

Est.
1841

YORK
ST JOHN
UNIVERSITY

Vidal-Durà, Andrea, Burke, Ian T., Stewart, Douglas I. and Mortimer, Robert (2018) Reoxidation of estuarine sediments during simulated resuspension events: Effects on nutrient and trace metal mobilisation. *Estuarine, Coastal and Shelf Science*, 207. pp. 40-55.

Downloaded from: <https://ray.yorks.ac.uk/id/eprint/4895/>

The version presented here may differ from the published version or version of record. If you intend to cite from the work you are advised to consult the publisher's version:
<https://www.sciencedirect.com/science/article/abs/pii/S0272771417308995?via%3Dihub#!>

Research at York St John (RaY) is an institutional repository. It supports the principles of open access by making the research outputs of the University available in digital form. Copyright of the items stored in RaY reside with the authors and/or other copyright owners. Users may access full text items free of charge, and may download a copy for private study or non-commercial research. For further reuse terms, see licence terms governing individual outputs. [Institutional Repositories Policy Statement](#)

RaY

Research at the University of York St John

For more information please contact RaY at
ray@yorks.ac.uk

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

3

4 Andrea Vidal-Durà¹, Ian T. Burke¹, Douglas I. Stewart² and Robert J.G. Mortimer³

5 ¹ School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK.

6 ² School of Civil Engineering, University of Leeds, Leeds, LS2 9JT, UK.

7 ³ School of Animal Rural & Environmental Sciences, Nottingham Trent University, Brackenhurst
8 Campus, Southwell, Nottinghamshire, NG25 0QF, UK

9 ***Correspondence:** Andrea Vidal-Durà, Cohen Laboratories, School of Earth and Environment,
10 University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK

11 andreavidaldura@gmail.com

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).

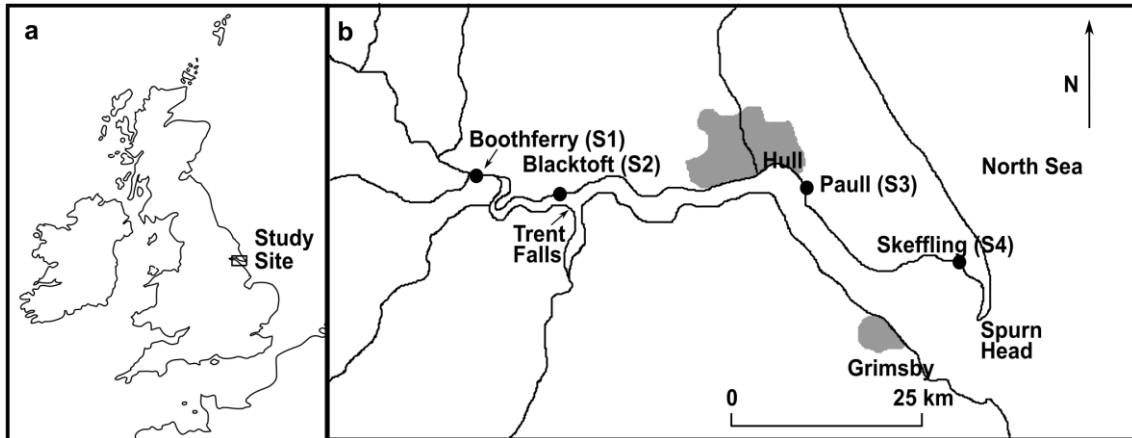
121 In this study sediments from four different sites along the salinity range of the
122 Humber Estuary (UK) were used in order to investigate the impact of sediment
123 resuspension on the redox cycling and transport of the major elements and TMs to the
124 coastal waters. The authors have worked in 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 km² 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 15th 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 HNO₃ 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 Fe²⁺_(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 °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 HNO₃ 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 HNO₃) 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 Fe²⁺_(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 MgCl₂ 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 NH₂OH·HCl in 25% v/v HAC

247 (for the bound to Fe/Mn oxides), and 30% H₂O₂ at pH 2 (with HNO₃) followed by
248 NH₄Ac (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
NO₃⁻ (µM)	266	250	248	<LDL
NH₄⁺ (µM)	7	7	12	23
Mn²⁺ (µM)	1.4	1.0	0.6	23
SO₄²⁻ (mM)	0.8	3.4	16	22
Fe²⁺ (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, 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 (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 ($\mu\text{mol/g}$ 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 ($\mu\text{g/g}$)	656±8	785±8	681±20	654±1	847±6	969±3	758±14	732±11
Zn ($\mu\text{g/g}$)	132±3	149±1	139±4	129±4	161±2	199±13	174±1	167±6
Cu ($\mu\text{g/g}$)	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 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).

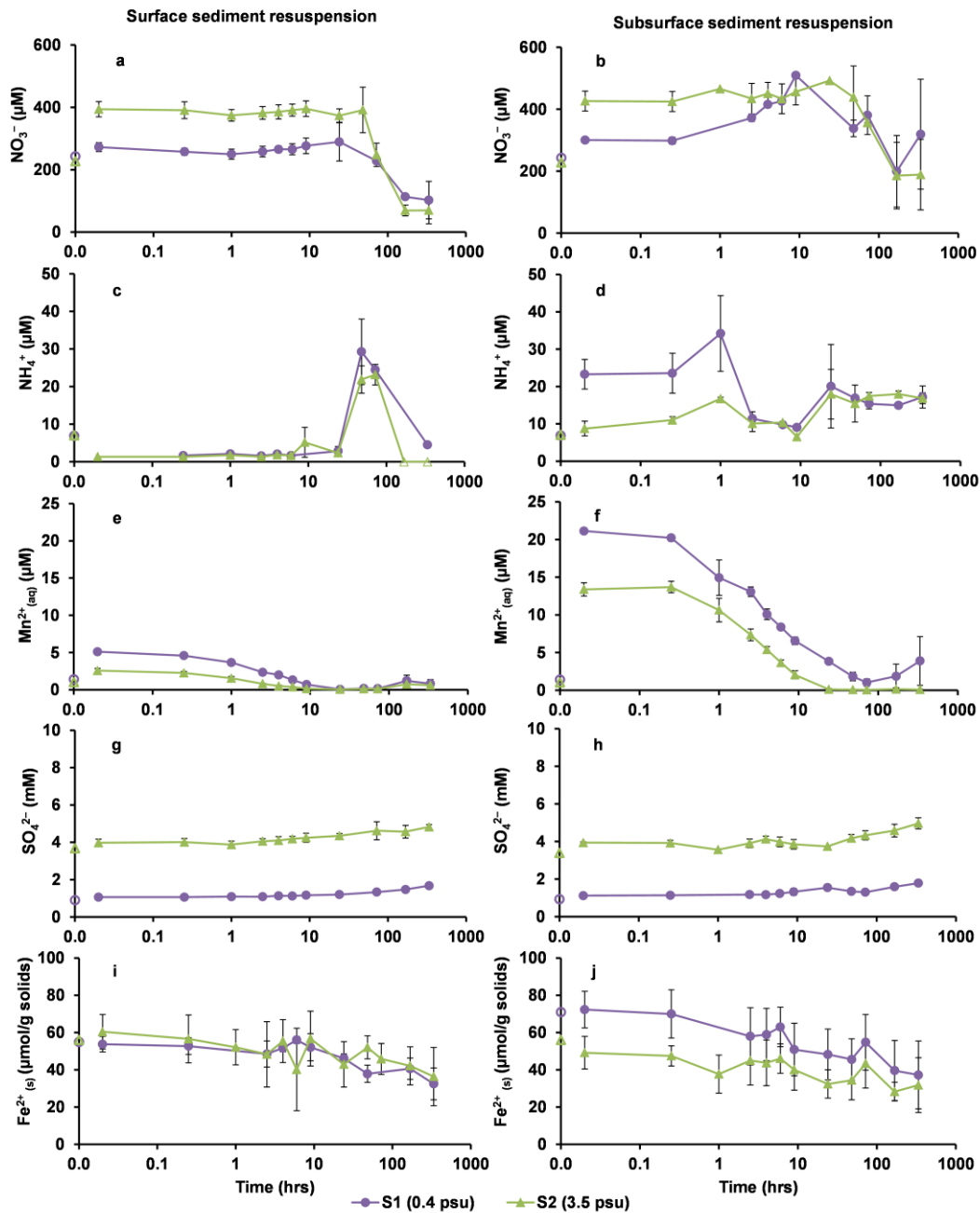
310 Ammonium concentrations in the experiments carried out with surface
311 sediments decreased immediately after resuspension started (Fig.2c) and remained close
312 to detection levels until 48 hrs, when concentrations transiently increased to around 20-
313 30 μM before decreasing to low concentrations 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

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 (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 ($190 \pm 30 \mu\text{M}$)
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.

