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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.

1. Introduction

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

River inputs are the main nitrogen sources to estuarine waters. Inorganic nitrogen is generally the major portion of the total dissolved nitrogen inputs to an estuary; however organic nitrogen may sometimes be significant (20-90% of the total nitrogen load) (Seitzinger & Sanders, 1997; Nedwell *et al.*, 1999). The speciation and distribution of nitrogen along the salinity continuum will be controlled by complex dissimilatory and assimilatory transformations coexisting at a range of oxygen concentrations (Thamdrup, 2012); but denitrification is considered the major removal process to the atmosphere in shallow aquatic environments (Statham, 2012). Anammox and dissimilatory nitrate reduction to ammonium (DNRA) can also play a role in the nitrogen cycle, although their relative importance in different coastal environments is still a matter of debate (Song *et al.*, 2013; Roberts *et al.*, 2014). The organic nitrogen 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^2 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).
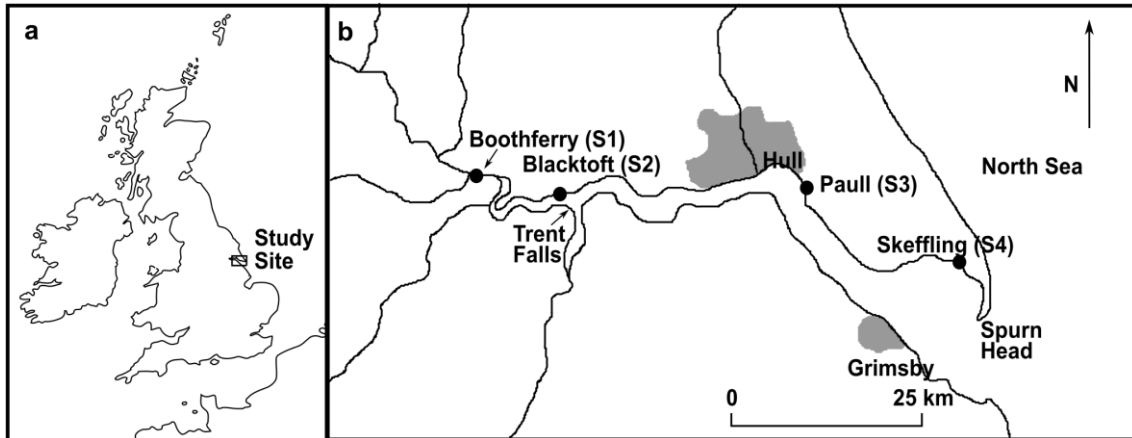
Figure 1: Map with the location of the Humber Estuary (a), and detail of the sampling sites (Boothferry (S1), Blacktoft (S2), Paull (S3), and Skeffling (S4)) (b).

Samples of intertidal mudflat sediments and river water were collected at low tide during the same tidal cycle on the 15th July 2014 along the north bank of the Humber Estuary (Fig.1). The four sites were Boothferry (S1) and Blacktoft (S2) on the inner estuary, and Paull (S3) and Skeffling (S4) on the outer estuary. These sites were selected to cover the estuarine salinity range (Mortimer *et al.*, 1998; Burke *et al.*, 2005; Uncles *et al.*, 2006). River water pH, conductivity, and temperature were determined in the field using a Myron Ultrameter PsiII handheld multimeter. For the resuspension experiments, river water was recovered from each sampling location into 2L acid washed polythene containers, and bulk samples of surface (0-1 cm) and subsurface sediment (5-10 cm) were taken with a trowel and transferred into 1L acid washed polythene containers. No airspace was left in the containers in order to minimise sediment air oxidation. These river water and sediments were stored at 4°C until used in resuspension experiments (started within 48 hrs). Extra samples of sediments and river water were collected in 0.5L containers. All river waters were filtered (<0.2μm Minisart®) and were stored for sample characterisation (see below). Within 6-8 hrs of sampling, at the laboratory, porewaters were recovered from sediment subsamples by 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_3 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 $Fe^{2+}_{(s)}$ 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 ºC), 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).

