Metal Composition and Fluxes of Sinking Particles and Post-Depositional Transformation in a Ria Coastal System (NW Iberian Peninsula)

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Abstract

The intrannual variation of the quantity and composition of the sinking particles in a ria coastal system (Vigo Ria, Galicia, NW Iberian Peninsula) has been studied. Levels of particulate metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, U, V and Zn) were determined both in the labile (1M HCl extraction) and in the total fraction. The levels and type of metals found in different seasons of the year depended upon oceanographic, physical, chemical and biological conditions but, in general, lithogenic type metals (Al, Fe, Ti, U and V) were more abundant during winter rainy campaigns when high quantities of SPM were recovered in the trap. However, the more biogenic metals (Cu, Pb, Zn) were more abundant in spring or summer associated to the higher quantities of organic matter found in the traps. The fluxes of these metals to the sediment were calculated being comparable to other European estuaries and coastal systems. The quantity of particulate metals deposited in the Vigo Ria seabed represents between 60-80% of their inputs through rivers and sewages. In special, the deposited labile fraction is subject to postdepositional diagenetic processes with subsequent benthic fluxes of dissolved Cr, Cu, Mn, Ni, Pb and Zn form of the metals to the water column. For Co and Cd, however, their higher enrichment in the sediments compared to the traps suggests that they are converted into a more refractory fraction upon postdepositional remineralization.

Keywords: trace elements; SPM; labile; sediment trap; vertical fluxes; Ria of Vigo; NW Spain; sediment core; postdepositional transformation.

INTRODUCTION

Estuarine suspended particulate matter arises from a variety of sources, which can be broadly categorized into the following components (Turner and Millward 2002): (i) lithogenic, which depends on the geology of the basin and draining area; (ii) hydrogenic, i.e. generated in-situ by chemical processes; (iii) biogenic, generated from biological processes; and (iv) anthropogenic. These particles comprise seston, with densities similar to water and with an abundance and

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32 distribution determined by the factors controlling primary production and therefore with a
33 strong seasonal component, and suspended sediments which are subject to successive cycles
34 of deposition and resuspension.

35 Processes controlling the interaction of trace elements with particles in estuarine and coastal
36 systems are generally more active than in the open ocean, due to stronger physico-chemical
37 gradients, higher primary production and continental runoff. These processes include removal
38 from solution by biological uptake (Turekian, 1977; Kuss and Kremling, 1999) and chemical
39 scavenging (Kremling and Pohl, 1989), coagulation and flocculation of colloids (Sholkowitz,
40 1978; Morris, 1986; Boyle et al., 1977; Erisma, 1986), agglomeration and modification of
41 redox-sensitive elements (Pohl et al., 2004) or desorption from particle surfaces by
42 competition from major ions of seawater (Van der Weiden et al., 1977; Li et al., 1984).

43 Direct measurements of the transport of particulate trace elements from the water column to
44 bottom sediments in estuarine and coastal systems are rather limited. Sediment traps offer a
45 convenient method for the collection of settling particles in the aquatic environment
46 (Blomqvist & Häkansson, 1981) and have been used in previous work for the analysis of sinking
47 particles in the water column (Broman et al., 1994; Leivuori et al., 1998; Kuss and Kremling,
48 1999; Matthai et al., 2002; Ergül et al., 2008; Nordmyr et al., 2008). Diagenesis of this
49 particulate material deposited on bottom sediments induce the release of trace elements to
50 the water column (Haley and Klinkhammer, 2004), implying that a fraction of the matter
51 derived from continental runoff will eventually be exported to ocean margins. This process
52 has been documented for some first-row transition metals (Elrod *et al.*, 2004; Johnson *et al.*,
53 2003), but the extent to which this represents a net source, by diagenetic mobilization of
54 continentally derived material versus the regeneration of biogenic and authigenic marine
55 phases, remains poorly known.

56 Thus, the objectives of this study are: (i) to characterize the chemical composition and
57 seasonal changes of the sinking particles from samples collected in sediment traps of the Vigo
58 Ria (NW Iberian Peninsula); (ii) to estimate particulate matter and metal fluxes to the
59 sediments; and (iii) to compare the composition of sinking particles with surface sediments in
60 order to determine postdepositional processes.

61 **MATERIAL & METHODS**

62 *Study area*

63 The Vigo Ria, is the southernmost of the Galician Rias, which are located in the northwest of
64 the Iberian Peninsula (Figure 1). This type of estuarine-coastal systems were formed by

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65 flooding of river valleys in the Pleistocene–Holocene in regions of high relief during the last

66 interglacial transgression, and are typical of other World areas such as SW England or SE Asia

67 (Bianchi, 2007). The Vigo Ria occupies an area of 156 km^2 with a volume of 3275 km^3 of water.

68 The residence time of ria waters ranges from a few days to one month (Prego and Fraga,

69 1992). The main land-derived inputs of suspended matter to the Vigo Ria come from the

70 discharge of rivers, streams and several sewage treatment plants. The Oitavén river,

71 discharging at the ria head, constitutes the main freshwater input with an annual average flow

72 of 17m^3 s^{-1} (55 m^3 s^{-1} in February to 1 m^3 s^{-1} in August; Figure 1). The geology of the watershed

73 is mainly composed by igneous and metamorphic rocks (Nombela et al., 1995). The Vigo Ria

74 has an oceanic climate with relatively dry periods during summer (Perez-Alberti, 1982),

75 resulting in an average annual rainfall of 1950 ± 330 mm (2850 mm in January and 31 mm in

76 August). Due to the frequent upwelling events (Fraga, 1981; Prego and Bao, 1997; Prego et al.,

77 2007), the primary production in the Vigo Ria is elevated (annual average of 350 mgCm^{-2} d^{-1};

78 Prego, 1993), leading to the production of 250,000 tons of mussels per year, representing

79 about 50% of the European Union production (Smaal, 2002). This ria is the most industrialised

80 and populated in the Galician coast with approx. 400,000 inhabitants, 80% of which are settled

81 at the southern margin (city of Vigo; Fig.1). Industrial and port activities have occupied the ria

82 banks for decades, especially the Bouzas shipyard (Fig.1). Anthropogenic inputs of trace metals

83 into the ria are mainly derived from food factories and metal industries linked to shipyard and

84 dock activities (Prego et al., 2008). As a result, sediments in the middle zone of the ria are

85 contaminated by metals, while more pristine conditions are found in the outer zone (Belzunce-

86 Segarra et al., 2008).

87 ***Sample collection and pre-treatment***

88 Two sediment traps were deployed five meters above sea bottom, one in the middle-outer

89 part of the ria and the other in the inner-middle ria (Stations T1 and T2; Figure 1). Traps

90 consisted on a homemade 4-PVC cylinders of 0,28 dm^2 collecting area and an aspect *ratio of*

91 *10.76*, were deployed for 24 hours. A hyper saline solution was placed inside the cylinders in

92 order to maintain the deposited material inside of them. Sampling was carried out onboard

93 the R/V Mytilus belonging to IIM-CSIC during 2004 and was designed to cover different

94 seasonal oceanographic scenarios (winter: 29-Jan. and 04-Feb.; spring: 06-May and 12-May;

95 summer: 06-Sep. and 13-Sep.).

96 After recovery of the traps, the particulate material was obtained by filtration through acid-

97 washed 0.45 µm polycarbonate membranes. In order to determine the amount of labile

98 elements, filters were subject to digestion overnight with 1M HCl in Teflon® vials (Savillex) at

99 ambient temperature (Bryan and Langston, 1992). The digest was then syringed-filtered (0.45

100 µm) using a Swinnex filtration unit and stored pending analysis; filters containing the remnant

101 particles were microwave digested using a mixture of HF and HNO_3 (1:3) in order to analyze the

102 total fraction (Biscombe, 2004).

103 Another portion of the particulate trap material was filtered through previously combusted

104 (450°C) GF/F filter (Whatman) to quantify organic matter.

105 Short sediment cores (approx. 10 cm) were taken at station C (Figure 1), located between both

106 traps, using acid-washed methacrylate tubes placed inside a *Rouvilloise* grab sampler. Once at

107 the onshore lab, sediment cores were stored in plastic bags at -18° C. Sample treatment was

108 undertaken inside a glove box filled with N_2 (815-PGB, Plas-Labs). Frozen cores were extruded

109 from the tube and sliced into 2-3 cm layers and allowed to thaw in acid-cleaned polyethylene

110 centrifuge tubes. Before digestion, sediments were sieved (2 mm) and freeze-dried. About 150

111 mg of sediment was subject to 1M HCl digestion as described above. Digests were filtered

112 through GF/F membranes and stored pending analysis. Remnant sediments were digested in

113 screw-capped Teflon® vials in a hot plate following the procedure described by Biscombe

114 (2004). A fraction of 1 g of sediment was dried gently (50°C) in an oven and kept in plastic

115 storage for subsequent analysis of PIC, POC and PON.

