
Seasonal trace metal distribution, partition and fluxes in the temperate macrotidal Loire Estuary (France)

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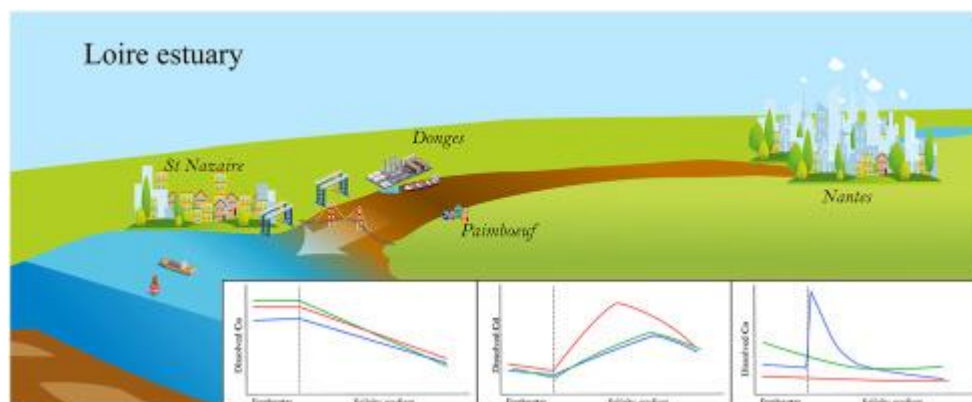
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Abstract :

Estuaries can be considered as biogeochemical reactors, acting both as sinks or sources for trace metals depending on environmental factors. Distribution of dissolved and particulate Cd, Co, Cu, Mn, Ni, and Zn were determined in samples collected from the Loire river estuary (France) during seasonal contrasting flow conditions (summer, spring and winter). Mean concentrations of dissolved Cd (0.13 ± 0.07 nM) were below concentrations previously observed in the estuary, while Cu (23.00 ± 8.07 nM) concentrations were similar to those found ten years ago. The results also demonstrated a wide fluctuation of the TMZ (Turbidity Maximum Zone) following the water discharge conditions and various reactivity behaviours depending on the type of metal even if all metals presented stable log KD values along the estuary. Rapid adsorption of suspended matter occurs at the salinity front, and only Ni and Cu are conservative through the salinity gradient. Organic matter appeared to be a major factor in metals fractioning and its role though the estuary is discussed. Riverine particulate and dissolved metal inputs, and estuary dissolved efflux have been estimated, and show a large export of Cu and Zn to the sea. However, the Loire river outputs only play a minor contribution to the ocean at the global scale. These results provide unique information concerning the contemporary distribution of dissolved and particulate trace metals in the Loire estuary, and provide a geochemical baseline dataset to assess the evolution of historical contaminants in the estuary. Ongoing studies on emerging metallic elements must be carried out to understand the impact of urban development in this part of the river.

Graphical abstract



Highlights

► Metal concentrations and behavior exhibit small differences between hydrological regimes. ► Temporal decrease of metal fluxes from the river to the sea. ► Cu and Zn are the most exported metals from the estuary.

Keywords : Estuary, Flux, Trace metals, Loire river

34 **1. Introduction**

35

36 Estuaries represent a transfer box for particles along the land-sea continuum and are
37 geochemical reactors. They are characterised by strong physicochemical gradients (in e.g.
38 salinity, temperature, flow velocity, and suspended matter composition (Elliott and McLusky
39 2002) that play an important role for the elemental mass balances of coastal zones. The
40 knowledge of particulate (Nolting et al. 1990; Turner and Millward 2000; Che et al. 2003) and
41 dissolved (Apte et al. 1990; Boyle et al. 1982; Chaudry & Zwolsman, 2008; Chiffoleau et al.
42 1994; Elbaz-Poulichet et al. 1987; Zwolsman & Van Eck, 1999) heavy metal compositions in
43 the estuary is essential in understanding the fluxes of riverine materials transported into the
44 coastal zones, and thus, the influence of weathering and anthropogenically-derived materials
45 on the marine ecosystems and the health of this environment. Trace elements are also an
46 interesting aspect of estuarine chemistry because their differing physical chemistries lead to
47 various geochemical behaviours (Shiller and Boyle 1991). In macrotidal estuaries, internal
48 cycling of resuspendable sediment can push dissolved metals towards a non-conservative
49 behaviour (Morris 1990). Processes such as solubilisation, speciation, and precipitation, as
50 well as diffusion and advection, are also critical for determining metal spatial distribution
51 (Benoit et al. 1994).

52 Loire river dissolved and particulate metal contamination have been studied and well
53 documented upstream from Montjean (Negrel 1997; Grosbois et al. 2012; Dhivert et al.
54 2016) which is not the case for the estuarine section (downstream from Montjean). In contrast
55 to other French main rivers such as the Seine River, the Gironde Estuary, or the Rhône River,
56 the Loire estuary has few studies describing the behaviour of dissolved or particulate trace
57 metals such as cadmium, copper, lead and mercury (Boutier et al. 1993; Coquery et al. 1997;
58 Waeles et al. 2004, 2009).

59 This study focuses on the distribution of particulate and dissolved trace metal elements such
60 as cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), manganese (Mn) and zinc (Zn) along
61 the salinity gradient of the Loire estuary from the freshwater upstream (Montjean), to the
62 seawater downstream (coastal area), during three contrasting water discharge periods
63 representing three seasons (summer 2012, spring 2013 and winter 2014). The aim was to
64 understand the biogeochemical functioning of the Loire estuary with respect to the mobility of
65 metallic contaminants. The data will provide metal distributions along the salinity gradient to
66 characterise different types of biogeochemical behaviour. In addition, they enable the
67 estimation of the gross and net metal flows in and out of the estuary depending on the
68 hydrological conditions.

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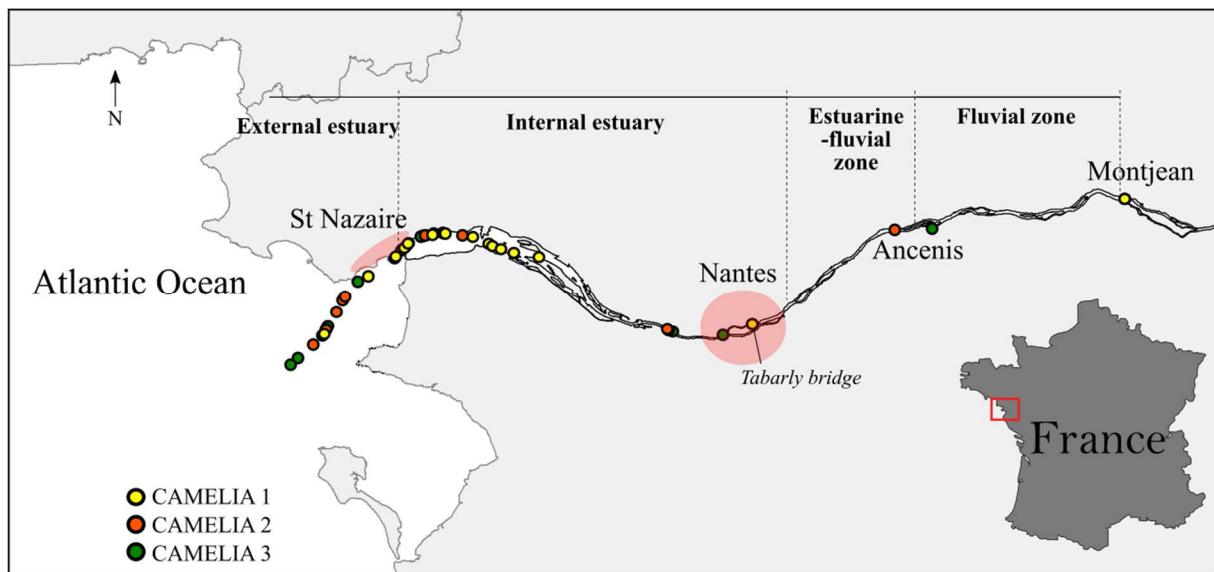
70 **2. Material and Methods**

71

72 *Study site*

73 Loire river is the longest river in France and one of the main riverine inputs to the
74 European western Atlantic Ocean. The average annual water discharge over the last century
75 was around $850 \text{ m}^3 \text{ s}^{-1}$ (Figueres et al. 1985; Negrel 1997; Dauvin 2008). In 1985, the annual
76 solid load output was established at 10^6 T for a sediment volume representing $4 \cdot 10^6 \text{ m}^3$
77 (Figueres et al. 1985). The drainage basin of Loire river is $117,356 \text{ km}^2$. It covers one fifth of
78 the French territory but mainly rural areas and midsize cities. Devoid of dams, Loire river is
79 considered "the last wild river in France" (Gautier and Grivel 2006). However, in its internal
80 estuarine section, chemical industries (fertilizer, acid plants and soap factory) have been
81 operating since the middle of the XIXth century (Martin 2014). During the First World War,
82 plants were requisitioned to the war effort and increased their productions up to 1918,
83 followed by a slow decrease (Martin 2014). Currently, a major commercial port (Nantes-St

84 Nazaire) has caused severe alterations to the natural ecosystem of the Loire estuary (Demaure
85 1979; Ottmann 1979).



86
87 **Figure 1:** Sampling stations map during the three CAMELIA cruises in the estuarine section

88 of the Loire river.

89 The Loire estuary is a 60 km long macrotidal estuary, artificially modified and partially
90 canalised. The water residence time within the Loire estuary ranges from 3 days in floods to
91 30 days at times of low river flow (Guillaud et al. 2008). Like most tidal estuarine systems, a
92 high suspended sediment concentrations zone (the turbidity maximum zone, TMZ) is present
93 most of the time. The spatial and temporal evolutions of the TMZ govern the transport and
94 deposition of fine sediments (Uncles et al. 2006), and hence, may cause significant
95 morphological changes such as the siltation in channels and ports (Pontee et al. 2004).
96 Moreover, the TMZ influences biogeochemical processes of chemical substances associated
97 with particles like nutrients and hydrophobic substances (Turner and Millward 2002; Etcheber
98 et al. 2007). In the Loire estuary, the TMZ moves upstream during periods of low discharge
99 (summer) and its upstream boundary may reach up to 62 km from the mouth (Tarbarly bridge
100 – Fig. 1). The TMZ displacement is faster during its downstream flushing by river floods than
101 during its upstream migration by tidal pumping. However, the expulsion of the TMZ from the

102 upper reaches requires higher discharge levels than its setting up (respective discharge
103 thresholds of 497–1034 m³ s⁻¹ and 300–360 m³ s⁻¹). Clockwise turbidity-discharge hysteresis
104 patterns (Jalón-Rojas et al. 2016) observed in the Loire estuary are due to the presence of
105 mobile and fluid mud that has sedimented and remains in place.

106 *Water, SPM and nutrients sampling and quantification*

107 Filtered water and suspended particulate matter (SPM) samples were collected during three
108 sampling cruises CAMELIA in September 2012, April 2013 and February 2014. They were
109 conducted along the estuarine salinity gradient from Nantes city to over the estuarine mouth
110 on board of the R/V *Thalia* (IFREMER) during contrasting freshwater discharges. The Loire
111 freshwater discharges (Supplementary file – Fig. S1) were ~ 210 m³ s⁻¹ during the 2012
112 campaign, ~ 1673 m³ s⁻¹ during the 2013 campaign, and ~ 2790 m³ s⁻¹ during the 2014
113 campaign. The average discharge of the Loire river over the period 2012-2014 was ~ 940 m³
114 s⁻¹. The sampling strategy was designed to sample waters from salinity 0 to 30 along the
115 estuary.

