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1 **Cu and Zn stable isotopes in suspended particulate matter sub-fractions from the**  
2 **Northern Bay of Biscay help identify biogenic and geogenic particle pools**

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13

14 **Abstract**

15 Marine suspended particulate matter (SPM) plays a pivotal role in the marine biogeochemical  
16 cycling of trace elements. This study investigates metal distributions and copper (Cu) and zinc  
17 (Zn) stable isotope ratios in different size fractions of SPM from two sampling stations on the  
18 inner continental shelf of northern Bay of Biscay (NE Atlantic), a zone highly influenced by  
19 the macrotidal Loire estuary, the outlet of a major European river. The objective of this study  
20 is to test stable isotopes as tools to infer the origins of particles and their formation processes,  
21 and to infer relevant Cu and Zn biogenic pools involved in marine trophic transfers of these  
22 metals. SPM samples were nearly quantitatively mineralized (i.e., without HF) to determine  
23 metals and Cu and Zn isotopes in their more labile and reactive phases. Their  $\delta^{65}\text{Cu}_{\text{SRM-976}}$   
24 values ranged from -0.45 to +0.51‰, with higher Cu concentrations accompanying particle size  
25 decreasing. The  $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$  values in SPM sub-fractions varied from +0.14 to +0.76‰, and  
26 were uncorrelated to both Zn concentrations and particle size. Compared to larger size fractions,  
27 increased Al and Fe levels (proxies for terrigenous materials) and enrichments in lighter Cu and  
28 Zn isotopes observed in the smaller size SPM sub-fractions suggest that a major proportion of  
29 SPM Cu and Zn is associated with geogenic particles. Conversely, the relative enrichment of  
30 heavy isotopes in coarser particles is attributable to an increase of Cu and Zn metabolically  
31 incorporated into biogenic organic particles (e.g., plankton), and by surface adsorption onto  
32 organic detrital particles. The higher  $\delta$ -values attributed to biogenic particles likely represents  
33 the isotope composition of the local marine organic matter available to primary consumers like  
34 filter-feeders (oysters). Thus, this study shows that targeting particles of specific size classes  
35 allows to identify relative dominances of biogenic and geogenic carrier phases. Identifying  
36 these pools and their isotopic composition may help track Cu and Zn transfers through marine  
37 food-web metal in future studies.

38 **Keywords:** Biscay Bay; Loire estuary; trace metal biogeochemistry; isotope tracer; Cu and Zn  
39 stable isotopes; MC-ICP-MS

## 40 **1. Introduction**

41 In aquatic environments, suspended particulate matter (SPM) plays a pivotal role in controlling  
42 reactivity, transport and biological uptake of trace elements (Dang, Schäfer, et al., 2015; Mason,  
43 2013; Petit et al., 2015; Turner & Millward, 2002). It encompasses a wide range of particle  
44 sizes, from nanometers to millimeters, and includes a combination of allochthonous and  
45 autochthonous compounds of lithogenic, hydrogenic, biogenic and anthropogenic origins (Lam  
46 et al., 2018; Schulz & Zabel, 2006; Turner & Millward, 2002). It accounts for various organic  
47 compounds, including biofilms coated on clay mineral surfaces that can modify the surface  
48 texture and act as a cementing agent for sediment particles (Coutaud et al., 2014; Turner &  
49 Millward, 2002).

50 Trace metals can be associated with SPM as lattice structural components, or interact  
51 physico-chemically with them via adsorption, complexation, occlusion and (co)-precipitation  
52 processes (Brown & Calas, 2011; Dekov et al., 2014; Köbberich & Vance, 2018; Sparks, 2005;  
53 von der Heyden & Roychoudhury, 2015). Geochemical and biological processes (such as  
54 weathering, primary activity and hydrology) modulate interactions and distributions of trace  
55 metals in the different physicochemical SPM sub-fractions (Bianchi, 2007; de Souza Machado  
56 et al., 2016; Sparks, 2005; Tonhá et al., 2020). Therefore, their analysis in target particle classes  
57 can provide information about underlying biogeochemical processes controlling the behavior  
58 of these elements in aquatic systems, including continental shelves.

59 In recent years, the determination of stable copper ( $^{65}\text{Cu}$ ,  $^{63}\text{Cu}$ ) and zinc ( $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  
60  $^{67}\text{Zn}$ ,  $^{68}\text{Zn}$ ,  $^{70}\text{Zn}$ ) isotope abundances in environmental matrices have emerged as a new tool to  
61 examine the origins and interactions of these elements with compounds in the aquatic  
62 environment, including particles and dissolved ligands (Albarède et al., 2016; Ducher et al.,  
63 2016; Moynier et al., 2017). Heavy and light isotopes of these elements exhibit subtle  
64 differences in their chemical reactivities related to bond energies. They are unevenly distributed  
65 among reactants and products, phases, molecules, or compartments, involved in  
66 biogeochemical processes: biological uptake, redox reactions, scavenging and others (Araújo  
67 et al., 2022; Fujii et al., 2014; Little et al., 2014; Sherman & Little, 2020; Wiederhold, 2015).  
68 This isotope fractionation phenomenon occurs in a variety mechanisms and magnitudes,  
69 yielding isotope ratio changes that allow tracking Cu and Zn controlling processes (Aranda et  
70 al., 2012; Borrok et al., 2008; Skierszkan et al., 2016; Viers et al., 2018; Weiss et al., 2007).

71 In aquatic systems, the characterization of Cu and Zn isotope signatures of SPM present  
72 in fluvial, lacustrine and estuarine environments has been used to trace the sources and sinks of  
73 these elements (Araújo et al., 2017; Babcsányi et al., 2014; El Azzi et al., 2013; Guinoiseau et  
74 al., 2018; Liang et al., 2020; Peel et al., 2009; Petit et al., 2013, 2015). However, isotope  
75 description of the distribution of these elements in different size classes of aquatic SPM is  
76 lacking and hence, deserves major investigations. Since particle size depends only on  
77 weathering processes, biological activity and contaminant transport in the watersheds (Chester,  
78 2003; Schulz & Zabel, 2006; Unda-Calvo et al., 2019), describing Cu and Zn isotope  
79 compositions in the different size classes of SPM sub-fractions can provide additional  
80 information about sources and processes that is not accessible when analyzing only bulk SPM.  
81 For an example, in the context of Cu-contaminated soils by vineyard activity, analyses of silt  
82 and fine clay fractions of the soils showed distinct Cu isotope compositions related to the  
83 mineralogical and geochemical phases (Babcsányi et al., 2016; El Azzi et al., 2013). In  
84 atmospheric environments, Cu and Zn isotope distribution among particle size fractions of  
85 mineral dust presented a “U-shape” pattern, with lighter isotopic compositions in the mid  
86 particle size fractions and heavier isotopic compositions in the smaller and larger particles  
87 (Schleicher et al., 2020).

