

1 **Reoxidation of estuarine sediments during simulated resuspension events: Effects**  
2 **on nutrient and trace metal mobilisation**

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12 ***Abstract***

13 Estuarine environments are considered to be nutrient buffer systems as they regulate the  
14 delivery of nutrients from rivers to the ocean. In the Humber Estuary (UK) seawater and  
15 freshwater mixing during tidal cycles leads to the mobilisation of oxic surface  
16 sediments (0-1 cm). However, less frequent seasonal events can also mobilise anoxic  
17 subsurface (5-10 cm) sediments, which may have further implications for the estuarine  
18 geochemistry. A series of batch experiments were carried out on surface and subsurface  
19 sediments taken from along the salinity gradient of the Humber Estuary. The aim was to  
20 investigate the geochemical processes driving major element (N, Fe, S, and Mn) redox  
21 cycling and trace metal behaviour during simulated resuspension events. The magnitude  
22 of major nutrient and metal release was significantly greater during the resuspension of  
23 outer estuarine sediments rather than from inner estuarine sediments. When comparing  
24 resuspension of surface versus subsurface sediment, only the outer estuary experiments  
25 showed significant differences in major nutrient behaviour with sediment depth. In  
26 general, any ammonium, manganese and trace metals (Cu and Zn) released during the  
27 resuspension experiments were rapidly removed from solution as new sorption sites (i.e.  
28 Fe/Mn oxyhydroxides) formed. Therefore Humber estuary sediments showed a  
29 scavenging capacity for these dissolved species and hence may act as an ultimate sink  
30 for these elements. Due to the larger aerial extent of the outer estuary intertidal mudflats  
31 in comparison with the inner estuary area, the mobilisation of the outer estuary  
32 sediments (more reducing and richer in sulphides and iron) may have a greater impact  
33 on the transport and cycling of nutrients and trace metals. Climate change-associated  
34 sea level rise combined with an increasing frequency of major storm events in temperate  
35 zones, which are more likely to mobilise deeper sediment regions, will impact the

36 nutrient and metal inputs to the coastal waters, and therefore enhance the likelihood of  
37 eutrophication in this environment.

## 38        **1. Introduction**

39            Estuaries are highly dynamic coastal environments regulating delivery of  
40 nutrients and trace metals (TMs) to the ocean (Sanders *et al.*, 1997; Statham, 2012). In  
41 most coastal ecosystems in the temperate zone, nitrogen controls primary productivity  
42 as it is usually the limiting nutrient; therefore an increased load flowing into such  
43 oligotrophic waters could lead to eutrophication, and the subsequent environmental  
44 impacts due to hypoxia, shifts in the biological community and harmful algal blooms  
45 (Howarth, 1996; Abril *et al.*, 2000; Boyer & Howarth, 2002; Roberts *et al.*, 2012;  
46 Statham, 2012). This has been the focus of attention because human activities over the  
47 last century have increased nitrogen fluxes to the coast due to intensive agricultural  
48 practices, and wastewater and industrial discharges (Howarth, 1996; Canfield *et al.*,  
49 2010).

50            River inputs are the main nitrogen sources to estuarine waters. Inorganic  
51 nitrogen is generally the major portion of the total dissolved nitrogen inputs to an  
52 estuary; however organic nitrogen may sometimes be significant (20-90% of the total  
53 nitrogen load) (Seitzinger & Sanders, 1997; Nedwell *et al.*, 1999). The speciation and  
54 distribution of nitrogen along the salinity continuum will be controlled by complex  
55 dissimilatory and assimilatory transformations coexisting at a range of oxygen  
56 concentrations (Thamdrup, 2012); but denitrification is considered the major removal  
57 process to the atmosphere in shallow aquatic environments (Statham, 2012). Anammox  
58 and dissimilatory nitrate reduction to ammonium (DNRA) can also play a role in the  
59 nitrogen cycle, although their relative importance in different coastal environments is  
60 still a matter of debate (Song *et al.*, 2013; Roberts *et al.*, 2014). The organic nitrogen  
61 pool will be cycled during microbial metabolism, and thus it also plays an important

62 role in estuarine geochemistry. However, this pool is difficult to characterise as it  
63 comprises a wide variety of compounds, mostly complex high molecular weight  
64 compounds that are more refractory and less bioavailable than low molecular weight  
65 compounds (Seitzinger & Sanders, 1997). Organic matter buried in the sediments will  
66 be involved in early diagenesis through a combination of biological, chemical and  
67 physical processes. In fact, high rates of organic matter oxidation are expected in  
68 estuaries due to the sediment accumulation rates, organic matter flux into the sediment  
69 and organic matter burial (Henrichs, 1992).

70         Estuarine sediments may also have accumulated contaminants such as TMs  
71 carried by river loads. Sediment geochemistry and dynamics will control the mobility  
72 and bioavailability of TMs, and therefore sediments subjected to reoxidation processes  
73 may be a potential source (Salomons *et al.*, 1987; Di Toro *et al.*, 1990; Allen *et al.*,  
74 1993; Calmano *et al.*, 1993; Simpson *et al.*, 1998; Saulnier & Mucci, 2000; Caetano *et*  
75 *al.*, 2003). Trace metals can be in solution, sorbed to or co-precipitated with different  
76 mineral surfaces and organic matter, but in anoxic sediments, iron sulphides are thought  
77 to be the main solid phases controlling TM mobility (Salomons *et al.*, 1987; Huerta-  
78 Diaz & Morse, 1990; Allen *et al.*, 1993). When sediments are exposed to oxic  
79 conditions, dissolved Fe and Mn will precipitate rapidly as amorphous and poorly  
80 crystalline Fe/Mn oxyhydroxides, incorporating the released TMs by co-precipitation  
81 and/or adsorption (Burdige, 1993; Calmano *et al.*, 1993; Simpson *et al.*, 1998; Saulnier  
82 & Mucci, 2000; Gunnars *et al.*, 2002; Caetano *et al.*, 2003). These newly formed  
83 minerals will be transported, mixed, and maybe, eventually buried into the underlying  
84 anoxic sediment again.

85         In aquatic sediments, there is a vertical progression of metabolic processes  
86 determined by the use of the available electron acceptors during organic matter

87 mineralisation (Canfield & Thamdrup, 2009). The sequential utilization of the terminal  
88 electron acceptors is based on the thermodynamics of the process and the free energy  
89 yield (Stumm & Morgan, 1970; Froelich *et al.*, 1979; Berner, 1980). At the surface,  
90 dissolved oxygen can diffuse a few millimetres into the sediments (the *oxic* zone),  
91 where aerobic respiration is the dominant metabolic pathway. Beneath, there is often a  
92 suboxic zone where nitrate is actively reduced and nitrite accumulates as its reduction  
93 intermediate (the *nitrogenous* zone). Below, zones dominated by metal reduction (the  
94 *manganous* and *ferruginous* zones), sulphate reduction (the *sulphidic* zone), and  
95 methanogenesis (the *methanic* zone) occur in sequence (Canfield & Thamdrup, 2009).  
96 Dissolved Fe normally accumulates below Mn in the sediment column since it is less  
97 mobile and more sensible to oxygen. In general, besides the effects of advection and  
98 bioturbation, Mn and Fe cycling in aquatic sediments imply vertical diffusion that  
99 depends on gradient concentrations and different environmental factors (pH, oxygen,  
100 hydrogen sulphide concentrations, organic matter, suspended particulate matter, etc.)  
101 (Canfield *et al.*, 2005). Finally, in anoxic sediments, sulphate reduction, the major  
102 anaerobic mineralization process in coastal sediments, results in the accumulation of  
103 dissolved sulphide (Jørgensen, 1977, 1982; Middelburg & Levin, 2009).

104         However, in coastal and estuarine sediments, these geochemical zones, and the  
105 correspondent metabolic zones, are not normally well delineated and they tend to  
106 overlap because sediment profiles are often disturbed by mixing and bioturbation  
107 (Sørensen & Jørgensen, 1987; Aller, 1994; Postma & Jakobsen, 1996; Mortimer *et al.*,  
108 1998; Canfield & Thamdrup, 2009). Rapid redox changes at the sediment-water  
109 interface due to successive cycles of sediment suspension and settling will control the  
110 speciation and cycling of nutrients and trace elements on a tidal-cycle timescale  
111 (Morris, 1986). Yet, less frequently, seasonal or annual resuspension events can affect

112 sediment to depths that are not disturbed normally, which will alter the biogeochemistry  
113 of the system (Eggleton & Thomas, 2004). The pairing of in situ hydrodynamic and  
114 erosion observations during a moderate storm and estimates of the magnitude of benthic  
115 nutrient release at increasing erosion thresholds show that resuspension events may  
116 significantly influence nutrient budget of shallow estuarine systems (Kalnejais *et al.*,  
117 2010; Couceiro *et al.*, 2013; Percuoco *et al.*, 2015; Wengrove *et al.*, 2015). Nutrient  
118 release during resuspension can be associated to the entrainment of particles and  
119 porewaters into the water column and also to reactions of freshly suspended particles  
120 (Kalnejais *et al.*, 2010; Couceiro *et al.*, 2013).

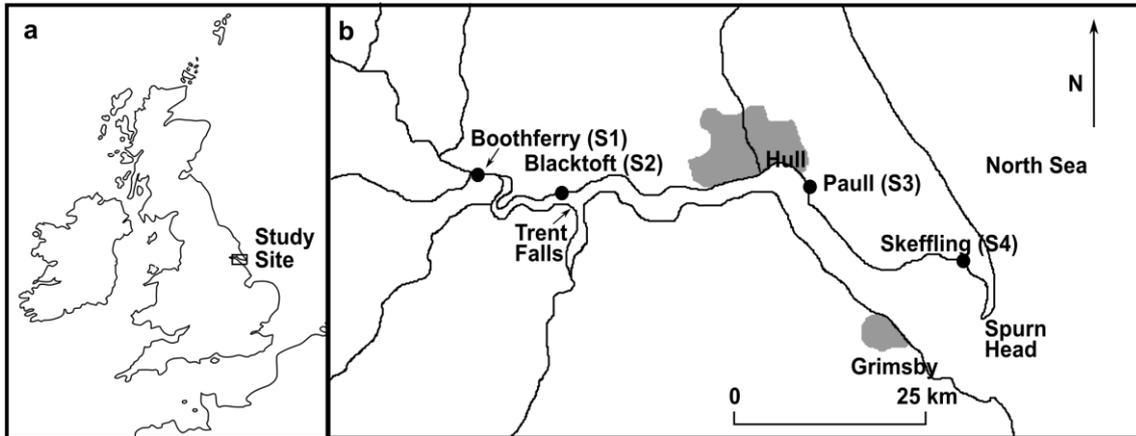
121 In this study sediments from four different sites along the salinity range of the  
122 Humber Estuary (UK) were used in order to investigate the impact of sediment  
123 resuspension on the redox cycling and transport of the major elements and TMs to the  
124 coastal waters. The authors have worked in the Humber since 1994 (Mortimer *et al.*,  
125 1998; Mortimer *et al.*, 1999; Burke *et al.*, 2005) and have observed the frequency and  
126 magnitude of resuspension events. Small-scale resuspension of the upper 1-2 mm  
127 occurs on a tidal cycle; medium scale resuspension of the order of centimetres occurs  
128 during large flooding or moderate storm events which occur approximately twice a year.  
129 Very significant resuspension events that strip off the mud from intertidal areas occur  
130 on a timescale of several decades (a removal of about 10 cm deep in the intertidal  
131 mudflat was observed following a storm in early 1996) (Mortimer *et al.*, 1998).  
132 Accordingly, for this experiment, two sediment depths (the mobile oxic/suboxic surface  
133 layer, 0-1 cm, and the suboxic/anoxic subsurface layer, 5-10 cm) were selected to  
134 simulate different timescales of resuspension and to analyse their effects on nutrient and  
135 TM behaviour.