116 An all-Teflon pumping system, consisting of PFA 15 mm diameter tubing, connected to a
117 pneumatic-driven piston PTFE pump (ASTI, France), was used to bring water directly and
118 continuously at 2 L/min flow into the positive pressure, clean van on the ship's deck. To
119 avoid contamination, the end of the Teflon tubing was kept 1 m below the water surface and 5
120 m off the side of the ship during the sampling. Samples were discretised by collecting the
121 pump outflow into 2 L acid-cleaned Teflon (PFA) bottles under a laminar flow bench.
122 Subsamples were filtered through dry, pre-cleaned and weighed filters (Whatman -
123 Nuclepore®, polycarbonate membrane, 0.45 µm) in the clean van within 1 h after sampling,
124 for quantification of SPM concentrations. After filtration, the filters were then rinsed with
125 ultra-pure water (Merck Millipore®, 18 MΩ cm⁻¹), dried, and stored folded in acid cleaned
126 polystyrene Petri dishes. Back in the laboratory, the filters were dried in a drying stove then

127 weighed under clean conditions. Filtered water samples were stored in acid-cleaned high-
128 density polyethylene bottles and acidified with 0.1% v/v concentrated nitric acid (Suprapur,
129 Merck®).

130 All elemental analyses were performed with a Q-ICP-MS (iCAP-Q Thermo®) in KED
131 mode (He). External calibration using multi-elemental standard solutions (SCP Science) was
132 done at the beginning of each analytical session. Internal correction with In was done to
133 correct for potential matrix effects, and the data was corrected with procedural blanks. Prior to
134 analyses, dissolved trace element samples were pre-concentrated using the APDC-
135 DDDC/Freon method (Danielsson et al. 1982). Recoveries from the seawater certified
136 reference materials (CRM NRC-CASS-5, processed every 12 extractions) were $92 \pm 14\%$.
137 The data presented here were corrected using average recoveries on the day of extraction.

138 Particulate metals retained on the filters were determined with the same analytical
139 procedure after microwaved total acid digestion (2 mL HCl, 4 mL HNO₃, 2 mL HF).

140 Dissolved inorganic nitrogen (nitrate and nitrite), phosphorus, and silicate were measured.
141 Samples were obtained by filtering sea water through 25 mm Whatman GF/F filters under low
142 filtration pressure. The filtrate was stored frozen at -20°C except for the silicate, which was
143 stored at 4°C , until analyses. Analyses were carried out with a Seal Analytical auto analyser
144 using colorimetric techniques (Bendschneider and Robinson 1952) optimised by Aminot et al.
145 (2009). Particulate organic carbon was measured with a CHN analyser (Carlo Erba, Model
146 1106), and salinity by conductivity measurements.

147 *Distribution coefficient (K_D)*

148 Metal partitioning between dissolved and particulate concentrations can be described by
149 the particle-water distribution coefficient expressed as K_D (L kg^{-1}) (Sung 1995):

$$150 \quad K_D = \text{Me}_p / \text{Me}_d \quad (\text{Equation 1})$$

151 where Me_p is the mass fraction of metal in the particulate phase ($mg\ kg^{-1}$), and Me_d is the
152 volumetric mass of metal in the dissolved phase ($mg\ L^{-1}$).

153 Such experimental K_D can be used to estimate the dissolved metal concentrations from
154 particulate data, assuming equilibrium conditions.

155 *Loire river fluxes*

156 Fluxes of Me_d and Me_p were estimated by combining mean river discharges during the
157 campaigns obtained from the National Hydrographic Databank (DIREN, website
158 <http://www.hydro.eaufrance.fr/>) with the observed Me_d , Me_p and SPM concentrations. Fluxes
159 equations are given in Table III.

160 *Statistical methods*

161 All descriptive (mean, min-max, standard deviation) and multivariate statistics were
162 performed using R software with $\alpha = 0.05$. Comparison of individual metal concentrations
163 were conducted using Wilcoxon and Kruskal-Wallis non-parametric tests.

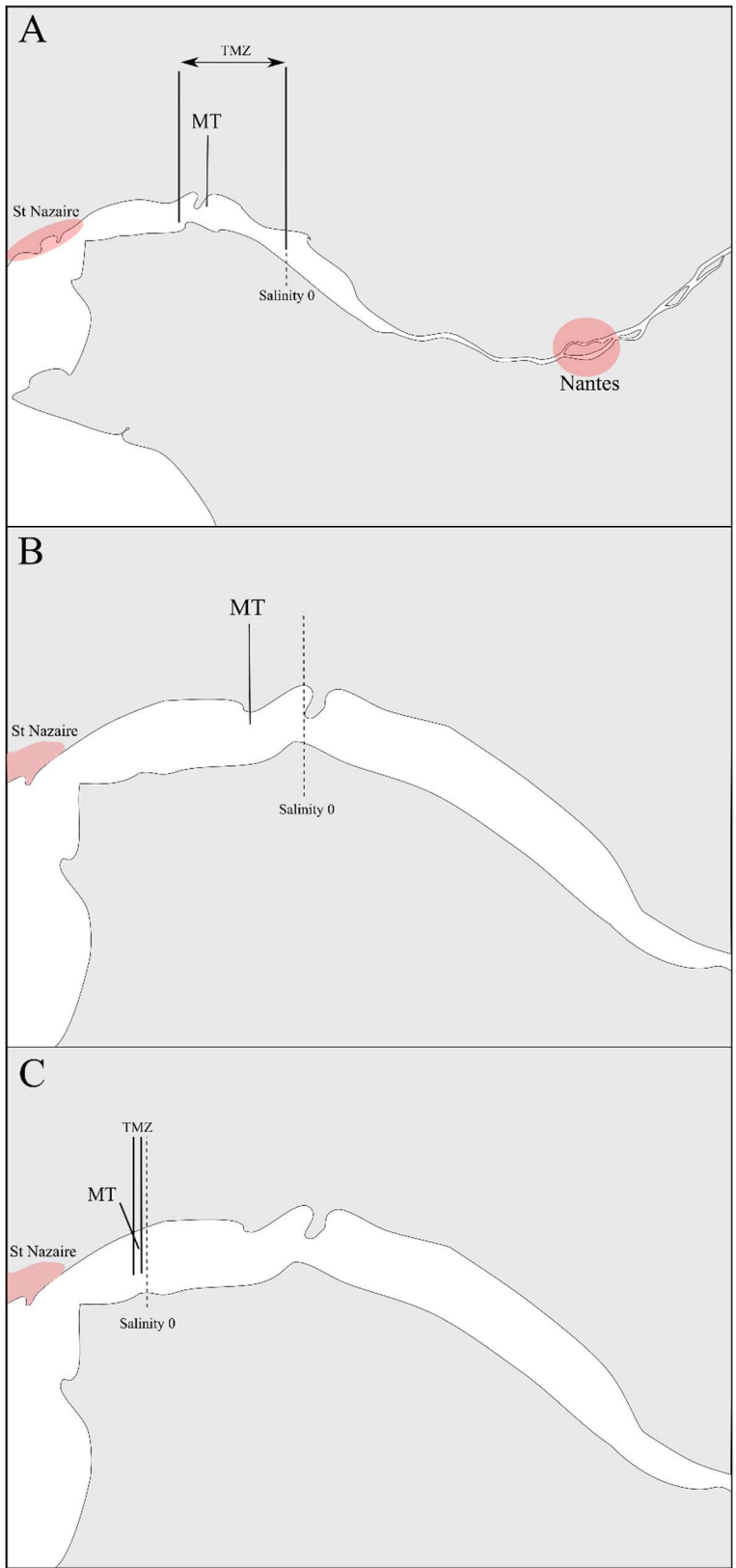
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165 **3. Results and Discussion**

166

167 *Hydrographic settings*

168 River discharges during the three campaigns were contrasted, with a very dry season
169 with low discharge ($210 \pm 10\ m^3\ s^{-1}$) in summer 2012, and a high-water discharge in winter
170 2014 ($2790 \pm 404\ m^3\ s^{-1}$). The TMZ defined as $SPM > 500\ mg\ L^{-1}$ (Gallenne 1974; Jalón-
171 Rojas et al. 2016) that were encountered during the cruises, fluctuated according to the water
172 discharges (Fig. 2).



173

174 **Figure 2:** Spatial distribution of the TMZ ($\text{SPM} > 500 \text{ mg L}^{-1}$) during A) summer CAMELIA
 175 1, B) spring CAMELIA 2 and C) winter CAMELIA 3 conditions. MT corresponds to the
 176 maximum SPM concentration determined during the cruise.

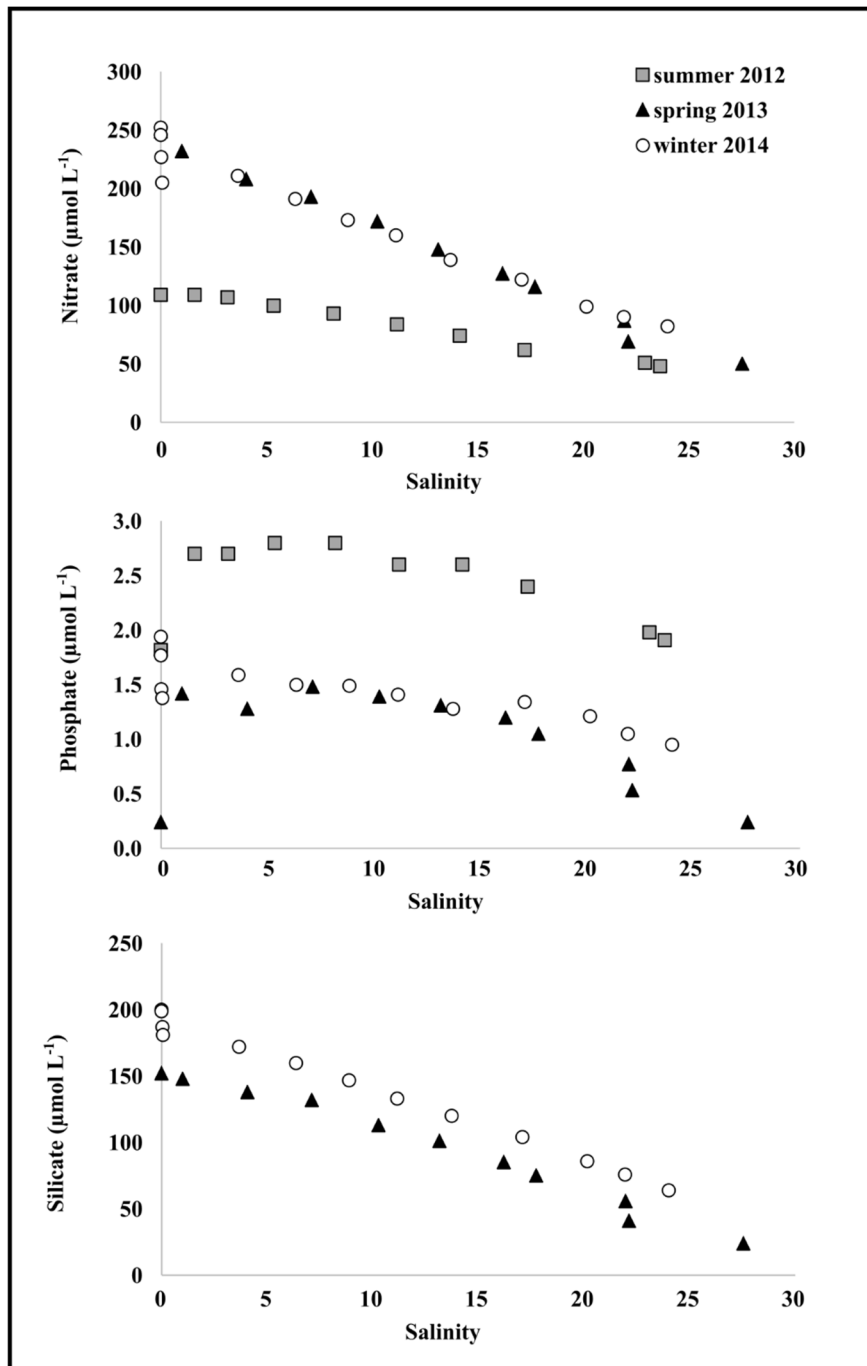
177 During summer 2012, the TMZ was upstream and over 20 km long. The concentration
178 of suspended particles rose up to 2100 mg L⁻¹, which is the highest concentration of the three
179 cruises. During high water discharge conditions (spring 2013 and winter 2014), linked to
180 seasonal rains, water discharges were 1673 ± 528 and 2790 ± 404 m³ s⁻¹ respectively, and the
181 TMZ was not observed or was shifted seawards. The maximum concentrations of suspended
182 particles were 410 and 680 mg L⁻¹ respectively. The TMZ movement in macrotidal estuaries
183 affects sediment resuspension or particulate sedimentation (Avoine and Larssonneur 1987) as
184 already described in various studies (Chiffolleau et al. 1994; Martino et al. 2002). Jalón-Rojas
185 et al. (2016) also observed that the TMZ moves upstream during periods of low discharge
186 (summer) in the Loire estuary. Moreover, the TMZ displacement is faster during its
187 downstream flushing by river floods than during its upstream migration by tidal pumping.
188 However, the expulsion of the TMZ from the upper reaches requires higher discharge levels
189 than its installation (respective discharge thresholds of 497–1034 m³ s⁻¹ and 300–360 m³ s⁻¹).
190 This is due to the presence of mobile mud remaining after the TMZ presence, as confirmed by
191 clockwise turbidity-discharge hysteresis patterns (Jalón-Rojas et al. 2016).

