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1 **Biogeochemical cycling of manganese and iron in a macrotidal**  
2 **and hyperturbid estuary subject to flow-driven sedimentation**

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20        **Abstract**

21        The study of manganese (Mn) and iron (Fe) cycling in early diagenetic processes in  
22 estuaries is crucial for understanding the functioning of these vital ecosystems and predicting  
23 their responses to environmental change. The present study investigates the dynamic interplay  
24 of Mn and Fe in early diagenetic processes at highly contrasted hydrosedimentary conditions  
25 in the Loire estuary, which is very rare and allows a comprehensive framework to understand  
26 diagenetic processes in a very dynamic environment. One campaign took place in the  
27 Brillantes intertidal mudflat in March 2015 (PV1), while 3 others took place in a muddy  
28 riverbed along the navigation channel off the city of Paimboeuf during a decennial flood in  
29 February (RR1-4), under moderate discharge in June (RRK-4) and low in August 2021 (RR2-  
30 4). The monitored riverbed station was upstream, under and downstream the maximum  
31 turbidity zone, respectively. By combining sequential extraction techniques for Mn and Fe in  
32 solid phases and pore-water analysis, the study provides insights into the behaviour of these  
33 elements in sedimentary environments and reveals their speciation and association with  
34 specific mineral phases and forms during different diagenesis stages. The remobilization of  
35 Mn and Fe in the surface sediments of the Brillantes mudflat (PV1) allows iron sulphide  
36 formation within the upper 50 cm of the sediment column (above the sulphate penetration  
37 depth). The deeper layers show other authigenic phases formation, such as the probable  
38 precipitation of vivianite below the sulphate depletion depth and progressive precipitation of  
39 carbonate at depth, leading to definitive burial and accumulation. At the muddy riverbed,  
40 following the exceptional flood in February 2021 (RR1-4), significant sediment erosion  
41 occurred unveiling to the water column old and reduced sediments. Sharp pore-water  
42 gradients for dissolved Mn, Fe and sulphate indicated the sudden exposure of the old <sup>7</sup>Be-free  
43 and anoxic sediment to low-salinity, well-oxygenated water. Despite its dark colour, this  
44 sediment showed no authigenic FeS/FeS<sub>2</sub> phases. Four months later, changes in the estuarine  
45 environment (low river discharge) and the presence of a maximum turbidity zone (TMZ) led  
46 to a new deposition of a sediment layer (RRK-4) triggering transient diagenetic reactions. The  
47 freshly deposited sediment layer developed important recycling of dissolved Mn, Fe and  
48 sulphate above the precedent sediment water interface (SWI) generating a double peak,  
49 accompanied by consistently low concentrations of solid Mn and Fe phases specially  
50 FeS/FeS<sub>2</sub> and Mn bound to FeS/FeS<sub>2</sub> compared to PV1. Six months after the flood event, in  
51 August (RR2-4), the discernible attenuation of dissolved Mn and Fe peaks and sulphate  
52 concentration, indicated a gradual recovery of characteristic sediment profiles with the well-  
53 known redox layer succession. Overall, despite important sulphate reduction within

54 sediments from both the river and its adjacent mudflats, pyritization is not a major process for  
55 Mn and Fe burial. The intense hydrodynamics of the mid estuary prevents thermodynamical  
56 equilibrium between pore-water chemistry and solid phases not allowing pyrite formation  
57 while in the calmer conditions of intertidal mudflats, pyrite accumulates in intermediate  
58 depths but carbonates and phosphates seem to be the preferential phases of burial probably  
59 related to methane production and phosphate availability.

60 **Keywords:** Loire, speciation, diagenesis, transient state, sedimentation, disturbance.

## 61 **1. Introduction**

62 Estuaries are unique and dynamic systems formed at the meeting point of freshwater rivers  
63 or streams and saline marine waters and are subject to the influence of tidal and fluvial  
64 processes (Perillo, 1995). Most macrotidal estuaries have a region of elevated suspended  
65 sediment concentrations called the estuarine turbidity maximum zone (TMZ) (Ciffroy et al.,  
66 2003). The TMZ is usually located near the landward end of the salinity intrusion (Woodruff  
67 et al., 2001). Different hydrodynamic processes can support the TMZ such as the increase in  
68 tidal range (hypersynchronous estuary), which is favoured by the convergence/roughness ratio  
69 of the shore (Allen et al., 1980). In macrotidal estuaries, fluctuations in tidal cycles and shifts  
70 in freshwater discharge may alter the position of the TMZ along the estuarine axis and change  
71 sediment deposition patterns (Jalón-Rojas et al., 2016; Migniot, 1972). These variations result  
72 in a seasonal shift of the sediment accumulation zone, affecting the transport and cycling of a  
73 variety of biogeochemical elements, including essential micronutrients such as manganese  
74 (Mn) and iron (Fe) (Morris et al., 1982).

75 Mn and Fe are key elements for living organisms (Burdige, 1993; Raven, 1990). Thanks to  
76 their redox properties, in particular in sediment, they can serve as important alternative  
77 oxidants for carbon degradation (Thamdrup and Dalsgaard, 2000; Vandieken et al., 2006). In  
78 estuaries, the interplay between the release of Mn and Fe into the pore-water or the water  
79 column then their reincorporation and storage in the solid phase influence their availability  
80 and persistence in the sediments. Under conditions where sediments are low in oxygen and  
81 with low sulphide concentrations, Fe(II) and Mn(II) can be released into the water column as  
82 the formation of insoluble compounds such as FeS<sub>x</sub>, which would trap these metals, is  
83 avoided (Wytze K. Lenstra et al., 2021; Scholz et al., 2014). Conversely, Fe(III) and Mn(IV)  
84 tend to precipitate under oxidizing conditions (Froelich et al., 1979). The reactivity of Mn and  
85 Fe may influence the behaviour of many other elements. For example, Mn and Fe oxides  
86 strongly adsorb trace metals (Shaw et al., 1990). Additionally, Fe oxides can adsorb and

87 sequester phosphorus, limiting its bioavailability (Anschutz et al., 1998; Pant and Reddy,  
88 2001), while Mn affects nitrogen dynamics through interactions with organic matter and  
89 microbial processes (Luther et al., 1997). Finally, authigenic precipitation of the reduced  
90 metals with carbonates, sulphides, or phosphate anions and subsequent solid phase  
91 equilibrium can control their respective cycles (Mehner, 2009).

92 While early diagenesis in marine sediments is often described as a steady-state process  
93 (Berner, 1980), the geochemical composition of the sediments evolves through transient  
94 states. These changes can be attributed to factors such as changes in organic carbon input,  
95 oxygen content, sedimentation rates, and local biological activity (Sundby, 2006). Numerous  
96 studies have highlighted how changing environmental conditions affect transient diagenesis.  
97 Rozan et al. (2002) described the conversion of reactive Fe oxides to the FeS/FeS<sub>2</sub> in a  
98 shallow coastal bay and attributed it to sulphate reduction increasing with temperature while  
99 Saulnier and Mucci (2000) demonstrated that the release of Mn in pore-water seems to be  
100 mainly controlled by the dissolution of Mn-carbonate or a mixed Mn–Ca-carbonate.  
101 Phenomena leading to transient states can occur at different temporal and spatial scales. In  
102 continental margins, significant disruptions can occur due to remobilization of bottom  
103 sediments during flood events (Deflandre et al., 2002; Mucci et al., 2003; Mucci and  
104 Edenborn, 1992; Pastor et al., 2018; Sundby, 2006). In estuaries, bed reworking, sediment  
105 transport and deposition, especially during extreme flood events, may have a significant  
106 impact on diagenetic processes and the associated benthic community (Hulot et al., 2023).  
107 This is evident as several decimetres of sediment can be rapidly suspended and deposited  
108 instantaneously (Hulot et al., 2023; Pastor et al., 2018). In estuarine intertidal mudflats, flood  
109 events combined to strong winds can affect the Fe and Mn cycles through the combination of  
110 resuspension/deposition of a freshly transported material from the watershed that is rich in  
111 metallic oxides (Thibault de Chanvalon et al., 2016). After deposition, the classical vertical  
112 diagenetic series is gradually restored by successive release of dissolved Mn and Fe towards  
113 pore-water over a period of few weeks until reaching steady state during summer (Thibault de  
114 Chanvalon et al., 2016). As the sediment becomes compact and the microphytobenthos  
115 biofilm develops, macrofauna increase biological reworking drastically enhancing metal  
116 benthic effluxes and potentially limiting their burial as authigenic sulfidic phases (Thibault de  
117 Chanvalon et al., 2017).