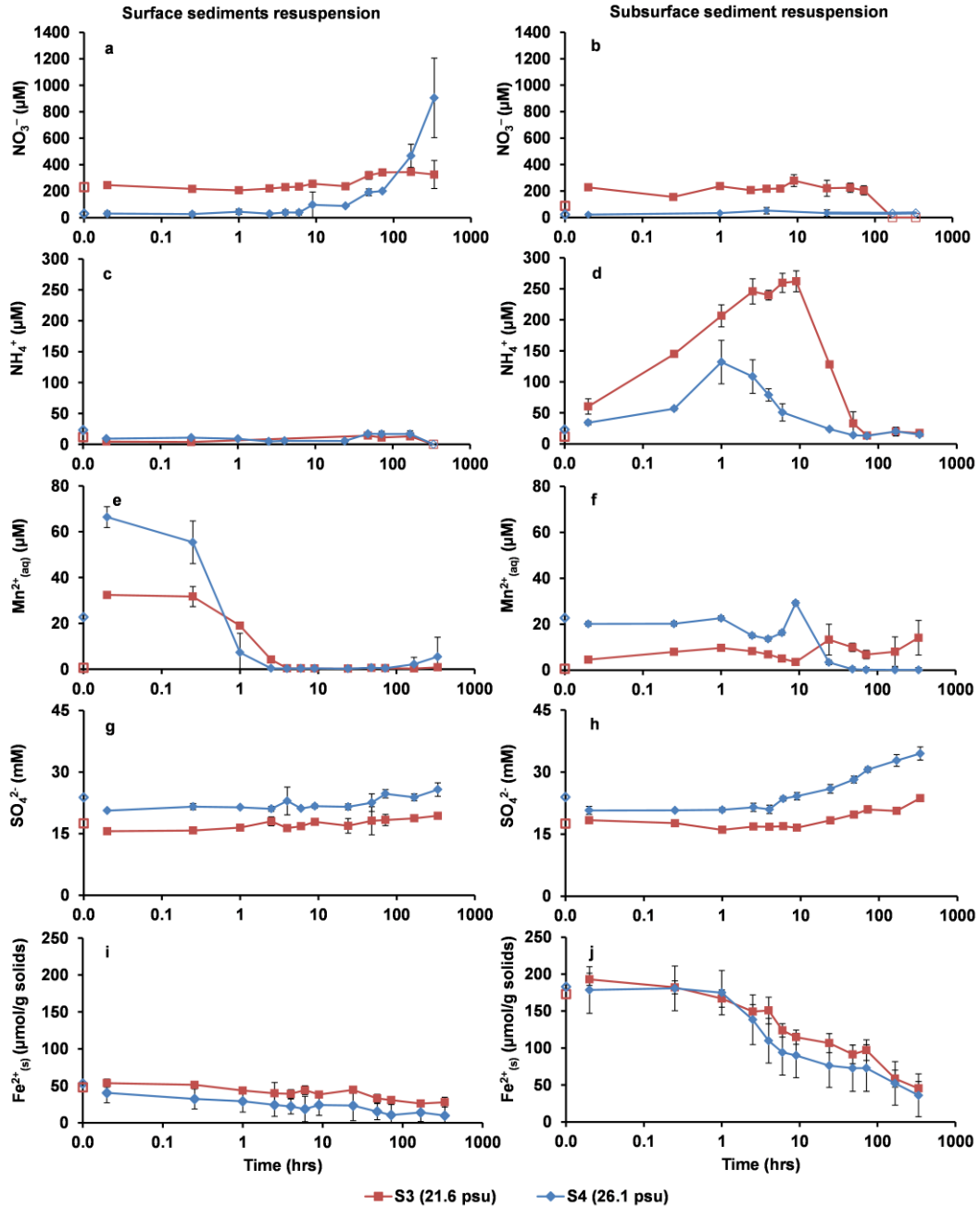
354 Ammonium concentrations in experiments using outer estuary surface sediments
355 were initially low ($< 20 \mu\text{M}$), similar to the concentrations in the original river water,
356 and remained so until the end of the tests (Fig.3c). There was a very different trend in
357 ammonium concentrations in the experiments using subsurface sediments (Fig.3d),
358 which increased significantly (by ~ 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 $\sim 20 \mu\text{M}$
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 ± 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 ± 3 (S3) and 40 ± 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 ± 8 (S3) and 179 ± 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 ± 3 (S3) and 36 ± 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.



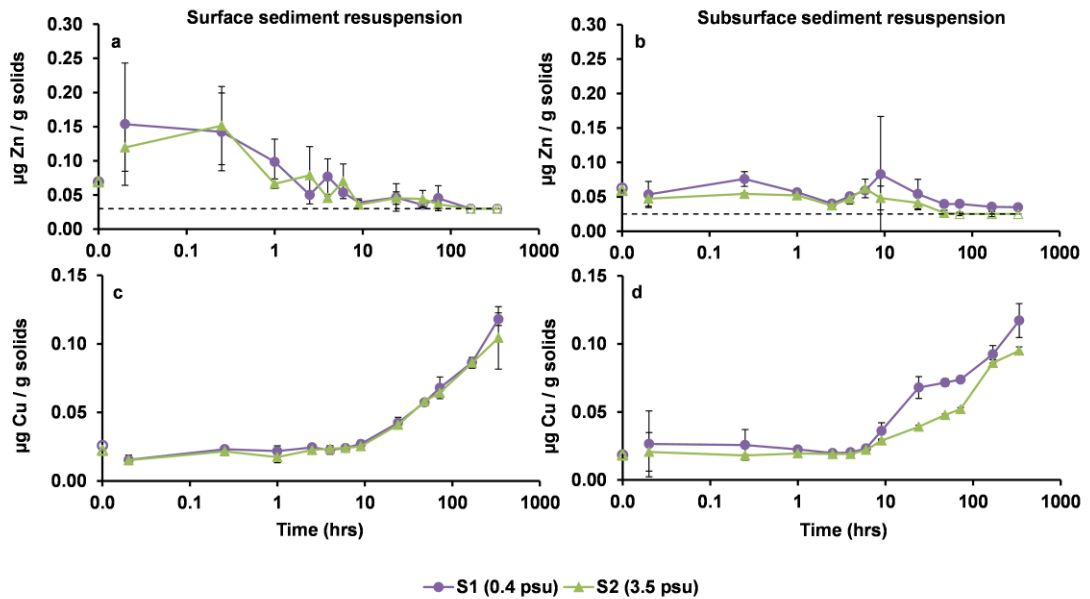
387

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 (1σ) 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 μg of
398 metal released per g (dry weight) of sediment used in the experiment, therefore the
399 concentrations have been corrected for moisture content.

