Article:

Vidal-Dura, A, Burke, IT, Stewart, DI orcid.org/0000-0001-5144-1234 et al. (1 more author) (2018) Reoxidation of estuarine sediments during simulated resuspension events: Effects on nutrient and trace metal mobilisation. Estuarine, Coastal and Shelf Science, 207. pp. 40-55. ISSN 0272-7714

https://doi.org/10.1016/j.ecss.2018.03.024

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

Andrea Vidal-Durà[1], Ian T. Burke[1], Douglas I. Stewart[2] and Robert J.G. Mortimer[3]

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

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

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

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

andreavidaldura@gmail.com

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 km^2 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).

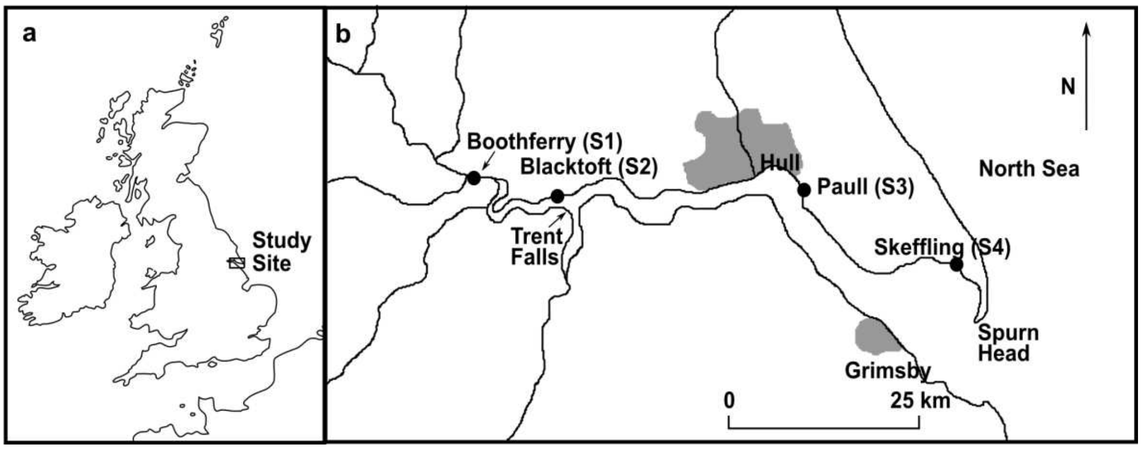

Figure 1: Map with the location of the Humber Estuary (a), and detail of the sampling sites (Boothferry (S1), Blacktoft (S2), Paull (S3), and Skeffling (S4)) (b).

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 HNO_3 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 $Fe^{2+}_{(s)}$ 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 ºC), 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 HNO_3 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±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 HNO_3) 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 $Fe^{2+}_{(s)}$ 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 $MgCl_2$ 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 $NH_2OH{\cdot}HCl$ in 25% v/v HAc (for the bound to Fe/Mn oxides), and 30% H_2O_2 at pH 2 (with HNO_3) followed by NH_4Ac (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
NO_3^- (μM)	266	250	248	<LDL
NH_4^+ (μM)	7	7	12	23
Mn^{2+} (μM)	1.4	1.0	0.6	23
SO_4^{2-} (mM)	0.8	3.4	16	22
Fe^{2+} (μM)	0.1	0.1	1.2	1.8

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, clinochlore, 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 $Fe^{2+}_{(s)}$ 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).

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

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

3.2 Major Element behaviour during sediment resuspension

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

3.2.1 Inner estuary

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

Ammonium concentrations in the experiments carried out with surface sediments decreased immediately after resuspension started (Fig.2c) and remained close to detection levels until 48 hrs, when concentrations transiently increased to around 20-30 µM before decreasing to low concentrations by the end of the test. On the other hand, ammonium concentrations in experiments using subsurface sediments (Fig.2d) increased immediately after resuspension started from <10 to ~20 µM in S1 experiments. The ammonium increase was more progressive in S2 experiments, in which concentrations doubled within the first hour. Then, levels of ammonium in the subsurface sediment experiments remained relatively constant after the first day of resuspension.

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

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

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

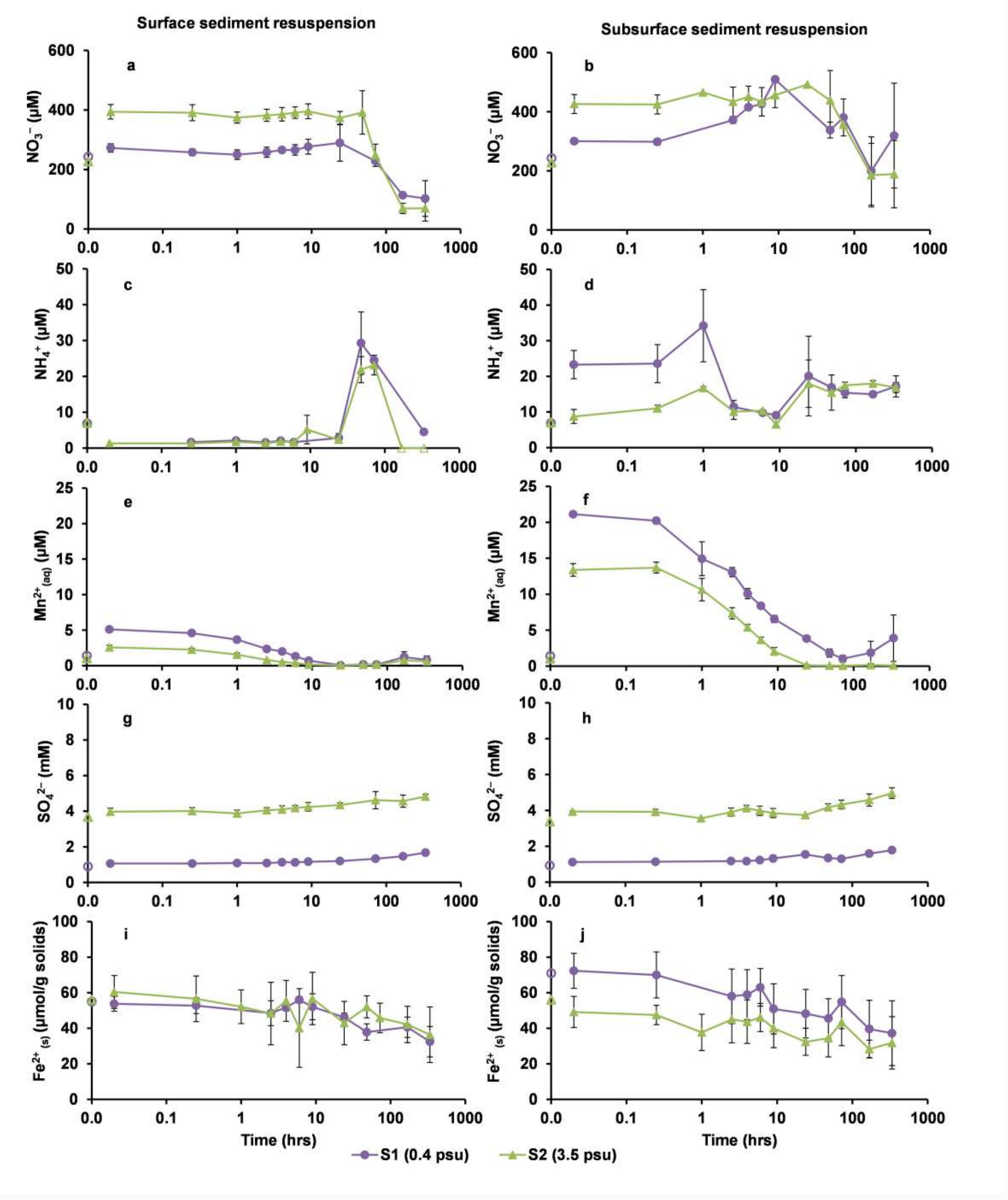

Figure 2: Major element behaviour during resuspension of inner estuary sediments. The purple line with circles represents S1 (Boothferry) and the green line with triangles represents S2 (Blacktoft). Open symbols on the y-axis indicate the initial concentrations of the major elements in the experiments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

3.2.2 Outer estuary

The experiments using surface sediments from the outer estuary (S3 and S4), showed differences in the nitrate behaviour between the sites (Fig.3a and 3b). The initial nitrate concentrations in S3 experiments were higher than in S4 experiments and similar to those found in the inner estuary sites; they remained relatively constant over the tests. In contrast, in the experiments using surface sediments from S4, nitrate concentrations were initially very low, but increased by six-fold within the first 48 hrs (190±30 µM) and nearly by 30-fold (~900±300 µM) by the end of the experiment. In the tests using subsurface sediments from S3, nitrate concentrations behaved initially similarly than in the surface sediment tests; however, after a week, the concentrations dropped below detectable levels (~40 µM). The experiments using S4 subsurface sediments showed very low nitrate concentrations (close to or below detection levels) throughout.