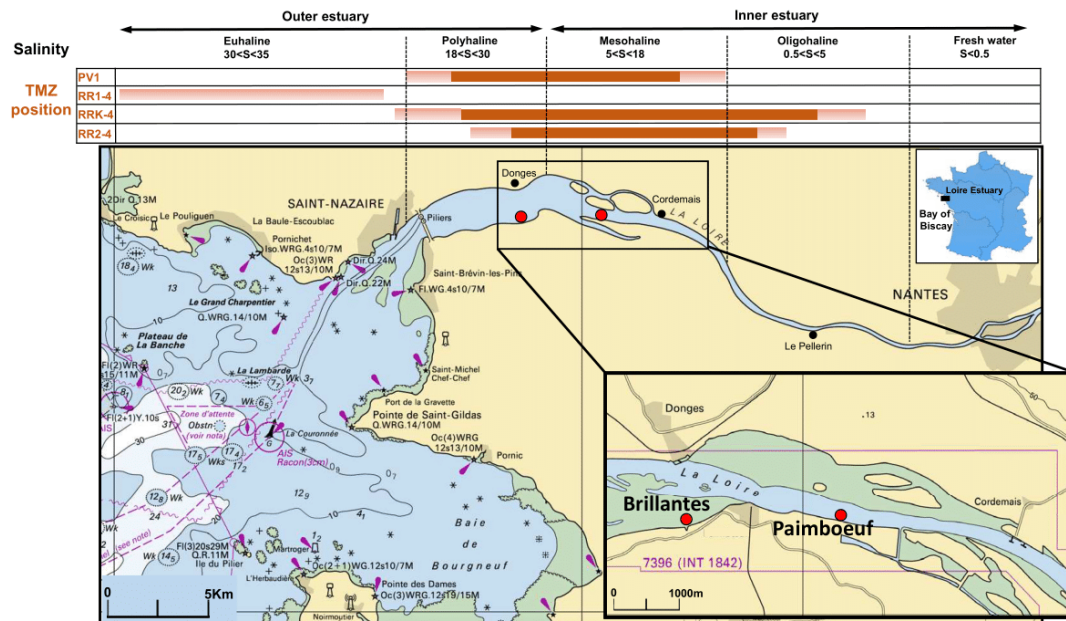
118 Given the complexity of Mn and Fe cycling processes after sediment deposition, the aim of  
119 this study is to investigate the burial and recycling of Mn and Fe in the middle Loire estuary,  
120 focusing on two contrasting hydrodynamic environments: a muddy riverbed near the

121 navigation channel and an adjacent large intertidal mudflat. We hypothesize that extreme  
122 hydrodynamic events, such as the exceptional flood in February 2021 and the TMZ shift,  
123 significantly affect the geochemical behaviour of Mn and Fe and deviate from traditional  
124 diagenetic steady-state models. These events are likely to shift redox conditions, altering the  
125 geochemical profiles of the metals and affecting their interaction at the sediment-water  
126 interface. The application of sequential extraction allows a detailed investigation of Mn and  
127 Fe speciation in the different sediment layers and provides insights into their dynamic  
128 behaviour during and after sediment deposition, which is influenced by extreme hydrological  
129 conditions. In addition, the integration of pore-water chemistry and radionuclide profiles, such  
130 as  $^{210}\text{Pb}$  and  $^7\text{Be}$ , provides a unique temporal resolution that captures short-term changes and  
131 the long-term effects of these events on the metal cycle in the land-sea continuum.

## 132 **2. Material and methods**

### 133 **2.1. Study site**

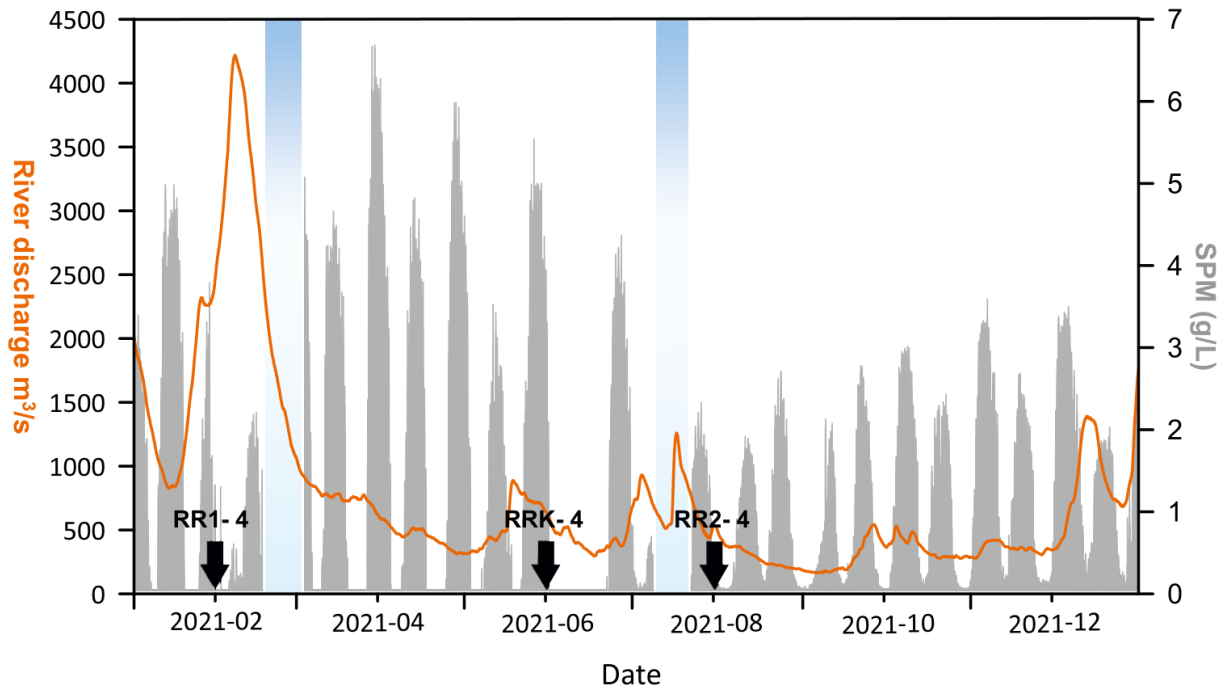
134 The Loire River is the longest river in France (1012 km), draining a watershed of ~  
135 118,000 km<sup>2</sup>, covering one-fifth of metropolitan France. The average annual flow of the Loire  
136 River is 900 m<sup>3</sup> s<sup>-1</sup>, fluctuating between periods of low water in summer and autumn (300 m<sup>3</sup>  
137 s<sup>-1</sup>) and high discharge in winter and spring (>1800 m<sup>3</sup> s<sup>-1</sup>) (Hydro B, 2021). The Loire  
138 estuary extends over 80 km, and covers an area of ~ 217 km<sup>2</sup> and a catchment area of 7470  
139 km<sup>2</sup> (Fig. 1; Ciffroy et al., 2003; OFB, 2017). The limits of the salinity ranges fluctuate daily,  
140 monthly and seasonally with hydrological conditions. Based on the average annual discharge  
141 and tidal conditions, five areas are defined from the estuary to Nantes (Fig.1; Gallene, 1974):  
142 1) the euhaline zone (salinity = 35–30) from the estuary to Saint-Nazaire, 2) the polyhaline  
143 zone (30–18) from Saint-Nazaire to Donges, 3) the mesohaline zone (18–5) from Donges to  
144 Cordemais, 4) the oligohaline zone (5–0.5) from Cordemais to Nantes and 5) the freshwater  
145 zone (< 0.5) upstream of Nantes. Being macrotidal (tidal range: 3 to 6 m), the estuary is  
146 characterised by turbidity maximum zone (TMZ) defined as the region where suspended  
147 particles matter (SPM) concentrations exceeds 500 mg L<sup>-1</sup> (Gallenne, 1974) and extending  
148 over 20 km (Migniot, 1993). During periods of low flow, typically in summer, the TMZ tends  
149 to shift farther upstream (Jalón-Rojas et al., 2016). This results locally in high SPM  
150 concentrations, often reaching several hundred milligrams per litre (Hulot et al., 2023).



151  
 152 **Fig1.** Map of the Loire estuarine zone with morphological subdivisions of the estuary, salinity domains under  
 153 annual averaged flow conditions (after Gallene, 1974) and the position of the turbidity maximum zone (dark orange)  
 154 and its extension (light orange) during each campaign (after GIP Loire, 2023). Red circles represent the sampling sites  
 155 (the muddy riverbed station at Paimboeuf and the Brillantes intertidal mudflat). Bathymetric maps are sourced from  
 156 DATA.SHOM (2024).

## 157 2.2. Sampling

158 The first site is located on the unvegetated part of the Brillantes intertidal mudflat (largest  
 159 mudflat of the Loire estuary; ~1350 ha) about 150 m from the shoreline (47°16'59.05"N;  
 160 2°3'47.63"W; Fig.1) and was sampled in March 2015 (PV1) when the water discharge was  
 161 about 950 m<sup>3</sup> s<sup>-1</sup>. The second one is located on the left subtidal bank of the inner Loire estuary  
 162 at Paimboeuf (47°17'12.2"N 1°59'46.2"W; depth range 5 to 10 m; Fig.1), 7 km upstream of  
 163 the Brillantes mudflat and was sampled three times during REBELRED cruises in 2021  
 164 (Metzger and Maillet, 2021): (1) in February (RR1-4) when the Loire experienced an  
 165 exceptional flood event with a peak discharge up to 4300 m<sup>3</sup> s<sup>-1</sup> that expelled the TMZ  
 166 beyond the western limit of the Fig.1 map as a plume, after intense rainfall episodes (Fig.2),  
 167 (2) in June (RRK-4) with a water discharge around 384 m<sup>3</sup> s<sup>-1</sup> and, (3) in August (RR2-4)  
 168 when the water discharge dropped to 231 m<sup>3</sup> s<sup>-1</sup> (Fig.2) and the TMZ was centred on the  
 169 sampling zone. During sampling at Paimboeuf station, bottom salinity varied from 0.1 in  
 170 February to 2.5 and 22.9 in June and August respectively.



171

172 **Fig 2. Daily averaged river discharge records at Montjean-sur-Loire gauging station and high frequency**  
 173 **records of suspended particulate matter (SPM) in surface waters at Paimboeuf in 2021. Data provided by Hydro**  
 174 **B(2021) and SYVEL, (2021). Black arrows indicate different REBELRED sampling campaigns. Blue rectangles**  
 175 **indicate periods when SPM data were not available.**  
 176

177 At the Brillantes mudflat, two long sediment cores (PV1a: 5.4 m; PV1b: 5.3 m) were  
 178 recovered using a percussion corer. The core PV1a was collected for sedimentological  
 179 analyses (grain-size, photography, x-ray imagery and sedimentary columns). To characterize  
 180 grain-size distribution of the different facies in the cores, samples were selected on the basis  
 181 of visual description of the sediment core and analysed using a Malvern™ laser  
 182 diffractometer Mastersizer 3000 laser diffractometer. Photographs were obtained using a  
 183 NIKON Reflex D5600 camera, lens 35/1.8G, mounted on a photo bench and X-ray imagery  
 184 was carried out using an X-ray imaging system SCOPIX2 at EPOC (Univ Bordeaux). PV1b  
 185 was collected to determine the chemical composition of both pore-water and particles. The  
 186 core was sliced in a N<sub>2</sub> purged glove bag into 2 cm slices every 5 cm for the first meter, and  
 187 every 10 cm deeper. At the same station, an interface core (PV1b.i: 0.35 m) was sampled by  
 188 hand using a PVC tube to obtain a well-preserved sediment surface and to avoid the possible  
 189 loss of surface sediment due to the percussion coring used to obtain the long core. The  
 190 sediment of this core was also sliced in a N<sub>2</sub> purged glove bag into 2 mm slices for the first 2  
 191 cm, 0.5 cm slices from 2 to 5 cm depth, 1 cm slices from 5 to 20 cm depth and 2 cm slices  
 192 every 5 cm deeper. A fraction of each sampled sediment slice was frozen for porosity and  
 193 radionuclides determinations and chemical extractions. The rest was centrifuged (15 min at



194 3500 rpm) and pore-water recovered and filtered through 0.2  $\mu\text{m}$  Minisart® RC25 cellulosic  
195 syringe filters and separated into different aliquots for analyses.