136 Climate change-associated impacts will have effects on estuarine morphodynamics  
137 (Townend *et al.*, 2007; Robins *et al.*, 2016). For the UK, an increase in the extreme  
138 rainfall events (during the winter season) and long periods of low flow conditions have  
139 been predicted (Jones & Reid, 2001; Christensen *et al.*, 2007; IPCC, 2013; Robins *et*  
140 *al.*, 2016). This combined with the sea-level rise will increase estuarine flood risk and  
141 will have further implications on sediment transport patterns; on the position of the  
142 estuarine turbidity maximum (ETM); and on the retention time of river-borne  
143 substances (i.e. sediments and contaminants) (Robins *et al.*, 2016). The aim of this work  
144 is to better understand the environmental impact of different sediment remobilisation  
145 events within the estuary. The more frequent disruption of subsurface sediments will  
146 affect the geochemistry of estuarine sediments; porewater profiles may not reach steady  
147 state between resuspension episodes, and there may be impacts on the nutrient and TM  
148 fluxes to the sea.

## 149 **2. Material and Methods**

### 150 **2.1 Field sampling**

151 The Humber Estuary is a macrotidal estuary on the east coast of northern  
152 England (Fig.1). It is 60 km in length, there are ~115 km<sup>2</sup> of mudflats, and is highly  
153 turbid (Pethick, 1990). The Humber is also considered a major source of nutrients for  
154 the North Sea (Pethick, 1990; Mortimer *et al.*, 1998; Uncles *et al.*, 1998).



155

156 Figure 1: Map with the location of the Humber Estuary (a), and detail of the sampling  
 157 sites (Boothferry (S1), Blacktoft (S2), Paull (S3), and Skeffling (S4)) (b).

158 Samples of intertidal mudflat sediments and river water were collected at low  
 159 tide during the same tidal cycle on the 15<sup>th</sup> July 2014 along the north bank of the  
 160 Humber Estuary (Fig.1). The four sites were Boothferry (S1) and Blacktoft (S2) on the  
 161 inner estuary, and Paull (S3) and Skeffling (S4) on the outer estuary. These sites were  
 162 selected to cover the estuarine salinity range (Mortimer *et al.*, 1998; Burke *et al.*, 2005;  
 163 Uncles *et al.*, 2006). River water pH, conductivity, and temperature were determined in  
 164 the field using a Myron Ultrameter PsiII handheld multimeter. For the resuspension  
 165 experiments, river water was recovered from each sampling location into 2L acid  
 166 washed polythene containers, and bulk samples of surface (0-1 cm) and subsurface  
 167 sediment (5-10 cm) were taken with a trowel and transferred into 1L acid washed  
 168 polythene containers. No airspace was left in the containers in order to minimise  
 169 sediment air oxidation. These river water and sediments were stored at 4°C until used in  
 170 resuspension experiments (started within 48 hrs). Extra samples of sediments and river  
 171 water were collected in 0.5L containers. All river waters were filtered (<0.2µm  
 172 Minisart®) and were stored for sample characterisation (see below). Within 6-8 hrs of  
 173 sampling, at the laboratory, porewaters were recovered from sediment subsamples by  
 174 centrifugation (30 min, 6000 g), filtered (<0.2µm Minisart ®) and stored for further

175 analysis (see below). All the subsamples of the dissolved phase used for metal analysis  
176 were acidified (1% v/v) with concentrated HNO<sub>3</sub> to prevent metal losses to the walls of  
177 the sample tubes and/or precipitation of oxyhydroxides.

## 178 **2.2 Sample characterisation and analytical methods**

179 All the following physicochemical analyses of sediments and water samples  
180 were carried out in triplicate (pseudoreplicates from bulk samples). Sediments were  
181 oven dried at 70°C (until constant weight) prior to X-Ray diffraction analysis on a  
182 Bruker D8 Advance diffractometer and X-Ray fluorescence (XRF) analysis on an  
183 Olympus Innovex X-5000 spectrometer. The percentages of acid volatile sulphide  
184 (AVS) and pyrite were determined on freeze-dried sediments using the methods  
185 described in Canfield *et al.* (1986) and Fossing and Jørgensen (1989) respectively. Total  
186 extractable Fe and extractable Fe<sup>2+</sup><sub>(s)</sub> were determined after 60 min extractions in 0.25  
187 M hydroxylamine HCl (Lovley & Phillips, 1987) and 0.5 N HCl respectively (Lovley &  
188 Phillips, 1986), both followed by ferrozine assay (Viollier *et al.*, 2000). Subsamples of  
189 10% v/v HCl acid and non-acid washed, oven dried (70 °C), and ground sediment  
190 samples were analysed for total sulphur (TS), total carbon and total organic carbon  
191 (TOC) on a LECO SC-144DR Sulphur and Carbon Analyser by combustion with non-  
192 dispersive infrared detection. Total inorganic carbon (TIC) was determined by the  
193 difference between non-acid washed and acid washed samples. Wet sediments were  
194 analysed for particle size by laser diffraction on a Malvern Mastersizer 2000E.

195 Ammonium was measured in all the pre-filtered dissolved phase samples on a  
196 continuous segmented flow analyser (SEAL AutoAnalyser 3 HR) (%RSD was 3% and  
197 1% for fresh and brackish-saline waters respectively). Ion chromatography was carried  
198 out to determine inorganic anions (nitrate, nitrite, sulphate, and chloride).

199 Chromatographic analysis of high chloride samples required the use of a column-  
200 switching method (Bruno *et al.*, 2003) where matrix chloride anions were pre-separated  
201 from the other analytes by a double in-line pre-column (AG9-HC 4 mm). Then, nitrate  
202 and nitrite were analysed without dilution by conductivity (DIONEX CD20, ED40  
203 Electrochemical detector, 8% RSD) and spectrophotometry for differentiation of nitrite  
204 and nitrate (DIONEX AD20 UV absorbance detector (225 nm)). In order to measure  
205 chloride and sulphate concentrations, 20-fold dilution samples were analysed on a  
206 DIONEX 500 (%RSD  $\leq$  2%). Iron and Mn in solution were determined after  
207 acidification with 1% v/v HNO<sub>3</sub> for TM analysis by ion-coupled plasma-mass  
208 spectroscopy (ICP-MS) on a Thermo Scientific iCAPQc ICP-MS. For the analysis of  
209 brackish-saline waters a special protocol, in which precautions were taken to avoid  
210 polyatomic interferences, was applied, and Certified Reference Material (CRM) was run  
211 throughout (see Supporting Information for more details).

### 212 **2.3 Resuspension experiments**

213 The 2L samples of river water collected were directly used to make up the  
214 suspensions without any pre-treatment (no deoxygenation or filtration was applied). The  
215 preparation of the sediment slurries prior to the starting of the mechanical resuspension  
216 was carried out under nitrogen gas conditions to minimise the oxidation. From the 1L  
217 bulk sediment samples collected, subsamples of 30 g (w/w) were weighed in triplicate,  
218 and 120 ml of the corresponding river water was added in an open 500 ml Erlenmeyer  
219 flask, which was covered with a foam bung that allowed gas exchange with the  
220 atmosphere, but excluded dust. Thereafter, the slurries were maintained in suspension  
221 using an orbital shaker (120 rpm) at laboratory temperature (21 $\pm$ 1°C). Sediment  
222 erodibility was assumed to be homogeneous among samples. Aliquots of 5 ml were

223 withdrawn from all flasks at different intervals from 0.02 hrs (1 min) to 336 hrs (two  
224 weeks). The sampling frequency was progressively decreased with time in order to  
225 more intensively monitor changes occurring at the start of the experiment (short-term  
226 changes, tidal cycle scale) relative to those occurring over longer time periods (medium-  
227 term changes, 2-3 days), which would represent the duration of a very significant  
228 resuspension event like suggested in Kalnejais *et al.* (2010). From the 5 ml aliquots, the  
229 aqueous phase was separated from solids by centrifugation (5 min; 16,000 g). Eh and  
230 pH were determined using a Hamilton PolyPlast ORP BNC and an Orion Dual Star  
231 meter (with the electrode calibrated at pH 4, 7 and 10) respectively. Aqueous phase  
232 samples were filtered and retained for analysis. Subsamples were acidified (1% v/v  
233 HNO<sub>3</sub>) for metal analysis by ICP-MS, as mentioned above, with the correspondent  
234 precautions for high salinity samples. Nutrients in the aqueous phase were measured as  
235 described above, and acid extractable Fe<sup>2+</sup><sub>(s)</sub> was determined immediately on solid  
236 residues from centrifugation following the method described above.

#### 237 **2.4 Sequential Extractions**

238 To support the understanding of the changes in TM speciation due to  
239 resuspension, sequential extractions were performed concurrently. The partitioning of  
240 selected metals (Zn and Cu) between different operationally-defined geochemical  
241 fractions was determined using the Tessier *et al.* (1979) procedure as optimised for  
242 riverine sediments by Rauret *et al.* (1989). The extractions were carried out with the  
243 original wet sediments and with the dried solid residues recovered at the end of the  
244 resuspension experiments. Four extractants were used: 1 M MgCl<sub>2</sub> at pH 7 (to  
245 determine the “exchangeable” fraction), 1 M NaOAc at pH 5 (for the bound-to-  
246 carbonates or “weak acid-extractable” fraction), 0.04 M NH<sub>2</sub>OH·HCl in 25% v/v HAC

247 (for the bound to Fe/Mn oxides), and 30% H<sub>2</sub>O<sub>2</sub> at pH 2 (with HNO<sub>3</sub>) followed by  
248 NH<sub>4</sub>Ac (for the bound to organic matter and sulphides). The third step of the extraction  
249 protocol was modified by reducing the extraction temperature (from 96°C to room  
250 temperature), and increasing the extraction time (from 6 to 14 hrs (overnight)). With the  
251 original wet sediments, the first three steps of the extraction protocol were carried out in  
252 an anaerobic chamber with deoxygenated reactants. Metal concentrations associated  
253 with the residual phase were not determined. The concentration of the metals in the  
254 extractant solutions was analysed by ICP-MS following the pertinent precautions (see  
255 more details in Supporting Information).

## 256 **3. Results**

### 257 **3.1 Sample Characterisation**

#### 258 3.1.1 Site characterisation

259 The basic physicochemical parameters at the four sampling sites are reported in  
260 Table 1. During sampling, the light brown surface sediments contrasted visually with  
261 the underlying dark grey materials, except at S2 (Blacktoft), where there was no colour  
262 change but abundant plant material throughout. The full chemical characterisation of the  
263 river waters and porewaters is given in the SI.

264 Table 1: Characterisation of the river waters at the four study sites. Conductivity,  
 265 temperature, and pH were measured *in situ*. Eh was measured prior to resuspension in  
 266 the laboratory.