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

In experiments using surface sediments, $Mn^{2+}_{(aq)}$ concentrations increased immediately on resuspension to three times (~30-70 µM) the concentration of the river water (Fig.3e). This rapid release of Mn to the solution was followed by a very rapid decrease to close to detection levels (0.1 µM) after about 4 hrs. In the experiments using subsurface sediments from S4, $Mn^{2+}_{(aq)}$ concentrations sharply decreased from ~20 µM to detection limits after the first 10 hrs of resuspension; whereas for subsurface S3 experiments, there was no clear release-uptake trend in $Mn^{2+}_{(aq)}$ concentrations (Fig.3f).

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

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

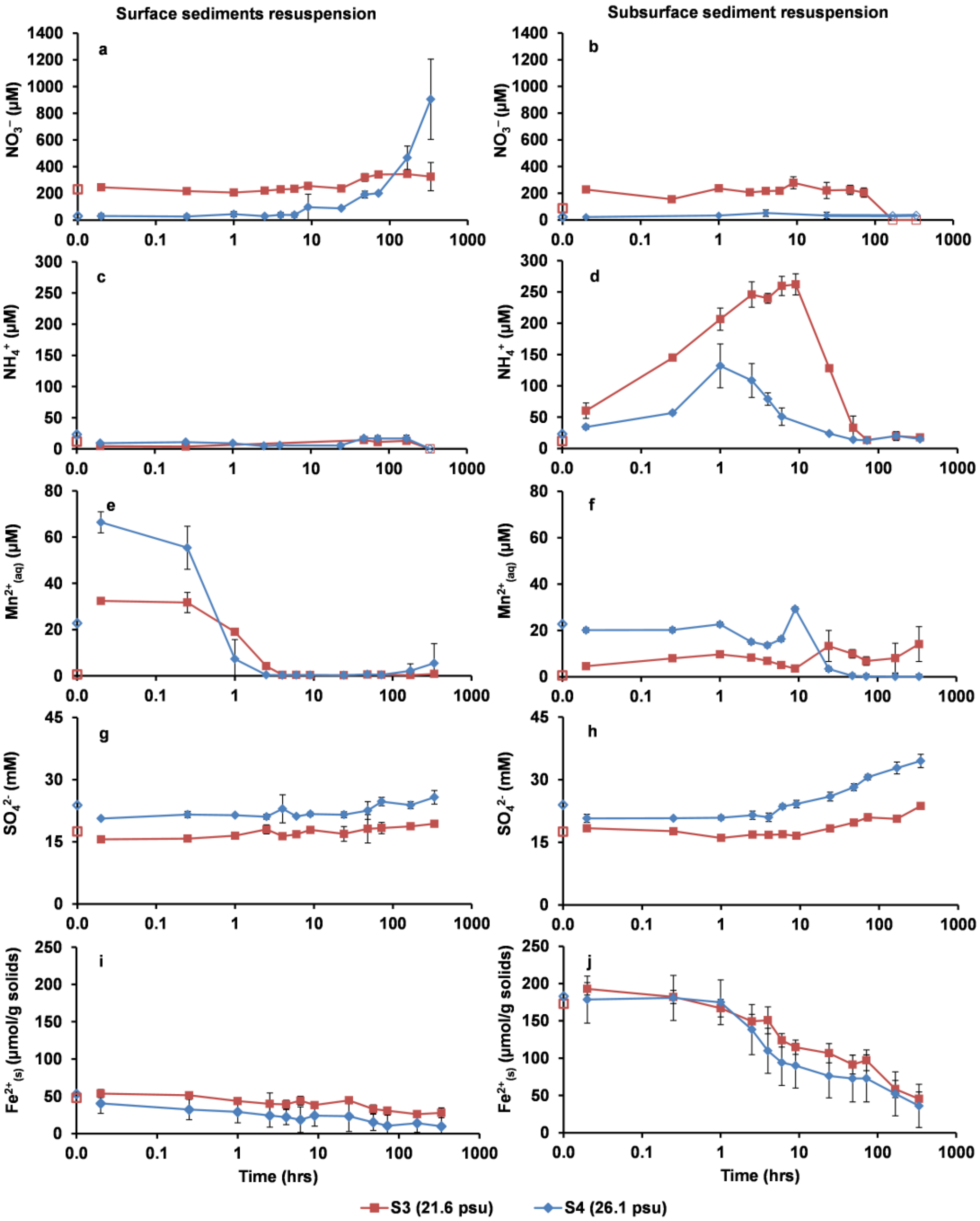

Figure 3: Major element behaviour during resuspension of outer estuary sediments. The red line with squares represents S3 (Paull) and the blue line with diamonds represents S4 (Skeffling). Open symbols on the y-axis indicate the initial concentrations of the major elements in the experiments (river water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

3.3 Trace metal mobility during sediment resuspension

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

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

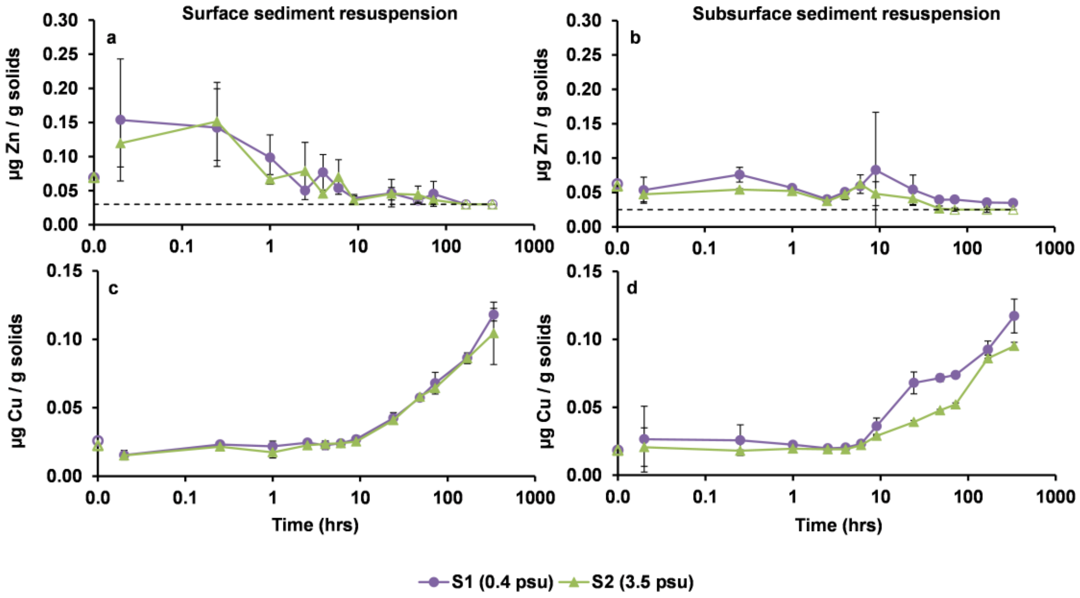

Figure 4: Zinc and copper released to the solution from solids during resuspension experiments using S1 and S2 sediments. Zinc released from surface (a) and subsurface (b) sediments; Cu released from surface (c) and subsurface (d) sediments. Open symbols on the y-axis indicate the initial concentrations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

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

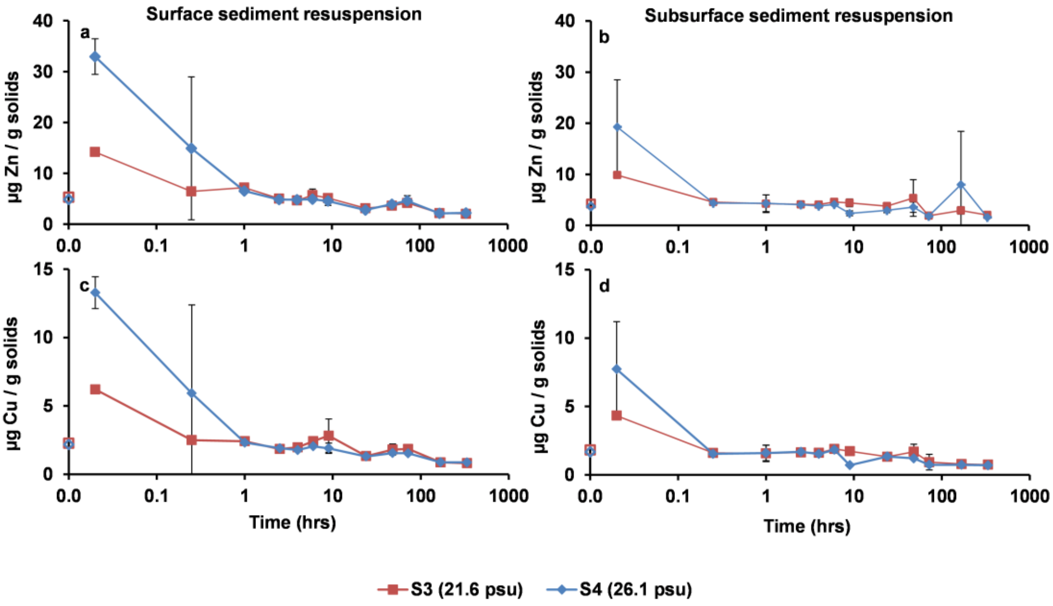

Figure 5: Zinc and copper released to the solution from solids during resuspension experiments using S3 and S4 sediments. Zinc released from surface (a) and subsurface (b) sediments; Cu released from surface (c) and subsurface (d) sediments. Open symbols on the y-axis indicate the initial concentrations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