116 ***Sediment and suspended particulate matter analysis***

117 A Varian Flame-Atomic Absorption Spectrophotometer model SpectrAA 220FS equipped with

118 SPS-5 Sample Preparation System was used for Al, Fe and Zn determination both in the labile

119 and the total fractions. Cadmium, Co, Cr, Cu, Mn, Ni, Pb, U and V were analyzed by means of

120 Electrothermal Atomic Absorption Spectrometry with a Varian SpectrAA 220 apparatus

121 equipped with Zeeman background correction. One blank every ten samples was run and

122 results were blank-corrected. The accuracy of the analytical procedure was assessed by the

123 analysis of certified reference material PACS-2 (harbour sediment, National Research Council

124 of Canada) obtaining good agreement with the certified values (Table 1). The precision of the

125 analysis depended on the concentrations of a given metal in the sample and were, as RSD

126 (relative standard deviation), less than 10% for all elements.

127 Total C and P in the sediments were determined with a Carlo Erba CHNS-O 1108 elemental

128 analyzer. Organic carbon was calculated as the difference between total carbon and PIC as

129 weight loss at 550 and 975°C. POC and PON in the SPM were analyzed as above but carbonate

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130 was not removed from the filters since the contribution of carbonate to total sedimented

131 carbon does not exceed 2% (Fernández et al. 1995).

132 *Sedimentation fluxes of the particulate material*

133 Transport of particulate material from the water column to bottom sediments can be easily

134 estimated from the sedimentation rates of particulate matter and trace elements

135 concentrations. This was calculated using the deposited matter recovered in the traps,

136 deployment time (24 h) and the cylinder trap area (0,28 dm^2).

137 *Statistics*

138 Statistical software (Statistica 7.0) was used for data analysis. Correlations between elements

139 and aluminium were analyzed by Spearman rank correlations (Zar, 1999).

140 **RESULTS**

141 *Composition and spatio-temporal variation of sediment trap material and bottom sediments*

142 Significantly higher amount of material was recovered from the outer sediment trap (177-710

143 mg) than for the inner (76-217 mg; Figure 2), though they shown a similar seasonal trend with

144 the lowest values obtained in summer. It is interest noting that the highest amount recovered

145 occurred when downwelling conditions prevailed in the ria.

146 Aluminium, often used as a tracer of lithogenic material (Windom et al., 1989; Pohl et al.,

147 2004), showed a range of 6.5 to 10.4%; accordingly, a slight decrease was observed from

148 winter to summer as the freshwater input to the ria decreases. The amount of organic matter,

149 calculated as 1.72 the percentage of particulate organic carbon (POC), did show no trend in

150 both traps during the winter and spring sampling dates, with higher values in Trap 2 (12.8-

151 18.1%) than Trap 1 (8.5-13.6%); however, a clear peak was found during the first summer

152 campaign reaching 28.6% in Tap 1 and 82.2% of POM in Trap 2.

153 A clear seasonal trend on the sedimenting particle composition is observed in the C:N ratios

154 (Figure 2), which is a good measure to discriminate marine from terrestrial organic matter in

155 sediments (Meyers, 1994; 1997; Thornton and McManus, 1994; Ruiz-Fernández *et al*., 2002)

156 due to the differences between vascular plants (C:N>17) and marine microalgae (5<C:N<7).

157 Values ranged from 15.9 (Trap 1) and 13.2 (Trap 2) in winter to about 9.2 in spring-summer as

158 the continental input decreases and the primary production – based on the amount of

159 chlorophyll collected (Figure 2) – increases.

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160 The organic matter content of bottom sediments did not show a variation with depth (Table 2),

161 with average values of (mean ± 1σ) 5.6 ± 0.3 (winter), 5.5 ± 0.3 (spring) and 5.2 ± 1.0

162 (summer), which are 2-3 times lower than those for the sediment trap material. Average C:N

163 ratios did not show any seasonal trend or variation with depth (Table 2), with average values

164 of 10.9 ± 0.8 (summer) to 11.3 ± 0.5 (winter) suggesting some degree of organic matter

165 remineralization.

Total and labile trace metal concentrations in sediment traps and bottom sediments

167 Trace metal concentrations in the sediment trap material and bottom sediments in the

168 different sampling campaigns are displayed in Table 3. Data shows no evident seasonal or

169 spatial differences in the trap material. Nevertheless, lithogenic metals like Al, Fe, Ti, U and V

170 showed higher levels in winter and decreasing towards spring and summer. On the contrary,

171 metals with higher affinity to organic matter (i.e. Cu, Pb and Zn) followed a sinusoidal time

172 course variation at both traps (Figure S1). This tendency is coincident with POM trend (Figure

173 2) and opposite to Al trend (Figure 2). In the sediment cores, however, a decreasing trend from

174 winter to summer was found for most elements with the exception of Cd, Co and U. Average

175 metal concentrations in the sediment traps were generally higher than those in the sediments,

176 even for elements with a dominant lithogenic source (e.g. Al, Fe, Ti), with the exception of Cd

177 and Co. In order to check for significant differences between metal enrichment in the trap

178 material compared to sediments, unpaired two-tailed t-tests were run for the metal/Al ratios.

179 Results given in Table 4 indicate that Me/Al ratios are significantly different (at the 99.5% or

180 higher) for all the elements with the exception of Ti, U and Zn. For those elements showing a

181 significant difference, normalized values are higher in trap material than in sediments, except

182 for Co and especially Cd.

183 Trace metal lability in trap material and sediment are displayed in Figure 3. A high degree of

184 lability in the traps was found for elements like Pb (83 ± 6 %) and Cu (92 ± 6 %), whereas for

185 refractory elements like Al and Ti lability was less than 15%. Lability in sediments was lower for

186 most of the elements (Figure 3). Statistical analysis of these data indicated that this decrease in

187 metal lability for the sediments was significant (at the 99.5% or higher), with the only

188 exception of U, V, and Zn (Table 4).

Suspended particulate matter and trace metal deposition rates in the water column

190 Sedimentation rates of SPM and downward particulate metal fluxes are shown in Table 5.

191 Metals with higher lithogenic fraction (Fe, Al, Ti, U, V, Cr, Co) showed proportional fluxes to the

192 SPM amount, being higher on 4th February and 12th May. At that time, values oscillated

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193 between 1.0-1.3 g m^{-2} d^{-1} for Fe, 2.2-6.1 g m^{-2} d^{-1} for Al, 2.7-7.9 g m^{-2} d^{-1} for Ti, 0.2-0.6 mg m^{-2} d^{-}

194 ^{1} for U, 2.5-7.2 mg m^{-2} d^{-1} for V, 1.6-6.4 mg m^{-2} d^{-1} for Cr and 0.3-0.6 mg m^{-2} d^{-1} for Co while

195 during the rest of the year, fluxes were lower than a half of the previous ones. Maximum fluxes

196 of Cu, Pb and Zn were estimated for the 6th May at both traps (4.8-6.1 mg m^{-2} d^{-1} for Cu, 5.6-

197 6.1 mg m^{-2} d^{-1} for Pb and 3.6-4.2 mg m^{-2} d^{-1} for Zn), with the exception of Pb in the outer trap

198 when the maximum was found on the 4th February (7.9 mg m^{-2} d^{-1}). Nickel, Mn and Cd showed

199 a similar pattern to the lithogenic metals in the outer trap, but higher fluxes on the 12th May

200 for the inner trap.

201 **DISCUSSION**

202 A summary of total trace metal concentration ranges and percentages of lability in both

203 sediment traps (T1 and T2) are shown in Table 6. The obtained results are comparable to

204 values published by (Prego et al., 2006) in the Vigo Ria. With the exception of Zn, metal

205 concentrations are higher in the Vigo Ria traps than in the Ferrol Ria northern to the Galician

206 coast (Cobelo-García et al., 2005). Concentrations of metals sinking particles of the Vigo Ria

207 were similar with those recovered from sediment traps located in the Black Sea (Ergül et al.,

208 2008) or Baltic Sea (Broman et al., 1994; Leivuori et al., 1998; Pohl et al., 2004) (Table 6).

209 Otherwise, concentrations were up to two times lower in studies conducted with traps in

210 continental shelf waters (Matthai et al., 2002) or up to 15 times lower in open ocean waters

211 (Kuss and Kremling, 1999). A single study was found concerning the lability of trace metals in

212 sediment traps (Nordmyr et al., 2008) in the Vöra River Estuary (Finland) that showed similar

213 lability percentages to the ones found for the Vigo Ria (Table 6).

214 *Origin and sources of suspended sedimentary material*

215 The quantity and composition of the material recovered from the traps is different among

216 traps and all over the year. The amount of SPM recovered in the outer part of the Ria (T1) was

217 higher (316 ± 217 mg) and more variable than in the inner part of the Ria (T2; 160 ± 52 mg).

218 There are two main factors influencing the amount and variability of the sedimenting material.

219 Accordingly, currents are higher in the inner ria due to the proximity to the main freshwater

220 inputs and the Rande strait, allowing the transport of particulate material to the outer ria

221 where the currents are lower favoring its deposition. These outer parts of the Galician rias are

222 greatly influenced by upwelling-downwelling conditions. During downwelling events, the water

223 mass is retained for a longer time inside the Vigo Ria (Prego et al., 2001). It is no surprise,

224 therefore, that the highest amount of SPM recovered in the outer Ria (700 mg) was recorded

225 when downwelling prevailed (Figure 2).