	S1	S2	S3	S4
<b>Location</b>				
Longitude	0°53'25"(W)	0°43'57"(W)	0°14'01"(W)	0°04'13"(E)
Latitude (N)	53°43'38"	53°42'28"	53°43'04"	53°38'37"
<b>Conductivity (mS/cm)</b>	0.7383	5.731	30.48	36.42
<b>Salinity</b>	0.4	3.5	21.6	26.1
<b>Temperature (°C)</b>	20.0	19.7	19.2	19.5
<b>pH</b>	7.87	7.52	7.90	8.02
<b>Eh (mV)</b>	+151±24	+109±23	+75±8	+75±4
<b>NO<sub>3</sub><sup>-</sup> (µM)</b>	266	250	248	<LDL
<b>NH<sub>4</sub><sup>+</sup> (µM)</b>	7	7	12	23
<b>Mn<sup>2+</sup> (µM)</b>	1.4	1.0	0.6	23
<b>SO<sub>4</sub><sup>2-</sup> (mM)</b>	0.8	3.4	16	22
<b>Fe<sup>2+</sup> (µM)</b>	0.1	0.1	1.2	1.8

267

### 268 3.1.2 Solid phase

269 The bulk mineralogy of the dried sediments was characterised and all sediments  
 270 contained a mixture of quartz, carbonates (calcite and dolomite), and silicates (kaolinite,  
 271 muscovite, clinocllore, albite, microcline). Pyrite was only detected by XRD in the  
 272 subsurface sediments from S4. The average TIC, TOC and TS contents of inner estuary  
 273 sediments (S1 and S2) were 1.1%, 2.0%, and 0.17% respectively, with little systematic  
 274 variation with depth (Table 2). The average TIC, TOC and TS contents of outer estuary  
 275 sediments (S3 and S4) were 1.6%, 2.4%, and 0.35%, respectively, with both TOC and  
 276 TS increasing with sample depth. The average amounts of Fe in the inner and outer  
 277 estuary sediments were 3% and 4% by weight, respectively, with 0.09% and 0.13%  
 278 associated with pyrite. AVS were only detected in the samples from the outer estuary  
 279 but not in all the replicates. The Fe associated with AVS in S3 and S4 subsurface  
 280 sediments was 0.01 and 0.09% respectively; however, it was not possible to quantify the  
 281 very little amount extracted from surface samples. The average amount of 0.5 N HCl

282 extractable  $\text{Fe}^{2+}_{(s)}$  was 108 and 153  $\mu\text{mol g}^{-1}$  in the inner and outer estuary sediments  
283 respectively, with no depth trend in the inner estuary, but a trend of increase with depth  
284 in the outer estuary. The bulk concentrations of Mn, Zn, and Cu in solids are also  
285 included in Table 2. Finally, the particle grain size data (as the upper bound diameter of  
286 50% of cumulative percentage of particles by volume, D50), showed that sediments  
287 were finer in the outer estuary mudflats. Sediments in the inner estuary sites had less  
288 water content and were classified as finer sands/coarse silt (Supporting Information).

289 Table 2: Characterisation of the solid phase of estuarine sediments from the four study sites. The errors associated are the standard deviation ( $1\sigma$ )  
 290 of three (or two replicates in the case of XRF measurements of Mn, Zn, and Cu).

291

	<b>S1</b>		<b>S2</b>		<b>S3</b>		<b>S4</b>	
	<b>Surface</b>	<b>Subsurface</b>	<b>Surface</b>	<b>Subsurface</b>	<b>Surface</b>	<b>Subsurface</b>	<b>Surface</b>	<b>Subsurface</b>
% TIC	1.71±0.31	1.01±0.69	0.69±0.22	1.09±0.19	1.43±0.06	1.38±0.21	1.75±0.10	1.76±0.04
% TOC	1.28±0.29	2.34±0.68	2.48±0.21	1.75±0.15	2.06±0.04	2.58±0.17	2.17±0.04	2.69±0.03
% TS	0.16±0.01	0.18±0.01	0.18±0.00	0.14±0.01	0.22±0.00	0.35±0.00	0.31±0.00	0.52±0.01
Total Fe (%)	2.77±0.76	3.30±0.74	3.05±0.63	2.89±0.52	3.75±0.74	4.07±0.85	4.48±0.99	4.28±0.89
% Fe-AVS	nd	nd	nd	nd	<LDL	0.01	<LDL	0.09
% Fe-Pyrite	0.08	0.10	0.09	0.10	0.10	0.12	0.12	0.18
0.5 N HCl extractable Fe (µmol/g solids)	106±1	116±10	106±6	105±4	123±3	206±8	93±9	191±28
0.5 N HCl extractable Fe <sup>2+</sup> (% Fe <sup>2+</sup> / extractable Fe)	52±2	61±5	53±1	53±2	39±1	84±6	57±3	96±3
Mn (µg/g)	656±8	785±8	681±20	654±1	847±6	969±3	758±14	732±11
Zn (µg/g)	132±3	149±1	139±4	129±4	161±2	199±13	174±1	167±6
Cu (µg/g)	30±4	33±4	31±2	27±2	39±2	31±3	33±2	37±11
Grain size (D50) (µm)	53	37	47	47	16	19	13	16

## 292 **3.2 Major Element behaviour during sediment resuspension**

293 Changes in the concentration of the major elements (nitrate, ammonium,  
294 manganese, and sulphate) in solution, and 0.5 N HCl extractable  $\text{Fe}^{2+}_{(s)}$  during the  
295 resuspension of estuarine sediments are shown in Fig.2 (inner estuary) and Fig.3 (outer  
296 estuary). The initial concentrations (i.e. prior to slurry preparation and mechanical  
297 resuspension) of each species in the river waters (and solids in the case of reduced Fe)  
298 have been plotted with an open symbol on the y-axis. Nitrite was below the detection  
299 limit (0.1  $\mu\text{M}$ ) and has not been included.

### 300 3.2.1 Inner estuary

301 In the experiments using surface sediments from the inner estuary sites (S1 and  
302 S2) nitrate seemed to be released immediately on resuspension, particularly in S2  
303 experiments (~400  $\mu\text{M}$ ) (Fig.2a). Nitrate concentrations then remained relatively  
304 constant in these tests until 72 hrs, after which time concentrations steadily decreased  
305 towards the end of the test. In the experiments using inner estuary subsurface sediments,  
306 nitrate concentrations followed similar trends to those exhibited in the surface sediment  
307 experiments (Fig.2b), with S1 experiments showing a progressive increase in  
308 concentrations within the first 10 hrs. There was significantly more data scatter  
309 observed in these tests (especially at the later time points).

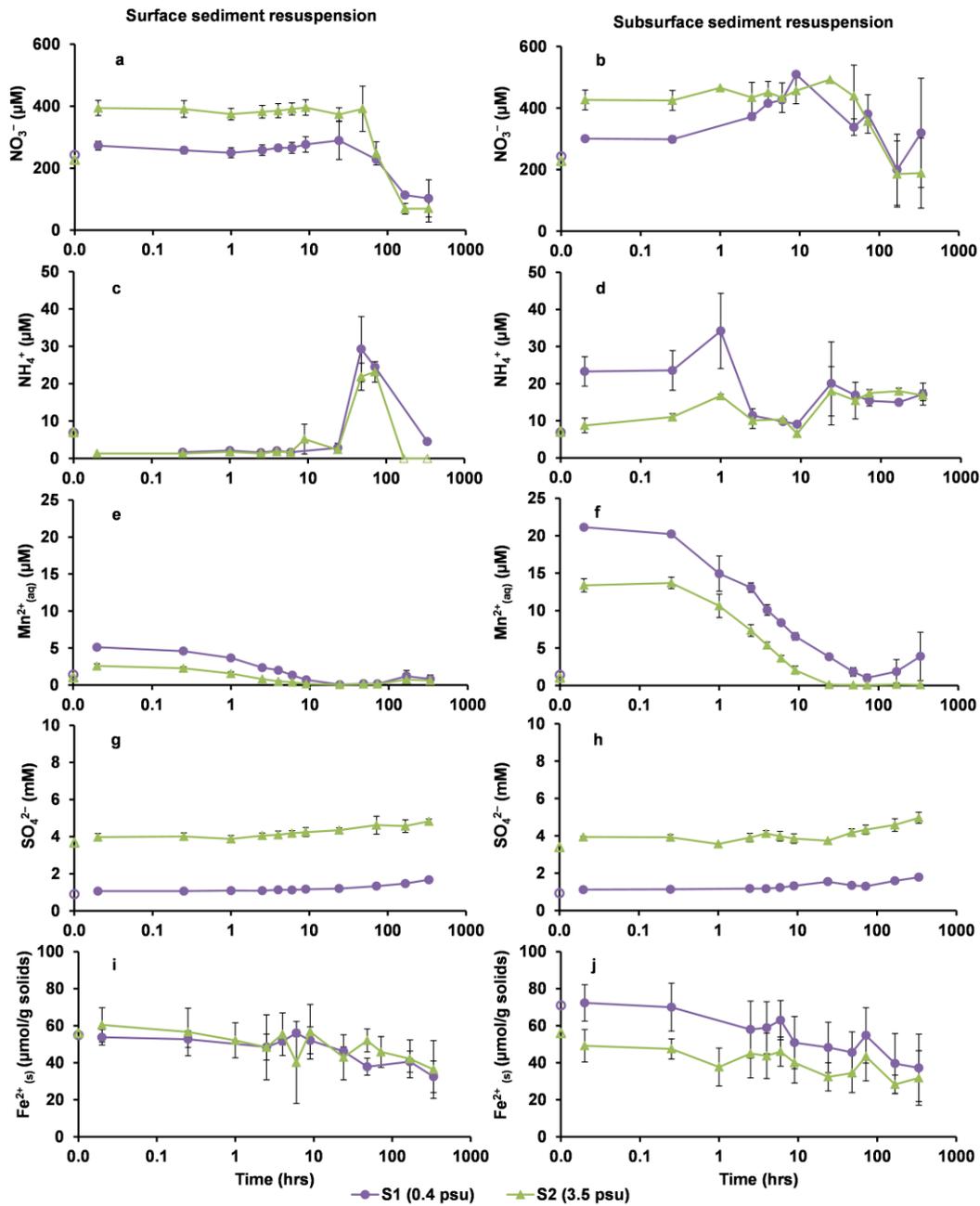
310 Ammonium concentrations in the experiments carried out with surface  
311 sediments decreased immediately after resuspension started (Fig.2c) and remained close  
312 to detection levels until 48 hrs, when concentrations transiently increased to around 20-  
313 30  $\mu\text{M}$  before decreasing to low concentrations by the end of the test. On the other hand,  
314 ammonium concentrations in experiments using subsurface sediments (Fig.2d)  
315 increased immediately after resuspension started from <10 to ~20  $\mu\text{M}$  in S1

316 experiments. The ammonium increase was more progressive in S2 experiments, in  
317 which concentrations doubled within the first hour. Then, levels of ammonium in the  
318 subsurface sediment experiments remained relatively constant after the first day of  
319 resuspension.

320 In the experiments using surface sediments,  $Mn^{2+}_{(aq)}$  concentrations were  
321 initially very low ( $\leq 5 \mu M$ ), yet higher than the initial concentration in the water column  
322 (Fig.2e), and decreased to detection limit levels after the first day of the resuspension,  
323 coinciding with the peak observed in ammonium. In the experiments using subsurface  
324 sediments,  $Mn^{2+}_{(aq)}$  concentrations showed an immediate increase to  $\sim 10-20 \mu M$ ,  
325 followed by a very rapid decrease (within hours) to close to detection levels (Fig.2f).

326 The sulphate concentrations were low in the inner estuary experiments, although  
327 slightly higher at S2 due to its position on the salinity gradient, and increased only  
328 marginally during resuspension (Fig.2g and 2h).

329 The 0.5 N HCl extractable  $Fe^{2+}_{(s)}$  represented between 12-18% of the total Fe in  
330 these experiments, being slightly lower in the surface than in the subsurface sediments  
331 experiments (Fig. 2i and 2j). The percentage of acid extractable  $Fe^{2+}_{(s)}$  decreased with  
332 time to a similar extent in all inner estuary experiments (between 20-40  $\mu mol Fe^{2+} g^{-1}$   
333 were removed which represented 4-7% of the total Fe in the sediments).



334

335 Figure 2: Major element behaviour during resuspension of inner estuary sediments. The  
 336 purple line with circles represents S1 (Boothferry) and the green line with triangles  
 337 represents S2 (Blacktoft). Open symbols on the y-axis indicate the initial concentrations  
 338 of the major elements in the experiments (river water plus porewater contribution) (a-h)  
 339 and the initial 0.5 N HCl extractable  $\text{Fe}^{2+}_{(s)}$  in the sediments (i, j). Empty markers  
 340 indicate measurements <LDL. The vertical error bars in all the figures represent one  
 341 standard deviation ( $1\sigma$ ) of triplicates.

