Unravelling metal mobility under complex contaminant signatures

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HIGHLIGHTS

- Laboratory experiments and field survey were performed for pollution assessment.
- Contaminated sediments leached significant amounts of metals to overlying water.
- Metal mobilisation varied ~1000-fold depending on sediment pH, salinity, and redox.
- Metal mobility affected concentration in sediment and contamination signatures.
- Assessment of metal mobility in estuarine sediments is essential to infer environmental impacts.

GRAPHICAL ABSTRACT
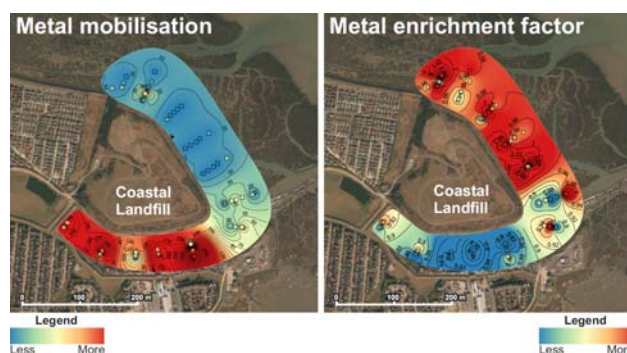
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ABSTRACT

Metals are concerning pollutants in estuaries, where contamination can undergo significant remobilisation driven by physico-chemical forcing. Environmental concentrations of metals in estuarine sediments are often higher than natural backgrounds, but show no contiguity to potential sources. Thus, better understanding the metal mobility in estuaries is essential to improve identification of pollution sources and their accountability for environmental effects. This study aims to identify the key biogeochemical drivers of metal mobilisation on contaminated estuarine sediments through (1) evaluation of the potential mobilisation under controlled conditions, and (2) investigation of the relevance of metal mobilisation for in situ pollution levels in an area with multiple contaminant sources. Sediments from a saltmarsh adjacent to a coastal landfill, a marina, and a shipyard on the Thames Estuary (Essex, UK) were exposed in the laboratory (24 h, N = 96, 20 °C) to water under various salinity, pH, and redox potential. Major cations, Fe(II), and trace metal concentrations were analysed in the leachate and sediment. Salinity, pH and redox had a significant effect on metal mobilisation (p < 0.001), e.g. under certain conditions Fe(II) leaching was increased ~1000-fold. Measurements in situ of surface and subsurface sediment cores revealed that landfill proximity poorly explained metal spatial distribution. However, physico-chemical parameters explained up to 97% of geochemically normalized metal concentrations in sediments. Organic matter and pH were dominant factors for most of the metal concentrations at the sediment surface. At subsurface, major cations (Ca, Na, Mg and K) were determinant predictors of metal concentrations. Applying the empirical model obtained in the laboratory to geochemical conditions of the studied saltmarsh it was possible to demonstrate that Fe mobilisation regulates the fate of this (and other) metal in that area. Thus, present results highlight the importance of metal mobility to control sediment pollution and estuarine fate of metals.

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1. Introduction

Estuaries are transitional ecosystems between land and sea that provide a multitude of services (Millennium Ecosystem Assessment, 2005). These areas are amongst the most biologically productive of the planet, and therefore of extreme relevance for marine and freshwater biodiversity protection. Additionally, the provisioning of privileged access to marine, freshwater and continental resources made estuarine systems preferable places for urbanization and industrialization (Kennish, 1991). In fact, many important large metropolitan areas of current commercial and industrial centres, such as London, New York, Shanghai, Lagos, Istanbul and Tokyo are situated in estuarine systems. Therefore, estuarine environments have globally experienced both historical and current intense anthropogenic activities and consequent contamination (Chapman and Wang, 2001; Ridgway and Shimmield, 2002).

Metal contaminants have been traditionally problematic in estuaries because they tend to present non conservative behaviour, while still concentrating and accumulating in estuarine sediments (Machado et al., 2016). In fact, metal-contaminated sediments are commonly reported as of potential concern for the quality of estuarine waters and benthic organism worldwide (Bianchi, 2007). For instance, legacy contaminated sediments in estuaries from Southeast England might display up to 70% of bioavailable metals, many of which at levels that threat wildlife and environmental services (Spencer and MacLeod, 2002). Many estuaries receive substantial inputs of metals such as Cd, Cu, Cr, Hg, Pb, Zn that concentrate in the sediment at levels up to one million-fold higher than the water concentrations (Förstner and Wittmann, 1979; Zwolsman et al., 1993; Attrill and Thomes, 1995).

On the other hand, the non-conservative behaviour of metals (Machado et al., 2016) driven by mobilisation hampers the assessment of pollution sources and misleads inference of pollution levels. For instance, the Newlands saltmarsh (Thames Estuary, UK) presents metal concentrations at concerning levels but with weak association to the main known sources (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995), which obstructs accountability for pollution. Indeed, O'Shea (2016) determined that a combination of proximity to contaminant source and post-depositional mobility accounted for spatial variability in metal concentrations in those intertidal sediments. Many of the physic, chemical and biological gradients present in estuaries affect the metal speciation, partitioning, transport, and consequently spatial distributions (Zwolsman et al., 1993). As an example, the decay of organic matter, periodic flooding, and air exposure of sediments on intertidal areas provoke a cyclic covariation of pH and redox (Machado et al., 2016), with consequent changes on chemical speciation and cycling of several metals (Du Laing et al., 2009c). The diagenetic remobilisation and the difference on sediment pH and salinization due to seawater inflow similarly affects metal speciation and fate (Zwolsman et al., 1993; Du Laing et al., 2009a,b; Johnston et al., 2011). As a result, complex contaminant signatures arising from multiple sources and high environmental mobility make identification of potential impacts particularly challenging.

Notwithstanding, metal pollution is still investigated in estuaries as in fully fresh or marine sediments, i.e. in terms of continuity of high contaminant levels to the contamination sources (Chapman and Wang, 2001). That is partially because it is still unclear how relevant the impacts of metal mobility are in estuarine sediments near contamination sources. Consequently, such lack of information obstructs a realistic understanding of the estuarine pollution and a quantification of the metal mobilised from the sediment to the bioavailable water fraction that mostly impacts aquatic biota.

The present study aimed to quantify the potential effects of the key biogeochemical drivers of metal mobilisation on the metal pollution levels in estuarine sediments. Therefore, laboratory experiments, field measurements and modeling methods were combined in a manner that could be easily implemented in environmental health assessments. The laboratory experiments aimed to provide an estimation of the potential for metal leaching on surface sediments and served as basis for empirical models of geochemical metal mobilisation. Additionally, the in situ relationships between metal enrichment factors and sediment geochemistry were investigated in an intertidal area surrounded by multiple potential contamination sources to compare the influence of mobilisation and proximity to the emission source. The study site chosen here is under influence of a historical coastal landfill and multiple current metal sources (i.e. shipyard and docking area) in one of the estuaries most heavily impacted by metal pollution in the world (Thames Estuary, UK). Metal enrichment factors were used for the assessment of pollution level because they represent the most commonly employed proxy of metal contamination. Finally, an empirical model from laboratory experiments was combined with the in situ sediment geochemistry to compare pollution levels and metal mobilisation. This approach allowed inference of the importance of metal mobility for pollution levels and its interference on the identification of metal sources in estuarine systems.

2. Material & methods

For the purpose of the present study we define some terms that are broadly used in pollution science with potentially ambiguous meaning. The term "metal immobilisation" is defined as the collection of processes such as adsorption, absorption, precipitation and co-precipitation, crystallization that remove metal from the water column to a solid sedimentary phase (Förstner and Wittmann, 1979). The term "metal mobilisation" is then used here as the sum of physical, chemical and biological processes complementary to immobilisation that result into a transfer of metal as dissolved or particulate to the aqueous phase with potential to be transported by water hydrodynamics. The term "metal mobility" is thus defined as the interaction of immobilisation and mobilisation, in which low metal mobility implies high net immobilisation whereas high metal mobility implies high net mobilisation. Moreover, salinity is presented here as practical salinity units 1978 (Unesco/ICES/SCOR/IAPSO, 1981), which is proportional to the conductivity of the sample and its salt content. Therefore, the term salinization is used here as the increase in salinity (and salt contents) of water, slurry or sediments.