192

193 *Nutrients (nitrate, phosphate and silicate) behaviour*

194 Silicate from summer 2012 could not be analysed. For all seasons, near-conservative
195 behaviour of nutrients along the salinity gradient was evident (Fig. 3). Such patterns and
196 correlation (Pearson test, r² = -0.998 for nitrate, r² = -0.782 for phosphate and r² = -0.993 for
197 silicate, *p* value < 0.05) between nutrients and salinity were also observed by Boutier et al.
198 (1993). The near-conservative behaviour of nutrients suggests that no large sinks or sources of
199 nutrients are present within the estuary. As described by Guillaud et al. (2008), it appears that
200 similar to the Seine estuary (Guillaud 1983; Aminot et al. 1998), most of the nitrate and
201 silicate entering the estuary reach the coastal zone because of the relatively low residence

202 time of water within the Loire estuary, ranging from 3 days in floods to 30 days at low river
203 flow (Gallenne 1974). Cloern (2001) has estimated these low residence times result in a
204 nitrogen export of between 75% and 95% of the input.



205
206 **Figure 3:** Nitrate, phosphate and silicate distributions along the salinity gradient. Silicate
207 during summer 2012 was not determined. Correlation values are described in the text.

208

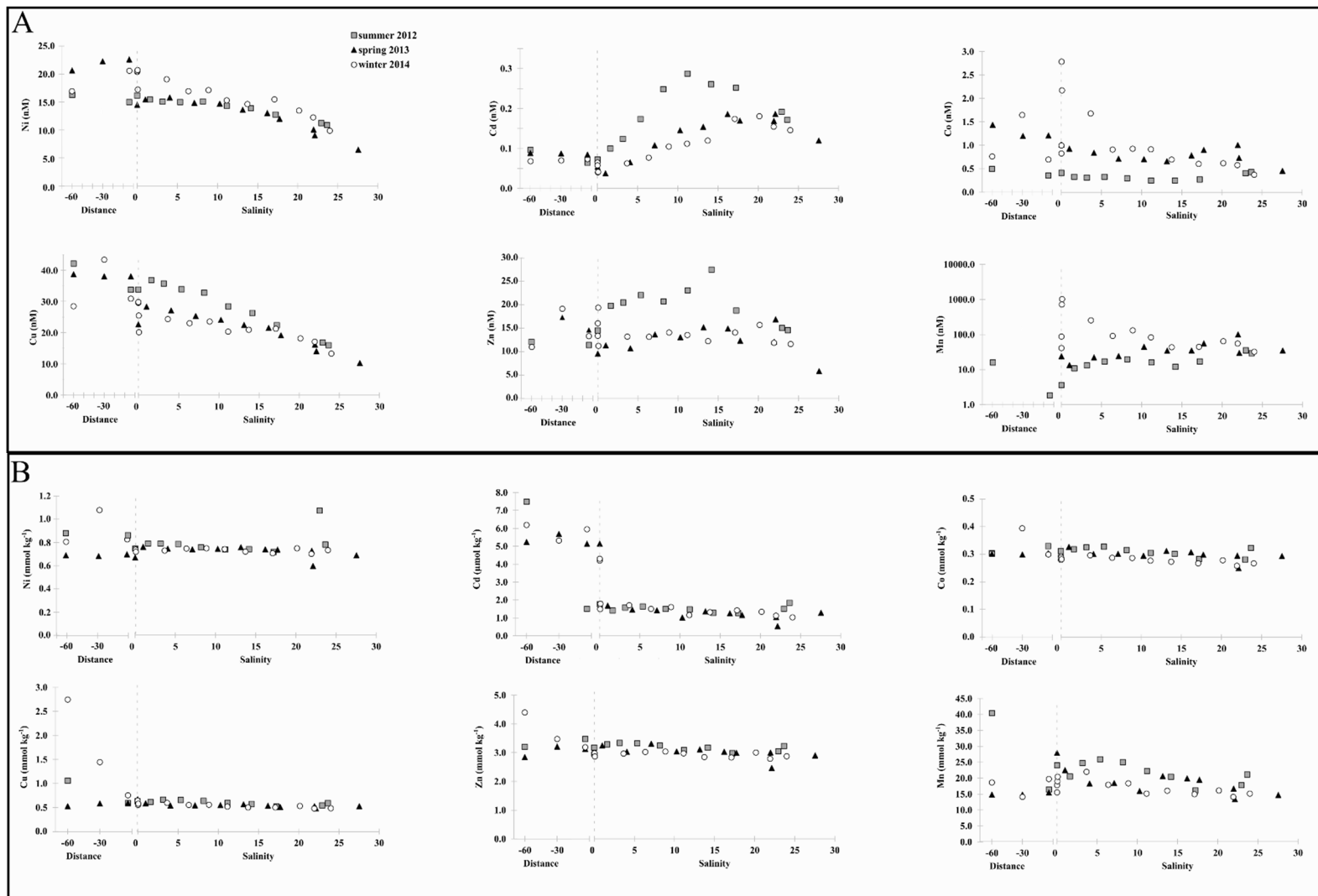
209 The main exception was an increase of phosphate concentrations and a decrease of nitrate
210 (about two-fold higher and two-fold lower at salinity 1, respectively) during summer within
211 the estuary. This could be caused by Nantes' urban wastewater disposal (2.5 t d^{-1} of
212 phosphorus) influence during low water discharge (Guillaud et al. 2008), and/or the potential
213 desorption of exchangeable particulate phosphate from the estuarine TMZ in summer tides
214 (Rincé et al. 1985). Particular summer conditions with higher temperature and low water
215 discharge could result in a phytoplankton bloom in the estuarine zone (Relexans et al. 1988),
216 with all the algal particulate organic carbon (POC) being mineralised in the TMZ, where, in
217 addition, the light penetration is too low to sustain important primary production (Meybeck et
218 al. 1988). As a result, the estuarine waters in the TMZ are dramatically oxygen depleted
219 (Thouvenin et al. 1997). Meybeck et al. (1988) also observed and described the process which
220 results in a regeneration of dissolved PO_4^{3-} , while NO_3^{2-} is conserved or depleted when the
221 TMZ is nearly anoxic (Meybeck et al. 1988). Unfortunately, no oxygen measurement was
222 made, and this hypothesis cannot be verified.

223

224 *Dissolved metals*

225 Concentrations of dissolved trace metals are shown as a function of salinity and, for salinity
226 approaching zero, as a function of distance up-estuary from the point of saline intrusion
227 defined as $S = 0.05$ (salinometer detection limit) in Fig. 4. This combined representation
228 allows a clearer visualisation of the entire dataset in freshwater as well as in the estuary.
229 Dissolved metals exhibit different distribution patterns along the salinity gradient, so three
230 groups have been distinguished: *i*) elements mobilised in low salinities during intense
231 discharge (Co and Mn); *ii*) elements with a conservative pattern (Ni and Cu); and *iii*) elements
232 with a more or less pronounced mid-salinity concentration maximum (Zn and Cd).

233



234

235 **Figure 4:** Metal dissolved (A) and particulate (B) concentrations along the Loire Estuary salinity gradient for the three seasonal surveys.

236 Group i: Manganese and Cobalt

237 Dissolved manganese levels during the three cruises ranged from 2.8 nM to 1.02 μ M with
238 some similar patterns and lower levels during summer 2012 and spring 2013. For these two
239 cruises, Mn_d did not follow the expected conservative mixing line nor exhibit estuarine
240 removal, but rather showed inputs of Mn_d . Dissolved Mn levels showed non-conservative
241 distributions with increasing concentrations downstream from the riverine end-members.
242 However, during winter 2014 when SPM concentrations were the highest, Mn_d concentrations
243 rose up to 1.02 μ M. This large Mn_d enrichment in the TMZ suggests reductive conditions in
244 this high-particle zone, or possibly sediment resuspension linked to mobilisation of the Mn
245 present in the sediment porewater (Yeats, 1990; Chiffoleau et al. 1994). Winter oxic
246 conditions do not appear to be conducive to *in situ* (water-column) reduction, even in the
247 TMZ. However, it should be noted that Mn oxides are susceptible to reduction and their
248 solubility is influenced by light, pH, surface reactivity, and organic matter. In systems where
249 freshwater and seawater meet, many chemical species of Mn can coexist and rapidly cycle
250 between one another. Oldham et al. (2017) have described 20 possible reactions or pathways
251 for manganese cycling in estuarine systems.

252 Dissolved cobalt concentrations over the three cruises exhibited a non-conservative
253 distribution with constant concentrations around 0.6 ± 0.2 nM along the salinity gradient.
254 During winter 2014, a peak of concentration up to 2.8 nM was observed, when SPM and Mn_d
255 concentrations were the highest and salinity was 0.1. Dissolved Co concentration patterns are
256 similar to manganese patterns as already observed (Moffett and Ho 1996). Knowing the high
257 affinity of Co for Mn oxides, it is suggested that the dissolution of Mn oxides in a likely more
258 reductive environment such as the TMZ, releases adsorbed Co, and thus induces a similar
259 behaviour between both dissolved elements (Moffett and Ho 1996). Moreover, changes in
260 salinity contribute to the particle-solution exchange of Co (Takata et al. 2010).

261

262 Group ii: Copper and Nickel

263 These two metals, characterized by a potentially complex biogeochemical behaviour, exhibit
264 an approximately conservative mixing, with small differences between seasons. For both
265 metals, the role of complexation by strong organic ligands is predominant in estuarine
266 systems.

267 Dissolved Cu concentrations can exhibit both conservative (Boyle, Husted and Grant,
268 1982; Shiller and Boyle, 1991) and non-conservative (Windom et al. 1983; Waeles et al.
269 2004) behaviours along estuarine salinity gradients. During CAMELIA cruises, Cu_d
270 concentrations measured in the Loire estuary varied between 10 to 37 nM. These
271 concentrations are in the range of previous studies in the Loire River estuary (Waeles et al.
272 2004), and in the lower range of worldwide estuaries (Table I). During the three sampled
273 seasons, Cu_d exhibited a conservative behaviour along the estuarine salinity gradient (Fig. 4
274 A). The Cu_d behaviour through the salinity gradient is not impacted by environmental
275 seasonal changes. A small concentration decrease is observed at low salinity (0.1-0.5) follow
276 by a rapid increase before taking a conservative mixing pattern. Copper is highly particle
277 reactive and is known to be subject to scavenging by surface reactions on particles (Bruland
278 and Lohan 2003) and strongly complexes with humic ligands (Skrabal et al. 2006). Studies on
279 the speciation of copper in estuarine systems showed that, Cu_d is also mainly complexed by
280 colloidal organic ligands (van den Berg et al. 1987; Shank et al. 2004; Abualhaija et al. 2015;
281 Dulaquais et al. 2020). The slight decrease near the riverine water could be explained by the
282 decrease of the Cu complexing ligand concentrations in the dissolved fraction with increasing
283 salinity, in agreement with the general pattern observed for other estuaries (van den Berg et al.
284 1987; Apte et al. 1990; Tang et al. 2001; Wong et al. 2018). Dulaquais et al. (2020) studied
285 the organic speciation of Cu_d in the Loire estuary for the soluble (sCu, <0.02 μm) and

286 dissolved (Cu_d , $<0.45 \text{ nm}$) fractions. They observed a non-conservative distribution of Cu_d
287 with an increase in the TMZ which was not observed for sCu which showed a conservative
288 distribution in the estuary as observed in the present study. The inorganic speciation of Cu is
289 not expected to change with salinity since Cu forms weak chloride or sulphate complexes
290 (Dulaquais et al. 2020). In the Loire estuarine system, as in many others, dissolved organic
291 matter (DOM) is derived from relatively refractory, terrestrially dominated material (mostly
292 humic substances, Dulaquais et al. 2020) that is conservatively mixed with respect to salinity
293 (Avery et al. 2003). However, it has been shown that thiol-like and amino-like acids/proteins
294 could also account for Cu_d ligand in the estuary (Dulaquais et al. 2020).