196 At the muddy riverbed station (Paimboeuf), in February, two interface cores were collected  
197 using a MC6 Octopus multicorer (RR1-4a.i: 0.4 m; RR1-4b.i: 0.5 m). RR1-4a.i was collected  
198 for sedimentological analyses. RR1-4b.i was dedicated to pore-water separation and related  
199 analyses. In June, 145 days later, two long sediment cores (RRK-4a: 1.2 m; RRK-4b: 1.8 m)  
200 were recovered using a Kullenberg corer. RRK-4a was collected for sedimentological  
201 analyses and RRK-4b was collected to determine the chemical composition of both pore-  
202 water and solid phase. At the same station, an interface core (RRK-4b.i: 0.35 m) was sampled  
203 using a Fantacore multicorer to obtain a well-preserved sediment surface and to avoid the  
204 possible loss of surface sediment due to the Kullenberg coring. In August, an interface core  
205 was collected, (RR2 -4b.i: 0.45 m) following the same treatment as for RR1. All cores  
206 collected during REBELRED cruises were processed using the same slicing and analysis  
207 protocol as in the Brillantes mudflat. To simplify the result descriptions, mission names will  
208 be used instead of individual core names.

### 209 **2.3. Porosity and $^{210}\text{Pb}$ and $^7\text{Be}$ profiles**

210 The frozen sediment aliquots were freeze-dried and the weight lost during freeze-drying,  
211 corrected for the sea salt content, was used to calculate sediment porosity.

212 Profiles of radionuclides of interest ( $^{210}\text{Pb}$ , and  $^7\text{Be}$ ) were established on all interface and  
213 long sediment cores from the riverbed station. For PV1,  $^7\text{Be}$  could not be investigated because  
214 activity measurements were done too long after sampling and  $^7\text{Be}$  was no longer detectable.  
215 Gamma emitter activities were measured on about 5 g of dry sediment using a Broad Energy  
216 Germanium detector BEGe<sup>TM</sup> (Dubosq et al., 2021). First, rapidly after the cruises due to the  
217 rapid decay of  $^7\text{Be}$  ( $T_{1/2} = 53$  days), the uppermost layers of the interface cores were measured  
218 downcore until negligible  $^7\text{Be}$  activities were reached. Several weeks later, sediment layers  
219 were measured to determine  $^{210}\text{Pb}$ . Excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}$ ) was calculated by subtracting the  
220 parent isotope  $^{226}\text{Ra}$  from the total  $^{210}\text{Pb}$  measured in the sediments. Different models could  
221 be used to estimate sediment age or accumulation rates (Sanchez-Cabeza and Ruiz-Fernández,  
222 2012). When sedimentation tend to be continuous, the CF:CS (constant flux and constant  
223 sedimentation) model is the simplest one to estimate sediment accumulation rates from the  
224 exponential decay of  $^{210}\text{Pb}_{\text{xs}}$  with depth. If sedimentation is more erratic and does not satisfy  
225 the CF:CS condition, an alternative is to use the CIC (constant initial concentration) model to  
226 calculate the age (t, in year) of the sediment layer according to (1):

$$t = \left(\frac{1}{\lambda}\right) \ln\left(\frac{A_0}{A_z}\right) \quad (1)$$

227 where  $A_0$  and  $A_z$  are the  $^{7}\text{Be}$  activities, respectively, at the sediment-water interface (SWI) and  
228 at the depth  $z$  respectively, and  $\lambda$  is the decay constant ( $0.0311 \text{ yr}^{-1}$ ) of  $^{210}\text{Pb}$ .

#### 229 **2.4. Pore-water analyses**

230 Pore-water was filtered and an aliquot for total dissolved manganese, iron, sulphur  
231 (interpreted as sulphate, after Metzger et al. (2007)), calcium and sodium was acidified with a  
232 single drop of ultrapure  $\text{HNO}_3$  for less than 5 mL of sample and then diluted 10-fold with a  
233 1%  $\text{HNO}_3$  solution for ICP-AES analysis using a Thermo Scientific iCAP 6300 spectrometer  
234 with a precision below 2 %. Sulphide was analysed in another interface core from the same  
235 multicorer during RR1-4 and RR2-4 cruises. Concentrations were always below the  
236 quantification limit ( $1 \mu\text{mol L}^{-1}$ , data not shown) using the blue methylene method for pore-  
237 waters (Metzger et al., 2007).

#### 238 **2.5. Sequential chemical extractions and analyses**

239 To determine Mn and Fe partitioning in the solid-phase of PV1, RR1-4 and RRK-4, 100  
240 mg of freeze-dried grounded sediment of each sample were subjected to a five-step sequential  
241 extraction procedure (Table 1). 10 mL of extractant was used in each step. Sediment was  
242 fractionated as followed: (1) ascorbic acid (pH 7.5) to extract poorly ordered Mn oxides and  
243 ferrihydrite (Anschutz et al., 2005; Kostka and Luther, 1994; Raiswell et al., 2010; Rennert et  
244 al., 2021); (2) 1 M HCl to dissolve Mn and Fe carbonates, reducible crystalline Fe oxides  
245 (Chester and Hughes, 1967; Lenstra et al., 2019), mackinawite and vivianite (Kubeneck et al.,  
246 2021); (3) citrate buffered dithionite to extract crystalline Mn and Fe oxides (W. K. Lenstra et  
247 al., 2021; Poulton and Canfield, 2005); (4) ammonium oxalate to dissolve recalcitrant Mn  
248 oxides and magnetite (Phillips and Lovley, 1987; Poulton and Canfield, 2005) and (5)  
249 concentrated  $\text{HNO}_3$  to extract pyrite ( $\text{FeS}/\text{FeS}_2$ ) and Mn bound to pyrite (Lord III, 1982; Claff  
250 et al., 2010). The samples were centrifugated and the supernatant was recovered and diluted  
251 with 1%  $\text{HNO}_3$ . Mn and Fe concentrations were analysed using ICP-AES 6300 Thermo-  
252 Fischer.

253 **Table 1. Sediment sequential extraction scheme for Mn and Fe and targeted mineral phases.**

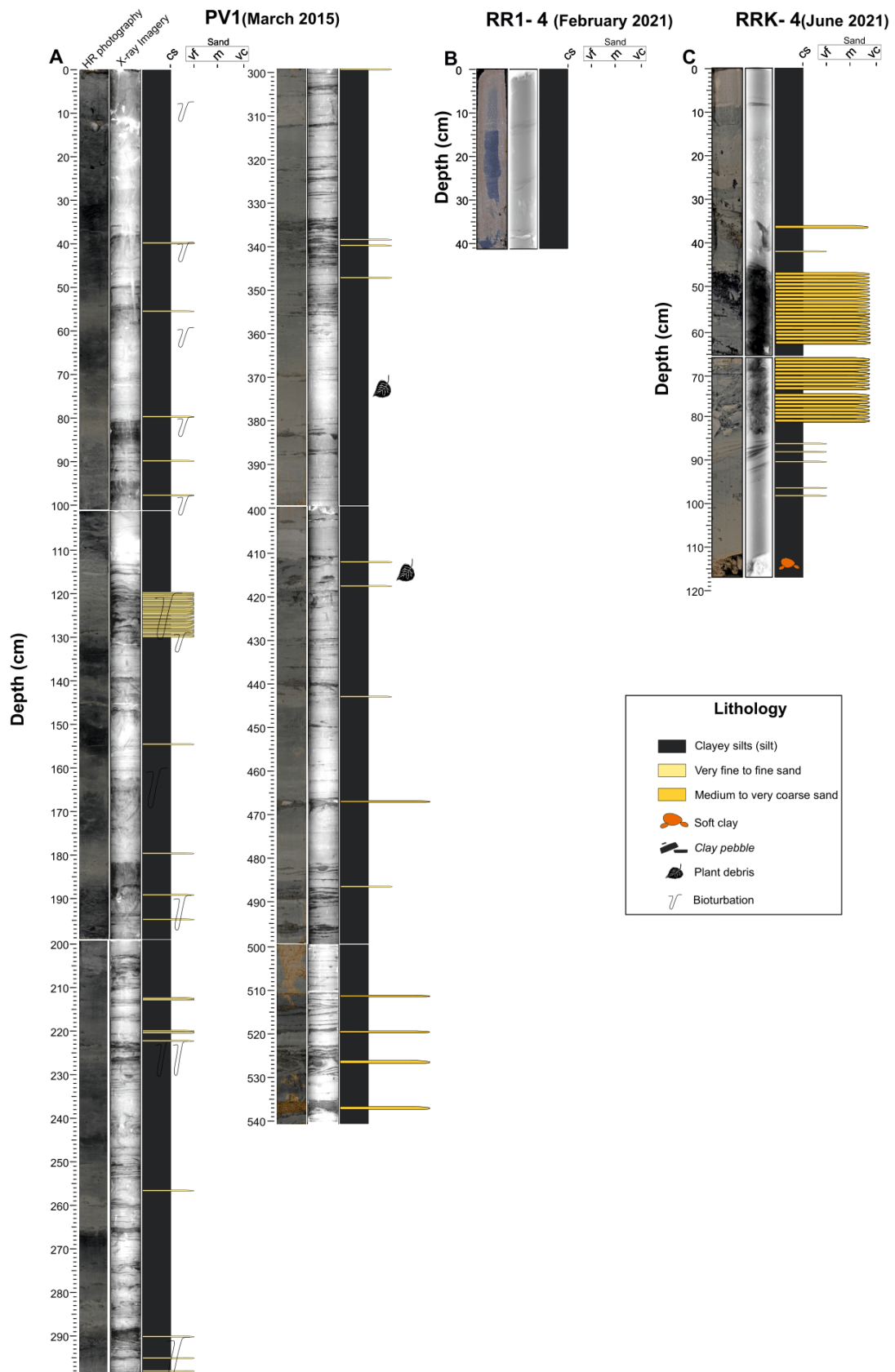
Step	Extractant	Time (hours)	Terminology	Target phases	References
1	0.17 M sodium citrate, 0.6 M sodium bicarbonate and 0.057 M ascorbic acid (pH 7.5)	24	Mn Asc Fe Asc	Poorly ordered Mn oxides Ferrihydrite	Kotska and Luther, 1994; Anschutz et al., 2005; Raiswell et al., 2010
2	1 M HCl	4	Mn HCl Fe HCl	Mn carbonates, Reducible crystalline Fe oxides, Fe carbonates, Mackinawite and Vivianite	Chester and Hughes, 1967; Lenstra et al., 2019; Kubeneck et al., 2021
3	50 g L <sup>-1</sup> sodium dithionite solution buffered to pH 4.8 with 0.35 M acetic acid/ 0.2 M sodium citrate	4	Mn CDB Fe CDB	Crystalline Mn oxides Crystalline Fe oxides	Poulton and Canfield, 2005; Lenstra et al., 2021
4	0.2 M ammonium oxalate/ 0.17 M oxalic acid (pH 3.2)	6	Mn Oxalate Fe Oxalate	Recalcitrant Mn oxides Magnetite	Phillips and Lovley, 1987; Poulton and Canfield, 2005
5	65% HNO <sub>3</sub>	2	Mn HNO <sub>3</sub> Fe HNO <sub>3</sub>	Mn bound to pyrite Pyrite	Lord III, 1982; Claff et al., 2010