2.1. Study area

The Thames Estuary is a tidally dominated estuary with strong anthropogenic influence and noticeable metal contamination (Spencer and MacLeod, 2002; van der Wal and Pye, 2004; Vane et al., 2015). This estuary is amongst the first industrial centres in the world, which summed to the influence of the City of London are the main the causes of a high metal pollution (Attrill and Thomes, 1995). Moreover, several landfills were constructed based on the attenuation principle in the Thames intertidal areas (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995), which today constitute potential additional contamination source.

The study area is situated on an intertidal saltmarsh of the Thames Estuary (south east England, 58° 21′ 25″ N and 18° 37′ 37″ E) receiving both current and legacy contamination from multiple sources (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995), including the Newlands historic landfill, and the shipyard and docking areas on the Oyster Creek (Fig. 1). The Newlands Landfill, hereafter referred as Newlands, is a historical coastal landfill situated on the northern bank of lower portion of the Thames Estuary (Essex, UK). As many other historic coastal landfills from western Europe, Newlands was constructed with no basal or side wall engineering, which allowed release of contaminated leachate, relying on attenuation by surrounding sediments (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995). The site was actively receiving waste from 1954 to 1989 when it was dumped approximately 1,000,000 m^3 of diverse toxic waste including oil-contaminated material from beach clean ups as well as household and
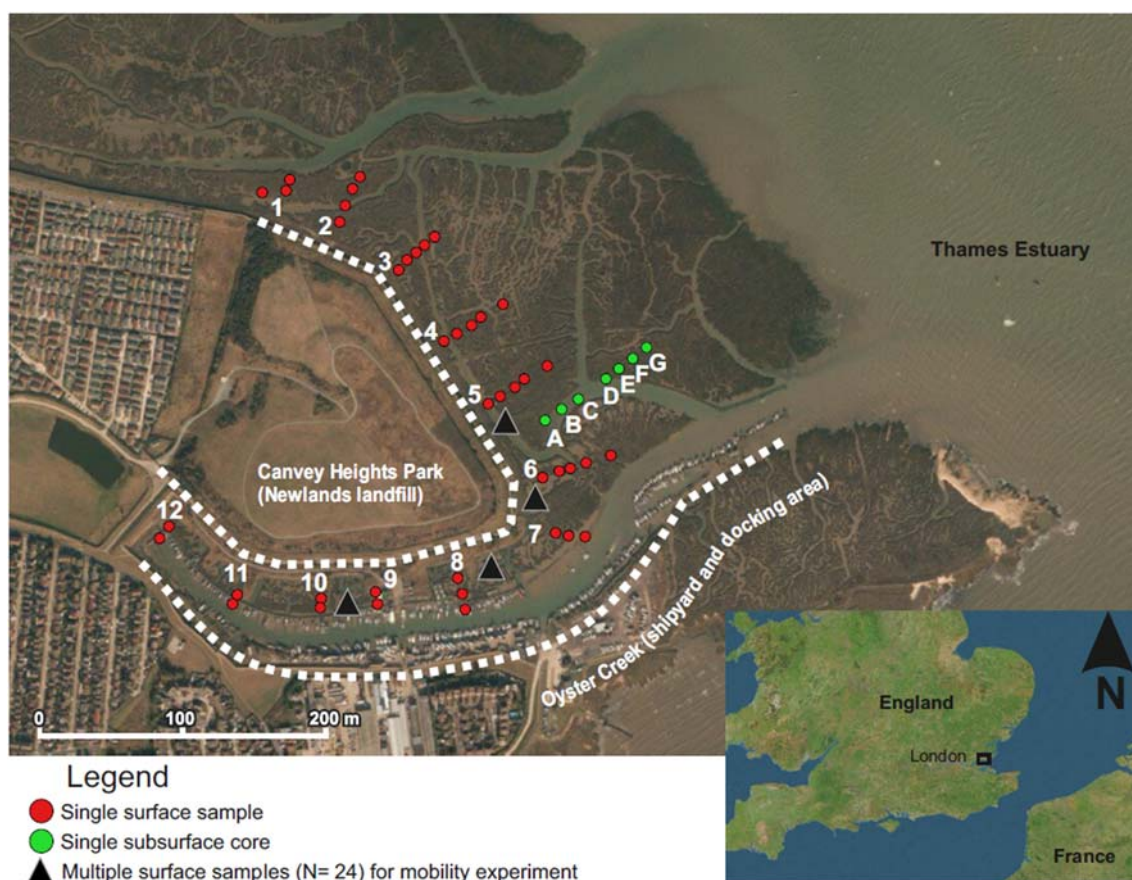
Fig. 1. Schematic of the study area: intertidal saltmarshes adjacent to the Canvey Heights Country Park (Essex, UK). The main potential fronts of metal contamination (the historic Newlands landfill and Oyster Creek shipyard and docks) are highlighted with a white dashed line. Transects are denoted by numbers (1–12), while subsurface individual cores are represented by uppercase letters (A–G). Each triangle points the area where 24 individual samples were taken for the leachate experiment.

commercial waste (Caulmert Limited, 2011a,b). The Newlands is currently underneath the recreational Canvey Heights Country Park. At the south side of the Newlands there is the Oyster Creek, in which many storm water drains and docks from the Small Gains Marina and the Island Yacht Club are located. The metal distributions in that area have been investigated and suggest that historically the landfill was a source of Cr, Cu, Pb and Zn (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995) which is now recorded at depth in the saltmarsh sediments.

2.2. Laboratory experiments

The main goal of the experiments was to quantify the metal leaching from surface sediments under various redox, salinity and pH, so that the rate of metal leaching was used to develop empirical models of potential metal mobilisation on estuarine sediments. For that surface sediment rings (2 cm) were collected in 4 points (24 samples each) of the intertidal mud flat (Fig. 1). The samples were then wrapped with cling film, brought to the Geography laboratory of Queen Mary, University of London in refrigerated coolers, and stored at 4 °C for up to 4 weeks. Redox potential (Eh) of the slurry ranged from −229 mV to −1 mV.

Sediment slurries were prepared with 10 ± 0.1 g wet sediment placed in 50 mL conical centrifuge plastic tubes with 25 mL of nanopure water. The original pH of this sediment slurry ranged from 7.4 to 8.5 and it was recorded with a pH probe (VWR pH 110). Four treatments of salt were added to experimental slurries (0.000 g, 0.125 g, 0.375 g or 0.875 g of sea salt - S9883, Sigma Aldrich) were considered to investigate effects of salinization on metal mobility. The sea salt used in this study is a composition of Cl, Na, SO_4, K, Ca, HCO_3, Sr, B, Br, I, Li, F, Mg and trace elements of typical sea water (Supplementary Table A. 1). After salt addition, the

slurry was stirred with vortex for ~1 min. The mass of marine salt added created leachates with salinities of 0, 5, 15 and 30 had complete dissolution occurred. It is worth to mention that only partial dissolution was achieved since the sediment interacted with salinity adjustments. A summary of the effect of salt addition on salinity and major ion concentration on the leachates is presented on Supplementary Fig. A. 1, and Supplementary Table A. 2.

After salt addition, the original pH was adjusted by adding hydrochloric acid 1 M or sodium hydroxide 1 M, which resulted in a pH initial ranging from 5.9 to 9.1. The experimental slurry (with modified salinity and pH) was then gently shaken for 24 ± 1 h at 24 ± 2 °C. After this 24 h-period of water-sediment interaction, the pH was recorded as pH final (Table 1). Redox potential (Eh) of the slurry was also determined with a redox probe (VWR pH110). The experimental slurry was then centrifuged for 10 min at 3000 rpm, and the resulting supernatant was considered the leachate for the purpose of the present study.

Table 1
Range of geochemical parameters measured at the end of 24 h on laboratory experiments. Salinity and pH were arranged as multivariate, pH and redox as covariate (Supplementary Fig. A. 2).

Parameter	Range	Experimental size
	Min to max	N[a]
pH	6.3 to 8.6[b]	96
Salinity	2.6 to 31.5	96
Eh (mV)	−229 to −1	96

[a] 24 surface samples were collected at each of the 4 points of the saltmarsh (Fig. 1) and posteriorly equally distributed along the range of pH and salinity treatments.
[b] The monitored variation of pH within the experimental 24 h was generally smaller than 12%.