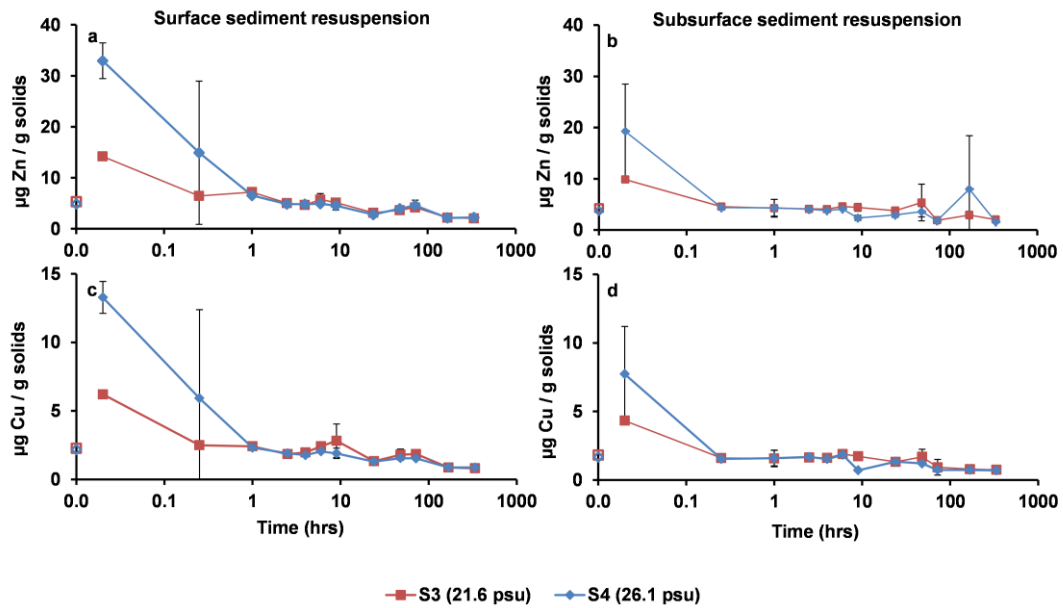
400 In the experiments carried out with inner estuarine sediments, the pattern of Zn
401 behaviour depended on the sediment depth. In the surface sediment experiments, Zn
402 concentrations increased immediately upon resuspension to values 2-3 times the initial
403 concentrations in the experiments (0.15 ± 0.09 (S1) and 0.12 ± 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 ~ 10 hrs of resuspension,
409 reaching concentrations $\sim 3-4$ times their initial values (about 0.12 ± 0.02 (S1) and
410 0.1 ± 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 (1σ) 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.



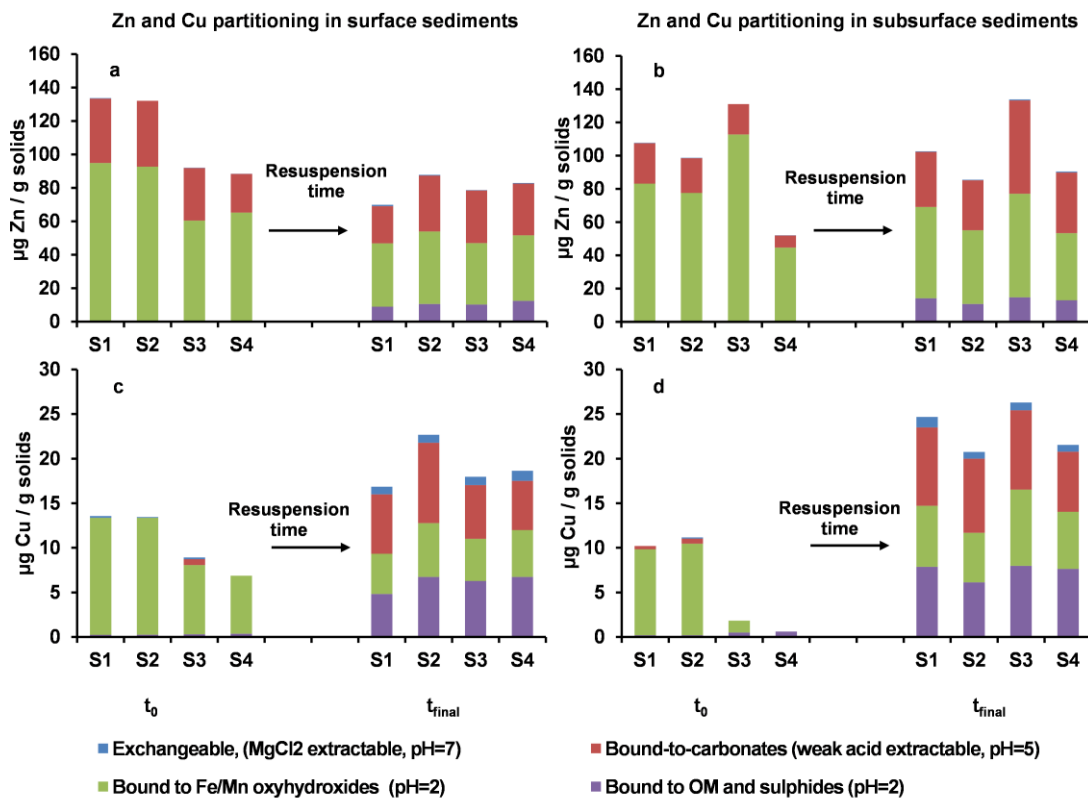
428

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 (1σ) 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 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 $\text{Fe}^{2+}_{(\text{aq})}$ 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 ~ 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.

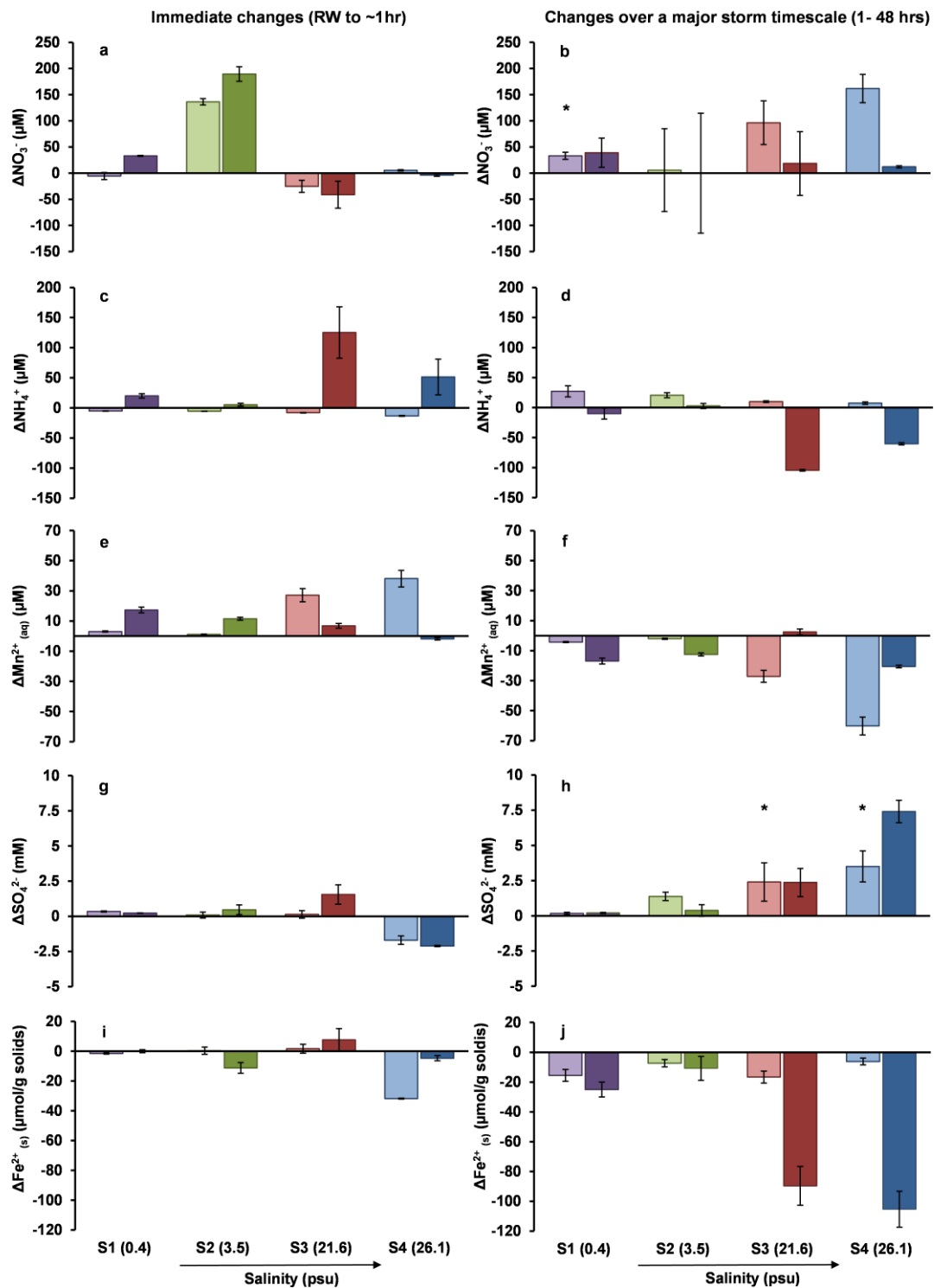
507 Furthermore, the mudflats of the outer Humber estuary accumulated finer
508 materials and they appeared to have a slightly higher TOC content than the inner estuary