295 Observed concentrations of Ni_d range from $6 \pm 1 \text{ nM}$ at the vicinity of the marine water
296 (salinity >25) to $19 \pm 4 \text{ nM}$ in the river water (salinity <1). Concentrations of Ni_d in the river
297 and estuary are in the same range, or lower, compared to other estuaries such as the Danube
298 (Guieu et al. 1998), the Gironde (Kraepiel et al. 1997), the Mersey river (Martino et al. 2002)
299 or the Thames (Turner & Millward, 2000), reflecting the low contamination of the Loire
300 River. As expected in a well-mixed estuary such as the Loire River, and knowing the affinity
301 of Ni for dissolved organic matter, Ni exhibited a nearly conservative behaviour (Shiller and
302 Boyle 1991; Gaulier et al. 2021) during the summer and spring cruises. However, for winter
303 2014, the river water samples had lower concentrations than anticipated by conservative
304 behaviour. The Ni_d winter pattern could be due to fluvial nickel dilution linked to high river
305 discharge, and nickel desorption at low salinities as observed in other estuaries (Edmond et al.
306 1985; Chiffoleau et al. 1994). Ni speciation and distribution through the estuarine system is
307 mainly controlled by the presence of strong organic ligand (Nimmo et al. 1989; Donat et al.
308 1994). Turner et al. (1998) have studied the influence of dissolved organic matter and particle
309 character on Ni partitioning. They observed that the presence of dissolved organic matter
310 inhibits uptake of Ni by suspended particles which implies the conservative behaviour of Ni_d

311 along the estuary. Even if DOC concentrations have not been determined in this study, Turner
312 et al (1998) have demonstrated that Ni adsorption is largely determined by the presence of a
313 specific fraction of organic ligands rather than concentration.

314 Group *iii*: Cadmium and Zinc

315 Dissolved Cd concentrations were in the range of 0.04 to 0.29 nM over the CAMELIA cruises
316 which is in good agreement with the concentrations determined earlier by Boutier et al. (1993)
317 and Waeles et al. (2004). Concentrations are low in comparison to other French estuaries such
318 as the Gironde (Kraepiel et al. 1997; Michel et al. 2000) or Seine (Chiffoleau et al. 1994). A
319 non-conservative distribution is always observed for Cd_d with peak concentrations (~0.15 to
320 0.30 nM) found between salinities of 10 (summer low flow) and 22 (high flow, winter and
321 spring). This pattern is observed in other French estuaries (Boutier et al. 1993; Chiffoleau et
322 al. 1994; Kraepiel et al. 1997; Michel et al. 2000; Waeles et al. 2004), and attributed to Cd
323 desorbing from suspended particles in the estuarine mixing zone when the river water mixes
324 with the marine water. This desorption is the consequence of the complexation of free Cd²⁺
325 activity in solution by seawater chloride ions (Cl⁻), and the concomitant effects of increasing
326 ionic strength (Comans and Van Dijk 1988; Shiller and Boyle 1991). However, laboratory
327 experiments have shown a rapid complexation of free Cd at salinities of 10. Waeles et al.
328 (2004) have demonstrated that a labile Cd species is formed between salinities 0 and 12, and
329 then decreases when the salinity rises. From these observations and the Cd_d concentration
330 patterns during CAMELIA cruises, it can be hypothesised that during the summer, a majority
331 of Cd_d comes from newly formed, labile Cd (chloro-complexes) up to the peak of Cd_d
332 concentrations. If so, simple Cd desorption from newly arrived particles is not sufficient to
333 reflect the patterns in the salinity range 15-25 observed during winter and spring. During these
334 seasons, Cd_d concentration maximums come at a higher salinity than the expected range of
335 desorption peak salinity shown by mixing experiments. As Cd desorption occurs on the order

336 of minutes, it is not likely to be a kinetic effect (Shiller and Boyle 1991). A sedimentary input
337 is indicated. Moreover, cadmium enriched sediments have been reported close to the urban
338 centres of the estuary (St. Nazaire) (Coynel et al. 2016) in the area of the 15-25 salinity range.
339 These contaminated sediment particles could exchange with the water column leading to a
340 punctual increase in the Cd_d phase. In the absence of known or identified anthropogenic
341 inputs, estuarine sediments could be a source of Cd. As demonstrated in the Gironde estuary,
342 the suspended and bed particles are known to exchange with each other under the influence of
343 tidal mixing (Allen et al. 1977; Kraepiel et al. 1997).

344

345 Zn is a particle-reactive element in the estuarine environment (Hatje et al. 2003) and has been
346 found to be strongly organically complexed to ligands (Bruland 1989). During high discharge
347 conditions (spring and winter), no difference in Zn_d behaviour is observed ($p > 0.05$).
348 Concentrations though the salinity gradient are constant from 5.8 nM to 16.9 nM. In general,
349 concentrations of Zn_d are in the range of moderately impacted estuaries (San Francisco Bay
350 (Sañudo-Wilhelmy et al. 1996) or Cape Fear estuary (O'Connell 1999)) and significantly less
351 than more highly impacted estuaries (Yangtze estuary (Yin et al. 2016)). However, during
352 summer 2012, the Loire river mid-salinity maximum concentration (27.5 nM at salinity 15)
353 reached up to twice the river Zn_d concentrations (~11.9 nM). The highest concentrations of
354 trace metals in the water coincide with high turbidity zones in the middle region. This
355 highlights the role of resuspension and sediment remobilization due to tidal forcing as a
356 critical driver of pollution in contaminated areas (Premier et al. 2019). Like Cd_d , the Zn_d
357 concentration's increase could be due to the desorption caused by the increasing inorganic
358 complexation with the major seawater anions (Cl^- and SO_4^{2-}) and/or from increasing particle
359 load due to resuspended estuarine sediment (Ackroyd et al. 1986; Pearson et al. 2017). Non-
360 conservative mixing has already been observed in various temperate estuaries (Ackroyd et al.

1986; Yan et al. 1991; Guieu and Martin 2002). In the Loire estuary system, during low discharge, hypoxic (Schmidt et al. 2019) summer conditions, natural and anthropogenic sources of Zn adsorbed to the sediment and organic matter can be released from the degraded organic matter or released from Fe and Mn diagenesis, and that sediment fluxes could be a significant source of trace metals in the water column (Thibault de Chanvalon et al. 2016b; Duan et al. 2019). Moreover, the anthropogenic Zn associated to urban particles (Schäfer et al. 2009; Araújo et al. 2019) could also be susceptible to desorption processes in saline waters.

369

370 **Table I:** Comparison of dissolved metal concentrations with previous studies.

Rivers		Co (nM)	Ni (nM)	Cu (nM)	Zn (nM)	Cd (nM)	Pb (nM)	Mn (nM)	Reference
Loire Estuary	<i>mean</i>	0.76 ± 0.54	14 ± 4	23 ± 8	15 ± 4	0.13 ± 0.07	0.12 ± 0.05	93 ± 203	This study
Thames 1995	<i>mean</i>		107	168	445	2,85	48		Power et al. 1999
Krka				2		0.04	0.08		Elbaz-Poulichet et al. 1991
Tagus Estuary	<i>min-max</i>		5.3–14.0	6–26	52–230	0.4–3.4			Cotté-Krief et al. 2000
Hudson Estuary	<i>min-max</i>			15 - 110		0.9 -4.4			Klinkhammer and Bender 1981
Gironde Estuary	<i>mean</i>			22	93	0,44	1.17		Masson et al. 2006
Seine River	<i>mean</i>			35		0,28	1.71		Françoise Elbaz-Poulichet et al. 2006
Pearl River Estuary	<i>mean</i>			64 ± 10	123 ± 68	1.33 ± 0.27	8 ± 4		Zhen et al. 2016
Yangtze Estuary	<i>mean</i>	1.19 ± 0.63	23 ± 12	45 ± 20	146 ± 115	0.82 ± 0.62	6.47 ± 2.75		Yin et al. 2016
NE Atlantic Ocean	<i>min-max</i>		1.7–3.1	0.7–1.9	0.5–1.6	0.003–0.05			Saager et al. 1997

371

372

373 *Particulate metals concentrations*

374 Moving through the estuary, particles are subject to numerous deposition-resuspension
375 cycles, and redox variations that could modify their properties. Nevertheless, for all evaluated
376 metals, the composition of suspended particles throughout the estuary (Fig. 4 B) is uniform.
377 This seems to reflect a homogenous composition made of a comparatively large pool of
378 particles in equilibrium with the physical/chemical conditions encountered within the estuary.

379 This observation is a fact for Ni, Co, Zn and to a lesser extent for Cu, regardless of the season.
380 This homogenous composition would conceal the expected variations of a much smaller pool
381 of particles newly introduced to the estuary. Collectively, new and old particles form the
382 suspended matter which has a long residence time, up to 10 months for the Loire estuary
383 (Ciffroy et al. 2003b), and thus represents a well-mixed system as also suggested by various
384 studies in other estuaries, such as in the Gironde estuary (Kraepiel et al. 1997). According to
385 the study of Ciffroy et al. (2003) on the residence time of particles in the Loire estuary, the
386 “standard half-life” of suspended particles in its TMZ depends on the season, and varies from
387 6 to 10 months in summer, 4 to 5 months in winter, and is about 0.7 month during flood
388 periods. In the present study, seasonal cruises through flood or low flow showed a uniform
389 pattern for particulate metal concentrations. An exception can be made for Mn during summer
390 2012. Particulate Mn concentrations increase linearly from freshwater levels up to 26.5 mmol
391 kg⁻¹ encountered at a low salinity ($\sim \leq 5$). Particulate Mn has already been discussed in a
392 previous publication (Thibault de Chanvalon et al. 2016a), where the authors have concluded
393 that Mn transformations (and hence Mn_d) are largely dependent on Mn oxides whose input is
394 seasonal. The degree of crystallinity of Mn oxides seems to increase as soon as they settle,
395 indicating a specific and not yet identified transformation occurring in the TMZ (Thibault de
396 Chanvalon et al. 2016a).

