

1 **The relevance of defining trace metal baselines in coastal waters at a regional scale:**
2 **The case of the Portuguese coast (SW Europe)**

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6 **Abstract**

7 The Water Framework Directives aims a reduction in concentration of hazardous substances in
8 the marine environment. Consequently, there is a need to distinguish between
9 anthropogenically influenced metal concentrations from natural background levels. To better
10 achieve this goal in the Portuguese coast, dissolved and particulate trace metal (TM)
11 concentrations along the Portuguese coast were determined in 46 sites distance 1-3 km from
12 the shoreline. Dissolved values ranged within the following intervals: 0.01-0.89 nM for Cd,
13 0.01-3.37 nM for Co, 0.90-45.4 nM for Cu, 3.30-140 pM for Hg, **1.88-15.1 nM for Ni**, 0.01-0.15
14 nM for Pb and 1.40-62.0 nM for Zn. Whereas Cd, Co, Cu, Ni and Zn were enhanced in the
15 southern coast, while Pb values were higher in the central part of the western coast. Mercury
16 concentrations showed punctual increases all along the coast. Values of trace metals in
17 suspended particulate matter varied in a broad range: 36-2902 $\mu\text{mol g}^{-1}$ for Al, 0.10-15.1 nmol
18 g^{-1} for Cd, 1.50-165 nmol g^{-1} for Co, 50.0-990 nmol g^{-1} for Cu, 2.80-76.4 nmol g^{-1} for Hg, **22-**
19 **1471 nmol g^{-1} for Ni**, 10.0-347 nmol g^{-1} for Pb and 416-10981 nmol g^{-1} for Zn. Higher values for
20 Al, Ni and Co were found in the central part of the western coast. However, Cd, Cu, Pb and Zn
21 increased their levels from the north coast towards the central and south areas. The variability
22 of both dissolved and particulate metals appears to be mainly associated with oceanographic
23 conditions and continental inputs at North and central areas of the coast, and in the south
24 coast to geological features rather than to anthropogenic pressures. On the basis of these
25 results, regional baseline concentrations are proposed for the three typologies in Portuguese
26 coastal waters defined under the Water Framework Directive.

27 **Keywords:** dissolved, particulate, metals, coastal waters, SW Europe, upwelling, poleward
28 current, Pyritic Belt.

29 **1. INTRODUCTION**

30 The ocean margin is the critical land-ocean interface. At its inner boundary, coastal waters are
31 characterized by steep physical and chemical gradients although being highly dynamic over
32 short time-scales (Braungardt et al., 1998). Several studies have shown that coastal waters
33 contain higher trace element concentrations than open ocean waters (eg., Bruland and Franks,

34 1983; Kremling, 1985; Kremling and Hydes, 1988; Kremling and Pohl, 1989; Landing et al.,
35 1995; Le Gal et al., 1999; Cotté, 1997). Natural weathering processes at basins of major world
36 wide rivers have been pointed as major supplier of dissolved and particulate material to the
37 ocean (Martin & Meybeck, 1979). The enrichment of coastal waters in trace metals has been
38 ascribed to river discharges (Martin and Whitfield, 1983), atmospheric transport (Martin et al.,
39 1989), and anthropogenic sources (Cotté-Krief et al., 2000). Major internal sources are
40 diagenetic exchanges of trace elements across the water-sediment interface (Klinkhammer et
41 al., 1982; Cotté-Krief et al., 2000) and upwelling of bottom waters (Bruland et al., 1978, van
42 Geen et al., 1990). Multiple factors influence the chemical speciation and water-particle
43 partitioning of trace elements in coastal waters, namely complexation by dissolved organic
44 matter, formation of colloids, precipitation, sorption to particulate phases and biological
45 uptake (Muller, 1996, Morris et al., 1986, Olsen et al., 1982). In addition, accidental episodes of
46 contamination may lead to punctual enhancement of trace-element concentrations. Examples
47 are Aznalcollar mining spill (Grimalt et al., 1999; Achterberg et al., 1999; Elbaz-Poulichet et al.,
48 2001), Erika and Prestige oil spills (Baars, 2002, Amiard et al., 2004, Chiffoleau et al., 2004,
49 Prego and Cobelo-García, 2003, Santos-Echeandia et al., 2005, Santos-Echeandia et al., 2008).
50 The intensity and extension of these contaminating events could not be determined if baseline
51 concentrations are not previously established.

52 Trace-element concentrations in dissolved and suspended particulate matter (SPM) along the
53 Portuguese coast are reported in a few works, covering the south and south-west sectors (van
54 Geen et al., 1997, Cotté-Krief et al., 2000) and nearby estuarine mouths (Caetano and Vale,
55 2003). These works show a high variability in trace metal concentrations with several
56 hypotheses to explain it. However, results with a high spatial resolution of the entire coast are
57 still lacking.

58 The current work reports the Cd, Co, Cu, Hg, Ni, Pb and Zn concentrations at 46 sites sampled
59 in March 2010. Water was sampled within the first 3 km of the entire Portuguese coast, which
60 correspond to the coastal waters defined within the Water Framework Directive. On the basis
61 of these results, the anthropogenic influence and the regional differences are examined, and
62 baseline concentrations of these elements for the three typologies of Portuguese coastal
63 waters are proposed.

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69 2. MATERIAL AND METHODS

70 2.1. Brief description of the Portuguese Coast

71 The Portuguese coast is 943 km long. In the northern west coast, several funnel-shaped rivers
72 discharge to coastal waters, like the Minho, Lima, Douro and Mondego rivers (annual average
73 is $388\pm 444\text{ m}^3\text{ s}^{-1}$, $74\pm 64\text{ m}^3\text{ s}^{-1}$, $650\pm 300\text{ m}^3\text{ s}^{-1}$, $2\pm 3\text{ m}^3\text{ s}^{-1}$ respectively, <http://www.inag.pt>)
74 (Figure 1a). Higher freshwater discharges in winter induce stratification of the coastal waters
75 (Moita, 2001). Conversely, the major rivers in the southwest coast, Tagus and Sado rivers
76 (annual average is $324\pm 436\text{ m}^3\text{ s}^{-1}$, $11\pm 15\text{ m}^3\text{ s}^{-1}$ respectively, <http://www.inag.pt>) end into
77 large estuaries. Their morphology favors the trapping of river-borne material inside the
78 estuaries under moderate to low flow conditions (Figure 1a). The Mira and Guadiana rivers
79 (SW and S coast) have lower discharges ($3\pm 3\text{ m}^3\text{ s}^{-1}$ and $37\pm 59\text{ m}^3\text{ s}^{-1}$, respectively,
80 <http://www.inag.pt>) and estuaries consist of single channels. SPM concentration and Al
81 concentration presented by Caetano and Vale (2003) evidenced the contrasting north-south
82 influence of river inputs to the Portuguese coastal waters. Episodically, some of these estuaries
83 receive abrupt quantities of freshwater and land-derived contaminants (Vale, 1990; Martins et
84 al., 2005; Caetano and Vale, 2003; Quental et al, 2003). The geology of the north Portugal river
85 basins is dominated by granitic complexes while the south is greatly influenced by the Iberian
86 Pyritic belt (Munha et al., 1986) (Figure 1b), which is admittedly the largest sulphide
87 mineralization in the world (Leistel et al., 1998). Weathering and mining activities have led to
88 extremely high metal concentrations and acidity (pH <3) in the rivers crossing this belt
89 (Delgado et al., 2009). **The most densely populated areas in the Portuguese coast are Porto,**
90 **Aveiro, Lisbon and Faro (Figure 1b) while the industrialized regions are located in the north**
91 **part (Aveiro-Porto) and close to the Lisbon area.**

92 Surface waters of the Iberian coast change circulation according to the season (Wooster et al.,
93 1976; Frouin et al., 1990; Barton, 1998), being, in autumn-winter, northwards to the Bay of
94 Biscay in France, and in spring-summer, it becomes weaker and reverses due to the North
95 trade wind regime (Fiuza, 1983). This southward current promotes cooling and wind-induced
96 upwelling along the shelf break (Fiuza, 1983; Abrantes and Moita, 1999). The Portuguese
97 continental shelf is crossed by several canyons influencing the water circulation (Fiuza, 1983).
98 The Nazaré canyon cuts-cross the NW continental shelf and has its head located close to the
99 present-day shoreline. Northern from this canyon, coastal waters are characterized by a
100 homogeneous upwelling of **ENACW (Eastern North Atlantic Central Water)** along the shore
101 (Fiuza, 1983). From Lisbon to Cape Sines, the upwelling is affected by several canyon-systems

102 like the Cascais, Lisbon and Setúbal canyons. South of the Cape Sines until Cape S. Vicente, the
103 upwelling structure becomes more regular but is affected by warmer and saltier offshore
104 surface waters (Moita et al., 2003). Finally, the southern Portuguese coast is controlled by a
105 cyclonic gyre circulation in winter that turns anticyclonic in summer (Batteen et al., 2000;
106 Mauritzen et al., 2001; García-Lafuente et al., 2006) affecting the entire Gulf of Cadiz. In
107 addition, several studies have referred to a coastal current of warm water that flows westward
108 near the shore, reaching Cape San Vicente and proceeds even northwards (Fiúza, 1983; Relvas
109 and Barton, 2002; García-Lafuente et al., 2006) reaching the Spanish NW coast. The presence
110 of eddies derived from the Mediterranean Sea has been reported offshore the south coast of
111 Portugal (Brogueira et al., 2004).

112 Within the Water Framework Directive three typologies for the Portuguese coast have been
113 defined (Bettencourt, 2004; Ferreira et al., 2005): A5 – Mesotidal exposed Atlantic coast, from
114 the Minho estuary until Cape Carvoeiro; A6 – Mesotidal moderately exposed Atlantic coast,
115 between this cape and the Ponta da Piedade; and A7 – Mesotidal sheltered Atlantic coast, until
116 the Guadiana estuary.