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 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 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 $\text{Mn}^{2+}_{(\text{aq})}$ 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

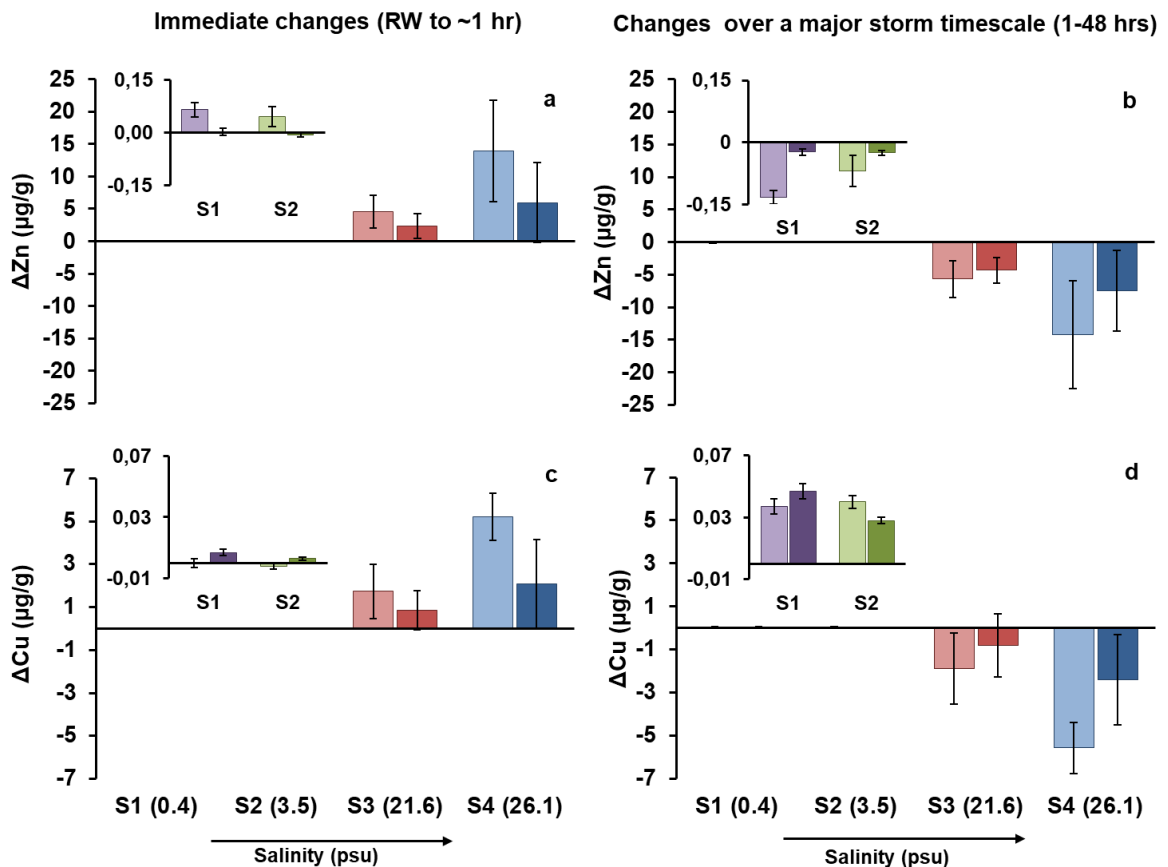
660 they aggregate to larger particles) may have passed the filters used, and therefore any
661 metal associated would have been deemed as solutes. Nevertheless, the releases of Zn
662 and Cu were generally reversed to a considerable extent by the time of a major storm
663 (Fig.8b and 8d) as a result, 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 ± 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 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 mmol/m²/day in the inner estuary, and from -12.1 to -3.9
776 mmol/m²/day in the outer estuary. Ammonium fluxes would increase from -2.0 to 4.6
777 mmol/m²/day in the inner estuary, and from -3.9 to 32.3 mmol/m²/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, $Mn^{2+}_{(aq)}$ 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.

832 **6. Acknowledgements**

833 The authors acknowledge funding from a University of Leeds Doctoral Training
834 Award to A. Vidal-Durà. We are grateful to S. Reid, A. Stockdale, for technical support
835 with the ICP-MS analysis, AA3 autoanalyser respectively; and to A. Connelly, F. Keay
836 and D. Ashley (all from University of Leeds) for their help in the column-switching
837 setting up for saline water analysis by IC. We also thank S. Poulton and his team for the
838 iron extraction training, and the technical support from L. Neve in the XRF and XRD
839 analysis, and from G. Keevil and R. Thomas in the grain size analysis.

840 **7. References**

- 841 [1] Abril, G., Riou, S. A., Etcheber, H., Frankignoulle, M., de Wit, R., &
842 Middelburg, J. J. (2000). Transient, tidal time-scale, nitrogen transformations in an
843 estuarine turbidity maximum-fluid mud system (The Gironde, south-west France).
844 *Estuarine Coastal and Shelf Science*, 50(5), 703-715. doi: 10.1006/ecss.1999.0598
- 845 [2] Allen, H. E., Fu, G. M., & Deng, B. L. (1993). Analysis of acid-volatile sulfide
846 (AVS) and simultaneously extracted metals (SEM) for the estimation of potential
847 toxicity in aquatic sediments. *Environmental Toxicology and Chemistry*, 12(8), 1441-
848 1453. doi: 10.1897/1552-8618(1993)12[1441:aoasaa]2.0.co;2
- 849 [3] Aller, R. C. (1994). Bioturbation and remineralization of sedimentary organic-
850 matter - effects of redox oscillation. *Chemical Geology*, 114(3-4), 331-345. doi:
851 10.1016/0009-2541(94)90062-0
- 852 [4] Andrews, J. E., Samways, G., & Shimmield, G. B. (2008). Historical storage
853 budgets of organic carbon, nutrient and contaminant elements in saltmarsh sediments:
854 Biogeochemical context for managed realignment, Humber Estuary, UK. *Science of*
855 *The Total Environment*, 405(1-3), 1-13. doi: 10.1016/j.scitotenv.2008.07.044
- 856 [5] Anju, M., & Banerjee, D. K. (2010). Comparison of two sequential extraction
857 procedures for heavy metal partitioning in mine tailings. *Chemosphere*, 78(11), 1393-
858 1402. doi: 10.1016/j.chemosphere.2009.12.064
- 859 [6] Anschutz, P., Sundby, B., Lefrancois, L., Luther, G. W., & Mucci, A. (2000).
860 Interactions between metal oxides and species of nitrogen and iodine in bioturbated
861 marine sediments. *Geochimica et Cosmochimica Acta*, 64(16), 2751-2763. doi:
862 10.1016/s0016-7037(00)00400-2

