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

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Abstract

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

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

1. Introduction

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

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

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

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

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

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

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

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

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

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

2. Material and Methods

2.1 Field sampling

The Humber Estuary is a macrotidal estuary on the east coast of northern England (Fig.1). It is 60 km in length, there are ~115 km² of mudflats, and is highly turbid (Pethick, 1990). The Humber is also considered a major source of nutrients for the North Sea (Pethick, 1990; Mortimer *et al.*, 1998; Uncles *et al.*, 1998a; Uncles *et al.*, 1998b).

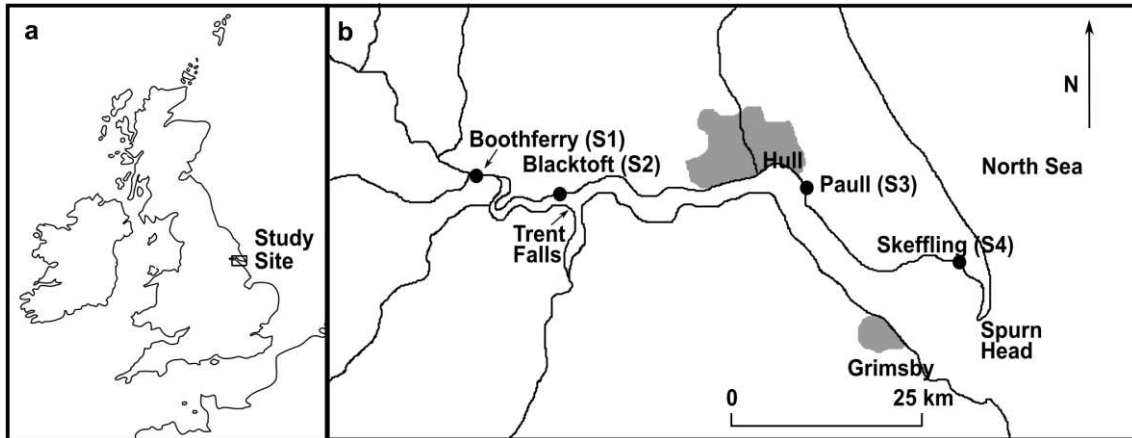


Figure 1: Map with the location of the Humber Estuary (a), and detail of the sampling sites (Boothferry (S1), Blacktoft (S2), Paull (S3), and Skeffling (S4)) (b).

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

analysis (see below). All the subsamples of the dissolved phase used for metal analysis were acidified (1% v/v) with concentrated HNO₃ to prevent metal losses to the walls of the sample tubes and/or precipitation of oxyhydroxides.

2.2 Sample characterisation and analytical methods

All the following physicochemical analyses of sediments and water samples were carried out in triplicate (pseudoreplicates from bulk samples). Sediments were oven dried at 70°C (until constant weight) prior to X-Ray diffraction analysis on a Bruker D8 Advance diffractometer and X-Ray fluorescence (XRF) analysis on an Olympus Innovex X-5000 spectrometer. The percentages of acid volatile sulphide (AVS) and pyrite were determined on freeze-dried sediments using the methods described in Canfield *et al.* (1986) and Fossing and Jørgensen (1989) respectively. Total extractable Fe and extractable Fe²⁺_(s) were determined after 60 min extractions in 0.25 M hydroxylamine HCl (Lovley & Phillips, 1987) and 0.5 N HCl respectively (Lovley & Phillips, 1986), both followed by ferrozine assay (Viollier, 2000). Subsamples of 10% v/v HCl acid and non-acid washed, oven dried (70 °C), and ground sediment samples were analysed for total sulphur (TS), total carbon and total organic carbon (TOC) on a LECO SC-144DR Sulphur and Carbon Analyser by combustion with non-dispersive infrared detection. Total inorganic carbon (TIC) was determined by the difference between non-acid washed and acid washed samples. Wet sediments were analysed for particle size by laser diffraction on a Malvern Mastersizer 2000E.

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

Chromatographic analysis of high chloride samples required the use of a column-switching method (Bruno *et al.*, 2003) where matrix chloride anions were pre-separated from the other analytes by a double in-line pre-column (AG9-HC 4 mm). Then, nitrate and nitrite were analysed without dilution by conductivity (DIONEX CD20, ED40 Electrochemical detector, 8% RSD) and spectrophotometry for differentiation of nitrite and nitrate (DIONEX AD20 UV absorbance detector (225 nm)). In order to measure chloride and sulphate concentrations, 20-fold dilution samples were analysed on a DIONEX 500 (%RSD \leq 2%). Iron and Mn in solution were determined after acidification with 1% v/v HNO₃ for TM analysis by ion-coupled plasma-mass spectroscopy (ICP-MS) on a Thermo Scientific iCAPQc ICP-MS. For the analysis of brackish-saline waters a special protocol, in which precautions were taken to avoid polyatomic interferences, was applied, and Certified Reference Material (CRM) was run throughout (see Supporting Information for more details).

2.3 Resuspension experiments

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

withdrawn from all flasks at different intervals from 0.02 hrs (1 min) to 336 hrs (two weeks). The sampling frequency was progressively decreased with time in order to more intensively monitor changes occurring at the start of the experiment (short-term changes, tidal cycle scale) relative to those occurring over longer time periods (medium-term changes, 2-3 days), which would represent the duration of a very significant resuspension event like suggested in Kalnejais *et al.* (2010). From the 5 ml aliquots, the aqueous phase was separated from solids by centrifugation (5 min; 16,000 g). Eh and pH were determined using a Hamilton PolyPlast ORP BNC and an Orion Dual Star meter (with the electrode calibrated at pH 4, 7 and 10) respectively. Aqueous phase samples were filtered and retained for analysis. Subsamples were acidified (1% v/v HNO₃) for metal analysis by ICP-MS, as mentioned above, with the correspondent precautions for high salinity samples. Nutrients in the aqueous phase were measured as described above, and acid extractable Fe²⁺_(s) was determined immediately on solid residues from centrifugation following the method described above.

2.4 Sequential Extractions

To support the understanding of the changes in TM speciation due to resuspension, sequential extractions were performed concurrently. The partitioning of selected metals (Zn and Cu) between different operationally-defined geochemical fractions was determined using the Tessier *et al.* (1979) procedure as optimised for riverine sediments by Rauret *et al.* (1989). The extractions were carried out with the original wet sediments and with the dried solid residues recovered at the end of the resuspension experiments. Four extractants were used: 1 M MgCl₂ at pH 7 (to determine the “exchangeable” fraction), 1 M NaOAc at pH 5 (for the bound-to-carbonates or “weak acid-extractable” fraction), 0.04 M NH₂OH·HCl in 25% v/v HAC

(for the bound to Fe/Mn oxides), and 30% H₂O₂ at pH 2 (with HNO₃) followed by NH₄Ac (for the bound to organic matter and sulphides). The third step of the extraction protocol was modified by reducing the extraction temperature (from 96°C to room temperature), and increasing the extraction time (from 6 to 14 hrs (overnight)). With the original wet sediments, the first three steps of the extraction protocol were carried out in an anaerobic chamber with deoxygenated reactants. Metal concentrations associated with the residual phase were not determined. The concentration of the metals in the extractant solutions was analysed by ICP-MS following the pertinent precautions (see more details in Supporting Information).

3. Results

3.1 Sample Characterisation

3.1.1 Site characterisation

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

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

3.1.2 Solid phase

The bulk mineralogy of the dried sediments was characterised and all sediments contained a mixture of quartz, carbonates (calcite and dolomite), and silicates (kaolinite, muscovite, clinocllore, albite, microcline). Pyrite was only detected by XRD in the subsurface sediments from S4. The average TIC, TOC and TS contents of inner estuary sediments (S1 and S2) were 1.1%, 2.0%, and 0.17% respectively, with little systematic variation with depth (Table 2). The average TIC, TOC and TS contents of outer estuary sediments (S3 and S4) were 1.6%, 2.4%, and 0.35%, respectively, with both TOC and TS increasing with sample depth. The average amounts of Fe in the inner and outer estuary sediments were 3% and 4% by weight, respectively, with 0.09% and 0.13% associated with pyrite. AVS were only detected in the samples from the outer estuary but not in all the replicates. The Fe associated with AVS in S3 and S4 subsurface sediments was 0.01 and 0.09% respectively; however, it was not possible to quantify the very little amount extracted from surface samples. The average amount of 0.5 N HCl extractable Fe²⁺_(s) was 108 and 153 µmol g⁻¹ in the inner and outer estuary sediments

respectively, with no depth trend in the inner estuary, but a trend of increase with depth in the outer estuary. The bulk concentrations of Mn, Zn, and Cu in solids are also included in Table 2. Finally, the particle grain size data (as the upper bound diameter of 50% of cumulative percentage of particles by volume, D50), showed that sediments were finer in the outer estuary mudflats. Sediments in the inner estuary sites had less water content and were classified as finer sands/coarse silt (Supporting Information).

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

3

	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

4 **3.2 Major Element behaviour during sediment resuspension**

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

12 3.2.1 Inner estuary

13 In the experiments using surface sediments from the inner estuary sites (S1 and
14 S2) nitrate seemed to be released immediately on resuspension, particularly in S2
15 experiments (~400 μM) (Fig.2a). Nitrate concentrations then remained relatively
16 constant in these tests until 72 hrs, after which time concentrations steadily decreased
17 towards the end of the test. In the experiments using inner estuary subsurface sediments,
18 nitrate concentrations followed similar trends to those exhibited in the surface sediment
19 experiments (Fig.2b), with S1 experiments showing a progressive increase in
20 concentrations within the first 10 hrs. There was significantly more data scatter
21 observed in these tests (especially at the later time points).