Salinity in the leachate was measured (VWR pH110), and 1 mL of it was immediately preserved for Fe(II) analysis. We devoted especial attention to iron behaviour as it is known to affect the fate of other metals, and because Fe(II) was an important metal species that we could measure in a simpler manner without filtering the leachate (see Section 2.4.3). The remaining leachate was passed through filters with 8 μm mesh (Whatman 542) for later ICP OES quantification of total mobilised metal during leaching experiment. Despite filters of 0.45 μm or smaller are commonly used to infer dissolved or bioavailable metal, the current study focused on the mass of metal mobilised, which is more accurately assessed via total metal proxies. In this sense, the 8 μm used here constituted the minimum filtering required to quantify total metal with the ICP OES procedures used here. Yet, during this filtering part of the colloidal metal was retained, as discussed in the Supplementary material A (Box A. 1). Inferences about bioavailable metal are beyond the scope of the current study.

2.3. Field assessment

The field data within this paper for surface and subsurface metal concentrations and enrichment factors are presented elsewhere (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995), therefore only a brief overview of the data collection methods is outlined here.

Surface grab samples were taken every 50 m in triplicate along 12 radial transects perpendicular to the site boundary (Fig. 1). Additionally, seven sediment cores were extracted at 10 m intervals along a transect perpendicular to the site boundary using a polycarbonate pipe for the first 30 cm or a Russian corer for deeper samples (Jowsey, 1966). Samples kept at −12 °C until required.

Subsurface samples were analysed at 5 cm intervals for the top 1 m, then 10 cm intervals at depths below this. Samples were homogenized and split, with a sub-sample used for pH, particle size and organic matter content while the other was freeze-dried for 24 h for later metal analysis. Original pH was measured in these samples as in the leachate experiments.

The surface sediments were classified as silty clay or clayey silt (Shepard, 1954), with predominance of mud-sized (<3.9 μm) and silt-sized (3.9–63 μm) sediment fractions. There was only little spatial variation on surface grain size. However, subsurface sediment shifted from clayey silt near the sediment surface to silty sand at depth (deeper than 70 cm) (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995). Further mineralogical characterization of the sediment samples was not performed.

Data from these field samples are discussed within the Sections 3.2 and 3.3 and combined with laboratory experimental data for the mobilisation presented in Section 3.4.

2.4. Additional physico-chemical parameters analysed

A broad suite of geochemical parameters influencing metal mobility were measured in both leachate experiment and field assessment data as described below. Procedures reported in Sections 2.4.1 to 2.4.3 refer to laboratory leachate experiment. Methods for the field assessment are similar and can be found in more detail in O'Shea, 2016 (https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995).

2.4.1. Water percentage and loss of ignition

Water percentage was quantified by the mass difference between overnight dried (60 °C) sediment and the initial a wet mass (24.2 ± 3.3 g). Loss of ignition (LOI) was then measured as a proxy for organic matter content on the sediment. For that a mass of 13.4 ± 2.2 g of dried sediment was ignited in a furnace (550 °C, 5 h). The difference on weight before and after ignition was interpreted in terms of percentage of organic matter combusted.

2.4.2. Aqua Regia extraction

Trace metals were extracted from all sediment samples on a hotplate using Aqua Regia (HNO_3:3HCl). This method quantifies pseudototal metal, which provides insights on the potential environmentally mobile and bioavailable metal. Therefore, such metal extracted is considered as environmentally available metal (National Water Research Institute, 2001) and this terminology is adopted here.

All the materials in contact with metals during leachate experiment and Aqua Regia extraction were washed with nitric acid 10% during 24 h and rinsed 3 times with nanopure water. All the chemicals used in the present study were analytical grade. Sediment from metal leaching experiment and from field assessment were freeze-dried overnight (vacuum, −56 °C). The extraction involved placing 0.50 ± 0.02 g of sediment in Erlenmeyer flasks, adding freshly prepared Aqua Regia, and heat this mixture for in hot plate (5 h, ~85 °C) (Chen and Ma, 2001). The Aqua Regia was then filtered (542 Whatman, 8 μm) and made up to 50 mL with nanopure water. To assess accuracy of metal extraction additionally 2 certified materials (SUD1- Environment Canada, and the CRMLGC 6187) and method blanks were analysed in triplicate (Supplementary material, Table A.5). Also, two samples were measured in duplicate, which were considered together with the certified materials to assess extraction precision (Supplementary material, Table A.5). Metal extracts were kept at 4 °C until analysis.

2.4.3. Metal quantification

Fe(II) in the leachate was measured with the colorimetric method based on the reaction of Fe(II) with the 1,10-phenanthroline as in Lee and Stumm (1960). Other metal concentrations (Al, Co, Fe, Li, Mn, Pb, Sr) on the leachate and sediments were quantified by inductively coupled plasma optical emission spectrometry (ICP OES) on a Varian Vista-Pro ICP OES instrument using internal standard settings of the Geography laboratory of Queen Mary, University of London. Analytical further information and quality control data is presented in Supplementary Tables A. 3, A. 4 and A. 5.

2.4.4. Geochemical speciation model with Visual MINTEQ

In order to provide mechanistic insights on the geochemical processes driving the mobility of metals in the laboratory experiments, computations of equilibrium concentrations of Fe and trace metal species in the pore water were performed with Visual MINTEQ 3.0. In total 96 scenarios were computed (one for each leachate) according to Table 2. Note that such settings were designed to consider the effects of parameters with the strongest association with metal mobility in the laboratory and in the field, namely Fe mobility and its relationship to pH and organic matter (see section on Results and discussion). Such computations did not consider all the activity of ions from saltwater and sediments or the full diversity of mineral and sorption sites potentially available in those systems. This simplification might limit the accuracy of Visual MINTEQ outputs. Introduction of these variables in the model would cause a very great number of possible reactions and products that lead to numerical instabilities. Therefore, the model outputs displayed in the figure of Box 1 should be interpreted as an indication of general patterns only.

2.4.5. Geochemical normalization and enrichment factors

Metal concentrations in sediments vary with grain size, which makes necessary to normalize environmental metal concentrations (Kersten and Smedes, 2002). Variations in the distribution of fine sediments, which are negatively charged surfaces and have large surface/volume ratios that increase cation exchange capacity, affects the concentrations of sediment-bound metals (Förstner and Wittmann, 1979). Thus, different types of "normalization" of metal concentration are used to interpret environmental metal concentrations (Kersten and Smedes, 2002). Broadly, normalization consists to divide measured metal concentrations by a proxy element that could account for the different adsorption at various grain sizes. Al and Li are amongst the

Table 2
Parameters for the computations of metal speciation with Visual MINTEQ.

Parameter	Model settings	
pH	Varied as pH measured for each sample	Variable with major effects on Fe mobility
Eh (mV)	Constant at −150	Average redox of sediments
Temperature (°C)	Constant at 24	Experimental condition
DOC (mg L^{-1})	Varied according to measured at each sample	Variable with major effects on metal concentrations on the field surveys
	The concentration of DOC was estimated based on the empirical quadratic relationship between LOI and DOC by Craft et al., 1991. The reactivity of DOC to metals was simulated with the Stockholm Humic Model (SHM) within Visual MINTEQ. The SHM accounts for metal complexation by both dissolved and particulate organic matter.	
Adsorption surface model	4.8 g L^{-1} of matter allocated to ferrihydrite, and the Hydrous Ferric Oxide Model (HFO- Dzombak & Morel) was used to compute surface complexation of metals to iron oxyhydroxide minerals.	This represents the allocation of ~80% of total Fe measured to the HFO model, which is the most complete database for the interaction of precipitated metal minerals and other ions.
Counter-ion function	Activated	Accounts for the changes in the surface charges resulting from ion-surface interactions.
Fe(II)	Varied as Fe^{2+} for each sample	~20% of the total Fe measured
Cobalt	Varied as Co^{2+} for each sample	Total Co measured for each sample
Manganese	Varied as Mn^{2+} for each sample	Total Mn measured for each sample
Lead	Varied as Pb^{2+} for each sample	Total Pb measured for each sample
Strontium	Varied as Sr^{2+} for each sample	Total Sr measured for each sample
Lithium	Varied as Li^{2+} for each sample	Total Li measured for each sample

Other parameters were set as default of Visual MINTEQ 3.0 for all samples, and readers are referred to user guide of Visual MINTEQ for further information on assumptions and parametrization.

most common normalizing elements (Kersten and Smedes, 2002) and were adopted in the present study. Therefore, metal concentrations presented here were normalized by the Al as this metal was used in relevant estuarine geochemistry studies (Zhang and Liu, 2002). Al concentrations needed to be normalized by Li to avoid mathematical artefacts of normalization.