- 863 [7] Barnes, J., & Owens, N. J. P. (1998). Denitrification and nitrous oxide
864 concentrations in the Humber estuary, UK, and adjacent coastal zones. *Marine Pollution*
865 *Bulletin*, 37(3-7), 247-260.
- 866 [8] Berner, R. A. (1980). *Early diagenesis: A theoretical approach*. New York:
867 Princeton University Press.
- 868 [9] Blanchard, G. F., Paterson, D. M., Stal, L. J., Richard, P., Galois, R., Huet, V.,
869 Kelly, J., Honeywill, C., de Brouwer, J., Dyer, K., Christie, M., & Seguignes, M.
870 (2000). The effect of geomorphological structures on potential biostabilisation by
871 microphytobenthos on intertidal mudflats. *Continental Shelf Research*, 20(10), 1243-
872 1256. doi: [https://doi.org/10.1016/S0278-4343\(00\)00021-2](https://doi.org/10.1016/S0278-4343(00)00021-2)
- 873 [10] Boyer, E. W., & Howarth, R. W. (2002). *The Nitrogen Cycle at Regional to*
874 *Global Scales. Report of the International SCOPE Nitrogen Project (Vol. 57/58)*.
875 Dordrecht, Netherlands: Springer.
- 876 [11] Bruno, P., Caselli, M., de Gennaro, G., De Tommaso, B., Lastella, G., &
877 Mastrolitti, S. (2003). Determination of nutrients in the presence of high chloride
878 concentrations by column-switching ion chromatography. *Journal of Chromatography*
879 *A*, 1003(1-2), 133-141. doi: 10.1016/s0021-9673(03)00785-4
- 880 [12] Burdige, D. J. (1993). The biogeochemistry of manganese and iron reduction in
881 marine-sediments. *Earth-Science Reviews*, 35(3), 249-284. doi: 10.1016/0012-
882 8252(93)90040-e
- 883 [13] Burke, I. T., Boothman, C., Lloyd, J. R., Mortimer, R. J. G., Livens, F. R., &
884 Morris, K. (2005). Effects of Progressive Anoxia on the Solubility of Technetium in
885 Sediments. *Environmental Science & Technology*, 39, 4109-4116.
- 886 [14] Caetano, M., Madureira, M. J., & Vale, C. (2003). Metal remobilisation during
887 resuspension of anoxic contaminated sediment: short-term laboratory study. *Water Air*
888 *and Soil Pollution*, 143(1-4), 23-40. doi: 10.1023/a:1022877120813
- 889 [15] Calmano, W., Hong, J., & Forstner, U. (1993). Binding and mobilization of
890 heavy-metals in contaminated sediments affected by pH and redox potential. *Water*
891 *Science and Technology*, 28(8-9), 223-235. doi: 10.15480/882.450
- 892 [16] Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., & Berner, R. A.
893 (1986). The use of chromium reduction in the analysis of reduced inorganic sulfur in
894 sediments and shales. *Chemical Geology*, 54(1-2), 149-155. doi: 10.1016/0009-
895 2541(86)90078-1
- 896 [17] Canfield, D. E., Kristensen, E., & Thamdrup, B. (2005). *Aquatic*
897 *Geomicrobiology (Vol. 48)*. London: Elsevier Academic Press.
- 898 [18] Canfield, D. E., & Thamdrup, B. (2009). Towards a consistent classification
899 scheme for geochemical environments, or, why we wish the term 'suboxic' would go
900 away. *Geobiology*, 7(4), 385-392. doi: 10.1111/j.1472-4669.2009.00214.x

- 901 [19] Canfield, D. E., Glazer, A. N., & Falkowski, P. G. (2010). The Evolution and
902 Future of Earth's Nitrogen Cycle. *Science*, 330(6001), 192-196. doi:
903 10.1126/science.1186120
- 904 [20] Cantwell, M. G., Burgess, R. M., & Kester, D. R. (2002). Release and phase
905 partitioning of metals from anoxic estuarine sediments during periods of simulated
906 resuspension. *Environmental Science & Technology*, 36(24), 5328-5334. doi:
907 10.1021/es0115058
- 908 [21] Cave, R. R., Andrews, J. E., Jickells, T., & Coombes, E. G. (2005). A review of
909 sediment contamination by trace metals in the Humber catchment and estuary, and the
910 implications for future estuary water quality. *Estuarine, Coastal and Shelf Science*,
911 62(3), 547-557. doi: 10.1016/j.ecss.2004.09.017
- 912 [22] Christensen, J. H., Hewitson, B., Busuioc, A., Chen, A., Gao, X., Held, I., Jones,
913 R., Kolli, R. K., Kwon, W.-T., Laprise, R., Magaña Rueda, V., Mearns, L., Menéndez,
914 C. G., Räisänen, J., Rinke, A., Sarr, A., & Whetton, P. (2007). Regional Climate
915 Projections. In S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt,
916 M. Tignor & H.L. Miller (Eds.), *Climate Change 2007: The Physical Science Basis*.
917 Contribution of Working Group I to the Fourth Assessment Report of the
918 Intergovernmental Panel on Climate Change (pp. 847-940). Cambridge, United
919 Kingdom and New York, NY, USA: Cambridge University Press.
- 920 [23] Couceiro, F., Fones, G. R., Thompson, C. E. L., Statham, P. J., Sivyer, D. B.,
921 Parker, R., Kelly-Gerreyn, B. A., & Amos, C. L. (2013). Impact of resuspension of
922 cohesive sediments at the Oyster Grounds (North Sea) on nutrient exchange across the
923 sediment-water interface. *Biogeochemistry*, 113(1-3), 37-52. doi: 10.1007/s10533-012-
924 9710-7
- 925 [24] Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Hicks, M. B., Mayr,
926 S. M., & Redmond, M. S. (1990). Toxicity of cadmium in sediments the role of acid
927 volatile sulfide. *Environmental Toxicology and Chemistry*, 9(12), 1487-1502. doi:
928 10.1002/etc.5620091208
- 929 [25] Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F. M. G., &
930 Verloo, M. G. (2008). Effect of salinity on heavy metal mobility and availability in
931 intertidal sediments of the Scheldt estuary. *Estuarine Coastal and Shelf Science*, 77(4),
932 589-602. doi: 10.1016/j.ecss.2007.10.017
- 933 [26] Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. M. G.
934 (2009). Trace metal behaviour in estuarine and riverine floodplain soils and sediments:
935 A review. *Science of The Total Environment*, 407(13), 3972-3985. doi:
936 10.1016/j.scitotenv.2008.07.025
- 937 [27] EASAC (2013). Trends in extreme weather events in Europe: implications for
938 national and European Union adaptation strategies (EASAC policy report 22 ed.):
939 EASAC. Retrieved from
940 [http://www.easac.eu/fileadmin/PDF_s/reports_statements/Easac_Report_Extreme_Weat](http://www.easac.eu/fileadmin/PDF_s/reports_statements/Easac_Report_Extreme_Weather_Events.pdf)
941 [her_Events.pdf](http://www.easac.eu/fileadmin/PDF_s/reports_statements/Easac_Report_Extreme_Weather_Events.pdf)