### 342 3.2.2 Outer estuary

343 The experiments using surface sediments from the outer estuary (S3 and S4),  
344 showed differences in the nitrate behaviour between the sites (Fig.3a and 3b). The initial  
345 nitrate concentrations in S3 experiments were higher than in S4 experiments and similar  
346 to those found in the inner estuary sites; they remained relatively constant over the tests.  
347 In contrast, in the experiments using surface sediments from S4, nitrate concentrations  
348 were initially very low, but increased by six-fold within the first 48 hrs ( $190\pm 30\ \mu\text{M}$ )  
349 and nearly by 30-fold ( $\sim 900\pm 300\ \mu\text{M}$ ) by the end of the experiment. In the tests using  
350 subsurface sediments from S3, nitrate concentrations behaved initially similarly than in  
351 the surface sediment tests; however, after a week, the concentrations dropped below  
352 detectable levels ( $\sim 40\ \mu\text{M}$ ). The experiments using S4 subsurface sediments showed  
353 very low nitrate concentrations (close to or below detection levels) throughout.

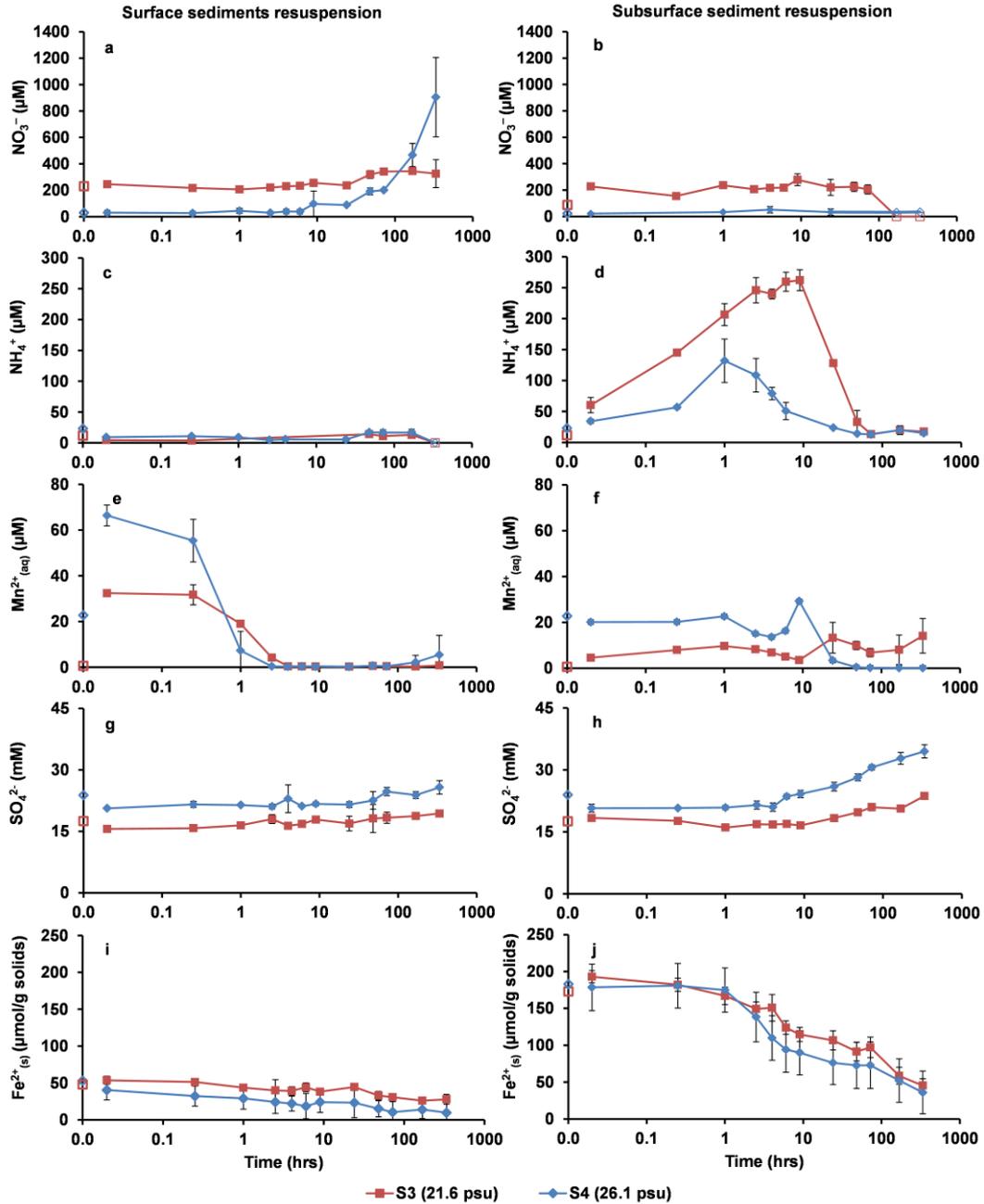
354 Ammonium concentrations in experiments using outer estuary surface sediments  
355 were initially low ( $< 20\ \mu\text{M}$ ), similar to the concentrations in the original river water,  
356 and remained so until the end of the tests (Fig.3c). There was a very different trend in  
357 ammonium concentrations in the experiments using subsurface sediments (Fig.3d),  
358 which increased significantly (by  $\sim 2.5$  times) within the first few hours of resuspension.  
359 Ammonium concentration peaks in the experiments were  $260\pm 20$  (S3) and  $130\pm 40$  (S4)  
360  $\mu\text{M}$ . Following these initial releases, ammonium levels in solution decreased to  $\sim 20\ \mu\text{M}$   
361 by the end of the first week to remain stable until the end of the tests.

362 In experiments using surface sediments,  $\text{Mn}^{2+}_{(\text{aq})}$  concentrations increased  
363 immediately on resuspension to three times ( $\sim 30\text{-}70\ \mu\text{M}$ ) the concentration of the river  
364 water (Fig.3e). This rapid release of Mn to the solution was followed by a very rapid  
365 decrease to close to detection levels ( $0.1\ \mu\text{M}$ ) after about 4 hrs. In the experiments using

366 subsurface sediments from S4,  $\text{Mn}^{2+}_{(\text{aq})}$  concentrations sharply decreased from  $\sim 20 \mu\text{M}$   
367 to detection limits after the first 10 hrs of resuspension; whereas for subsurface S3  
368 experiments, there was no clear release-uptake trend in  $\text{Mn}^{2+}_{(\text{aq})}$  concentrations (Fig.3f).

369 Sulphate is a more important species in solution in the outer estuary samples due  
370 to the position of the sampling sites within the estuarine salinity gradient. In  
371 experiments using surface sediments, sulphate concentrations remained fairly constant  
372 throughout (Fig.3g). However, in the experiments using subsurface sediments (Fig.3h),  
373 sulphate concentrations increased with time, particularly in S4 experiments (from  $21 \pm 1$   
374 to  $34 \pm 2 \text{ mM}$ ).

375 Iron oxidation trends differed between the experiments carried out with surface  
376 and subsurface sediments. The initial amounts of 0.5 N HCl extractable  $\text{Fe}^{2+}_{(\text{s})}$  in the  
377 surface sediments were  $54 \pm 3$  (S3) and  $40 \pm 6$  (S4)  $\mu\text{mol Fe}^{2+} \text{ g}^{-1}$  (Fig.3i), which  
378 represented around 40% of the total 0.5 N HCl extractable Fe and  $< 9\%$  of the total Fe.  
379 By the end of the 2-weeks, the  $\text{Fe}^{2+}_{(\text{s})}$  decreased to around 20% and 10% in the S3 and  
380 S4 surface sediment slurries respectively. The initial amounts of acid extractable  $\text{Fe}^{2+}_{(\text{s})}$   
381 in the subsurface sediments ( $193 \pm 8$  (S3) and  $179 \pm 27$  (S4)  $\mu\text{mol Fe}^{2+} \text{ g}^{-1}$  respectively)  
382 represented more than 90% of the total 0.5 N HCl extractable Fe pool and  $\sim 30\%$  of the  
383 total Fe. By the end of the tests, the percentages of the  $\text{Fe}^{2+}_{(\text{s})}$  decreased to  $\sim 21\%$  of the  
384 total Fe ( $45 \pm 3$  (S3) and  $36 \pm 6$  (S4)  $\mu\text{mol Fe}^{2+} \text{ g}^{-1}$ ) (Fig.3j). These outer estuary  
385 subsurface sediments experienced a rapid colour change (from black to brown) during  
386 the first hours of the experiment.



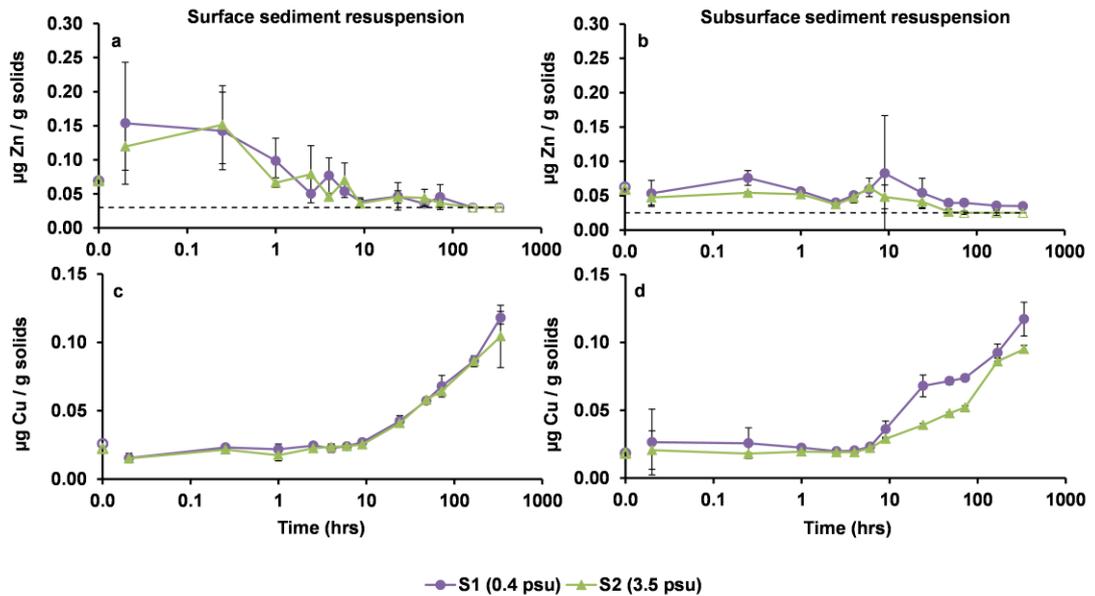
387

388 Figure 3: Major element behaviour during resuspension of outer estuary sediments. The  
 389 red line with squares represents S3 (Paull) and the blue line with diamonds represents  
 390 S4 (Skeffling). Open symbols on the y-axis indicate the initial concentrations of the  
 391 major elements in the experiments (river water plus porewater contribution) (a-h) and  
 392 the initial 0.5 N HCl extractable  $\text{Fe}^{2+}_{(s)}$  in the sediments (i, j). Empty markers indicate  
 393 measurements <LDL. The vertical error bars in all the figures represent one standard  
 394 deviation ( $1\sigma$ ) of triplicates.

### 395 **3.3 Trace metal mobility during sediment resuspension**

396 The release of Zn and Cu during sediment resuspension experiments is shown in  
397 Fig.4 and Fig.5. Data of Zn and Cu in solution have been normalised to show  $\mu\text{g}$  of  
398 metal released per g (dry weight) of sediment used in the experiment, therefore the  
399 concentrations have been corrected for moisture content.