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226   In agreement with previous studies (Prego et al., 1993; Gago et al., 2003; Zuñiga et al., 2010; Alonso-Pérez et al., 2010), higher organic matter content was found in the inner trap due to a more intense phytoplankton activity in this part of the Ria (Gago et al., 2003) and the proximity of the main continental inputs to the Vigo Ria (Gago et al., 2005). During winter, continental particulate material dominates the composition of the sediment trap material, as depicted from the C:N ratios (Figure 2). In spring-summer, the lower freshwater input and the higher primary production – favored by upwelling conditions – as observed from the chlorophyll concentrations, leading to a dominant marine-borne (e.g. phytoplankton) sedimenting material (C:N 9-11; Figure 2).

Trace metal seasonal concentration and trend vs. composition of sinking particles

236   Concentration, lability and type of metals in retained particles are strongly related to the composition and type of material that reaches the traps and therefore to the hydrologic and oceanographic conditions. In general, during winter period, the lithogenic-like metals (i.e. Al, Fe, Ti, U and V) are more abundant. However, in spring and summer periods, the levels of the biogenic metals associated with the organic matter (i.e. Cd, Co, Cu, Ni, Pb and Zn) increased (Figure S1). A few exceptions were found to this general behavior. Although during winter the trap material was more terrigenous, the low levels of lithogenic elements on the first winter campaign results from the high POM content from terrestrial origin (confirmed by the high C:N ratio). The increase of lithogenic elements on the 12th May, may be related to increasing SPM that reaches the highest value for the inner trap, probably due to the input of terrestrial origin material and lithogenic characteristics according to the POM% that did not increase during that sampling cruise.

248   As indicated before, the intra-annual evolution of biogenic metals (i.e. Cd, Co, Cu, Ni, Pb and Zn) co-varies with the %POM. Rubio et al., 2000 indicated a good correlation between Ni, Co and organic matter for the sediments of the Vigo Ria. This behavior has also been observed in the South China Sea (Ho et al., 2010). Biogenic metals present similar or higher values in the inner trap all along the year coincident with the higher POM percentage found in that trap with respect to the outer one. This relation is also observed on the 6th May and 6th September campaigns when the highest Cu and Zn values were measured for the inner trap matching up with the highest POM percentages among all the sampling campaigns.

256   Even with the same tendency all along the year, Cu, Pb and Zn concentrations are higher for the inner than for the outer trap. A diffuse source (i.e. shipyard area or sewage treatment plant) of these type of metals considered as anthropogenic could increase their dissolved

259 levels that would be complexed or/and adsorbed by dissolved or particulate organic matter
260 respectively. The dissolved organic matter can flocculate or coagulate acting as a road for
261 these metals to the trap (Coale and Bruland, 1985; Jickels et al., 1990). Nevertheless, levels of
262 these elements decrease, mainly the labile fraction (Figure S2), under downwelling conditions.
263 This may be related with the remineralization process (Zuñiga et al., 2010) that will be more
264 intense when water keeps retained for a longer time. These particular conditions allows labile
265 fraction to be released from the particulate to the dissolved phase leading to a decrease of the
266 trace metal labile fraction in the SPM and therefore the total concentration (Figure S1).

267 Finally, it seems that Cd evolution is controlled by the productive periods in the Ria as it co-
268 varies with the chlorophyll along the year. Some authors have indicated that an uptake of this
269 element by phytoplankton or microalgae is possible (Collier and Edmond, 1984; Fehrmann and
270 Pohl, 1993; Turner and Millward, 2002). Both Cd and Zn have been related with the uptake by
271 marine phytoplankton and the increase in chlorophyll values during spring and summer
272 campaigns can confirm that these metals could have been incorporated into phytoplanktonic
273 cells acting as vehicles of metals from the water column to the traps.

274 Suspended particulate matter and metal sedimentation rates measured in the Vigo Ria are
275 similar to a recent study carried out in this ria (Alonso-Pérez et al., 2010) and comparable to
276 other studies conducted in the Black Sea (Ergül et al., 2008), in the Baltic Sea (Broman et al.,
277 1994; Leivuori et al., 1998) or in the Vöra River Estuary (Nordmyr et al., 2008) but between 10
278 and 1000 times higher than the rates or fluxes measured in the continental shelf waters
279 (Matthai et al., 2002) or open ocean waters (Kuss and Kremling, 1999) (Table 5).

280 Based on the total surface area of the Vigo Ria (156 km^2) an annual estimation of the
281 particulate matter and metals that reach the Ria can be done. Approximately 7752 tons of
282 particulate matter reaches the seabed. From this, 686 ton is Al, 315 is Fe and 23 is Ti. The rest
283 of the elements participate in a minor proportion but important quantities are deposited in
284 the Vigo Ria sediments all along the year. In this way, around 1kg of Cd, 73 kg of Co, 880 kg of
285 Cr, 1100 kg of Cu, 2254 kg of Mn, 497 kg of Ni, 1522 kg of Pb, 63 kg of U, 807 kg of V and 988
286 kg of Zn reach the Vigo Ria seabed each year. As an example, we can state that the amount of
287 particulate Cu deposited in a year period in the Ria seabed (1100 kg) is from the same order of
288 magnitude as the quantity of particulate Cu that enters the Vigo Ria from rivers and sewages
289 (1915 kg) each year (Santos-Echeandia et al., 2008).

290 The lability of most of the metals in the inner trap is higher than in the outer trap. The
291 sedimentation of these metal-labile particles will make the sediments of the inner part more

292   labile with respect to metals than the outer sediments. This distribution has been shown in

293   previous studies (Prego et al., 2008; Belzunce-Segarra et al., 2008) and implies a higher

294   contamination risk of metals like Cd, Cu, Pb and Zn from the point of view of the

295   biodisponibility (Beiras et al., 2003) and the release of metals to the dissolved phase after the

296   degradation of the organic matter (Froelich et al., 1979; Santos-Echeandia et al., 2009).

297   ***Metal enrichment in the traps and bottom sediments***

298   Aluminium is a lithogenic parameter because mimics the abundance in particulate lithogenic

299   material entering the Vigo Ria via atmosphere and rivers (Windom et al., 1989; Rubio et al.,

300   2000; Prego et al., 2008). Metal concentrations were normalized to Al in order to minimize

301   differences associated with changes of sediment nature. Furthermore, by plotting metal

302   concentrations against Al content two different patterns can be observed (Figure 4). For Fe, Ti,

303   U and V plots vs Al a single relationship ($p \ll 0.01$; $R > 0.67$) was found that includes bottom and

304   trap particles (Figure 4 a,b,c). This indicates that both the particles deposited in the seabed and

305   sediment-trap material is mainly related to the aluminosilicate fraction. Moreover, the settling

306   particles are not enriched in Fe, Ti, U and V. The other group of metals (Cr, Cu, Mn, Ni, Pb and

307   Zn) showed a different pattern when concentrations are plotted to Al content: significant

308   correlations ($p < 0.05$; $R > 0.48$) were found for Cr, Cu, Mn, Ni, Pb and Zn in bottom sediments

309   but not for sediment trap material (Figure 4 d,e,f). Different explanation hypothesis are

310   advanced depending on metals. The absence of correlation between Mn and Al in sediment

311   trap material indicates that settling particles are enriched in diagenetic manganese. In fact,

312   Mn(II) in pore waters of Vigo Ría exhibited a maximum at subsurface layers over all year

313   (Santos-Echeandia et al., 2009), which suggests that Mn(IV) in the trap sediments may be

314   generated through upward diffusion of dissolved Mn, as commonly observed in marine

315   sediments (Sundby et al., 1986). The lack of correlations between Co, Cu, Pb, Zn, Cd, Ni and Cr

316   with Al in sediment trap material indicates that those particles act as a vehicle for these metals

317   to the sediments due to contamination or uptake by plankton. This particulate material metal-

318   enriched is spread inside the Vigo Ria due to the large water mass exchanged over semi-

319   diurnal tidal cycles (Prego et al., 2010). The high Cu/Al, Pb/Al, Zn/Al, Cd/Al, Ni/Al and Cr/Al

320   ratios in sediment trap material relative to upper sediments, suggest that metals are

321   transported from the water column to sediments being rapidly remobilised from the solids

322   (Froelich et al., 1979; Berner, 1980) and transferred back to the water column (Skrabal et al.,

323   1997; Santos-Echeandía et al., 2009). Cadmium and Co are an exception to this behaviour. As

324   shown in Table 4 and Figure 4, these elements are enriched in the sediments respect to the

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325 trap material. However, the labile percentage is higher in the trap material (Fig. 3). This
326 suggests that instead of being remobilized from the sediments to the water column in
327 dissolved form, cadmium and cobalt suffer from post-depositional processes that bind them
328 with more refractory fractions of the sediments.