- 942 [28] Eggleton, J., & Thomas, K. V. (2004). A review of factors affecting the release
943 and bioavailability of contaminants during sediment disturbance events. *Environment*
944 *International*, 30(7), 973-980. doi: 10.1016/j.envint.2004.03.001
- 945 [29] Fang, T., Li, X., & Zhang, G. (2005). Acid volatile sulfide and simultaneously
946 extracted metals in the sediment cores of the Pearl River Estuary, South China.
947 *Ecotoxicology and Environmental Safety*, 61(3), 420-431. doi:
948 <http://dx.doi.org/10.1016/j.ecoenv.2004.10.004>
- 949 [30] Fossing, H., & Jørgensen, B. B. (1989). Measurement of bacterial sulfate
950 reduction in sediments - evaluation of a single-step chromium reduction method.
951 *Biogeochemistry*, 8(3), 205-222. doi: 10.1007/BF00002889
- 952 [31] Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G.
953 R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., & Maynard, V. (1979). Early
954 oxidation of organic-matter in pelagic sediments of the eastern equatorial atlantic -
955 suboxic diagenesis. *Geochimica et Cosmochimica Acta*, 43(7), 1075-1090. doi:
956 10.1016/0016-7037(79)90095-4
- 957 [32] Gunnars, A., Blomqvist, S., Johansson, P., & Andersson, C. (2002). Formation
958 of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with
959 incorporation of phosphate and calcium. *Geochimica et Cosmochimica Acta*, 66(5),
960 745-758. doi: 10.1016/s0016-7037(01)00818-3
- 961 [33] Gerringa, L. J. A., de Baar, H. J. W., Nolting, R. F., & Paucot, H. (2001). The
962 influence of salinity on the solubility of Zn and Cd sulphides in the Scheldt estuary.
963 *Journal of Sea Research*, 46(3-4), 201-211. doi: 10.1016/s1385-1101(01)00081-8
- 964 [34] Gleyzes, C., Tellier, S., & Astruc, M. (2002). Fractionation studies of trace
965 elements in contaminated soils and sediments: a review of sequential extraction
966 procedures. *Trac-Trends in Analytical Chemistry*, 21(6-7), 451-467. doi:
967 10.1016/s0165-9936(02)00603-9
- 968 [35] Henrichs, S. M. (1992). Early diagenesis of organic matter in marine sediments:
969 progress and perplexity. *Marine Chemistry*, 39(1), 119-149. doi: 10.1016/0304-
970 4203(92)90098-U
- 971 [36] Hirst, J. M., & Aston, S. R. (1983). Behavior of copper, zinc, iron and
972 manganese during experimental resuspension and reoxidation of polluted anoxic
973 sediments. *Estuarine Coastal and Shelf Science*, 16(5), 549-558. doi: 10.1016/0272-
974 7714(83)90085-9
- 975 [37] Howarth, R. W., Billen, G., Swaney, D., Townsend, A., Jaworsky, N., Lajtha, K.,
976 Downing, J. A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov,
977 V., Murdoch P., and Zhao-Liang Zhu. (1996). Regional Nitrogen budgets and riverine
978 N & P fluxes for the drainages to the North Atlantic Ocean: natural and human
979 influences. *Biogeochemistry*, 35, 75-139.

- 980 [38] Huerta-Diaz, M. A., & Morse, J. W. (1990). A quantitative method for
981 determination of trace metal concentrations in sedimentary pyrite. *Marine Chemistry*,
982 29(2-3), 119-144. doi: 10.1016/0304-4203(90)90009-2
- 983 [39] Hulth, S., Aller, R. C., & Gilbert, F. (1999). Coupled anoxic nitrification
984 manganese reduction in marine sediments. *Geochimica et Cosmochimica Acta*, 63(1),
985 49-66. doi: 10.1016/s0016-7037(98)00285-3
- 986 [40] IPCC. (2013). Summary for policymakers. In T.F. Stocker, D. Qin, G.K.
987 Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex & P.M.
988 Midgley (Eds.), *Climate Change 2013: the Physical Science Basis*. Contribution of
989 Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on
990 Climate Change. United Kingdom and New York, NY, USA: Cambridge University
991 Press.
- 992 [41] Jerez Vegueria, S. F., Godoy, J. M., de Campos, R. C., & Goncalves, R. A.
993 (2013). Trace element determination in seawater by ICP-MS using online, offline and
994 bath procedures of preconcentration and matrix elimination. *Microchemical Journal*,
995 106, 121-128. doi: 10.1016/j.microc.2012.05.032
- 996 [42] Jones, P. D., & Reid, P. A. (2001). Assessing future changes in extreme
997 precipitation over Britain using regional climate model integrations. *International*
998 *Journal of Climatology*, 21(11), 1337-1356. doi: 10.1002/joc.677
- 999 [43] Jørgensen, B. B. (1977). Sulfur cycle of a coastal marine sediment (Limfjorden,
1000 Denmark). *Limnology and Oceanography*, 22(5), 814-832. doi:
1001 10.4319/lo.1977.22.5.0814
- 1002 [44] Jørgensen, B. B. (1982). Mineralization of organic-matter in the sea bed - the
1003 role of sulfate reduction. *Nature*, 296(5858), 643-645. doi: 10.1038/296643a0
- 1004 [45] Joye, S. B., & Hollibaugh, J. T. (1995). Influence of sulfide inhibition of
1005 nitrification on nitrogen regeneration in sediments. *Science*, 270(5236), 623-625. doi:
1006 10.1126/science.270.5236.623
- 1007 [46] Kalnejais, L. H., Martin, W. R., & Bothner, M. H. (2010). The release of
1008 dissolved nutrients and metals from coastal sediments due to resuspension. *Marine*
1009 *Chemistry*, 121(1-4), 224-235. doi: 10.1016/j.marchem.2010.05.002
- 1010 [47] Lamb, H., & Frydendahl, K. U. (1991). *Historic Storms of the North Sea, British*
1011 *Isles and Northwest Europe*: Cambridge University Press.
- 1012 [48] Lansdown, K., Heppell, C. M., Dossena, M., Ullah, S., Heathwaite, A. L.,
1013 Binley, A., Zhang, H., & Trimmer, M. (2014). Fine-Scale in Situ Measurement of
1014 Riverbed Nitrate Production and Consumption in an Armored Permeable Riverbed.
1015 *Environmental Science & Technology*, 48(8), 4425-4434. doi: 10.1021/es4056005
- 1016 [49] Lansdown, K., Heppell, C. M., Trimmer, M., Binley, A., Heathwaite, A. L.,
1017 Byrne, P., & Zhang, H. (2015). The interplay between transport and reaction rates as
1018 controls on nitrate attenuation in permeable, streambed sediments. *Journal of*
1019 *Geophysical Research-Biogeosciences*, 120(6), 1093-1109. doi: 10.1002/2014jg002874