254

### 255 3. Results

#### 256 3.1. Sediment characteristics

257 Core PV1, from the Brillantes mudflat, consisted primarily of silty clays with alternating  
 258 layers of very fine to fine sand showing evidence of bioturbation, that can be centimetric at  
 259 40, 55, 75, 95 cm depth for the first meter of the core, and decimetric at 120 cm depth  
 260 (Fig.3A). The lower part of the core (from 360 cm depth to the bottom) consisted mainly of  
 261 silty sands with sandy layers of few centimetres (470 and 550 cm depth) without any trace of  
 262 bioturbation. The cores from the riverbed station present well-consolidated silty clayey mud  
 263 in the top 30 cm depth (Fig.3, RR1-4b.i and RRK- 4b). Below, punctual layers of coarse sand  
 264 mixed with clay are observed in RRK-4 whose widths vary from 1 cm to 10 cm (Fig.3C). The  
 265 lower part of the core had a clayey-sandy aspect, characterised by the presence of well-  
 266 consolidated silt level with the presence of some layers of fine sand and soft clay pebbles  
 267 throughout the core at 117 cm depth.



268

269

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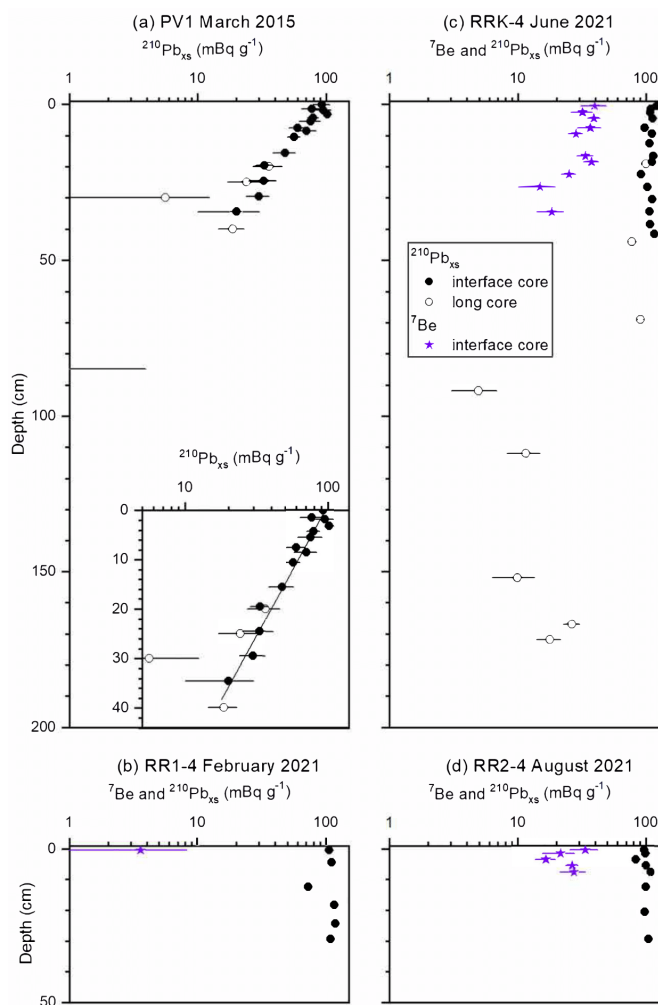
271

**Fig 3.** HD photographs, X-ray images and synthetic sedimentary columns of the 3 cores (PV1a, RR1-4a and RRK-4a) with their lithology. The light-coloured layers appearance observed on the X-ray images correspond to fine sediments, while the dark-coloured layers correspond to coarse sediments.

272 **3.2.  $^{210}\text{Pb}$  and  $^7\text{Be}$  activities**

273 For the Brillantes mudflat,  $^{210}\text{Pb}_{\text{xs}}$  profile showed a surface mixed layer of 3-4 cm, with  
 274 activity ranging around 90-100  $\text{mBq g}^{-1}$ , followed by an exponential decrease with depth.  
 275 Negligible excesses were reached deeper than 50 cm (Fig.4a).

276 For the muddy riverbed, the  $^{210}\text{Pb}_{\text{xs}}$  profiles were quite different. While surface activities  
 277 were also about 100  $\text{mBq g}^{-1}$ , there was no significant decrease with depth in the upper 40 cm.  
 278 In June 2021, there was still an excess of  $^{210}\text{Pb}$  at the bottom of the long core ( $18\pm 4 \text{ mBq g}^{-1}$   
 279 at 172 cm; Fig.4c). On the other hand,  $^7\text{Be}$  showed an important seasonal variability. In  
 280 February 2021, during the flood event,  $^7\text{Be}$  presented already negligible values in the upper  
 281 sediment (0-1 cm) (Fig.4b). In June,  $^7\text{Be}$  presented the highest activities in surface sediment  
 282 ( $40 \text{ mBq g}^{-1}$ ), followed by a gradual decrease to reach  $18 \text{ mBq g}^{-1}$  at 34.5 centimetres (Fig.4c).  
 283 In August, the surface  $^7\text{Be}$  activities were also high ( $35 \text{ mBq g}^{-1}$ ) but decreased more rapidly  
 284 with depth (Fig.4d).



285

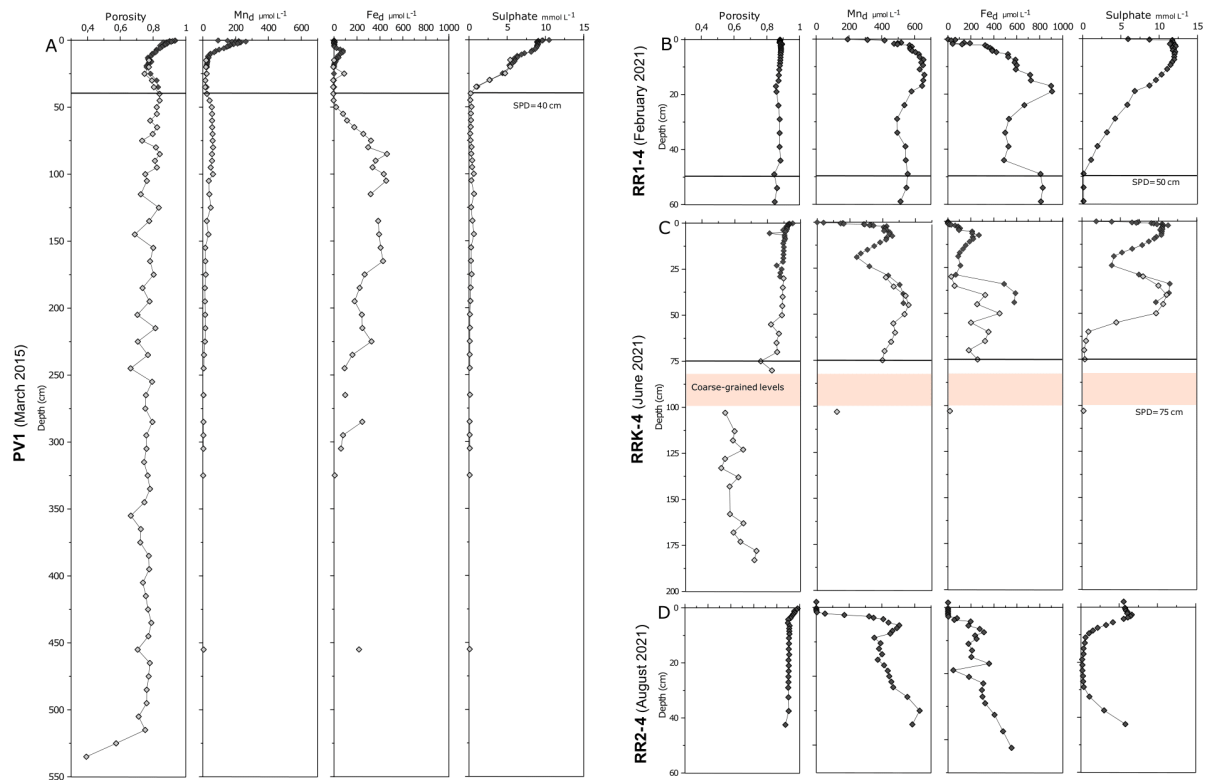
286 **Fig 4.  $^{210}\text{Pb}_{\text{xs}}$  and  $^7\text{Be}$  profiles with depth in sediments of PV1 at the intertidal mudflat (a) and at the muddy riverbed**  
 287 **during the cruises RR1 (b), RRK (c) and RR2 (d). Only interface cores were collected during RR1 and RR2 cruises.**  
 288 **The inset in the figure 4a shows the exponential curve that was used to estimate the sedimentation rate of core PV1.**