Enrichment factor (EF) was also computed as this parameter is perhaps the most common indicator used for environmental assessment of metal pollution. EF was calculated empirically according to Eq. (1). The background concentrations for the studied area were determined by O'Shea, 2016 (https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995), i.e. the average metal concentrations between 3.4 and 4.4 m deep of core 2.

$$EF = \frac{\left(\frac{M_s}{N_s}\right)}{\left(\frac{M_b}{N_b}\right)} \qquad (1)$$

where:

EF = Enrichment factor
M_s = Metal concentration in the sample
N_s = Normalizing metal in the sample
M_b = Background metal concentration for the studied area
N_b = Background normalizing metal concentration for the studied area

2.5. Statistical methods and data presentation

Significant effects of geochemical parameters on metal mobilisation and sediment metal enrichment factors were detected with Kruskal-Nemenyi test with Tukey post hoc (Sachs, 1997) or linear regressions with the "lm" function from software R (R Core Team, 2013). The empirical linear relationships between geochemical parameters and metal mobility are presented in the figures so that interested readers could potentially compare them to values from other studies. All statistical analyses were performed with $\alpha = 0.05$.

The empirical linear model derived from the laboratory experiments (Fig. 2) was used to estimate Fe(II) leaching from in situ sediments. Then, spatial distribution of Fe enrichment factors, and Fe(II) leaching maps were created on the software QGIS 2.14.1 with interpolated surface sediment data. Interpolation was performed by inverse distance

weighting, and contour lines were extracted for EF (every 0.02) and metal mobilisation (every 10) intervals.

3. Results and discussion

In the next paragraphs the results on the potential for metal leaching from contaminated sediments are discussed in terms of drivers of metal mobilisation. Secondly, the influence of sediment geochemistry is compared to the proximity to potential contamination sources. Finally, the relevance of metal mobilisation to metal levels in that tidal flat and how ignoring metal mobilisation might mislead environmental health assessment are discussed in the context of estuarine sediments with complex contaminant signatures.

### 3.1. Potentially high metal leaching in estuarine sediments

The metal species with highest mobilisation flux was Fe(II). Mobilisation of Fe(II) varied from <0.2 up to 267.5 μg Fe(II) g^{-1} (dw) d^{-1} depending mostly on pH (Fig. 2). In fact, the empirical model devised here predicts a 2.66-fold increase on Fe(II) mobilisation for each unit of pH acidification (see equation on Fig. 2). The geochemical explanation for such a great changes in Fe(II) mobility might be on the formation of Fe hydroxides (see Box 1). Redox potential also affected Fe(II) leaching (p < 0.001), with maximum leaching occurring between −150 and −50 mV (Supplementary Fig. B. 1). Salinization presented only mild effects, with more saline slurry yielding leachates with slight higher Fe(II) concentration (Supplementary Fig. B. 1).

Sediment geochemistry also strongly influenced the leaching of Al, Co, Li, Mn, Pb and Sr. For the total mobilised metal, salinity and pH changes jointly accounted for 80% of metal leaching (Fig. 3). In this context, salinization is believed to increase metal leaching due to a combinatory effect of anions and cations in affecting the ionic forces on the slurry (Förstner and Wittmann, 1979; Bianchi, 2007). Saltwater anions as chloride form soluble complexes with weakly adsorbed metals, therefore enhancing solubility (Machado et al., 2016). That is because metals weakly adsorbed as Cd might interact with chloride and sulphate to form soluble inorganic species (Greger et al., 1995). Concurrently, Ca and Na cations can displace both weakly and moderately sorbed metals such as Cr, Cu, Zn and Pb (Fairbrother et al., 2007). Thus, via such mechanisms metal adsorption can be prevented as well as metal desorption increased.

Box 1
Geochemical insights on the effects of pH on the behaviour of Fe(II) and trace metals.

The computations of Fe(II) speciation with the chemical equilibrium model Visual MINTEQ suggest that the effects of pH on Fe(II) leaching are explained by a decrease in dissolved Fe(II) in combination to an increase in adsorbed Fe(II) (Fig. Box 1A). Moreover, the concentrations of Fe hydroxides were predicted to increase up to 6 orders of magnitude (Fig. Box 1B) with the increment of ~ 2.5 pH units. Indeed, the concentration of H^+ is reported to affect hydrolysis of metals, which was generally estimated by Hietanen and Sillén (1954) as:

$$q\, Me^{z+} + p\, H_2O \rightleftharpoons Me_q OH_p^{(qz-p)+} + p\, H^+$$
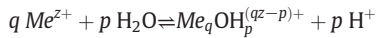
where "q" is the number of metal units in the complex, "Me" is the metal element, "z" is the charge of Me ion, "p" is the number of OH (hydroxyl) in the complex, and H is the hydrogen ion. Such hydrolytic reaction might produce one or more mono- or polynuclear metal complexes. In fact, three mononuclear ($q = 1$) hydroxyl complexes ($Fe(OH)_3^-$, $Fe(OH)^+$, and $Fe(OH)_2 \cdot aq$) were computed by Visual MINTEQ as the most relevant for the fate of Fe(II) under our experimental conditions (Fig. Box 1B). In turns, such increment on the concentrations of Fe hydroxides seems to play a role on the decreased mobility of Fe(II) (Fig. Box 1C). Trace metals were predicted by the model to undergo similar reactions, forming mononuclear as well as polynuclear complexes (e.g. $Co_4(OH)_4^{4+}$, $Mn_2(OH)_3^+$, and $Pb_4(OH)_4^{4+}$). As the concentrations of the trace metals hydroxides were computed to be about 15 orders of magnitude lower than Fe hydroxides (data not shown), most of trace metal adsorption occurred to Fe oxyhydroxides (ferrihydrite) species and organic matter. In this context, the formation of trace metal oxides might be negligible under the reducing conditions of the sediments investigated here (e.g. MnO_4^- and MnO_4^{2-} were the most relevant oxide species with concentrations from ~10^{-65} to ~10^{-95} g L^{-1}).
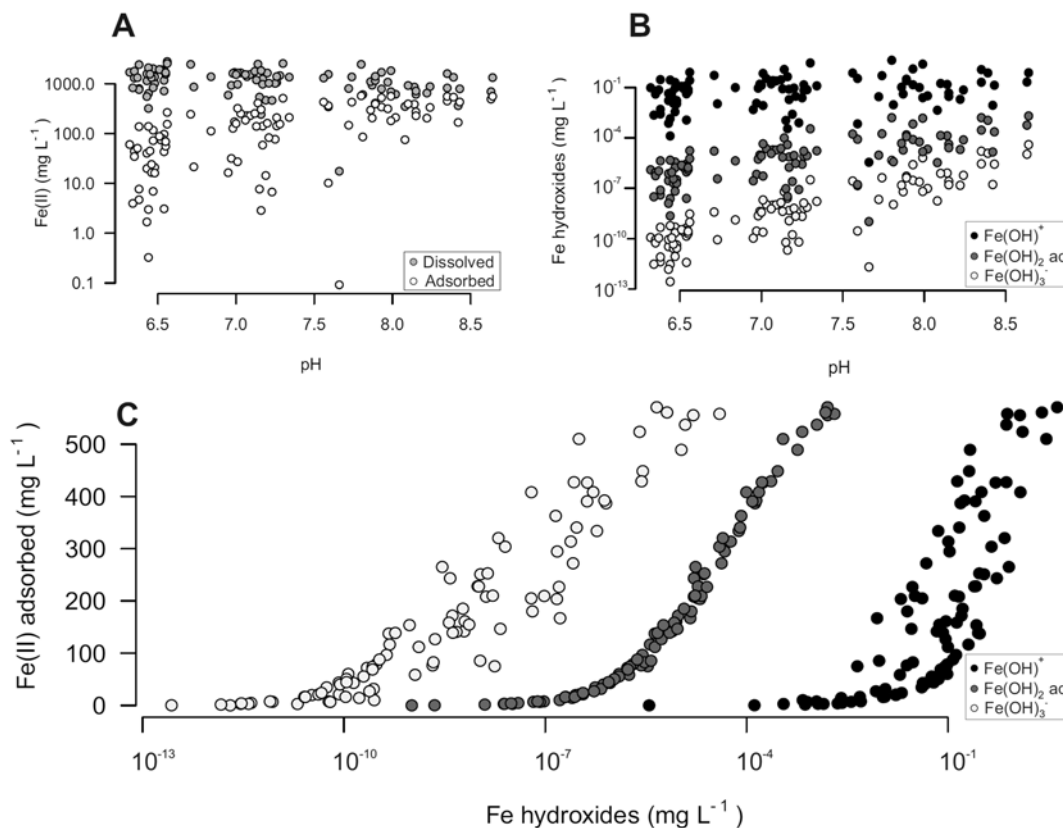

Fig. Box 1 Output of Visual MINTEQ for the speciation and adsorption of Fe(II) in pore waters of leachate experiments. Dissolved Fe(II) trends to decrease linearly with leachate pH while adsorption (A). Iron hydroxides directly increase with pH (B), concomitantly to a significant increment on Fe(II) adsorbed (C). Absolute values must be careful interpreted as some components of the systems (i.e. all active ions and adsorption sites) have not been included in the computations. Notwithstanding, general patterns and relative concentrations might hold in more realistic settings.