- 1020 [50] Lee, S. V., & Cundy, A. B. (2001). Heavy Metal Contamination and Mixing
1021 Processes in Sediments from the Humber Estuary, Eastern England. *Estuarine, Coastal*
1022 *and Shelf Science*, 53(5), 619-636. doi: 10.1006/ecss.2000.0713
- 1023 [51] Lovley, D. R., & Phillips, E. J. P. (1986). *Appl. Environ. Microbiol.*, 52, 751.
- 1024 [52] Lovley, D. R., & Phillips, E. J. P. (1987). Rapid assay for microbially reducible
1025 ferric iron in aquatic sediments. *Applied and Environmental Microbiology*, 53(7), 1536-
1026 1540.
- 1027 [53] Luther, G. W., Sundby, B., Lewis, B. L., Brendel, P. J., & Silverberg, N. (1997).
1028 Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen.
1029 *Geochimica et Cosmochimica Acta*, 61(19), 4043-4052. doi: 10.1016/s0016-
1030 7037(97)00239-1
- 1031 [54] Martin, J. M., Nirel, P., & Thomas, A. J. (1987). Sequential extraction
1032 techniques - promises and problems. *Marine Chemistry*, 22(2-4), 313-341. doi:
1033 10.1016/0304-4203(87)90017-x
- 1034 [55] Martino, M., Turner, A., Nimmo, A., & Millward, G. E. (2002). Resuspension,
1035 reactivity and recycling of trace metals in the Mersey Estuary, UK. *Marine Chemistry*,
1036 77(2-3), 171-186. doi: 10.1016/s0304-4203(01)00086-x
- 1037 [56] Mayer, L. M. (1994). Surface-area control of organic-carbon accumulation in
1038 continental-shelf sediments. *Geochimica et Cosmochimica Acta*, 58(4), 1271-1284. doi:
1039 10.1016/0016-7037(94)90381-6
- 1040 [57] Middelburg, J. J., & Herman, P. M. J. (2007). Organic matter processing in tidal
1041 estuaries. *Marine Chemistry*, 106(1-2), 127-147. doi: 10.1016/j.marchem.2006.02.007
- 1042 [58] Middelburg, J. J., & Levin, L. A. (2009). Coastal hypoxia and sediment
1043 biogeochemistry. *Biogeosciences*, 6(7), 1273-1293. doi: 10.5194/bg-6-1273-2009
- 1044 [59] Middleton, R., & Grant, A. (1990). Heavy Metals in the Humber Estuary:
1045 Scrobicularia Clay as a Pre-industrial Datum. *Proceedings of the Yorkshire Geological*
1046 *Society*, 48(pàg. 75-80).
- 1047 [60] Millward, G., & Liu, Y. (2003). Modelling metal desorption kinetics in
1048 estuaries. *Sci Total Environ*, 314-316, 613-623. doi: 10.1016/s0048-9697(03)00077-9
- 1049 [61] Millward, G. E., & Glegg, G. A. (1997). Fluxes and Retention of Trace Metals
1050 in the Humber Estuary. *Estuarine, Coastal and Shelf Science*, 44, 97-105.
- 1051 [62] Morgan, B., Rate, A. W., & Burton, E. D. (2012). Water chemistry and nutrient
1052 release during the resuspension of FeS-rich sediments in a eutrophic estuarine system.
1053 *Science of The Total Environment*, 432, 47-56. doi: 10.1016/j.scitotenv.2012.05.065
- 1054 [63] Morin, J., & Morse, J. W. (1999). Ammonium release from resuspended
1055 sediments in the Laguna Madre estuary. *Marine Chemistry*, 65(1-2), 97-110. doi:
1056 10.1016/s0304-4203(99)00013-4

- 1057 [64] Morris, A. W., Bale, A. J., Howland, R.J.M., Millward, G.E., Ackroyd, R.,
1058 Loring H. and Rantala, R.T.T. (1986). Sediment mobility and its contribution to trace
1059 metal cycling and retention in a macrotidal estuary. *Water Science and Technology*, 18,
1060 111-119.
- 1061 [65] Mortimer, R. J. G., Krom, M. D., Watson, P. G., Frickers, P. E., Davey, J. T., &
1062 Clifton, R. J. (1998). Sediment-water exchange of nutrients in the intertidal zone of the
1063 Humber estuary, UK. *Marine Pollution Bulletin*, 37(3-7), 261-279. doi: 10.1016/s0025-
1064 326x(99)00053-3
- 1065 [66] Mortimer, R. J. G., Davey, J. T., Krom, M. D., Watson, P. G., Frickers, P. E., &
1066 Clifton, R. J. (1999). The Effect of Macrofauna on Porewater Profiles and Nutrient
1067 Fluxes in the Intertidal Zone of the Humber Estuary. *Estuarine, Coastal and Shelf*
1068 *Science*, 48(6), 683-699. doi: <https://doi.org/10.1006/ecss.1999.0479>
- 1069 [67] Murray, J. W., Codispoti, L. A., & Friederich, G. E. (1995). Oxidation-reduction
1070 environments - the suboxic zone in the black-sea. *Aquatic Chemistry: Interfacial and*
1071 *Interspecies Processes*, 244, 157-176. doi: 10.1021/ba-1995-0244.ch007
- 1072 [68] Nedwell, D. B., Jickells, T. D., Trimmer, M., & Sanders, R. (1999). Nutrients in
1073 estuaries. In D. B. Nedwell & D. G. Raffaelli (Eds.), *Advances in Ecological Research*,
1074 *Estuaries* (Vol. 29, pp. 43-92): Academic Press.
- 1075 [69] NRA. (1995). *Sea Vigil Water Quality Monitoring: the Humber Estuary 1992-*
1076 *1993*. Peterborough: National Rivers Authority Anglian Region. Retrieved from
1077 <http://www.environmentdata.org/archive/ealit:2851>.
- 1078 [70] NRA. (1996). *Sea Vigil Water Quality Monitoring: The Humber Estuary 1994*.
1079 Peterborough: National Rivers Authority Anglian Region. Retrieved from
1080 <http://www.environmentdata.org/archive/ealit:2868>
- 1081 [71] Paerl, H. W. (2006). Assessing and managing nutrient-enhanced eutrophication
1082 in estuarine and coastal waters: Interactive effects of human and climatic perturbations.
1083 *Ecological Engineering*, 26(1), 40-54. doi: 10.1016/j.ecoleng.2005.09.006
- 1084 [72] Percuoco, V. P., Kalnejais, L. H., & Officer, L. V. (2015). Nutrient release from
1085 the sediments of the Great Bay Estuary, NH USA. *Estuarine Coastal and Shelf Science*,
1086 161, 76-87. doi: 10.1016/j.ecss.2015.04.006
- 1087 [73] Pethick, J. S. (1990). *The Humber Estuary*. In S. and Crowther Ellis, D.R. (Ed.),
1088 *Humber Perspectives, A region through the ages* (pp. 54-67). Hull: Hull University.
- 1089 [74] Postma, D., & Jakobsen, R. (1996). Redox zonation: Equilibrium constraints on
1090 the Fe(III)/SO₄-reduction interface. *Geochimica et Cosmochimica Acta*, 60(17), 3169-
1091 3175. doi: 10.1016/0016-7037(96)00156-1
- 1092 [75] Rauret, G., Rubio, R., & López-Sánchez, J. F. (1989). Optimization of Tessier
1093 Procedure for Metal Solid Speciation in River Sediments. *International Journal of*
1094 *Environmental Analytical Chemistry*, 36(2), 69-83. doi: 10.1080/03067318908026859