117 **2.2. Sampling and samples pretreatment**

118 The sampling campaign along the Portuguese Coast (Fig. 1) was performed **between the 16th-**
119 **22nd March 2010** on board the R/V Noruega; 46 surface water samples were collected from
120 Minho to Guadiana River (Figure 1) at 1-3 km distance from the shoreline. **An important**
121 **precipitation in Portugal (115 mm) was measured during the first two weeks of March in**
122 **comparison with the ancillary data registered for this period of the year (INAG). Consequently,**
123 **high river flows are expected. In addition, favorable upwelling indexes (Figure 2) were**
124 **measured during the first couple of days (CCMP: [http://podaac-
126 www.jpl.nasa.gov/datasetlist?search=ccmp](http://podaac-
125 www.jpl.nasa.gov/datasetlist?search=ccmp)) while the sampling cruise was collecting samples**
127 **between Carvoeiro Cape and Minho river mouth (Figure 1).** Surface samples (0.5 m below the
128 surface) were pumped into a class-100 laminar flow bench located in the lab onboard with the
129 aid of a tow-fish to be filtered through 0.45 µm acetate cellulose syringe filters (Millipore). In
130 addition, a depth profile (DP, 1800 m) was sampled north to the Tagus estuary using a Kevlar
131 cable and **Teflon coated** Niskin bottles with external closure (Fig. 1). After filtration, around
132 100 mL of the water was acidified to pH≈2 with HCl Trace Select (Fluka) for TMs analysis while
133 10 mL were stored in pre-cleaned HDPE vials and frozen at -20°C pending nutrient analysis. In
134 the case of mercury, an aliquot of each sample was directly transferred to a previously
decontaminated quartz flask while another aliquot was filtrated with a 0.45 µm to a previously

135 decontaminated quartz flask (around 40 mL) and preserved with a bromide monochloride
136 (BrCl) solution (EPA Method 1631). Furthermore, between 1 and 2 L of water were collected
137 for SPM quantification. Water was filtered using acid-washed polycarbonate filter holder
138 through acid cleaned acetate cellulose Nuclepore filters (0.45 μm and 47 mm). Filters were
139 placed inside Petri dishes and frozen pending particulate trace elements analysis. Finally,
140 around two liters of water were filtered through 0.7 μm GFF filters for chlorophyll
141 measurements. Samples for chlorophyll *a* were kept at dark conditions under refrigerated
142 environment and were filtered through a filtration slope as soon as possible. **Samples were**
143 **frozen at -18°C during the cruise and immediately analyzed as returned to the laboratory. The**
144 **maximum storing time was five days.**

145

146 **2.3.Measurement of master variables**

147 A previously calibrated multiparametric probe and a Seabird 911 plus CTD were used for direct
148 measurement of temperature, salinity, dissolved oxygen and pH in surface waters from the
149 vessel. **The pH was measured with a glass electrode (Mettler) calibrated with the following**
150 **Merck buffer solutions 4.0 \pm 0.1, 7.0 \pm 0.1 and 10.01 \pm 0.1. The oxygen was not measured on CTD**
151 **but in a Yellow Spring Instrument model 605QS probe calibrated with a 0% oxygen solution**
152 **and with a 100% oxygenated solution according to the YSI procedure. The errors for**
153 **temperature, salinity, pH, dissolved oxygen and SPM are 0.1 %, 0.1%, 0.1 units, 2.0 % and**
154 **1.0%.**

155 **2.4.Analytical procedure**

156 Dissolved (TMs) concentrations were determined by means of stripping voltammetry using a
157 Metrohm797 VA computrace equipped with a hanging mercury drop electrode (HMDE) as the
158 working electrode, Ag/AgCl as the reference electrode, and a Pt wire as the counter-electrode.
159 Prior to determination, samples were UV-digested for 1 h using an UV-Digestor equipped with
160 a high-pressure mercury lamp of 200 W (Achterberg and Van Den Berg, 1994). The
161 simultaneous determination of Cd, Cu, Pb and Zn in the dissolved phase was carried out using
162 the method of standard additions by differential pulse anodic stripping voltammetry (DPASV)
163 (Gardiner and Stiff., 1975) while the simultaneous determination of Co and Ni was performed
164 by Adsorptive Cathodic Stripping Voltammetry (ACSV) (Santos-Echeandía., 2011). The solution
165 was deaerated by purging (5 min) with nitrogen. Voltammetric parameters for the DPASV
166 method were: deposition 300-900 s at -1.1 V whilst stirring; 10 s quiescence at -1.1V;
167 potential scan using the differential pulse modulation: pulse amplitude of 50 mV, a pulse

168 duration of 40 ms, a pulse frequency of 5 s^{-1} and a scan rate of 20 mV s^{-1} , from -1.1 to 0 V. In
169 the case of the ACSV method, voltammetric parameter were: deposition 30-120 s at -0.35 V
170 whilst stirring; 10 s quiescence at -0.05V; potential scan using the differential pulse
171 modulation: pulse amplitude of 50 mV, a pulse duration of 40 ms, a pulse frequency of 5 s^{-1}
172 and a scan rate of 20 mV s^{-1} , from -0.05V to -1.2 V.

173 One blank was run every five samples and results were blank-corrected. The accuracy of the
174 analytical procedure was assessed by the analysis of two different certified reference materials
175 (CRMs) (CASS-4 and SLEW-3), obtaining good agreement with the certified concentrations
176 (Table 1). The detection limits of the analytical procedure, defined as three times the standard
177 deviation of the blanks, were 0.4 nM for Ni, 0.020 nM for Co, 0.5 nM for Zn, 0.7 nM for Cu,
178 **0.010 nM for Pb and 0.010 nM for Cd**. The precision of the method measured as relative
179 standard deviation was: 5-10% for Ni (at 6 nM), 3-6% for Co (at 0.5 nM), 5-10% for Zn (at 20
180 nM), 5-10% for Cu (at 10 nM), 5-10% for Pb (at 300 pM) and 25-40% for Cd (at 60 pM). In the
181 case of total dissolved Hg, prior to analysis by Cold Vapour Atomic Fluorescence Spectroscopy
182 (CV-AFS) each filtered sample was sequentially reduced with $\text{NH}_2\text{OH}\cdot\text{HCl}$ to destroy the free
183 halogens and with stannous chloride (SnCl_2) to convert Hg(II) to volatile Hg(0) (EPA Method
184 1631). Accuracy and precision were determined after preparing different stock solutions of
185 Hg^{2+} from 1000 ppm Merck stock solution in 2% HNO_3 . These solutions were prepared and
186 measured every 2 samples. Detection limit and precision error were 0.5 pM and 4.0%
187 respectively ($p < 0.05$). **Procedural blanks were prepared the same way as samples with Milli-Q**
188 **water instead of water samples and using the same reagents. The fluorescence signal of the**
189 **blanks was always lower than detection limit.**

190 Filters charged with SPM were completely mineralized with 1 cm^3 of HF (40%) and 1 mL of
191 Aqua-Regia (HCl-36%: HNO_3 -60%; 3:1) in closed Teflon bombs at $100 \text{ }^\circ\text{C}$ during 1 h. The bomb
192 contents were evaporated to near dryness in Teflon vials, taken up with HNO_3 , heated for 20
193 min at $75 \text{ }^\circ\text{C}$ and diluted to 50 mL with Milli-Q water. Concentrations of Cd, Co, Cu, Ni, Pb and
194 Zn were determined using a quadrupole ICP-MS (Thermo Elemental, X-Series) equipped with a
195 Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. A 7-points calibration
196 within a range of $1\text{--}100 \text{ } \mu\text{g L}^{-1}$ was used to quantify metal concentration. Coefficients of
197 variation for metal counts ($n=5$) varied between 0.5 and 2%. The precision and accuracy of
198 each metal concentration measurements were determined through repeated analysis of CRMs
199 (MESS2 and PACS2), using Indium as internal standard, were 1–4% and 2–5%, respectively.
200 Procedural blanks always accounted for less than 1% of the total metal concentrations in

201 samples. Mercury concentration in the particulate matter was calculated by subtraction of the
202 total mercury determined in filtered water samples from total mercury concentrations in
203 unfiltered samples. This methodology is frequently used for the determination of particulate
204 Hg and methyl mercury in aquatic systems. The result was then multiplied by the
205 concentration of SPM to obtain particulate mercury concentration in $\mu\text{g/g}$.

206 Finally, chlorophyll a was determined by the spectrophotometer method (Lorenzen, 1967)
207 while the ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (HPO_4^{2-}) and silicate
208 (H_4SiO_4) were determined using a Skalar autoanalyser following the methodology described by
209 Hansen and Grasshoff (1983). The detection limits were $0.01 \mu\text{M}$ for nitrate, $0.02 \mu\text{M}$ for
210 nitrite, $0.07 \mu\text{M}$ for ammonium, $0.03 \mu\text{M}$ for phosphate and $0.05 \mu\text{M}$ for silicate. Dissolved
211 inorganic nitrogen (DIN) was calculated as the sum of ammonium, nitrate and nitrite.

212 **2.5. Statistics**

213 Prior to statistical analyses, the log-normal of partition coefficient of each metal ($\log K_D$ (Me))
214 were tested for normality and equality of variances. Non-compliance with parametric ANOVA
215 assumptions led to employment of the Kruskal-Wallis H and Mann-Whitney non-parametric
216 tests to evaluate the existing differences between $\log K_D$ registered from samples in the west
217 Portuguese coast and south coast. The significance for statistical analyses was always $p < 0.05$.
218 The statistical analyses were performed using STATISTICA 6 (Statsoft).

219

220 **3. RESULTS**

221 **3.1. Oceanographic conditions and master variables**

222 Figure 3 shows the satellite images with the average conditions of temperature, salinity and
223 chlorophyll a obtained during the water sampling period (16th-22nd March). Temperature
224 ranged from 12°C , at the north coast of Portugal to 20°C close to Guadiana (south-east coast).
225 Salinity ranked from 34 to 37 with lower values in areas adjacent to the estuaries of Douro
226 (27), Tagus (33) and Guadiana (29). Chlorophyll a ranged between $1\text{-}10 \text{ mg m}^{-3}$, with higher
227 values at the north coast, between Minho and Mondego, in the Sado area and close to Santa
228 Maria Cape. The lowest values were observed between Cabo Carvoeiro and Tagus estuary
229 mouth.