329 Aluminium can also be used as reference element for the calculation of enrichment factors in
330 relation to the crustal Me/Al ratio and the influence of anthropogenic metals like Cd, Pb, Cu
331 and Zn, but also as a control base for other lithogenic elements like Fe. From the background
332 equations calculated by Prego et al. (2008) for the Vigo Ria sediments, trace metals
333 enrichment factors have been calculated for each trap (data not shown). Metals like Fe, Ni, V,
334 Co, Cr and Mn showed an enrichment factor (average of the traps and seasons) close to 1,
335 indicating mostly a lithogenic origin what is coincident with the explanations given above. On
336 the other hand Cu, Pb and Zn showed enrichment factors between 3 and 8, what indicates a
337 biogenic or anthropogenic origin apart from the lithogenic one. Elements like Fe, U, Ti and V
338 are not associated with the anthropogenic changes as indicated by Prego et al., 2008 for the
339 Vigo Ria sediments, where the enrichment factors (i.e. Fe and V) where close to 1 indicating a
340 lithogenic origin. By considering bottom sediments the obtained slopes metal vs aluminium
341 relationships (Figure 4) with those obtained by Prego et al., 2008 for the background equations
342 we can conclude that our sediments are enriched in Zn and impoverished in Ni, V and Cr. This
343 strengthens the assumption that these later metals (Ni, V and Cr) were remobilized from the
344 sediments to the water column by means of benthic fluxes. For the remained elements (Cu, Fe,
345 Pb and Mn) slopes were comparable indicating that sediment deposited in this site was neither
346 enriched nor impoverished.

347 ***Postdepositional transformation of trace metals in the sediments***

348 A summary of trace metal concentration ranges in the sediments are shown in Table 6 and we
349 have found that values are similar to sediment concentrations in the Vigo Ria documented in
350 previous studies (Rubio et al., 2000; Howarth et al., 2005; Prego et al., 2008). If we divide all
351 the layers into a superficial one comprising the first 2 centimeters and a depth one from 2 to
352 10 centimeters (Table 6) we can see that although concentrations of Al, Cd, Ti and U are similar
353 among layers, Co and Ni showed higher levels in the upper layer whereas Cr, Cu, Fe, Mn, Pb, V
354 and Zn presented higher concentrations in the deeper layer. With respect to lability, Co, U and
355 Zn showed lower percentages in the upper layer. On the contrary, Cu shows higher
356 percentages in the upper layer. The rest of the elements do not show a significant variation of
357 their labile percentages from the upper to the deepest layers.

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358 A noticeable decrease in Cr, Cu, Ni, Mn and Pb was observed when comparing concentrations

359 in the surface layers of the sediment with those found in traps. This decrease, which is

360 remarkable in the labile fraction (Table 6), occurs between the trap-water depth (5 m above

361 the bottom) and the bottom and/or in the sediment surface. This change may result from: a)

362 remineralization of the particulate organic matter with a subsequent release of dissolved

363 metals in the water column, which may have minor extension since the residence time of

364 particles in 5 m water column should be hours (Balistrieri et al., 1981); b) intense diagenetic

365 postdepositional processes that affect trace metal distribution between the sediments and

366 porewaters (Froelich et al., 1979; Berner, 1980). In fact, POC content in the traps varied

367 between 5 and 48% (Figure 2) decreasing sharply to up to 4 % in surface sediments (Table 2).

368 In addition, C:N ratios increase from 9.6±0.7 in the traps during spring and summer (Figure 2)

369 to up 12.3 in the sediments (Table 2) suggesting that a remineralization of settling particles has

370 occurred in surface sediment. Therefore to the oxidation of the particulate organic matter

371 follows the release of organic matter bound metals (i.e. Cu, Pb, Zn) to the interstitial waters. In

372 fact, trace metal lability percentages were lower in the surface sediments than in the

373 particulate material recovered from the trap (Table 6). As a consequence upward and

374 downward fluxes may transfer metals to the water column or deep into the sediment. In Vigo

375 Ria these diffusive transports have different magnitude depending on oxidizing conditions of

376 surface sediments (Santos-Echeandía et al., 2009). According to these authors when the

377 sediment upper layer is oxic, the exportation of dissolved Cu (0.7-1.1 nmol cm^{-2} y^{-1}) and V (3.1-

378 4.4 nmol cm^{-2} y^{-1}) to the overlying waters is pronounced, whereas during less oxidizing

379 conditions, Ni (0.6-1.7 nmol cm^{-2} y^{-1}) and Co (0.1-0.2 nmol cm^{-2} y^{-1}) exportation from the pore

380 water increases. Transport towards the pore waters appears to be less effective, since labile

381 fraction of Cu, Pb and Zn decreased with depth, although precipitation as sulphides would be

382 favoured by the presence of AVS just below the sediment-water interface (Skrabal et al.,

383 2000). Depending on the ria water circulation, these elements will be transported to the inner

384 part of the ria with the subsequent risk for the mariculture and mussel rafts of these area or to

385 the outer zone being finally transported out of the ria becoming an important source of metals

386 to the open ocean.

CONCLUSIONS

388 The seasonal dependence of the metal composition of the trap material in the Vigo Ria was

389 shown to be influenced by biological (i.e. presence/absence of phytoplankton, type of organic

390 matter), physical (i.e. upwelling indexes) and chemical processes (i.e. coagulation,

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391 aggregation). From %Al, %POM, C:N ratio and chlorophyll values, we can assume that the
392 material found in the trap was mainly of terrestrial origin during winter sampling campaigns,
393 changing to be mainly marine-like (phytoplanktonic) with higher or lower degree of
394 mineralization towards spring and summer.

395 The organic matter composition and percentage of the material in the traps takes control over
396 Cu, Pb, Zn and Cd distribution over the year by means of labile percentages and concentrations
397 of these metals. However, Al, Ti, U and V annual variation is controlled by the inputs of
398 terrestrial material. Elements like Co, Cr, Fe, Mn and Ni, with medium lability percentages
399 depend upon both factors (POM and terrestrial inputs) showing intermediate behavior with
400 respect to the previous groups. Metals associated to POM showed higher levels in the inner
401 trap, while more lithogenic elements showed similar levels in both traps.

402 The quantity of anthropogenically-impacted metals (Cu, Pb and Zn) deposited in the sediments
403 of the Vigo Ria are higher (and more labile) during the periods of favourable upwelling indexes.

404 The presence of higher quantity of organic matter (from terrestrial origin or locally produced
405 by phytoplanktonic species) induces an increase in the vertical fluxes of elements like Cu, Pb
406 and Zn from the water column to the ria sediment. However, fluxes of Al, Ti, U and V increase
407 during winter and matching up with important continental inputs of material.

408 The degradation of the organic matter of the sediment releases these elements to the
409 dissolved phase inducing benthic fluxes to the water column of Cu, Ni and Zn. For Co and Cd,
410 however, their higher enrichment in the sediments compared to the traps suggests that they
411 are converted into a more refractory fraction upon postdepositional remineralization.

412 This work represents one of the first studies about labile trace metal concentrations and intra
413 annual variation in the particulate matter recovered from a sediment trap.

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Table(s)

Table 1. Results for the certified reference sediment material (PACS-2) using the analytical procedure for the SPM (sediment traps) and sediments

		Al (mg g^{-1})	Cd (µg g^{-1})	Co (µg g^{-1})	Cr (µg g^{-1})	Cu (µg g^{-1})	Fe (mg g^{-1})	Mn (µg g^{-1})	Ni (µg g^{-1})	Pb (µg g^{-1})	Ti (mg g^{-1})	U (µg g^{-1})	V (µg g^{-1})	Zn (µg g^{-1})
SPM Procedure	[1]	65.4 ± 8.5	2.21 ± 0.12	10.3 ± 0.4	90.4 ± 8.7	294± 23	41.3 ± 2.6	402 ± 20	36.7 ± 2.7	187 ± 7	4.75 ± 0.69	2.9 ± 1.0	129 ± 6	317 ± 12
	[2]	69.9 ± 3.6	2.09 ± 0.10	9.5 ± 1.3	99.5 ± 4.8	302 ± 16	40.6 ± 2.0	415 ± 13	37.9 ± 1.6	181 ± 6	4.62 ± 0.20	4.3 ± 1.2	131 ± 4	351 ± 18
Sediments procedure	[2]	59.6 ± 3.6	2.28 ± 0.14	13.1 ± 1.8	94.9 ± 6.2	300 ± 24	43.9 ± 1.3	473 ± 30	40.3 ± 3.6	177 ± 4	4.43 ± 0.88	2.4 ± 0.3	141 ± 6	376 ± 77
Certified		66.1 ± 5.3	2.11 ± 0.15	11.5 ± 0.3	90.7 ± 4.6	310 ± 12	40.9 ± 0.6	440 ± 19	39.5 ± 2.3	183 ± 8	4.43± 0.32	3	133 ± 5	364 ± 23

(1) Sum of both partial (1M HCl) and total (HNO3:HF) digestion

(2) Total digestion

Table 2. Organic matter percentage (calculated from POC), organic carbon and C:N ratios measured in the Vigo Ria sediment cores.