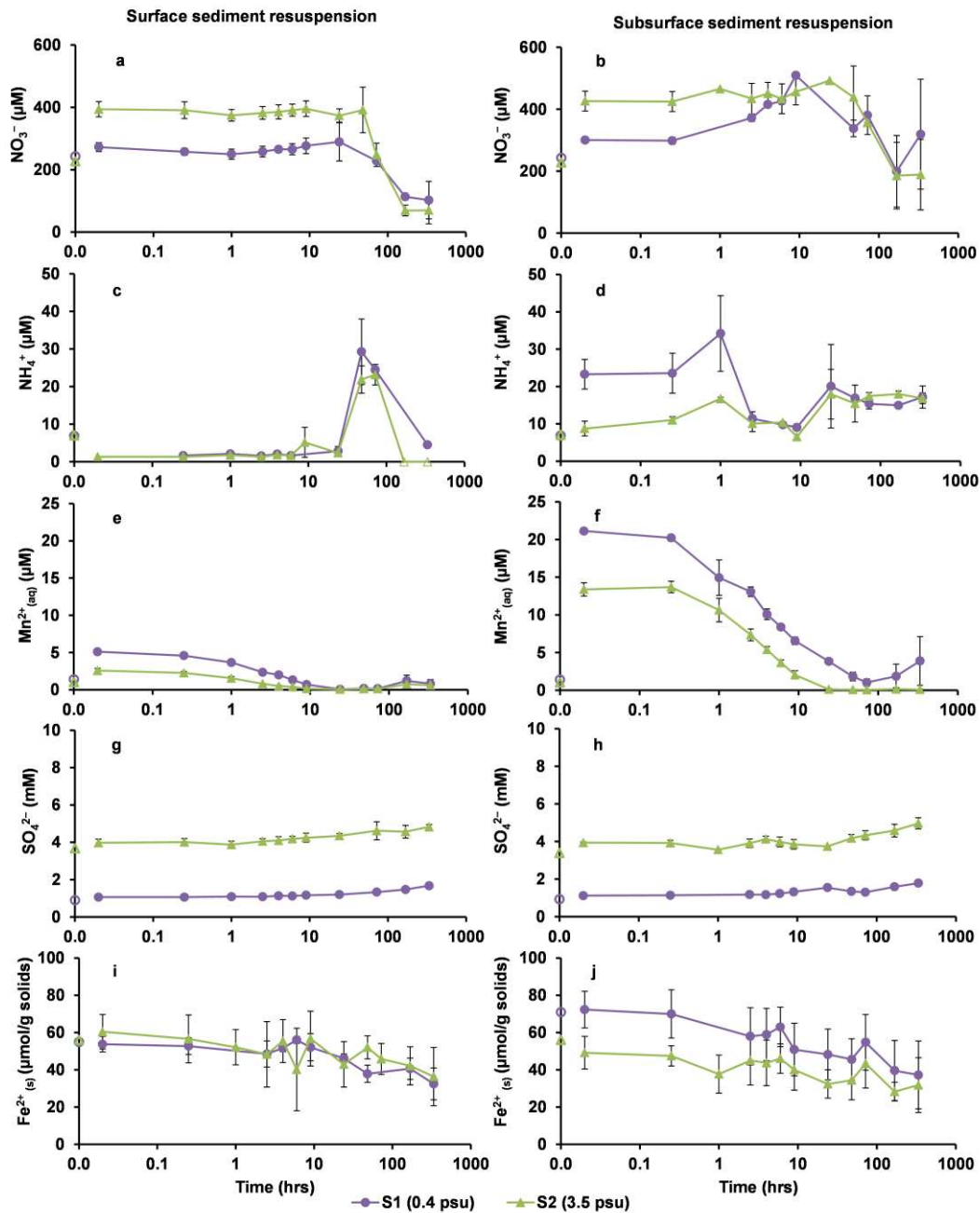
22 Ammonium concentrations in the experiments carried out with surface
23 sediments decreased immediately after resuspension started (Fig.2c) and remained close
24 to detection levels until 48 hrs, when concentrations transiently increased to around 20-
25 30 μM before decreasing to low concentrations by the end of the test. On the other hand,
26 ammonium concentrations in experiments using subsurface sediments (Fig.2d)
27 increased immediately after resuspension started from <10 to ~20 μM in S1

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

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

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

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



46

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

54 3.2.2 Outer estuary

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

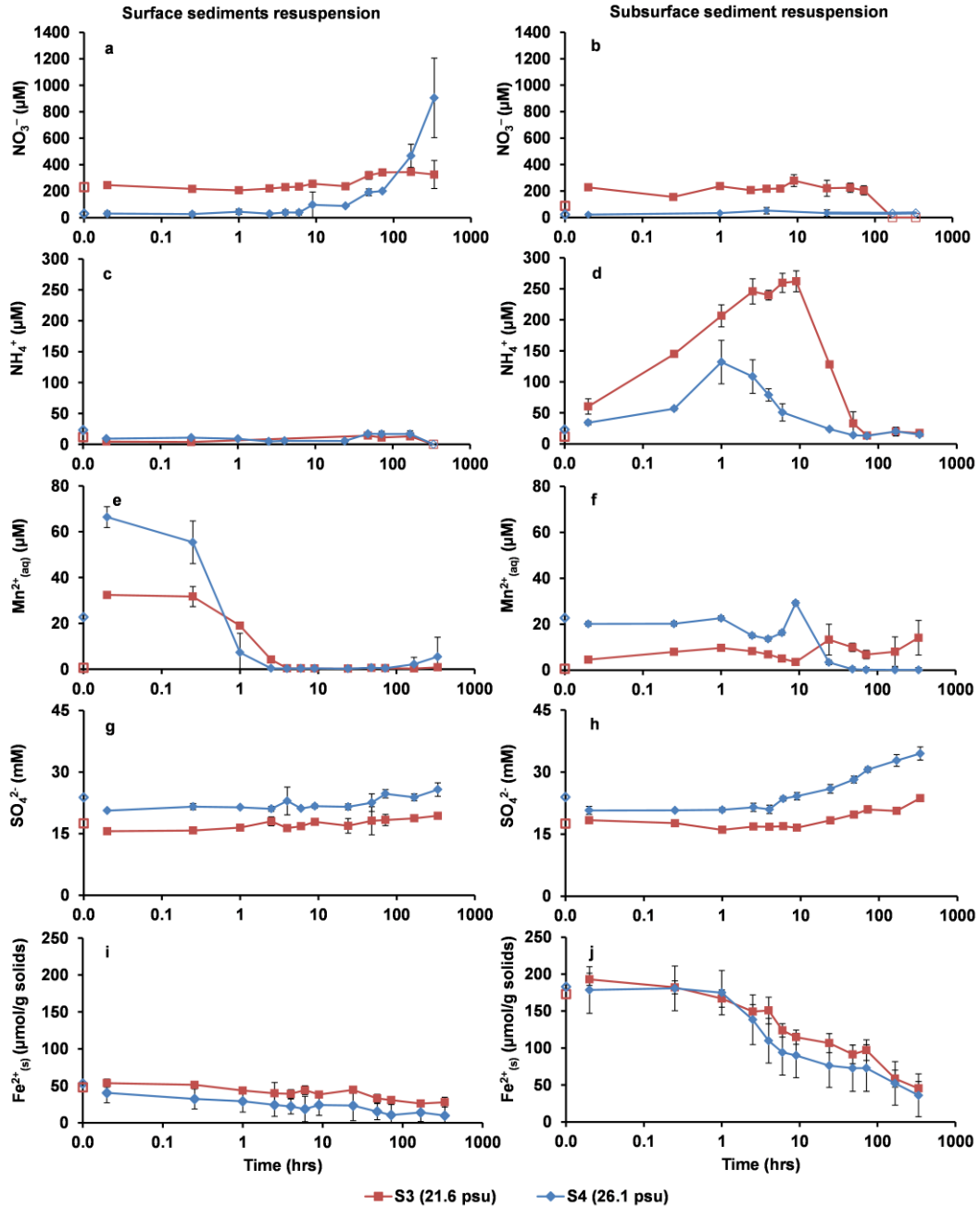
66 Ammonium concentrations in experiments using outer estuary surface sediments
67 were initially low ($< 20 \mu\text{M}$), similar to the concentrations in the original river water,
68 and remained so until the end of the tests (Fig.3c). There was a very different trend in
69 ammonium concentrations in the experiments using subsurface sediments (Fig.3d),
70 which increased significantly (by ~ 2.5 times) within the first few hours of resuspension.
71 Ammonium concentration peaks in the experiments were 260 ± 20 (S3) and 130 ± 40 (S4)
72 μM . Following these initial releases, ammonium levels in solution decreased to $\sim 20 \mu\text{M}$
73 by the end of the first week to remain stable until the end of the tests.