9

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_3 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±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_3) 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 $Fe^{2+}_{(s)}$ 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 $MgCl_2$ 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 $NH_2OH \cdot HCl$ in 25% v/v HAc

247 (for the bound to Fe/Mn oxides), and 30% H_2O_2 at pH 2 (with HNO_3) followed by

248 NH_4Ac (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
Location				
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"
Conductivity (mS/cm)	0.7383	5.731	30.48	36.42
Salinity	0.4	3.5	21.6	26.1
Temperature (°C)	20.0	19.7	19.2	19.5
pH	7.87	7.52	7.90	8.02
Eh (mV)	+151±24	+109±23	+75±8	+75±4
NO_3^- (μM)	266	250	248	<LDL
NH_4^+ (μM)	7	7	12	23
Mn^{2+} (μM)	1.4	1.0	0.6	23
SO_4^{2-} (mM)	0.8	3.4	16	22
Fe^{2+} (μM)	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, clinochlore, 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 $Fe^{2+}_{(s)}$ was 108 and 153 µmol 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).

14

289 Table 2: Characterisation of the solid phase of estuarine sediments from the four study sites. The errors associated are the standard deviation (1σ)

290 of three (or two replicates in the case of XRF measurements of Mn, Zn, and Cu).

291

	S1		S2		S3		S4	
	Surface	Subsurface	Surface	Subsurface	Surface	Subsurface	Surface	Subsurface
%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^{2+} (% Fe^{2+}/ 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 $Fe^{2+}_{(s)}$ 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 µM) 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 µM) (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 µM 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 µM in S1

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

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

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

The 0.5 N HCl extractable $Fe^{2+}_{(s)}$ represented between 12-18% of the total Fe in these experiments, being slightly lower in the surface than in the subsurface sediments experiments (Fig. 2i and 2j). The percentage of acid extractable $Fe^{2+}_{(s)}$ decreased with time to a similar extent in all inner estuary experiments (between 20-40 µmol Fe^{2+} g^{-1} were removed which represented 4-7% of the total Fe in the sediments).
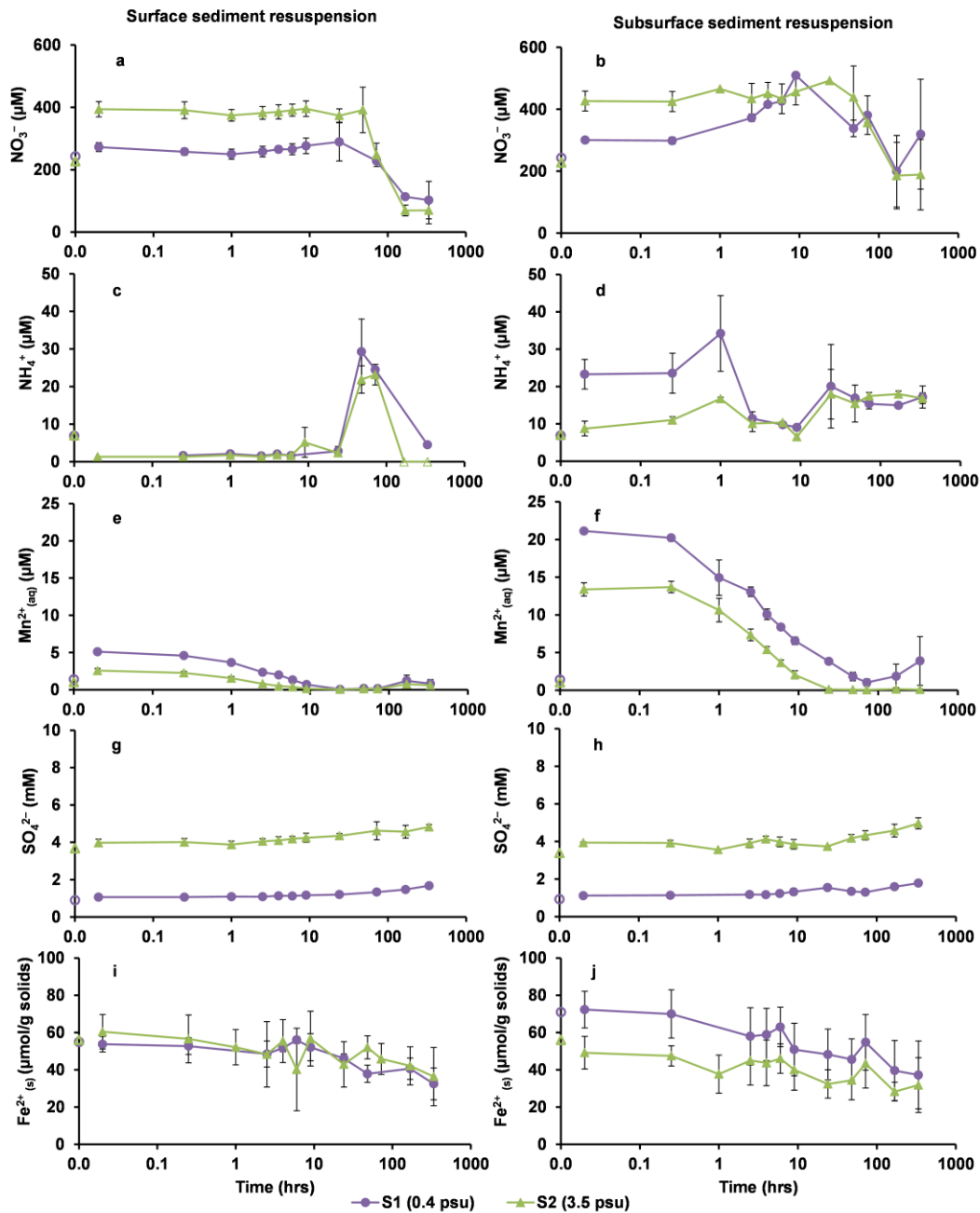
Figure 2: Major element behaviour during resuspension of inner estuary sediments. The purple line with circles represents S1 (Boothferry) and the green line with triangles represents S2 (Blacktoft). Open symbols on the y-axis indicate the initial concentrations of the major elements in the experiments (river water plus porewater contribution) (a-h) and the initial 0.5 N HCl extractable $Fe^{2+}_{(s)}$ in the sediments (i, j). Empty markers indicate measurements <LDL. The vertical error bars in all the figures represent one standard deviation (1σ) 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±30 μM)