Likewise, acidification (positive values of pH difference, Fig. 3B) of one unit of pH increased mobilisation by 7.3-fold (see equation on Fig. 3).

Interestingly, within the range of metal concentrations measured in the present study, the quantity of metal leached was minimally constrained by environmentally available metal concentrations (Fig. 4).

For most of the metals, either no significant or very low correlation indexes ($r^2 < 0.1$) were found between the sediment concentrations and the leached metal. In other words, the concentration of certain metals in the sediment fraction had small effects on the leachate concentrations compared to the physico-chemical mobility (i.e. empirical relationships were non-significant or slopes ≪1 on Fig. 4).
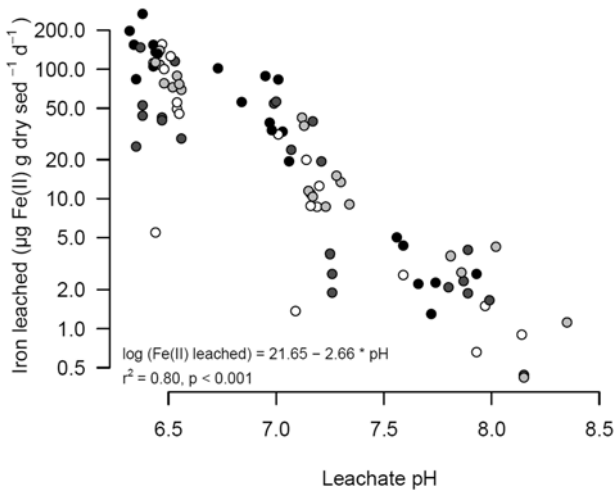
Fig. 2. Effects of pH on the mobilisation of Fe(II). The white, light grey, dark grey and black filled circles represent respectively 0.000 g, 0.125 g, 0.375 g or 0.875 g of marine salt added to the experimental slurry.
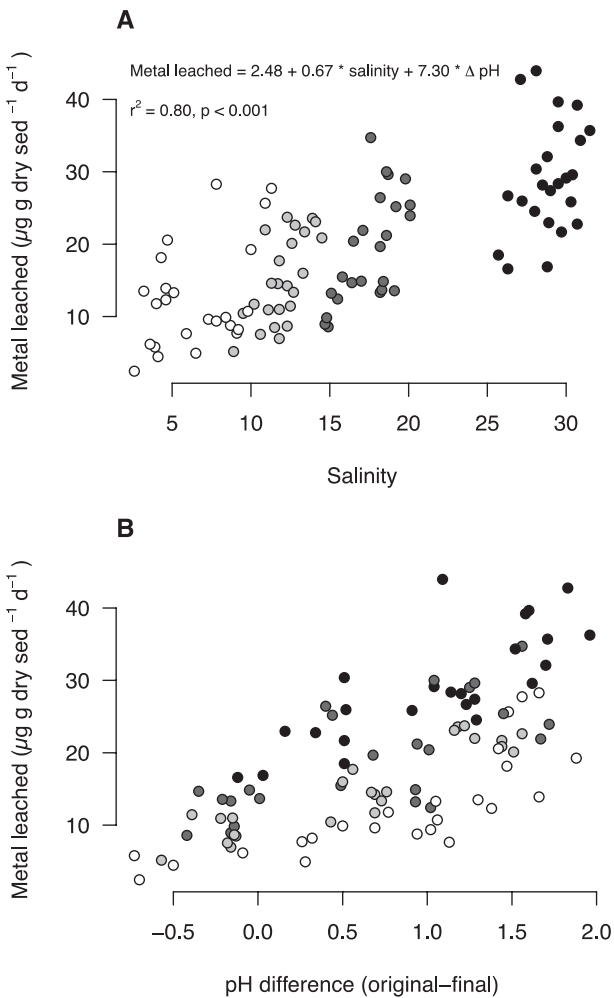

Fig. 3. Effects of salinity (A) and pH changes (B) on the total metal mobilisation ($\sum$ Al, Co, Fe, Li, Mn, Pb, Sr) from sediment to the 8 μm air-filtered leachate. The white, light grey, dark grey and black filled circles represent respectively 0.000 g, 0.125 g, 0.375 g or 0.875 g of marine salt added to the experimental slurry.
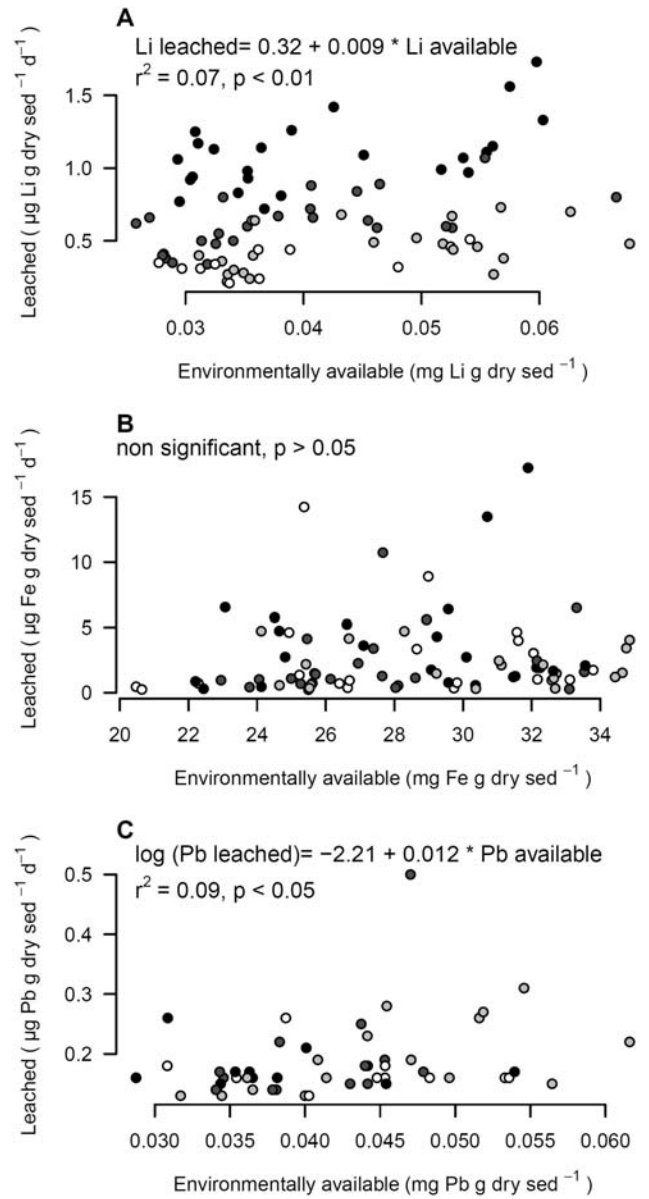

Fig. 4. Effects of environmentally available metals on the mobilisation of Li (A), Fe (B), and Pb (C) as examples of lithogenic, diagenetically highly mobile, and anthropogenic metals, respectively. The white, light grey, dark grey and black filled circles represent respectively 0.000 g, 0.125 g, 0.375 g or 0.875 g of marine salt added to the experimental slurry.