397 During winter conditions, Cu_p and Zn_p concentration differences are observed between
398 river and seawater end-members (from 2.75 to 0.50 mmol kg⁻¹ and from 4.40 to 2.83 mmol
399 kg⁻¹, respectively). A higher concentration of these elements is typical in freshwater than in
400 the estuary, where various ligands (organic matter (OM), chlorides (Cl⁻)) can complex these
401 two divalent cations (Luoma and Davis 1983). It is generally accepted that OM and hydrous
402 oxides of Fe and Mn are critical components of aquatic particles with respect to the sorptive
403 removal of transition metals (Young and Harvey 1992; Turner et al. 2004). The affinity of

404 metals for specific organic ligands can be described by the Irving-Williams series (Hg> Cu>
405 Zn, Ni> Co> Fe> Mn, Cd> Mg (Guo et al. 2000)) which shows that Cu and Zn are divalent
406 metals with the greatest affinity for OM. Variations in the extent of sorption to untreated
407 particles are caused, principally, by salinity-dependent interactions between Zn and POM
408 (Turner et al. 2004). Indeed, seawater ions compete with dissolved Zn for charged sorption
409 sites on the POM, while neutral organic complexes of Zn that are salted out interact with
410 hydrophobic regions of this phase (Turner et al. 2004). Likewise, Cd_p is depleted in the
411 estuarine part as observed by Boutier et al. (1993) and simulated by Thouvenin et al. (1997) in
412 Loire river estuary. Mean Cd_p concentrations in freshwater are almost five times higher than
413 in estuarine particles (5.31 ± 1.71 vs $1.70 \pm 1.00 \mu\text{mol kg}^{-1}$). The high concentration of
414 particles in the estuary, their lateral homogenisation, and inputs of freshwater particles with
415 high Cd_p concentrations do not allow the observation of measurable variations linked to
416 salinity-driven Cd sorption/desorption. Nowadays Cd_p concentrations in the river, as well as
417 in the estuarine section, are about 3 times lower than concentrations reported in 1993 (Boutier
418 et al. 1993). Given the long residence time of particles in the system, this could denote a
419 decrease in the cadmium contamination of the Loire river between the two studies. The
420 attenuation of Cd contamination in the SPM samples is coherent with the tendencies observed
421 in the sedimentary archives in the fluvial-estuarine continuum (Dhivert et al. 2016; Araújo et
422 al. 2019). No regulatory law has been imposed in the last decade which could explain the
423 attenuation. However, at the end of the World War II, Loire estuary became an important
424 industrial centre for the production of fertilizers (nitrogen and phosphorus) in France (Martin
425 2018). Natural phosphate contains some cadmium and the latter is found as an impurity in
426 phosphate fertilizers (Roberts 2014). This chemical industry, which provided a potential
427 source of Cd link to atmospheric dust or sewages, became anecdotal with the closure in 1975
428 of the last super-phosphate plants (Martin 2018).

430 The particle-water distribution coefficient, K_D , (Equation 1) enables the determination
431 of the relative affinities of ions for their dissolved and particulate phases. Because true or
432 apparent interactions of chemical constituents between suspended particles and water result
433 from a variety of physical, chemical, and biological processes (Turner and Millward 2002),
434 we will talk about the “apparent K_D ”. Apparent K_D for Cu, Zn, Ni, Cd, Co and Mn resulting
435 from the cruises are shown in Table II. No difference in the particle-water distribution
436 coefficient for the same metal was observed between the seasons (T-test for independent
437 samples, p -value > 0.05) nor in the function of the salinity, as already suggested by Turner

439 6). For all three seasons, the trend of decreasing apparent K_D among the metals is Co > Mn >
440 Zn > Ni > Cu > Cd. The sequence is quite similar to reported values by Balls (1994) on
441 British coasts, Turner et al. (1991) in the Weser estuary, and Chiffoleau et al. (1994) in the
442 Seine estuary. However, sorting K_D 's as a function of concentration of SPM reveals
443 systematic trends (Supplementary file – Fig. S2). Turner et al. (1991) also observed the same
444 trends and have suggested that variations in K_D with SPM concentrations are dominated by
445 variation in the available dissolved metal content. The increase in K_D^{Mn} with SPM suggests
446 that flocs or/and temporarily suspended particles of the TMZ are relatively enriched in these
447 metals through removal from solution by flocculation or sorption reactions at the particle
448 surfaces. In contrast, K_D 's for Cu, Ni and Zn, and possibly Co, decrease with increasing SPM
449 concentration. Low K_D 's in the TMZ, ignoring possible ionic strength effects, reflect the
450 dynamic nature of this zone in which particulate metals are depleted because their sorptive
451 equilibrium cannot be met. Moreover, the organic matter degradation could release metals
452 into the water column (Turner and Millward 2002).

453 **Table II:** Distribution coefficient ($\log K_D$) for Co, Cu, Zn, Ni, Cd and Mn and SPM
454 concentrations resulting from campaigns samples.

Station name	Salinity	Co <i>logK_D</i>	Ni <i>logK_D</i>	Cu <i>logK_D</i>	Zn <i>logK_D</i>	Cd <i>logK_D</i>	Mn <i>logK_D</i>	SPM ₅₅ <i>g L⁻¹</i>	
Mont Jean	0.0	5.8	4.7	4.4	5.4	4.9	6.4	0.01	
Tabarly	0.0	6.0	4.7	4.2	5.5	4.4	6.9	456	
ST24	0.0	5.9	4.7	4.3	5.3	4.4	6.8	0.08	
ST23	1.6	6.0	4.7	4.2	5.2	4.2	6.3	0.04	
ST22	3.2	6.0	4.7	4.3	5.2	4.1	6.3	457	B
ST21	5.4	6.0	4.7	4.3	5.2	4.0	6.2	0.21	
ST20	8.2	6.0	4.7	4.3	5.2	3.8	6.1	1.41	
ST19	11.2	6.1	4.7	4.3	5.1	3.7	6.2	458	ased
ST18	14.2	6.1	4.7	4.4	5.1	3.7	6.2	2.11	
ST17	17.2	6.0	4.7	4.4	5.2	3.7	6.0	1.32	
ST16	22.9	5.8	5.0	4.5	5.3	3.9	5.7	459	on
ST15	23.7	5.9	4.9	4.6	5.4	4.0	5.9	0.75	
								1.00	
CAMELIA 2								460	parti
Mont Jean	0.0	5.3	4.5	4.1	4.9	4.8	n.d	0.06	
Oudon	0.0	5.4	4.5	4.2	5.3	4.8	n.d	461	cula
Tabarly	0.0	5.4	4.5	4.2	5.3	4.8	n.d	0.06	
ST22	0.0	5.4	4.7	4.5	5.5	5.0	6.1	462	te
ST21	1.0	5.5	4.7	4.3	5.5	4.7	6.2	0.03	
ST20	4.1	5.5	4.7	4.3	5.5	4.4	5.9	0.02	
ST19	7.1	5.6	4.7	4.3	5.4	4.1	5.9	463	and
ST18	10.3	5.6	4.7	4.4	5.4	3.9	5.6	0.07	
ST17	13.2	5.7	4.7	4.4	5.3	4.0	5.8	0.07	
ST16	16.2	5.6	4.8	4.4	5.3	3.8	5.8	464	diss
ST15	17.7	5.5	4.8	4.4	5.4	3.8	5.6	0.10	
ST14	22.0	5.5	4.9	4.5	5.4	3.8	5.2	465	olve
ST13	22.1	5.5	4.8	4.5	5.2	3.5	5.7	0.41	
ST12	27.5	5.8	5.0	4.7	5.7	4.0	5.6	0.02	
								466	d
CAMELIA 3									
Mont Jean	0.0	5.6	4.7	5.0	5.6	5.0	n.d	467	met
Prairie Inondée	0.0	5.4	4.6	4.5	5.3	4.9	n.d	0.02	
Tabarly	0.0	5.6	4.6	4.4	5.4	4.9	n.d	0.06	
ST1	0.0	5.5	4.6	4.3	5.3	4.8	5.6	468	als
ST2	0.0	5.5	4.6	4.3	5.3	4.9	5.3	0.06	
ST3	0.0	5.0	4.5	4.3	5.2	4.6	4.4	0.38	
ST4	0.1	5.1	4.6	4.5	5.4	4.6	4.3	469	con
ST5	3.7	5.2	4.6	4.4	5.4	4.4	4.9	0.49	
ST6	6.4	5.5	4.6	4.4	5.4	4.3	5.3	470	cent
ST7	8.9	5.5	4.6	4.4	5.3	4.2	5.2	0.10	
ST8	11.2	5.5	4.7	4.4	5.3	4.0	5.3	0.05	
ST9	13.7	5.6	4.7	4.4	5.4	4.1	5.6	471	ratio
ST10	17.1	5.6	4.7	4.4	5.3	3.9	5.5	0.04	
ST11	20.2	5.6	4.7	4.5	5.3	3.9	5.4	0.03	
ST12	21.9	5.6	4.8	4.5	5.4	3.9	5.4	472	ns
ST13	24.0	5.8	4.9	4.6	5.4	3.9	5.7	0.02	
								473	in

474 the river, in the estuary, and water discharges during the cruises, metal fluxes have been
475 quantified using the linear regression between metal and salinity, following the Boyle et al.
476 (1974) model. This model assumes that a concentration of a given constituent is a continuous
477 function of salinity. The flux of a dissolved metal of unknown behaviour at a given salinity
478 corresponds to the product of the river water flux with the intersection of the tangent to the
479 concentration-salinity curve at a given salinity with this concentration axis (e.g. (Chiffolleau et

480 al. 1994)). In this study, the tangent to the concentration vs salinity curves correspond to the
 481 best fits for the salinity range 20-35. Estimated fluxes are presented in Table III. As dissolved
 482 metal concentrations are quite similar in the river end-member regardless of the season,
 483 dissolved metal fluxes are completely dependent on the water discharge. The importance of
 484 freshwater flow and season on chemical composition of upstream SPM has already been
 485 described by Grosbois et al. (2001). An increase of metal fluxes, up to two orders of
 486 magnitude, between summer low water flow ($\sim 210 \text{ m}^3 \text{ s}^{-1}$) and winter water flow ($\sim 2790 \text{ m}^3 \text{ s}^{-1}$)
 487 leads to a wide range of dissolved and particulate fluxes for all the metals.

488 **Table III:** Dissolved and particulate Co, Ni, Cu, Cd and Zn fluxes estimated in the Loire
 489 estuary.

		Riverine Inputs (kg day ⁻¹)		Net Outputs (kg day ⁻¹)
		Dissolved ^a	Particulate ^b	Dissolved ^c
Co	<i>Summer 2012</i>	0.5±0.0	4.5±0.2	0.2±0.0
	<i>Spring 2013</i>	12.1±3.8	153.2±48.4	22.0±6.9
	<i>Winter 2014</i>	10.9±1.6	221.4±32.1	28.0±4.1
Ni	<i>Summer 2012</i>	17.1±0.8	13.3±0.6	22.4±1.1
	<i>Spring 2013</i>	173.1±54.6	349.1±110.2	186.1±58.7
	<i>Winter 2014</i>	236.4±34.2	590.3±85.5	460.4±66.7
Cu	<i>Summer 2012</i>	48.6±2.3	17.6±0.8	52.5±2.5
	<i>Spring 2013</i>	355.2±112.1	295.2±93.2	321.7±101.5
	<i>Winter 2014</i>	434.9±63.0	2210.8±320.1	678.1±98.2
Cd	<i>Summer 2012</i>	0.2±0.0	0.2±0.0	1.7±0.1
	<i>Spring 2013</i>	1.4±0.4	5.2±1.6	6.6±2.1
	<i>Winter 2014</i>	1.7±0.2	8.8±1.3	9.7±1.4
Zn	<i>Summer 2012</i>	14.2±0.7	54.8±2.6	36.8±1.8
	<i>Spring 2013</i>	304.5±96.1	1634.5±515.9	462.6±146.0
	<i>Winter 2014</i>	173.0±25.0	3643.6±527.6	566.3±82.0

490 ^a Loire river discharge at Montjean during the sampling campaign multiplied by Me_d concentration at the same
 491 site.

492 ^b Loire river discharge at Montjean x SPM concentration x Me_p concentration at the same site.

493 ^c Loire river discharge at Montjean x hypothetical Me concentration in the dissolved phase at salinity 0
 494 extrapolated from the dilution line observed at salinity >20.

495

496 Dissolved metal net outputs were estimated to be 0.2 to 28.0 kg day⁻¹ for Co, 22.4 to 460.4 kg
 497 day⁻¹ for Ni, 52.5 to 678.1 kg day⁻¹ for Cu, 1.7 to 9.7 kg day⁻¹ for Cd and 36.8 to 566.3 kg day⁻¹

498 ¹ for Zn. With regard to fluxes of all dissolved and particulate metal fluxes, Cu and Zn
499 represent the most exported metals through the estuary whatever the season (Table II).