349   and nearly by 30-fold (~900±300 μM) 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 (~40 μM). 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 μM), 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 ~2.5 times) within the first few hours of resuspension.

359   Ammonium concentration peaks in the experiments were 260±20 (S3) and 130±40 (S4)

360   μM. Following these initial releases, ammonium levels in solution decreased to ~20 μM

361   by the end of the first week to remain stable until the end of the tests.

362   In experiments using surface sediments, $Mn^{2+}_{(aq)}$ concentrations increased

363   immediately on resuspension to three times (~30-70 μM) 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 μM) after about 4 hrs. In the experiments using

19

366 subsurface sediments from S4, $Mn^{2+}_{(aq)}$ concentrations sharply decreased from ~20 μM

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 $Mn^{2+}_{(aq)}$ 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±1

374 to 34±2 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 $Fe^{2+}_{(s)}$ in the

377 surface sediments were 54±3 (S3) and 40±6 (S4) μmol Fe^{2+} 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 $Fe^{2+}_{(s)}$ decreased to around 20% and 10% in the S3 and

380 S4 surface sediment slurries respectively. The initial amounts of acid extractable $Fe^{2+}_{(s)}$

381 in the subsurface sediments (193±8 (S3) and 179±27 (S4) μmol Fe^{2+} g^{-1} respectively)

382 represented more than 90% of the total 0.5 N HCl extractable Fe pool and ~30% of the

383 total Fe. By the end of the tests, the percentages of the $Fe^{2+}_{(s)}$ decreased to ~21% of the