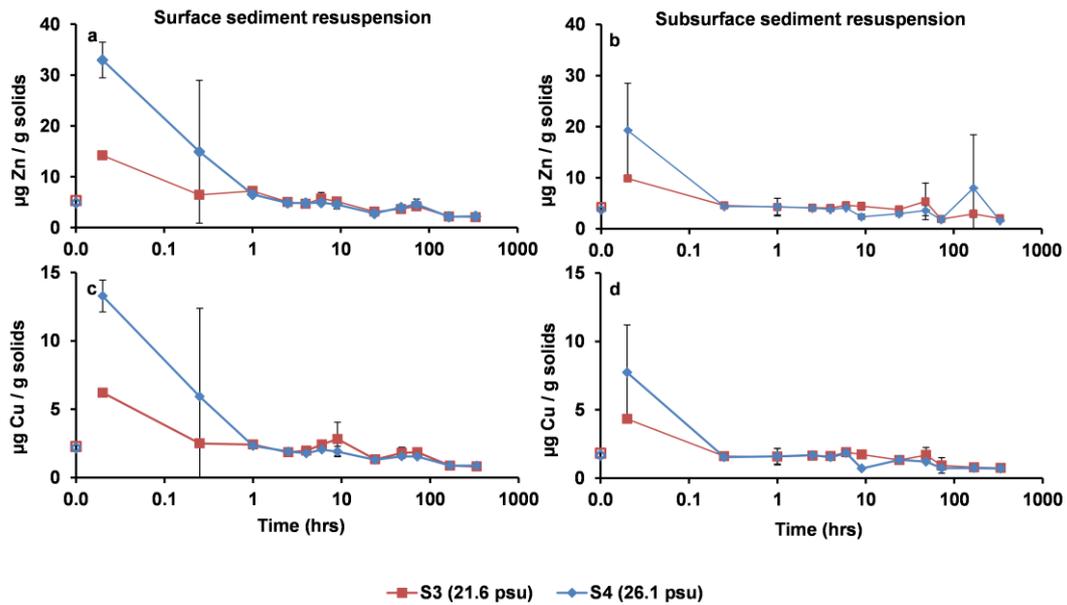
400 In the experiments carried out with inner estuarine sediments, the pattern of Zn  
401 behaviour depended on the sediment depth. In the surface sediment experiments, Zn  
402 concentrations increased immediately upon resuspension to values 2-3 times the initial  
403 concentrations in the experiments ( $0.15\pm 0.09$  (S1) and  $0.12\pm 0.04$  (S2)  $\mu\text{g Zn g}^{-1}$ ) but  
404 decreased with time to below the detection limit by the end of the experiment (Fig.4a).  
405 In contrast, in the experiments using subsurface sediments (Fig.4b), Zn concentrations  
406 did not increase upon resuspension and decreased gradually to a final level close to the  
407 detection limit. Initially, Cu concentrations remained stable at about the levels in the  
408 river water in the four sets of experiments, but increased after  $\sim 10$  hrs of resuspension,  
409 reaching concentrations  $\sim 3-4$  times their initial values (about  $0.12\pm 0.02$  (S1) and  
410  $0.1\pm 0.04$  (S2)  $\mu\text{g Cu g}^{-1}$ ) (Fig.4c and 4d).



411

412 Figure 4: Zinc and copper released to the solution from solids during resuspension  
 413 experiments using S1 and S2 sediments. Zinc released from surface (a) and subsurface  
 414 (b) sediments; Cu released from surface (c) and subsurface (d) sediments. Open  
 415 symbols on the y-axis indicate the initial concentrations in the experiment (river water  
 416 plus porewater contribution). Error bars in all the figures represent one standard  
 417 deviation ( $1\sigma$ ) of triplicates. Empty markers indicate measurements  $<LDL$  and dashed  
 418 lines indicate the LDL of the ICP-MS analysis.

419 The resuspension experiments using outer estuary sediments showed a clear  
 420 release-uptake trend for Zn and Cu. Zinc was immediately released to solution, reaching  
 421 concentrations 3 to 6 times higher than the initial concentrations in the experiment, and  
 422 then concentrations rapidly decreased to initial concentration levels ( $\sim 4.5 \mu\text{g g}^{-1}$ )  
 423 (Fig.5a and 5b). The greatest Zn concentrations were observed in experiments with S4  
 424 sediments. Similarly, there was an immediate release of Cu to the solution, followed by  
 425 a rapid decrease (within hours) to below initial concentration levels. The maximum  
 426 concentrations were  $\sim 5\text{-}13 \mu\text{g Cu g}^{-1}$  (Fig.5c and 5d), which were 2 to 6 times the  
 427 concentrations of Cu prior to the mixing.



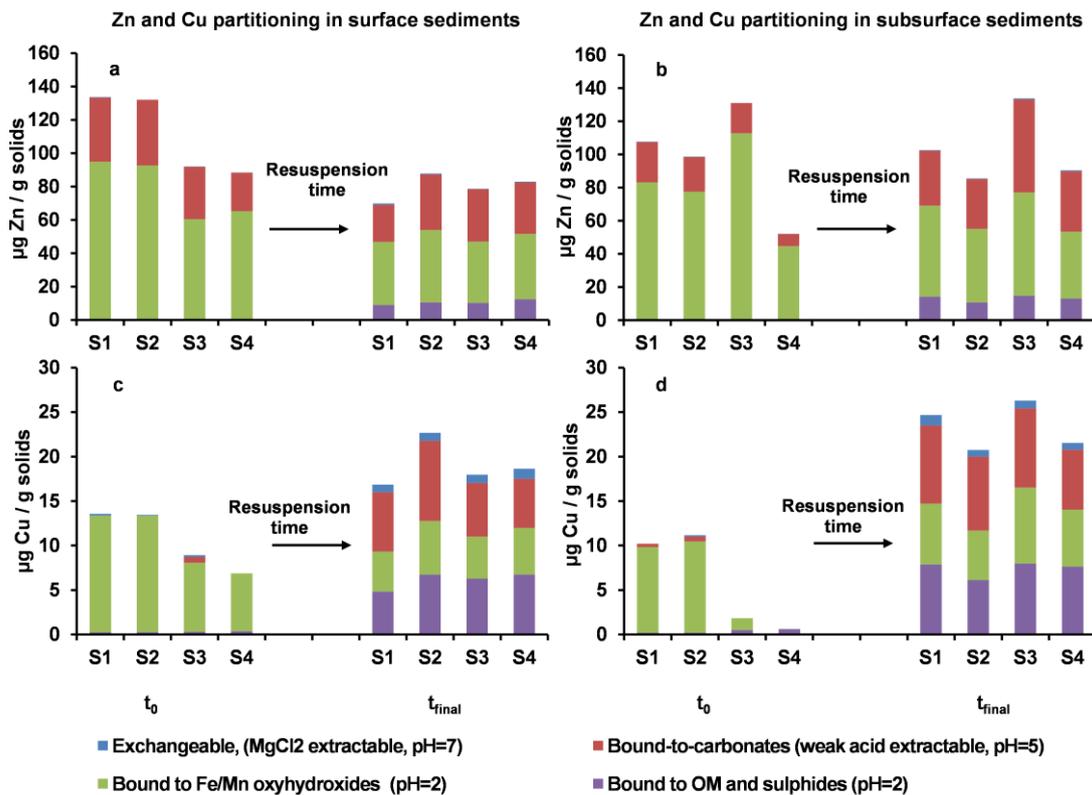
428

429 Figure 5: Zinc and copper released to the solution from solids during resuspension  
 430 experiments using S3 and S4 sediments. Zinc released from surface (a) and subsurface  
 431 (b) sediments; Cu released from surface (c) and subsurface (d) sediments. Open  
 432 symbols on the y-axis indicate the initial concentrations in the experiment (river water  
 433 plus porewater contribution). Error bars in all the figures represent one standard  
 434 deviation ( $1\sigma$ ) of triplicates.

### 435 3.4 Changes in metal partitioning during resuspension

436 Partitioning of Zn and Cu in the sediments before and after the resuspension  
 437 experiment, as determined by sequential extraction, is reported in Fig.6. In all the  
 438 original sediments, Zn was predominantly associated with weak acid-extractable  
 439 fractions and Fe/Mn oxyhydroxides. The trends for Zn partitioning changes were  
 440 similar in, both, surface and subsurface sediments (Fig.6a and 6b). After two weeks of  
 441 resuspension, Zn concentrations slightly decreased in the bound-to-Fe/Mn  
 442 oxyhydroxides fraction and increased in the more weakly-bound fractions  
 443 (exchangeable and bound-to-carbonates). In the bound-to-organic matter and sulphides  
 444 fraction, Zn was only detected at the endpoint samples. Copper partitioning (Fig.6c and

445 6d) showed similar changes in all the samples; although very little Cu was extracted  
 446 from S3 and S4 subsurface sediments. In the original sediments, almost all the Cu  
 447 extracted was associated with the Fe/Mn oxyhydroxides fraction. Upon resuspension,  
 448 there was a general shift from the Fe/Mn oxyhydroxides fraction to the weak acid-  
 449 extractable, and the organic matter-sulphide fraction. Copper concentrations for each  
 450 leachate were similar among samples.



451  
 452 Figure 6: Zinc and copper partitioning changes after estuarine sediment resuspension  
 453 determined by sequential extractions using Tessier *et al.* (1979) protocol with  
 454 modifications. The concentration (averaged from triplicates) is expressed in µg of metal  
 455 in the extractant solution by the mass of solids (dry sediments) used in the extraction.  
 456 Zinc partitioning in surface (a) and subsurface (b) sediments; and Cu partitioning in  
 457 surface (c) and subsurface (d) sediments. Sites are ordered according to their location  
 458 within the salinity gradient and the arrows represent the time of the experiment (2-  
 459 weeks).

## 460        **4. Discussion**

### 461        **4.1 Geochemical character of river water and estuarine sediments.**

462            The four sites along the Humber estuary represent the gradual change from a  
463 typical freshwater environment to an intertidal mudflat with brackish waters. This  
464 salinity profile was similar to that measured in other surveys (NRA, 1995, 1996;  
465 Sanders *et al.*, 1997; Mortimer *et al.*, 1998). Along the salinity gradient, nitrate  
466 concentrations in the overlying waters decreased with increasing salinity and were  
467 inversely correlated with the ammonium concentrations. Previously nitrate has been  
468 described to show a conservative behaviour along the mixing line, although there may  
469 be specific locations that show net nitrate production or removal during the year  
470 (Sanders *et al.*, 1997; Barnes & Owens, 1998). Generally, the ammonium  
471 concentrations measured were of the same order of magnitude, if not slightly higher,  
472 than typical Humber waters. We observed increasing ammonium concentrations with  
473 increasing salinity, but the 90s surveys showed that ammonium trends varied  
474 seasonally. All porewaters recovered were enriched in ammonium but not in nitrate.  
475 This ammonium enrichment was enhanced in the outermost estuary sites, which was  
476 most likely a reflection of *in situ* production from organic matter degradation during  
477 sulphate reduction (Mortimer *et al.*, 1998) and DNRA processes. Sulphate  
478 concentrations increased seawards.