230 Figure 4 shows the registered values of S, T, chl a , dissolved oxygen and SPM concentration.
231 Salinity, T and chl a were within the intervals of the satellite image data despite their broader
232 spatial resolution. Dissolved oxygen concentrations varied between 5.5 and 8.4 mg L^{-1} with
233 higher values at the north coast of Portugal (Figure 4d). Saturation was in general above 80%,

234 with the exception of areas located between the mouth of the Mondego and Tagus estuary
235 (68-79%). SPM concentration varied between 0.60 and 14.4 mg L⁻¹ (Figure 4e). The higher
236 values found in the proximities of the Douro, Ria of Aveiro, Tagus and Ria Formosa reflect the
237 influence of the plumes of the respective estuaries and lagoon. The lower values were
238 registered between Mondego and Cabo da Roca, and from Sado to S. Vicente Cape, which
239 correspond to the areas with low river discharges (Fig.1).

240 **3.2.Nutrients**

241 Figure 5 shows dissolved inorganic nitrogen (DIN), phosphate and silicate concentrations in the
242 surveyed sites. The distribution pattern is characterized by pronounced differences among
243 sites. Phosphate concentrations in the area adjacent to the Tagus estuary were up to 50 times
244 (3.1-15 μM) above the mean of all the other sampling sites (0.1-0.5 μM). The pattern found for
245 DIN displayed an irregular variation. Despite the higher values in the Tagus adjacent area (4.0-
246 17 μM), enhancements were also registered in other sites along the coast (0.5-4.0 μM). Silicate
247 distribution was also variable with concentrations varying between 0.06 and 11.0 μM. Unlike
248 the other nutrients, the highest values of silicate were not found nearby the Tagus estuary.

249 **3.3.Dissolved trace elements**

250 Figure 6 presents the concentration intervals of Cd, Co, Cu, Hg, Ni, Pb and Zn in the dissolved
251 fraction of surface waters from the 46 surveyed sites. Three distribution patterns can be
252 discerned along the coast. Levels of dissolved Cd (0.01-0.89 nM), Cu (0.90-45.0 nM) and Zn
253 (1.40-62.0 nM) were much higher in the south-western and southern coastal waters (WFD type
254 A6 and A7, respectively) than north of the Tagus (WFD type A5 and part of A6). Cobalt (0.03-
255 3.40 nM) and Ni (1.90-15.0 nM) showed a similar pattern to those elements, although with
256 enhanced values in the coastal areas nearby the Minho and Lima. Enhanced Hg concentrations
257 were registered in several sites (5.00-140 pM) namely near the mouth of certain estuarine
258 systems (i.e. Minho, Cavado, Tagus, Ria Formosa and Guadiana, Figure 1). Lead concentrations
259 (0.01-0.15 nM) were higher in the central part of the Portuguese coast, particularly adjacent to
260 Sado and Tagus areas, and lower levels at the southern coast. Depth variation of temperature
261 and salinity in the offshore station is shown in Figure 7. The profiles evidenced that the upper
262 400 m of the water column is characterized by North Atlantic Central Water. Enhanced values
263 of salinity and temperature between 800 and 1200m pointed to a Mediterranean Water mass
264 (MW). Deeper the cold and less saline North Atlantic Deep Water mass was found. Higher
265 concentrations of Cu and Pb were registered at surface waters than in deeper waters.
266 Otherwise, levels of Cd, Zn, Ni and Co increased with the depth with a maximum in the MW.

267 **3.4. Particulate trace elements**

268 Figure 8 presents the interval concentrations of Al, Cd, Co, Cu, Hg, Ni, Pb and Zn in the SPM
269 along the Portuguese coast. A broad range of particulate Al ($36\text{-}2902\ \mu\text{mol g}^{-1}$) was found along
270 the coast, with higher values from Carvoeiro Cape to Sines Cape and some hotspots closer to
271 Douro, Guadiana and Ria Formosa. Lower Al concentrations were found in the south-west and
272 south coasts ($<200\ \mu\text{mol g}^{-1}$). Cobalt ($1.50\text{-}170\ \text{nmol g}^{-1}$) and Ni ($22\text{-}1475\ \text{nmol g}^{-1}$) showed a
273 similar distribution pattern to Al. Cadmium ($0.03\text{-}15.0\ \text{nmol g}^{-1}$), Cu ($50.0\text{-}600\ \text{nmol g}^{-1}$), Pb
274 ($10.0\text{-}300\ \text{nmol g}^{-1}$) and Zn ($530\text{-}11000\ \text{nmol g}^{-1}$) exhibited a different distribution pattern
275 characterized by lower concentrations in the SPM from the northern coastal waters than from
276 the south of Carvoeiro Cape. Higher values were found in particles collected in the proximities
277 of the Sado and Tagus estuaries. Mercury ($4.0\text{-}80\ \text{nmol g}^{-1}$) showed an irregular distribution
278 with several punctual high values along the coast, mainly near estuarine systems (i.e. Minho,
279 Cavado, Tagus, Ria Formosa and Guadiana, Figure 1).

280 **3.5. Element/Al molar ratios**

281 Figure 9 shows the trace-element/Al molar ratios, as commonly used in order to minimize the
282 particle nature and size effect (Windom et al., 1989; Loring, 1990; Pohl et al., 2004). This
283 representation highlights the trace element enrichment observed in the suspended particles
284 from the southwest and south coast. Ratios pointed to enrichment of all determined elements
285 except Co in areas adjacent to the Tagus and Sado estuaries. In addition Cu, Ni, Zn Cd, Pb and
286 Hg showed high ratios to Al near Sines Cape and southern coast. For most of the determined
287 elements, ratios increased between the Ria Formosa and the Guadiana, being Co the most
288 remarkable case.

289 **3.6. Dissolved-Particle interactions (K_D)**

290 Assuming quasi-equilibrium conditions between the water and the suspended particulate
291 matter, the partitioning of trace element between dissolved and particulate fractions can be
292 estimated by the distribution coefficient, defined as $K_D = [P]/[D]$ (L kg^{-1}), where [P] represents
293 the particulate trace element concentration (w/w) and [D] the dissolved trace element
294 concentration (w/v) (Millward and Turner, 1995). Calculated mean values and standard
295 deviation of $\log K_D$ were: 4.1 ± 0.5 (Cd), 5.2 ± 0.7 (Co), 4.7 ± 0.5 (Cu), 6.1 ± 0.6 (Hg), 4.5 ± 0.4 (Ni),
296 6.1 ± 0.6 (Pb) and 5.2 ± 0.4 (Zn). The decreasing sequence was $\text{Hg}\approx\text{Pb}>\text{Zn}>\text{Co}>\text{Cu}>\text{Ni}>\text{Cd}$, within
297 an interval of two orders of magnitude for $\log K_D$. Although the coefficient variation of the
298 mean was in general lower than 15%, $\log K_D$ of Ni, Zn, Cd, Co and Cu were significantly ($p<0.05$)
299 lower at the south coast (WFD type A7) than at the rest of the Portuguese coast (WFD types A5

300 and A6). Conversely, the $\log K_D$ (Pb) showed an opposite trend being significantly ($p < 0.05$)
301 higher at the south coast. No significant differences ($p > 0.05$) were found for $\log K_D$ (Hg).

302

303 4. DISCUSSION

304 Despite the discharge of several rivers on the A5 typology coastal waters, the current work
305 shows low concentrations of nutrients and trace elements, as observed in previous works in
306 the NW coast of Iberian Peninsula (Santos-Echeandia et al., 2005; Santos-Echeandia et al.,
307 2009) or North Atlantic Ocean waters (Landing et al. 1995, Saager et al. 1997, Ellwood and van
308 den Berg 2001, and Cotté-Krief et al. 2002). This pattern points to minor contribution of rivers
309 to the dissolved trace elements composition of near-shore coastal waters, **probably due to the**
310 **presence of upwelling events that would retain the continental waters in the mouth of the**
311 **estuaries**. A similar pattern was found for trace elements in A6 coastal waters (Table 2).
312 Dissolved inorganic nitrogen and phosphate increased clearly near the Tagus estuary and
313 northwards presumably as a result of urban and industrial pressures from the Lisbon
314 metropolitan area (≈ 5 million inhabitants, GeoNames). Conversely, in the A7 typology (south
315 Portuguese coastal waters) trace metal concentrations rise up 30 times the values found for A5
316 and A6. These values were similar to those reported in south Spanish shelf waters (van Geen
317 1991; Cotté-Krief et al., 2000; van Geen et al., 1997). It is noteworthy that element
318 concentrations all over the coast, in both dissolved and particulate fractions, varied up to 2-3
319 orders of magnitude. These intervals may be related to the narrow band where surface waters
320 were sampled, between the coastline and closure line of coastal waters defined in Water
321 Framework Directive (Ferreira et al, 2005). The calculated values of $\log K_D$ are comparable to
322 the ones reported for other coastal systems (Balls, 1989 and references therein), suggesting
323 that affinity of trace elements to suspended matter is of major importance on the water-
324 particle partitioning. The adsorption tendency has been related to the first hydrolysis constant
325 of the element (Stumm and Morgan, 1981). Previous studies have shown the tendency of
326 dissolved lead to adsorb onto suspended particles decreasing the concentrations in solution
327 (Windom et al., 1989; Balls et al., 1994; Chiffoleau et al., 1994; Chiffoleau et al., 1999; Cobelo-
328 García et al., 2005). However, cadmium showed the lowest $\log K_D$, **probably due to its**
329 **association with chloride ions (Comans et al., 1988)** and to its strong association with organic
330 matter (Bruland, 1992). According to this author at least 70 % of dissolved Cd in surface waters
331 is in the form of organic complex. Strong Cd complexation may avoid binding to particles and
332 thus diminishing $\log K_D$ values. Despite of these processes, most $\log K_D$ of the determined

333 elements, except Pb, were lower at the south coast of Portugal. Concentrations, element/Al
334 ratios and K_D may thus reflect small-scale spatial variation related to different coastal
335 morphology and associated oceanographic processes, as well as river inputs.