384 total Fe (45±3 (S3) and 36±6 (S4) μmol Fe^{2+} 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
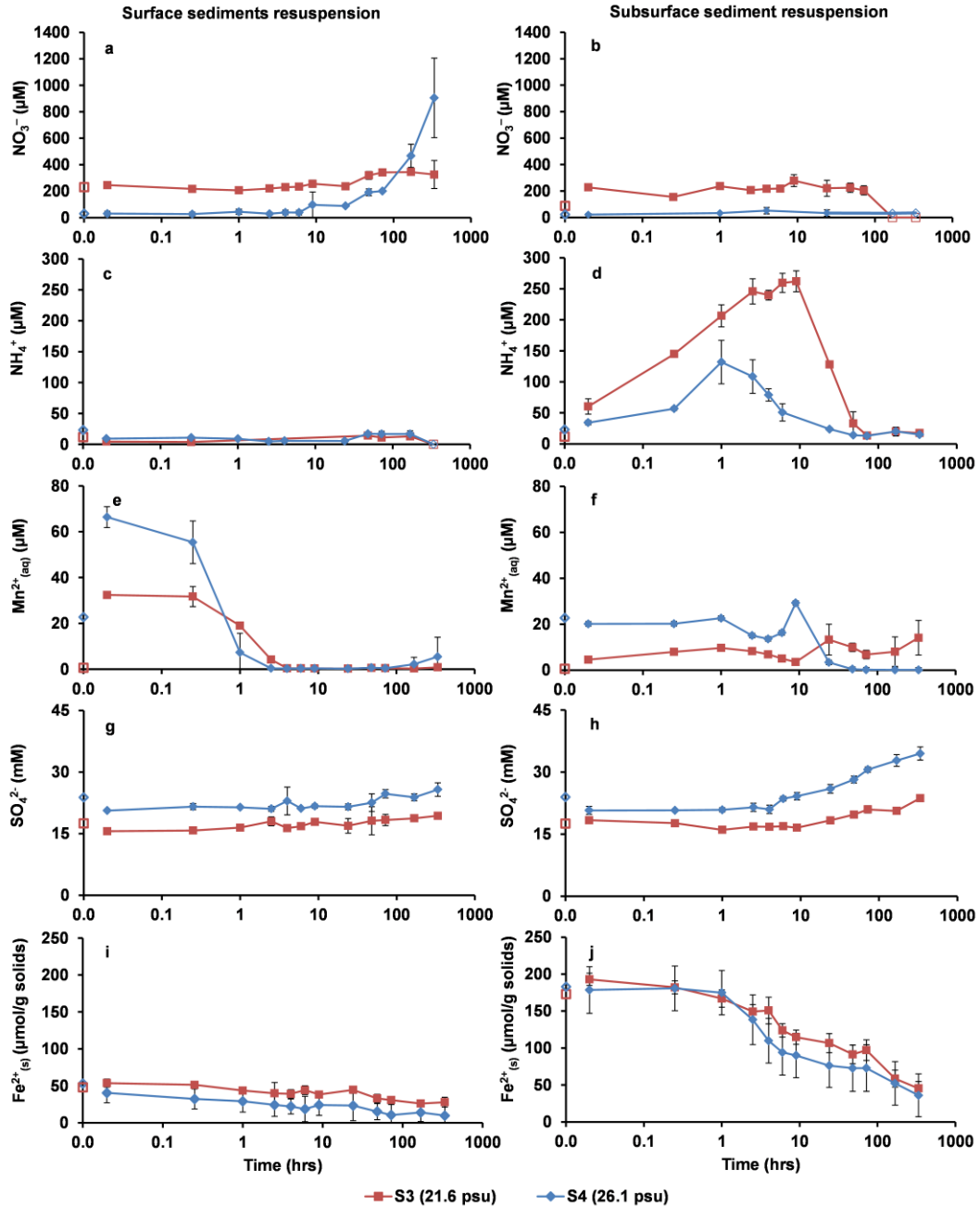
Figure 3: Major element behaviour during resuspension of outer estuary sediments. The red line with squares represents S3 (Paull) and the blue line with diamonds represents S4 (Skeffling). Open symbols on the y-axis indicate the initial concentrations of the major elements in the experiments (river water plus porewater contribution) (a-h) and the initial 0.5 N HCl extractable $Fe^{2+}_{(s)}$ in the sediments (i, j). Empty markers indicate measurements <LDL. The vertical error bars in all the figures represent one standard deviation (1σ) of triplicates.

3.3 Trace metal mobility during sediment resuspension

The release of Zn and Cu during sediment resuspension experiments is shown in Fig.4 and Fig.5. Data of Zn and Cu in solution have been normalised to show μg of metal released per g (dry weight) of sediment used in the experiment, therefore the concentrations have been corrected for moisture content.