88 To date, however, very little Cu and Zn isotope data exist for particulate material from  
89 the marine water column (Little et al., 2018). To fill this gap, this preliminary study examines  
90 possible Cu and Zn isotope variability in different particle size classes of the SPM from the  
91 northern Bay of Biscay (NE Atlantic), a local influenced by the macrotidal Loire estuary. We  
92 targeted the Cu and Zn isotopes in labile, reactive and biologically available fractions of  
93 particles, rather than the Cu and Zn atoms from solid lattice structures by using a “pseudo” total  
94 extraction (without hydrofluoric acid). With this approach, we intend to link the observed  
95 isotope patterns with biogeochemical processes, in order to constrain particle origins (inorganic  
96 vs. organic, natural vs. anthropogenic) and to identify the bioorganic pools (*e.g.*, plankton) that  
97 are relevant in transferring Cu and Zn to upper trophic levels. Analyses of other trace and major  
98 elements are used to support the discussion.

99

## 100 **2. Methods**

### 101 *2.1 SPM sampling and preparation*

102 The Bay of Biscay is an open oceanic basin in the north-eastern Atlantic Ocean, fringed by the  
103 Spanish and French coasts (Fig. 1). The continental shelf is up to about 100 miles (160 km)  
104 wide off the coast of Brittany but narrows to less than 65 km off the Spanish shore. The

105 counterclockwise surface currents of the Biscay Bay are influenced by the circulation in the  
106 North Atlantic. From mid-autumn to early spring (thus including winter as a whole), intense  
107 river flows associated with sustained wind activity maintain this region under the influence of  
108 the northward plumes of the Gironde and Loire rivers along the coast, with relatively low  
109 salinities between the coast and the 100 m isobath, at around 20–40 km from the coast (Penaud  
110 et al., 2020). Freshwater discharges from the main rivers (Loire, Gironde, Vilaine and Adour;  
111 cumulative annual mean flow around 4200 m<sup>3</sup>/s) in surface layers thus induce steep density  
112 gradients driving a poleward circulation (about 10 cm/s) modulated by wind forcing (Lazure et  
113 al., 2008; Lazure & Jegou, 1998). The climate on shore is maritime, with mild winters and cool  
114 summers (Penaud et al., 2020).

115 The macrotidal Loire estuary (~106 km long) is the seaward end of Loire River, a major  
116 European river, with a mean annual waterflow of 890 m<sup>3</sup> s<sup>-1</sup>. The well mixed and highly turbid  
117 sedimentary plume of this estuary extends over a large part of the northern Bay of Biscay  
118 continental shelf (Dulaquais et al., 2020) (Waeles et al. 2004). The maximum turbidity zone  
119 (MTZ), delimited where SPM in the water column water reach > 1g L<sup>-1</sup>, is estimated to be about  
120 20- to 50-km long (Briant et al., 2021; Dulaquais et al., 2020; Jalón-Rojas et al., 2016). The  
121 Loire estuary has an industrialized and urbanized watershed that comprises the metropolitan  
122 areas of Nantes and Saint-Nazaire with its more than 800,000 inhabitants (Grosbois et al., 2012;  
123 Coynel et al., 2016).

124 A previous Cu isotope characterization of surface and core sediments in this estuary  
125 indicated a dominant natural Cu origin and a spatial isotope variability related to the  
126 hydrodynamic particle sorting between silt, clay, organic and amorphous particles through the  
127 fluvial-estuarine continuum (Araújo et al., 2019b). In turn, Zn isotope compositions in this zone  
128 was explained by natural and anthropogenic mixing source processes (Araújo et al., 2019). A  
129 similar explanation was also proposed for the variations observed in oysters (*Crassostrea gigas*)  
130 harvested near this estuary (Araújo et al., 2021).

131 For this study, the SPM samples near the Loire estuary were collected in April 2013 at  
132 2 stations in the north Bay of Biscay inner shelf (LEP1 and LEP2). Sampling was performed  
133 by successive horizontal trawls using nylon nets (0.25 m<sup>2</sup> circular opening, 63 µm mesh size)  
134 coupled to a cylindrical polymer collector at its end, in order to collect enough material in the 5  
135 m below the surface for analyses. We thus considered contributions from remobilized particles  
136 from bottom sediments negligible.

137 At each station, seawater samples were collected through a WP2 sampling system and  
138 wet-sieved through a series of nylon sieves with mesh sizes of 2000, 1000, 500, 250 and 63 µm

139 previously cleaned with ultra-pure water in a containerized clean-room to prevent  
140 contamination. A total of four sub-samples representing the following size fractions were  
141 obtained for station LE1 south east of the river mouth (Fig. 1): >2000, 1000-500, 500-250, and  
142 250-63  $\mu\text{m}$ . The same fractions were chosen for station LE2 located north east of the river  
143 mouth, except 1000-500  $\mu\text{m}$ , where insufficient amounts of material were collected to allow  
144 analyses. These size fractions are operationally defined and commonly used in the study of  
145 trace elements in marine plankton assemblages (e.g. Chouvelon et al., 2019; Strady et al., 2015).  
146 Several studies showed that size fractions >60  $\mu\text{m}$  likely contain a greater fraction of (living)  
147 phyto- and/or zooplankton that mostly sustain higher trophic levels, and no more detritus, viro-  
148 or bacterioplankton (e.g. Rolff and Elmgren 2000, Espinasse et al. 2014).

149 Filtered seawater from the site was used to gently push SPM tangentially to the surface  
150 of the sieves. Then, SPM size fractions were poured in acid-cleaned polyethylene tubes and  
151 immediately frozen at  $-18^{\circ}\text{C}$ . Back at the laboratory, they were freeze-dried and then stored at  
152 room temperature, in the dark in the laboratory until analyses. A total between 5 and 7 g of  
153 sample mass were obtained for each sampling station (Supplementary Material -Table 1S). For  
154 LE1, 57% of total mass concentrated in the 63-250  $\mu\text{m}$  and 16% in 250-500  $\mu\text{m}$  (Table 1S). For  
155 LE2, 63-250 and 250-500  $\mu\text{m}$  contributed with 35 and 40% approximately. In both stations, the  
156 class 500-100  $\mu\text{m}$  had few materials, below 5%.

157 As noted, the SPM was collected with plankton nets and sampling protocols designed  
158 to preserve as much as possible the integrity of organisms it may contain for later identification  
159 and quantification (Chouvelon et al., 2019). However, these methods normally result in  
160 complex samples that include both planktonic organisms and non-living organic and inorganic  
161 particles. Nevertheless, this method is advantageous as it preserves cellular contents of  
162 organisms and allows their concentration from tens of cubic meters of seawater. Indeed, for an  
163 example, frontal-flow filtration rapidly clogs and likely induces plasmatic membrane rupture.  
164 In this work, "SPM" designates the range of particle matrices present in the surface of an  
165 estuarine water column and collected using a plankton net and serial wet sieving.

166

## 167 *2.2 Elemental and isotope analysis*

168 Dry SPM samples were weighted in Teflon® reactor vessels and digested with nitric acid  
169 solution (3 ml of concentrated  $\text{HNO}_3$  + 3 ml of  $\text{H}_2\text{O}$ ) assisted by microwave radiation. This  
170 method extracts metals from potentially bioavailable phases, commonly referred as water-  
171 soluble, and also the exchangeable, acid-soluble, reducible, oxidable, etc. phases (Gleyzes et  
172 al., 2002; Rao et al., 2008; Tessier & Turner, 1995; Tonhá et al., 2021). It is considered a partial

173 extraction of the sample, and since hydrofluoric acid (HF) that breaks down crystalline matrices  
 174 was not included, we consider negligible the fraction of extracted metals from crystal lattices  
 175 of silicates. Splits from the final solution were subsequently analyzed for metal concentrations  
 176 by ICP-MS (Cu, Zn, Pb, Cd, Ag, Co, Cr, Ni, Mn, Ti, V, Fe, and Al) and isotope compositions.  
 177 Plankton BCR 414 and oyster soft tissue SRM 1566b, as reference materials (RMs) of  
 178 biological matrices, were used since they are closest to the planktonic and marine characters of  
 179 our samples. They were processed jointly with each sample batch, including procedural blanks,  
 180 and recoveries are within  $\pm 10\%$  of certified values. Similar recoveries were obtained for MESS-  
 181 3 reference material (RM), digested using a total extraction (e.g., with HF, as described in  
 182 Araújo et al., 2019a,b). The latter was used only for analytical control of isotopic analyses.