3.4 Changes in metal partitioning during resuspension

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

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

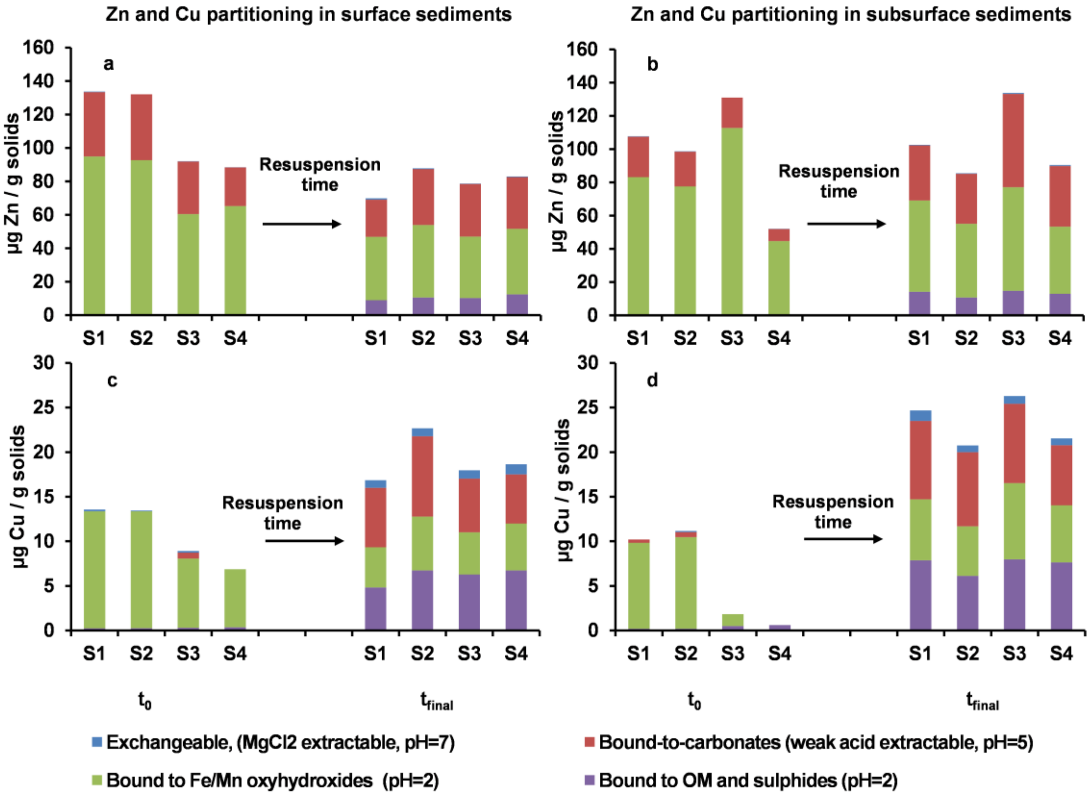

Figure 6: Zinc and copper partitioning changes after estuarine sediment resuspension determined by sequential extractions using Tessier et al. (1979) protocol with modifications. The concentration (averaged from triplicates) is expressed in µg of metal in the extractant solution by the mass of solids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

4. Discussion

4.1 Geochemical character of river water and estuarine sediments.

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

All surface sediments used in the resuspension experiments were in contact with air at the time of sampling. Precautions were taken during sampling to avoid oxidation of redox-sensitive elements, but we cannot discard partial oxidation of these elements during sampling and transport, before the sediment slurries were made up for the resuspension experiments. The subsurface sediments collected in the inner estuary sites appeared to be moderately reducing compared to the subsurface sediments from the outer estuary which appeared to become more reducing at depth. The AVS concentrations measured (<0.02 µmol AVS g^{-1}) in these Humber sediments were very low, but still in the range of concentrations reported in estuaries and other aquatic environments (Di Toro et al., 1990; Allen et al., 1993; Fang et al., 2005). The dynamic nature of the Humber leads to a continuous resuspension and reoxidation of sediments, which will buffer the AVS to low concentrations, whereas pyrite will accumulate in sediments with time as it is more stable than AVS. This would explain the presence of pyrite in all the samples regardless of the absence of AVS. Furthermore, the availability of dissolved Mn and nitrate will also influence the distribution of free sulphide within the sediments (Thamdrup et al., 1994; Sayama et al., 2005). Iron oxides react with free sulphides and, at the same time, the produced $Fe^{2+}_{(aq)}$ and H_2S reduce MnO_2 rapidly (Thamdrup et al., 1994), which could be another reason for the low AVS detected. Besides, the Fe oxides produced in the reaction of MnO_2 with $Fe^{2+}_{(aq)}$ will fuel this positive feedback mechanism. Alternatively, it cannot be discarded that the low AVS extracted was an artefact due to the partial oxidation of sediments during sampling and transport or during the handling in the laboratory, prior sediments were freeze-dried for AVS-pyrite extraction. The better-defined redox stratification between the two sediment depths sampled at the outer estuary sites was supported by in situ observations (colour change and odour of the sediments). Moreover, the total acid extractable $Fe^{2+}_{(s)}$ in the subsurface outer estuary sediments was ~2 times the content in the equivalent sediments from the inner estuary. Thus, it seems that the outer estuary mudflats hold the largest Fe-pool within the Humber.

Furthermore, the mudflats of the outer Humber estuary accumulated finer materials and they appeared to have a slightly higher TOC content than the inner estuary sediments. Organic matter often accumulates in finer grained sediments, and its concentrations in coastal sediments are often lower at the sediment-water interface (Mayer, 1994). The organic matter depletion in the surface layer relative to the immediate subsurface suggests that frequent mobilisation of surface sediments leads to greater organic matter degradation, which will be especially important in the areas of maximum sediment mobilisation (i.e. ETM, which is situated in the inner estuary) (Abril et al., 2002; Middelburg & Herman, 2007). Metabolizable organic matter is progressively depleted along the estuary, and despite the high rates of sediment accumulation in the outer estuary, which allow high organic matter burial, this organic matter will be likely more refractory and may be further degraded during early diagenesis (Henrichs, 1992; Tyson, 1995).

4.2 Geochemical responses of major elements to sediment resuspension

In order to compare the relative impact of a small-scale versus a more major resuspension event, the discussion about the changes in the geochemical behaviour of the major elements observed and their potential implications on estuarine geochemistry will be framed by two time-windows (Fig.7). Firstly, the immediate changes upon sediment resuspension in river water, which are important as they will occur naturally at any type of resuspension event (from regular tidal cycles to less frequent extreme events). Secondly, longer timescale changes expected during major storms, which potentially mobilise deeper sediments that are not normally disturbed and typically last 2-3 days in the Humber region (Lamb & Frydendahl, 1991; EASAC, 2013). For the immediate changes, net differences between the average concentration after the first hour of resuspension (as a final concentration datum) and the original concentrations of the river water (RW) have been calculated. Changes during a major storm timescale have been represented by the difference between the average concentration over the first hour and the concentration at 48 hrs of resuspension. Since an intense turbulent shear was reproduced, particle settling was not considered.