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

22

411
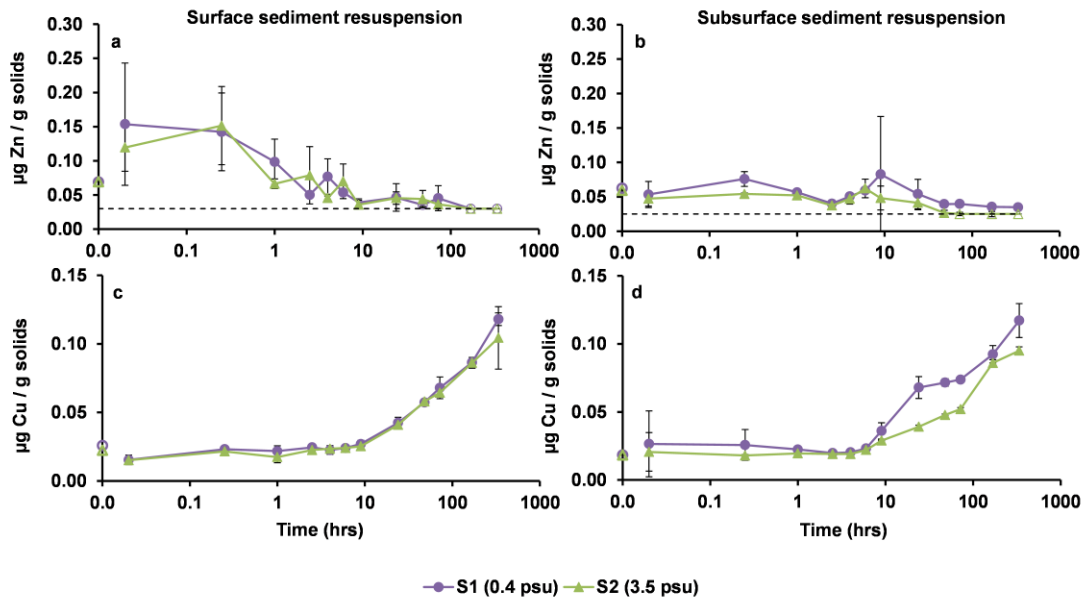
Figure 4: Zinc and copper released to the solution from solids during resuspension experiments using S1 and S2 sediments. Zinc released from surface (a) and subsurface (b) sediments; Cu released from surface (c) and subsurface (d) sediments. Open symbols on the y-axis indicate the initial concentrations in the experiment (river water plus porewater contribution). Error bars in all the figures represent one standard deviation (1σ) of triplicates. Empty markers indicate measurements <LDL and dashed lines indicate the LDL of the ICP-MS analysis.

The resuspension experiments using outer estuary sediments showed a clear release-uptake trend for Zn and Cu. Zinc was immediately released to solution, reaching concentrations 3 to 6 times higher than the initial concentrations in the experiment, and then concentrations rapidly decreased to initial concentration levels (~4.5 µg g^{-1}) (Fig.5a and 5b). The greatest Zn concentrations were observed in experiments with S4 sediments. Similarly, there was an immediate release of Cu to the solution, followed by a rapid decrease (within hours) to below initial concentration levels. The maximum concentrations were ~5-13 µg Cu g^{-1} (Fig.5c and 5d), which were 2 to 6 times the concentrations of Cu prior to the mixing.
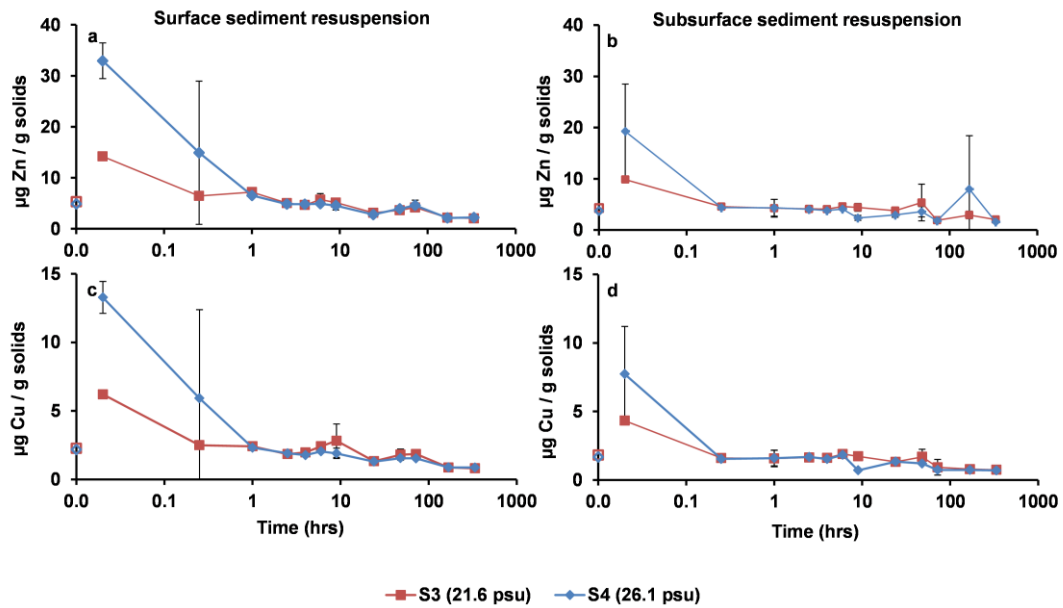
Figure 5: Zinc and copper released to the solution from solids during resuspension experiments using S3 and S4 sediments. Zinc released from surface (a) and subsurface (b) sediments; Cu released from surface (c) and subsurface (d) sediments. Open symbols on the y-axis indicate the initial concentrations in the experiment (river water plus porewater contribution). Error bars in all the figures represent one standard deviation (1σ) of triplicates.