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

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

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

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



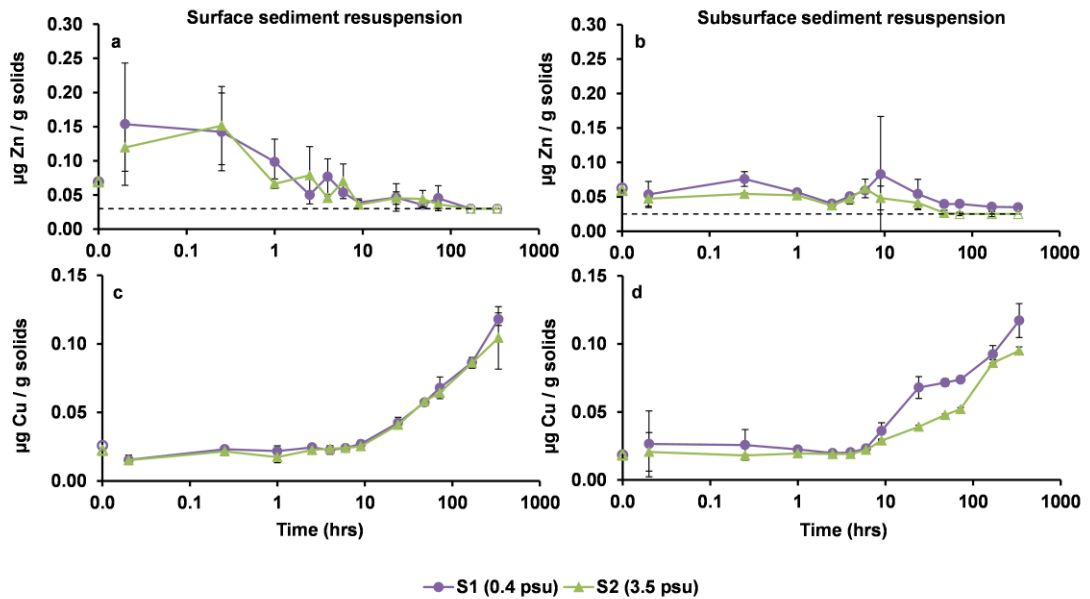
99

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

107 **3.3 Trace metal mobility during sediment resuspension**

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

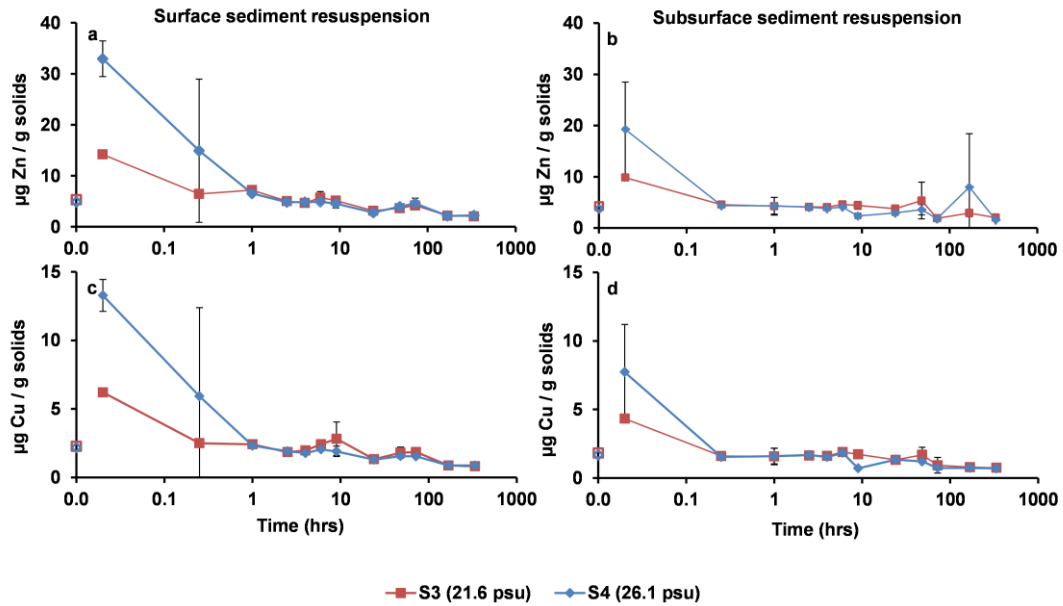
112 In the experiments carried out with inner estuarine sediments, the pattern of Zn
113 behaviour depended on the sediment depth. In the surface sediment experiments, Zn
114 concentrations increased immediately upon resuspension to values 2-3 times the initial
115 concentrations in the experiments (0.15 ± 0.09 (S1) and 0.12 ± 0.04 (S2) $\mu\text{g Zn g}^{-1}$) but
116 decreased with time to below the detection limit by the end of the experiment (Fig.4a).
117 In contrast, in the experiments using subsurface sediments (Fig.4b), Zn concentrations
118 did not increase upon resuspension and decreased gradually to a final level close to the
119 detection limit. Initially, Cu concentrations remained stable at about the levels in the
120 river water in the four sets of experiments, but increased after ~ 10 hrs of resuspension,
121 reaching concentrations $\sim 3-4$ times their initial values (about 0.12 ± 0.02 (S1) and
122 0.1 ± 0.04 (S2) $\mu\text{g Cu g}^{-1}$) (Fig.4c and 4d).



123

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

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



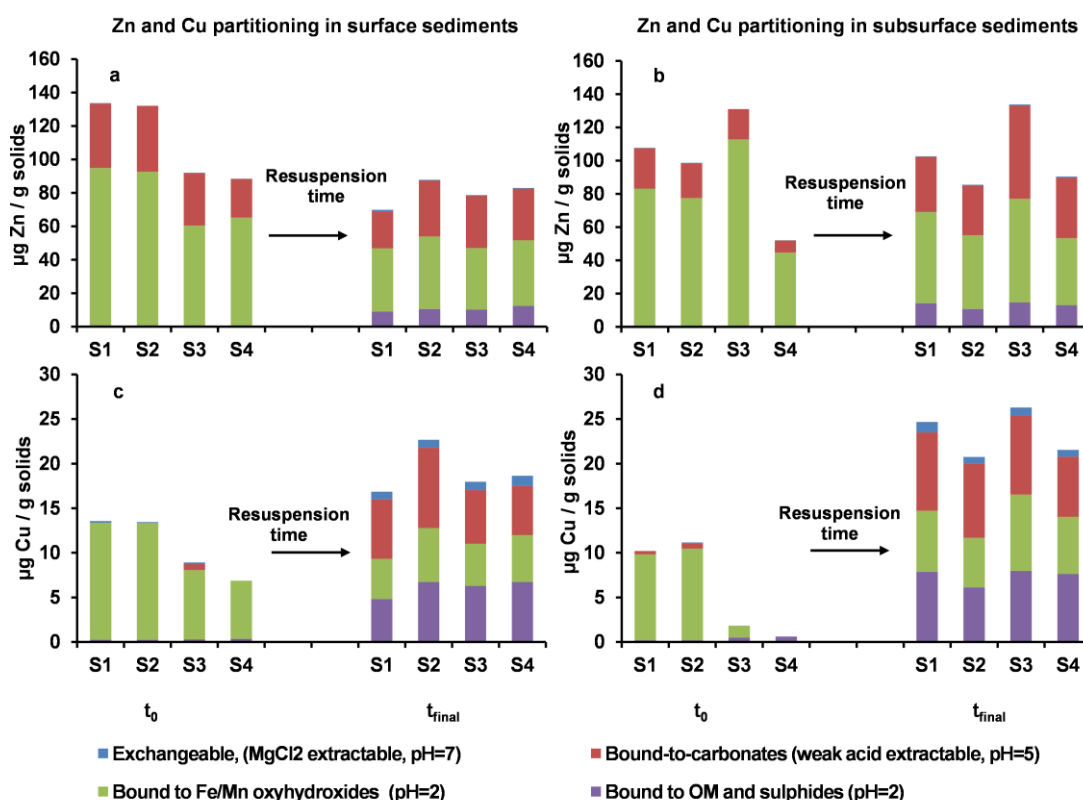
140

141 Figure 5: Zinc and copper released to the solution from solids during resuspension
 142 experiments using S3 and S4 sediments. Zinc released from surface (a) and subsurface
 143 (b) sediments; Cu released from surface (c) and subsurface (d) sediments. Open
 144 symbols on the y-axis indicate the initial concentrations in the experiment (river water
 145 plus porewater contribution). Error bars in all the figures represent one standard
 146 deviation (1σ) of triplicates.

147 3.4 Changes in metal partitioning during resuspension

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

157 6d) showed similar changes in all the samples; although very little Cu was extracted
 158 from S3 and S4 subsurface sediments. In the original sediments, almost all the Cu
 159 extracted was associated with the Fe/Mn oxyhydroxides fraction. Upon resuspension,
 160 there was a general shift from the Fe/Mn oxyhydroxides fraction to the weak acid-
 161 extractable, and the organic matter-sulphide fraction. Copper concentrations for each
 162 leachate were similar among samples.



163
 164 Figure 6: Zinc and copper partitioning changes after estuarine sediment resuspension
 165 determined by sequential extractions using Tessier *et al.* (1979) protocol with
 166 modifications. The concentration (averaged from triplicates) is expressed in µg of metal
 167 in the extractant solution by the mass of solids (dry sediments) used in the extraction.
 168 Zinc partitioning in surface (a) and subsurface (b) sediments; and Cu partitioning in
 169 surface (c) and subsurface (d) sediments. Sites are ordered according to their location
 170 within the salinity gradient and the arrows represent the time of the experiment (2-
 171 weeks).

172 **4. Discussion**

173 **4.1 Geochemical character of river water and estuarine sediments.**

174 The four sites along the Humber estuary represent the gradual change from a
175 typical freshwater environment to an intertidal mudflat with brackish waters. This
176 salinity profile was similar to that measured in other surveys (NRA, 1995, 1996;
177 Sanders *et al.*, 1997; Mortimer *et al.*, 1998). Along the salinity gradient, nitrate
178 concentrations in the overlying waters decreased with increasing salinity and were
179 inversely correlated with the ammonium concentrations. Previously nitrate has been
180 described to show a conservative behaviour along the mixing line, although there may
181 be specific locations that show net nitrate production or removal during the year
182 (Sanders *et al.*, 1997; Barnes & Owens, 1998). Generally, the ammonium
183 concentrations measured were of the same order of magnitude, if not slightly higher,
184 than typical Humber waters. We observed increasing ammonium concentrations with
185 increasing salinity, but the 90s surveys showed that ammonium trends varied
186 seasonally. All porewaters recovered were enriched in ammonium but not in nitrate.
187 This ammonium enrichment was enhanced in the outermost estuary sites, which was
188 most likely a reflection of *in situ* production from organic matter degradation during
189 sulphate reduction (Mortimer *et al.*, 1998) and DNRA processes. Sulphate
190 concentrations increased seawards.

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

196 appeared to be moderately reducing compared to the subsurface sediments from the
197 outer estuary which appeared to become more reducing at depth. The AVS
198 concentrations measured ($<0.02 \mu\text{mol AVS g}^{-1}$) in these Humber sediments were very
199 low, but still in the range of concentrations reported in estuaries and other aquatic
200 environments (Di Toro *et al.*, 1990; Allen *et al.*, 1993; Fang *et al.*, 2005). The dynamic
201 nature of the Humber leads to a continuous resuspension and reoxidation of sediments,
202 which will buffer the AVS to low concentrations, whereas pyrite will accumulate in
203 sediments with time as it is more stable than AVS. This would explain the presence of
204 pyrite in all the samples regardless of the absence of AVS. Furthermore, the availability
205 of dissolved Mn and nitrate will also influence the distribution of free sulphide within
206 the sediments (Thamdrup *et al.*, 1994; Sayama *et al.*, 2005). Iron oxides react with free
207 sulphides and, at the same time, the produced $\text{Fe}^{2+}_{(\text{aq})}$ and H_2S reduce MnO_2 rapidly
208 (Thamdrup *et al.*, 1994), which could be another reason for the low AVS detected.
209 Besides, the Fe oxides produced in the reaction of MnO_2 with $\text{Fe}^{2+}_{(\text{aq})}$ will fuel this
210 positive feedback mechanism. Alternatively, it cannot be discarded that the low AVS
211 extracted was an artefact due to the partial oxidation of sediments during sampling and
212 transport or during the handling in the laboratory, prior sediments were freeze-dried for
213 AVS-pyrite extraction. The better-defined redox stratification between the two sediment
214 depths sampled at the outer estuary sites was supported by *in situ* observations (colour
215 change and odour of the sediments). Moreover, the total acid extractable $\text{Fe}^{2+}_{(\text{s})}$ in the
216 subsurface outer estuary sediments was ~2 times the content in the equivalent sediments
217 from the inner estuary. Thus, it seems that the outer estuary mudflats hold the largest
218 Fe-pool within the Humber.