479            All surface sediments used in the resuspension experiments were in contact with  
480 air at the time of sampling. Precautions were taken during sampling to avoid oxidation  
481 of redox-sensitive elements, but we cannot discard partial oxidation of these elements  
482 during sampling and transport, before the sediment slurries were made up for the  
483 resuspension experiments. The subsurface sediments collected in the inner estuary sites

484 appeared to be moderately reducing compared to the subsurface sediments from the  
485 outer estuary which appeared to become more reducing at depth. The AVS  
486 concentrations measured ( $<0.02 \mu\text{mol AVS g}^{-1}$ ) in these Humber sediments were very  
487 low, but still in the range of concentrations reported in estuaries and other aquatic  
488 environments (Di Toro *et al.*, 1990; Allen *et al.*, 1993; Fang *et al.*, 2005). The dynamic  
489 nature of the Humber leads to a continuous resuspension and reoxidation of sediments,  
490 which will buffer the AVS to low concentrations, whereas pyrite will accumulate in  
491 sediments with time as it is more stable than AVS. This would explain the presence of  
492 pyrite in all the samples regardless of the absence of AVS. Furthermore, the availability  
493 of dissolved Mn and nitrate will also influence the distribution of free sulphide within  
494 the sediments (Thamdrup *et al.*, 1994; Sayama *et al.*, 2005). Iron oxides react with free  
495 sulphides and, at the same time, the produced  $\text{Fe}^{2+}_{(\text{aq})}$  and  $\text{H}_2\text{S}$  reduce  $\text{MnO}_2$  rapidly  
496 (Thamdrup *et al.*, 1994), which could be another reason for the low AVS detected.  
497 Besides, the Fe oxides produced in the reaction of  $\text{MnO}_2$  with  $\text{Fe}^{2+}_{(\text{aq})}$  will fuel this  
498 positive feedback mechanism. Alternatively, it cannot be discarded that the low AVS  
499 extracted was an artefact due to the partial oxidation of sediments during sampling and  
500 transport or during the handling in the laboratory, prior sediments were freeze-dried for  
501 AVS-pyrite extraction. The better-defined redox stratification between the two sediment  
502 depths sampled at the outer estuary sites was supported by *in situ* observations (colour  
503 change and odour of the sediments). Moreover, the total acid extractable  $\text{Fe}^{2+}_{(\text{s})}$  in the  
504 subsurface outer estuary sediments was  $\sim 2$  times the content in the equivalent sediments  
505 from the inner estuary. Thus, it seems that the outer estuary mudflats hold the largest  
506 Fe-pool within the Humber.

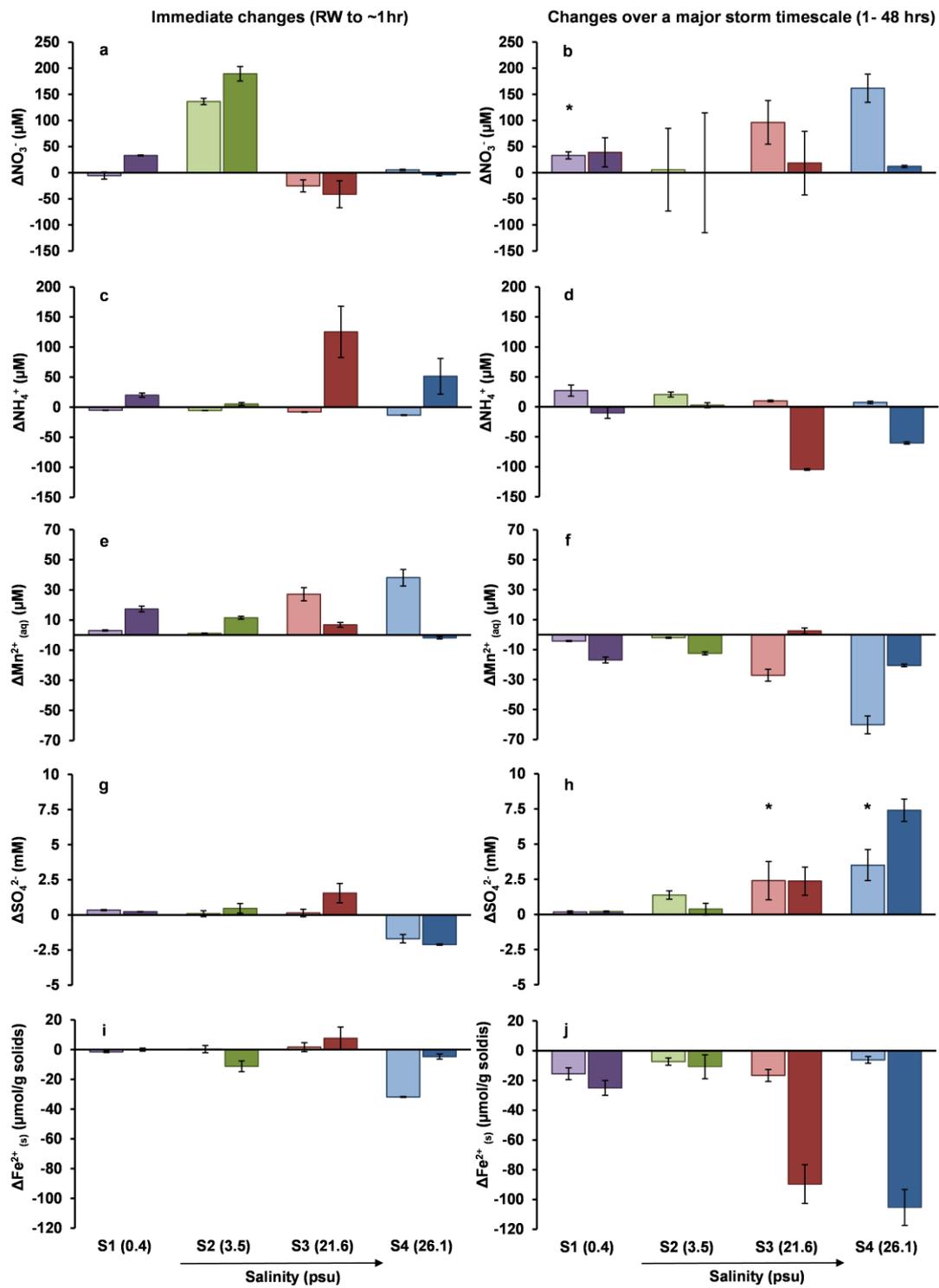
507           Furthermore, the mudflats of the outer Humber estuary accumulated finer  
508 materials and they appeared to have a slightly higher TOC content than the inner estuary

509 sediments. Organic matter often accumulates in finer grained sediments, and its  
510 concentrations in coastal sediments are often lower at the sediment-water interface  
511 (Mayer, 1994). The organic matter depletion in the surface layer relative to the  
512 immediate subsurface suggests that frequent mobilisation of surface sediments leads to  
513 greater organic matter degradation, which will be especially important in the areas of  
514 maximum sediment mobilisation (i.e. ETM, which is situated in the inner estuary)  
515 (Abril *et al.*, 2002; Middelburg & Herman, 2007). Metabolizable organic matter is  
516 progressively depleted along the estuary, and despite the high rates of sediment  
517 accumulation in the outer estuary, which allow high organic matter burial, this organic  
518 matter will be likely more refractory and may be further degraded during early  
519 diagenesis (Henrichs, 1992; Tyson, 1995).

#### 520 **4.2 Geochemical responses of major elements to sediment resuspension**

521 In order to compare the relative impact of a small-scale versus a more major  
522 resuspension event, the discussion about the changes in the geochemical behaviour of  
523 the major elements observed and their potential implications on estuarine geochemistry  
524 will be framed by two time-windows (Fig.7). Firstly, the immediate changes upon  
525 sediment resuspension in river water, which are important as they will occur naturally at  
526 any type of resuspension event (from regular tidal cycles to less frequent extreme  
527 events). Secondly, longer timescale changes expected during major storms, which  
528 potentially mobilise deeper sediments that are not normally disturbed and typically last  
529 2-3 days in the Humber region (Lamb & Frydendahl, 1991; EASAC, 2013). For the  
530 immediate changes, net differences between the average concentration after the first  
531 hour of resuspension (as a final concentration datum) and the original concentrations of  
532 the river water (RW) have been calculated. Changes during a major storm timescale

533 have been represented by the difference between the average concentration over the first  
 534 hour and the concentration at 48 hrs of resuspension. Since an intense turbulent shear  
 535 was reproduced, particle settling was not considered.



536

537 Figure 7: Major elements changes during sediment resuspension experiments at  
538 different time windows. Immediate changes (left) and changes over a major storm  
539 timescale (48 hrs) (right) for nitrate (a, b), ammonium (c, d), dissolved Mn (e, f),  
540 sulphate (g, h), and 0.5 N HCl extractable  $\text{Fe}^{2+}_{(s)}$  from solids (i, j). Light and dark  
541 coloured bars represent surface and subsurface sediments respectively. \*Delta  
542 calculated for 72 hrs when datum for 48 hrs was not available.

543 Nitrate showed no big releases in the short term (Fig.7a), with the exception of  
544 S2 which may be explained by oxidation of reduced nitrogen species because porewater  
545 did not accumulate nitrate. A combination of oxidation processes may also explain the  
546 nitrate increases in the longer timescale (Fig.7b). For example, the later significant  
547 increase in nitrate concentration in the experiments using S4 surface sediments may, in  
548 part, be associated with nitrification processes, as observed by Couceiro *et al.* (2013).  
549 Although a proportional ammonium consumption coupled to the production of nitrate  
550 was not observed in this experiment, coupled nitrification-denitrification can occur very  
551 fast, especially if other oxidants such as Mn oxides are competing with the oxygen for  
552 the oxidation of ammonia to  $\text{N}_2$  and organic-N (Luther *et al.*, 1997; Anschutz *et al.*,  
553 2000). Therefore, in this mosaic of redox reactions, a combination of aerobic oxidation  
554 of organic matter and nitrification may be the major nitrate sources. The nitrate  
555 produced could be subsequently used in other reactions. In fact under longer time  
556 intervals (1-2 weeks), the concentrations of nitrate decreased progressively possibly due  
557 to the development of suboxic conditions in the experiments (i.e. conditions developed  
558 perhaps in isolated micro-niches in the bottom of the flasks) (Triska *et al.*, 1993;  
559 Lansdown *et al.*, 2014; Lansdown *et al.*, 2015); such that denitrification could be  
560 supported despite the constant influx of air to the experiments. As such, the longer term  
561 removal of nitrate observed in these experiments may be an artefact of the experimental

562 set-up (i.e. the higher sediment to water ratios used) and may not be representative of  
563 nitrate dispersion following a large resuspension event.

564 Ammonium showed significant releases (70-140  $\mu\text{M}$ ) in the first hour of  
565 resuspension in the experiments carried out with subsurface sediments from S3 and S4  
566 (Fig.7c), likely due to the accumulation of ammonium in the porewater of outer estuary  
567 mudflats like suggested by Morgan *et al.* (2012). However, other processes, such as  
568 reversible desorption from sediments and/or ion-exchange reactions likely have also  
569 contributed to the ammonium increase (Morin & Morse, 1999; Kalnejais *et al.*, 2010;  
570 Morgan *et al.*, 2012; Percuoco *et al.*, 2015; Wengrove *et al.*, 2015) since porewater  
571 contribution to the mixture by simple diffusion cannot explain the concentrations  
572 reached. The ammonium released in those experiments was completely removed after  
573 48 hrs (Fig.7d). Transitory ammonium release also occurred in S1 and S2 surface  
574 sediment experiments and these peaks coincided with the depletion of  $\text{Mn}^{2+}$  in solution.  
575 Nitrification and ammonium oxidation to  $\text{N}_2$  by Mn oxides could have contributed to  
576 the ammonium removal processes. Any  $\text{Mn}^{2+}_{(\text{aq})}$  product of these reaction pathways  
577 would readily react with the oxygen present to regenerate reactive oxides, which will act  
578 as a catalysts to continue the oxidation of ammonium and organic-N (Luther *et al.*,  
579 1997); or, if suboxic conditions,  $\text{Mn}^{2+}_{(\text{aq})}$  may react with nitrate (Sørensen & Jørgensen,  
580 1987; Murray *et al.*, 1995; Luther *et al.*, 1997). In the natural environment, the  
581 occurrence and magnitude of nitrification depends on the availability of oxygen and  
582 ammonium (Canfield *et al.*, 2005), and it will play a major role in the nutrient exchange  
583 processes within the sediment-water interface as the nitrate produced will, in turn,  
584 sustain denitrification (Barnes & Owens, 1998; Mortimer *et al.*, 1998). In the Humber,  
585 an intense zone for nitrification-denitrification has been associated with the ETM due to  
586 the enhanced chemical and microbial activity as suspended particles provide a large

587 additional surface area (Barnes & Owens, 1998; Mortimer *et al.*, 1998; Uncles *et al.*,  
588 1998). On the other hand, nitrifiers can be inhibited by sulphide concentration, light,  
589 temperature, salinity and extreme pH (Canfield *et al.*, 2005). The inhibition of  
590 nitrification by sulphide could favour the preservation of ammonium in porewater (Joye  
591 & Hollibaugh, 1995; Morgan *et al.*, 2012), which may be a possible reason for the  
592 limited evidence of nitrification in some of these experiments and may help to explain  
593 spatial differences in coupled nitrification-denitrification within this estuary.  
594 Alternatively, re-adsorption of ammonium onto particles, is likely to be an important  
595 removal process (especially as Fe/Mn oxides were likely to be forming in experiments  
596 as a result of metal oxidation; see below) which, in the natural estuary systems may be  
597 key for the nutrient buffering capacity of the sediments (Morin & Morse, 1999; Song *et*  
598 *al.*, 2013).