3.4 Changes in metal partitioning during resuspension

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

24

6d) showed similar changes in all the samples; although very little Cu was extracted from S3 and S4 subsurface sediments. In the original sediments, almost all the Cu extracted was associated with the Fe/Mn oxyhydroxides fraction. Upon resuspension, there was a general shift from the Fe/Mn oxyhydroxides fraction to the weak acid-extractable, and the organic matter-sulphide fraction. Copper concentrations for each leachate were similar among samples.
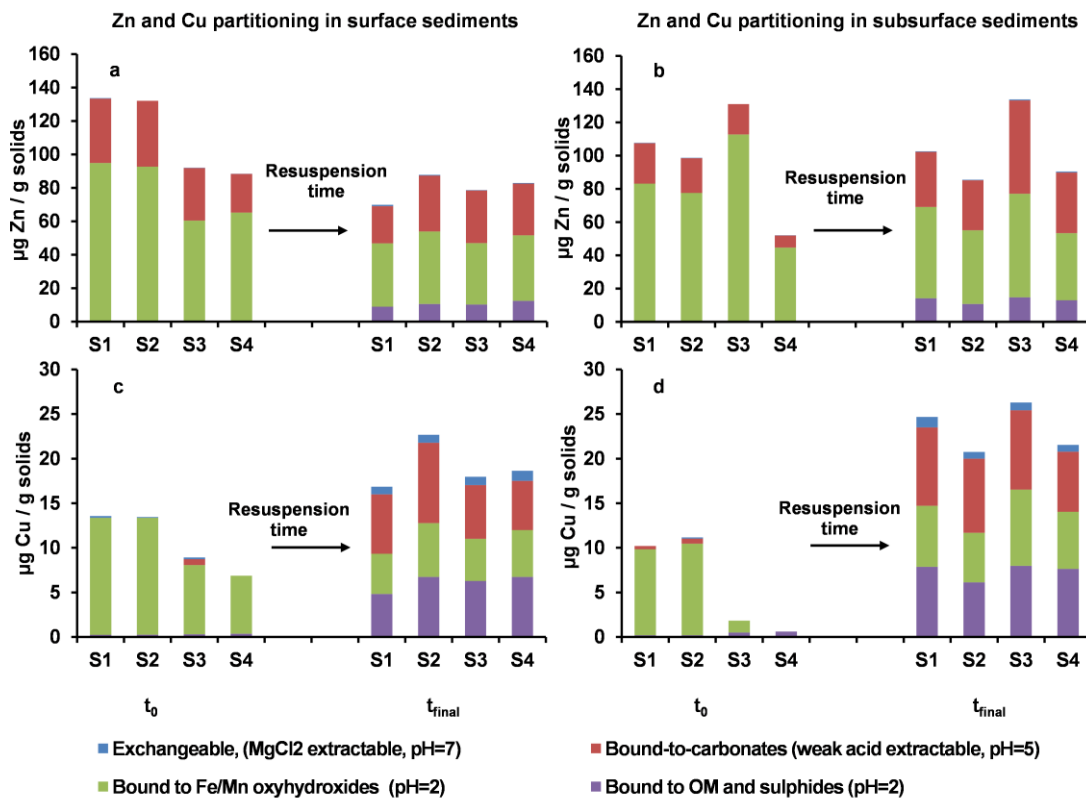
Figure 6: Zinc and copper partitioning changes after estuarine sediment resuspension determined by sequential extractions using Tessier *et al.* (1979) protocol with modifications. The concentration (averaged from triplicates) is expressed in µg of metal in the extractant solution by the mass of solids (dry sediments) used in the extraction. Zinc partitioning in surface (a) and subsurface (b) sediments; and Cu partitioning in surface (c) and subsurface (d) sediments. Sites are ordered according to their location within the salinity gradient and the arrows represent the time of the experiment (2-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 µmol 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 $Fe^{2+}_{(aq)}$ and H_2S reduce 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 MnO_2 with $Fe^{2+}_{(aq)}$ 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 $Fe^{2+}_{(s)}$ in the