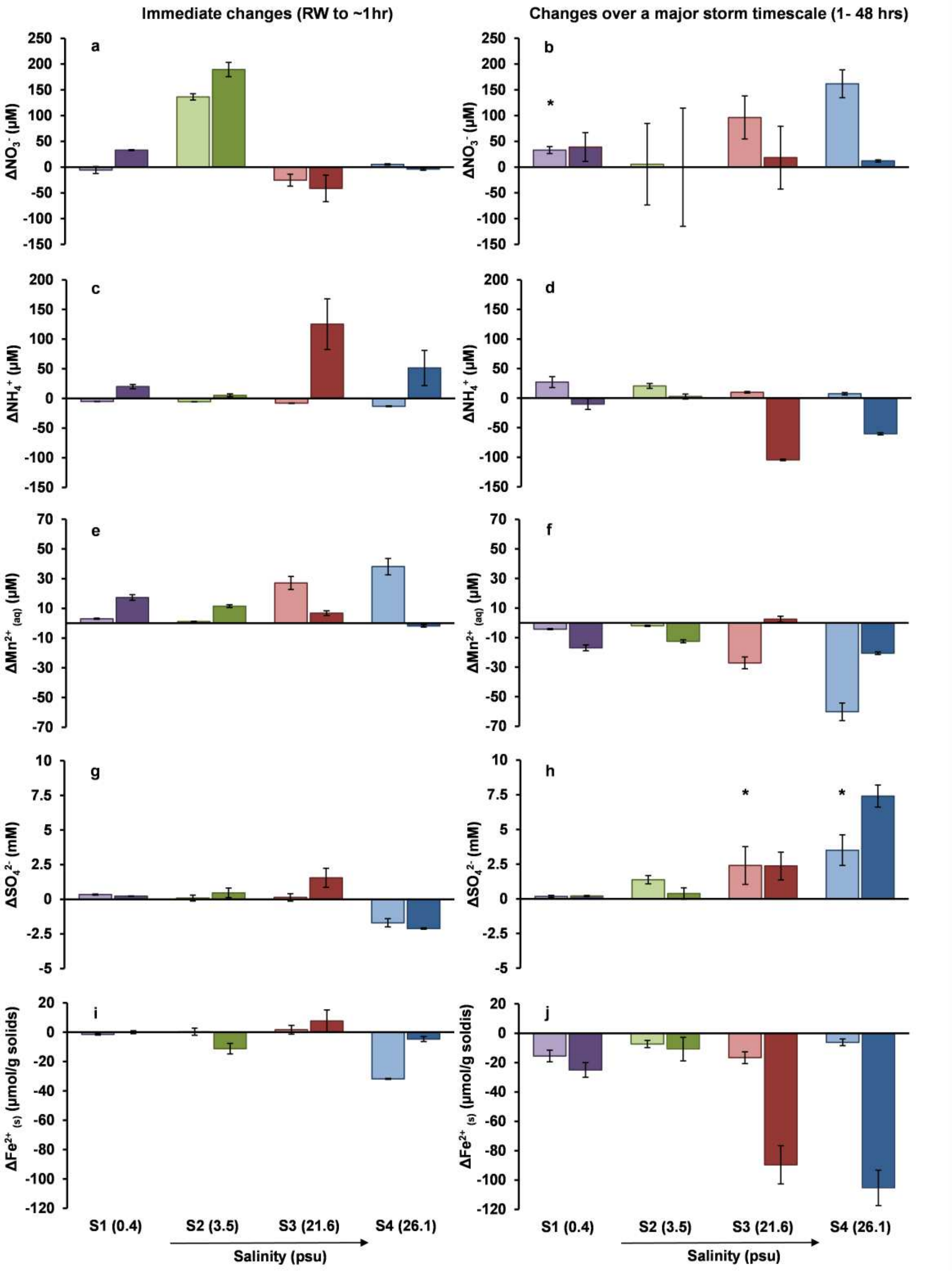

Figure 7: Major elements changes during sediment resuspension experiments at different time windows. Immediate changes (left) and changes over a major storm timescale (48 hrs) (right) for nitrate (a, b), ammonium (c, d), dissolved Mn (e, f), sulphate (g, h), and 0.5 N HCl extractable $Fe^{2+}_{(s)}$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

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

Ammonium showed significant releases (70-140 μM) in the first hour of resuspension in the experiments carried out with subsurface sediments from S3 and S4 (Fig.7c), likely due to the accumulation of ammonium in the porewater of outer estuary mudflats like suggested by Morgan et al. (2012). However, other processes, such as reversible desorption from sediments and/or ion-exchange reactions likely have also contributed to the ammonium increase (Morin & Morse, 1999; Kalnejais et al., 2010; Morgan et al., 2012; Percuoco et al., 2015; Wengrove et al., 2015) since porewater contribution to the mixture by simple diffusion cannot explain the concentrations reached. The ammonium released in those experiments was completely removed after 48 hrs (Fig.7d). Transitory ammonium release also occurred in S1 and S2 surface sediment experiments and these peaks coincided with the depletion of Mn^{2+} in solution. Nitrification and ammonium oxidation to N_2 by Mn oxides could have contributed to the ammonium removal processes. Any $Mn^{2+}_{(aq)}$ product of these reaction pathways would readily react with the oxygen present to regenerate reactive oxides, which will act as a catalysts to continue the oxidation of ammonium and organic-N (Luther et al., 1997); or, if suboxic conditions, $Mn^{2+}_{(aq)}$ may react with nitrate (Sørensen & Jørgensen, 1987; Murray et al., 1995; Luther et al., 1997). In the natural environment, the occurrence and magnitude of nitrification depends on the availability of oxygen and ammonium (Canfield et al., 2005), and it will play a major role in the nutrient exchange processes within the sediment-water interface as the nitrate produced will, in turn, sustain denitrification (Barnes & Owens, 1998; Mortimer et al., 1998). In the Humber, an intense zone for nitrification-denitrification has been associated with the ETM due to the enhanced chemical and microbial activity as suspended particles provide a large additional surface area (Barnes & Owens, 1998; Mortimer et al., 1998; Uncles et al., 1998b). On the other hand, nitrifiers can be inhibited by sulphide concentration, light, temperature, salinity and extreme pH (Canfield et al., 2005). The inhibition of nitrification by sulphide could favour the preservation of ammonium in porewater (Joye & Hollibaugh, 1995; Morgan et al., 2012), which may be a possible reason for the limited evidence of nitrification in some of these experiments and may help to explain spatial differences in coupled nitrification-denitrification within this estuary. Alternatively, re-adsorption of ammonium onto particles, is likely to be an important removal process (especially as Fe/Mn oxides were likely to be forming in experiments as a result of metal oxidation; see below) which, in the natural estuary systems may be key for the nutrient buffering capacity of the sediments (Morin & Morse, 1999; Song et al., 2013).

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

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

To summarise, the initial geochemical state of the sediments and their position along the estuarine continuum were the biggest influence on the geochemical progression during their resuspension. The availability of seawater sulphate, which likely promotes the development sulphidic sediments and $Fe^{2+}_{(s)}$ accumulation in the outer estuary mudflats, may be the major control on the biogeochemical processes, and hence Fe- and S-oxidation will dominate in this part of the Humber. However, the interlinks of N, Mn, Fe and S cycles and the spatiotemporal variability of the estuarine environments make extremely difficult to constrain which are the principal reaction pathways occurring during resuspension events in natural conditions.

4.3 Trace metal behaviour and changes during resuspension

Zinc and Cu were selected for analysis because they are known to be significantly enriched in the Humber sediments due to industrial contamination (Middleton & Grant, 1990; Cave et al., 2005; Andrews et al., 2008). Although the total concentrations in the solid phase were not significantly different between samples, during the resuspension experiments the release of Zn and Cu was significantly lower in the experiments carried out with inner estuarine sediments than in those with outer estuarine sediments. Despite all the precautions taken in the ICP-MS analysis, the determination of trace elements in saline waters has been analytically challenging due to the potential interference of the matrix in the sensitivity and the formation of polyatomic ions (Reed et al., 1994; Jerez Vegueria et al., 2013). However, the difference between the concentrations measured immediately after the resuspension started and the concentrations after 48 hrs indicated that, even if there were polyatomic interferences on the baseline, the trends were not an analytical artefact. Despite the differences in magnitude, Zn and Cu showed a general release-uptake trend in the experiments. The very rapid increase of Zn and Cu in solution upon resuspension (Fig.8a and 8c) probably occurred due to a combination of mixing and desorption from different mineral phases (Calmano et al., 1993; Cantwell et al., 2002). Salinity has been shown to promote metal desorption since metals can be mobilised as soluble chloride complexes (Gerringa et al., 2001; Millward & Liu, 2003; Du Laing et al., 2008), which may help to explain the higher concentrations of metals in the experiments carried out with outer estuarine sediments. Furthermore, very early Fe/Mn colloids formed (before they aggregate to larger particles) may have passed the filters used, and therefore any metal associated would have been deemed as solutes. Nevertheless, the releases of Zn and Cu were generally reversed to a considerable extend by the time of a major storm (Fig.8b and 8d) as a result, most probably, of co-precipitation and adsorption processes to newly formed Mn/Fe oxyhydroxides (Burdige, 1993; Calmano et al., 1993; Simpson et al., 1998; Saulnier & Mucci, 2000; Gunnars et al., 2002; Caetano et al., 2003). This will evidence the importance of Fe/Mn transformations in the transport and fate of TMs in the estuarine sediment-water interface (Du Laing et al., 2009). Further, the presence of soluble organic compounds may have influenced in the trends observed as well.

The mobilisation of TMs upon resuspension was also supported by the general shift observed towards ‘easier to extract’ fractions in metal partitioning (exchangeable and bound-to-carbonates). Although the metal release was reversed in a relatively short term, changes in metal partitioning may have implications in metal bioavailability. The Zn released in the inner estuary experiments was <0.1% of the total Zn in the experiment, which was within the range of the Zn associated with the exchangeable fraction. Zinc showed no significant changes in partitioning; but the decreases in the “weak acid extractable” and Fe/Mn oxides-associated fractions did not match quantitatively with any Zn increase in other fractions of the final sediments, which may be probably explained by protocol limitations (see below). In the outer estuary experiments, the average peak of Zn released was 11% of the total Zn in the experiments. The Zn released to the solution was higher than the Zn associated with the exchangeable fraction of these sediments, which suggests that Zn was likely mobilised from other fractions. Probably Zn experienced a transient release (i.e. Zn likely sourced from absorption complexes and returned to new absorption complexes). Zinc speciation varied among the outer estuary sediments, and only two of them showed changes that quantitatively matched (loss in the Fe/Mn oxides-bound fraction was equivalent to the increase in carbonates and organic matter-sulphide fraction). On the other hand, the Cu released to the solution in the inner estuary experiments represented about 0.1% of the total Cu in the solids, which coincided with the Cu found in the exchangeable fraction. In the outer estuary experiments, the average peak of Cu released to the solution was 22% of the total Cu in solids, which suggests that not only the Cu associated with the exchangeable fraction was mobilised. Generally, in the initial sediment samples, Cu was only found associated with the Fe/Mn oxides-bound fraction, whereas, for the reoxidised endpoint sediments, it was found in all the fractions. Thus, Cu may have been mobilised from high-energy binding sites to weaker binding sites. Nevertheless, errors introduced during the extractions or associated with protocol limitations cannot be discarded.