Season	Depth (cm)	%POM	%POC	C:N
Winter	0,0-1,5	5,52	3,21	11,7
	1,5-3,0	6,03	3,51	11,3
	3,0-5,0	5,42	3,15	11,4
	5,0-7,0	5,52	3,21	10,4
	7,0-10	5,44	3,16	11,6
Spring	0,0-1,0	5,19	3,02	10,1
	1,0-2,5	5,76	3,35	11,1
	2,5-4,0	5,53	3,21	11,7
	4,0-5,5	5,06	2,94	9,2
	5,5-7,0	5,40	3,14	11,7
	7,0-9,0	5,52	3,21	11,2
	9,0-10,5	5,78	3,36	12,0
Summer	0,0-1,0	6,45	3,75	10,8
	1,0-2,5	6,19	3,60	12,3
	2,5-4,0	5,14	2,99	10,9
	4,0-5,5	5,21	3,03	10,3
	5,5-7,0	3,66	2,13	11,4
	7,0-8,5	4,15	2,41	9,9

Table(s)

<p style="text-align:center">**Table 3.** Concentrations of trace elements in the sediment trap material and sediment cores (average ± 1σ).</p>

2004			Al (mg g^{-1})	Cd (µg g^{-1})	Co (µg g^{-1})	Cr (µg g^{-1})	Cu (µg g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})	Ni (µg g^{-1})	Pb (µg g^{-1})	Ti (mg g^{-1})	U (µg g^{-1})	V (µg g^{-1})	Zn (µg g^{-1})
Traps															
Winter	29-Jan	1	81.8	0.10	9.5	149.9	201.0	38.4	0.508	64.6	302.5	2.8	7.0	108.0	45.8
		2	73.3	0.05	8.6	123.0	166.4	32.9	0.393	64.7	360.7	2.4	5.9	96.0	*n.d.*
	04-Feb	1	99.8	0.12	9.7	104.3	75.4	44.5	0.322	47.7	129.5	3.4	9.0	117.7	45.3
		2	101.8	0.05	10.5	172.6	159.0	45.0	0.304	79.1	278.2	3.0	8.2	106.3	190.1
Spring	06-May	1	91.4	0.10	9.3	67.9	201.6	40.6	0.247	64.2	186.4	3.3	9.0	107.7	118.4
		2	91.7	0.10	10.7	153.3	307.7	39.6	0.217	98.6	395.6	2.9	9.1	98.4	268.3
	12-May	1	73.9	0.12	8.2	52.8	53.9	34.3	0.214	46.3	90.4	2.8	7.0	83.5	*n.d.*
		2	101.4	0.20	10.1	185.7	*n.d.*	45.0	0.225	109.9	157.6	3.2	8.3	111.3	155.6
Summer	06-Sep	1	76.4	0.17	10.4	117.7	204.7	37.8	0.285	68.0	189.1	2.3	7.6	101.1	298.9
		2	62.3	0.22	7.9	114.7	217.1	31.3	0.247	69.3	293.9	1.7	6.9	86.8	391.4
	13-Sep	1	75.5	0.11	8.7	110.8	76.9	35.1	0.221	52.8	133.4	3.0	8.3	90.3	90.5
	Average (±1σ)		84 ±13	0.12 ± 0.05	9.4 ± 1.0	123 ± 41	166 ± 78	39 ± 5	0.29 ± 0.09	70 ± 20	229 ±102	2.8 ± 0.5	7.8 ± 1.0	92 ± 30	178 ± 120
Cores															
Winter (0-9.0 cm; *n*=5)[1]			88 ± 8	1.0 ± 0.1	9.7 ± 0.6	64 ± 8	43 ± 5	33 ± 4	0.21 ± 0.03	35 ± 2	84 ± 5	2.6 ± 0.3	4.6 ± 0.4	73 ± 11	131 ± 15
Spring (0-10.5 cm; *n*=7)[1]			69 ± 5	0.9 ± 0.3	13 ± 4	51 ± 4	44 ± 9	25 ± 2	0.16 ± 0.01	36 ± 4	76 ± 12	2.4 ± 0.2	5.3 ± 0.8	71 ± 7	118 ± 15
Summer (0-8.5 cm; *n*=6)[1]			46 ± 7	1.9 ± 2.5	8.5 ± 1.1	43 ± 8	36 ± 8	19 ± 3	0.13 ± 0.02	27 ± 4	70 ± 13	1.9 ± 0.3	5.3 ± 1.9	57 ± 11	97 ± 14

[1]*n* represents the number of slices in which the core was sectioned

Table 4. Comparison of the Me/Al ratios and lability of trace elements in trap material and bottom sediments. Unpaired two-tailed t-tests for were run to check for significant differences between trap and sediment data

	Me/Al ratios			Metal Lability (in %)		
	Trap	Sediments	*P* value	Trap	Sediments	*P* value
Cd	0.002 ± 0.001	0.022 ± 0.029	<0.0001	65 ± 29	35 ± 21	<0.005
Co	0.11 ± 0.01	0.16 ± 0.04	<0.001	51 ± 11	29 ± 5	<0.0001
Cr	1.46 ± 0.43	0.80 ± 0.14	<0.001	32 ± 9	23 ± 4	<0.005
Cu	2.05 ± 1.01	0.65 ± 0.16	<0.005	92 ± 6	58 ± 10	<0.0001
Fe	0.46 ± 0.02	0.38 ± 0.04	<0.0001	45 ± 6	38 ± 8	<0.05
Mn	3.51 ± 1.25	2.52 ± 0.34	<0.05	62 ± 5	38 ± 7	<0.0001
Ni	0.83 ± 0.20	0.51 ± 0.10	<0.001	46 ± 12	32 ± 4	<0.005
Pb	2.79 ± 1.39	1.20 ± 0.30	<0.005	83 ± 6	71 ± 8	<0.0001
Ti	33.2 ± 3.7	35.3 ± 6.2	*n.s.*	11 ± 3	8 ± 2	<0.005
U	0.094 ± 0.011	0.082 ± 0.031	*n.s.*	26 ± 10	33 ± 9	*n.s.*
V	1.20 ± 0.12	1.04 ± 0.21	<0.05	34 ± 6	35 ± 4	*n.s.*
Zn	2.23 ± 1.88	1.78 ± 0.34	*n.s.*	67 ± 15	65 ± 12	*n.s.*

Table(s)

Table 5. Suspended particulate matter and trace metal fluxes from the water column to the Vigo Ria sediments during 2004.

2004			SPM (g·m⁻²·d⁻¹)	Al (g·m⁻²·d⁻¹)	Cd (µg·m⁻²·d⁻¹)	Co (mg·m⁻²·d⁻¹)	Cr (mg·m⁻²·d⁻¹)	Cu (mg·m⁻²·d⁻¹)	Fe (g·m⁻²·d⁻¹)	Mn (mg·m⁻²·d⁻¹)	Ni (mg·m⁻²·d⁻¹)	Pb (mg·m⁻²·d⁻¹)	Ti (g·m⁻²·d⁻¹)	U (mg·m⁻²·d⁻¹)	V (mg·m⁻²·d⁻¹)	Zn (mg·m⁻²·d⁻¹)
Ría Vigo																
Winter	29-jan	T1	17,7	1,44	1,86	0,17	2,66	3,56	0,68	9,01	1,14	5,36	0,05	0,12	1,91	0,81
		T2	13,9	1,02	0,69	0,12	1,71	2,32	0,46	5,47	0,90	5,02	0,03	0,08	1,34	-
	04-feb	T1	61,3	6,12	7,61	0,60	6,40	4,62	2,73	19,75	2,92	7,94	0,21	0,55	7,22	2,78
		T2	15,6	1,59	0,78	0,16	2,69	2,48	0,70	4,75	1,23	4,34	0,05	0,13	1,66	2,97
Spring	06-may	T1	30,3	2,77	3,0	0,28	2,05	6,10	1,25	7,47	1,94	5,64	0,10	0,27	3,26	3,58
		T2	15,5	1,42	1,5	0,17	2,37	4,76	0,63	3,36	1,53	6,12	0,05	0,14	1,52	4,15
	12-may	T1	29,3	2,16	3,5	0,24	1,55	1,58	1,00	6,26	1,36	2,65	0,08	0,20	2,45	-
		T2	18,2	1,85	3,7	0,18	3,38	-	0,82	4,11	2,00	2,87	0,06	0,15	2,03	2,84
Summer	06-sep	T1	8,8	0,67	1,50	0,09	1,04	1,80	0,33	2,51	0,60	1,67	0,02	0,07	0,89	2,64
		T2	7,4	0,46	1,62	0,06	0,85	1,60	0,26	1,82	0,51	2,17	0,01	0,05	0,64	2,88
	13-sep	T1	15,6	1,18	1,70	0,14	1,73	1,20	0,63	3,44	0,82	2,08	0,05	0,13	1,41	1,72
	Range	T1	8,8-61,3	0,67-6,12	1,50-7,61	0,09-0,60	1,04-6,40	1,20-6,10	0,33-2,73	2,51-19,75	0,60-2,92	1,67-7,94	0,02-0,21	0,07-0,55	0,89-7,22	0,81-24,60
	Mean		27,2	2,39	3,20	0,25	2,57	3,14	1,10	8,07	1,46	4,22	0,09	0,22	2,86	2,31
	Range	T2	7,4-18,2	0,46-1,85	0,69-3,7	0,06-0,18	0,85-3,38	1,60-10,88	0,26-0,82	1,82-5,47	0,51-2,00	2,17-6,12	0,01-0,06	0,05-0,15	0,64-2,03	2,84-39,83
	Mean		14,1	1,27	1,66	0,14	2,20	2,79	0,57	3,90	1,23	4,10	0,04	0,11	1,44	3,21
Black Sea			9,4-56,4		10,9-13,0	0,19-0,99	0,52-2,88	0,42-3,18	0,06-0,25	7,17-57,6	0,11-1,38	0,23-2,44				1,64-7,49
Baltic Sea			0,55-1,6	0,01-0,09	0,4-3	0,01-0,03	0,02-0,11	0,01-0,06	0,01-0,05	0,01-0,02	0,01-0,06	0,01-0,05	0,01		0,02-0,13	0,08-0,25
Baltic Sea			1,1-7,2	0,03-0,14	1-23	0,03-0,15	0,06-0,7	0,01-2	0,05-0,33	4-10	0,03-0,23	0,01-3				0,5-5
Vöra River Estuary (Finland)			5-120	0,27-9,72		0,16-11,4	0,20-5,76	0,16-8,52	0,19-5,04	4,09-1116	0,3-9,96		0,01-0,40	0,03-1,44	0,21-7,2	1,52-67,92