599         The net removal of reduced Mn and Fe in all the experiments is attributed to the  
600 series of oxidation reactions occurring during sediment resuspension in aerated  
601 conditions, and the consequent precipitation of insoluble Mn/Fe oxyhydroxides (e.g.  
602 birnessite and ferrihydrite). During oxic resuspension, abiotic oxidation processes are  
603 expected to be the dominant mechanism operating. In contrast, microbially mediated  
604 Mn- and Fe-oxidation are the dominant mechanism operating in micro-aerophilic and  
605 sub-oxic environments (Froelich *et al.*, 1979; Thamdrup *et al.*, 1994; Canfield *et al.*,  
606 2005). Dissolved Mn behaviour varied significantly between the two resuspension  
607 timescales examined. There was a general immediate release of  $\text{Mn}^{2+}_{(\text{aq})}$  from the  
608 porewater to the solution (Fig.7e) that was completely reversed within a major storm  
609 time interval (Fig.7f). The release and the later uptake of  $\text{Mn}^{2+}_{(\text{aq})}$  appeared to be more  
610 important in the experiments carried out with inner estuary surface sediments. For the  
611 inner estuary experiments, the release and uptake of  $\text{Mn}^{2+}_{(\text{aq})}$  closed numerically.

612 However, from the outer estuary, only the S3 surface sediment experiments, showed an  
613 equivalent Mn-release and uptake. This fact and the initial concentration of  $\text{Mn}^{2+}_{(\text{aq})}$  in  
614 surface porewater may indicate that these sediments were poised at Mn-reduction at the  
615 time of sampling. Site 4 surface experiments showed slightly more Mn-uptake because  
616  $\text{Mn}^{2+}_{(\text{aq})}$  decreased to levels below the initial  $\text{Mn}^{2+}_{(\text{aq})}$  concentrations in the river water.  
617 As mentioned above, coupled ammonium and/or organic-N oxidation with Mn oxides  
618 reduction may also have been a short-term source of  $\text{Mn}^{2+}_{(\text{aq})}$ . Sulphate and Fe did not  
619 show significant changes in the resuspension experiments during the first hour (Fig.7g  
620 and 7i). After 48-72 hrs, there was a net production of sulphate in the experiments with  
621 an increasing trend from S1 to S4. Although further conclusions about reaction  
622 pathways cannot be drawn from this type of resuspension experiment, this trend  
623 evidences again the more reducing conditions of the outer estuary sediments which  
624 probably contained intermediate reduced sulphur species (e.g. sulphides, thiosulphate,  
625 etc.) that were oxidised to form sulphate during the experiments (Fig.7h). The  
626 differences in the concentration of acid extractable  $\text{Fe}^{2+}_{(\text{s})}$  over 48 hrs of resuspension  
627 (Fig.7j) became also more important in the experiments using outer most estuary  
628 sediments due to their more reducing nature and their higher content of reactive Fe.

629 To summarise, the initial geochemical state of the sediments and their position  
630 along the estuarine continuum were the biggest influence on the geochemical  
631 progression during their resuspension. The availability of seawater sulphate, which  
632 likely promotes the development sulphidic sediments and  $\text{Fe}^{2+}_{(\text{s})}$  accumulation in the  
633 outer estuary mudflats, may be the major control on the biogeochemical processes, and  
634 hence Fe- and S-oxidation will dominate in this part of the Humber. However, the  
635 interlinks of N, Mn, Fe and S cycles and the spatiotemporal variability of the estuarine

636 environments make extremely difficult to constrain which are the principal reaction  
637 pathways occurring during resuspension events in natural conditions.

### 638 **4.3 Trace metal behaviour and changes during resuspension**

639 Zinc and Cu were selected for analysis because they are known to be  
640 significantly enriched in the Humber sediments due to industrial contamination  
641 (Middleton & Grant, 1990; Cave *et al.*, 2005; Andrews *et al.*, 2008). Although the total  
642 concentrations in the solid phase were not significantly different between samples,  
643 during the resuspension experiments the release of Zn and Cu was significantly lower in  
644 the experiments carried out with inner estuarine sediments than in those with outer  
645 estuarine sediments. Despite all the precautions taken in the ICP-MS analysis, the  
646 determination of trace elements in saline waters has been analytically challenging due to  
647 the potential interference of the matrix in the sensitivity and the formation of  
648 polyatomic ions (Reed *et al.*, 1994; Jerez Vegueria *et al.*, 2013). However, the  
649 difference between the concentrations measured immediately after the resuspension  
650 started and the concentrations after 48 hrs indicated that, even if there were polyatomic  
651 interferences on the baseline, the trends were not an analytical artefact. Despite the  
652 differences in magnitude, Zn and Cu showed a general release-uptake trend in the  
653 experiments. The very rapid increase of Zn and Cu in solution upon resuspension  
654 (Fig.8a and 8c) probably occurred due to a combination of mixing and desorption from  
655 different mineral phases (Calmano *et al.*, 1993; Cantwell *et al.*, 2002). Salinity has been  
656 shown to promote metal desorption since metals can be mobilised as soluble chloride  
657 complexes (Gerringa *et al.*, 2001; Millward & Liu, 2003; Du Laing *et al.*, 2008), which  
658 may help to explain the higher concentrations of metals in the experiments carried out  
659 with outer estuarine sediments. Furthermore, very early Fe/Mn colloids formed (before

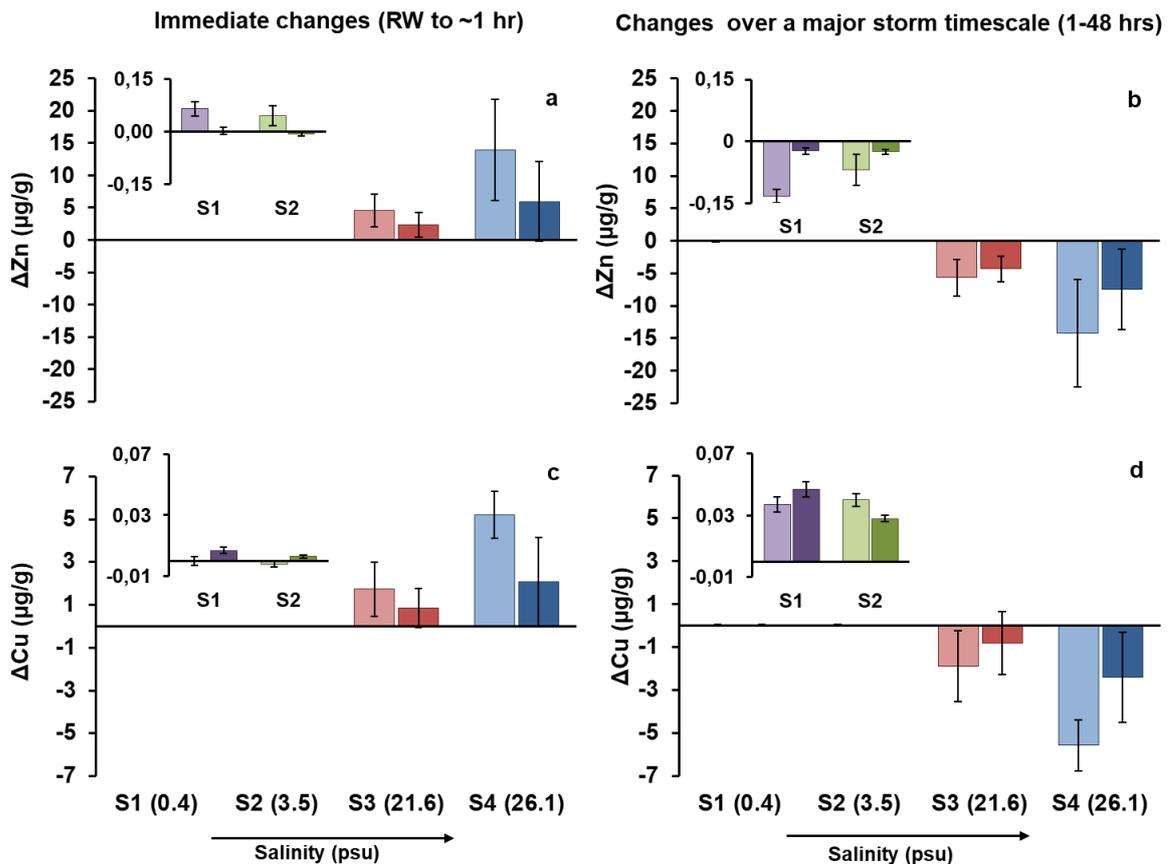
660 they aggregate to larger particles) may have passed the filters used, and therefore any  
661 metal associated would have been deemed as solutes. Nevertheless, the releases of Zn  
662 and Cu were generally reversed to a considerable extent by the time of a major storm  
663 (Fig.8b and 8d) as a result, most probably, of co-precipitation and adsorption processes  
664 to newly formed Mn/Fe oxyhydroxides (Burdige, 1993; Calmano *et al.*, 1993; Simpson  
665 *et al.*, 1998; Saulnier & Mucci, 2000; Gunnars *et al.*, 2002; Caetano *et al.*, 2003). This  
666 will evidence the importance of Fe/Mn transformations in the transport and fate of TMs  
667 in the estuarine sediment-water interface (Du Laing *et al.*, 2009). Further, the presence  
668 of soluble organic compounds may have influenced in the trends observed as well.

669         The mobilisation of TMs upon resuspension was also supported by the general  
670 shift observed towards ‘easier to extract’ fractions in metal partitioning (exchangeable  
671 and bound-to-carbonates). Although the metal release was reversed in a relatively short  
672 term, changes in metal partitioning may have implications in metal bioavailability. The  
673 Zn released in the inner estuary experiments was <0.1% of the total Zn in the  
674 experiment, which was within the range of the Zn associated with the exchangeable  
675 fraction. Zinc showed no significant changes in partitioning; but the decreases in the  
676 “weak acid extractable” and Fe/Mn oxides-associated fractions did not match  
677 quantitatively with any Zn increase in other fractions of the final sediments, which may  
678 be probably explained by protocol limitations (see below). In the outer estuary  
679 experiments, the average peak of Zn released was 11% of the total Zn in the  
680 experiments. The Zn released to the solution was higher than the Zn associated with the  
681 exchangeable fraction of these sediments, which suggests that Zn was likely mobilised  
682 from other fractions. Probably Zn experienced a transient release (i.e. Zn likely sourced  
683 from absorption complexes and returned to new absorption complexes). Zinc speciation  
684 varied among the outer estuary sediments, and only two of them showed changes that

685 quantitatively matched (loss in the Fe/Mn oxides-bound fraction was equivalent to the  
686 increase in carbonates and organic matter-sulphide fraction). On the other hand, the Cu  
687 released to the solution in the inner estuary experiments represented about 0.1% of the  
688 total Cu in the solids, which coincided with the Cu found in the exchangeable fraction.  
689 In the outer estuary experiments, the average peak of Cu released to the solution was  
690 22% of the total Cu in solids, which suggests that not only the Cu associated with the  
691 exchangeable fraction was mobilised. Generally, in the initial sediment samples, Cu was  
692 only found associated with the Fe/Mn oxides-bound fraction, whereas, for the  
693 reoxidised endpoint sediments, it was found in all the fractions. Thus, Cu may have  
694 been mobilised from high-energy binding sites to weaker binding sites. Nevertheless,  
695 errors introduced during the extractions or associated with protocol limitations cannot  
696 be discarded.