183 Cu and Zn were isolated from their matrix interferences before isotope analysis by ion  
 184 exchange column chromatography packed with AG-MP1 resin following an adaptation of the  
 185 protocol of Maréchal et al. (1999). Chromatographic recovery yields were checked by ICP-MS  
 186 and isotope ratios measured by MC-ICP-MS (Neptune, Thermo Scientific) at the analytical  
 187 platform (PSO *Pôle Spectrométrie Océan*, Ifremer, Brest, France). Samples dissolved in 2%  
 188 (v/v) HNO<sub>3</sub> medium at metal concentrations of 250 ng.ml<sup>-1</sup> were introduced using a stable  
 189 introduction system and mass bias corrected by a combination of a sample-standard bracketing  
 190 combined with external normalization technique (Cu doping Zn samples and vice-versa). The  
 191 Cu and Zn isotope compositions of samples are expressed as  $\delta^{65}\text{Cu}$  and  $\delta^{66}\text{Zn}$  values, using the  
 192 NIST SRM 976 and the “JMC-Lyon” as reference standards according to Equations 1 and 2,  
 193 respectively:

194

$$195 \quad \delta^{65}\text{Cu}_{\text{SRM-976}} (\text{‰}) = \left( \frac{R\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{sample}}}{R\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{SRM-976}}} - 1 \right) \times 1000 \quad (\text{Eq.1})$$

196

$$197 \quad \delta^{66}\text{Zn}_{\text{JMC-Lyon}} (\text{‰}) = \left( \frac{R\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}}\right)_{\text{sample}}}{R\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}}\right)_{\text{JMC-Lyon}}} - 1 \right) \times 1000 \quad (\text{Eq. 2})$$

198

199 The average precision (2s) obtained from two or three measurements for a single replicate  
 200 during a unique analytical session was  $\pm 0.04\text{‰}$  for both analytes. Our obtained  $\delta^{65}\text{Cu}_{\text{SRM-976}}$   
 201 value for the plankton RM BCR 414 ( $-0.27 \pm 0.02\text{‰}$ , 2s,  $n = 3$ ) agreed with reported values in

202 literature ( $-0.29 \pm 0.10\%$ ,  $2\sigma$ ,  $n = 3$ , Yang et al., 2020;  $-0.27 \pm 0.05\%$ , Takano et al., 2020),  
203 while the corresponding  $\delta^{66}\text{Zn}_{\text{JMC}}$  for this RM ( $+0.23 \pm 0.09\%$ ,  $2s$ ,  $n = 1$ ) fell in the same range  
204 of values reported by Takano et al.(2020) of  $+0.31 \pm 0.03\%$  ( $2s$ ,  $n = 10$ ). Longer time series of  
205 analyses of the oyster tissue SRM 1566b yielded reproducible  $\delta^{65}\text{Cu}_{\text{SRM-976}}$  and  $\delta^{66}\text{Zn}_{\text{JMC}}$  values  
206 of  $+0.23 \pm 0.03\%$  ( $2s$ ,  $n = 11$ ) and  $+0.70 \pm 0.05\%$  ( $2s$ ,  $n = 5$ ), respectively. These values are  
207 close to the  $\delta^{65}\text{Cu}_{\text{SRM-976}}$  value of  $+0.30 \pm 0.02$  ( $2s$ ,  $n = 4$ , Jeong et al., 2021) and  $\delta^{66}\text{Zn}_{\text{JMC}}$  values  
208 of  $+0.68 \pm 0.04\%$  ( $n = 14$ ,  $2s$ , Nitzsche et al., 2021). Measurements of the sediment MESS-3  
209 RM during several analytical sessions yielded a  $\delta^{66}\text{Zn}_{\text{JMC}}$  of  $+0.26 \pm 0.06\%$  ( $2s$ ,  $n = 9$ ), which  
210 agrees with another published value ( $+0.28 \pm 0.02\%$ ,  $2s$ ,  $n = 4$ , Druce et al., 2020). The  
211 corresponding  $\delta^{65}\text{Cu}_{\text{SRM-976}}$  for this sediment was  $+0.03 \pm 0.1$  ( $n = 9$ ), but no literature data are  
212 available for comparison.

213

### 214 2.3 Principal Component Analysis (PCA)

215 Principal Component Analysis (PCA) was applied to identify the main interrelations among the  
216 elemental variables, and hence, summarizing dataset information by grouping inter-correlated  
217 variables in principal components (Meglen, 1992). PCA factor loads were calculated using the  
218 correlation matrix with varimax rotation. The principal components (PCs) that had eigenvalues  
219 higher than 1 were selected for discussion (Mar da Costa et al., 2016; Mulholland et al., 2012).  
220 The communalities values of all variables equal or higher than 0.5 were used as thresholds for  
221 PCA results acceptance (Araújo, et al., 2019). PCA analysis was performed using the SPSS®  
222 software v.18.0 (IBM®). Linear relationship between variables were estimated using Pearson  
223 coefficients.

224

## 225 3. Results and discussion

226

### 227 3.1 Elemental and isotope distributions in the SPM sub-fractions

228 Concentrations of Cu vary from 2 to  $57 \mu\text{g g}^{-1}$  dry weight (dw) and display an overall tendency  
229 of increasing with decreasing particle size (Table 1; Fig. 2a,b). In turn, Zn concentrations range  
230 from 66 to  $200 \mu\text{g g}^{-1}$  dw and are uncorrelated with particle size, with the highest Zn  
231 concentrations observed in intermediate-size fractions (Table 1; Fig. 2c,d). The  $\delta^{65}\text{Cu}_{\text{SRM-976}}$   
232 values of both sampling stations range from  $-0.45$  to  $+0.51\%$ , while  $\delta^{66}\text{Zn}_{\text{JMC}}$  values vary from  
233  $+0.14$  to  $+0.76\%$ . For both sites, the elemental and isotope Cu systematics demonstrate a clear  
234 trend towards lighter Cu isotope compositions and higher concentrations with smaller particle  
235 sizes (Fig. 2a,b). Zinc stable isotope systematics are less clear (Fig. 2c,d), even if the lightest



236 isotope compositions occur in the smallest size class 63-250  $\mu\text{m}$  that was collected at both  
237 sampling stations, and in the 250-500  $\mu\text{m}$  class of the LE2 sample. A comparison of particle  
238 classes of the same sizes shows similar values at both sites, except for Zn in the class size 250-  
239 500  $\mu\text{m}$ .