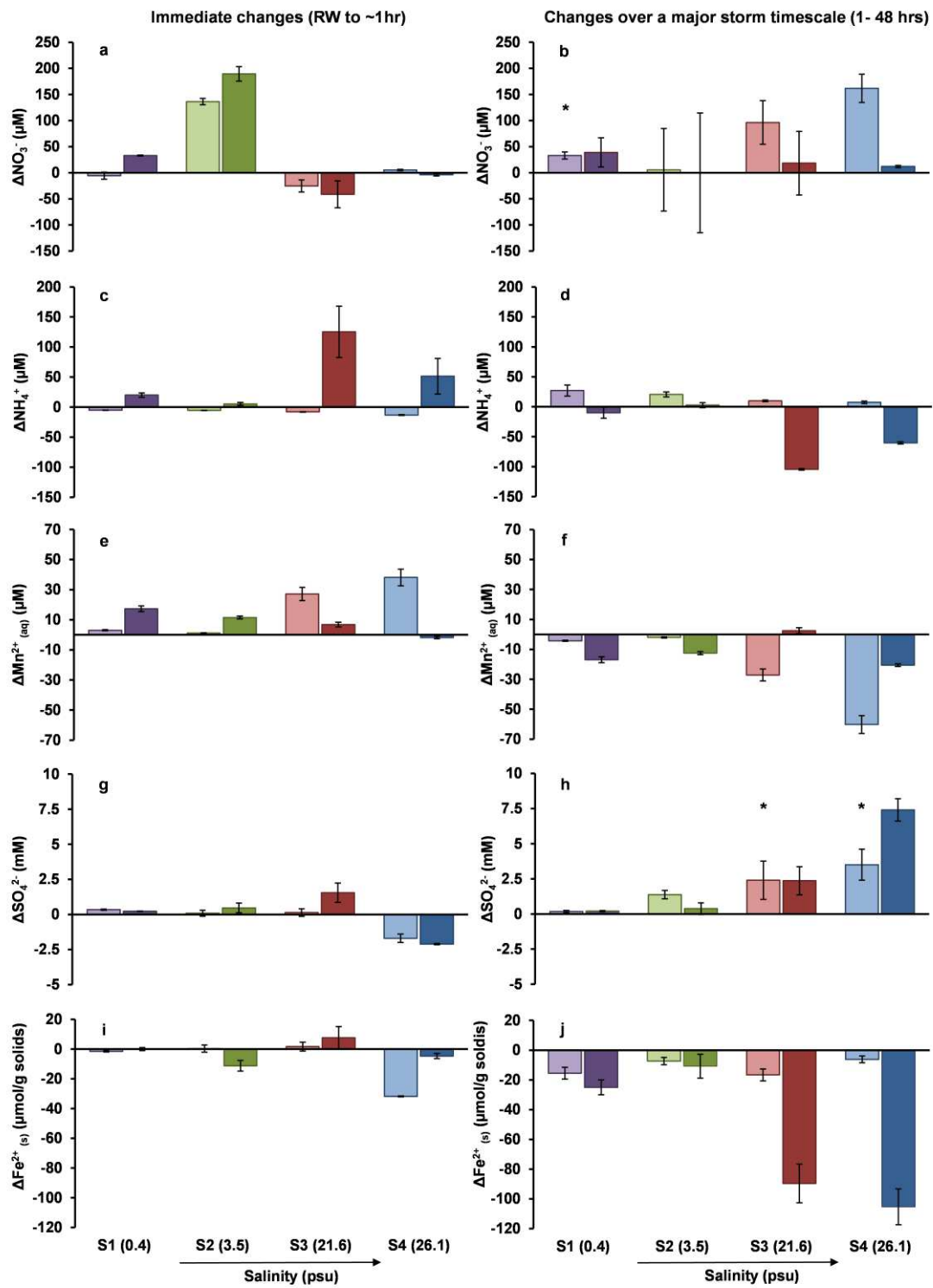
219 Furthermore, the mudflats of the outer Humber estuary accumulated finer
220 materials and they appeared to have a slightly higher TOC content than the inner estuary

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

232 **4.2 Geochemical responses of major elements to sediment resuspension**

233 In order to compare the relative impact of a small-scale versus a more major
234 resuspension event, the discussion about the changes in the geochemical behaviour of
235 the major elements observed and their potential implications on estuarine geochemistry
236 will be framed by two time-windows (Fig.7). Firstly, the immediate changes upon
237 sediment resuspension in river water, which are important as they will occur naturally at
238 any type of resuspension event (from regular tidal cycles to less frequent extreme
239 events). Secondly, longer timescale changes expected during major storms, which
240 potentially mobilise deeper sediments that are not normally disturbed and typically last
241 2-3 days in the Humber region (Lamb & Frydendahl, 1991; EASAC, 2013). For the
242 immediate changes, net differences between the average concentration after the first
243 hour of resuspension (as a final concentration datum) and the original concentrations of
244 the river water (RW) have been calculated. Changes during a major storm timescale

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



248

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

255 Nitrate showed no big releases in the short term (Fig.7a), with the exception of
256 S2 which may be explained by oxidation of reduced nitrogen species because porewater
257 did not accumulate nitrate. A combination of oxidation processes may also explain the
258 nitrate increases in the longer timescale (Fig.7b). For example, the later significant
259 increase in nitrate concentration in the experiments using S4 surface sediments may, in
260 part, be associated with nitrification processes, as observed by Couceiro *et al.* (2013).
261 Although a proportional ammonium consumption coupled to the production of nitrate
262 was not observed in this experiment, coupled nitrification-denitrification can occur very
263 fast, especially if other oxidants such as Mn oxides are competing with the oxygen for
264 the oxidation of ammonia to N_2 and organic-N (Luther *et al.*, 1997; Anschutz *et al.*,
265 2000). Therefore, in this mosaic of redox reactions, a combination of aerobic oxidation
266 of organic matter and nitrification may be the major nitrate sources. The nitrate
267 produced could be subsequently used in other reactions. In fact under longer time
268 intervals (1-2 weeks), the concentrations of nitrate decreased progressively possibly due
269 to the development of suboxic conditions in the experiments (i.e. conditions developed
270 perhaps in isolated micro-niches in the bottom of the flasks) (Triska *et al.*, 1993;
271 Lansdown *et al.*, 2014; Lansdown *et al.*, 2015); such that denitrification could be
272 supported despite the constant influx of air to the experiments. As such, the longer term
273 removal of nitrate observed in these experiments may be an artefact of the experimental

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

276 Ammonium showed significant releases (70-140 μM) in the first hour of
277 resuspension in the experiments carried out with subsurface sediments from S3 and S4
278 (Fig.7c), likely due to the accumulation of ammonium in the porewater of outer estuary
279 mudflats like suggested by Morgan *et al.* (2012). However, other processes, such as
280 reversible desorption from sediments and/or ion-exchange reactions likely have also
281 contributed to the ammonium increase (Morin & Morse, 1999; Kalnejais *et al.*, 2010;
282 Morgan *et al.*, 2012; Percuoco *et al.*, 2015; Wengrove *et al.*, 2015) since porewater
283 contribution to the mixture by simple diffusion cannot explain the concentrations
284 reached. The ammonium released in those experiments was completely removed after
285 48 hrs (Fig.7d). Transitory ammonium release also occurred in S1 and S2 surface
286 sediment experiments and these peaks coincided with the depletion of Mn^{2+} in solution.
287 Nitrification and ammonium oxidation to N_2 by Mn oxides could have contributed to
288 the ammonium removal processes. Any $\text{Mn}^{2+}_{(\text{aq})}$ product of these reaction pathways
289 would readily react with the oxygen present to regenerate reactive oxides, which will act
290 as a catalysts to continue the oxidation of ammonium and organic-N (Luther *et al.*,
291 1997); or, if suboxic conditions, $\text{Mn}^{2+}_{(\text{aq})}$ may react with nitrate (Sørensen & Jørgensen,
292 1987; Murray *et al.*, 1995; Luther *et al.*, 1997). In the natural environment, the
293 occurrence and magnitude of nitrification depends on the availability of oxygen and
294 ammonium (Canfield *et al.*, 2005), and it will play a major role in the nutrient exchange
295 processes within the sediment-water interface as the nitrate produced will, in turn,
296 sustain denitrification (Barnes & Owens, 1998; Mortimer *et al.*, 1998). In the Humber,
297 an intense zone for nitrification-denitrification has been associated with the ETM due to
298 the enhanced chemical and microbial activity as suspended particles provide a large

299 additional surface area (Barnes & Owens, 1998; Mortimer *et al.*, 1998; Uncles *et al.*,
300 1998b). On the other hand, nitrifiers can be inhibited by sulphide concentration, light,
301 temperature, salinity and extreme pH (Canfield *et al.*, 2005). The inhibition of
302 nitrification by sulphide could favour the preservation of ammonium in porewater (Joye
303 & Hollibaugh, 1995; Morgan *et al.*, 2012), which may be a possible reason for the
304 limited evidence of nitrification in some of these experiments and may help to explain
305 spatial differences in coupled nitrification-denitrification within this estuary.
306 Alternatively, re-adsorption of ammonium onto particles, is likely to be an important
307 removal process (especially as Fe/Mn oxides were likely to be forming in experiments
308 as a result of metal oxidation; see below) which, in the natural estuary systems may be
309 key for the nutrient buffering capacity of the sediments (Morin & Morse, 1999; Song *et*
310 *al.*, 2013).

311 The net removal of reduced Mn and Fe in all the experiments is attributed to the
312 series of oxidation reactions occurring during sediment resuspension in aerated
313 conditions, and the consequent precipitation of insoluble Mn/Fe oxyhydroxides (e.g.
314 birnessite and ferrihydrite). During oxic resuspension, abiotic oxidation processes are
315 expected to be the dominant mechanism operating. In contrast, microbially mediated
316 Mn- and Fe-oxidation are the dominant mechanism operating in micro-aerophilic and
317 sub-oxic environments (Froelich *et al.*, 1979; Thamdrup *et al.*, 1994; Canfield *et al.*,
318 2005). Dissolved Mn behaviour varied significantly between the two resuspension
319 timescales examined. There was a general immediate release of $\text{Mn}^{2+}_{(\text{aq})}$ from the
320 porewater to the solution (Fig.7e) that was completely reversed within a major storm
321 time interval (Fig.7f). The release and the later uptake of $\text{Mn}^{2+}_{(\text{aq})}$ appeared to be more
322 important in the experiments carried out with inner estuary surface sediments. For the
323 inner estuary experiments, the release and uptake of $\text{Mn}^{2+}_{(\text{aq})}$ closed numerically.

