	Fal estuary	Drowned River Valley	Macrotidal	*	24.8	Inputs from farming, sewage treatment discharges, shellfisheries, boating and historical mining catchment
Northern Ireland	Irish Sea	Belfast Lough	Man-made Port in a Coastal Plain	Mesotidal	*	73.6	Nutrient rich estuarine harbour, passing ships and ferry terminal

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Table 3

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

109 **Metals levels in Transitional and Coastal Waters by ICPMS and Voltammetry**  
 110 **analysis of spot samples and passive samplers (DGT)**

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112 *Supplementary information*

113 Table S1 – Samples collected at each sampling site for analysis by ICPMS, Voltammetry (Volt) and DGT and DGT deploying  
 114 time (days).

Sampling sites	n° samples (ICP)	n° of samples (Volt)	n° samples (DGT)	DGT deploying time (days)
La Luz	9	12	18	2-7
Jinámar	6	5	6	4-7
Taliarte	9	12	12	2-7
Gando	6	6	3	4-7
Oporto	5	10	4	3
Lisbon	6	12	8	5
Sesimbra	6	12	8	5
Port-en-Bessin	10	12	6	4
Saint-Nazaire	10	12	12	4
Saumonard	10	12	6	4
Dublin Bay-2	6	12	6	5
Dublin Bay-4	6	12	6	5
Liverpool	6	6	3	6
Buoy 38A	7	6	6	6-7
Newhaven	3	6	5	4
Molo Dogana	6	10	6	5
Molo Ichnusa	6	10	6	5
Molo Rinascita	6	10	6	5
Sant'Elmo Dock	6	10	12	2-5
Ria of Aveiro	12	24	8	5
Oiartzun	70	70	35	5
Deba	20	24	6	5
Charente estuary	20	20	6	4-7
Aulne Estuary	10	12	3	4
Alexandra Basin - River Liffey	8	11	8	5
River Lee - Lough Mahon	5	8	6	5
River Ballynacorra	5	6	6	5
Fal estuary	20	16	12	4
Belfast Lough	22	12	6	6-7

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117 Table S2 - Certified and measured average concentrations and standard deviations of Ni, Cd and Pb ( $\mu\text{g/L}$ ) in SLEW-3 CASS-  
 118 6 (National Research Council of Canada) using voltammetry and ICPMS.

CRM		Method	Cd ( $\mu\text{g/L}$ )	Pb ( $\mu\text{g/L}$ )	Ni ( $\mu\text{g/L}$ )
SLEW-3	Certified	Voltammetry	0.047 $\pm$ 0.004	0.009 $\pm$ 0.002	1.23 $\pm$ 0.07
	Measured		0.046 $\pm$ 0.003	0.013 $\pm$ 0.002	1.2 $\pm$ 0.1
CASS-6	Certified	Voltammetry	0.0217 $\pm$ 0.0018	0.0106 $\pm$ 0.0040	0.418 $\pm$ 0.040
	Measured		0.023 $\pm$ 0.003	0.014 $\pm$ 0.003	0.420 $\pm$ 0.003
CASS-6	Certified	ICPMS	0.0217 $\pm$ 0.0018	0.0106 $\pm$ 0.0040	0.418 $\pm$ 0.040
	Measured		0.024 $\pm$ 0.0028	0.0103 $\pm$ 0.0015	0.429 $\pm$ 0.035

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