240 Principal Component Analysis (PCA) was applied to the dataset to visualize the  
241 intercorrelations between the concentrations of Cu and Zn and other elements. It yields two  
242 main components that together explained 92% of total dataset variance and discriminated two  
243 clusters of elements, here labelled as “Group A” and “Group B”, respectively (Fig. 3a). Group  
244 A comprises Cu, Pb, Ni, Cr, Co, Mn, V, Ti, Al and Fe, while Group B includes Zn, Cd, and Ag  
245 (Fig. 3a). Elements from the first cluster show an overall tendency of concentration increase  
246 with particle size decrease, analogous to Cu (Table 1). In the second cluster, the elements  
247 display highest concentrations in intermediate size fractions, similarly to Zn (Table 1). In Group  
248 A, major elements (Al and Fe) and trace elements (Mn, V, Ti, Co, Cr, V, Pb, and Ni) showed  
249 strong coefficients of correlations ( $r > 0.9$ ,  $p < 0.01$ ), while in Group B, Cd and Ag are strongly  
250 correlated among them ( $r > 0.9$ ,  $p < 0.01$ ). Copper show affinities with Cr and Ni ( $0.7 < r < 0.9$ ,  
251  $p < 0.05$ ). In turn, Zn is not significantly correlated to Cd and Ag ( $0.1 < p > 0.05$ ), despite  
252 belonging in the same cluster.

253 In the southernmost LE1 sampling station, the finer SPM sub-fraction of 63-250  $\mu\text{m}$   
254 contribute with 73% of total Cu mass. Based on the mass sub-fractions and their respective Cu  
255 concentrations we estimate a bulk SPM concentration of 13  $\mu\text{g g}^{-1}$  and a  $\delta^{65}\text{Cu}$  value near -  
256 0.27‰ (Table 1S). This estimated isotope value is much lighter than the average obtained for  
257 the bottom sediments from the Loire estuary mouth and its vicinities ( $-0.04 \pm 0.18$ , 2s,  $n=31$ ,  
258 Araújo et al., 2019b). For Zn, estimations yield a concentration of 96  $\mu\text{g g}^{-1}$  and a  $\delta^{66}\text{Zn}$  value  
259 of +0.43‰, which fell above the average of the local sedimentary surface ( $+0.24 \pm 0.06$ , 2s,  
260  $n=25$ ). The difference between bulk SPM and bottom sediments suggest differences in their  
261 physicochemical compositions of each compartment. Surface sediments tend to be enriched in  
262 denser particles that settled through the water-column and their composition modified by early  
263 diagenesis occurring immediately below.(Coynel et al., 2016; Dang, et al., 2015). An  
264 unfortunately missing analysis of the (1000-500  $\mu\text{m}$ ) fractions did not allow to estimate bulk  
265 values at LE2.

266

### 267 *3.2 Using Cu isotope information to infer particle origins and underlying processes*

268 The northern continental shelf Bay of Biscay receives high loads of metals associated with i)  
269 inorganic and organic particles derived from weathering and erosion of the continental surface,

270 ii) in situ primary productivity, and iii) anthropogenic emissions from the Loire estuary  
271 watershed (Araújo, et al., 2019b; Briant et al., 2017, 2021; Coynel et al., 2016; Penaud et al.,  
272 2020). This particulate material is likely the main source of the elements from group “A” in the  
273 PCA analysis (Cu, Al, Fe, Mn, V, Cr, Ni, Ti, Pb, Co). The similar Fe to Al ratio in all the SPM  
274 samples indicates that the relative proportions of these two major elements are constant across  
275 the different particle size classes (Fig. 3b), which demonstrates that terrigenous materials are  
276 ubiquitous in the samples. Figure 3b also shows that, increased Fe and Al concentrations with  
277 decreasing particle size indicates a stronger imprint of “continental” inorganic (i.e., Fe and Al-  
278 containing) particles on the smaller size class particles (Fig. 3b). The accompanying  
279 concentration of the “continental” trace elements (group “A”), including Cu, point to the role  
280 of geogenic particles, mostly composed of clay minerals and their surface coatings, in  
281 transporting these elements from estuary mouth to the shelf of the bay.

282 The observed lighter Cu isotope compositions of finer particles are also consistent with  
283 the presence of weathered, smaller-size minerals and their increased capacity to adsorb this  
284 trace metal. In the critical zone, once released from their primary mineral structures, Cu isotopes  
285 tend to partition between aqueous organic complexes and residual particulate phases (Fe-Mn  
286 oxyhydroxides, clay minerals). The former become enriched with the heavy isotopes, while the  
287 latter become enriched with the light isotopes (Little et al., 2014; Vance et al., 2016). Field  
288 studies observed the link between enrichment of light isotopes in clay minerals with primary  
289 mineral depletion in soils (Guinoiseau et al., 2017, 2018b), while batch experiments showed  
290 the preferential light isotope adsorption on the surface of kaolinite (Li et al., 2015), and  
291 preferential heavy isotope losses in acid-leachates on natural basalts (Li & Liu, 2022). The  
292 coherence of our results with the cited field and laboratory studies point to weathering as the  
293 primary source of Cu with cumulative effects of organic ligands adsorption on solid surfaces as  
294 the principal controlling processes of group “A” (continental) elements in the finer particle size  
295 classes.

296 Conversely, the coarser SPM fractions exhibit lower concentration of crustal elements  
297 (Table 1), and hence, we infer that the relative fraction of organic matter, which includes living  
298 organisms and detrital forms of plants and micro-organisms, should increase. It is well known  
299 that Cu presents high affinity with organic matter (Ilina et al., 2013). Furthermore, experimental  
300 adsorption of Cu isotopes on organic matter (insolubilized humic acid-IHA) indicates the  
301 preferential retention of the heavy isotope in the organo-Cu complexes (Bigalke et al., 2010).  
302 Similarly, Cu adsorption onto phototrophic biofilm induces enrichment of biomass in heavy  
303 isotope (Coutaud et al., 2014). These observations suggest that Cu-organic matter-associations

304 in the SPM fractions could form a pool of isotopically heavy Cu. Indeed, the homeostatic  
305 regulation of Cu in microorganisms, such as in meso- and macro-plankton could result in an  
306 isotopically heavy, bioaccumulated Cu pool. It is well-known that Cu heavy isotopes  
307 preferentially tend to bound to O- and N- donors of proteins involved in metabolic functions  
308 (Albarède et al., 2016). Conversely, light Cu isotopes would be preferentially associated to S-  
309 ligands often used for detoxification and excretion processes. High positive  $\delta^{65}\text{Cu}$  values found  
310 in sheep and mouse kidney has been also interpreted in terms of isotope fractionation in redox  
311 reactions involving Cu (I) and Cu (II) species. These dual and opposite effects fractionation  
312 mechanisms were also used to explain Cu isotope systematic observed in mussels (Araújo, et  
313 al., 2021). It is unknown if the plankton of distinct size classes, composed of different species  
314 assemblages present different isotope enrichment patterns related to metabolic and homeostatic  
315 processes. In any case, the Cu isotope systematic presented here identifies two main Cu pools  
316 in suspended particulate matter: a mineral rich (continental) pool, enriched in light isotopes,  
317 and an organic-rich, labile pool, enriched in the heavy isotope. Such a systematic is very similar  
318 to the particulate phase of South Atlantic ocean waters (Little et al., 2018).