336 The presumed geographical pattern observed along the Portuguese coast is better illustrated
337 by the application of a principal component analysis (PCA) with the results presented in Figure
338 10. The southern stations, presenting enhanced metal concentrations, are projected
339 separately from the stations of the northern region. Moreover, the samples located in the river
340 or estuaries outflows are also well grouped (Figure 10). Attending to this, three different
341 features that take control over trace metal distribution can be distinguished along the coast.

342 **4.1. Upwelling conditions**

343 The lower temperatures at the northern coastal waters are related to the occurrence of
344 upwelling conditions during the campaign confirmed by the positive upwelling indexes
345 measured (Figure 2), which is in line with recurrent episodes registered in this season at this
346 region (Wooster et al., 1976; Fiuza, 1983; Relvas et al., 2007). Although nutrient
347 concentrations did not mirror the upwelling of nutrient enriched waters, chlorophyll *a*
348 presented enhanced values presumably due to the consumption of nutrients advected from
349 bottom waters. These results are in line with the exceptionally high chlorophyll values
350 registered in winter (Abrantes and Moita, 1999). In addition, typical spring chained-like
351 diatoms blooms composed mainly by *Chaetoceros decipiens*, *Detonula pumila*, *Dytilum*
352 *brightwelli* and *Lauderia annulata* have been found in the A5 area (Moita, T., personal
353 communication) associated with the higher values of chlorophyll *a* what would reinforce the
354 upwelling hypothesis.

355 Dissolved Co, Hg, Ni and Pb were enhanced in surface waters from the northern Portuguese
356 coast adjacent to rivers Minho, Lima and Douro. Nevertheless it is uncertain whether these
357 increases are attributed to upwelling, local feature or anthropogenic inputs. However, Hg and
358 Pb are probably associated to river inputs since their concentrations enhance close to the
359 estuaries. Otherwise, Co and Ni could be related to upwelling processes. In fact, depth profiles
360 evidence enhanced levels of these elements with depth (Figure 7). In addition, Pb and Cu
361 concentrations decreased in the first 200 m of the water column (Figure 7). These results
362 pointed that upwelling will result in the Co and Ni enrichment and in diminishing of Pb
363 concentrations. It has been reported for the Iberian Atlantic coast either a decrease in
364 dissolved Cu, Pb and Zn, or an enhancement in Cd, Ni and Co during upwelling events
365 happened (Cotté-Krieff et al., 2000; Santos-Echeandia et al., 2009). Increased metal

366 concentrations have been observed in other regions under frequent upwelling events (e.g., the
367 Celtic Sea: Cotté-Krief et al., 2002; San Francisco Bay: van Geen and Luoma, 1993).

368 **4.2. River/estuarine inputs**

369 The Portuguese coastline contains various morphological irregularities constituted by capes,
370 funnel-shaped estuaries, bays, broad estuaries, and coastal lagoons with permanent
371 connection to the sea. The plumes of the Douro, Tagus and Guadiana rivers were marked by
372 the salinity decrease, unlike freshwater discharges by estuaries of small rivers were not clearly
373 discerned in the salinity distribution along the coast at first glance. The pronounced increases
374 of DIN and phosphate concentrations evidence the influence of Tagus discharges on the
375 nearby coastal area. Two factors may have concurred to this pattern: the large water volume
376 of the estuary exchanged with the sea over semi-diurnal tidal scales; and the naturally turbid
377 water of the estuary (Vale and Sundby, 1987) inducing a light limitation to convert nutrients
378 into primary production. The Douro signal was minor and the input from other estuaries was
379 poorly marked. The silicate distribution was less clear with several peaks concentrations along
380 the coast. The estuarine water input into the coastal waters was poorly marked by metal
381 concentration distributions, both in dissolved and particulate forms. Although the dissolved
382 fraction of several elements presented enhanced concentrations in areas nearby the Minho,
383 Douro and Tagus (eg., Co, Hg, Ni, Pb) elevated values were also registered in other areas of the
384 coast far from the direct influence of river inputs. Strong negative correlations ($n=34$) between
385 salinity and dissolved metal concentrations have been found for: Ni ($R^2=0.82$); Co ($R^2=0.79$); Cu
386 ($R^2=0.65$); Cd ($R^2=0.62$) and; Zn ($R^2=0.52$). This suggests the influence of freshwater inputs that
387 may superimpose the role of chloride or organic complexes and nanoparticle formation in
388 metal chemistry. On the contrary, weak correlations between Pb or Hg and salinity ($R^2<0.3$)
389 suggest that other parameters than chlorine ions influences the distribution of these elements
390 in the water column. The variation of the trace-element/Al ratios did not show a clear relation
391 to the river inputs.

392 **4.3. Geographical patterns**

393 The highest concentration of several trace elements either in dissolved or particulate fractions
394 was registered in the south and southwest coast of the Portuguese coast (Figures 6 and 8). The
395 enhancements were more accentuated for dissolved Cd, Co, Cu and Zn, while less clear
396 differences were found for Hg and Ni. Lead, was the only elements with low concentrations in
397 this area, probably associated to high $\log K_D$ values confirmed by the high concentrations
398 found in the particulate phase. Several factors converge in this area. Firstly, the Guadiana River

399 drains the central-western part of the Iberian Pyrite Belt (Figure 1), an area with many
400 polymetallic sulfide deposits and residues of mining activities (Leistel et al., 1998). Under
401 oxidizing conditions it generates an acidic leachate with high quantities of sulfur species,
402 metals, and metalloids in solution (Delgado et al., 2009). Furthermore, the observed increase
403 of metal concentrations in the Mediterranean water mass has already been reported in other
404 works nearby the Strait of Gibraltar (Statham et al., 1985; van Geen et al., 1988) A coastal
405 current of warm water that flows westward near the shore reaches the Cape San Vicente and,
406 even, proceeds northwards (Fiúza, 1983; Relvas and Barton, 2002; García-Lafuente et al., 2006)
407 reaching the northwestern coast of Spain. The effect of this current was noticeable close to
408 Sines Cape by temperature satellite image (Figure 3a). Finally, the south coast of Portugal is
409 near the metal enriched rivers Guadalquivir and Tinto that reach the south coast of Spain
410 (Elbaz-Poulichet et al., 2001; Sarmiento et al., 2011). The enhanced metal concentrations have
411 been reported for the south coast of Portugal invoking similar explanations (van Geen and
412 Boyle, 1990; van Geen et al., 1997; Braungardt et al., 1998; Achterberg et al., 1999; Cotte-Krief
413 et al., 2000; Beckers et al., 2007). The higher spatial resolution of the sampling sites and the
414 extension of the surveyed area corroborate those previous findings.

415 **4.4. An attempt to define trace element baseline concentrations and comparison to other** 416 **European coastal areas**

417 On the basis of the results obtained with this high spatial resolution it was attempted to
418 establish the baseline concentrations for Cd, Co, Cu, Hg, Ni, Pb and Zn at each typology of the
419 Portuguese coast (A5, A6 and A7 of the Water Framework Directive). The methodology for
420 estimating the baseline values of these elements were the following: (i) at each typology,
421 selection the 20% of the sites presenting the lowest element concentrations; (ii) at each
422 typology, calculation of the concentration interval of each determined element for the
423 selected sites (Table 2). Low levels of trace elements in the A5 and A6 typologies point to
424 minor influence of anthropogenic pressures at the coastal waters of west coast of Portugal.
425 However, **punctual** increases of metal concentrations occur at northern coast of A5 associated
426 with high river flows following heavy rain periods (Caetano and Vale, 2003). Elevated dissolved
427 Cd, Co, Cu, Hg, Ni and Zn were found at the south Portuguese coast (A7 typology) except for
428 Pb, **mainly associated with particles (high log K_D)**. Baseline concentrations of Cu, Co and Cd in
429 A7 were 20 to 30 times above the values proposed for A5 and A6, while only 5 and 2 times
430 were found for Ni and Hg, respectively.

431 **As indicated before, there is an important lack of studies about trace metal concentration**
432 **along the European coasts. In the context of the Water Framework Directive, a unique work**

433 has been published regarding trace metal concentration in coastal waters (Tueros et al., 2008).
434 Background levels of heavy metals (As, Cu, Mn, Ni, Pb and Zn), in coastal waters within the
435 Basque Country (northern Spain), according to ranges are estimated. This study, together with
436 other European coastal and open ocean waters studies where dissolved and particulate trace
437 metal concentrations are reported have been summarized in Table 3 and Table 4. Dissolved
438 trace metal concentrations in the Portuguese coast are within the values reported for other
439 European coastal waters or North East Atlantic Ocean waters (Table 3) with the exception of
440 the A7 typology (Table 2). However, the values reported in this study for the A7 typology, are
441 quite similar to the ones reported for the Basque Country coastal waters (Tueros et al., 2008).
442 Regarding the particulate metals, we find a similar scenario, with similar levels between this
443 study and other European coastal or open ocean waters (Table 4) with the exception of the A7
444 typology.

445

446 5. CONCLUSIONS

447 The high variability of trace element concentrations registered in this study points to the
448 importance of examining concentration patterns at a regional scale. These changes may result
449 from anthropogenic effects as well as natural factors (i.e. oceanographic and hydrographic
450 conditions and geological features). It seems that geological features of the SW and S
451 Portuguese coast superimpose fluvial or oceanographic conditions in defining the trace
452 element distribution, both in dissolved and particulate fractions of this area. However, riverine
453 inputs and upwelling conditions determine trace element concentrations in the North coast.
454 Only punctual concentrations exceed the baseline values at each typology. The estimation of
455 baseline values and the influence of anthropogenic pressures are important at European level
456 for the implementation of the Water Framework Directive and Marine Strategic Framework
457 Directive. European state-members should supply information of descriptors related to
458 contamination in order to assessing Good Environmental Status. Due to the variability of
459 oceanographic and climate conditions all over the coast further studies involving the
460 characterization of the water column should considered the seasonal pattern contributing,
461 thus, to a better definition of baseline concentrations.

462

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469

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- 733

Table 1. Accuracy of the analytical procedure: AdCSV determination of Co and Ni and ASV of Cd, Cu, Pb, and Zn in different certified reference materials (CASS-4: near-shore waters and SLEW-3: estuarine water) compared with the certified values. The value below concentrations represents the replicates.