3.2. Mobilisation drives in situ metal concentrations in estuarine sediments

The spatial distributions of most metals were not contiguous to the main potential sources, i.e. the Newlands or Oyster Creek docks. As exemplified for subsurface in Fig. 5(A, B, C) metals levels range mostly between natural (EF < 1) and polluted (EF > 1), which confirmed the significant influence of anthropogenic sources of metals in an area where geochemistry and natural mineralogy are the main factors controlling metal fate (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995). In fact, only low correlation values (N ~ 600, $r^2 < 0.15$, $p < 0.001$) were found in the present study between proximity to the landfill and metal concentration. However, environmentally available metals were not randomly distributed (Fig. 5D, E, F). Normalized concentrations presented characteristic vertical and horizontal distributions that were significantly ($p < 0.001$) explained by geochemistry for all studied metals.
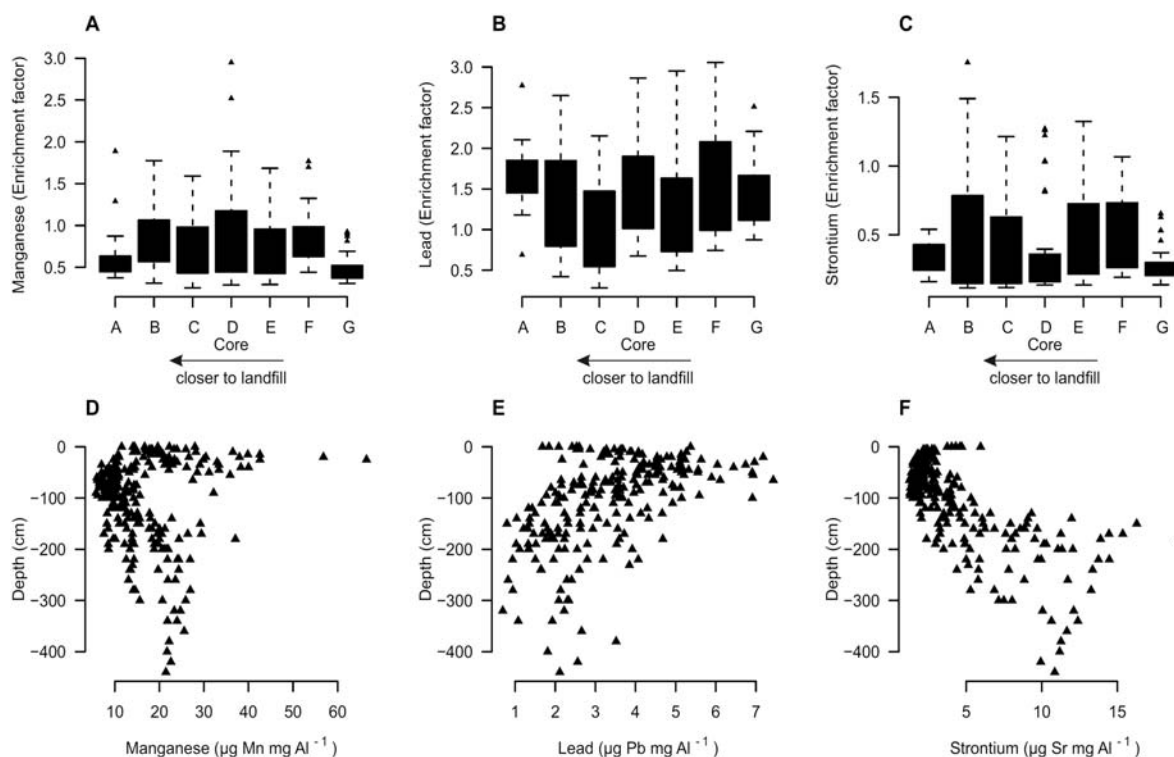
Fig. 5. Environmental behaviour of selected metals on subsurface sediments. Mn was selected as an example of diagenetic mobility dominated by redox gradients. Pb was selected as it is believed as anthropogenic (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995). Sr was selected as an example of metal mobility strongly dominated by the fate of Ca. A–C: Subsurface metal distributions displaying low contiguity to main potential metal contamination source (upper and lower limits of boxes represent respectively 75% and 25% quartiles, bar limits represent 99% and 1% quartiles, small triangles are extreme values). D–F: Metal distributions displaying high dependence of geochemical gradients (triangles represent individual measured data).

The mechanisms of metal distribution and physico-chemical mobility might vary. For instance, Mn is diagenetically mobile, i.e. tends to be remobilised in reduced conditions at depth in the profile and precipitate near the surface (Förstner and Wittmann, 1979; Du Laing et al., 2009a, b). Pb in those sediments is believed to represent the anthropogenic influence through the peak of industrialization from late 1800s to 20th century (O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995). Despite the potentially low mobility in soils (Li, 2006), the wide scattering of Pb distribution found in the currently studied estuarine sediments might also imply significant environmental mobility. Finally, Sr has its fate strongly determined by behaviour of Ca (Section 3.3). Thus, sediment chemistry was influential for all normalized metal concentrations through many mobility mechanisms (see also Box 1). It cannot be discarded that additional processes (e.g. bioturbation and hydrodynamic transport) might help to explain the metal compartmentation reported here. Tidal pumping and tidal trapping are known to promote residual circulation and asymmetric flow that determine the fate of particulate material and consequentially particulate metals (Machado et al., 2016).

3.3. Sediment geochemistry and pollution levels

This section shows selected examples of metals with representative effects of geochemistry on their pollution levels (either increasing or decreasing). Generally, the patterns of surface and vertical concentrations of Cu, Co, Zn and Pb are similar (see Supplementary Fig. B. 2 for major ion influence). Also, Fe and Mn presented similar behaviour. Enrichment factor of Fe and Mn were correlated to most of the trace metals ($p < 0.01$) in surface and relationships commonly faded with increasing depth (data not shown). Sr and Cr presented peculiar behaviour as discussed later.

Surface metal levels in the intertidal area were strongly influenced by pH and organic matter content ($p < 0.001$). The latter was positively correlated to water content and metal concentrations in the sediment (Fig. 6). It suggests that intertidal sediments flooded more frequently or for longer periods might present higher organic matter content, which provided important ligands for metal immobilisation. It has been noticed that increased flooding generally enhances organic matter content in sediments due to less optimal degradation conditions (Du Laing et al., 2009b). Nevertheless, the effect of organic matter on the concentration of trace metals might be ignored in environmental health assessment of metal pollution if normalization of metal concentration is based exclusively on sediment granulometry of mineral phases. Organic matter must be taken into account when assessing metal contamination in intertidal areas. Du Laing et al. (2009a) found that a 25% increment in organic matter might result in 200-fold increase in metal concentrations. In the present results, enrichment factors show a more modest sensitivity to organic content. Notwithstanding, metal immobilisation by organic matter was noteworthy and ignoring it might further contribute to hamper identification on the reason of metal accumulation in estuarine sediments and lead to false positive indication of presence of anthropogenic sources.

The Fig. 6(B, C) exemplifies the effect of organic matter on the environmental levels of a potentially anthropogenic trace metal (Co) and a lithogenic redox sensitive metal (Fe). In turn, Fe influences the concentration of many trace metal through precipitation and co-precipitation during the formation of oxy-hydroxide iron colloids (Fairbrother et al., 2007; Du Laing et al., 2009c). Therefore, a synergistic effect on organic matter and redox cycling metals (as Fe and Mn) on the immobilisation of trace metals cannot be discarded.