500 In the Loire river, previous studies have been focused only on dissolved Cd and Cu
501 metals (Boutier et al. 1993; Waeles et al. 2004). For Cd_d, Boutier et al. (1993) have calculated
502 a net efflux of 7.2 kg day⁻¹, while Waeles et al. (2004) have calculated a flux of dissolved Cd
503 of 14 kg day⁻¹. Both studies have the same Cd_d concentration at 0 of salinity (0.8 nM).
504 Nowadays, Cd_d concentrations have decreased (0.13 ± 0.07 nM) with a calculated net efflux
505 close to that reported by Boutier et al. (1993).

506 Concerning Cu, a first estimate by Waeles et al. (2004) in the spring of 2001 mentions
507 a daily Cu_d flux of 343 kg day⁻¹. Same values have been estimated for this study during spring
508 2013. However, fluxes variations are visible for both the dissolved and the particulates
509 depending on the flow conditions of the river. The dissolved Cu net output is more than 10
510 times higher during high discharge conditions (winter) than low discharge conditions
511 (summer).

512 In comparison with the Gironde or Tagus Rivers, which are the main sources of metal input to
513 the North East Atlantic Ocean (Figueres et al. 1985), the Loire river dissolved net output over
514 the winter-time is higher than the Tagus and Gironde for Cu, Zn and Ni but lower for Cd
515 (Table SI). At the global scale, the Loire metal fluxes are relatively low in comparison with
516 the main world rivers (Liu et al. 2020) and dependent on the flow conditions of the river.
517 Taking mean particulate and dissolved concentrations (summer and winter values) with a
518 mean water discharge (835 m³ s⁻¹, Banque HYDRO database), it could be estimated that the
519 Loire river could transport 19 Mg of Co, 45 Mg of Ni, 50 Mg of Cu, 195 Mg of Zn and 0.98
520 Mg of Cd into the coastal North East of the Atlantic Ocean. In comparison with the 32 Gg of
521 heavy metals discharged by the Yangtze River into the East China Sea (Liu et al. 2020), the
522 Loire river does not serve as a significant source of heavy metal pollution for the global

523 ocean. Moreover, using the concentrations of total suspended solids (Cs^*) parameter defined
524 by Meybeck et al. (2003), the Loire river has a mean Cs^* of 50 mg.L^{-1} . Compared to the 60
525 global rivers of Meybeck et al. study, which covers natural conditions ranging from the humid
526 tropics to subarctic and arid regions, located in all types of relief around the world, the Loire
527 river discharge is classified as “low” far behind Colorado, Rio Grande or El Abid rivers
528 (Meybeck et al. 2003). However, it has been shown that the effect of the Loire inflows could
529 be detected up to the north of the Bay of Biscay (Waeles et al. 2004).

530 It is recognised that the cities discharge stormwater and treated wastewater that carry
531 pollutants like metals into the river, posing a risk to both humans and the ecosystem
532 (Landrigan et al. 2018). Although the Loire crosses Nantes city (6th largest French
533 metropolis), which experiences a constant increase in its population (+ 0.7% each year), it
534 seems that the Loire river is only slightly affected by urban discharges, or that the urban
535 contributions are diluted and masked by the natural contributions of the very large catchment
536 area. Overall, concentrations are stable or have decreased since the studies of the 1990s
537 (Boutier et al. 1993; Waeles et al. 2004).

538 It would be interesting to link *in situ* biogeochemical observations to modelling the
539 remobilisation and exchange of trace metals at sediment-water-biota interfaces. In addition, it
540 would be interesting to carry out new campaigns in order to determine the concentrations in
541 emerging elements that can lead to changes in concentrations linked to growing technological
542 uses.

543
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545

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550

551

552 **Authors contributions**

553 All authors contributed to the study conception and design. Material preparation, data
554 collection and analysis were performed by Sylvette Crochet and Bastien Thomas. The first
555 draft of the manuscript was written by Nicolas Briant and all authors collaborated and
556 commented on previous versions of the manuscript. All authors read and approved the revised
557 manuscript.

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560 **Reference**

- 561 Abualhaija MM, Whitby H, van den Berg CMG (2015) Competition between copper and iron for humic ligands
562 in estuarine waters. *Mar Chem* 172:46–56. <https://doi.org/10.1016/j.marchem.2015.03.010>
- 563 Ackroyd D, Bale A, Howland R, et al (1986) Distributions and behaviour of dissolved Cu, Zn and Mn in the
564 Tamar estuary. *Estuar Coast Shelf Sci* 23:621–640. [https://doi.org/10.1016/0272-7714\(86\)90103-4](https://doi.org/10.1016/0272-7714(86)90103-4)
- 565 Allen G, Sauzay G, Castaing P, Jouanneau J (1977) Transport and deposition of suspended sediment in the
566 Gironde Estuary, France. *Estuar Process (PROC THIRD INT Estuar Res CONF GALVESTON, USA*
567 *OCT 7-9, 1975) WILEY, M 2, Cirulc:63–81. https://doi.org/10.1016/b978-0-12-751802-2.50013-8*
- 568 Aminot A, Guillaud J, Andrieux-Loyer F, K erouel R (1998) Nutrients and phytoplanktonic growth in the Bay of
569 Seine, France. *Oceanol Acta* 6:923–935
- 570 Aminot A, K erouel R, Coverly S (2009) Nutrients in seawater using segmented flow analysis. In: *Practical*
571 *guidelines for the analysis of seawater. pp 143–178*
- 572 Apte SC, Gardner MJ, Gunn AM, et al (1990) Trace metals in the Severn estuary: a reappraisal. *Mar Pollut Bull*
573 21:393–396. [https://doi.org/10.1016/0025-326X\(90\)90649-S](https://doi.org/10.1016/0025-326X(90)90649-S)
- 574 Ara ujo D, Ponzevera E, Briant N, et al (2019) Assessment of the metal contamination evolution in the Loire
575 estuary using Cu and Zn stable isotopes and geochemical data in sediments. *Mar Pollut Bull* 143:12–23.
576 <https://doi.org/10.1016/j.marpolbul.2019.04.034>
- 577 Avery GB, Willey JD, Kieber RJ, et al (2003) Flux and bioavailability of Cape Fear River and rainwater
578 dissolved organic carbon to Long Bay, southeastern United States. *Global Biogeochem Cycles* 17:1042.
579 <https://doi.org/10.1029/2002gb001964>
- 580 Avoine J, Larsonneur C (1987) Dynamics and behaviour of suspended sediment in macrotidal estuaries along the
581 south coast of the English Channel. *Cont Shelf Res* 7:1301–1305. [https://doi.org/10.1016/0278-](https://doi.org/10.1016/0278-4343(87)90033-1)
582 [4343\(87\)90033-1](https://doi.org/10.1016/0278-4343(87)90033-1)
- 583 Balls P (1994) Nutrient Inputs to Estuaries from Nine Scottish East Coast Rivers; Influence of Estuarine
584 Processes on Inputs to the North Sea. *Estuar Coast Shelf Sci* 39:329–352.
585 <https://doi.org/10.1006/ecss.1994.1068>
- 586 Bendschneider K, Robinson R (1952) A new spectrophotometric method for the determination of nitrite in sea
587 water
- 588 Benoit G, Oktay-Marshall S, Cantu A, et al (1994) Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-
589 retained particles, colloids, and solution in six Texas estuaries. *Mar Chem* 45:307–336.
590 [https://doi.org/10.1016/0304-4203\(94\)90076-0](https://doi.org/10.1016/0304-4203(94)90076-0)
- 591 Boutier B, Chiffolleau J, Auger D, Truquet I (1993) Influence of the Loire River on Dissolved Lead and
592 Cadmium Concentrations in Coastal Waters of Brittany. *Estuar Coast Shelf Sci* 36:133–145.
593 <https://doi.org/10.1006/ecss.1993.1009>

- 594 Boyle E, Collier R, Dengler A, et al (1974) On the chemical mass-balance in estuaries. *Geochim Cosmochim*
595 *Acta* 38:1719–1728. [https://doi.org/10.1016/0016-7037\(74\)90188-4](https://doi.org/10.1016/0016-7037(74)90188-4)
- 596 Boyle EA, Husted SS, Grant B (1982) The chemical mass balance of the amazon plume-II. Copper, nickel, and
597 cadmium. *Deep Sea Res Part A, Oceanogr Res Pap* 29:1355–1364. [https://doi.org/10.1016/0198-](https://doi.org/10.1016/0198-0149(82)90013-9)
598 [0149\(82\)90013-9](https://doi.org/10.1016/0198-0149(82)90013-9)
- 599 Bruland K, Lohan M (2003) Controls of trace metals in seawater
- 600 Bruland KW (1989) Complexation of zinc by natural organic ligands in the central North Pacific. *Limnol*
601 *Oceanogr* 34:269–285. <https://doi.org/10.4319/lo.1989.34.2.0269>
- 602 Chaudry MA, Zwolsman JJG (2008) Seasonal dynamics of dissolved trace metals in the Scheldt estuary:
603 Relationship with redox conditions and phytoplankton activity. *Estuaries and Coasts* 31:430–443.
604 <https://doi.org/10.1007/s12237-007-9030-7>
- 605 Che Y, He Q, Lin W (2003) Distributions of particulate heavy metals and its indication to the transfer of
606 sediment in high turbidity estuaries. *Mar Pollut Bull* 57
- 607 Chiffolleau J, Cossa D, Auger D, Truquet I (1994) Trace metal distribution, partition and fluxes in the Seine
608 estuary (France) in low discharge regime. *Mar Chem* 47:145–158. [https://doi.org/10.1016/0304-](https://doi.org/10.1016/0304-4203(94)90105-8)
609 [4203\(94\)90105-8](https://doi.org/10.1016/0304-4203(94)90105-8)
- 610 Ciffroy P, Garnier JM, Benyahya L (2003a) Kinetic partitioning of Co, Mn, Cs, Fe, Ag, Zn and Cd in fresh
611 waters (Loire) mixed with brackish waters (Loire estuary): Experimental and modelling approaches. *Mar*
612 *Pollut Bull* 46:626–641. [https://doi.org/10.1016/S0025-326X\(02\)00517-9](https://doi.org/10.1016/S0025-326X(02)00517-9)
- 613 Ciffroy P, Reyss JL, Siclet F (2003b) Determination of the residence time of suspended particles in the turbidity
614 maximum of the Loire estuary by ⁷Be analysis. *Estuar Coast Shelf Sci* 57:553–568.
615 [https://doi.org/10.1016/S0272-7714\(02\)00339-6](https://doi.org/10.1016/S0272-7714(02)00339-6)
- 616 Cloern J (2001) Our evolving conceptual model of the coastal eutrophication problem. *Mar Ecol Prog Ser*
617 210:223–253
- 618 Comans R, Van Dijk C (1988) Role of complexation processes in cadmium mobilization during estuarine
619 mixing. *Nature* 336:151–154. <https://doi.org/10.1038/336151a0>
- 620 Coquery M, Cossa D, Sanjuan J (1997) Speciation and sorption of mercury in two macro-tidal estuaries. In:
621 *Marine Chemistry*. Elsevier, pp 213–227
- 622 Cotté-Krief M, Guieu C, Thomas A, Martin J (2000) Sources of Cd, Cu, Ni and Zn in Portuguese coastal waters.
623 *Mar Chem* 71:199–214. [https://doi.org/10.1016/S0304-4203\(00\)00049-9](https://doi.org/10.1016/S0304-4203(00)00049-9)
- 624 Coynel A, Gorse L, Curti C, et al (2016) Spatial distribution of trace elements in the surface sediments of a
625 major European estuary (Loire Estuary, France): Source identification and evaluation of anthropogenic
626 contribution. *J Sea Res* 118:77–91. <https://doi.org/10.1016/j.seares.2016.08.005>
- 627 Danielsson LG, Magnusson B, Westerlund S, Zhang K (1982) Trace metal determinations in estuarine waters by

628 electrothermal atomic absorption spectrometry after extraction of dithiocarbamate complexes into freon.
629 *Anal Chim Acta* 144:183–188. [https://doi.org/10.1016/S0003-2670\(01\)95531-X](https://doi.org/10.1016/S0003-2670(01)95531-X)