(1) Ergül et al.,2008
(2) Leivuori et al., 1998
(3) Broman et al., 1994
(4) Nordmyr et al., 2008

Table(s)

Table 6. Comparison of total trace metal concentration ranges found in the Vigo Ria traps and sediment cores with the levels measured in surface sediments and suspended particulate matter (SPM) in Rias by other authors. Values in brackets represent the percentage of lability (HCl extraction).

		Al (mg g⁻¹)	Cd (µg g⁻¹)	Co (µg g⁻¹)	Cr (µg g⁻¹)	Cu (µg g⁻¹)	Fe (mg g⁻¹)	Mn (µg g⁻¹)	Ni (µg g⁻¹)	Pb (µg g⁻¹)	Ti (mg g⁻¹)	U (µg g⁻¹)	V (µg g⁻¹)	Zn (µg g⁻¹)	Reference
Trap 1		74-100	0,10-0,17	8-10	53-150	54-205	34-45	214-508	48-68	90-303	2,3-3,4	7-9	83-118	45-299	This study
		(9-13%)	*(11-94%)*	*(41-65%)*	*(23-44%)*	*(81-95%)*	*(39-54%)*	*(56-66%)*	*(37-53%)*	*(71-87%)*	*(8-11%)*	*(13-41%)*	*(28-38%)*	*(64-92%)*	
Trap 2		62-102	0,05-0,22	8-11	115-186	159-308	31-45	217-393	65-110	158-396	1,7-3,2	6-9	87-111	156-391	This study
		(10-15%)	*(50-80%)*	*(38-67%)*	*(16-39%)*	*(91-99%)*	*(39-53%)*	*(55-69%)*	*(21-65%)*	*(74-89%)*	*(9-18%)*	*(10-42%)*	*(27-48%)*	*(55-76%)*	
Ferrol Ria (trap)		26-37	0,06-0,10			51-70	21-30			62-108				211-415	(1)
Black Sea (trap)			0,23-1,20	16-20	38-74	16-60	45-49	430-1096	4-25	9-47				133-175	(2)
Baltic Sea (trap)		31-42	0,4-3,2	15-26	60-90	40-300	18-23	950-4000	25-28	50-400				300-700	(3)
Baltic Sea (trap)		4,9-38	0,33-14			16-222	2,2-50	5,5-58	23-176	21-1181				131-2092	(4)
Baltic Sea (trap)		21-62	0,27-4,60	6-29	23-92	12-44	12-40	3,4-101	13-51	13-38	0,7-2,7		28-98	78-317	(5)
VoraRiver Estuary (Finland) (trap)		54-81		32-95	40-48	32-71	38-42	817-9300	60-83		1,9-3,3	5-12	42-60	304-566	(6)
		(6-19%)		*(34-62%)*	*(35-41%)*	*(90-97%)*	*(49-60%)*	*(60-70%)*	*(40-59%)*		*(13-18%)*	*(22-27%)*	*(36-46%)*	*(56-74%)*	
Vigo Ria (SPM)			0,24±0,12			44±21			33±8	156±112				167±132	(7)
Vigo Ria (surface sediment)		101-115	0,09-0,32	8-10	86-87	42-61	41-50	212-239	44-64	76-141	2,9-3,7*	2-7**	95-126	121-232	(8)(9)(10)
Sediment core	0-2 cm	50-93	0,08-0,12	10-21	48-58	35-46	24-30	151-183	31-41	72-88	2,2-2,4	4-6	46-71	113-140	This study
		(6-14%)	*(10-66%)*	*(14-32%)*	*(21-25%)*	*(54-79%)*	*(32-44%)*	*(29-43%)*	*(25-36%)*	*(57-87%)*	*(5-9%)*	*(19-33%)*	*(31-43%)*	*(52-94%)*	
	2-10 cm	39-98	0,07-0,14	9-12	46-75	38-64	23-37	147-231	30-39	65-99	2,2-3,0	4-6	44-86	97-154	
		(6-16%)	*(10-72%)*	*(26-37%)*	*(16-31%)*	*(31-69%)*	*(25-52%)*	*(25-48%)*	*(27-42%)*	*(46-83%)*	*(4-10%)*	*(14-46%)*	*(30-42%)*	*(52-77%)*	

(1) Cobelo-García et al., 2005
(2) Ergül et al.,2008
(3) Broman et al., 1994
(4) Pohl et al., 2004
(5) Leivuori et al., 1998
(6) Nordmyr et al., 2008 (Mean extraction of hydroxylamin and Aqua Regia)
(7) Prego et al., 2006
(8) Prego et al., 2008
(9) Rubio et al., 2000*
(10) Howarth et al., 2005**

Table S1. Trace metal labile percentages in the traps.

2004		Trap	Al (%)	Cd (%)	Co (%)	Cr (%)	Cu (%)	Fe (%)	Mn (%)	Ni (%)	Pb (%)	Ti (%)	U (%)	V (%)	Zn (%)
Winter	29-Jan	1	9	14	65	39	95	51	66	53	87	11	13	31	64
		2	12	80	61	39	99	51	69	65	85	12	10	34	-
	04-Feb	1	13	11	60	29	81	54	65	44	71	8	27	38	92
		2	11	80	67	25	96	53	69	35	84	12	17	34	75
Spring	06-May	1	10	70	46	44	90	40	56	41	84	9	25	30	70
		2	10	50	38	27	91	41	55	48	89	11	25	34	65
	12-May	1	11	75	47	43	82	42	58	37	76	9	26	28	-
		2	10	80	39	16	-	39	55	21	83	9	25	27	71
Summer	06-Sep	1	12	94	55	34	94	45	64	52	87	11	41	38	39
		2	15	73	47	38	95	45	62	61	89	18	42	48	50
	13-Sep	1	10	91	41	23	95	39	58	46	81	9	30	30	76
	Range	1	9-13	11-94	41-65	23-44	81-95	39-54	56-66	37-53	71-87	8-11	13-41	28-38	39-92
	Mean		11	59	52	35	90	45	61	46	81	10	27	33	68
	Range	2	10-15	50-88	38-67	16-39	91-99	39-53	55-69	21-65	74-89	9-18	10-42	27-48	50-75
	Mean		12	73	50	29	95	46	62	46	86	12	24	35	65

Figure captions.

Figure 1. Map of the study area showing the positions of the inner (T2) and outer (T1) traps and the sediment core C collected during 2004.

Figure 2. Annual evolution of the chlorophyll (in mg L^{-1}), suspended particulate matter (SPM, in mg) in the traps, river flow (in m^3 seg^{-1}), upwelling index (in m^3 s^{-1} km^{-1}), aluminum and particulate organic matter (POM) percentages and C:N ratios for both traps during 2004 in the Vigo Ria.

Figure 3. Lability (%) of trace elements in the SPM (sediment traps) and sediments. See text for details on the estimation of the labile fraction.

Figure 4. Correlation between trace elements and Al. Closed and open symbols represent sediment and SPM data, respectively. Regression lines were calculated using sediment data only. Broken lines represent the 95% prediction intervals. These lines are not shown for Cd and Co because no significant correlation was found.

Supplementary information.

Figure S1. Trace metal concentrations found in both traps during 2004. Units are in μg g^{-1} except from Al, Fe and Ti which are in mg g^{-1} (a) Al, Fe (left axis), Ti and U (right axis). (b) Cu, Pb and Zn. (c) Cd (right axis), Ni and V (left axis). (d) Co (right axis), Cr and Mn (left axis).

Figure S2. Trace metal labile concentrations found in both traps during 2004. Units are in μg g^{-1} except from Al, Fe and Ti which are in mg g^{-1} (a) Al, Fe, U (left axis) and V (right axis). (b) Cu, Pb, Zn (left axis), Ni and Cr (right axis). (c) Co (left axis) and Mn (right axis). (d) Cd and Ti.