697         Numerous limitations have been reported for the ‘Tessier’ extraction protocol  
698 (Gleyzes *et al.*, 2002). The concentrations in the exchangeable phase were generally  
699 very low or below the detection limit, probably because the adsorption-desorption  
700 processes are normally pH-dependent, and therefore desorption of the specifically  
701 adsorbed metals may not be complete at neutral pH (Tessier *et al.*, 1979; Du Laing *et*  
702 *al.*, 2009). Furthermore, none of the Zn and Cu bound to organic matter-sulphides were  
703 extracted from the original sediments, which may seem contrary to what was expected  
704 for initially sulphate reducing sediments (Di Toro *et al.*, 1990; Allen *et al.*, 1993).  
705 However, the absence of Zn and Cu in this fraction may be explained by protocol  
706 limitations since organic matter and sulphide dissolution may not be completed with the  
707 reagents used (Gleyzes *et al.*, 2002; Anju & Banerjee, 2010). The incomplete  
708 dissolution of some phases, matrix effects, and changes in pH can lead to readsorption  
709 (by complexation, precipitation, coprecipitation, adsorption and loss on the vial walls)

710 and redistribution of some metals during the extraction (Martin *et al.*, 1987). Further  
 711 limitations of the extraction procedure used may be the underestimation of the metals  
 712 bound to Fe/Mn oxides (i.e. the changes applied in the extraction time to compensate  
 713 the reduction of the extracting temperature, may have not been enough to dissolve all  
 714 the hydrous oxides, Gleyzes *et al.*, 2002).



715

716 Figure 8: Zinc and Copper changes over time during sediment resuspension experiments  
 717 at different time windows. Immediate changes (left) and changes over a major storm  
 718 timescale (48 hrs) (right) for Zn (a, b) and Cu (c, d). Light and dark coloured bars  
 719 represent surface and subsurface sediments respectively.

720 **4.4 General implications of sediment resuspension for nutrient and trace metal**  
721 **transport and mobility in estuaries**

722         The oxidation of estuarine sediment due to remobilisation events enhanced the  
723 release of both, nutrients and metals. The major element geochemical progression was  
724 conditioned by the depth of the sediment being mobilised, whereas the release-uptake  
725 trend in TMs behaviour was observed in all sediment types. These findings are in  
726 agreement with other field and laboratory studies which used more sophisticated erosion  
727 devices that showed how sediment erosion depth varies with turbulence (Kalnejais *et*  
728 *al.*, 2010; Couceiro *et al.*, 2013; Wengrove *et al.*, 2015). Under natural conditions,  
729 estuarine sediments are eroded when the eroding forcing exceeds a particular bed shear  
730 stress or erosion threshold (Van Prooijen & Winterwerp, 2010). The dynamics of the  
731 cohesive sediment in estuaries is extremely complex due to the interaction between  
732 abiotic (hydrodynamics, cohesion, armouring flocculation, consolidation, deposition)  
733 and biotic processes (bioturbation, biodeposition, bioestabilisation) (Wu *et al.*, 1999;  
734 Blanchard *et al.*, 2000; Sanford, 2008; Van Prooijen & Winterwerp, 2010). However, in  
735 this resuspension experiment, the natural progressive erosion of sediments was  
736 simplified and differences in sediment erodibility were not considered. It was assumed  
737 that the cohesive particulate matter was not armoured to any extent and it was  
738 resuspended fairly uniformly. Also, this study aimed to reproduce a potential maximum  
739 release of nutrient and metals; but under natural conditions, there will be further  
740 seasonal variations associated with temperature, riverine loads, the intensity of storms,  
741 and tides (Sanders *et al.*, 1997; Barnes & Owens 1998; Mortimer *et al.*, 1998).

742         Nitrate (autochthonous or as a product of nitrification processes) was the only  
743 major nutrient that seemed to remain in solution for few days in both resuspension  
744 scenarios simulated. Hence, although nitrate concentrations were low in the outer

745 estuary, during a major storm, important nitrate inputs from the estuary to the coastal  
746 waters may occur. During sediment resuspension, any ferrous iron present (in solution  
747 or associated with particles) will be rapidly oxidised, and hence Fe will be transported  
748 mainly as ferric iron (as particles, colloids, organic-matter complexed). Therefore Fe  
749 supplied from resuspended sediments is likely to be an important source of Fe to the  
750 coastal environment as suggested by Kalnejais *et al.* (2010).

751         The area of the outer estuary intertidal mudflats is the largest in terms of aerial  
752 extent (see Mortimer *et al.*, 1998), and therefore the potential amount of sediments, and  
753 consequently nutrients and metals, mobilised will be significantly larger during an  
754 extraordinary resuspension event than during normal circumstances. Also nutrient and  
755 metal fluxes will be determined largely by the flow conditions, which means that a  
756 turbulent release (e.g. in storm conditions) may be relevant to the overall nutrient and  
757 metal budgets (see more in Supporting Information, SI.7). In the outer estuary mudflats,  
758 the larger amount of Fe and the continuous availability of sulphate seem to promote the  
759 development of sulphidic conditions at a depth, which are not observed in the inner  
760 estuary sites. The total oxidation of the inorganic species released during the  
761 resuspension of estuary sediments would equate to an oxygen consumption of  $20\pm 10$   
762  $\text{mmol O}_2 \text{ kg}^{-1}$ , and to  $70\pm 40$   $\text{mmol O}_2 \text{ kg}^{-1}$  for the inner and outer estuary sediments  
763 respectively. This amount of oxygen removal could result in full deoxygenation of  
764 surface waters at relatively low solid-solution ratios ( $15 \text{ g L}^{-1}$  for the inner estuary;  $4 \text{ g}$   
765  $\text{L}^{-1}$  for the outer estuary). However, well-mixed estuaries rarely exhibit water column  
766 hypoxia (Paerl, 2006). The kinetics of the reoxidation processes (especially those of Fe  
767 and S) are such that supply of oxygen (by diffusion from the atmosphere or mixing with  
768 adjacent oxygenated waters) is likely to prevent anoxic conditions from developing in  
769 all but the very largest of remobilisation events.

770 Humber sediments may act as an ultimate sink for the major (Fe and Mn) and  
771 trace metals; while for nutrients, they may act as a major source on some occasions, as  
772 argued by Millward and Glegg (1997). Nutrient fluxes estimations showed important  
773 differences in nitrate and ammonium fluxes when comparing resuspension of surface  
774 and subsurface sediments. If subsurface sediments are mobilised, nitrate fluxes would  
775 increase from 23.8 to 40.8 mmol/m<sup>2</sup>/day in the inner estuary, and from -12.1 to -3.9  
776 mmol/m<sup>2</sup>/day in the outer estuary. Ammonium fluxes would increase from -2.0 to 4.6  
777 mmol/m<sup>2</sup>/day in the inner estuary, and from -3.9 to 32.3 mmol/m<sup>2</sup>/day in the outer  
778 estuary. Considering the areas of the inner and outer estuary, these estimations suggest  
779 that the whole estuary may act as an overall source of DIN rather than a sink when  
780 subsurface sediments are mobilised.

781 During estuarine resuspension events changes in TM speciation due to redox  
782 changes and desorption from resuspendable sediments are likely to be the main source  
783 of TMs to the water column; although direct diffusion of porewaters from undisturbed  
784 sediments can be also an important source of dissolved species (Martino *et al.*, 2002;  
785 Kalnejais *et al.*, 2010). In these experiments, the release of Zn and Cu was followed by  
786 an uptake in a relatively short time-window (<48 hrs). Hirst and Aston (1983)  
787 suggested, that the metal concentrations in the fluxes coming into the coastal waters  
788 may remain at normal levels even when extraordinary amounts of sediments are  
789 mobilised due to the rapid scavenging capacity of the newly formed minerals surfaces.  
790 This is supported by data presented here as only transient metal releases were observed.  
791 Others suggested that dissolved metals display a non-conservative mixing in macrotidal  
792 environments which can be explained by the presence of additional metal sources  
793 associated with sediments, and supports the importance of sediment mobilisation  
794 patterns and frequency on TM bioavailability and transport (Martino *et al.*, 2002).

795 Furthermore, these experiments showed that sediment resuspension led to a shift in TM  
796 partitioning (i.e. a greater proportion of Zn and Cu were associated with more weakly  
797 bound fractions). In the natural environment, before sediments are ultimately scavenged  
798 deeper in the sediment column, they will be continuously resuspended (Lee & Cundy,  
799 2001), so the transfer of TMs to weaker bound fractions will have implications in their  
800 bioavailability over time.

801           Climate change will impact upon morphodynamics and ecological processes in  
802 UK estuaries (Robins *et al.*, 2016). More frequent and intense episodes of extreme  
803 precipitations over Britain have been predicted (Jones & Reid, 2001; Christensen *et al.*,  
804 2007; IPCC, 2013). Therefore, in terms of budget, the more regular mobilisation of  
805 undisrupted subsurface sediment will lead to increased nutrient and metal inputs to the  
806 estuarine water column and maybe ultimately to coastal waters, which will have  
807 important environmental implications. Furthermore, changes in the estuarine dynamics  
808 could compromise the conditions needed for estuarine sediments to reach steady state  
809 before the next mixing event takes place, which may affect the sediment redox  
810 stratification and the development of well-defined geochemical zonations within the  
811 sediment profile.

## 812           **5. Conclusions**

813           This study gives an insight into the complex mosaic of processes that result from  
814 physical disturbances along the Humber estuary continuum. The position in the salinity  
815 gradient was the dominant control on sediment geochemistry with a change from a  
816 Mn/Fe-dominated redox chemistry in the inner estuary to a Fe/S-dominated system in  
817 the outer estuary. Therefore, understanding the system dynamics and sediment

818 characteristics is key when studying nutrients and metal cycling along a salinity  
819 continuum. Sediment resuspension resulted in the release of ammonium (where  
820 enriched) to surface waters. The nitrate released appears to remain in solution for more  
821 than 2-3 days. Reduced pools of Mn, Fe and, sulphur species in sediments were  
822 oxidised during resuspension resulting in Mn and Fe oxyhydroxides precipitation,  
823 which produced new sorption sites for the TMs released to solution upon resuspension.  
824 Thus, rapid releases of ammonium,  $\text{Mn}^{2+}_{(\text{aq})}$  and TMs may be reversed in relatively short  
825 (few days) timescales, which is important when assessing the overall environmental  
826 effects of resuspension episodes on surface waters composition and nutrient and metal  
827 cycling. In the Humber estuary, the potential resuspension of outer estuary subsurface  
828 sediments would have a greater effect on the coastal environment (in terms of Chemical  
829 Oxygen Demand (COD), nutrient and metal release), and it may become a more  
830 important process in the future as it is predicted an increase in the frequency of major  
831 storms that can mobilise these deeper sediments due to global warming.

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