319

### 320 *3.3 Using Zn isotope composition to infer particle origins and underlying processes*

321 The inter-correlations among Cd, Zn, and Ag identified in PCA analysis suggest that these  
322 elements are less influenced by the detrital, terrigenous materials that are preferentially present  
323 in the smaller-size SPM sub-fractions. Their concentrations and mass contents do not increase  
324 with decreasing particulate size. Rather, they tend to be highest in intermediate size fractions  
325 of SPM (Fig. 2c,d, for Zn; Table 1, for Ag and Cd). A similar pattern was also reported, but not  
326 explained, in another study conducted in Gulf of Lions (NW Mediterranean Sea, Chouvelon et  
327 al., 2019) using an analogous sample preparation, that is, seawater passed through sieves of  
328 decreasing mesh (200, 60 and 6  $\mu\text{m}$ ). The authors related the observed Cd, Zn and Ag  
329 distributions in SPM sub-fractions to the assimilation of Zn, Cd and Ag by copepods via  
330 protozoa diet (Chouvelon et al., 2019), despite the lack of detailed information about actual  
331 species distribution in the various SPM fractions. Indeed, the literature shows biomagnification  
332 of Zn, Cd and Ag in the low part of the trophic chain (Reinfelder et al. 1998). A higher Zn  
333 association with biologically-influenced particles is consistent with its status as the second-  
334 most abundant micronutrient in phytoplankton biomass (Morel, 2003; Twining & Baines,  
335 2013).

336 The smallest size-classes of the SPM in LE1 (250-63  $\mu\text{m}$ ) and LE2 (500-250  $\mu\text{m}$  and  
337 250-63 and) displayed  $\delta^{66}\text{Zn}$  values within the range for Loire estuary bottom sediments, about

338 +0.24 ± 0.11 (2s, n=26, Araújo et al., 2019). Zinc concentration of the surface sediment in the  
339 Loire estuary mouth is influenced by geogenic ( $\delta^{66}\text{Zn}_{\text{JMC}} \sim 0.3\text{‰}$ ) and anthropogenic Zn  
340 ( $\delta^{66}\text{Zn}_{\text{JMC}} \sim 0.1\text{‰}$ ). Thus, these natural and anthropic Zn sources may also be reflected in the  
341 Zn isotope compositions observed in the finer particle fractions of LE1 and LE2 sampling  
342 stations.

343 Overall, Zn isotope variability of smaller, geogenic particles is close to crustal rocks  
344 since isotope fractionation along weathering processes is small, but a subtle isotope  
345 fractionation with preferential allocation of the heavy and light isotope in particulate and  
346 dissolved phases is noticeable in most field samples (Desaulty & Petelet-Giraud, 2020;  
347 Guinoiseau et al., 2018b; Little et al., 2014; Moynier et al., 2017; Suhr et al., 2018; Vance et  
348 al., 2016). Like for Cu, geogenic Zn isotope signatures seems to result from the balance between  
349 complexation by organic ligands and sorption on solid surfaces in weathering processes.

350 It is important to note that, like models, laboratory work does not include the complexity  
351 and conditions of real systems, which may yield findings different than field observations. For  
352 example, Zn batch adsorption experiments have mostly demonstrated a preferential binding of  
353 the heavy isotope in surfaces of clay minerals and Fe-Mn-Al oxyhydroxides (Komárek et al.,  
354 2021). However, in estuaries (e.g., Gironde and Pearl Harbor), it has observed an unexpected  
355 preferential removal of the light Zn isotope from the dissolved fraction via sorption processes  
356 on surface particles through the maximum turbidity zones (Ma et al., 2020; Petit et al., 2015).  
357 The mismatch between field and laboratory results can also be related to equilibrium conditions  
358 built into experimental designs, whereas natural processes in dynamic areas close estuaries can  
359 occur kinetically-driven.

360 Anthropogenic Zn from urban and industrial emissions, mainly released by the erosion  
361 of Zn-plated materials, vehicular traffic (tires and brake pad wear, and combustion), and sewage  
362 has lighter isotope values centered around 0.1‰ (Desaulty & Petelet-Giraud, 2020; Nitzsche et  
363 al., 2021; Thapalia et al., 2015). Urban and industrial agglomerations close to estuaries  
364 represent several anthropogenic sources, and thus multi Zn emissions should occurs almost  
365 concomitantly (Barletta et al., 2019; Burt et al., 2019; Desaulty & Petelet-Giraud, 2020). Their  
366 mixing along the fluvial-estuarine continuum and in continental run-off makes pinpointing  
367 specific Zn sources challenging, generally requiring the combination of additional elemental  
368 and isotope source proxies (Gonzalez et al., 2016; Souto-Oliveira et al., 2019). Here,  $\delta^{66}\text{Zn}$   
369 values has been proved a good proxy to detect “Zn urban fingerprints” in the coastal  
370 environments (Zhang et al., 2018).

371           Nonetheless, the source mixing processes involving anthropogenic and geogenic Zn do  
372 not explain the heavier isotope enrichments (above 0.6‰) in the coarser fractions (> 250 μm in  
373 LE1 and > 500 μm in LE2). Such as inferred for Cu, a relative increase of a Zn-rich organic  
374 pool in the SPM coarser fractions should occur along with a decrease in the geogenic pool.  
375 Indeed, zinc associates with organic matter via physico-chemical reactions with organic solid  
376 surfaces of humic and fulvic acids, and with cell walls of living organisms, or with detrital  
377 material resulting of microbial degradation of plant or animal (Brown & Calas, 2011). Previous  
378 studies have argued that the scavenging of Zn from a marine water column onto organic particle  
379 surfaces favors the retention of heavier Zn isotopes in the particulate phase (Gélabert et al.,  
380 2006; John & Conway, 2014; Weber et al., 2018). This is coherent with the observed  $\delta^{66}\text{Zn}$   
381 distributions in vertical seawater profiles from the Atlantic and Pacific oceans (John et al.,  
382 2018). The isotope distribution pattern resulting from this open ocean process also seems to  
383 hold true for our study site on the continental shelf. There, in parallel to physico-chemical  
384 sorption processes, intracellular uptake of Zn can also occur favoring the light isotope  
385 enrichment in living cells via kinetically-driven isotope fractionation (Twining & Baines, 2013;  
386 Araújo et al., 2018; Caldelas et al., 2011; John et al., 2007; Köbberich & Vance, 2019).  
387 However, given the relatively high  $\delta^{66}\text{Zn}$  values from biogenic particles, the hypothesis of  
388 cellular uptake seems to be a minor influence on the Zn isotope compositions in the studied  
389 sub-fractions.

390

### 391 *3.4 Isotope identification of biogenic pools and their relevance for marine trophic web studies*

392 For our samples, the previous sections suggested that biogenic pools predominate in coarser  
393 sub-fractions and have heavier isotope compositions than geogenic ones. Indeed, for Zn, as the  
394 biogenic pool increases in larger sized SPM sub-fractions,  $\delta^{66}\text{Zn}$  values increase, approaching  
395 that of local filter-feeding organisms (oysters) (Fig. 4). The nearing SPM and biota isotope  
396 signatures suggest that the “biogenic Zn” pool from SPM is available for bioaccumulation in  
397 upper trophic levels via dietary intake, and therefore, does represent the local marine trophic  
398 baseline. Below are the main arguments in support of our suggestion that  $\delta^{66}\text{Zn}$  isotope values  
399 in oysters are consistent with the hypothesis of a bioavailable biogenic Zn pool.