Numerous limitations have been reported for the 'Tessier' extraction protocol (Gleyzes et al., 2002). The concentrations in the exchangeable phase were generally very low or below the detection limit, probably because the adsorption-desorption processes are normally pH-dependent, and therefore desorption of the specifically adsorbed metals may not be complete at neutral pH (Tessier et al., 1979; Du Laing et al., 2009). Furthermore, none of the Zn and Cu bound to organic matter-sulphides were extracted from the original sediments, which may seem contrary to what was expected for initially sulphate reducing sediments (Di Toro et al., 1990; Allen et al., 1993). However, the absence of Zn and Cu in this fraction may be explained by protocol limitations since organic matter and sulphide dissolution may not be completed with the reagents used (Gleyzes et al., 2002; Anju & Banerjee, 2010). The incomplete dissolution of some phases, matrix effects, and changes in pH can lead to readsorption (by complexation, precipitation, coprecipitation, adsorption and loss on the vial walls) and redistribution of some metals during the extraction (Martin et al., 1987). Further limitations of the extraction procedure used may be the underestimation of the metals bound to Fe/Mn oxides (i.e. the changes applied in the extraction time to compensate the reduction of the extracting temperature, may have not been enough to dissolve all the hydrous oxides, Gleyzes et al., 2002).

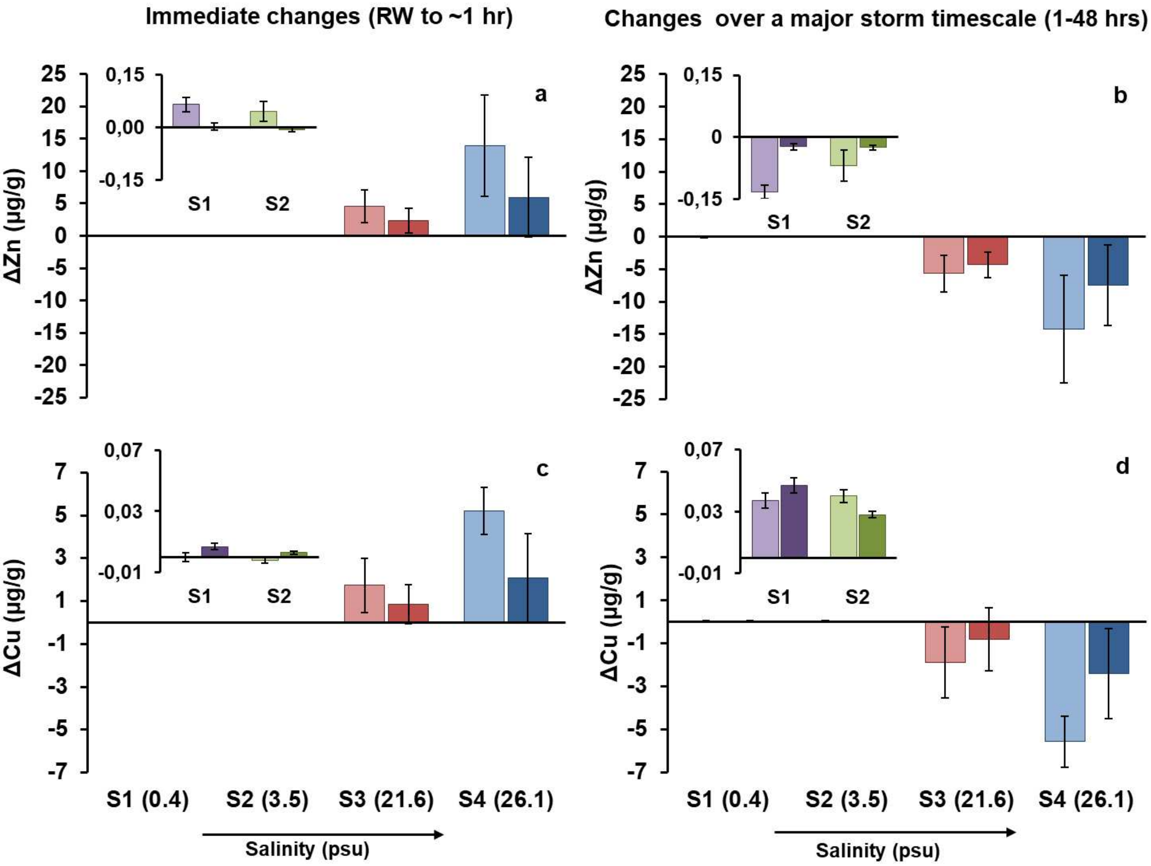

Figure 8: Zinc and Copper changes over time during sediment resuspension experiments at different time windows. Immediate changes (left) and changes over a major storm timescale (48 hrs) (right) for Zn (a, b) and Cu (c, d). Light and dark coloured bars represent surface and subsurface sediments respectively.

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

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

Nitrate (autochthonous or as a product of nitrification processes) was the only major nutrient that seemed to remain in solution for few days in both resuspension scenarios simulated. Hence, although nitrate concentrations were low in the outer estuary, during a major storm, important nitrate inputs from the estuary to the coastal waters may occur. During sediment resuspension, any ferrous iron present (in solution or associated with particles) will be rapidly oxidised, and hence Fe will be transported mainly as ferric iron (as particles, colloids, organic-matter complexed). Therefore Fe supplied from resuspended sediments is likely to be an important source of Fe to the coastal environment as suggested by Kalnejais et al. (2010).

The area of the outer estuary intertidal mudflats is the largest in terms of aerial extent (see Mortimer et al., 1998), and therefore the potential amount of sediments, and consequently nutrients and metals, mobilised will be significantly larger during an extraordinary resuspension event than during normal circumstances. Also nutrient and metal fluxes will be determined largely by the flow conditions, which means that a turbulent release (e.g. in storm conditions) may be relevant to the overall nutrient and metal budgets (see more in Supporting Information, SI.7). In the outer estuary mudflats, the larger amount of Fe and the continuous availability of sulphate seem to promote the development of sulphidic conditions at a depth, which are not observed in the inner estuary sites. The total oxidation of the inorganic species released during the resuspension of estuary sediments would equate to an oxygen consumption of 20±10 mmol O_2 kg^{-1}, and to 70±40 mmol O_2 kg^{-1} for the inner and outer estuary sediments respectively. This amount of oxygen removal could result in full deoxygenation of surface waters at relatively low solid-solution ratios (15 g L^{-1} for the inner estuary; 4 g L^{-1} for the outer estuary). However, well-mixed estuaries rarely exhibit water column hypoxia (Paerl, 2006). The kinetics of the reoxidation processes (especially those of Fe and S) are such that supply of oxygen (by diffusion from the atmosphere or mixing with adjacent oxygenated waters) is likely to prevent anoxic conditions from developing in all but the very largest of remobilisation events.

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

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

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

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

5. Conclusions

This study gives an insight into the complex mosaic of processes that result from physical disturbances along the Humber estuary continuum. The position in the salinity gradient was the dominant control on sediment geochemistry with a change from a Mn/Fe-dominated redox chemistry in the inner estuary to a Fe/S-dominated system in the outer estuary. Therefore, understanding the system dynamics and sediment characteristics is key when studying nutrients and metal cycling along a salinity continuum. Sediment resuspension resulted in the release of ammonium (where enriched) to surface waters. The nitrate released appears to remain in solution for more than 2-3 days. Reduced pools of Mn, Fe and, sulphur species in sediments were oxidised during resuspension resulting in Mn and Fe oxyhydroxides precipitation, which produced new sorption sites for the TMs released to solution upon resuspension. Thus, rapid releases of ammonium, $Mn^{2+}_{(aq)}$ and TMs may be reversed in relatively short (few days) timescales, which is important when assessing the overall environmental effects of resuspension episodes on surface waters composition and nutrient and metal cycling. In the Humber estuary, the potential resuspension of outer estuary subsurface sediments would have a greater effect on the coastal environment (in terms of Chemical Oxygen Demand (COD), nutrient and metal release), and it may become a more important process in the future as it is predicted an increase in the frequency of major storms that can mobilise these deeper sediments due to global warming.