In the Fig. 6B it is also possible to distinguish two clusters of data on the relationship between organic matter and Co, which were also observed for Cu, Pb, Cr and Zn. The upper cluster (EF > 1) represent the samples taken from the intertidal areas facing the main channel to the Thames Estuary (transects 1–5, Fig. 1), in which pH of the sediment was higher. While the lower cluster of data (Fig. 6B, EF < 1) are sampling
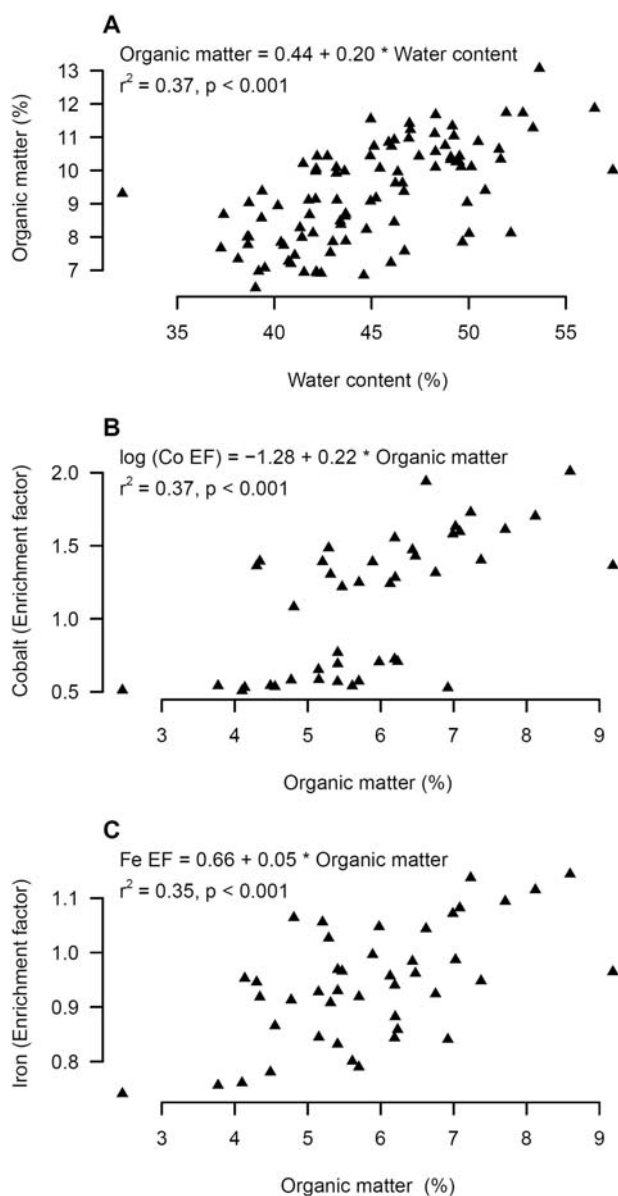
Fig. 6. Environmental behaviour of organic matter and selected metals on surface sediments. A: Organic matter increases with water content. B: Relationship of cobalt and organic matter. C: Relationship of iron and organic matter. Empirical relationships reported here might explain 35–37% of metal enrichment factors (see fitting equations).

points under the influence of Oyster Creek (transects 6–12), where a drop of approximately a unit of pH was observed. From the current results it is impossible to speculate whether the changes on pH are purely natural or have an anthropogenic influence. The gradient on sediment pH clearly influenced the metal behaviour in sediment surface samples. Enrichment factors smaller than 1 were observed for most of metal in the area of potentially higher contamination (e.g. under influence of the Newlands, adjacent docks, and with more enclosed hydrodynamic). In fact, the surface level metal concentrations considered in the present study ($\sum$ Al, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, Zn) could be also described as function of sediment pH ($r^2 = 0.46$, p < 0.001; Supplementary material B. 3), which exemplifies the decisive effect of surface sediment pH on environmental metal levels.

The effect of pH was not consistent throughout the sediment profile. Despite the strong correlation on the surface, subsurface sediments presented weaker or even reverse relationship with pH (Fig. 7A–B). This ambiguous effect of pH on metal concentrations on surface and subsurface reflect the different processes taking place at these two

compartments. Surface sediments (top 5 cm layer) are successively exposed to air and water. Metal solubilized by lower pH values on the surface sediments can be easily transferred to the water column and removed from the intertidal area within a tidal cycle (Machado et al., 2016). Thus, pH-driven mobilisation in the surface sediments implies decreasing levels of metals. On the other hand, metals solubilized in the subsurface sediments move much slower. Maximum advection of water within sediment layers is of order of 10^{-6} m s^{-1} (Brand et al., 2013). Therefore, the pH-driven mobilisation in subsurface might instead transport metals to places of preferential accumulation, where interaction with strong metal immobilisers (e.g. sulphide) could actually increase metal levels.

Moreover, subsurface sediments undergo several diagenetic processes that also affect the metal fate. For instance, Sr distribution is strongly determined by the fate of Ca (Fig. 7C). As an alkali Earth metal, Sr presents high affinity for carbonates (in which it can readily replace Ca) (Lerouge et al., 2010; O'Shea, 2016 https://qmro.qmul.ac.uk/xmlui/handle/123456789/12995). Therefore, a decrease of pH in the sediment profile would cause decalcification, with consequent dissolution of carbonates and release of both Ca and Sr (Du Laing et al., 2009b). The relationship between Sr enrichment factors and Ca was also present in the surface but with smaller explanatory power ($r^2 = 0.53$, p < 0.001). A stronger correlation at depth was also observed for Mg, Na, K and many trace metal enrichment factors (Supplementary material B. 2), suggesting that diagenetic provisioning of adsorption/co-precipitation sites, and the interaction with sea water ions might have a predominant role on the mobility of metals within the subsurface sedimentary layers.

Such influence of major cations (i.e. alkaline and alkali Earth metals) on the behaviour of trace metals was weaker at the surface. The only evident exception was the relationship between Al and K (Fig. 7D). Geochemically normalized Al concentrations significantly (p < 0.001) decreased with the increment of K concentrations. Likewise, geochemically normalized concentrations of Li increased proportionally to K concentrations (p < 0.001) since it presented exactly the opposite surface fate as Al. Regarding metal pollution levels, the presence of major cations might be considered influential at the sediment surface and determining at subsurface with an explanatory power between 19% to 97% (see fitting equations on Fig. 7).

Altogether, the results from the field assessment of metal levels also suggest that sediment geochemistry determines contamination levels of most of the metals in this tidal flat and partially accounts for the complex contaminant signatures. The most geochemical influential parameters at surface were pH and organic matter content, followed by major cations and Fe-Mn. In subsurface, the diagenetic processes and slower advection favoured the higher influence of major cations on metal concentrations.