400           Oysters are filter-feeders capable of filtering large quantities of seawater to extract their  
401 sustenance from seston (e.g., phytoplankton and algae debris). (Dame, 2012; Gosling, 2003;  
402 Wang and Wang, 2019). Being primary consumers, the isotope composition of carbon and  
403 nitrogen in their tissues are reliable proxies to assess their organic dietary sources (Briant et al.,  
404 2018). Furthermore, they accumulate metals through both particulate and dissolved pathways.

405 The particulate phase is associated with the diet and is considered the main route of  
406 bioaccumulation (Akcha et al., 2022; Griscom & Fisher, 2004). Oysters' ability to uptake  
407 contaminants and especially metals in their tissues justifies their wide use for biomonitoring  
408 marine environments. Recently, determinations of metal isotopes in oysters from biomonitoring  
409 sample banks has inferred anthropogenic origins and bioaccumulation routes for these  
410 elements. Since internal biological Zn fractionation of oysters does not affect the isotope record  
411 of Zn sources, these organisms are a reliable proxy of the Zn to which they are exposed in the  
412 surrounding medium (Ma et al., 2019; Ma & Wang, 2021). Therefore, Zn isotopes in the  
413 temporal series of bivalves have helped reconstruct anthropogenic Zn bioaccumulation  
414 tendencies in French estuaries (Araújo, et al., 2021).

415 Furthermore, in a spatial sampling of these organisms paired with SPM and water  
416 samples from the Pearl Harbor estuary, (Ma et al., 2021) quantified relative fractions of Zn  
417 bioaccumulated via dissolved and particulate routes, assuming that Zn from bulk SPM was  
418 entirely bioavailable. This assumption, however, is not necessarily true in natural systems and  
419 it may be necessary to refine uptake models for quantifying relative fractions contributions  
420 more accurately. Indeed, selective extractions using organic solvents (e.g., isopropanol) in  
421 continental margin sediments worldwide revealed that soluble organic fractions have heavier  
422 Zn isotope compositions ( $>0.5\text{‰}$  than the bulk material ( $\sim 0.3\text{‰}$ ) analyzed (Y. Zhang et al.,  
423 2021). Like our samples, the prevalent heavy isotope in these organic fractions has also been  
424 associated with biological activity and scavenging processes. Interestingly, the heavy isotope  
425 enrichment in biogenic materials seems coherent with organic-derived materials, such as  
426 bituminous coal ( $\sim 1.3\text{‰}$ , Gonzalez & Weiss, 2015). With oyster isotope records as a proxy of  
427 bioavailable Zn, the all mentioned evidence supports our hypothesis that a biogenic pool  
428 enriched in the heavy isotope is a primary Zn source for these organisms.

429

#### 430 **4. Conclusions**

431 This study reports for the first-time the isotope compositions of Cu and Zn in different size  
432 fractions of SPM (63-250; 250-500; 500-1000; and 1000-2000  $\mu\text{m}$ ) from a continental shelf.  
433 These data showed significant isotope variability between particle size fractions greater than  
434 that observed for bulk bottom sediment collected over the entire study site (e.g., for Zn, Fig. 4).  
435 The Cu and Zn isotope systematics, combined with the elemental composition dataset, allowed  
436 to distinguish two main Cu and Zn pools within the SPM. These pools control the behavior of  
437 these elements: the (relatively) refractory geogenic pool is enriched in light isotopes, while the  
438 (relatively) labile pool is enriched in heavy isotopes. Both pools are present in all SPM sub-

439 fractions, but their relative proportions vary according to particle size. The observed heavier  
440 isotope composition of biogenic particles likely reflects the local trophic marine baseline and  
441 explains the close isotope values observed in secondary consumers (i.e., oysters). We suggest  
442 that combining target-specific size classes and using selective extractions may improve the  
443 isotope characterization of different metal pools which may have different bioavailabilities. For  
444 bivalves, isotope characterization of metals in particles from the size range of food particles (1-  
445 10  $\mu\text{m}$ , Gosling, 2003) is suggested, to enable source apportionment of bioaccumulation routes  
446 (dissolved vs. particulate).

447 This study confirms that isotope analyses in distinct class-sized particles can provide  
448 additional information related to host phases of Cu and Zn, and their entry at the base of the  
449 trophic food-web. For future studies on trace metals, we recommend combining mineralogical  
450 and plankton assemblages with speciation and isotope characterization. This information will  
451 allow to better understand the influence of particle composition on the input, dissolution,  
452 scavenging, (dis-)aggregation, and transport of these elements in the marine environment.