6. Acknowledgements

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

7. References

[1] Abril, G., Riou, S. A., Etcheber, H., Frankignoulle, M., de Wit, R., & Middelburg, J. J. (2000). Transient, tidal time-scale, nitrogen transformations in an estuarine turbidity maximum-fluid mud system (The Gironde, south-west France). Estuarine Coastal and Shelf Science, 50(5), 703-715. doi: 10.1006/ecss.1999.0598

[2] Abril, G., Nogueira, M., Etcheber, H., Cabeçadas, G., Lemaire, E., & Brogueira, M. J. (2002). Behaviour of organic carbon in nine contrasting European estuaries. Estuarine, coastal and shelf science, 54(2), 241-262. doi: 10.1006/ecss.2001.0844

[3] Allen, H. E., Fu, G. M., & Deng, B. L. (1993). Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. Environmental Toxicology and Chemistry, 12(8), 1441-1453. doi: 10.1897/1552-8618(1993)12[1441:aoasaa]2.0.co;2

[4] Aller, R. C. (1994). Bioturbation and remineralization of sedimentary organic-matter - effects of redox oscillation. Chemical Geology, 114(3-4), 331-345. doi: 10.1016/0009-2541(94)90062-0

[5] Andrews, J. E., Samways, G., & Shimmield, G. B. (2008). Historical storage budgets of organic carbon, nutrient and contaminant elements in saltmarsh sediments: Biogeochemical context for managed realignment, Humber Estuary, UK. Science of The Total Environment, 405(1-3), 1-13. doi: 10.1016/j.scitotenv.2008.07.044

[6] Anju, M., & Banerjee, D. K. (2010). Comparison of two sequential extraction procedures for heavy metal partitioning in mine tailings. Chemosphere, 78(11), 1393-1402. doi: 10.1016/j.chemosphere.2009.12.064

[7] Anschutz, P., Sundby, B., Lefrancois, L., Luther, G. W., & Mucci, A. (2000). Interactions between metal oxides and species of nitrogen and iodine in bioturbated

marine sediments. Geochimica et Cosmochimica Acta, 64(16), 2751-2763. doi: 10.1016/s0016-7037(00)00400-2

[8] Barnes, J., & Owens, N. J. P. (1998). Denitrification and nitrous oxide concentrations in the Humber estuary, UK, and adjacent coastal zones. Marine Pollution Bulletin, 37(3-7), 247-260.

[9] Berner, R. A. (1980). Early diagenesis: A theoretical approach. New York: Princeton University Press.

[10] Blanchard, G. F., Paterson, D. M., Stal, L. J., Richard, P., Galois, R., Huet, V., Kelly, J., Honeywill, C., de Brouwer, J., Dyer, K., Christie, M., & Seguignes, M. (2000). The effect of geomorphological structures on potential biostabilisation by microphytobenthos on intertidal mudflats. Continental Shelf Research, 20(10), 1243-1256. doi: https://doi.org/10.1016/S0278-4343(00)00021-2

[11] Boyer, E. W., & Howarth, R. W. (2002). The Nitrogen Cycle at Regional to Global Scales. Report of the International SCOPE Nitrogen Project (Vol. 57/58). Dordrecht, Netherlands: Springer.

[12] Bruno, P., Caselli, M., de Gennaro, G., De Tommaso, B., Lastella, G., & Mastrolitti, S. (2003). Determination of nutrients in the presence of high chloride concentrations by column-switching ion chromatography. Journal of Chromatography A, 1003(1-2), 133-141. doi: 10.1016/s0021-9673(03)00785-4

[13] Burdige, D. J. (1993). The biogeochemistry of manganese and iron reduction in marine-sediments. Earth-Science Reviews, 35(3), 249-284. doi: 10.1016/0012-8252(93)90040-e

[14] Burke, I. T., Boothman, C., Lloyd, J. R., Mortimer, R. J. G., Livens, F. R., & Morris, K. (2005). Effects of Progressive Anoxia on the Solubility of Technetium in Sediments. Environmental Science & Technology, 39, 4109-4116.

[15] Caetano, M., Madureira, M. J., & Vale, C. (2003). Metal remobilisation during resuspension of anoxic contaminated sediment: short-term laboratory study. Water Air and Soil Pollution, 143(1-4), 23-40. doi: 10.1023/a:1022877120813

[16] Calmano, W., Hong, J., & Forstner, U. (1993). Binding and mobilization of heavy-metals in contaminated sediments affected by pH and redox potential. Water Science and Technology, 28(8-9), 223-235. doi: 10.15480/882.450

[17] Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., & Berner, R. A. (1986). The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chemical Geology, 54(1-2), 149-155. doi: 10.1016/0009-2541(86)90078-1

[18] Canfield, D. E., Kristensen, E., & Thamdrup, B. (2005). Aquatic Geomicrobiology (Vol. 48). London: Elsevier Academic Press.

[19] Canfield, D. E., & Thamdrup, B. (2009). Towards a consistent classification scheme for geochemical environments, or, why we wish the term 'suboxic' would go away. Geobiology, 7(4), 385-392. doi: 10.1111/j.1472-4669.2009.00214.x

[20] Canfield, D. E., Glazer, A. N., & Falkowski, P. G. (2010). The Evolution and Future of Earth's Nitrogen Cycle. Science, 330(6001), 192-196. doi: 10.1126/science.1186120

[21] Cantwell, M. G., Burgess, R. M., & Kester, D. R. (2002). Release and phase partitioning of metals from anoxic estuarine sediments during periods of simulated resuspension. Environmental Science & Technology, 36(24), 5328-5334. doi: 10.1021/es0115058

[22] Cave, R. R., Andrews, J. E., Jickells, T., & Coombes, E. G. (2005). A review of sediment contamination by trace metals in the Humber catchment and estuary, and the implications for future estuary water quality. Estuarine, Coastal and Shelf Science, 62(3), 547-557. doi: 10.1016/j.ecss.2004.09.017

[23] Christensen, J. H., Hewitson, B., Busuioc, A., Chen, A., Gao, X., Held, I., Jones, R., Kolli, R. K., Kwon, W.-T., Laprise, R., Magaña Rueda, V., Mearns, L., Menéndez, C. G., Räisänen, J., Rinke, A., Sarr, A., & Whetton, P. (2007). Regional Climate Projections. In S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor & H.L. Miller (Eds.), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (pp. 847-940). Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

[24] Couceiro, F., Fones, G. R., Thompson, C. E. L., Statham, P. J., Sivyer, D. B., Parker, R., Kelly-Gerreyn, B. A., & Amos, C. L. (2013). Impact of resuspension of cohesive sediments at the Oyster Grounds (North Sea) on nutrient exchange across the sediment-water interface. Biogeochemistry, 113(1-3), 37-52. doi: 10.1007/s10533-012-9710-7

[25] Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Hicks, M. B., Mayr, S. M., & Redmond, M. S. (1990). Toxicity of cadmium in sediments the role of acid volatile sulfide. Environmental Toxicology and Chemistry, 9(12), 1487-1502. doi: 10.1002/etc.5620091208

[26] Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F. M. G., & Verloo, M. G. (2008). Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. Estuarine Coastal and Shelf Science, 77(4), 589-602. doi: 10.1016/j.ecss.2007.10.017

[27] Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. M. G. (2009). Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. Science of The Total Environment, 407(13), 3972-3985. doi: 10.1016/j.scitotenv.2008.07.025

[28] EASAC (2013). Trends in extreme weather events in Europe: implications for national and European Union adaptation strategies (EASAC policy report 22 ed.): EASAC. Retrieved from http://www.easac.eu/fileadmin/PDF_s/reports_statements/Easac_Report_Extreme_Weather_Events.pdf

[29] Eggleton, J., & Thomas, K. V. (2004). A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. Environment International, 30(7), 973-980. doi: 10.1016/j.envint.2004.03.001

[30] Fang, T., Li, X., & Zhang, G. (2005). Acid volatile sulfide and simultaneously extracted metals in the sediment cores of the Pearl River Estuary, South China. Ecotoxicology and Environmental Safety, 61(3), 420-431. doi: http://dx.doi.org/10.1016/j.ecoenv.2004.10.004

[31] Fossing, H., & Jørgensen, B. B. (1989). Measurement of bacterial sulfate reduction in sediments - evaluation of a single-step chromium reduction method. Biogeochemistry, 8(3), 205-222. doi: 10.1007/BF00002889

[32] Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., & Maynard, V. (1979). Early oxidation of organic-matter in pelagic sediments of the eastern equatorial atlantic - suboxic diagenesis. Geochimica et Cosmochimica Acta, 43(7), 1075-1090. doi: 10.1016/0016-7037(79)90095-4

[33] Gunnars, A., Blomqvist, S., Johansson, P., & Andersson, C. (2002). Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. Geochimica et Cosmochimica Acta, 66(5), 745-758. doi: 10.1016/s0016-7037(01)00818-3

[34] Gerringa, L. J. A., de Baar, H. J. W., Nolting, R. F., & Paucot, H. (2001). The influence of salinity on the solubility of Zn and Cd sulphides in the Scheldt estuary. Journal of Sea Research, 46(3-4), 201-211. doi: 10.1016/s1385-1101(01)00081-8

[35] Gleyzes, C., Tellier, S., & Astruc, M. (2002). Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. Trac-Trends in Analytical Chemistry, 21(6-7), 451-467. doi: 10.1016/s0165-9936(02)00603-9

[36] Henrichs, S. M. (1992). Early diagenesis of organic matter in marine sediments: progress and perplexity. Marine Chemistry, 39(1), 119-149. doi: 10.1016/0304-4203(92)90098-U

[37] Hirst, J. M., & Aston, S. R. (1983). Behavior of copper, zinc, iron and manganese during experimental resuspension and reoxidation of polluted anoxic sediments. Estuarine Coastal and Shelf Science, 16(5), 549-558. doi: 10.1016/0272-7714(83)90085-9

[38] Howarth, R. W., BIllen,G., Swaney, D., Townsend, A., Jaworsky,N., Lajtha, K., Downing, J.A., Elmgren, R.,Caraco, N., Jordan, T., Berendse, F.,Freney, J.,Kudeyarov,

V., Murdoch P., and Zhao-Liang Zhu. (1996). Regional Nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlanthic Ocean: natural and human influences. Biogeochemistry, 35, 75-139.