### 289 3.3. Porosity and pore-water profiles

290 Porosity on PV1 was 0.93 at the top core, gradually decreased to 0.78 at 25 cm depth  
291 (Fig.5A), increasing again to 0.82 at 50 cm depth, decreasing slightly with depth over 4 m,  
292 and decreasing rapidly from 5 m depth below 0.4. Off Paimboeuf, in February 2021 (RR1-4,  
293 Fig.5B), porosity at the top of the core was about 0.88 and remained constant throughout the  
294 profile. The long core collected in June at the same station (RRK-4) showed below 50 cm  
295 depth a decrease to 0.50 at 100 cm depth (Fig.5C). Porosity in August (RR2-4, Fig.5D) was  
296 around 0.98 at the surface, decreased to 0.90 in the first 5 cm, and then remained stable in the  
297 next 40 cm.

298 Vertical pore-water profiles of dissolved Mn ( $Mn_d$ ), dissolved Fe ( $Fe_d$ ), and sulphate  
299 showed significant variations throughout the cores from the intertidal mudflat (Fig.5A).  
300 Dissolved manganese presented a first intense and narrow maximum at 1 cm depth ( $[Mn]_{max} =$   
301  $262 \mu\text{mol L}^{-1}$  with FWHM = 5 cm) and a second light and smooth maximum between 40 to  
302 125 cm depth ( $[Mn]_{max} = 62 \mu\text{mol L}^{-1}$ ) superimposed to a background concentration of about  
303  $20 \mu\text{mol L}^{-1}$ . Sulphate decreased from  $10 \text{ mmol L}^{-1}$  at the top of the core to depletion at 40 cm  
304 depth, which was defined as the sulphate penetration depth (SPD). Dissolved iron was almost  
305 absent in the first 3 cm before increasing to reach  $78 \mu\text{mol L}^{-1}$  at 8 cm depth. Below this  
306 depth,  $Fe_d$  decreased to depletion at 25 cm depth. Below the SPD,  $Fe_d$  increased again and  
307 reached a maximum at 85 cm depth ( $461 \mu\text{mol L}^{-1}$ ), followed by a decrease with depth along  
308 the rest of the core. It should be noted that the absence of data at the bottom of the cores was  
309 generally related to the absence or negligible amounts of pore-water in the samples, especially  
310 in sandy or coarse-grained layers. In the riverbed mudpatch, during winter (RR1-4),  $Mn_d$  and  
311  $Fe_d$  presented much higher concentrations with more intense maximum ( $[Mn]_{max} = 660 \mu\text{mol}$   
312  $\text{L}^{-1}$  at 5 cm depth,  $[Fe]_{max} = 910 \mu\text{mol L}^{-1}$  at 20 cm depth) followed by a less pronounced  
313 decrease below ( $[Mn]_{min} = 500 \mu\text{mol L}^{-1}$ ,  $[Fe]_{min} = 400 \mu\text{mol L}^{-1}$ ). Sulphate concentrations at  
314 the surface sediment were about  $6 \mu\text{mol L}^{-1}$  and increased to  $12 \text{ mmol L}^{-1}$  at 9 cm depth and  
315 then decreased to disappear at 50 cm depth. In June (RRK-4),  $Mn_d$ ,  $Fe_d$  and sulphate profiles  
316 exhibited a specific pattern characterised by two peaks above the SPD at 8 cm depth and 44  
317 cm depth. Maximum concentrations were higher in the deeper peak for redox metals while  
318 they presented similar concentrations of sulphate:  $[Mn]_{max} = 460$  and  $530 \mu\text{mol L}^{-1}$ ,  $[Fe]_{max} =$   
319  $270 \mu\text{mol L}^{-1}$  and  $580 \mu\text{mol L}^{-1}$ ,  $[S]_{max} = 10$  and  $9.6 \text{ mmol L}^{-1}$  for shallower and deeper peaks  
320 respectively. In August (RR2-4), dissolved element profiles showed the absence of  $Mn_d$  and  
321  $Fe_d$  in the upper part of the core down to 2 cm depth (Fig.5D), followed by an increase to  
322 concentrations of  $506 \mu\text{mol L}^{-1}$  for  $Mn_d$  and  $313 \mu\text{mol L}^{-1}$  for  $Fe_d$  at 6.5 and 7.5 cm depth

323 respectively. Below this depth,  $Mn_d$  decreased to a concentration of  $374 \mu\text{mol L}^{-1}$  at 19 cm  
 324 depth and then increased to a maximum concentration of  $586 \mu\text{mol L}^{-1}$  at 42.5 cm depth.  $Fe_d$   
 325 decreased sharply at 19 cm depth to attain a concentration of  $46 \mu\text{mol L}^{-1}$  before reaching the  
 326 maximum of  $554 \mu\text{mol L}^{-1}$  at 42.5 cm depth. The SPD was not reached. Sulphate  
 327 concentration decreased in the first 19 cm depth from  $6.4 \text{ mmol L}^{-1}$  to reach a minimum  
 328 concentration of  $0.16 \text{ mmol L}^{-1}$  before increasing back to  $5.8 \text{ mmol L}^{-1}$  at 42.5 cm depth.



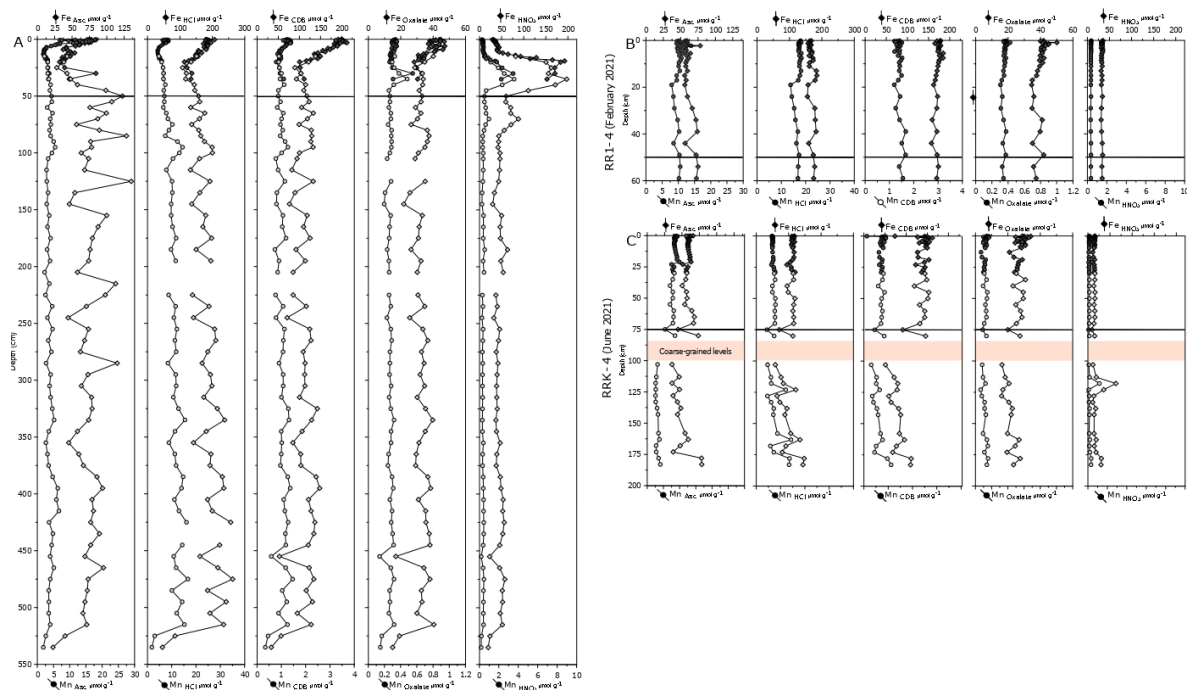
329  
 330 **Fig 5. Porosity and pore-water profiles of dissolved Mn ( $Mn_d$ ), dissolved Fe ( $Fe_d$ ), and dissolved S (sulphate)**  
 331 **concentrations with depth in PV1, RR1-4, RRK-4 and RR2-4. Horizontal black lines indicate the sulphate**  
 332 **penetration depth (SPD), dark symbols representing interface cores (PV1b.i, RR1-4b.i, RRK-4b.i and RR2-4b.i) and clear symbols**  
 333 **representing long cores (PV1b, RR1-4b, RRK-4b and RR2-4b) . The depth scale is different for each graphic.**