		Cd (nM)	Co (nM)	Cu (nM)	Ni (nM)	Pb (nM)	Zn (nM)
CASS-4	Certified	0.23±0.03	0.44±0.05	9.32±0.87	5.35±0.51	0.05±0.02	5.83±0.87
	Obtained	0.23±0.09	0.42±0.11	9.04±1.45	5.44±0.77	0.06±0.02	5.85±1.49
		<i>n</i> =6	<i>n</i> =5	<i>n</i> =6	<i>n</i> =6	<i>n</i> =5	<i>n</i> =6
SLEW-3	Certified	0.43±0.04	0.71±0.17	24.39±1.89	20.96±1.19	0.04±0.01	3.07±0.57
	Obtained	0.38±0.04	0.88±0.19	25.92±3.71	22.18±0.98	0.06±0.03	3.20±1.57
		<i>n</i> =5	<i>n</i> =5	<i>n</i> =4	<i>n</i> =5	<i>n</i> =5	<i>n</i> =4

Table 2. Trace metal baseline concentrations (dissolved and particulate phases) for each typology defined in the Water Framework Directive for the Portuguese coast.

<i>Dissolved</i>		Cd (nM)	Co (nM)	Cu (nM)	Hg (pM)	Ni (nM)	Pb (nM)	Zn (nM)
A5		0.01-0.02	0.03-0.06	1.1-1.3	5-8	2.2-2.5	0.01-0.02	1.4-2.3
A6		0.01-0.06	0.01-0.08	0.9-1.3	5-7	1.9-2.5	0.01-0.04	2.3-3.4
A7		0.20-0.40	1.50-1.80	30-35	3-12	9.0-12	0.02-0.03	17-21
<i>Particulate</i>	Al ($\mu\text{mol g}^{-1}$)	Cd (nmol g^{-1})	Co (nmol g^{-1})	Cu (nmol g^{-1})	Hg (nmol g^{-1})	Ni (nmol g^{-1})	Pb (nmol g^{-1})	Zn (nmol g^{-1})
A5	240-340	0.3-0.4	10-16	53.0-114	4.2-21	35-56	10.0-14.0	420-590
A6	36-135	0.4-0.9	2.0-6.0	51.0-210	4.0-11	22-62	11.0-28.0	750-1250
A7	122-124	1.8-2.1	7.0-13	160-360	2.8-3.1	47-55	122-138	1000-1200

Table 3. Dissolved metal concentrations and ranges measured along the western European Atlantic coast and in the North Atlantic Ocean.

Continental Shelf area	Cd(nM)	Co(nM)	Cu (nM)	Hg (pM)	Ni(nM)	Pb (nM)	Zn (nM)	N Stations	
NE Atlantic Ocean	0.02-0.19	0.03-0.10	0.6-2.7	1-4	0.5-3.6	0.03-0.22	0.1-3.0	18	(1)
North Biscay shelf	0.11-0.24		2.0-8.0					33	Waeles et al., 2004
English Channel	0.09-0.25	0.08-1.48	2.0-7.0	2-3	2-14	0.10-0.29	2.0-15	19	(2)
Irish Sea	0.12-0.72	0.02-0.18	3.0-24		2-15	0.10-0.82	3.0-54	14	(3)
North Sea	0.04-0.45	0.11-0.59	3.1-13	1-4	3.1-17	0.06-0.34	1.7-34	28	(4)
N Spanish Coast			4.7-39		5.1-8.5	1.45-7.24	61-443		Tueros et al., 2008
NW Spanish Coast	0.01-0.08	0.18-0.46	0.7-8.2	9-180	1.3-5.2	0.03-0.43	0.8-6.3	11	Santos-Echeandía et al., 2005;2009; Beiras et al., 2002
Portuguese Coast	0.01-0.89	0.01-3.32	0.9-45	3-140	1.9-15	0.01-0.15	1.4-62	46	<i>This study</i>
SW Spanish coast	0.06-0.29		10-17	2-4	3-10		5.0-100	31	(5)

(1) Landing et al., 1995; Saager et al., 1997; Ellwood and van den Berg, 2000; Ellwood and van den Berg, 2001; Cotté-Krief et al, 2002, Cossa et al., 2004

(2) Kremling and Hydes, 1988; Laslett, 1995; Statham et al., 1999; Cossa and Fileman., 1991; Cossa et al., 1994

(3) Kremling and Hydes, 1988; Laslett, 1995; Achterberg and van den Berg, 1996.

(4) Laslett, 1995; Schmidt, 1992; Fileman et al., 1991; Leermakers et al., 2001

(5) Van Geen et al., 1991; van Geen et al., 1997 ; Braungardt et al., 1998; Achterberg et al., 1999 ; Elbaz-Poulichet et al., 2001, Cossa et al., 2001

Table 4. Particulate metal concentrations and ranges measured along the western European Atlantic coast and in the North Atlantic Ocean.

Continental Shelf area	SPM (mg L ⁻¹)	Al (μmol g ⁻¹)	Cd (nmol g ⁻¹)	Co (nmol g ⁻¹)	Cu (nmol g ⁻¹)	Hg (nmol g ⁻¹)	Ni (nmol g ⁻¹)	Pb (nmol g ⁻¹)	Zn (nmol g ⁻¹)	N Stations	
Portuguese Coast	0.6-14	36-2900	0.03-15.1	1.5-165	51-614	4.0-76.4	22-1471	10-306	416-10981	46	<i>This study</i>
SW Spanish coast						0.4-2.1				31	Cossa et al., 2001
English Channel (Dover)	0.7-19	300-1400	0.9-38.0		205-283	2.1-8.8	341-409	70-320	1162-4892		(1)
Irish Sea			3.8-11.6		126-1338		204-647	92-482	2140-15000	14	Laslett, 1995
French Coast	0.3-10		3.9-23.1							15	Boutier et al., 2000
North Sea	0.2-0.9	17-230	0.9-12.5		20-676	0.1-1.6	17-1073	77-425	1116-16820	28	Laslett, 1995; Fileman et al., 1991; Leermaker et al., 2001
North Atlantic	0.1-0.4	10-80	24-150	25-60	150-660		100-350	20-28	250-950	13	Kuss and Kremling., 1999

(1) James et al., 1993; Laslett, 1995; Statham et al., 1993; Cossa and Fileman., 1991

Figure Captions.

Figure 1. Study area map with the a) surface water sampling stations and main river inputs and b) main capes and lithological facies.

Figure 2. Upwelling index conditions (in $\text{m}^3 \text{s}^{-1} \text{km}^{-1}$) during March 2010.

Figure 3. Satellite images for: a) Temperature, b) Salinity and c) Chlorophyll during the sampling cruise in the study area.

Figure 4. Master variables measured “in situ” at each sampling station during the campaign: a) Temperature, b) Salinity, c) Chlorophyll, d) Dissolved oxygen and e) Suspended particulate matter.

Figure 5. Nutrient concentration at each station: a) Dissolved inorganic Nitrogen, b) Phosphate and c) Silicate.

Figure 6. Dissolved trace element concentration ranges along the Portuguese coastal waters.

Figure 7. Deep profile of Temperature, Salinity and dissolved trace metal concentrations in the DP sampling station (Figure 1). The Mediterranean Water mass is observed between 800-1200 m depth.

Figure 8. Particulate trace element concentration ranges along the Portuguese coastal waters.

Figure 9. Trace metal to aluminum ratios in the particulate phase of the Portuguese coastal waters.

Figure 10. Principal component analysis for the dissolved trace metal levels along the Portuguese coast.

Figure 1.