[39] Huerta-Diaz, M. A., & Morse, J. W. (1990). A quantitative method for determination of trace metal concentrations in sedimentary pyrite. Marine Chemistry, 29(2-3), 119-144. doi: 10.1016/0304-4203(90)90009-2

[40] IPCC. (2013). Summary for policymakers. In T.F. Stocker, D. Qin, G.K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex & P.M. Midgley (Eds.), Climate Change 2013: the Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. United Kingdom and New York, NY, USA: Cambridge University Press.

[41] Jerez Vegueria, S. F., Godoy, J. M., de Campos, R. C., & Goncalves, R. A. (2013). Trace element determination in seawater by ICP-MS using online, offline and bath procedures of preconcentration and matrix elimination. Microchemical Journal, 106, 121-128. doi: 10.1016/j.microc.2012.05.032

[42] Jones, P. D., & Reid, P. A. (2001). Assessing future changes in extreme precipitation over Britain using regional climate model integrations. International Journal of Climatology, 21(11), 1337-1356. doi: 10.1002/joc.677

[43] Jørgensen, B. B. (1977). Sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnology and Oceanography, 22(5), 814-832. doi: 10.4319/lo.1977.22.5.0814

[44] Jørgensen, B. B. (1982). Mineralization of organic-matter in the sea bed - the role of sulfate reduction. Nature, 296(5858), 643-645. doi: 10.1038/296643a0

[45] Joye, S. B., & Hollibaugh, J. T. (1995). Influence of sulfide inhibition of nitrification on nitrogen regeneration in sediments. Science, 270(5236), 623-625. doi: 10.1126/science.270.5236.623

[46] Kalnejais, L. H., Martin, W. R., & Bothner, M. H. (2010). The release of dissolved nutrients and metals from coastal sediments due to resuspension. Marine Chemistry, 121(1-4), 224-235. doi: 10.1016/j.marchem.2010.05.002

[47] Lamb, H., & Frydendahl, K. U. (1991). Historic Storms of the North Sea, British Isles and Northwest Europe: Cambridge University Press.

[48] Lansdown, K., Heppell, C. M., Dossena, M., Ullah, S., Heathwaite, A. L., Binley, A., Zhang, H., & Trimmer, M. (2014). Fine-Scale in Situ Measurement of Riverbed Nitrate Production and Consumption in an Armored Permeable Riverbed. Environmental Science & Technology, 48(8), 4425-4434. doi: 10.1021/es4056005

[49] Lansdown, K., Heppell, C. M., Trimmer, M., Binley, A., Heathwaite, A. L., Byrne, P., & Zhang, H. (2015). The interplay between transport and reaction rates as controls on nitrate attenuation in permeable, streambed sediments. Journal of Geophysical Research-Biogeosciences, 120(6), 1093-1109. doi: 10.1002/2014jg002874

[50] Lee, S. V., & Cundy, A. B. (2001). Heavy Metal Contamination and Mixing Processes in Sediments from the Humber Estuary, Eastern England. Estuarine, Coastal and Shelf Science, 53(5), 619-636. doi: 10.1006/ecss.2000.0713

[51] Lovley, D. R., & Phillips, E. J. P. (1986). Appl. Environ. Microbiol., 52, 751.

[52] Lovley, D. R., & Phillips, E. J. P. (1987). Rapid assay for microbially reducible ferric iron in aquatic sediments. Applied and Environmental Microbiology, 53(7), 1536-1540.

[53] Luther, G. W., Sundby, B., Lewis, B. L., Brendel, P. J., & Silverberg, N. (1997). Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen. Geochimica et Cosmochimica Acta, 61(19), 4043-4052. doi: 10.1016/s0016-7037(97)00239-1

[54] Martin, J. M., Nirel, P., & Thomas, A. J. (1987). Sequential extraction techniques - promises and problems. Marine Chemistry, 22(2-4), 313-341. doi: 10.1016/0304-4203(87)90017-x

[55] Martino, M., Turner, A., Nimmo, A., & Millward, G. E. (2002). Resuspension, reactivity and recycling of trace metals in the Mersey Estuary, UK. Marine Chemistry, 77(2-3), 171-186. doi: 10.1016/s0304-4203(01)00086-x

[56] Mayer, L. M. (1994). Surface-area control of organic-carbon accumulation in continental-shelf sediments. Geochimica et Cosmochimica Acta, 58(4), 1271-1284. doi: 10.1016/0016-7037(94)90381-6

[57] Middelburg, J. J., & Herman, P. M. J. (2007). Organic matter processing in tidal estuaries. Marine Chemistry, 106(1-2), 127-147. doi: 10.1016/j.marchem.2006.02.007

[58] Middelburg, J. J., & Levin, L. A. (2009). Coastal hypoxia and sediment biogeochemistry. Biogeosciences, 6(7), 1273-1293. doi: 10.5194/bg-6-1273-2009

[59] Middleton, R., & Grant, A. (1990). Heavy Metals in the Humber Estuary: Scrobicularia Clay as a Pre-industrial Datum. Proceedings of the Yorkshire Geological Society, 48(pàg. 75-80).

[60] Millward, G., & Liu, Y. (2003). Modelling metal desorption kinetics in estuaries. Sci Total Environ, 314-316, 613-623. doi: 10.1016/s0048-9697(03)00077-9

[61] Millward, G. E., & Glegg, G. A. (1997). Fluxes and Retention of Trace Metals in the Humber Estuary. Estuarine, Coastal and Shelf Science, 44, 97-105.

[62] Morgan, B., Rate, A. W., & Burton, E. D. (2012). Water chemistry and nutrient release during the resuspension of FeS-rich sediments in a eutrophic estuarine system. Science of The Total Environment, 432, 47-56. doi: 10.1016/j.scitotenv.2012.05.065

[63] Morin, J., & Morse, J. W. (1999). Ammonium release from resuspended sediments in the Laguna Madre estuary. Marine Chemistry, 65(1-2), 97-110. doi: 10.1016/s0304-4203(99)00013-4

[64] Morris, A. W., Bale, A. J., Howland, R.J.M., Millward, G.E., Ackroyd, R., Loring H. and Rantala, R.T.T. (1986). Sediment mobility and its contribution to trace metal cycling and retention in a macrotidal estuary. Water Science and Technology, 18, 111-119.

[65] Mortimer, R. J. G., Krom, M. D., Watson, P. G., Frickers, P. E., Davey, J. T., & Clifton, R. J. (1998). Sediment-water exchange of nutrients in the intertidal zone of the Humber estuary, UK. Marine Pollution Bulletin, 37(3-7), 261-279. doi: 10.1016/s0025-326x(99)00053-3

[66] Mortimer, R. J. G., Davey, J. T., Krom, M. D., Watson, P. G., Frickers, P. E., & Clifton, R. J. (1999). The Effect of Macrofauna on Porewater Profiles and Nutrient Fluxes in the Intertidal Zone of the Humber Estuary. Estuarine, Coastal and Shelf Science, 48(6), 683-699. doi: https://doi.org/10.1006/ecss.1999.0479

[67] Murray, J. W., Codispoti, L. A., & Friederich, G. E. (1995). Oxidation-reduction environments - the suboxic zone in the black-sea. Aquatic Chemistry: Interfacial and Interspecies Processes, 244, 157-176. doi: 10.1021/ba-1995-0244.ch007

[68] Nedwell, D. B., Jickells, T. D., Trimmer, M., & Sanders, R. (1999). Nutrients in estuaries. In D. B. Nedwell & D. G. Raffaelli (Eds.), Advances in Ecological Research, Estuaries (Vol. 29, pp. 43-92): Academic Press.

[69] NRA. (1995). Sea Vigil Water Quality Monitoring: the Humber Estuary 1992-1993. Peterborough: National Rivers Authority Anglian Region. Retrieved from http://www.environmentdata.org/archive/ealit:2851.