### 334 3.4. Mn and Fe sequential extraction from the solid phase

335 Figure 6 illustrates the distribution of Mn and Fe phases for PV1, RR1-4 and RRK-4  
 336 according to the sequential extraction procedure. In the Brillantes mudflat (PV1; Fig.6A),  
 337 most of the Mn and Fe phases showed a surface enrichment, except for oxalate-extracted Mn  
 338 and  $\text{HNO}_3$ -extracted Mn and Fe. The highest concentration was observed for CDB-extracted  
 339 Fe with  $212 \mu\text{mol g}^{-1}$  at 3 cm depth. Ascorbate- and HCl-extracted Mn and Fe concentrations  
 340 were  $16.6 \mu\text{mol g}^{-1}$  and  $77 \mu\text{mol g}^{-1}$ ,  $8.7 \mu\text{mol g}^{-1}$  and  $196 \mu\text{mol g}^{-1}$ , respectively at the top of  
 341 the core. CDB-extracted Mn also showed surface enrichment, albeit at lower concentrations  
 342 ( $1.1 \mu\text{mol g}^{-1}$ ). The extractable Mn enrichment zone was limited to the first 8 cm, while the  
 343 extractable Fe enrichment zone extends to a depth of 20 cm. It should be noted that near the

344 surface, Fe was extracted in higher concentrations by HCl and CDB, and Mn by ascorbate and  
345 HCl. The HNO<sub>3</sub>-extracted Mn and Fe presented a specific pattern with a peak between 20 and  
346 30 cm depth at concentrations reaching 3.5 μmol g<sup>-1</sup> and 193 μmol g<sup>-1</sup> respectively. Below  
347 this depth, HNO<sub>3</sub>-extracted Mn and Fe decreased sharply to a depth of 45 cm, reaching  
348 relatively stable concentrations of 0.4 μmol g<sup>-1</sup> and 40 μmol g<sup>-1</sup>, respectively, down to the  
349 core while HCl-extracted Fe and Mn exhibited an increase with increasing depth. At the  
350 muddy riverbed, RR1-4 showed low variations of all Mn and Fe phases with depth showing  
351 similar trends for Mn and Fe (Fig.6B). CDB-extracted Fe presented higher concentrations at  
352 around 180 μmol g<sup>-1</sup> compared to ascorbate- and HCl-extracted Fe with around 60 μmol g<sup>-1</sup>  
353 and 170 μmol g<sup>-1</sup> respectively, while for Mn, the highest concentrations were observed for  
354 HCl-extracted Mn with around 18 μmol g<sup>-1</sup> compared to ascorbate- and CDB-extracted Mn  
355 with 11 μmol g<sup>-1</sup> and 1.5 μmol g<sup>-1</sup> respectively. For the other phases, concentrations remained  
356 consistently low throughout the core. HNO<sub>3</sub>-extracted Mn and Fe were around 0.35 μmol g<sup>-1</sup>  
357 and 34 μmol g<sup>-1</sup> respectively, and for oxalate-extracted Mn and Fe, concentrations were  
358 around 0.37 μmol g<sup>-1</sup> and 41 μmol g<sup>-1</sup> respectively. In June, at the same station, RRK-4  
359 showed a clear gradient between levels, above and below the coarser-grained layers (Fig.6C).  
360 Above the coarser-grained layers, concentrations of Mn and Fe phases showed relatively  
361 consistent variations with depth. In particular, HNO<sub>3</sub>-extracted Mn and Fe remained stable  
362 regardless of depth, while concentrations of other phases increased at 80 cm depth. Below the  
363 coarser-grained layers, ascorbate-HCl- CDB- and oxalate-extracted Mn and Fe showed an  
364 increasing trend with depth, reaching their highest concentrations at 183 cm depth. For  
365 HNO<sub>3</sub>-extracted Mn and Fe, the highest concentrations were reached at a depth of 125 cm.





366

367 **Fig 6. Solid phase depth profiles of different forms of Mn and Fe in PV1, RR1-4 and RRK-4 as determined with the**  
 368 **sequential extraction procedure showing poorly ordered Mn oxides and ferrihydrite (Mn Asc and Fe Asc), Mn and Fe**  
 369 **carbonates, reducible crystalline Fe oxides, mackinawite and vivianite (Mn HCl and Fe HCl), Mn and Fe crystalline**  
 370 **oxides (Mn CDB and Fe CDB), Mn recalcitrant oxides and magnetite (Mn oxalate and Fe oxalate), and Mn bound to**  
 371 **pyrite (Mn HNO<sub>3</sub> and Fe HNO<sub>3</sub>). Circles represent Mn and squares represent Fe. Dark symbols represent interface**  
 372 **cores (PV1b.i, RR1-4b.i, RRK-4b.i and RR2-4b.i), while clear symbols represent long cores (PV1b, RR1-4b, RRK-4b**  
 373 **and RR2-4b). Depth scale is different for each graphic.**  
 374

## 375 4. Discussion

### 376 4.1. Temporal context and sedimentary dynamics

377 Sediment dynamics in estuaries play a critical role in shaping these coastal ecosystems. A  
 378 number of processes take place in these environments, including remobilization of previously  
 379 deposited sediments and temporary interruptions in deposition (e.g. Deflandre et al., 2002).  
 380 PV1 core is composed mainly of silty clays, indicating a relatively calm environment. The  
 381 application of the CF:CS model to PV1 <sup>210</sup>Pb<sub>xs</sub> profile had permitted to estimate a mean  
 382 sedimentation rate of 0.7 cm yr<sup>-1</sup> for the top 40 centimetres of the record.

383 At the riverbed, in February 2021 (RR1-4), the high cohesivity, the dark colour and the  
 384 relatively low and constant porosity of the interface core sediment suggest a stable and well-  
 385 consolidated composition primarily consisting of silty clayey mud (Fig.3B, 5B). The  
 386 negligible <sup>7</sup>Be in surface sediments tends to indicate the absence of recent sediment  
 387 deposition (Fig.4B). In June (RRK-4), we observed various sediment types and structures at  
 388 different depths (Fig.3C) indicating variable depositional conditions. In particular, the  
 389 presence of a distinct coarse to very coarse sand layer in the middle of the core (from 45 to 85  
 390 cm depth) strongly suggests that the environment experienced a period of higher energy and

391 more dynamic conditions, probably related to an unusually high river discharge or a marine  
392 storm (Edmiston et al., 2008).

393 After the February exceptional flood (Fig.2), the water discharge decreased from 4300 to  
394  $384 \text{ m}^3 \text{ s}^{-1}$  in June, which led to favourable conditions for a shift of the TMZ upstream.  
395 Accordingly, the rather constant activities of  $^{210}\text{Pb}_{\text{xs}}$  in the top 70 cm support a single and  
396 recent (< 5 years) deposition event (Fig.4c). The  $^7\text{Be}$  signal allows more precise investigation  
397 with the top 20 cm being less than 1 month old while the sediments at 34 cm are estimated to  
398 be about 62 days by applying the CIC model to  $^7\text{Be}$ . These elements offer valuable insights  
399 into the timing and dynamics of recent deposition events in the muddy riverbed, which  
400 experiences episodes of resuspension/sedimentation of variable intensity depending on fluvial  
401 discharge and the position of the TMZ. This hydrodynamical context prevents the regular  
402 accumulation of fine sediment in the estuarine bed, unlike the nearby intertidal mudflat, and  
403 creates non-steady state conditions.

#### 404 **4.2. Mn and Fe cycling in the Brillantes mudflat**

405 In the upper 10 cm of PV1,  $\text{Mn}_d$  and  $\text{Fe}_d$  are successively released towards pore-water  
406 (Fig.5A). The increase in  $\text{Mn}_d$  with ascorbate-extracted Mn decrease in the first centimetre  
407 can be attributed to reductive dissolution of reactive Mn oxides. The same process can be seen  
408 for Fe a few centimetres below, as  $\text{Fe}_d$  gradually increases from 3 cm depth, indicating a  
409 transition of the dominant oxidant from Mn oxides to Fe oxides (ascorbate-extracted Fe).  
410 According to Thibault de Chanvalon et al. (2016), the well-established and separated peaks of  
411 Mn and Fe suggest that the transitional phase of diagenetic processes after flood deposition is  
412 already in a fairly stable condition. Furthermore, the surface concentration of ascorbate-  
413 extracted metals corresponded to Loire suspended particles composition (Thibault de  
414 Chanvalon et al., 2016b) indicating negligible metal diagenetic enrichment contrasting with  
415 frequent observation in continental margins systems (Anschutz et al., 1998; Mouret et al.,  
416 2009). Once reductively dissolved, Fe and Mn can either leave the sediment or reprecipitate  
417 generally as carbonates, sulphides or phosphates (Aller, 2014).

418 Sulphate concentrations in PV1 showed a complete depletion at 40 cm depth (Fig.5A),  
419 suggesting that sulphate is consumed as the dominant oxidant between 10 cm and 40 cm  
420 depth for metabolic processes and/or as an anaerobic oxidant of methane (not measured in this  
421 study but likely produced by methanogenesis after the total depletion of sulphate (Burdige,  
422 2006)). This layer corresponds to a depletion of  $\text{Fe}_d$  (Fig.5A) and the maximum of  $\text{HNO}_3$ -  
423 extracted Fe and associated Mn (Fig.6A), suggesting that Fe sulfides formation is important at

424 this depth. The formation of iron sulphides in sediments is a complex process influenced by  
425 several factors, such as the amount and reactivity of organic matter, reactive iron minerals  
426 deposited in the sediment, and the availability of dissolved sulphate (Berner, 1984). The  
427 residence time of particles in sediments can also affect FeS/FeS<sub>2</sub> formation. Pyrite formation  
428 may occur where the deposition rate is very high (Berner, 1984) as it is observed in the  
429 Brillantes mudflat.