453

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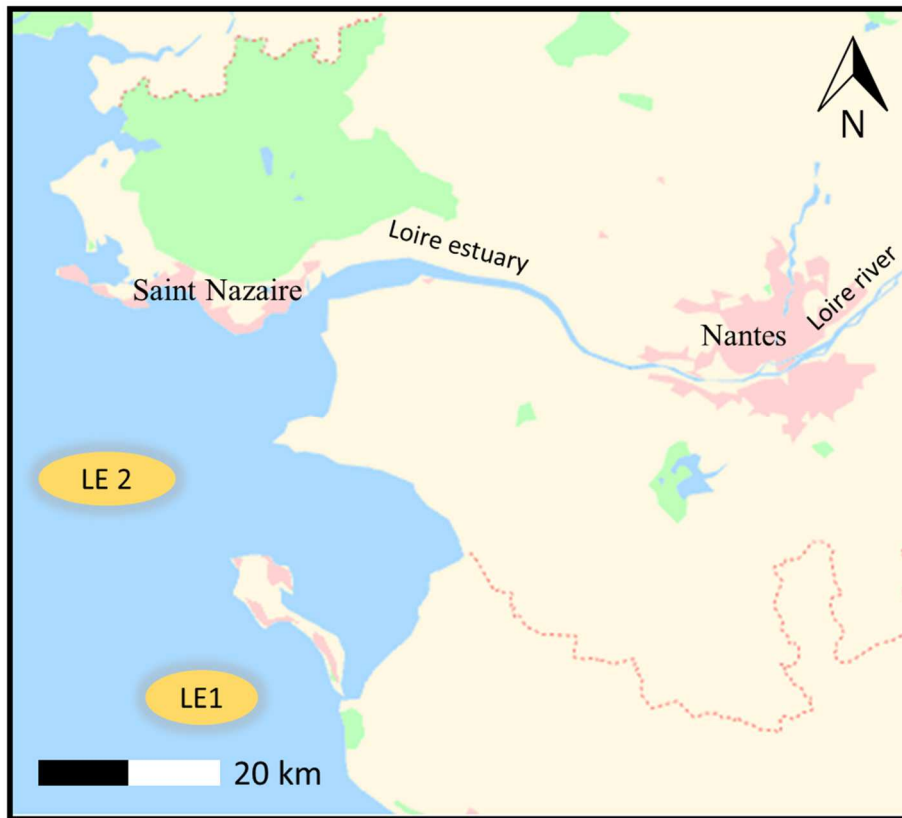
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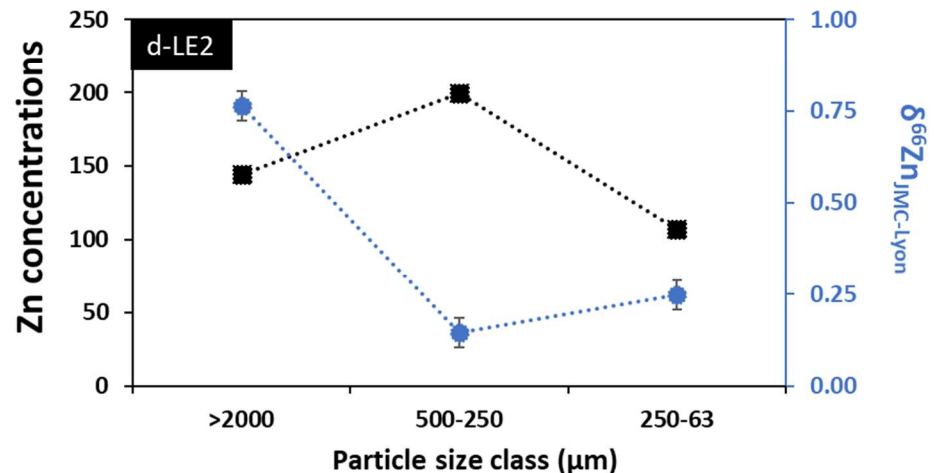
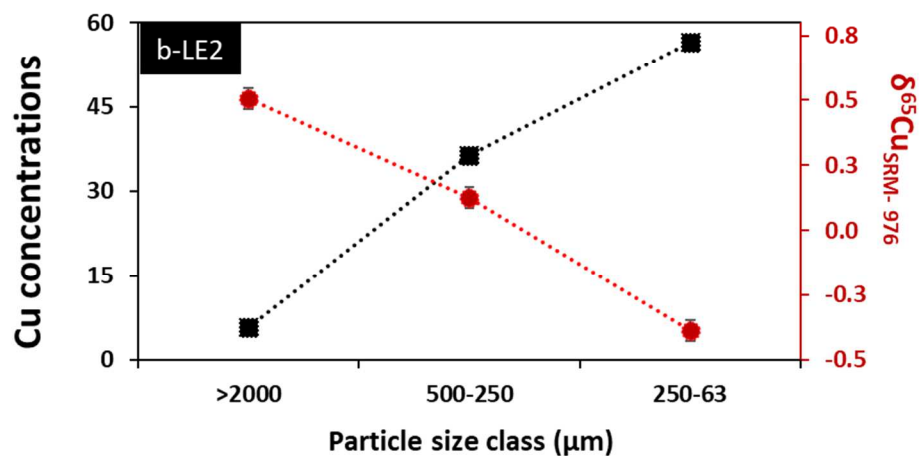
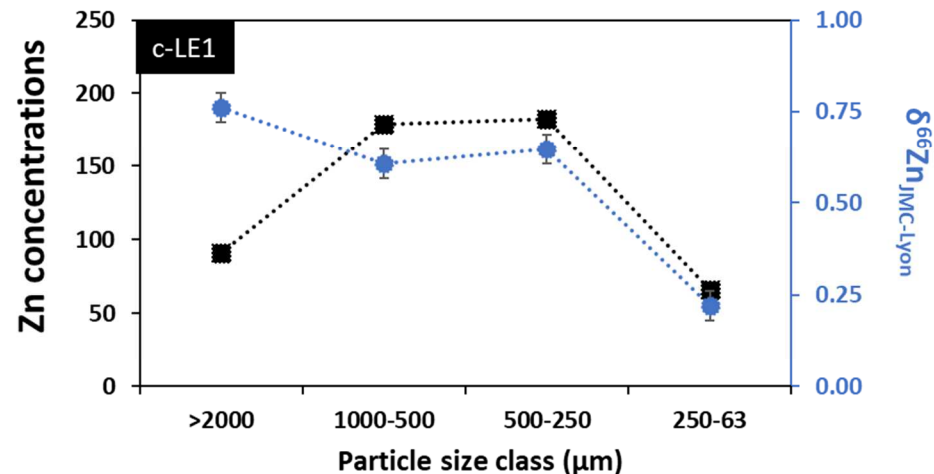
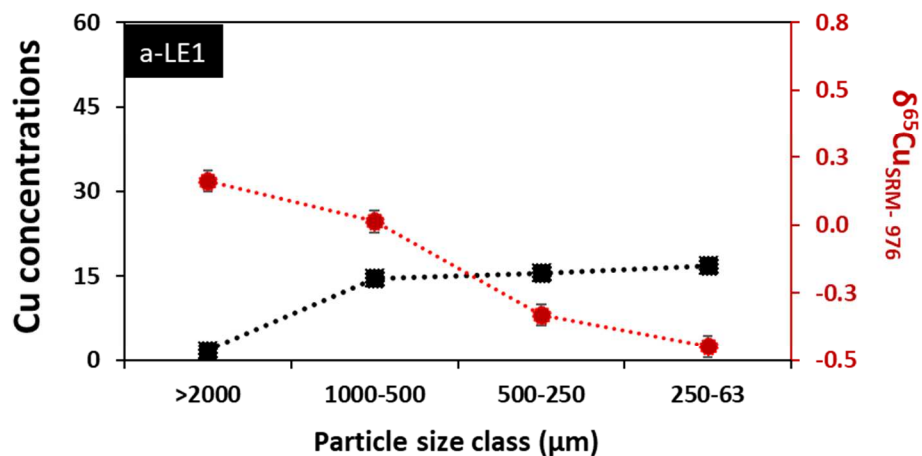
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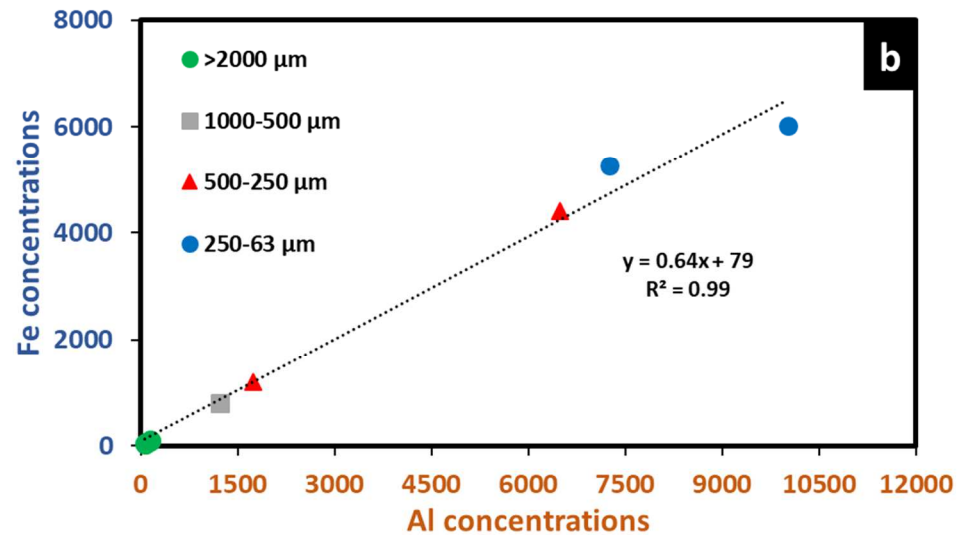
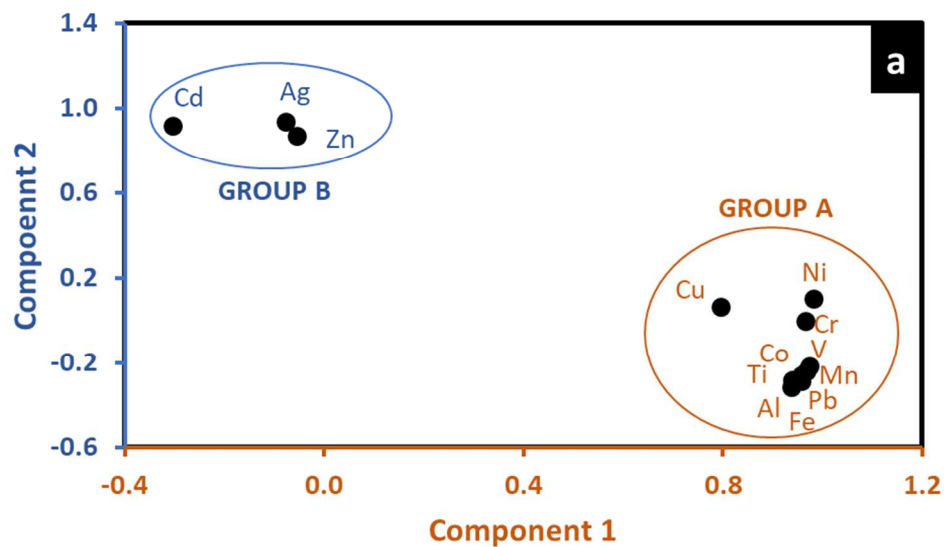
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823 **Fig. 1** Sampling stations (LE1 and LE2) for suspended particulate matter in the Northern Bay of Biscay.  
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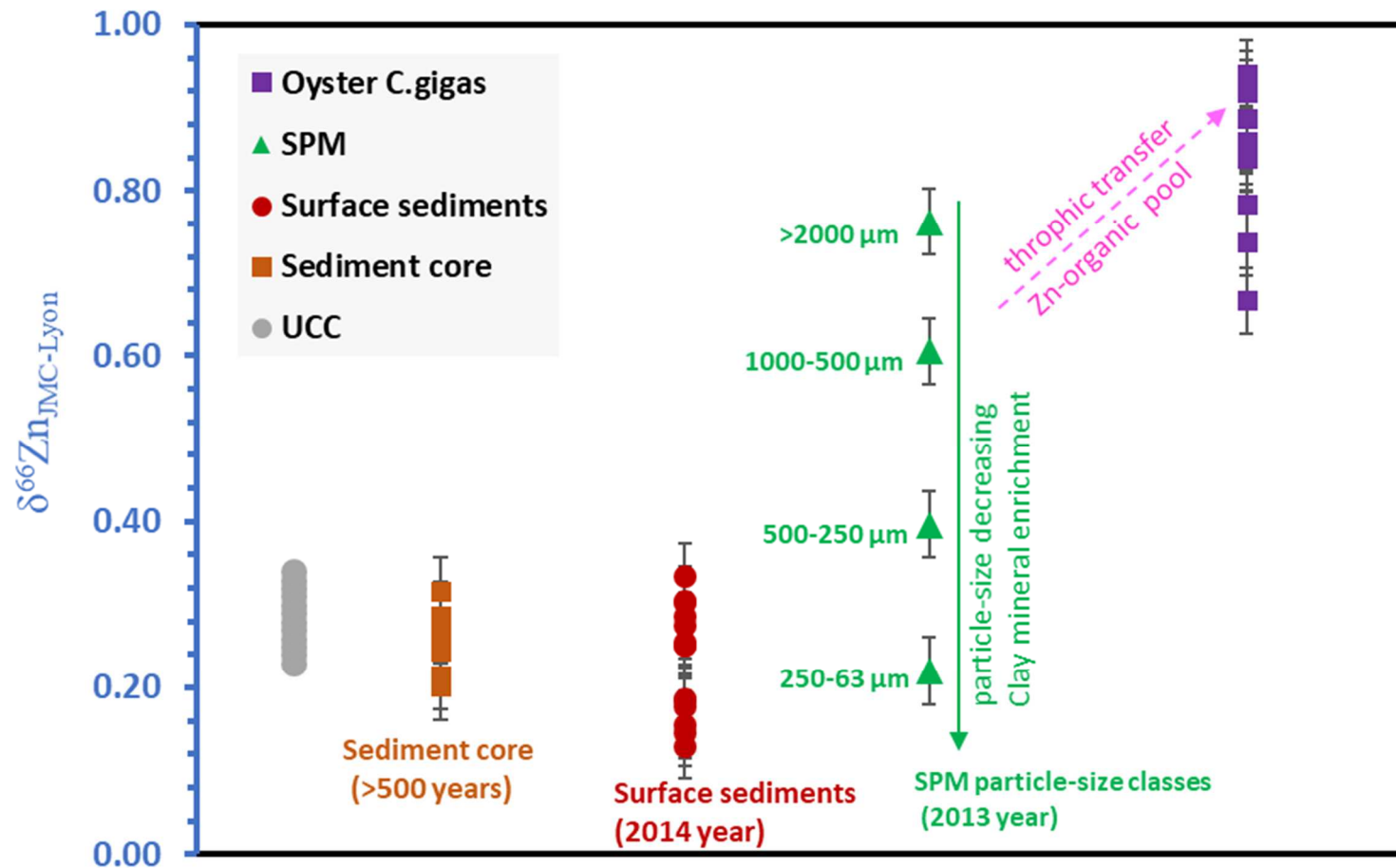