Figure S3. Trace metal concentrations in the sediment cores of the Vigo Ria: refractory concentration in dark, labile concentration in grey and labile percentages. Units are in μg g^{-1} except from Aland Fe which are in mg g^{-1}
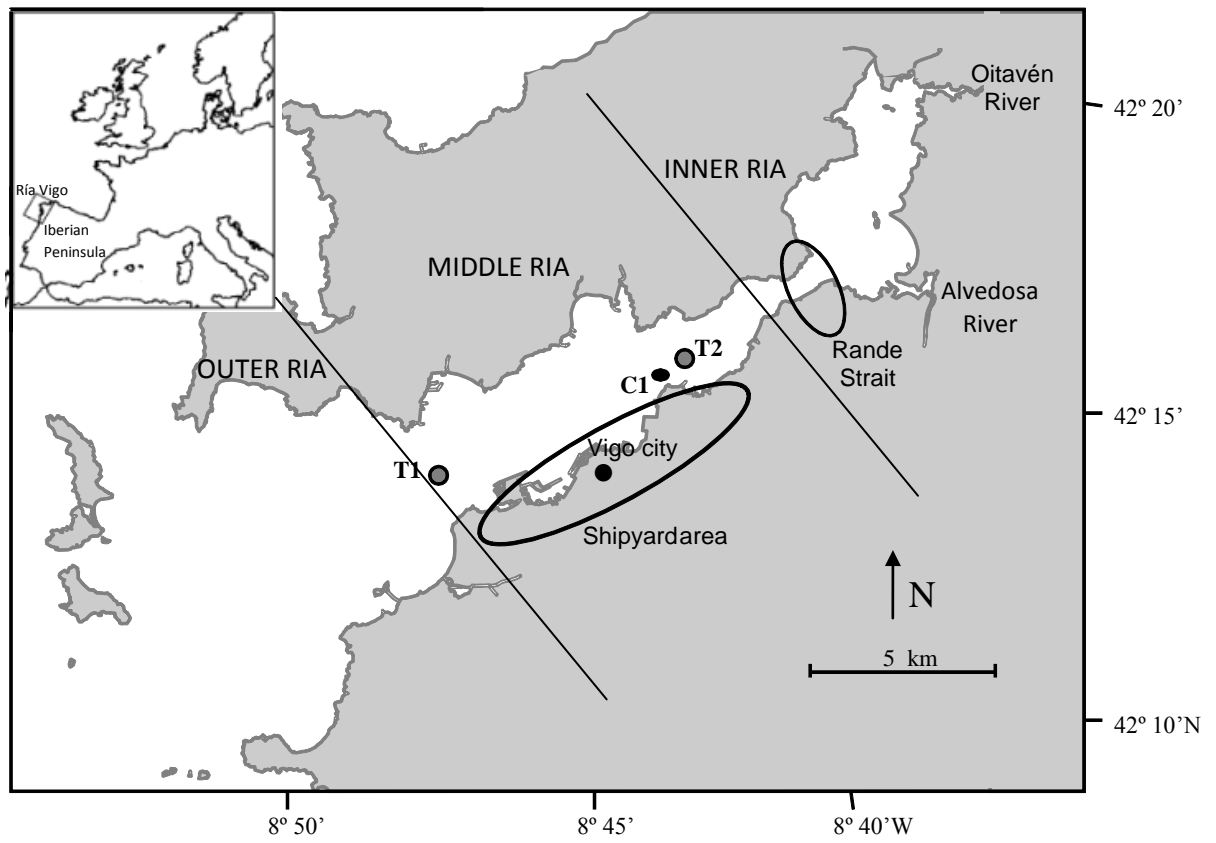
Figure 1.

Figure 2
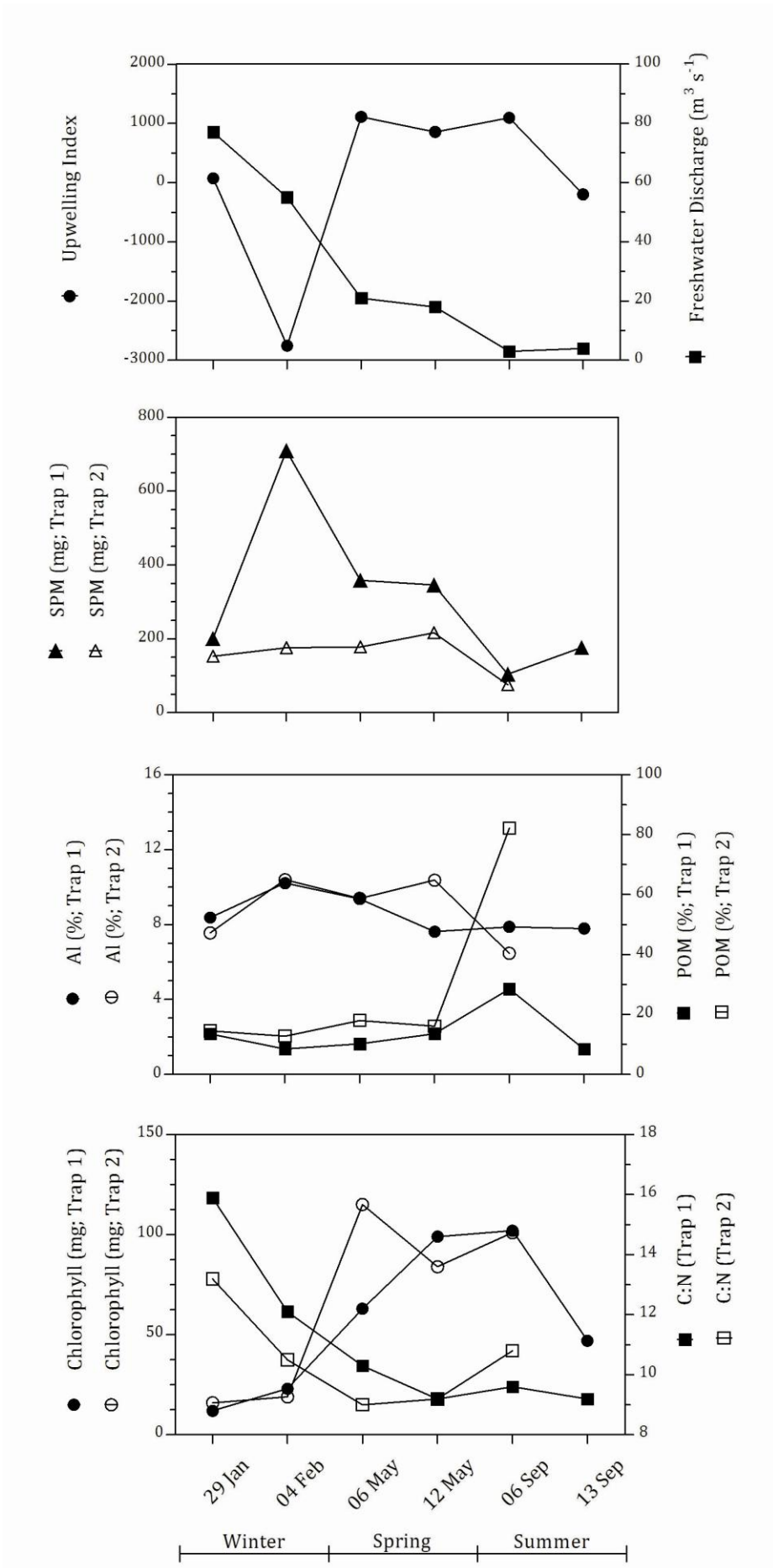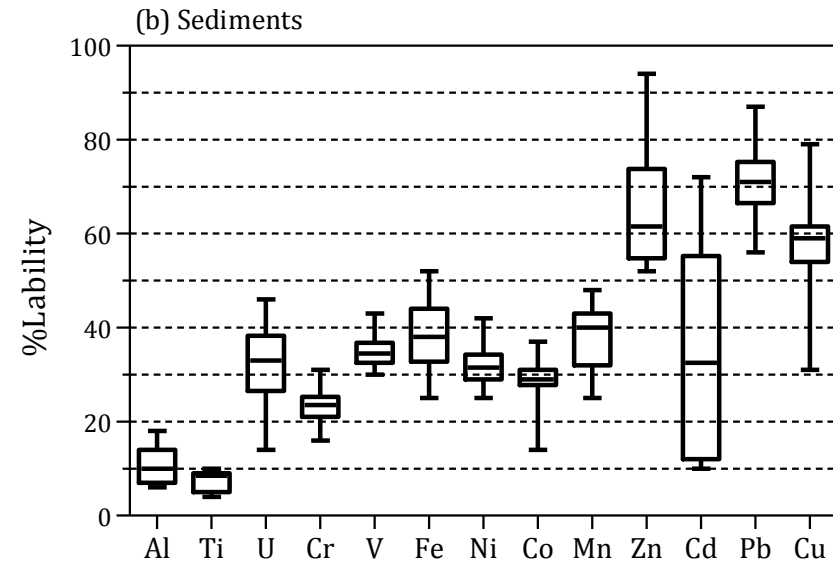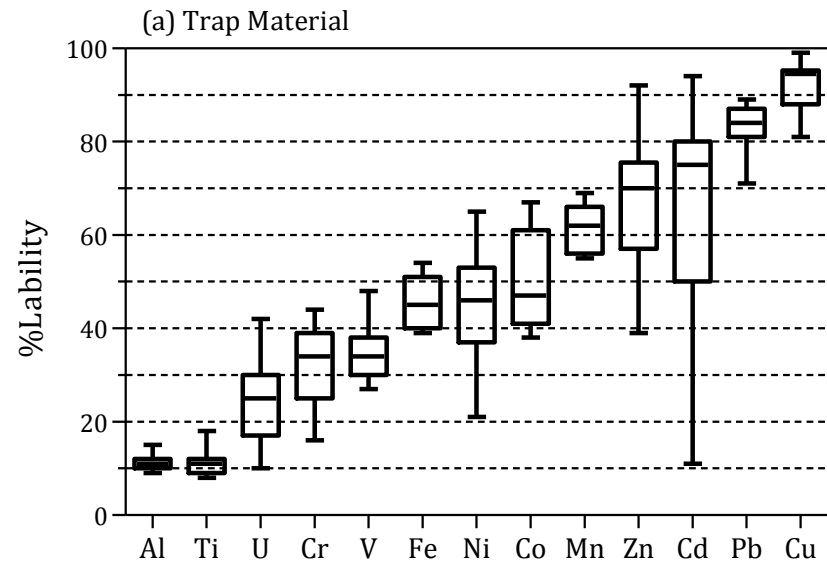
Figure 3