504   subsurface outer estuary sediments was ~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.
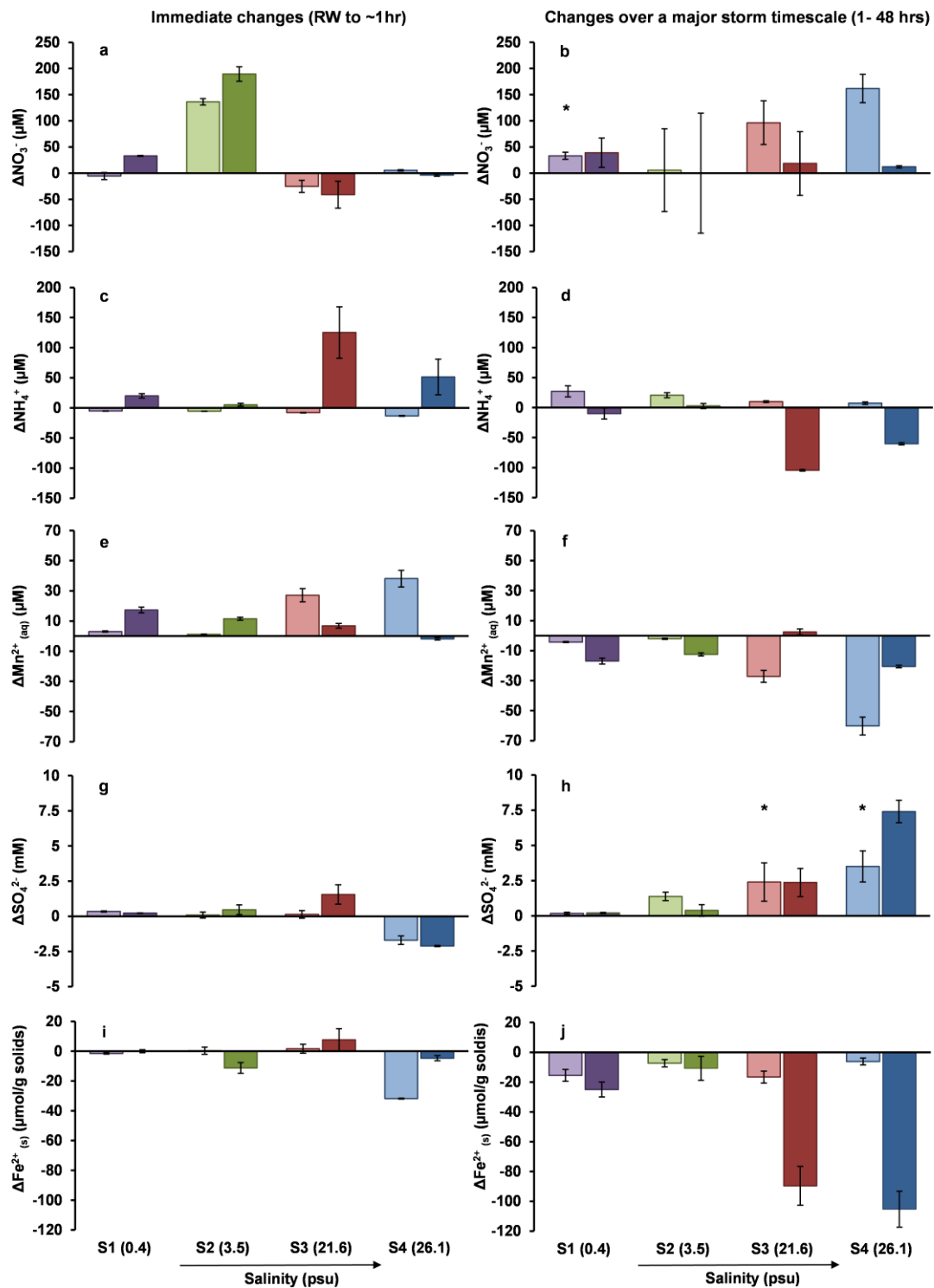
536

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 $Fe^{2+}_{(s)}$ 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 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

30

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 μM) 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 Mn^{2+} in solution.