324 However, from the outer estuary, only the S3 surface sediment experiments, showed an
325 equivalent Mn-release and uptake. This fact and the initial concentration of $\text{Mn}^{2+}_{(\text{aq})}$ in
326 surface porewater may indicate that these sediments were poised at Mn-reduction at the
327 time of sampling. Site 4 surface experiments showed slightly more Mn-uptake because
328 $\text{Mn}^{2+}_{(\text{aq})}$ decreased to levels below the initial $\text{Mn}^{2+}_{(\text{aq})}$ concentrations in the river water.
329 As mentioned above, coupled ammonium and/or organic-N oxidation with Mn oxides
330 reduction may also have been a short-term source of $\text{Mn}^{2+}_{(\text{aq})}$. Sulphate and Fe did not
331 show significant changes in the resuspension experiments during the first hour (Fig.7g
332 and 7i). After 48-72 hrs, there was a net production of sulphate in the experiments with
333 an increasing trend from S1 to S4. Although further conclusions about reaction
334 pathways cannot be drawn from this type of resuspension experiment, this trend
335 evidences again the more reducing conditions of the outer estuary sediments which
336 probably contained intermediate reduced sulphur species (e.g. sulphides, thiosulphate,
337 etc.) that were oxidised to form sulphate during the experiments (Fig.7h). The
338 differences in the concentration of acid extractable $\text{Fe}^{2+}_{(\text{s})}$ over 48 hrs of resuspension
339 (Fig.7j) became also more important in the experiments using outer most estuary
340 sediments due to their more reducing nature and their higher content of reactive Fe.

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

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

350 **4.3 Trace metal behaviour and changes during resuspension**

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

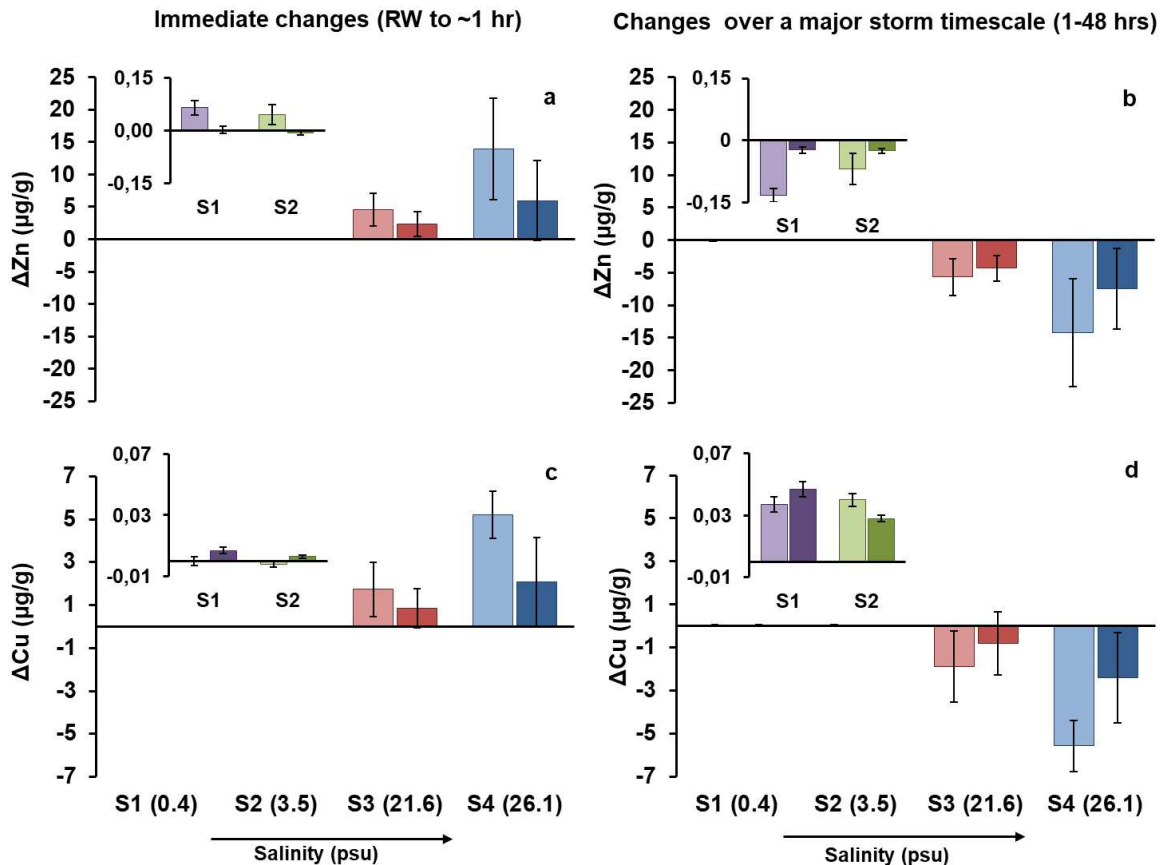
372 they aggregate to larger particles) may have passed the filters used, and therefore any
373 metal associated would have been deemed as solutes. Nevertheless, the releases of Zn
374 and Cu were generally reversed to a considerable extent by the time of a major storm
375 (Fig.8b and 8d) as a result,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

381 The mobilisation of TMs upon resuspension was also supported by the general
382 shift observed towards ‘easier to extract’ fractions in metal partitioning (exchangeable
383 and bound-to-carbonates). Although the metal release was reversed in a relatively short
384 term, changes in metal partitioning may have implications in metal bioavailability. The
385 Zn released in the inner estuary experiments was <0.1% of the total Zn in the
386 experiment, which was within the range of the Zn associated with the exchangeable
387 fraction. Zinc showed no significant changes in partitioning; but the decreases in the
388 “weak acid extractable” and Fe/Mn oxides-associated fractions did not match
389 quantitatively with any Zn increase in other fractions of the final sediments, which may
390 be probably explained by protocol limitations (see below). In the outer estuary
391 experiments, the average peak of Zn released was 11% of the total Zn in the
392 experiments. The Zn released to the solution was higher than the Zn associated with the
393 exchangeable fraction of these sediments, which suggests that Zn was likely mobilised
394 from other fractions. Probably Zn experienced a transient release (i.e. Zn likely sourced
395 from absorption complexes and returned to new absorption complexes). Zinc speciation
396 varied among the outer estuary sediments, and only two of them showed changes that

397 quantitatively matched (loss in the Fe/Mn oxides-bound fraction was equivalent to the
398 increase in carbonates and organic matter-sulphide fraction). On the other hand, the Cu
399 released to the solution in the inner estuary experiments represented about 0.1% of the
400 total Cu in the solids, which coincided with the Cu found in the exchangeable fraction.
401 In the outer estuary experiments, the average peak of Cu released to the solution was
402 22% of the total Cu in solids, which suggests that not only the Cu associated with the
403 exchangeable fraction was mobilised. Generally, in the initial sediment samples, Cu was
404 only found associated with the Fe/Mn oxides-bound fraction, whereas, for the
405 reoxidised endpoint sediments, it was found in all the fractions. Thus, Cu may have
406 been mobilised from high-energy binding sites to weaker binding sites. Nevertheless,
407 errors introduced during the extractions or associated with protocol limitations cannot
408 be discarded.

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

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



427

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

432 **4.4 General implications of sediment resuspension for nutrient and trace metal**
433 **transport and mobility in estuaries**

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

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

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

463 The area of the outer estuary intertidal mudflats is the largest in terms of aerial
464 extent (see Mortimer *et al.*, 1998), and therefore the potential amount of sediments, and
465 consequently nutrients and metals, mobilised will be significantly larger during an
466 extraordinary resuspension event than during normal circumstances. Also nutrient and
467 metal fluxes will be determined largely by the flow conditions, which means that a
468 turbulent release (e.g. in storm conditions) may be relevant to the overall nutrient and
469 metal budgets (see more in Supporting Information, SI.7). In the outer estuary mudflats,
470 the larger amount of Fe and the continuous availability of sulphate seem to promote the
471 development of sulphidic conditions at a depth, which are not observed in the inner
472 estuary sites. The total oxidation of the inorganic species released during the
473 resuspension of estuary sediments would equate to an oxygen consumption of 20 ± 10
474 $\text{mmol O}_2 \text{ kg}^{-1}$, and to $70\pm 40 \text{ mmol O}_2 \text{ kg}^{-1}$ for the inner and outer estuary sediments
475 respectively. This amount of oxygen removal could result in full deoxygenation of
476 surface waters at relatively low solid-solution ratios (15 g L^{-1} for the inner estuary; 4 g
477 L^{-1} for the outer estuary). However, well-mixed estuaries rarely exhibit water column
478 hypoxia (Paerl, 2006). The kinetics of the reoxidation processes (especially those of Fe
479 and S) are such that supply of oxygen (by diffusion from the atmosphere or mixing with
480 adjacent oxygenated waters) is likely to prevent anoxic conditions from developing in
481 all but the very largest of remobilisation events.

482 Humber sediments may act as an ultimate sink for the major (Fe and Mn) and
483 trace metals; while for nutrients, they may act as a major source on some occasions, as
484 argued by Millward and Glegg (1997). Nutrient fluxes estimations showed important
485 differences in nitrate and ammonium fluxes when comparing resuspension of surface
486 and subsurface sediments. If subsurface sediments are mobilised, nitrate fluxes would
487 increase from 23.8 to 40.8 mmol/m²/day in the inner estuary, and from -12.1 to -3.9
488 mmol/m²/day in the outer estuary. Ammonium fluxes would increase from -2.0 to 4.6
489 mmol/m²/day in the inner estuary, and from -3.9 to 32.3 mmol/m²/day in the outer
490 estuary. Considering the areas of the inner and outer estuary, these estimations suggest
491 that the whole estuary may act as an overall source of DIN rather than a sink when
492 subsurface sediments are mobilised.

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

507 Furthermore, these experiments showed that sediment resuspension led to a shift in TM
508 partitioning (i.e. a greater proportion of Zn and Cu were associated with more weakly
509 bound fractions). In the natural environment, before sediments are ultimately scavenged
510 deeper in the sediment column, they will be continuously resuspended (Lee & Cundy,
511 2001), so the transfer of TMs to weaker bound fractions will have implications in their
512 bioavailability over time.

513 Climate change will impact upon morphodynamics and ecological processes in
514 UK estuaries (Robins *et al.*, 2016). More frequent and intense episodes of extreme
515 precipitations over Britain have been predicted (Jones & Reid, 2001; Christensen *et al.*,
516 2007; IPCC, 2013). Therefore, in terms of budget, the more regular mobilisation of
517 undisrupted subsurface sediment will lead to increased nutrient and metal inputs to the
518 estuarine water column and maybe ultimately to coastal waters, which will have
519 important environmental implications. Furthermore, changes in the estuarine dynamics
520 could compromise the conditions needed for estuarine sediments to reach steady state
521 before the next mixing event takes place, which may affect the sediment redox
522 stratification and the development of well-defined geochemical zonations within the
523 sediment profile.