[70] NRA. (1996). Sea Vigil Water Quality Monitoring: The Humber Estuary 1994. Peterborough: National Rivers Authority Anglian Region. Retrieved from http://www.environmentdata.org/archive/ealit:2868

[71] Paerl, H. W. (2006). Assessing and managing nutrient-enhanced eutrophication in estuarine and coastal waters: Interactive effects of human and climatic perturbations. Ecological Engineering, 26(1), 40-54. doi: 10.1016/j.ecoleng.2005.09.006

[72] Percuoco, V. P., Kalnejais, L. H., & Officer, L. V. (2015). Nutrient release from the sediments of the Great Bay Estuary, NH USA. Estuarine Coastal and Shelf Science, 161, 76-87. doi: 10.1016/j.ecss.2015.04.006

[73] Pethick, J. S. (1990). The Humber Estuary. In S. and Crowther Ellis, D.R. (Ed.), Humber Perspectives, A region through the ages (pp. 54-67). Hull: Hull University.

[74] Postma, D., & Jakobsen, R. (1996). Redox zonation: Equilibrium constraints on the Fe(III)/SO4-reduction interface. Geochimica et Cosmochimica Acta, 60(17), 3169-3175. doi: 10.1016/0016-7037(96)00156-1

[75] Rauret, G., Rubio, R., & López-Sánchez, J. F. (1989). Optimization of Tessier Procedure for Metal Solid Speciation in River Sediments. International Journal of Environmental Analytical Chemistry, 36(2), 69-83. doi: 10.1080/03067318908026859

[76] Reed, N. M., Cairns, R. O., Hutton, R. C., & Takaku, Y. (1994). Characterization of polyatomic ion interferences in inductively-coupled plasma-mass spectrometry using a high-resolution mass-spectrometer. Journal of Analytical Atomic Spectrometry, 9(8), 881-896. doi: 10.1039/ja9940900881

[77] Roberts, K. L., Eate, V. M., Eyre, B. D., Holland, D. P., & Cook, P. L. M. (2012). Hypoxic events stimulate nitrogen recycling in a shallow salt-wedge estuary: The Yarra River estuary, Australia. Limnology and Oceanography, 57(5), 1427-1442. doi: 10.4319/lo.2012.57.5.1427

[78] Roberts, K. L., Kessler, A. J., Grace, M. R., & Cook, P. M. L. (2014). Increased rates of dissimilatory nitrate reduction to ammonium (DNRA) under oxic conditions in a periodically hypoxic estuary. Geochimica et Cosmochimica Acta, 133, 313-324. doi: http://dx.doi.org/10.1016/j.gca.2014.02.042

[79] Robins, P. E., Skov, M. W., Lewis, M. J., Giménez, L., Davies, A. G., Malham, S. K., Neill, S. P., McDonald, J. E., Whitton, T. A., Jackson, S. E., & Jago, C. F. (2016). Impact of climate change on UK estuaries: A review of past trends and potential projections. Estuarine, Coastal and Shelf Science, 169(Supplement C), 119-135. doi: https://doi.org/10.1016/j.ecss.2015.12.016

[80] Salomons, W., Derooij, N. M., Kerdijk, H., & Bril, J. (1987). Sediments as a source of contaminants. Hydrobiologia, 149, 13-30. doi: 10.1007/bf00048643

[81] Sanders, R. J., Jickells, T., Malcolm, S., Brown, J., Kirkwood, D., Reeve, A., Taylor, J., Horrobin, T., & Ashcroft, C. (1997). Nutrient Fluxes through the Humber estuary. Journal of Sea Research, 37, 3-23.

[82] Sanford, L. P. (2008). Modeling a dynamically varying mixed sediment bed with erosion, deposition, bioturbation, consolidation, and armoring. Comput. Geosci., 34(10), 1263-1283. doi: 10.1016/j.cageo.2008.02.011

[83] Saulnier, I., & Mucci, A. (2000). Trace metal remobilization following the resuspension of estuarine sediments: Saguenay Fjord, Canada. Applied Geochemistry, 15(2), 191-210. doi: 10.1016/s0883-2927(99)00034-7

[84] Sayama, M., Risgaard-Petersen, N., Nielsen, L. P., Fossing, H., & Christensen, P.B. (2005). Impact of bacterial NO3- transport on sediment biogeochemistry. Applied and Environmental Microbiology, 71(11), 7575-7577. doi: 10.1128/aem.71.11.7575-7577.2005

[85] Seitzinger, S. P., & Sanders, R. W. (1997). Contribution of dissolved organic nitrogen from rivers to estuarine eutrophication. Marine Ecology Progress Series, 159, 1-12. doi: 10.3354/meps159001

[86] Simpson, S. L., Apte, S. C., & Batley, G. E. (1998). Effect of short term resuspension events on trace metal speciation in polluted anoxic sediments. Environmental Science & Technology, 32(5), 620-625. doi: 10.1021/es970568g

[87] Song, G. D., Liu, S. M., Marchant, H., Kuypers, M. M. M., & Lavik, G. (2013). Anammox, denitrification and dissimilatory nitrate reduction to ammonium in the East

China Sea sediment. Biogeosciences, 10(11), 6851-6864. doi: 10.5194/bg-10-6851-2013

[88] Sørensen, J., & Jørgensen, B. B. (1987). Early diagenesis in sediments from Danish coastal waters - microbial activity and Mn-Fe-S geochemistry. Geochimica et Cosmochimica Acta, 51(6), 1583-1590. doi: 10.1016/0016-7037(87)90339-5

[89] Statham, P. J. (2012). Nutrients in estuaries--an overview and the potential impacts of climate change. Sci Total Environ, 434, 213-227. doi: 10.1016/j.scitotenv.2011.09.088

[90] Stumm, W., & Morgan, J. J. (1970). Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. New York: Wiley-Interscience.

[91] Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace-metals. Analytical Chemistry, 51(7), 844-851. doi: 10.1021/ac50043a017

[92] Thamdrup, B., Fossing, H., & Jørgensen, B. B. (1994). Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. Geochimica et Cosmochimica Acta, 58(23), 5115-5129. doi: 10.1016/0016-7037(94)90298-4

[93] Thamdrup, B. (2012). New Pathways and Processes in the Global Nitrogen Cycle. Annual Review of Ecology, Evolution, and Systematics, 43, 407-428. doi: 10.1146/annurev-ecolsys-102710-145048

[94] Townend, I. H., Wang, Z. B., & Rees, J. (2007). Millennial to annual volume changes in the Humber Estuary. Paper presented at the Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences.

[95] Triska, F. J., Duff, J. H., & Avanzino, R. J. (1993). The role of water exchange between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial aquatic interface. Hydrobiologia, 251(1-3), 167-184. doi: 10.1007/bf00007177

[96] Tyson, R. V. (1995). The nature of organic matter in sediments Sedimentary organic matter: Organic facies and palynofacies (pp. 7-28). London: Chapman & Hall.

[97] Uncles, R. J., Wood, R. G., Sthephens, J. A., & Howland, R. J. M. (1998a). Estuarine Nutrient Fluxes to the Humber Coastal Zone, UK, during June 1995. Marine Pollution Bulletin, 37, 225-233.

[98] Uncles, R. J., Stephens, J. A., & Law, D. J. (2006). Turbidity maximum in the macrotidal, highly turbid Humber Estuary, UK: Flocs, fluid mud, stationary suspensions and tidal bores. Estuarine, Coastal and Shelf Science, 67(1-2), 30-52. doi: 10.1016/j.ecss.2005.10.013

[99] Uncles, R. J., Joint, I., & Stephens, J. A. (1998b). Transport and retention of suspended particulate matter and bacteria in the Humber-Ouse Estuary, United Kingdom, and their relationship to hypoxia and anoxia. Estuaries, 21(4A), 597-612. doi: 10.2307/1353298

[100] Van Prooijen, B. C., & Winterwerp, J. C. (2010). A stochastic formulation for erosion of cohesive sediments. Journal of Geophysical Research: Oceans, 115(C1), n/a-n/a. doi: 10.1029/2008JC005189

[101] Viollier, E., Inglett, P.W., Huntrer, K., Roychoudhury, A. N., and Van Cappellen, P. (2000). The ferrozine method revised: Fe(II)/Fe(III) determination in natural waters. Applied Geochemistry, 15, 785-790.

[102] Wengrove, M. E., Foster, D. L., Kalnejais, L. H., Percuoco, V., & Lippmann, T. C. (2015). Field and laboratory observations of bed stress and associated nutrient release in a tidal estuary. Estuarine, Coastal and Shelf Science, 161(Supplement C), 11-24. doi: 10.1016/j.ecss.2015.04.005

[103] Wu, Y., Falconer, R. A., & Uncles, R. J. (1999). Modelling of Water Flows and Cohesive Sediment Fluxes in the Humber Estuary, UK. Marine Pollution Bulletin, 37(3), 182-189. doi: https://doi.org/10.1016/S0025-326X(99)00103-4