(a) Trap Material

(b) Sediments
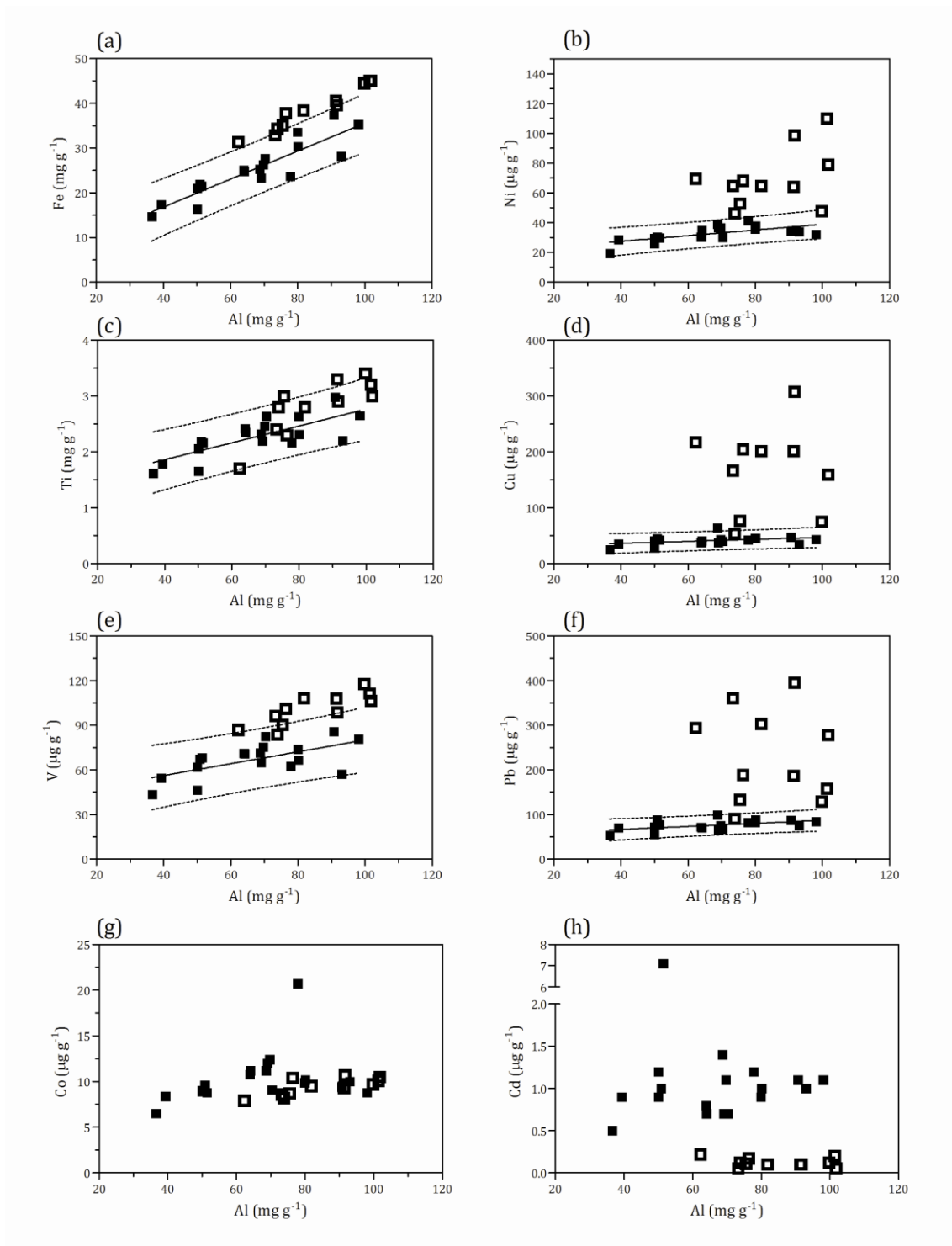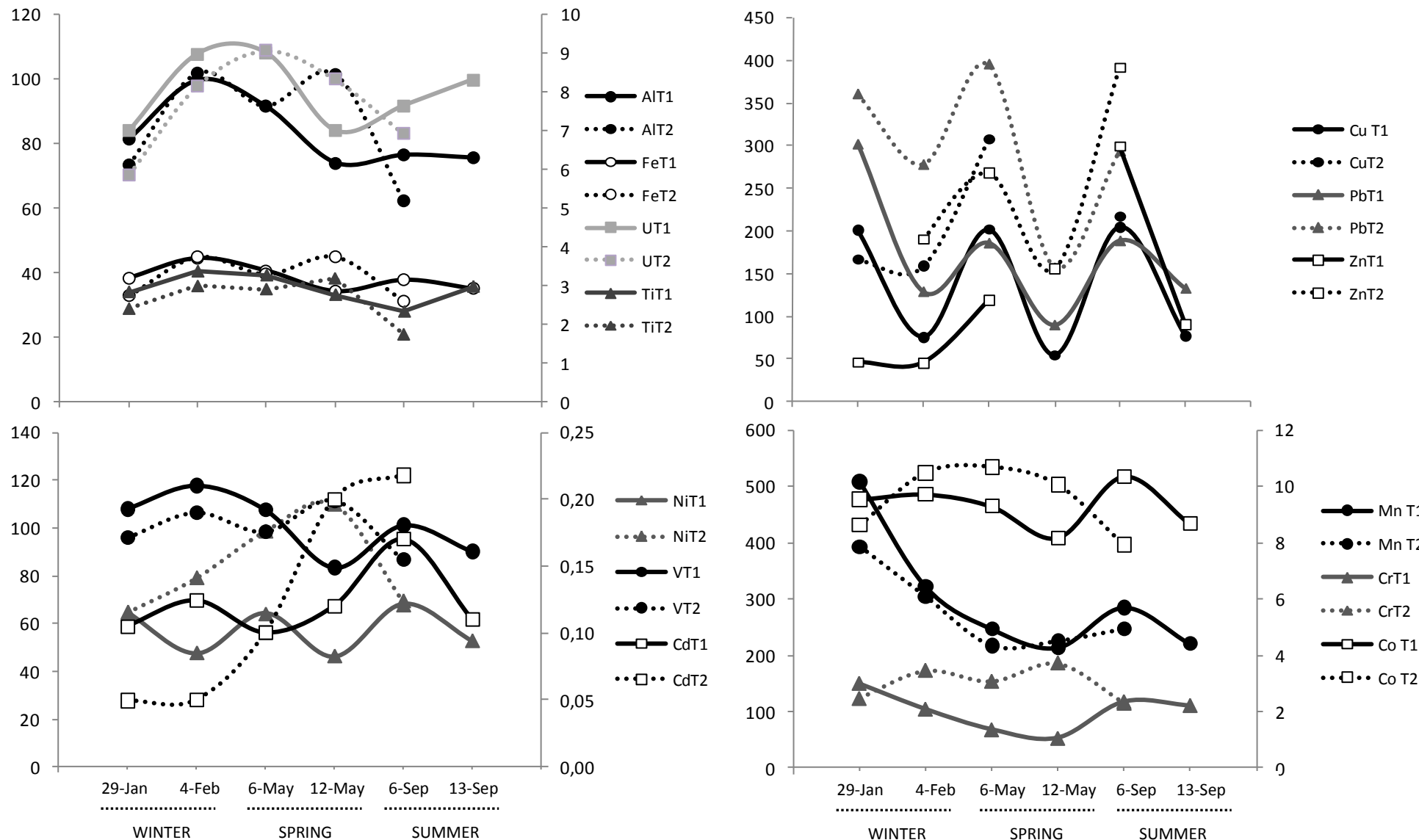
Figure 4.

Figure S1

Figure S2.

Figure S3