575 Nitrification and ammonium oxidation to N_2 by Mn oxides could have contributed to

576 the ammonium removal processes. Any $Mn^{2+}_{(aq)}$ 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, $Mn^{2+}_{(aq)}$ 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 $Mn^{2+}_{(aq)}$ 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 $Mn^{2+}_{(aq)}$ 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 $Mn^{2+}_{(aq)}$ 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 $Mn^{2+}_{(aq)}$ 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 $Mn^{2+}_{(aq)}$ decreased to levels below the initial $Mn^{2+}_{(aq)}$ 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 $Mn^{2+}_{(aq)}$. 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 $Fe^{2+}_{(s)}$ 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 $Fe^{2+}_{(s)}$ 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

33

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 extend 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

35

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).
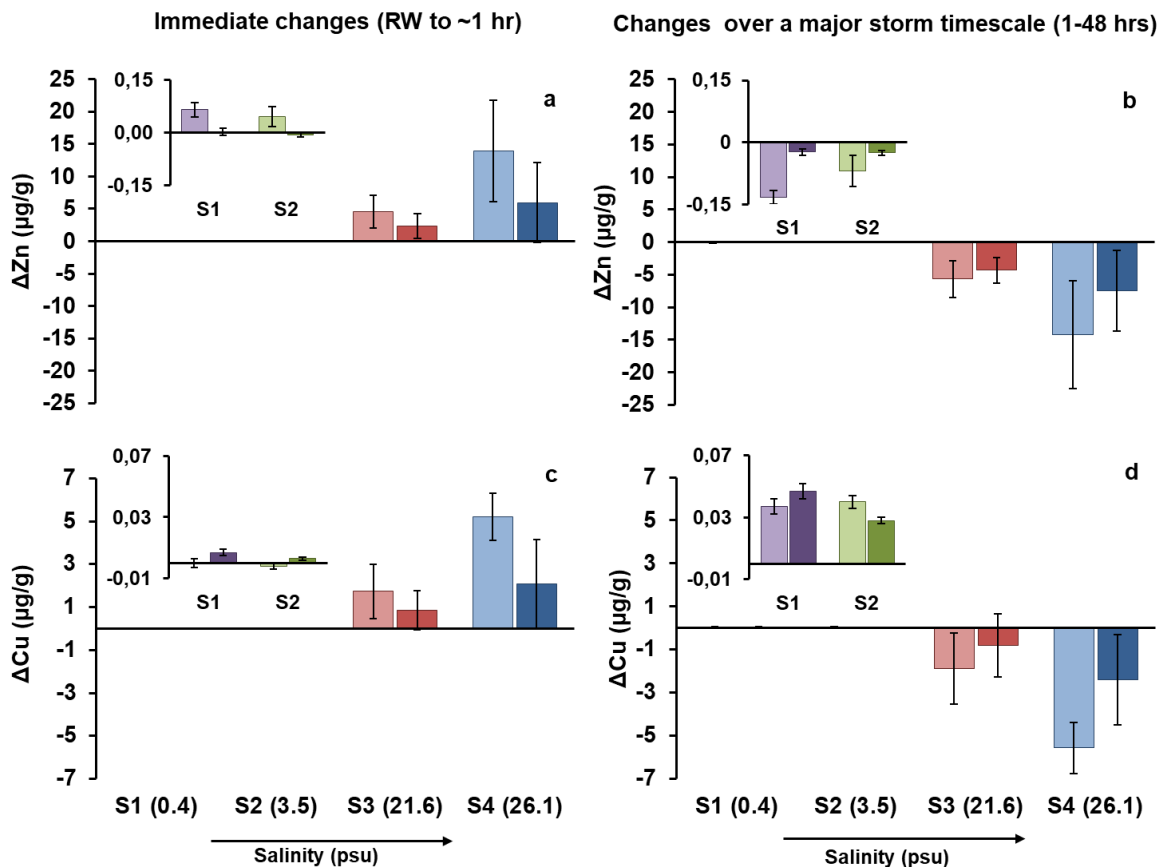
715

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.

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

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

Nitrate (autochthonous or as a product of nitrification processes) was the only major nutrient that seemed to remain in solution for few days in both resuspension 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 ± 10

762 mmol O_2 kg^{-1}, and to 70 ± 40 mmol O_2 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 g L^{-1} for the inner estuary; 4 g

765 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 mmoles/m^2/day in the inner estuary, and from −12.1 to −3.9

776   mmoles/m^2/day in the outer estuary. Ammonium fluxes would increase from −2.0 to 4.6

777   mmoles/m^2/day in the inner estuary, and from −3.9 to 32.3 mmoles/m^2/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

41

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, $Mn^{2+}_{(aq)}$ 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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7. References

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