430 Below 40 cm depth, the HNO<sub>3</sub>-extracted Mn and Fe decrease (Fig.6A) would indicate  
431 that iron sulphides production stops limiting their burial in the sediment archives. The lack of  
432 FeS/FeS<sub>2</sub> formation is well explained by the absence of sulphate at that depth which prevents  
433 sulphide formation (Fig.5A). However, it is difficult to explain the absence of FeS/FeS<sub>2</sub> burial  
434 while this mineral is commonly observed in geological records and is known to be stable in  
435 anoxic conditions (Berner, 1980; Rickard and Luther, 2007). The distinct enrichment in  
436 Fe<sub>HNO3</sub> between 10 and 40 cm depth could therefore indicate non-steady state conditions due  
437 to increased inputs of organic matter induced by human activities, as previously observed in  
438 other environments with similar FeS/FeS<sub>2</sub> records (e.g. Egger et al., 2015; Slomp et al., 2013).  
439 Between 40 and 50 cm depth, the decrease of Fe<sub>HNO3</sub> occurs simultaneously to an increase of  
440 Fe<sub>ASC</sub> (Fig.6A). Ferrihydrite formation is unlikely due to the lack of oxidant at these depths  
441 but other minerals such as vivianite or illite-bound metals (W. K. Lenstra et al., 2021; Rennert  
442 et al., 2021) can be extracted with the ascorbate reagent. Several studies showed the possible  
443 formation of vivianite below the sulphate/methane transition zone (e.g. Egger et al., 2015;  
444 Kubeneck et al., 2021; Rothe et al., 2015). Deeper, between 50 cm to 300 cm depth, a  
445 progressive increase in HCl-extractable Mn and Fe coincide with the highest Fe<sub>d</sub> measured in  
446 this core and an increase in Mn<sub>d</sub>, reinforcing the impression of a slow formation of Mn and Fe  
447 carbonates as end member of the early diagenesis transformation. The high dissolved metal  
448 concentrations in the pore- water could be explained by several processes (Slomp et al.,  
449 2013). A first mechanism is the reduction of Fe and Mn oxides coupled to organic matter  
450 degradation. Although these pathways are energetically more favourable than sulphate  
451 reduction, studies that focused on Fe suggested that kinetic control may limit the rate and  
452 extent of Fe oxide reduction (Postma, 1967; Sivan et al., 2011). This kinetic limitation would  
453 favour the persistence of un sulphidized Fe oxides (März et al., 2008; Xiong et al., 2019)  
454 allowing their reduction below the SPD. Another possible mechanism is the oxidation of  
455 methane with Mn and Fe oxides (Beal et al., 2009; Cai et al., 2018; Leu et al., 2020). Finally,  
456 Ma et al., (2023) demonstrated recently that the dissolution of mackinawite (FeS) releases HS<sup>-</sup>  
457 , which can be removed by transport or oxidation, and Fe<sub>d</sub>, which can react with phosphate to

458 precipitate vivianite. The increase of  $Fe_d$  below 50 cm depth occurs simultaneously with an  
459 almost equimolar increase of sulphate (Fig.5A), which could be induced by the dissolution of  
460 this metastable intermediate in the pyrite formation process. There is no extractive step  
461 presenting a symmetric decrease to the presence of dissolved iron and manganese  
462 accumulation in the pore-water below 50 cm depth. Contrastingly, CDB- and oxalate-  
463 extractable Mn and Fe represent a constant fraction, indicating the burial of less reactive/non-  
464 reactive forms in the sediment (Lenstra et al., 2019; W. K. Lenstra et al., 2021).

465 The observed diagenetic sequence of Mn and Fe in the Brillantes mudflat can be  
466 summarized as the following sequence: (1) deposition of reactive riverine Fe and Mn oxides,  
467 then (2) reduction of metal oxides by bacterial respiration or by sulphide from depth, (3)  
468 precipitation of sulphide mineral such as mackinawite or pyrite, then (4) transition from  
469  $FeS/FeS_2$  formation to vivianite formation and pore-water enrichment, finally (5) precipitation  
470 at depth of Mn and Fe carbonate depleting  $Mn_d$  and  $Fe_d$  from the pore-water. This sequence  
471 highlights the complex interplay between sedimentary processes evolving geochemical  
472 conditions in the different layers of the Brillantes mudflat. Up to stage 3, the present study is  
473 in agreement with the processes highlighted in the upper St-Lawrence estuary (Lefort et al.,  
474 2012; Oldham et al., 2019). However, both studies are based on 20 and 50 cm-deep cores and  
475 missed ultimate burial processes that highlight the importance of phosphates and carbonates  
476 to authigenic formation (stages 4 and 5). Another difference is the significative burial of Mn  
477 as carbonates in the Loire. Oldham et al., (2019) attributed the limited Mn burial to the  
478 important amount of Mn(III)-organic ligands complexes in pore-water favouring mobility  
479 during early diagenesis. In the Vörå creek estuary, located in the Finnish Baltic Sea, the study  
480 of Fe solid speciation from a long core (4.5m) showed another feature. Fe oxides were fairly  
481 stable along the sedimentary series (stage 1; Yu et al., 2015). The authors attributed this  
482 feature to the lack of sulphate that limits the formation of sulphur compounds despite a high  
483 sedimentary rate and an important organic carbon content. This is probably representative of  
484 the Bothnian Gulf estuaries as Widerlund and Ingri, (1996) showed the same efficiency of Mn  
485 and Fe oxides burial in the Kalix estuary.

#### 486 **4.3. Early diagenesis in the estuarine bed subjected to hydrodynamic events**

487 In February 2021, the remarkable flood of the Loire resulted in significant erosion of  
488 surface sediments in the upper estuary, including the muddy riverbed at Paimboeuf, revealing  
489 to the water column a very dark and cohesive sediment with some gas ebullition (Hulot et al.,  
490 2023). The geochemical signature of the surface sediments sampled after the erosion (RR1-4)

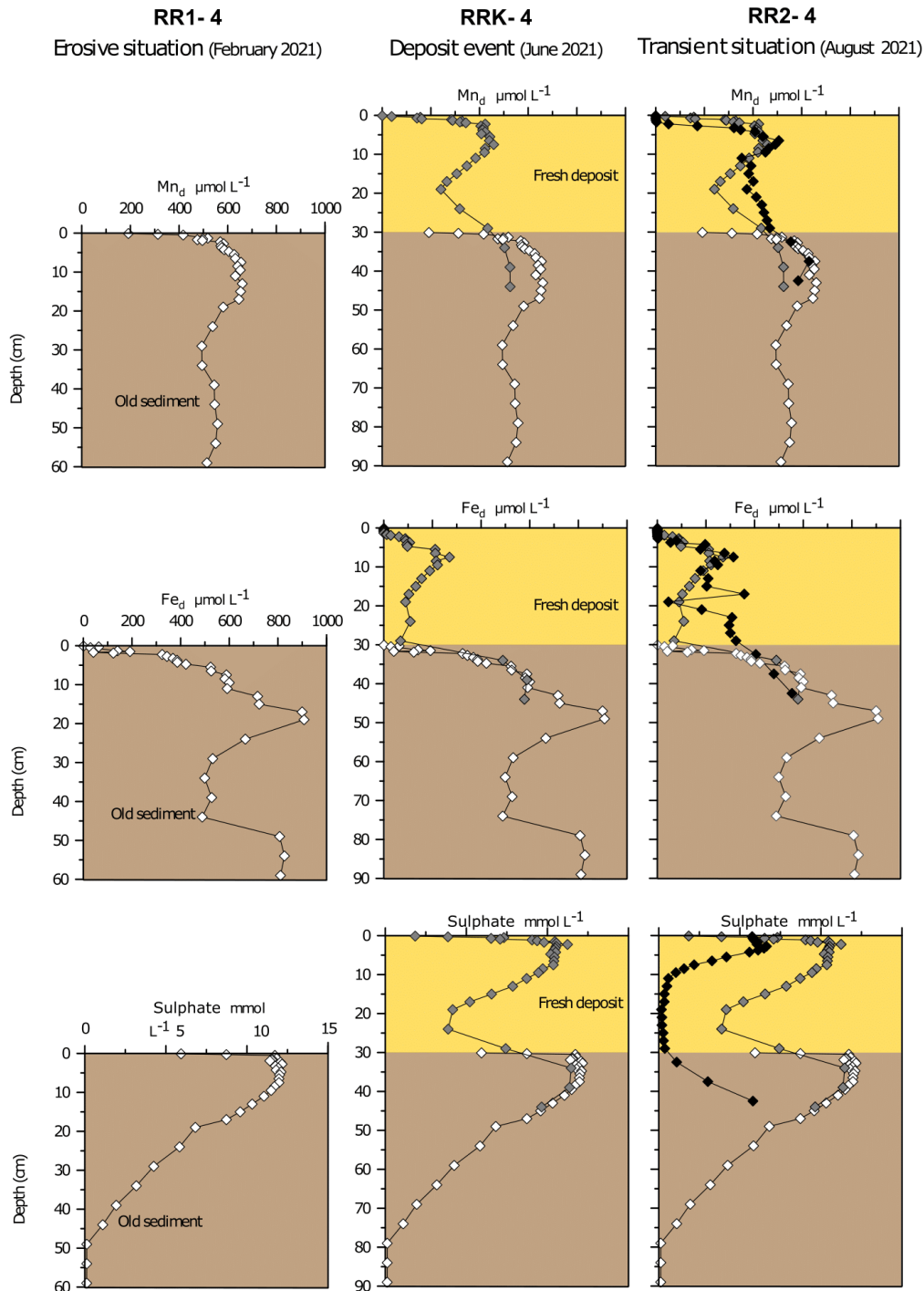
491 was characterised by relatively high and constant concentrations of different extracted Mn and  
492 Fe phases compared to PV1 (Fig.6B). Sharp pore-water gradients for  $Mn_d$ ,  $Fe_d$  and sulphate at  
493 the SWI indicated the sudden exposure of the old  $^7Be$ -free and anoxic sediment (Fig.4b) to  
494 low salinity, well oxygenated waters. In the surface sediment,  $Mn_d$  and  $Fe_d$  were high with no  
495 enrichment of ascorbate-extracted Mn and Fe. The same geochemical signatures were  
496 documented 24 km upstream (RR1-2) during the same sampling cruise (Hulot et al., 2023).  
497 This erosion phenomenon at the muddy riverbed had a significant impact on iron sulphides  
498 formation in the sediment. Despite sulphate reduction (attested by the decrease of S/Na in  
499 pore-water, see Supplementary Fig.S1), no Mn and Fe peaks were observed in the  $HNO_3$   
500 extracted fraction in this core (Fig.6B). This is probably related to the adjustment of the  
501 sulphate-methane transition zone following the intense erosional forces triggered by this  
502 extraordinary flood event. This erosion process disturbed the otherwise stable sedimentary  
503 layers, interrupted chemical reactions that occur in a steady-state context, and shifted redox  
504 conditions (changes in the availability of oxygen and other electron acceptors) within the  
505 sediment which explains the relatively constant concentrations of Mn and Fe  
506 particulate/mineral phases, especially  $HNO_3$ -extracted Mn and Fe.