524 **5. Conclusions**

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

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

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552 **7. References**

- 553 [1] Abril, G., Riou, S. A., Etcheber, H., Frankignoulle, M., de Wit, R., &
554 Middelburg, J. J. (2000). Transient, tidal time-scale, nitrogen transformations in an
555 estuarine turbidity maximum-fluid mud system (The Gironde, south-west France).
556 *Estuarine Coastal and Shelf Science*, 50(5), 703-715. doi: 10.1006/ecss.1999.0598
- 557 [2] Abril, G., Nogueira, M., Etcheber, H., Cabçadas, G., Lemaire, E., & Brogueira,
558 M. J. (2002). Behaviour of organic carbon in nine contrasting European estuaries.
559 *Estuarine, coastal and shelf science*, 54(2), 241-262. doi: 10.1006/ecss.2001.0844
- 560 [3] Allen, H. E., Fu, G. M., & Deng, B. L. (1993). Analysis of acid-volatile sulfide
561 (AVS) and simultaneously extracted metals (SEM) for the estimation of potential
562 toxicity in aquatic sediments. *Environmental Toxicology and Chemistry*, 12(8), 1441-
563 1453. doi: 10.1897/1552-8618(1993)12[1441:aoasaa]2.0.co;2
- 564 [4] Aller, R. C. (1994). Bioturbation and remineralization of sedimentary organic-
565 matter - effects of redox oscillation. *Chemical Geology*, 114(3-4), 331-345. doi:
566 10.1016/0009-2541(94)90062-0
- 567 [5] Andrews, J. E., Samways, G., & Shimmield, G. B. (2008). Historical storage
568 budgets of organic carbon, nutrient and contaminant elements in saltmarsh sediments:
569 Biogeochemical context for managed realignment, Humber Estuary, UK. *Science of*
570 *The Total Environment*, 405(1-3), 1-13. doi: 10.1016/j.scitotenv.2008.07.044
- 571 [6] Anju, M., & Banerjee, D. K. (2010). Comparison of two sequential extraction
572 procedures for heavy metal partitioning in mine tailings. *Chemosphere*, 78(11), 1393-
573 1402. doi: 10.1016/j.chemosphere.2009.12.064
- 574 [7] Anschutz, P., Sundby, B., Lefrancois, L., Luther, G. W., & Mucci, A. (2000).
575 Interactions between metal oxides and species of nitrogen and iodine in bioturbated

- 576 marine sediments. *Geochimica et Cosmochimica Acta*, 64(16), 2751-2763. doi:
577 10.1016/s0016-7037(00)00400-2
- 578 [8] Barnes, J., & Owens, N. J. P. (1998). Denitrification and nitrous oxide
579 concentrations in the Humber estuary, UK, and adjacent coastal zones. *Marine Pollution*
580 *Bulletin*, 37(3-7), 247-260.
- 581 [9] Berner, R. A. (1980). *Early diagenesis: A theoretical approach*. New York:
582 Princeton University Press.
- 583 [10] Blanchard, G. F., Paterson, D. M., Stal, L. J., Richard, P., Galois, R., Huet, V.,
584 Kelly, J., Honeywill, C., de Brouwer, J., Dyer, K., Christie, M., & Seguignes, M.
585 (2000). The effect of geomorphological structures on potential biostabilisation by
586 microphytobenthos on intertidal mudflats. *Continental Shelf Research*, 20(10), 1243-
587 1256. doi: [https://doi.org/10.1016/S0278-4343\(00\)00021-2](https://doi.org/10.1016/S0278-4343(00)00021-2)
- 588 [11] Boyer, E. W., & Howarth, R. W. (2002). *The Nitrogen Cycle at Regional to*
589 *Global Scales. Report of the International SCOPE Nitrogen Project (Vol. 57/58)*.
590 Dordrecht, Netherlands: Springer.
- 591 [12] Bruno, P., Caselli, M., de Gennaro, G., De Tommaso, B., Lastella, G., &
592 Mastrolitti, S. (2003). Determination of nutrients in the presence of high chloride
593 concentrations by column-switching ion chromatography. *Journal of Chromatography*
594 *A*, 1003(1-2), 133-141. doi: 10.1016/s0021-9673(03)00785-4
- 595 [13] Burdige, D. J. (1993). The biogeochemistry of manganese and iron reduction in
596 marine-sediments. *Earth-Science Reviews*, 35(3), 249-284. doi: 10.1016/0012-
597 8252(93)90040-e
- 598 [14] Burke, I. T., Boothman, C., Lloyd, J. R., Mortimer, R. J. G., Livens, F. R., &
599 Morris, K. (2005). Effects of Progressive Anoxia on the Solubility of Technetium in
600 Sediments. *Environmental Science & Technology*, 39, 4109-4116.
- 601 [15] Caetano, M., Madureira, M. J., & Vale, C. (2003). Metal remobilisation during
602 resuspension of anoxic contaminated sediment: short-term laboratory study. *Water Air*
603 *and Soil Pollution*, 143(1-4), 23-40. doi: 10.1023/a:1022877120813
- 604 [16] Calmano, W., Hong, J., & Forstner, U. (1993). Binding and mobilization of
605 heavy-metals in contaminated sediments affected by pH and redox potential. *Water*
606 *Science and Technology*, 28(8-9), 223-235. doi: 10.15480/882.450
- 607 [17] Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., & Berner, R. A.
608 (1986). The use of chromium reduction in the analysis of reduced inorganic sulfur in
609 sediments and shales. *Chemical Geology*, 54(1-2), 149-155. doi: 10.1016/0009-
610 2541(86)90078-1
- 611 [18] Canfield, D. E., Kristensen, E., & Thamdrup, B. (2005). *Aquatic*
612 *Geomicrobiology (Vol. 48)*. London: Elsevier Academic Press.

- 613 [19] Canfield, D. E., & Thamdrup, B. (2009). Towards a consistent classification
614 scheme for geochemical environments, or, why we wish the term 'suboxic' would go
615 away. *Geobiology*, 7(4), 385-392. doi: 10.1111/j.1472-4669.2009.00214.x
- 616 [20] Canfield, D. E., Glazer, A. N., & Falkowski, P. G. (2010). The Evolution and
617 Future of Earth's Nitrogen Cycle. *Science*, 330(6001), 192-196. doi:
618 10.1126/science.1186120
- 619 [21] Cantwell, M. G., Burgess, R. M., & Kester, D. R. (2002). Release and phase
620 partitioning of metals from anoxic estuarine sediments during periods of simulated
621 resuspension. *Environmental Science & Technology*, 36(24), 5328-5334. doi:
622 10.1021/es0115058
- 623 [22] Cave, R. R., Andrews, J. E., Jickells, T., & Coombes, E. G. (2005). A review of
624 sediment contamination by trace metals in the Humber catchment and estuary, and the
625 implications for future estuary water quality. *Estuarine, Coastal and Shelf Science*,
626 62(3), 547-557. doi: 10.1016/j.ecss.2004.09.017
- 627 [23] Christensen, J. H., Hewitson, B., Busuioc, A., Chen, A., Gao, X., Held, I., Jones,
628 R., Kolli, R. K., Kwon, W.-T., Laprise, R., Magaña Rueda, V., Mearns, L., Menéndez,
629 C. G., Räisänen, J., Rinke, A., Sarr, A., & Whetton, P. (2007). Regional Climate
630 Projections. In S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt,
631 M. Tignor & H.L. Miller (Eds.), *Climate Change 2007: The Physical Science Basis*.
632 Contribution of Working Group I to the Fourth Assessment Report of the
633 Intergovernmental Panel on Climate Change (pp. 847-940). Cambridge, United
634 Kingdom and New York, NY, USA: Cambridge University Press.
- 635 [24] Couceiro, F., Fones, G. R., Thompson, C. E. L., Statham, P. J., Sivyer, D. B.,
636 Parker, R., Kelly-Gerreyn, B. A., & Amos, C. L. (2013). Impact of resuspension of
637 cohesive sediments at the Oyster Grounds (North Sea) on nutrient exchange across the
638 sediment-water interface. *Biogeochemistry*, 113(1-3), 37-52. doi: 10.1007/s10533-012-
639 9710-7
- 640 [25] Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Hicks, M. B., Mayr,
641 S. M., & Redmond, M. S. (1990). Toxicity of cadmium in sediments the role of acid
642 volatile sulfide. *Environmental Toxicology and Chemistry*, 9(12), 1487-1502. doi:
643 10.1002/etc.5620091208
- 644 [26] Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F. M. G., &
645 Verloo, M. G. (2008). Effect of salinity on heavy metal mobility and availability in
646 intertidal sediments of the Scheldt estuary. *Estuarine Coastal and Shelf Science*, 77(4),
647 589-602. doi: 10.1016/j.ecss.2007.10.017
- 648 [27] Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. M. G.
649 (2009). Trace metal behaviour in estuarine and riverine floodplain soils and sediments:
650 A review. *Science of The Total Environment*, 407(13), 3972-3985. doi:
651 10.1016/j.scitotenv.2008.07.025