630 Dauvin JC (2008) The main characteristics, problems, and prospects for Western European coastal seas. *Mar*
631 *Pollut Bull* 57:22–40. <https://doi.org/10.1016/j.marpolbul.2007.10.016>

632 Demaure J. (1979) Les contraintes écologiques de l'aménagement de la Loire. *Penn ar Bed* 12:57–72

633 Dhivert E, Grosbois C, Courtin-Nomade A, et al (2016) Dynamics of metallic contaminants at a basin scale —
634 Spatial and temporal reconstruction from four sediment cores (Loire fluvial system, France). *Sci Total*
635 *Environ* 541:1504–1515. <https://doi.org/10.1016/j.scitotenv.2015.09.146>

636 Donat J, Lao K, Bruland K (1994) Speciation of dissolved copper and nickel in South San Francisco Bay: a
637 multi-method approach. *Anal Chim Acta* 284:547–571. [https://doi.org/10.1016/0003-2670\(94\)85061-5](https://doi.org/10.1016/0003-2670(94)85061-5)

638 Duan L, Song J, Liang X, et al (2019) Dynamics and diagenesis of trace metals in sediments of the Changjiang
639 Estuary. *Sci Total Environ* 675:247–259. <https://doi.org/10.1016/j.scitotenv.2019.04.190>

640 Dulaquais G, Waeles M, Breitenstein J, et al (2020) Links between size fractionation, chemical speciation of
641 dissolved copper and chemical speciation of dissolved organic matter in the Loire estuary. *Environ Chem*
642 17:385–399. <https://doi.org/10.1071/EN19137>

643 Edmond J, Spivack A, Grant B, et al (1985) Chemical dynamics of the Changjiang estuary. *Cont Shelf Res* 4:17–
644 36. [https://doi.org/10.1016/0278-4343\(85\)90019-6](https://doi.org/10.1016/0278-4343(85)90019-6)

645 Elbaz-Poulichet F, Guan D, Martin J (1991) Trace metal behaviour in a highly stratified Mediterranean estuary:
646 the Krka (Yugoslavia). *Mar Chem* 32:211–224

647 Elbaz-Poulichet F, Martin JM, Huang WW, Zhu JX (1987) Dissolved Cd behaviour in some selected french and
648 chinese estuaries. Consequences on Cd supply to the ocean. *Mar Chem* 22:125–136.
649 [https://doi.org/10.1016/0304-4203\(87\)90004-1](https://doi.org/10.1016/0304-4203(87)90004-1)

650 Elbaz-Poulichet F, Seidel J, Casiot C, Tusseau-Vuillemin M (2006) Short-term variability of dissolved trace
651 element concentrations in the Marne and Seine Rivers near Paris. *Sci Total Environ* 367:278–287.
652 <https://doi.org/10.1016/j.scitotenv.2005.11.009>

653 Elliott M, McLusky D (2002) The need for definitions in understanding estuaries. *Estuar Coast Shelf Sci*
654 55:815–827

655 Etcheber H, Taillez A, Abril G, et al (2007) Particulate organic carbon in the estuarine turbidity maxima of the
656 Gironde, Loire and Seine estuaries: origin and lability. *Hydrobiologia* 588:245–259.
657 <https://doi.org/10.1007/s10750-007-0667-9>

658 Figueres G, Martin J, Meybeck M, Seyler P (1985) A comparative study of mercury contamination in the Tagus
659 estuary (Portugal) and major French estuaries (Gironde, Loire, Rhône). *Estuar Coast Shelf Sci* 20:183–
660 203. [https://doi.org/10.1016/0272-7714\(85\)90037-X](https://doi.org/10.1016/0272-7714(85)90037-X)

661 Gallenne B (1974) Les accumulations turbides de l'estuaire de la Loire. Etude de la crème de vase

- 662 Gaulier C, Zhou C, Gao Y, et al (2021) Investigation on trace metal speciation and distribution in the Scheldt
663 estuary. *Sci Total Environ* 757:143827. <https://doi.org/10.1016/j.scitotenv.2020.143827>
- 664 Gautier E, Grivel S (2006) Multi-scale analysis of island formation and development in the Middle Loire River,
665 France. In: IAHS-AISH Publication. pp 179–187
- 666 Grosbois C, Meybeck M, Lestel L, et al (2012) Severe and contrasted polymetallic contamination patterns
667 (1900-2009) in the Loire River sediments (France). *Sci Total Environ* 435–436:290–305.
668 <https://doi.org/10.1016/j.scitotenv.2012.06.056>
- 669 Grosbois C, Négrel P, Grimaud D, Fouillac C (2001) An overview of dissolved and suspended matter fluxes in
670 the Loire River Basin: Natural and anthropogenic inputs. *Aquat Geochemistry* 7:81–105.
671 <https://doi.org/10.1023/A:1017518831860>
- 672 Guieu C, Martin J, Tankéré S, et al (1998) On trace metal geochemistry in the Danube River and western Black
673 Sea. *Estuar Coast Shelf Sci* 47:471–485. <https://doi.org/10.1006/ecss.1998.0377>
- 674 Guieu C, Martin JM (2002) The level and fate of metals in the Danube River plume. *Estuar Coast Shelf Sci*
675 54:501–512. <https://doi.org/10.1006/ecss.2000.0660>
- 676 Guillaud J (1983) Les flux de sels nutritifs dans l'estuaire de la Seine (France); rôle et importance du bouchon
677 vaseux au cours du mélange estuarien. *Can J Fish Aquat Sci* 40:s180–s187. <https://doi.org/10.1139/f83-280>
- 679 Guillaud J, Aminot A, Delmas D, et al (2008) Seasonal variation of riverine nutrient inputs in the northern Bay
680 of Biscay (France), and patterns of marine phytoplankton response. *J Mar Syst* 72:309–319.
681 <https://doi.org/10.1016/j.jmarsys.2007.03.010>
- 682 Guo L, Santschi PH, Warnken KW (2000) Trace metal composition of colloidal organic material in marine
683 environments. *Mar Chem* 70:257–275. [https://doi.org/10.1016/S0304-4203\(00\)00031-1](https://doi.org/10.1016/S0304-4203(00)00031-1)
- 684 Hatje V, Apte S, Hales L, Birch G (2003) Dissolved trace metal distributions in Port Jackson estuary (Sydney
685 Harbour), Australia. *Mar Pollut Bull* 46:719–30. [https://doi.org/10.1016/S0025-326X\(03\)00061-4](https://doi.org/10.1016/S0025-326X(03)00061-4)
- 686 Jalón-Rojas I, Schmidt S, Sottolichio A, Bertier C (2016) Tracking the turbidity maximum zone in the Loire
687 Estuary (France) based on a long-term, high-resolution and high-frequency monitoring network. *Cont
688 Shelf Res* 117:1–11. <https://doi.org/10.1016/j.csr.2016.01.017>
- 689 Klinkhammer GP, Bender ML (1981) Trace metal distributions in the Hudson River estuary. *Estuar Coast Shelf
690 Sci* 12:629–643. [https://doi.org/10.1016/S0302-3524\(81\)80061-8](https://doi.org/10.1016/S0302-3524(81)80061-8)
- 691 Kraepiel A, Chiffoleau J, Martin J, Morel F (1997) Geochemistry of trace metals in the Gironde estuary.
692 *Geochim Cosmochim Acta* 61:1421–1436. [https://doi.org/10.1016/S0016-7037\(97\)00016-1](https://doi.org/10.1016/S0016-7037(97)00016-1)
- 693 Landrigan PJ, Fuller R, Hu H, et al (2018) Pollution and global health – An agenda for prevention. *Environ
694 Health Perspect* 126:. <https://doi.org/10.1289/EHP3141>
- 695 Liu M, He Y, Baumann Z, et al (2020) The impact of the Three Gorges Dam on the fate of metal contaminants

696 across the river–ocean continuum. *Water Res* 185:. <https://doi.org/10.1016/j.watres.2020.116295>

697 Luoma SN, Davis JA (1983) Requirements for modeling trace metal partitioning in oxidized estuarine
698 sediments. *Mar Chem* 12:159–181. [https://doi.org/10.1016/0304-4203\(83\)90078-6](https://doi.org/10.1016/0304-4203(83)90078-6)

699 Martin P (2014) L'industrie chimique de l'estuaire de la Loire dans l'effort de guerre pendant la Première Guerre
700 mondiale. *Ann Bretagne des Pays l'Ouest* 121:167–185

701 Martin P (2018) Histoire de l'industrie des engrais dans l'estuaire de la Loire à l'époque contemporaine.
702 Université de Nantes

703 Martino M, Turner A, Nimmo M, Millward G (2002) Resuspension, reactivity and recycling of trace metals in
704 the Mersey Estuary, UK. *Mar Chem* 77:171–186. [https://doi.org/10.1016/S0304-4203\(01\)00086-X](https://doi.org/10.1016/S0304-4203(01)00086-X)

705 Masson M, Blanc G, Schäfer J (2006) Geochemical signals and source contributions to heavy metal (Cd, Zn, Pb,
706 Cu) fluxes into the Gironde Estuary via its major tributaries. *Sci Total Environ* 370:133–146.
707 <https://doi.org/10.1016/j.scitotenv.2006.06.011>

708 Meybeck M, Cauwet G, Dessery S, et al (1988) Nutrients (organic C, P, N, Si) in the eutrophic River Loire
709 (France) and its estuary. *Estuar Coast Shelf Sci* 27:595–624. [https://doi.org/10.1016/0272-7714\(88\)90071-](https://doi.org/10.1016/0272-7714(88)90071-6)
710 6

711 Meybeck M, Laroche L, Dürr HH, Syvitski JPM (2003) Global variability of daily total suspended solids and
712 their fluxes in rivers. *Glob Planet Change* 39:65–93. [https://doi.org/10.1016/S0921-8181\(03\)00018-3](https://doi.org/10.1016/S0921-8181(03)00018-3)

713 Michel P, Boutier B, Chiffolleau J (2000) Net Fluxes of Dissolved Arsenic, Cadmium, Copper, Zinc, Nitrogen
714 and Phosphorus from the Gironde Estuary (France): Seasonal Variations and Trends. *Estuar Coast Shelf*
715 *Sci* 51:451–462. <https://doi.org/10.1006/ecss.2000.0691>

716 Moffett J, Ho J (1996) Oxidation of cobalt and manganese in seawater via a common microbially catalyzed
717 pathway. *Geochim Cosmochim Acta* 60:3415–3424. [https://doi.org/10.1016/0016-7037\(96\)00176-7](https://doi.org/10.1016/0016-7037(96)00176-7)

718 Morris AW (1990) Kinetic and equilibrium approaches to estuarine chemistry. *Sci Total Environ* 97–98:253–
719 266. [https://doi.org/10.1016/0048-9697\(90\)90244-O](https://doi.org/10.1016/0048-9697(90)90244-O)

720 Negrel P (1997) Multi-element chemistry of Loire estuary sediments: Anthropogenic vs. natural sources. *Estuar*
721 *Coast Shelf Sci* 44:395–410. <https://doi.org/10.1006/ecss.1996.0139>

722 Nimmo M, van den Berg CMG, Brown J (1989) The chemical speciation of dissolved nickel, copper, vanadium
723 and iron in Liverpool Bay, Irish Sea. *Estuar Coast Shelf Sci* 29:57–74. [https://doi.org/10.1016/0272-](https://doi.org/10.1016/0272-7714(89)90073-5)
724 7714(89)90073-5

725 Nolting RF, Sundby B, Duinker JC (1990) Behaviour of minor and major elements in suspended matter in the
726 Rhine and Meuse rivers and estuary. *Sci Total Environ* 97–98:169–183. [https://doi.org/10.1016/0048-](https://doi.org/10.1016/0048-9697(90)90238-P)
727 9697(90)90238-P

728 O'Connell C (1999) The geochemistry of silver and zinc in the Cape Fear estuary. University of North Carolina
729 Wilmington, Wilmington, NC