3.4. High metal mobility in situ in estuarine sediments

Intertidal estuarine sediments might present high spatial chemical heterogeneity where metal levels are homogeneously controlled by biogeochemical processes (Mouret et al., 2016). Amongst those processes, the exchange of Fe between water and intertidal sediments is suggested as a vitally important mechanism of metal flux (Johnston et al., 2011). The results presented here from laboratory leachate experiments and field assessments of geochemical influence on metal levels suggest that potentially high metal mobilisation might occur within contaminated estuarine sediments. Applying the pH of the surface sediments from the saltmarsh studied here on the equation presented in Fig. 2 it was possible to confirm that mobilisation is the key factor for metal concentrations in sediments despite the strong anthropogenic influence in this tidal marsh (Fig. 8A–B). Fe enrichment factors were higher in the tidal flats, away from the potential main anthropogenic sources (Fig. 8B). As mentioned earlier, several trace metals presented similar patterns. Instead denoting absence of impacts, the low enrichment
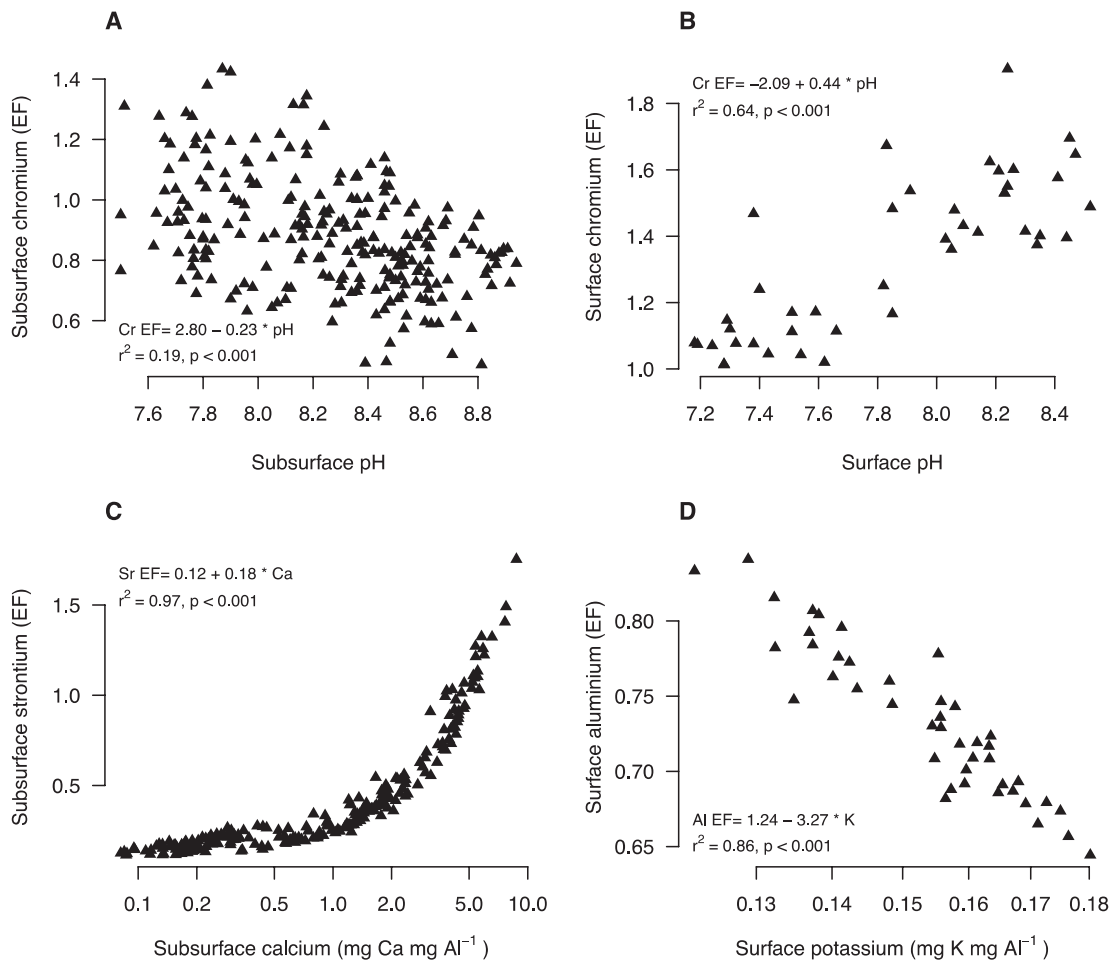
Fig. 7. Geochemistry determining pollution levels, in terms of enrichment factors (EF), of trace metals on both surface and subsurface sediments. Chromium is differently influenced by pH in subsurface (A) and surface (B) sediments. Precipitation and co-precipitation (C) and negative interaction (D) with major cations influences Sr and Al levels, respectively.
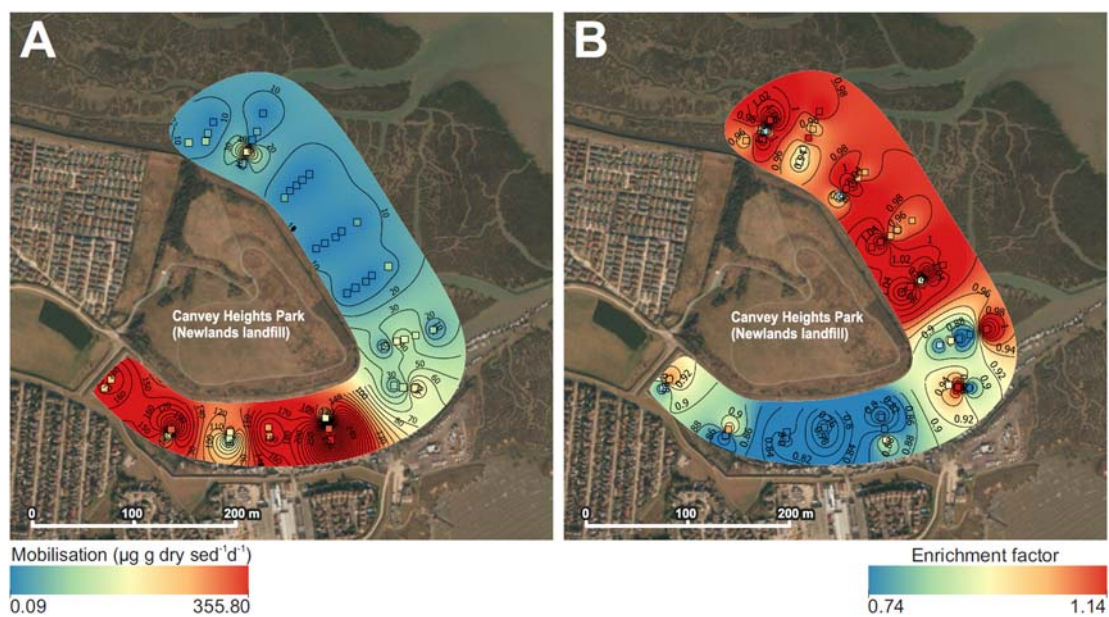

Fig. 8. Effect of metal mobility on pollution levels. Iron mobilisation (panel A, µg Fe(II) g dry sed^{-1} d^{-1}) was negatively correlated to iron enrichment factor (panel B) in the sediment surface ($r^2 = 0.42$, $p < 0.001$). In both panels, squares represent measured points and the colour scale for their values is presented in the graph. The contour lines are presented for the interpolated values in the whole study area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

factors of several metals in the area of Oyster Creek denounce the ~1000-fold higher metal mobilisation in that area. In other words, it means that the most human-impacted area is exporting significant amounts of metals to the adjacent waters. In the case of Fe(II) the main driver of mobility was the gradient of sediment pH (Fig. 8A). Mobilisation of Fe(II) also explains 39% of the observed pollution levels of other metals and more anthropogenic metals (Supplementary Fig. B. 3). Indeed, it has been extensively demonstrated that Fe behaviour correlates with the fate of other metals (Fairbrother et al., 2007; Machado et al., 2016; Prajith et al., 2016). The geochemical explanations for such effects are presented in Box 1. Nonetheless, given the current results from the laboratory experiments, salinity might also play an important role in explaining part of the remaining variability for the other metals.

4. Conclusions and future directions

In a recent study, O'Shea (2016) found that a historical leachate plume from Newlands Landfill resulted in elevated sediment metal concentrations. This zone of enrichment only extended to ca. 20 m from the landfill edge as a result of the effective natural attenuation by the fine-grained sediment and/or post depositional mobility. Therefore, as in many estuaries, beyond this enrichment zone, metal levels were moderately high but without spatial continuity to the main anthropogenic source. Our results demonstrate that the observed impacted zone may have been much larger because sediment geochemical gradients affected metal mobility and pollution levels for all studied metals. Metal mobility was found to potentially transfer significant amounts of metals from sediments to the aqueous phase in the laboratory. In the field, gradients of pH and organic matter at the sediment surface were the most important for most of the metals, while major cations were decisive in the subsurface.

The significant observed effects of salinization and acidification on the mobility of metals have implications in terms of global change impacts on industrialized estuaries. Sea-level rise might cause salinization in many coastal systems such as the Thames Estuary, which faces about 9 mm year^{-1} sea-level rise (last 20 years, Environment Agency data) associated to a projected decrease in annual precipitation (Johnson et al., 2009). Additionally, sea-level rise will increase the frequency of flooding, therefore increasing the content of organic matter in the sediments (see Section 3.3) and consequently affecting the pH. For instance, Du Laing et al. (2009b) found that decomposition of organic matter in sediments released CO_2 that accounted for the acidification and mobilisation of Ca, Fe, Mn, and Ni at low sulphide concentrations. This remobilisation of metals might be especially concerning for many industrialized countries, in which tons of metal contaminated material were disposed in coastal environments. For instance, between 1976 and 1977 about 9000 tons of metals ($\sum$ Cd, Cr, Cu, Hg, Pb, and Zn) were dumped in British estuarine and coastal systems (Förstner and Wittmann, 1979). Like at Newlands, most of these landfills relied on environmental natural attenuation of the pollution plumes. In fact, a recent review found >1200 coastal landfills at risk of flooding and/or erosion only in England and Wales (Brand et al., 2017). The remobilisation of sediment-immobilised metals increases the potential for biological impacts. In estuarine water, metals may present high bioavailability, and are subjected to long environmental persistence driven by hydrodynamic and geochemical processes (Machado et al., 2016). Therefore, the risk of remobilisation of contaminants from historic contaminated estuarine sediments might contribute to exacerbate pollution and habitat loss in a context of global changes.

The comparison of the leachate empirical regression with environmental levels ratifies that metal mobilisation is an important variable that explains for at least ~40% the pollution levels in estuarine tidal sediments. Further studies are required to verify whether the empirical models for mobilisation provided here are valid for other estuaries in order to derive a method to isolate the effect of metal mobility and allow inference of the real impact anthropogenic sources of metal contamination in estuarine environments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.11.239.

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