**Fig. 2** Concentrations ( $\mu\text{g g}^{-1}$ , dry weight) and isotope compositions of Cu and Zn (in per mil, ‰) in SPM sub-fractions collected at the LE1 and LE2 sampling stations. Sub-fractions comprise the different particle size classes of SPM ( $\mu\text{m}$ ): >2000; 1000-500; 500-250; 250-63. The fraction 1000-5000  $\mu\text{m}$  is missing for LE2 due lack of sufficient material for analyses.



**Fig. 3 (a)** Principal component analysis for trace and major elemental dataset of SPM and the identification of intercorrelated elements in clusters: Group A and Group B, respectively; **(b)** regression analysis for Fe and Al concentrations ( $\mu\text{g g}^{-1}$ , dry weight).





**Fig.4** Zn multi-compartmental isotope variability in the Loire estuary and Upper Continental Crust (UCC).  $\delta^{66}\text{Zn}$  value average of SPM particle-size fractions (this study) is compared to sediments (Araújo et al., 2019b) and primary consumers (oysters, Araújo, et al., 2021) reported in previous studies. A sediment core (“PV1”) integrate an isotope record of at least 500 years. Zinc isotope range of the UCC is reported by (Moynier et al., 2017). Clay mineral may be coated by Fe and Al oxides and biofilms. As clay minerals contents decrease with particle-size increasing, Zn organic pool becomes prevalent, and the SPM  $\delta^{66}\text{Zn}$  value shifts up. This tendency implies that the Zn-organic pool present in the different SPM fractions presents heavier isotope compositions. Therefore, the high  $\delta^{66}\text{Zn}$  values of oyster's soft tissues are consistent with the hypothesis of bioaccumulation of a local available Zn-organic pool enriched in the heavy Zn isotope.



Graphic abstract