- 652 [28] EASAC (2013). Trends in extreme weather events in Europe: implications for
653 national and European Union adaptation strategies (EASAC policy report 22 ed.):
654 EASAC. Retrieved from
655 [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)
656 [her_Events.pdf](http://www.easac.eu/fileadmin/PDF_s/reports_statements/Easac_Report_Extreme_Weather_Events.pdf)
- 657 [29] Eggleton, J., & Thomas, K. V. (2004). A review of factors affecting the release
658 and bioavailability of contaminants during sediment disturbance events. *Environment*
659 *International*, 30(7), 973-980. doi: 10.1016/j.envint.2004.03.001
- 660 [30] Fang, T., Li, X., & Zhang, G. (2005). Acid volatile sulfide and simultaneously
661 extracted metals in the sediment cores of the Pearl River Estuary, South China.
662 *Ecotoxicology and Environmental Safety*, 61(3), 420-431. doi:
663 <http://dx.doi.org/10.1016/j.ecoenv.2004.10.004>
- 664 [31] Fossing, H., & Jørgensen, B. B. (1989). Measurement of bacterial sulfate
665 reduction in sediments - evaluation of a single-step chromium reduction method.
666 *Biogeochemistry*, 8(3), 205-222. doi: 10.1007/BF00002889
- 667 [32] Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G.
668 R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., & Maynard, V. (1979). Early
669 oxidation of organic-matter in pelagic sediments of the eastern equatorial atlantic -
670 suboxic diagenesis. *Geochimica et Cosmochimica Acta*, 43(7), 1075-1090. doi:
671 10.1016/0016-7037(79)90095-4
- 672 [33] Gunnars, A., Blomqvist, S., Johansson, P., & Andersson, C. (2002). Formation
673 of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with
674 incorporation of phosphate and calcium. *Geochimica et Cosmochimica Acta*, 66(5),
675 745-758. doi: 10.1016/s0016-7037(01)00818-3
- 676 [34] Gerringa, L. J. A., de Baar, H. J. W., Nolting, R. F., & Paucot, H. (2001). The
677 influence of salinity on the solubility of Zn and Cd sulphides in the Scheldt estuary.
678 *Journal of Sea Research*, 46(3-4), 201-211. doi: 10.1016/s1385-1101(01)00081-8
- 679 [35] Gleyzes, C., Tellier, S., & Astruc, M. (2002). Fractionation studies of trace
680 elements in contaminated soils and sediments: a review of sequential extraction
681 procedures. *Trac-Trends in Analytical Chemistry*, 21(6-7), 451-467. doi:
682 10.1016/s0165-9936(02)00603-9
- 683 [36] Henrichs, S. M. (1992). Early diagenesis of organic matter in marine sediments:
684 progress and perplexity. *Marine Chemistry*, 39(1), 119-149. doi: 10.1016/0304-
685 4203(92)90098-U
- 686 [37] Hirst, J. M., & Aston, S. R. (1983). Behavior of copper, zinc, iron and
687 manganese during experimental resuspension and reoxidation of polluted anoxic
688 sediments. *Estuarine Coastal and Shelf Science*, 16(5), 549-558. doi: 10.1016/0272-
689 7714(83)90085-9
- 690 [38] Howarth, R. W., Billen, G., Swaney, D., Townsend, A., Jaworsky, N., Lajtha, K.,
691 Downing, J. A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov,

- 692 V., Murdoch P., and Zhao-Liang Zhu. (1996). Regional Nitrogen budgets and riverine
693 N & P fluxes for the drainages to the North Atlantic Ocean: natural and human
694 influences. *Biogeochemistry*, 35, 75-139.
- 695 [39] Huerta-Diaz, M. A., & Morse, J. W. (1990). A quantitative method for
696 determination of trace metal concentrations in sedimentary pyrite. *Marine Chemistry*,
697 29(2-3), 119-144. doi: 10.1016/0304-4203(90)90009-2
- 698 [40] IPCC. (2013). Summary for policymakers. In T.F. Stocker, D. Qin, G.K.
699 Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex & P.M.
700 Midgley (Eds.), *Climate Change 2013: the Physical Science Basis*. Contribution of
701 Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on
702 Climate Change. United Kingdom and New York, NY, USA: Cambridge University
703 Press.
- 704 [41] Jerez Vegueria, S. F., Godoy, J. M., de Campos, R. C., & Goncalves, R. A.
705 (2013). Trace element determination in seawater by ICP-MS using online, offline and
706 bath procedures of preconcentration and matrix elimination. *Microchemical Journal*,
707 106, 121-128. doi: 10.1016/j.microc.2012.05.032
- 708 [42] Jones, P. D., & Reid, P. A. (2001). Assessing future changes in extreme
709 precipitation over Britain using regional climate model integrations. *International*
710 *Journal of Climatology*, 21(11), 1337-1356. doi: 10.1002/joc.677
- 711 [43] Jørgensen, B. B. (1977). Sulfur cycle of a coastal marine sediment (Limfjorden,
712 Denmark). *Limnology and Oceanography*, 22(5), 814-832. doi:
713 10.4319/lo.1977.22.5.0814
- 714 [44] Jørgensen, B. B. (1982). Mineralization of organic-matter in the sea bed - the
715 role of sulfate reduction. *Nature*, 296(5858), 643-645. doi: 10.1038/296643a0
- 716 [45] Joye, S. B., & Hollibaugh, J. T. (1995). Influence of sulfide inhibition of
717 nitrification on nitrogen regeneration in sediments. *Science*, 270(5236), 623-625. doi:
718 10.1126/science.270.5236.623
- 719 [46] Kalnejais, L. H., Martin, W. R., & Bothner, M. H. (2010). The release of
720 dissolved nutrients and metals from coastal sediments due to resuspension. *Marine*
721 *Chemistry*, 121(1-4), 224-235. doi: 10.1016/j.marchem.2010.05.002
- 722 [47] Lamb, H., & Frydendahl, K. U. (1991). *Historic Storms of the North Sea, British*
723 *Isles and Northwest Europe*: Cambridge University Press.
- 724 [48] Lansdown, K., Heppell, C. M., Dossena, M., Ullah, S., Heathwaite, A. L.,
725 Binley, A., Zhang, H., & Trimmer, M. (2014). Fine-Scale in Situ Measurement of
726 Riverbed Nitrate Production and Consumption in an Armored Permeable Riverbed.
727 *Environmental Science & Technology*, 48(8), 4425-4434. doi: 10.1021/es4056005
- 728 [49] Lansdown, K., Heppell, C. M., Trimmer, M., Binley, A., Heathwaite, A. L.,
729 Byrne, P., & Zhang, H. (2015). The interplay between transport and reaction rates as
730 controls on nitrate attenuation in permeable, streambed sediments. *Journal of*
731 *Geophysical Research-Biogeosciences*, 120(6), 1093-1109. doi: 10.1002/2014jg002874

- 732 [50] Lee, S. V., & Cundy, A. B. (2001). Heavy Metal Contamination and Mixing
733 Processes in Sediments from the Humber Estuary, Eastern England. *Estuarine, Coastal*
734 *and Shelf Science*, 53(5), 619-636. doi: 10.1006/ecss.2000.0713
- 735 [51] Lovley, D. R., & Phillips, E. J. P. (1986). *Appl. Environ. Microbiol.*, 52, 751.
- 736 [52] Lovley, D. R., & Phillips, E. J. P. (1987). Rapid assay for microbially reducible
737 ferric iron in aquatic sediments. *Applied and Environmental Microbiology*, 53(7), 1536-
738 1540.
- 739 [53] Luther, G. W., Sundby, B., Lewis, B. L., Brendel, P. J., & Silverberg, N. (1997).
740 Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen.
741 *Geochimica et Cosmochimica Acta*, 61(19), 4043-4052. doi: 10.1016/s0016-
742 7037(97)00239-1
- 743 [54] Martin, J. M., Nirel, P., & Thomas, A. J. (1987). Sequential extraction
744 techniques - promises and problems. *Marine Chemistry*, 22(2-4), 313-341. doi:
745 10.1016/0304-4203(87)90017-x
- 746 [55] Martino, M., Turner, A., Nimmo, A., & Millward, G. E. (2002). Resuspension,
747 reactivity and recycling of trace metals in the Mersey Estuary, UK. *Marine Chemistry*,
748 77(2-3), 171-186. doi: 10.1016/s0304-4203(01)00086-x
- 749 [56] Mayer, L. M. (1994). Surface-area control of organic-carbon accumulation in
750 continental-shelf sediments. *Geochimica et Cosmochimica Acta*, 58(4), 1271-1284. doi:
751 10.1016/0016-7037(94)90381-6
- 752 [57] Middelburg, J. J., & Herman, P. M. J. (2007). Organic matter processing in tidal
753 estuaries. *Marine Chemistry*, 106(1-2), 127-147. doi: 10.1016/j.marchem.2006.02.007
- 754 [58] Middelburg, J. J., & Levin, L. A. (2009). Coastal hypoxia and sediment
755 biogeochemistry. *Biogeosciences*, 6(7), 1273-1293. doi: 10.5194/bg-6-1273-2009
- 756 [59] Middleton, R., & Grant, A. (1990). Heavy Metals in the Humber Estuary:
757 Scrobicularia Clay as a Pre-industrial Datum. *Proceedings of the Yorkshire Geological*
758 *Society*, 48(pàg. 75-80).
- 759 [60] Millward, G., & Liu, Y. (2003). Modelling metal desorption kinetics in
760 estuaries. *Sci Total Environ*, 314-316, 613-623. doi: 10.1016/s0048-9697(03)00077-9
- 761 [61] Millward, G. E., & Glegg, G. A. (1997). Fluxes and Retention of Trace Metals
762 in the Humber Estuary. *Estuarine, Coastal and Shelf Science*, 44, 97-105.
- 763 [62] Morgan, B., Rate, A. W., & Burton, E. D. (2012). Water chemistry and nutrient
764 release during the resuspension of FeS-rich sediments in a eutrophic estuarine system.
765 *Science of The Total Environment*, 432, 47-56. doi: 10.1016/j.scitotenv.2012.05.065
- 766 [63] Morin, J., & Morse, J. W. (1999). Ammonium release from resuspended
767 sediments in the Laguna Madre estuary. *Marine Chemistry*, 65(1-2), 97-110. doi:
768 10.1016/s0304-4203(99)00013-4