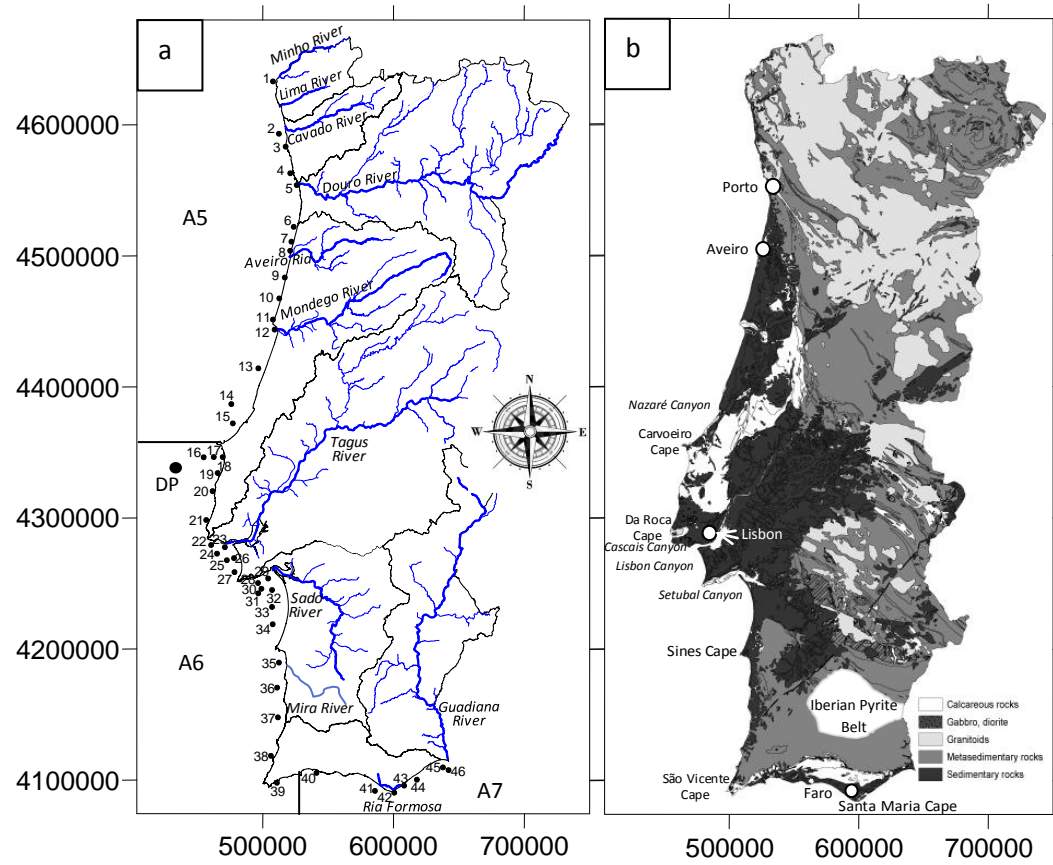


Figure2

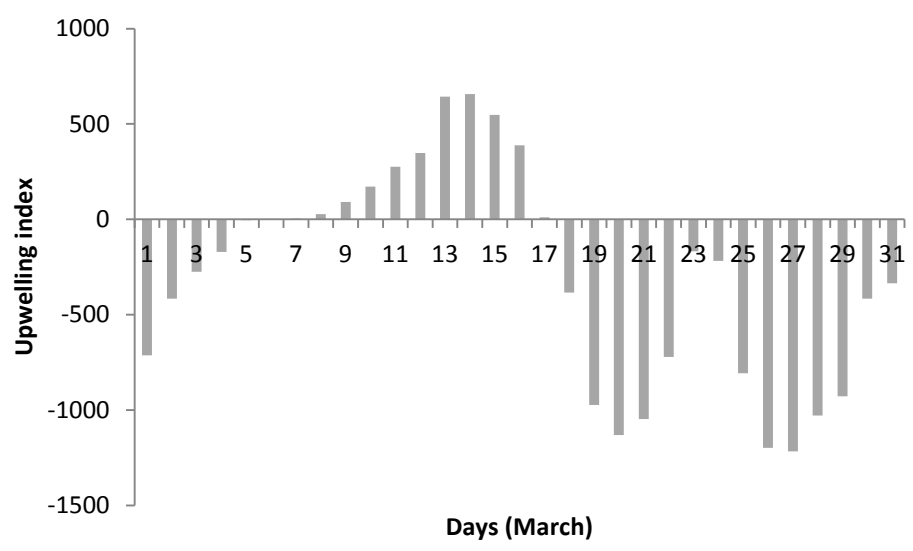


Figure 2

Figure 3.