- 1095 [76] Reed, N. M., Cairns, R. O., Hutton, R. C., & Takaku, Y. (1994).
1096 Characterization of polyatomic ion interferences in inductively-coupled plasma-mass
1097 spectrometry using a high-resolution mass-spectrometer. *Journal of Analytical Atomic*
1098 *Spectrometry*, 9(8), 881-896. doi: 10.1039/ja9940900881
- 1099 [77] Roberts, K. L., Eate, V. M., Eyre, B. D., Holland, D. P., & Cook, P. L. M.
1100 (2012). Hypoxic events stimulate nitrogen recycling in a shallow salt-wedge estuary:
1101 The Yarra River estuary, Australia. *Limnology and Oceanography*, 57(5), 1427-1442.
1102 doi: 10.4319/lo.2012.57.5.1427
- 1103 [78] Roberts, K. L., Kessler, A. J., Grace, M. R., & Cook, P. M. L. (2014). Increased
1104 rates of dissimilatory nitrate reduction to ammonium (DNRA) under oxic conditions in
1105 a periodically hypoxic estuary. *Geochimica et Cosmochimica Acta*, 133, 313-324. doi:
1106 <http://dx.doi.org/10.1016/j.gca.2014.02.042>
- 1107 [79] Robins, P. E., Skov, M. W., Lewis, M. J., Giménez, L., Davies, A. G., Malham,
1108 S. K., Neill, S. P., McDonald, J. E., Whitton, T. A., Jackson, S. E., & Jago, C. F. (2016).
1109 Impact of climate change on UK estuaries: A review of past trends and potential
1110 projections. *Estuarine, Coastal and Shelf Science*, 169(Supplement C), 119-135. doi:
1111 <https://doi.org/10.1016/j.ecss.2015.12.016>
- 1112 [80] Salomons, W., Derooij, N. M., Kerdijk, H., & Bril, J. (1987). Sediments as a
1113 source of contaminants. *Hydrobiologia*, 149, 13-30. doi: 10.1007/bf00048643
- 1114 [81] Sanders, R. J., Jickells, T., Malcolm, S., Brown, J., Kirkwood, D., Reeve, A.,
1115 Taylor, J., Horrobin, T., & Ashcroft, C. (1997). Nutrient Fluxes through the Humber
1116 estuary. *Journal of Sea Research*, 37, 3-23.
- 1117 [82] Sanford, L. P. (2008). Modeling a dynamically varying mixed sediment bed with
1118 erosion, deposition, bioturbation, consolidation, and armoring. *Comput. Geosci.*, 34(10),
1119 1263-1283. doi: 10.1016/j.cageo.2008.02.011
- 1120 [83] Saulnier, I., & Mucci, A. (2000). Trace metal remobilization following the
1121 resuspension of estuarine sediments: Saguenay Fjord, Canada. *Applied Geochemistry*,
1122 15(2), 191-210. doi: 10.1016/s0883-2927(99)00034-7
- 1123 [84] Sayama, M., Risgaard-Petersen, N., Nielsen, L. P., Fossing, H., & Christensen,
1124 P.B. (2005). Impact of bacterial NO₃- transport on sediment biogeochemistry. *Applied*
1125 *and Environmental Microbiology*, 71(11), 7575-7577. doi: 10.1128/aem.71.11.7575-
1126 7577.2005
- 1127 [85] Seitzinger, S. P., & Sanders, R. W. (1997). Contribution of dissolved organic
1128 nitrogen from rivers to estuarine eutrophication. *Marine Ecology Progress Series*, 159,
1129 1-12. doi: 10.3354/meps159001
- 1130 [86] Simpson, S. L., Apte, S. C., & Batley, G. E. (1998). Effect of short term
1131 resuspension events on trace metal speciation in polluted anoxic sediments.
1132 *Environmental Science & Technology*, 32(5), 620-625. doi: 10.1021/es970568g
- 1133 [87] Song, G. D., Liu, S. M., Marchant, H., Kuypers, M. M. M., & Lavik, G. (2013).
1134 Anammox, denitrification and dissimilatory nitrate reduction to ammonium in the East

- 1135 China Sea sediment. *Biogeosciences*, 10(11), 6851-6864. doi: 10.5194/bg-10-6851-
1136 2013
- 1137 [88] Sørensen, J., & Jørgensen, B. B. (1987). Early diagenesis in sediments from
1138 Danish coastal waters - microbial activity and Mn-Fe-S geochemistry. *Geochimica et*
1139 *Cosmochimica Acta*, 51(6), 1583-1590. doi: 10.1016/0016-7037(87)90339-5
- 1140 [89] Statham, P. J. (2012). Nutrients in estuaries--an overview and the potential
1141 impacts of climate change. *Sci Total Environ*, 434, 213-227. doi:
1142 10.1016/j.scitotenv.2011.09.088
- 1143 [90] Stumm, W., & Morgan, J. J. (1970). *Aquatic chemistry: an introduction*
1144 *emphasizing chemical equilibria in natural waters*. New York: Wiley-Interscience.
- 1145 [91] Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction
1146 procedure for the speciation of particulate trace-metals. *Analytical Chemistry*, 51(7),
1147 844-851. doi: 10.1021/ac50043a017
- 1148 [92] Thamdrup, B., Fossing, H., & Jørgensen, B. B. (1994). Manganese, iron, and
1149 sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Geochimica et*
1150 *Cosmochimica Acta*, 58(23), 5115-5129. doi: 10.1016/0016-7037(94)90298-4
- 1151 [93] Thamdrup, B. (2012). New Pathways and Processes in the Global Nitrogen
1152 Cycle. *Annual Review of Ecology, Evolution, and Systematics*, 43, 407-428. doi:
1153 10.1146/annurev-ecolsys-102710-145048
- 1154 [94] Townend, I. H., Wang, Z. B., & Rees, J. (2007). Millennial to annual volume
1155 changes in the Humber Estuary. Paper presented at the Proceedings of the Royal
1156 Society of London A: Mathematical, Physical and Engineering Sciences.
- 1157 [95] Triska, F. J., Duff, J. H., & Avanzino, R. J. (1993). The role of water exchange
1158 between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial
1159 aquatic interface. *Hydrobiologia*, 251(1-3), 167-184. doi: 10.1007/bf00007177
- 1160 [96] Tyson, R. V. (1995). The nature of organic matter in sediments *Sedimentary*
1161 *organic matter: Organic facies and palynofacies* (pp. 7-28). London: Chapman & Hall.
- 1162 [97] Uncles, R. J., Wood, R. G., Stephens, J. A., & Howland, R. J. M. (1998).
1163 Estuarine Nutrient Fluxes to the Humber Coastal Zone, UK, during June 1995. *Marine*
1164 *Pollution Bulletin*, 37, 225-233.
- 1165 [98] Uncles, R. J., Stephens, J. A., & Law, D. J. (2006). Turbidity maximum in the
1166 macrotidal, highly turbid Humber Estuary, UK: Flocs, fluid mud, stationary suspensions
1167 and tidal bores. *Estuarine, Coastal and Shelf Science*, 67(1-2), 30-52. doi:
1168 10.1016/j.ecss.2005.10.013
- 1169 [99] Uncles, R. J., Joint, I., & Stephens, J. A. (1998). Transport and retention of
1170 suspended particulate matter and bacteria in the Humber-Ouse Estuary, United
1171 Kingdom, and their relationship to hypoxia and anoxia. *Estuaries*, 21(4A), 597-612. doi:
1172 10.2307/1353298

- 1173 [100] Van Prooijen, B. C., & Winterwerp, J. C. (2010). A stochastic formulation for
1174 erosion of cohesive sediments. *Journal of Geophysical Research: Oceans*, 115(C1), n/a-
1175 n/a. doi: 10.1029/2008JC005189
- 1176 [101] Viollier, E., Inglett, P.W., Huntrer, K., Roychoudhury, A. N., and Van
1177 Cappellen, P. (2000). The ferrozine method revised: Fe(II)/Fe(III) determination in
1178 natural waters. *Applied Geochemistry*, 15, 785-790.
- 1179 [102] Wengrove, M. E., Foster, D. L., Kalnejais, L. H., Percuoco, V., & Lippmann, T.
1180 C. (2015). Field and laboratory observations of bed stress and associated nutrient
1181 release in a tidal estuary. *Estuarine, Coastal and Shelf Science*, 161(Supplement C), 11-
1182 24. doi: 10.1016/j.ecss.2015.04.005
- 1183 [103] Wu, Y., Falconer, R. A., & Uncles, R. J. (1999). Modelling of Water Flows and
1184 Cohesive Sediment Fluxes in the Humber Estuary, UK. *Marine Pollution Bulletin*,
1185 37(3), 182-189. doi: [https://doi.org/10.1016/S0025-326X\(99\)00103-4](https://doi.org/10.1016/S0025-326X(99)00103-4)