507 In June 2021, about four months later, the decreased low river discharge recorded during  
508 the sampling cruise (about  $384 \text{ m}^3 \text{ s}^{-1}$ ) resulted in favourable conditions for an upstream shift  
509 of the TMZ above the studied area of the river (Fig.1; Fig.2). The rather constant  $^{210}Pb_{xs}$   
510 activities in the interface core (RRK-4b.i) and the  $^7Be$  penetration up to 30 cm indicated either  
511 active bioturbation or recent and high sediment deposition (Fig.4c), the latter being more  
512 likely according to X-ray images from the topmost layer of the Kullenberg core (RRK-4a)  
513 that showed a very fine and homogenous deposit (Fig.3), and to the double peak observed in  
514 pore-water profiles. This phenomenon is consistent with documented cases of deposition of  
515 TMZ-derived particles in macrotidal estuaries (Grabemann et al., 1997; Migniot, 1972;  
516 Woodruff et al., 2001). Based on these observations (Fig.4 and 7), it is likely that this  
517 sediment deposition occurred between March and June 2021 and its thickness can be  
518 estimated at around 30 cm. This deposit was characterised by  $Mn_d$  and  $Fe_d$  peaks associated  
519 with a zone of intense, localized production, separated from another production zone observed  
520 at 30 cm depth (Fig.7). It is likely that these deeper peaks of  $Mn_d$  and  $Fe_d$  are the legacy of the  
521 remobilization layer below the previous SWI and corresponded to the production observed in  
522 February 2021 (Fig.7). Mn and Fe oxides (ascorbate-extracted Mn and Fe) remained high and  
523 constant at the new SWI and below (Fig.6C). Several studies have already highlighted the  
524 significant effects of turbidity deposition on benthic communities and diagenetic processes in

525 the sediment (Mucci and Edenborn, 1992). Typically, after the deposition event, oxygen  
526 quickly re-establishes in the uppermost part of the freshly deposited layer, allowing Mn and  
527 Fe oxides to accumulate by oxidation of  $Mn_d$  and then  $Fe_d$  diffusing from the underlying  
528 layers (Anschutz et al., 2002; Deflandre et al., 2002; Guilhermic, 2023). The absence of  
529 significant variation of Mn and Fe oxides within the first centimetres of RRK-4 sediment  
530 (Fig.6C) suggests that the fresh deposit rich in metal oxides started to be consumed recently.  
531 In the same core (RRK-4), below the coarse layers, there is a marked decrease in the  
532 occurrence of Mn and Fe phases. A low peak in  $HNO_3$ -extracted Mn and Fe at 125 cm depth  
533 could correspond to the formation of iron sulphides. The fact that  $FeS/FeS_2$  can be present at  
534 this depth indicates that the specific conditions for  $FeS/FeS_2$  formation were met at some time  
535 in the history of the sediment suggesting calmer hydrodynamic conditions over a period that  
536 can hardly be dated.

537 In August (RR2-4), about 6 months after the flood,  $Mn_d$ ,  $Fe_d$  and sulphate double peaks  
538 observed in June were much less marked for Mn and especially for Fe while sulphate showed  
539 a downward shift of its second peak, the first remaining at the SWI despite a concentration  
540 decrease. These observations strongly indicate that both  $Mn_d$  and  $Fe_d$  that were located more  
541 than 30 centimetres below the surface (i.e., the RRK-4 second peak) were likely able to  
542 undergo precipitation, potentially forming carbonates or sulphides as shown in the muddy  
543 sediments of the Bay of Biscay (Hyacinthe et al., 2001). In the new SWI, the decrease of  $Mn_d$   
544 and  $Fe_d$  within the first 2 and 3 centimetres respectively (Fig.5D) strongly suggests their  
545 precipitation into Mn and Fe oxides that would generate an enriched metal-oxide layer as  
546 observed from ascorbate extracted Mn and Fe. The attenuation of  $Mn_d$ ,  $Fe_d$  and sulphate  
547 double peaks observed between June and August is indicative of redox fronts undergoing  
548 relaxation within this recently deposited layer (Guilhermic, 2023). The time required for the  
549 recovery process, known as the relaxation time, is influenced by several factors, including  
550 sediment porosity, the grain size, organic matter content and thickness of the deposit (Nmor  
551 et al., 2022). It is important to note that different species have different recovery rates in pore-  
552 water. For example, oxygen can recover within a few days (Cathalot et al., 2010) while  
553 sulphate takes around four months to recover (Nmor et al., 2022). In addition, Chaillou et al.  
554 (2007) indicate that it can take about several months for both Mn and Fe to fully recover after  
555 turbidite deposition or even years in Canadian fjords (Deflandre et al., 2002). Our results of  
556 August show that the recovery of  $Mn_d$ ,  $Fe_d$  and sulphate steady-state levels is not yet  
557 complete. These transient conditions illustrate the dynamic nature of estuarine environments,  
558 where complex interactions between physical, chemical and biological factors constantly

559 shape the geochemical profiles of Mn and Fe and influence their availability, speciation and  
 560 cycling within the sediment matrix, resulting in a lack of thermodynamic equilibrium between  
 561 the dissolved and solid phases with, for example, the absence of FeS/FeS<sub>2</sub> accumulation  
 562 within the sediment in the estuarine bed.



563

564 **Fig 7. Pore-water profiles of dissolved Mn ( $Mn_d$ ), dissolved Fe ( $Fe_d$ ), and sulphate concentrations with depth,**  
 565 **temporally contextualized after a hydrosedimentary interpretation based on radioelements at the muddy riverbed**  
 566 **(Paimboeuf) in winter, spring, and summer 2021. White squares show February data, dark grey squares show June**  
 567 **data, and black squares show August data.**

568 **5. Conclusion**

569 The present study sheds light on the dynamic interplay of Mn and Fe in early diagenetic  
570 processes of burial and recycling in the Loire mid-estuary, in two different hydrodynamic  
571 contexts regarding deposition/resuspension, a muddy riverbed near the navigation channel  
572 and the major intertidal mudflat nearby. The 5m-long cores sampled at the Brillantes intertidal  
573 mudflat showed a sequence of authigenic mineral formation with a transition within the first  
574 metre from an expected FeS/FeS<sub>2</sub> formation layer and a layer of another authigenic phase  
575 which could be vivianite, probably because of a past higher organic matter production in the  
576 estuary under the influence of human activities. Finally, the slow formation of Mn and Fe  
577 carbonates constitutes an end member of the early diagenesis transformation. This intricate  
578 interplay between dissolution, precipitation and redox transformations underlines the complex  
579 relationship between sedimentary processes and the several pathways for the recycling and  
580 ultimate burial of Mn and Fe at different depths of the Brillantes mudflat that alters the  
581 sedimentary archive.

582 Within the river, the February flood event had a significant impact on the sediment,  
583 causing erosion and subsequent changes in the geochemical signature. The intense erosional  
584 forces ruptured stable sediment layers and prevented effective conversion of dissolved  
585 constituents to solid phases. This resulted in low and constant concentrations of Mn and Fe  
586 solid phases, especially ascorbate and HNO<sub>3</sub>-extracted Mn and Fe (amorphous oxides and  
587 pyrite or pyrite-bound Mn, respectively). The subsequent lowering of the river discharge  
588 allowed the formation of a 30 cm-thick deposit layer four months later, in June. The new  
589 deposit generated a second metal remobilisation zone 30 cm above the previous one still  
590 visible despite the distance from the new SWI. Progressively this peculiar feature evolved  
591 towards a more classic redox zonation. The high sedimentary dynamics in this riverbed  
592 generated transient conditions illustrating the dynamic nature of estuarine environments,  
593 where complex interactions between physical, chemical and biological factors influence the  
594 availability, speciation and cycling of Mn and Fe within the sediment matrix. This transient  
595 state leads to a lack of thermodynamic equilibrium between dissolved and solid phases with,  
596 for example, no FeS/FeS<sub>2</sub> accumulation within the sediment of the estuarine bed.

597 The well-established burial diagenetic sequence observed in the Loire estuarine mudflats  
598 differs from the observation made in the St-Lawrence and estuaries from the Bothnian Gulf.  
599 The St-Lawrence is characterized by little burial of Mn and important burial of Fe sulphides  
600 while the Bothnian Gulf estuaries show little transformation of trapped particles with efficient  
601 burial of reactive oxides. The Loire estuary mudflats show that these metals are buried as



602 carbonates and phosphates following a more complex sequential transformation and could  
603 represent another burial pathway typical for temperate macrotidal estuaries which catchment  
604 provides detrital reactive oxides and carbonates.

605 Investigating the behaviour of Mn and Fe in sediments holds considerable potential for  
606 improving the quality of estuarine systems. Our research in this area provide valuable insights  
607 into disruption of sedimentation patterns and subsequent rebalancing in these dynamic  
608 environments. These studies are particularly important for estuarine systems, which are  
609 characterised by complicated interactions between solid and dissolved phases. Understanding  
610 the non-equilibrium dynamics of these systems is critical as they deviate from traditional  
611 steady-state conditions and require a nuanced understanding especially when interpreting  
612 sedimentary historical records. Recognizing that sediment is both a source and a sink for  
613 essential nutrients such as Mn and Fe and their recycling by-products is critical for developing  
614 comprehensive strategies to improve the overall water quality of estuarine ecosystems.

615

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633

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