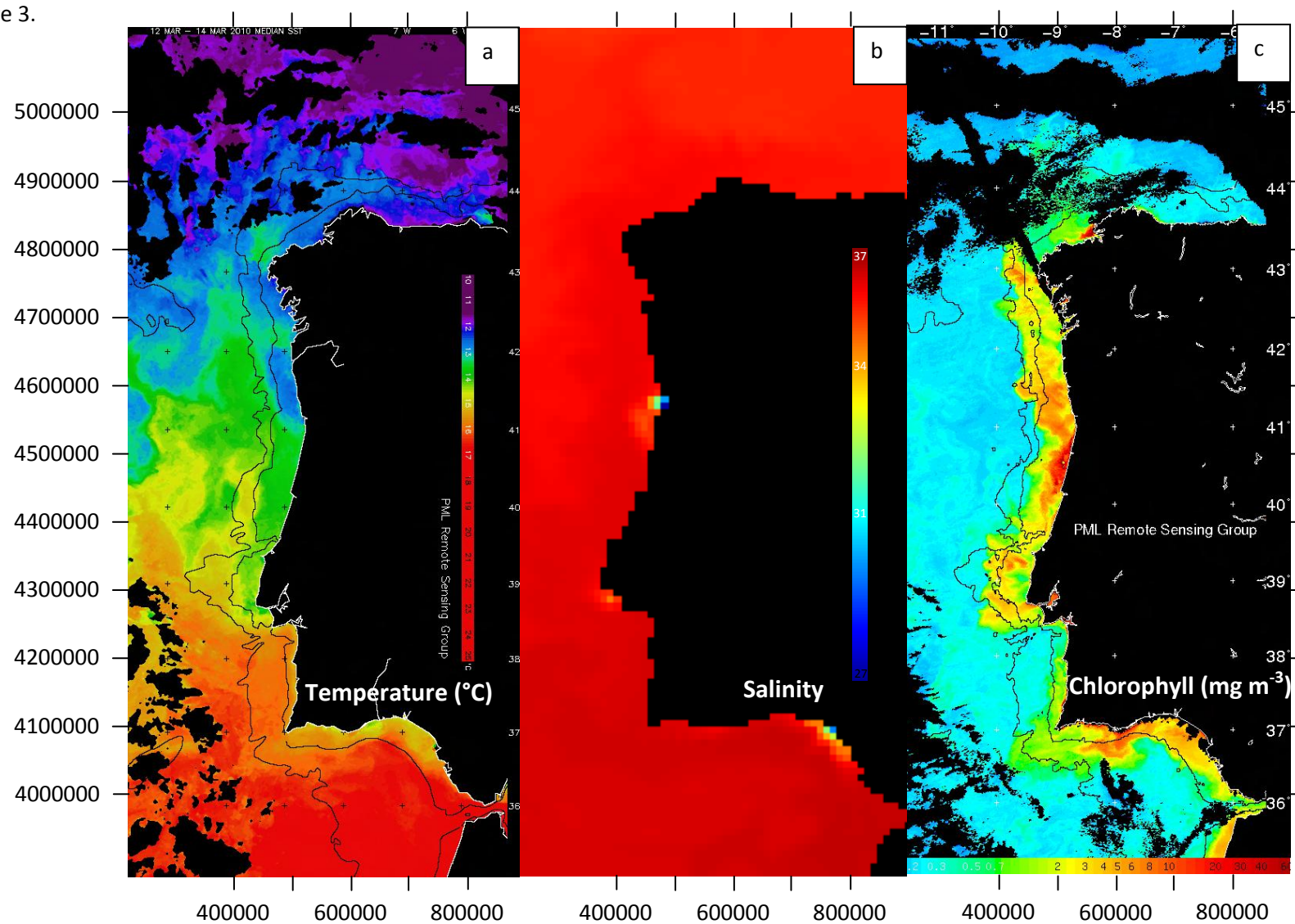


Figure4

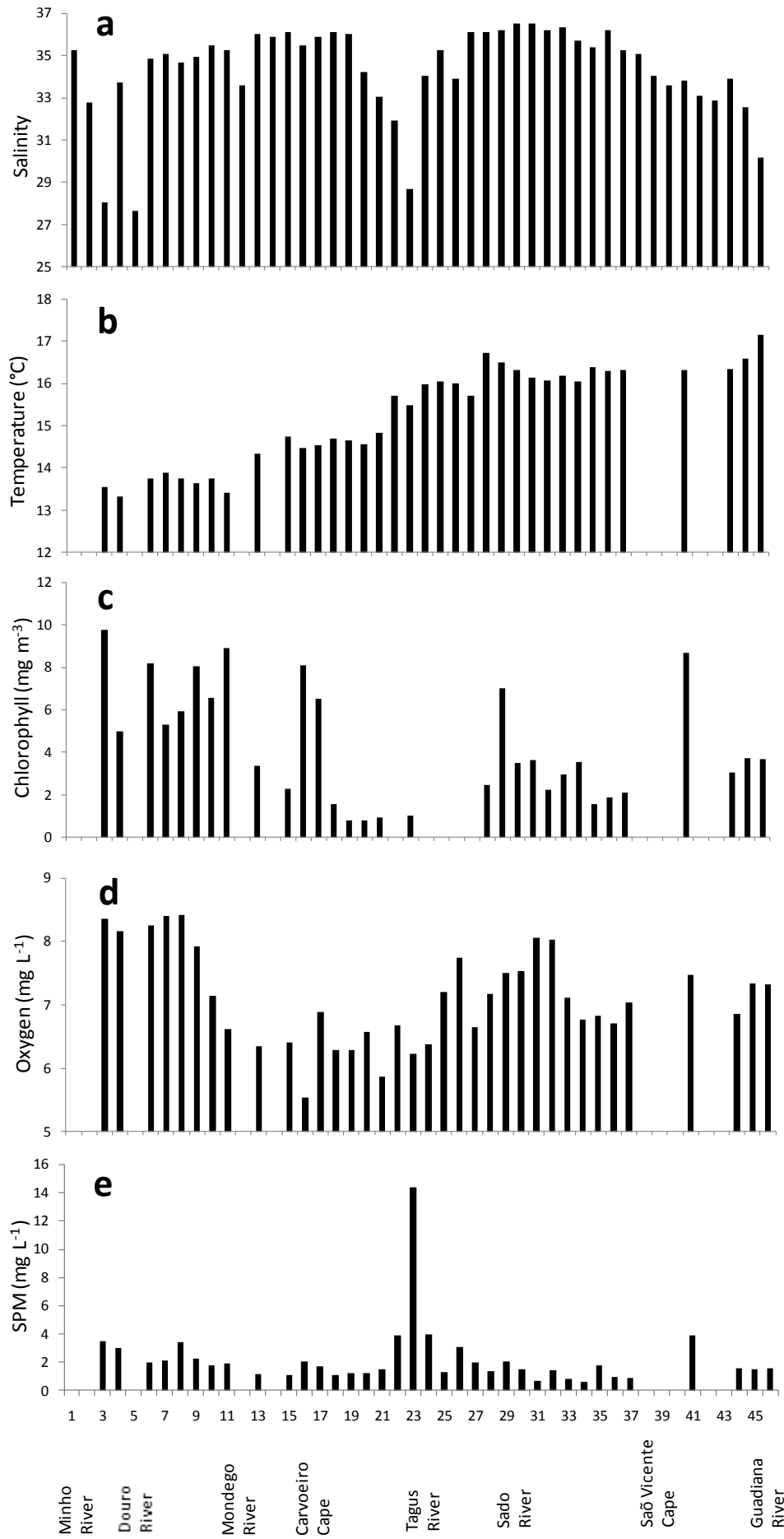


Figure 5

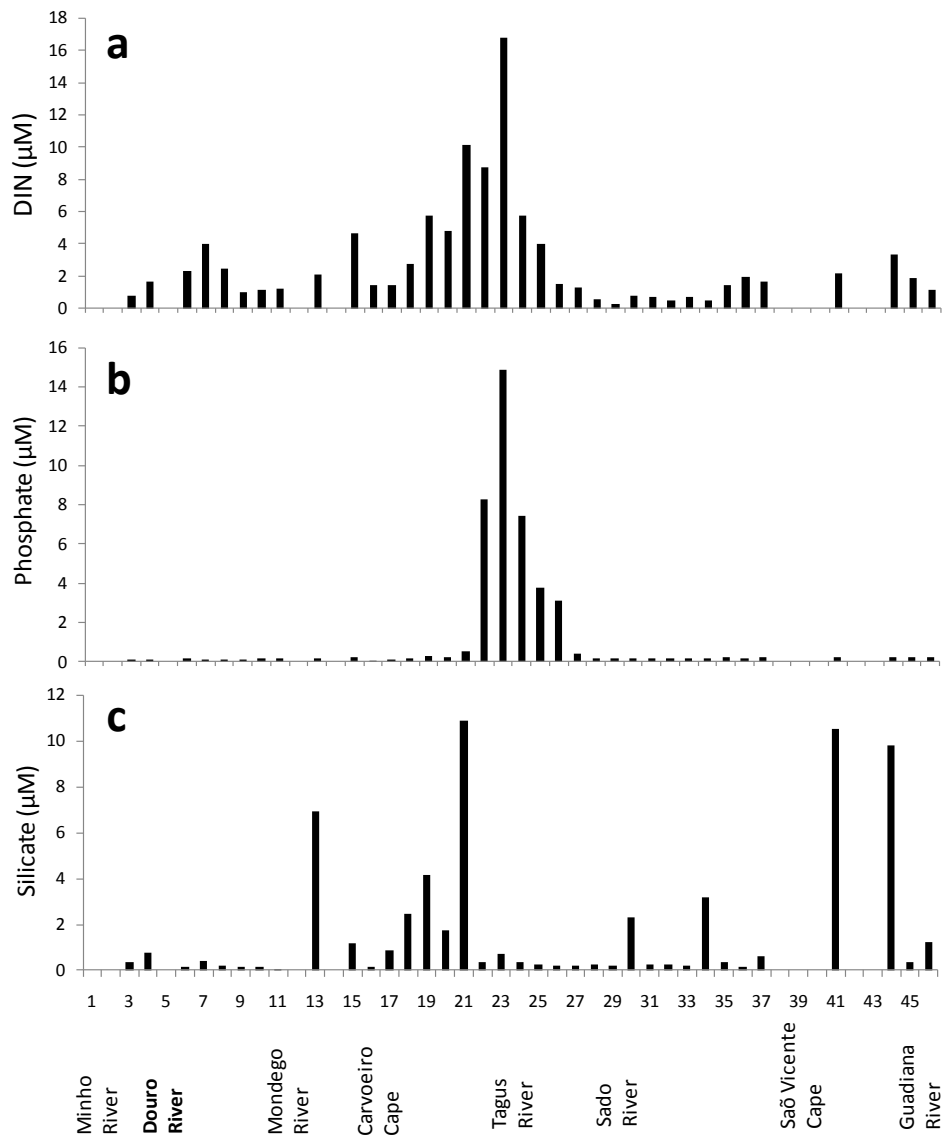


Figure6

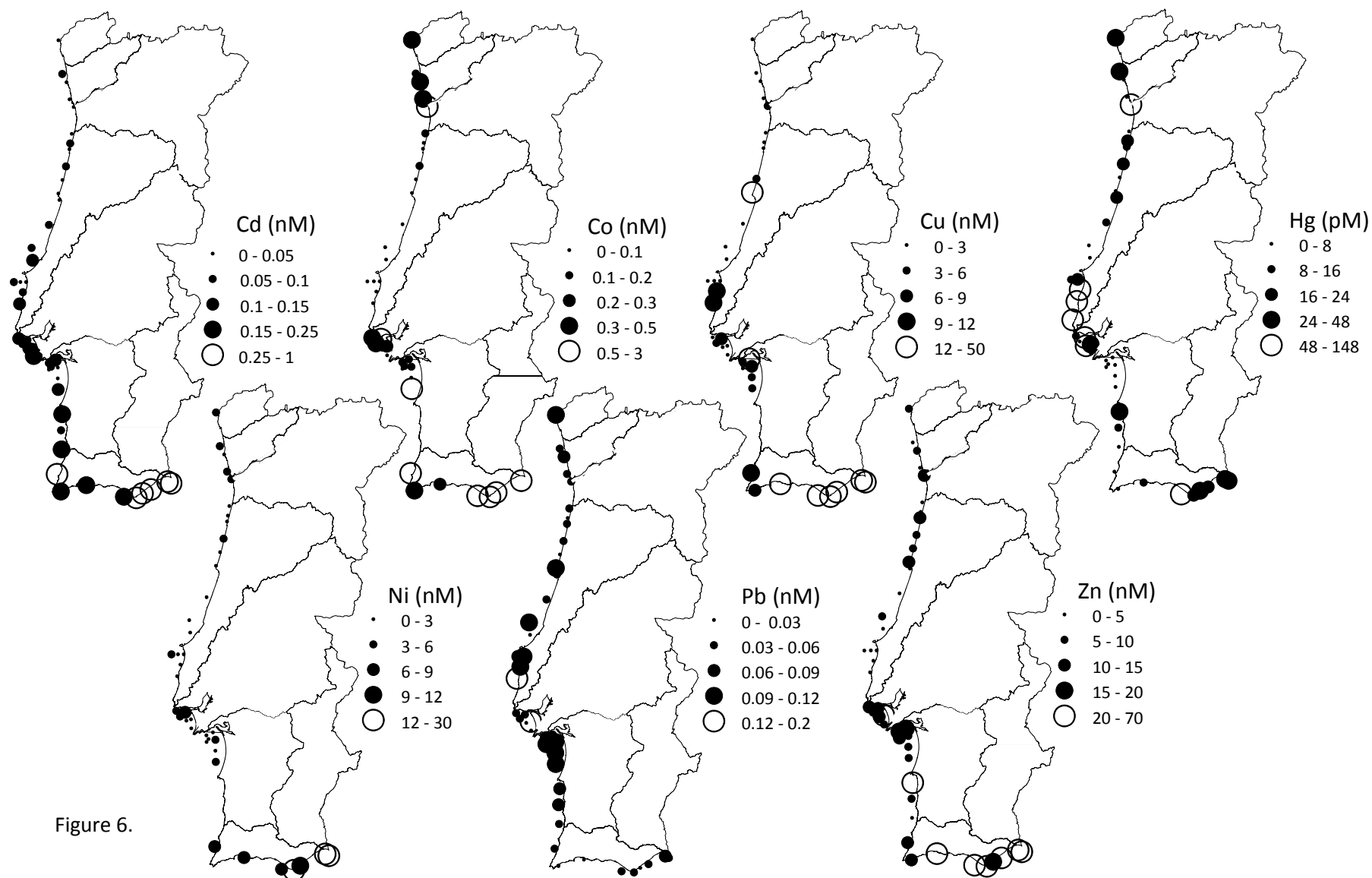


Figure 6.

Figure 7.