- 730 Oldham V, Miller M, Jensen L, Luther G (2017) Revisiting Mn and Fe removal in humic rich estuaries.
731 *Geochim Cosmochim Acta* 209:267–283. <https://doi.org/10.1016/j.gca.2017.04.001>
- 732 Ottmann F (1979) Conséquences des aménagements sur le milieu estaurien. *J Rech en Océanographie* 4:11–24
- 733 Pearson HBC, Comber SDW, Braungardt C, Worsfold PJ (2017) Predicting Copper Speciation in Estuarine
734 Waters—Is Dissolved Organic Carbon a Good Proxy for the Presence of Organic Ligands? *Environ Sci*
735 *Technol* 51:2206–2216. <https://doi.org/10.1021/acs.est.6b05510>
- 736 Pontee NI, Whitehead PA, Hayes CM (2004) The effect of freshwater flow on siltation in the Humber Estuary,
737 north east UK. *Estuar Coast Shelf Sci* 60:241–249. <https://doi.org/10.1016/j.ecss.2004.01.002>
- 738 Power M, Attrill M, Thomas R (1999) Heavy metal concentration trends in the Thames estuary. *Water Res*
739 33:1672–1680
- 740 Premier V, Machado AA de S, Mitchell S, et al (2019) A model-based analysis of metal fate in the thames
741 estuary. *Estuaries and Coasts* 42:1185–1201. <https://doi.org/10.1007/s12237-019-00544-y>
- 742 Relexans J, Meybeck M, Billen G, Brugeaille M (1988) Algal and microbial processes involved in particulate
743 organic matter dynamics in the Loire estuary. *Estuar Coast Shelf Sci* 27:625–644
- 744 Rincé Y, Guillaud J, Gallenne B (1985) Qualité des eaux en milieu estuarien: Suivi annuel de critères physiques
745 et chimiques dans les eaux de l'estuaire de la Loire. *Hydrobiologia* 124:199–210.
746 <https://doi.org/10.1007/BF00015236>
- 747 Roberts T (2014) Cadmium and phosphorous fertilizers: The issues and the science. In: *Procedia Engineering*.
748 Elsevier Ltd, pp 52–59
- 749 Saager P, De Baar K, De Jong J, et al (1997) Hydrography and local sources of dissolved trace metals Mn, Ni,
750 Cu, and Cd in the northeast Atlantic Ocean. *Mar Chem* 57:195–216. [https://doi.org/10.1016/S0304-4203\(97\)00038-8](https://doi.org/10.1016/S0304-4203(97)00038-8)
- 752 Sañudo-Wilhelmy SA, Rivera-Duarte I, Flegal AR (1996) Distribution of colloidal trace metals in the San
753 Francisco Bay estuary. *Geochim Cosmochim Acta* 60:4933–4944. [https://doi.org/10.1016/S0016-7037\(96\)00284-0](https://doi.org/10.1016/S0016-7037(96)00284-0)
- 755 Schäfer J, Norra S, Klein D, Blanc G (2009) Mobility of trace metals associated with urban particles exposed to
756 natural waters of various salinities from the Gironde Estuary, France. *J Soils Sediments* 9:374–392.
757 <https://doi.org/10.1007/s11368-009-0096-7>
- 758 Schmidt S, Diallo II, Derriennic H, et al (2019) Exploring the susceptibility of turbid estuaries to hypoxia as a
759 prerequisite to designing a pertinent monitoring strategy of dissolved oxygen. *Front Mar Sci* 6:352
- 760 Shank GC, Skrabal SA, Whitehead RF, Kieber RJ (2004) Strong copper complexation in an organic-rich estuary:
761 The importance of allochthonous dissolved organic matter. *Mar Chem* 88:21–39.
762 <https://doi.org/10.1016/j.marchem.2004.03.001>
- 763 Shiller A, Boyle E (1991) Trace elements in the Mississippi River Delta outflow region: Behavior at high

764 discharge. *Geochim Cosmochim Acta* 55:3241–3251. [https://doi.org/10.1016/0016-7037\(91\)90486-O](https://doi.org/10.1016/0016-7037(91)90486-O)

765 Skrabal SA, Lieseke KL, Kieber RJ (2006) Dissolved zinc and zinc-complexing ligands in an organic-rich
766 estuary: Benthic fluxes and comparison with copper speciation. *Mar Chem* 100:108–123.
767 <https://doi.org/10.1016/j.marchem.2005.12.004>

768 Sung W (1995) Some observations on surface partitioning of Cd, Cu, and Zn in estuaries. *Environ Sci Technol*
769 29:1303–1312

770 Takata H, Aono T, Tagami K, Uchida S (2010) Processes controlling cobalt distribution in two temperate
771 estuaries, Sagami Bay and Wakasa Bay, Japan. *Estuar Coast Shelf Sci* 89:294–305.
772 <https://doi.org/10.1016/j.ecss.2010.08.003>

773 Tang D, Warnken K, Santschi P (2001) Organic complexation of copper in surface waters of Galveston Bay.
774 *Limnol Oceanogr* 46:321–330. <https://doi.org/10.4319/lo.2001.46.2.0321>

775 Thibault de Chanvalon A, Metzger E, Mouret A, et al (2016a) Particles transformation in estuaries: Fe, Mn and
776 REE signatures through the Loire Estuary. *J Sea Res* 118:103–112.
777 <https://doi.org/10.1016/j.seares.2016.11.004>

778 Thibault de Chanvalon A, Mouret A, Knoery J, et al (2016b) Manganese, iron and phosphorus cycling in an
779 estuarine mudflat, Loire, France. *J Sea Res* 118:92–102. <https://doi.org/10.1016/j.seares.2016.10.004>

780 Thouvenin B, Gonzalez JL, Boutier B (1997) Modelling of pollutant behaviour in estuaries: Application to
781 cadmium in the Loire estuary. In: *Marine Chemistry*. pp 147–161

782 Turner A (1996) Trace-metal partitioning in estuaries: Importance of salinity and particle concentration. *Mar*
783 *Chem* 54:27–39. [https://doi.org/10.1016/0304-4203\(96\)00025-4](https://doi.org/10.1016/0304-4203(96)00025-4)

784 Turner A, Millward G (2002) Suspended particles: Their role in Estuarine biogeochemical cycles. *Estuar Coast*
785 *Shelf Sci* 55:857–883. <https://doi.org/10.1006/ecss.2002.1033>

786 Turner A, Millward GE (2000) Particle dynamics and trace metal reactivity in estuarine plumes. *Estuar Coast*
787 *Shelf Sci* 50:761–774. <https://doi.org/10.1006/ecss.2000.0589>

788 Turner A, Millward GE, Le Roux SM (2004) Significance of oxides and particulate organic matter in controlling
789 trace metal partitioning in a contaminated estuary. *Mar Chem* 88:179–192.
790 <https://doi.org/10.1016/j.marchem.2004.03.008>

791 Turner A, Millward GE, Morris AW (1991) Particulate metals in five major North Sea estuaries. *Estuar Coast*
792 *Shelf Sci* 32:325–346. [https://doi.org/10.1016/0272-7714\(91\)90047-F](https://doi.org/10.1016/0272-7714(91)90047-F)

793 Turner A, Nimmo M, Thuresson KA (1998) Speciation and sorptive behaviour of nickel in an organic-rich
794 estuary (Beaulieu, UK). *Mar Chem* 63:105–118. [https://doi.org/10.1016/S0304-4203\(98\)00054-1](https://doi.org/10.1016/S0304-4203(98)00054-1)

795 Uncles RJ, Stephens JA, Law DJ (2006) Turbidity maximum in the macrotidal, highly turbid Humber Estuary,
796 UK: Flocs, fluid mud, stationary suspensions and tidal bores. *Estuar Coast Shelf Sci* 67:30–52.
797 <https://doi.org/10.1016/j.ecss.2005.10.013>

798 van den Berg C, Merks A, Duursma E (1987) Organic complexation and its control of the dissolved
799 concentrations of copper and zinc in the Scheldt estuary. *Estuar Coast Shelf Sci* 24:785–797.
800 [https://doi.org/10.1016/0272-7714\(87\)90152-1](https://doi.org/10.1016/0272-7714(87)90152-1)

801 Waeles M, Riso R, Cabon J, et al (2009) Speciation of dissolved copper and cadmium in the Loire estuary and
802 over the North Biscay continental shelf in spring. *Estuar Coast Shelf Sci* 84:139–146.
803 <https://doi.org/10.1016/j.ecss.2009.06.011>

804 Waeles M, Riso R, Maguer J, Le Corre P (2004) Distribution and chemical speciation of dissolved cadmium and
805 copper in the Loire estuary and North Biscay continental shelf, France. *Estuar Coast Shelf Sci* 59:49–57.
806 <https://doi.org/10.1016/j.ecss.2003.07.009>

807 Windom H, Wallace G, Smith R, et al (1983) Behavior of copper in southeastern United States estuaries. *Mar*
808 *Chem* 12:183–193. [https://doi.org/10.1016/0304-4203\(83\)90079-8](https://doi.org/10.1016/0304-4203(83)90079-8)

809 Wong K, Obata H, Kim T, et al (2018) Organic complexation of copper in estuarine waters: An assessment of
810 the multi-detection window approach. *Mar Chem* 204:144–151.
811 <https://doi.org/10.1016/j.marchem.2018.07.001>

812 Yan L, Stallard RF, Key RM, Crerar DA (1991) Trace metals and dissolved organic carbon in estuaries and
813 offshore waters of New Jersey, USA. *Geochim Cosmochim Acta* 55:3647–3656.
814 [https://doi.org/10.1016/0016-7037\(91\)90062-A](https://doi.org/10.1016/0016-7037(91)90062-A)

815 Yeats P (1990) Reactivity and transport of nutrients and metals in the St. Lawrence Estuary. In: *Oceanography of*
816 *a Large-Scale Estuarine System*. Springer New York, pp 155–169

817 Yin S, Wu Y, Xu W, et al (2016) Contribution of the upper river, the estuarine region, and the adjacent sea to the
818 heavy metal pollution in the Yangtze Estuary. *Chemosphere* 155:564–572.
819 <https://doi.org/10.1016/j.chemosphere.2016.04.095>

820 Young LB, Harvey HH (1992) The relative importance of manganese and iron oxides and organic matter in the
821 sorption of trace metals by surficial lake sediments. *Geochim Cosmochim Acta* 56:1175–1186.
822 [https://doi.org/10.1016/0016-7037\(92\)90055-N](https://doi.org/10.1016/0016-7037(92)90055-N)

823 Zhen G, Li Y, Tong Y, et al (2016) Temporal variation and regional transfer of heavy metals in the Pearl
824 (Zhujiang) River, China. *Environ Sci Pollut Res* 23:8410–8420. [https://doi.org/10.1007/s11356-016-6077-](https://doi.org/10.1007/s11356-016-6077-7)
825 [7](https://doi.org/10.1007/s11356-016-6077-7)

826 Zwolsman JJG, Van Eck GTM (1999) Geochemistry of major elements and trace metals in suspended matter of
827 the Scheldt estuary, southwest Netherlands. *Mar Chem* 66:91–111. [https://doi.org/10.1016/S0304-](https://doi.org/10.1016/S0304-4203(99)00026-2)
828 [4203\(99\)00026-2](https://doi.org/10.1016/S0304-4203(99)00026-2)

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830

831 **Captions**

832 **Figure 1:** Sampling stations map during the three CAMELIA cruises.

833 **Figure 2:** Spatial distribution of the TMZ (SPM > 500 mg L⁻¹) during A) summer CAMELIA
834 1, B) spring CAMELIA 2 and C) winter CAMELIA 3 conditions. Max Turbi corresponds to
835 the maximum SPM concentration determined during the cruise.

836 **Figure 3:** Nutrient distributions along the salinity gradient.

837 **Figure 4:** Metal dissolved (A) and particulate (B) concentrations along the Loire Estuary
838 salinity gradient for the three seasonal surveys.

839 **Table I:** Comparison of dissolved metal concentrations with previous studies.

840 **Table II:** Distribution coefficient (log K_D) for Co, Cu, Zn, Ni, Cd and Mn and SPM
841 concentrations resulting from campaigns samples.

842 **Table III:** Dissolved and particulate Cd, Co, Cu, Ni and Zn fluxes.

Loire estuary