- 769 [64] Morris, A. W., Bale, A. J., Howland, R.J.M., Millward, G.E., Ackroyd, R.,
770 Loring H. and Rantala, R.T.T. (1986). Sediment mobility and its contribution to trace
771 metal cycling and retention in a macrotidal estuary. *Water Science and Technology*, 18,
772 111-119.
- 773 [65] Mortimer, R. J. G., Krom, M. D., Watson, P. G., Frickers, P. E., Davey, J. T., &
774 Clifton, R. J. (1998). Sediment-water exchange of nutrients in the intertidal zone of the
775 Humber estuary, UK. *Marine Pollution Bulletin*, 37(3-7), 261-279. doi: 10.1016/s0025-
776 326x(99)00053-3
- 777 [66] Mortimer, R. J. G., Davey, J. T., Krom, M. D., Watson, P. G., Frickers, P. E., &
778 Clifton, R. J. (1999). The Effect of Macrofauna on Porewater Profiles and Nutrient
779 Fluxes in the Intertidal Zone of the Humber Estuary. *Estuarine, Coastal and Shelf*
780 *Science*, 48(6), 683-699. doi: <https://doi.org/10.1006/ecss.1999.0479>
- 781 [67] Murray, J. W., Codispoti, L. A., & Friederich, G. E. (1995). Oxidation-reduction
782 environments - the suboxic zone in the black-sea. *Aquatic Chemistry: Interfacial and*
783 *Interspecies Processes*, 244, 157-176. doi: 10.1021/ba-1995-0244.ch007
- 784 [68] Nedwell, D. B., Jickells, T. D., Trimmer, M., & Sanders, R. (1999). Nutrients in
785 estuaries. In D. B. Nedwell & D. G. Raffaelli (Eds.), *Advances in Ecological Research*,
786 *Estuaries* (Vol. 29, pp. 43-92): Academic Press.
- 787 [69] NRA. (1995). *Sea Vigil Water Quality Monitoring: the Humber Estuary 1992-*
788 *1993*. Peterborough: National Rivers Authority Anglian Region. Retrieved from
789 <http://www.environmentdata.org/archive/ealit:2851>.
- 790 [70] NRA. (1996). *Sea Vigil Water Quality Monitoring: The Humber Estuary 1994*.
791 Peterborough: National Rivers Authority Anglian Region. Retrieved from
792 <http://www.environmentdata.org/archive/ealit:2868>
- 793 [71] Paerl, H. W. (2006). Assessing and managing nutrient-enhanced eutrophication
794 in estuarine and coastal waters: Interactive effects of human and climatic perturbations.
795 *Ecological Engineering*, 26(1), 40-54. doi: 10.1016/j.ecoleng.2005.09.006
- 796 [72] Percuoco, V. P., Kalnejais, L. H., & Officer, L. V. (2015). Nutrient release from
797 the sediments of the Great Bay Estuary, NH USA. *Estuarine Coastal and Shelf Science*,
798 161, 76-87. doi: 10.1016/j.ecss.2015.04.006
- 799 [73] Pethick, J. S. (1990). *The Humber Estuary*. In S. and Crowther Ellis, D.R. (Ed.),
800 *Humber Perspectives, A region through the ages* (pp. 54-67). Hull: Hull University.
- 801 [74] Postma, D., & Jakobsen, R. (1996). Redox zonation: Equilibrium constraints on
802 the Fe(III)/SO₄-reduction interface. *Geochimica et Cosmochimica Acta*, 60(17), 3169-
803 3175. doi: 10.1016/0016-7037(96)00156-1
- 804 [75] Rauret, G., Rubio, R., & López-Sánchez, J. F. (1989). Optimization of Tessier
805 Procedure for Metal Solid Speciation in River Sediments. *International Journal of*
806 *Environmental Analytical Chemistry*, 36(2), 69-83. doi: 10.1080/03067318908026859

- 807 [76] Reed, N. M., Cairns, R. O., Hutton, R. C., & Takaku, Y. (1994).
808 Characterization of polyatomic ion interferences in inductively-coupled plasma-mass
809 spectrometry using a high-resolution mass-spectrometer. *Journal of Analytical Atomic*
810 *Spectrometry*, 9(8), 881-896. doi: 10.1039/ja9940900881
- 811 [77] Roberts, K. L., Eate, V. M., Eyre, B. D., Holland, D. P., & Cook, P. L. M.
812 (2012). Hypoxic events stimulate nitrogen recycling in a shallow salt-wedge estuary:
813 The Yarra River estuary, Australia. *Limnology and Oceanography*, 57(5), 1427-1442.
814 doi: 10.4319/lo.2012.57.5.1427
- 815 [78] Roberts, K. L., Kessler, A. J., Grace, M. R., & Cook, P. M. L. (2014). Increased
816 rates of dissimilatory nitrate reduction to ammonium (DNRA) under oxic conditions in
817 a periodically hypoxic estuary. *Geochimica et Cosmochimica Acta*, 133, 313-324. doi:
818 <http://dx.doi.org/10.1016/j.gca.2014.02.042>
- 819 [79] Robins, P. E., Skov, M. W., Lewis, M. J., Giménez, L., Davies, A. G., Malham,
820 S. K., Neill, S. P., McDonald, J. E., Whitton, T. A., Jackson, S. E., & Jago, C. F. (2016).
821 Impact of climate change on UK estuaries: A review of past trends and potential
822 projections. *Estuarine, Coastal and Shelf Science*, 169(Supplement C), 119-135. doi:
823 <https://doi.org/10.1016/j.ecss.2015.12.016>
- 824 [80] Salomons, W., Derooij, N. M., Kerdijk, H., & Bril, J. (1987). Sediments as a
825 source of contaminants. *Hydrobiologia*, 149, 13-30. doi: 10.1007/bf00048643
- 826 [81] Sanders, R. J., Jickells, T., Malcolm, S., Brown, J., Kirkwood, D., Reeve, A.,
827 Taylor, J., Horrobin, T., & Ashcroft, C. (1997). Nutrient Fluxes through the Humber
828 estuary. *Journal of Sea Research*, 37, 3-23.
- 829 [82] Sanford, L. P. (2008). Modeling a dynamically varying mixed sediment bed with
830 erosion, deposition, bioturbation, consolidation, and armoring. *Comput. Geosci.*, 34(10),
831 1263-1283. doi: 10.1016/j.cageo.2008.02.011
- 832 [83] Saulnier, I., & Mucci, A. (2000). Trace metal remobilization following the
833 resuspension of estuarine sediments: Saguenay Fjord, Canada. *Applied Geochemistry*,
834 15(2), 191-210. doi: 10.1016/s0883-2927(99)00034-7
- 835 [84] Sayama, M., Risgaard-Petersen, N., Nielsen, L. P., Fossing, H., & Christensen,
836 P.B. (2005). Impact of bacterial NO₃- transport on sediment biogeochemistry. *Applied*
837 *and Environmental Microbiology*, 71(11), 7575-7577. doi: 10.1128/aem.71.11.7575-
838 7577.2005
- 839 [85] Seitzinger, S. P., & Sanders, R. W. (1997). Contribution of dissolved organic
840 nitrogen from rivers to estuarine eutrophication. *Marine Ecology Progress Series*, 159,
841 1-12. doi: 10.3354/meps159001
- 842 [86] Simpson, S. L., Apte, S. C., & Batley, G. E. (1998). Effect of short term
843 resuspension events on trace metal speciation in polluted anoxic sediments.
844 *Environmental Science & Technology*, 32(5), 620-625. doi: 10.1021/es970568g
- 845 [87] Song, G. D., Liu, S. M., Marchant, H., Kuypers, M. M. M., & Lavik, G. (2013).
846 Anammox, denitrification and dissimilatory nitrate reduction to ammonium in the East

- 847 China Sea sediment. *Biogeosciences*, 10(11), 6851-6864. doi: 10.5194/bg-10-6851-
848 2013
- 849 [88] Sørensen, J., & Jørgensen, B. B. (1987). Early diagenesis in sediments from
850 Danish coastal waters - microbial activity and Mn-Fe-S geochemistry. *Geochimica et*
851 *Cosmochimica Acta*, 51(6), 1583-1590. doi: 10.1016/0016-7037(87)90339-5
- 852 [89] Statham, P. J. (2012). Nutrients in estuaries--an overview and the potential
853 impacts of climate change. *Sci Total Environ*, 434, 213-227. doi:
854 10.1016/j.scitotenv.2011.09.088
- 855 [90] Stumm, W., & Morgan, J. J. (1970). *Aquatic chemistry: an introduction*
856 *emphasizing chemical equilibria in natural waters*. New York: Wiley-Interscience.
- 857 [91] Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction
858 procedure for the speciation of particulate trace-metals. *Analytical Chemistry*, 51(7),
859 844-851. doi: 10.1021/ac50043a017
- 860 [92] Thamdrup, B., Fossing, H., & Jørgensen, B. B. (1994). Manganese, iron, and
861 sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Geochimica et*
862 *Cosmochimica Acta*, 58(23), 5115-5129. doi: 10.1016/0016-7037(94)90298-4
- 863 [93] Thamdrup, B. (2012). New Pathways and Processes in the Global Nitrogen
864 Cycle. *Annual Review of Ecology, Evolution, and Systematics*, 43, 407-428. doi:
865 10.1146/annurev-ecolsys-102710-145048
- 866 [94] Townend, I. H., Wang, Z. B., & Rees, J. (2007). Millennial to annual volume
867 changes in the Humber Estuary. Paper presented at the Proceedings of the Royal
868 Society of London A: Mathematical, Physical and Engineering Sciences.
- 869 [95] Triska, F. J., Duff, J. H., & Avanzino, R. J. (1993). The role of water exchange
870 between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial
871 aquatic interface. *Hydrobiologia*, 251(1-3), 167-184. doi: 10.1007/bf00007177
- 872 [96] Tyson, R. V. (1995). The nature of organic matter in sediments *Sedimentary*
873 *organic matter: Organic facies and palynofacies* (pp. 7-28). London: Chapman & Hall.
- 874 [97] Uncles, R. J., Wood, R. G., Stephens, J. A., & Howland, R. J. M. (1998a).
875 Estuarine Nutrient Fluxes to the Humber Coastal Zone, UK, during June 1995. *Marine*
876 *Pollution Bulletin*, 37, 225-233.
- 877 [98] Uncles, R. J., Stephens, J. A., & Law, D. J. (2006). Turbidity maximum in the
878 macrotidal, highly turbid Humber Estuary, UK: Floccs, fluid mud, stationary suspensions
879 and tidal bores. *Estuarine, Coastal and Shelf Science*, 67(1-2), 30-52. doi:
880 10.1016/j.ecss.2005.10.013
- 881 [99] Uncles, R. J., Joint, I., & Stephens, J. A. (1998b). Transport and retention of
882 suspended particulate matter and bacteria in the Humber-Ouse Estuary, United
883 Kingdom, and their relationship to hypoxia and anoxia. *Estuaries*, 21(4A), 597-612. doi:
884 10.2307/1353298

- 885 [100] Van Prooijen, B. C., & Winterwerp, J. C. (2010). A stochastic formulation for
886 erosion of cohesive sediments. *Journal of Geophysical Research: Oceans*, 115(C1), n/a-
887 n/a. doi: 10.1029/2008JC005189
- 888 [101] Viollier, E., Inglett, P.W., Huntrer, K., Roychoudhury, A. N., and Van
889 Cappellen, P. (2000). The ferrozine method revised: Fe(II)/Fe(III) determination in
890 natural waters. *Applied Geochemistry*, 15, 785-790.
- 891 [102] Wengrove, M. E., Foster, D. L., Kalnejais, L. H., Percuoco, V., & Lippmann, T.
892 C. (2015). Field and laboratory observations of bed stress and associated nutrient
893 release in a tidal estuary. *Estuarine, Coastal and Shelf Science*, 161(Supplement C), 11-
894 24. doi: 10.1016/j.ecss.2015.04.005
- 895 [103] Wu, Y., Falconer, R. A., & Uncles, R. J. (1999). Modelling of Water Flows and
896 Cohesive Sediment Fluxes in the Humber Estuary, UK. *Marine Pollution Bulletin*,
897 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)