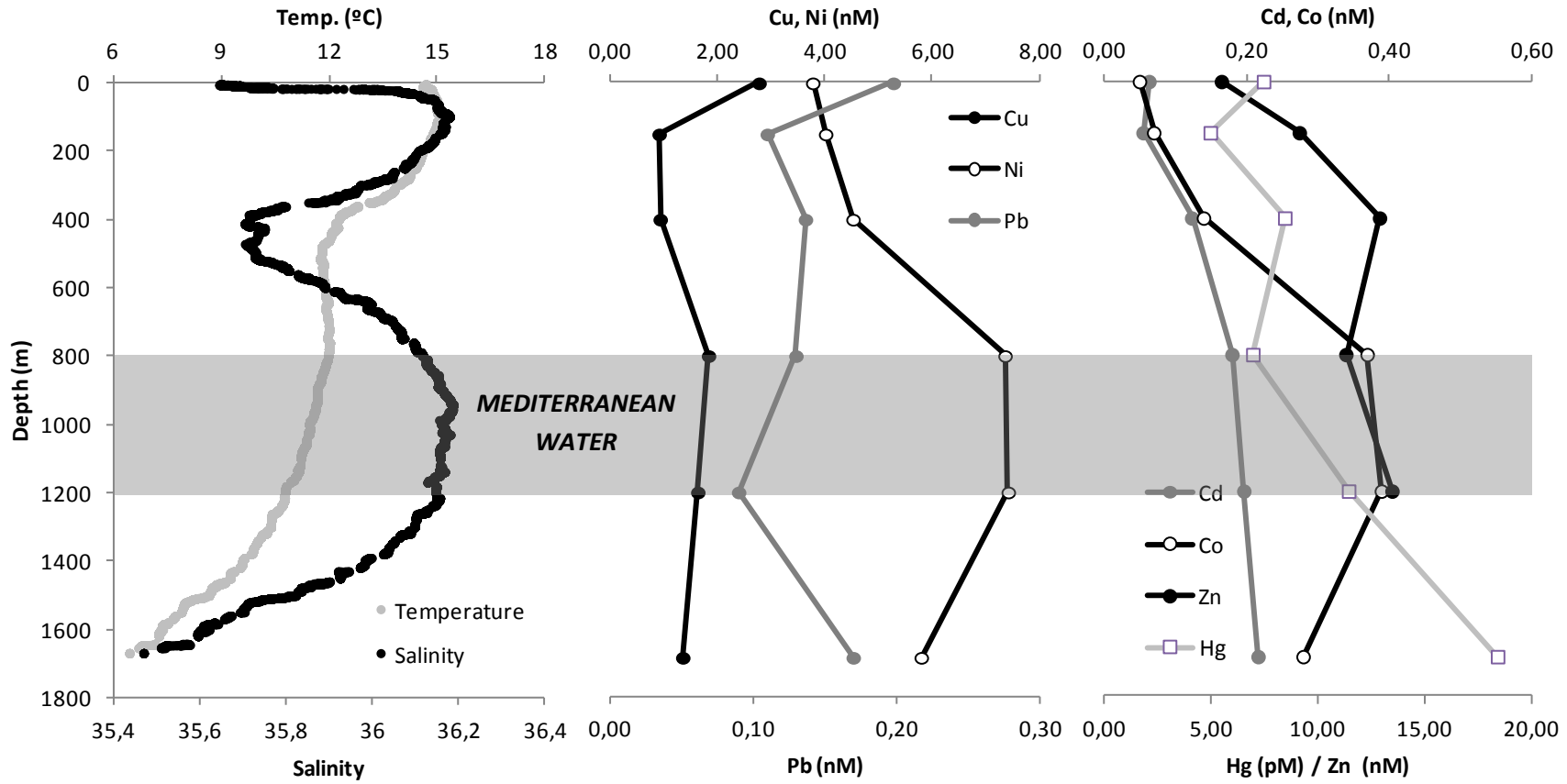


Figure8

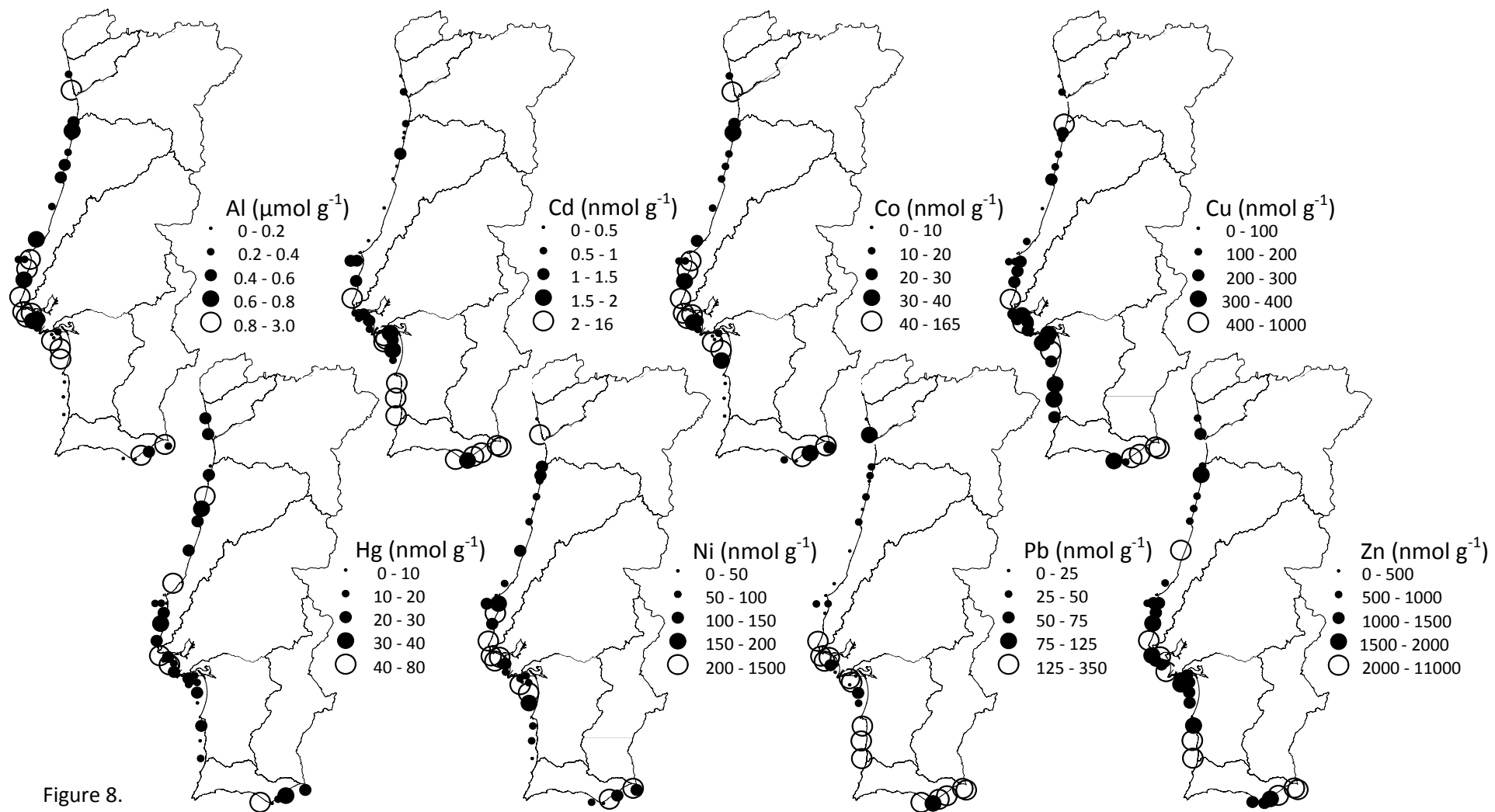


Figure 8.

Figure9

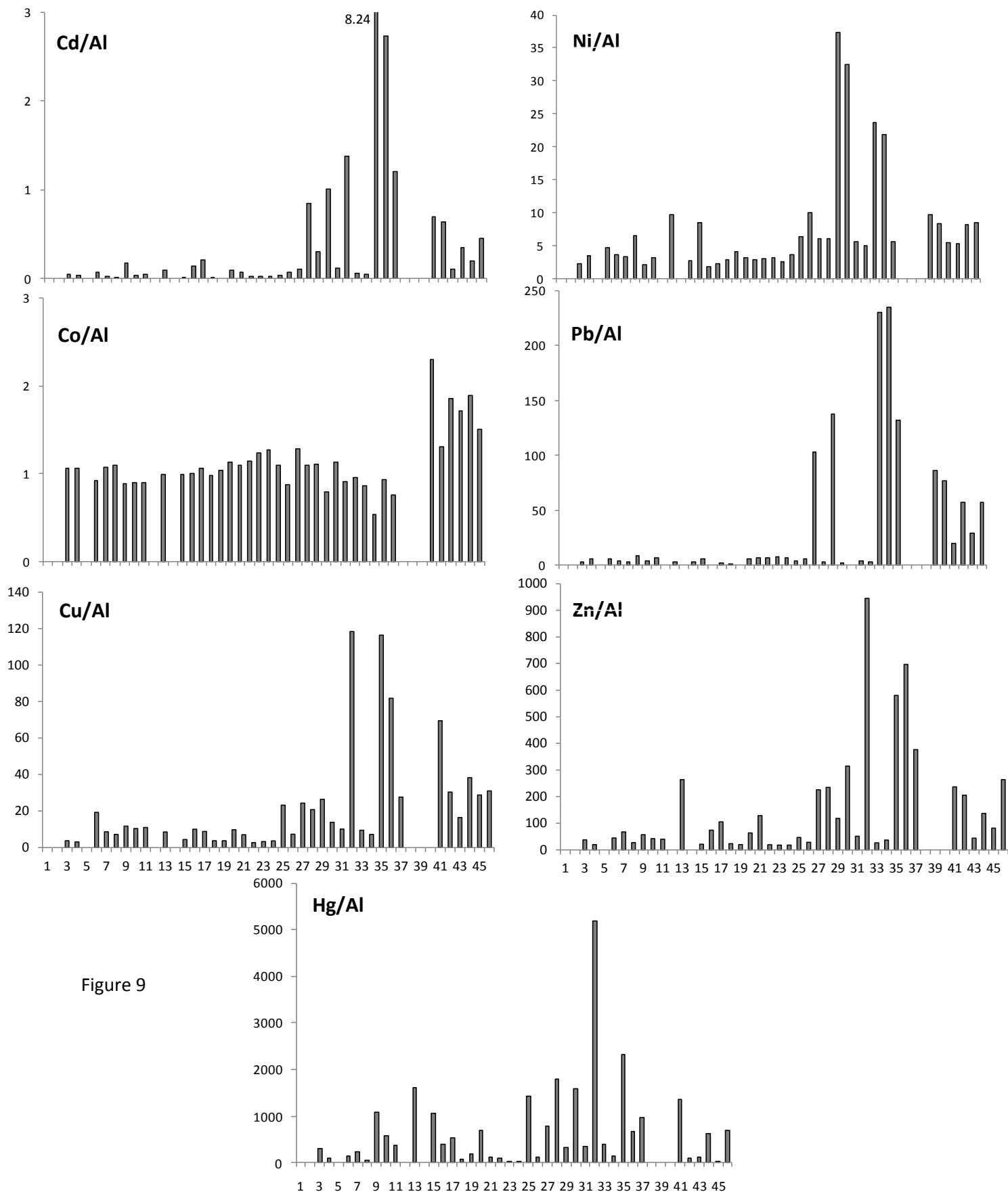
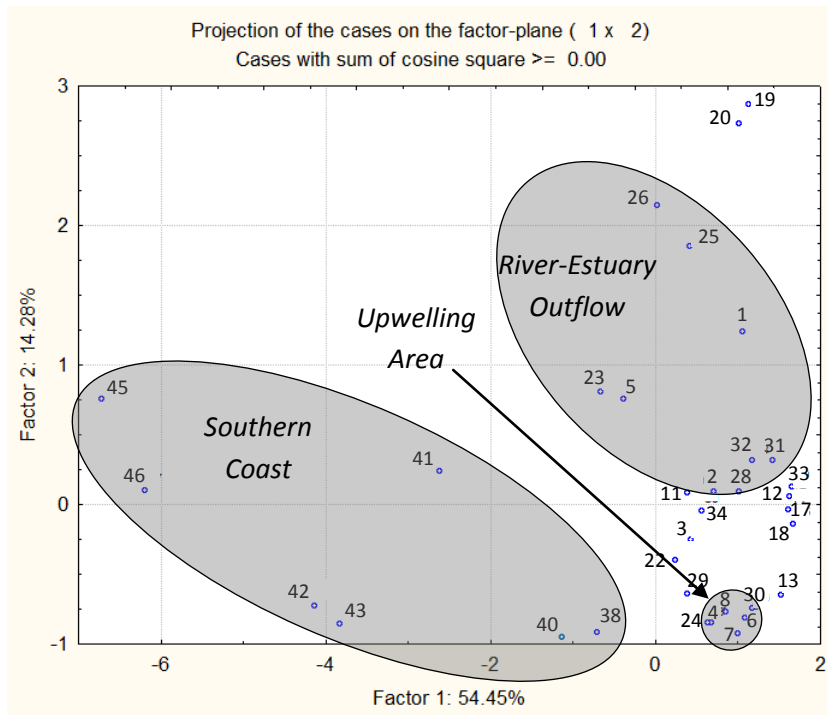


Figure 9

Figure 10.



TableS1

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TableS2

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TableS3

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