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The contaminant legacy from historic coastal landfills and their potential as sources of diffuse pollution

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ABSTRACT

Prior to modern environmental regulation landfills in low-lying coastal environments were frequently constructed without leachate control, relying on natural attenuation within inter-tidal sediments to dilute and disperse contaminants reducing environmental impact. With sea level rise and coastal erosion these sites may now pose a pollution risk, yet have received little investigation. This work examines the extent of metal contamination in saltmarsh sediments surrounding a historic landfill in the UK.

Patterns of sediment metal data suggest typical anthropogenic pollution chronologies for saltmarsh sediments in industrialised nations. However, many metals were also enriched at depth in close proximity to the landfill boundary and are indicative of a historical leachate plume. Though this total metal load is low, e.g., c. 1200 and 1650 kg Pb and Zn respectively, with > 1000 historic landfills on flood risk or eroding coastlines in the UK this could represent a significant, yet under-investigated, source of diffuse pollution.

1. Introduction

Historically (in the UK and elsewhere) many landfills were built within the coastal zone on low value land, particularly on or near saltmarsh habitats, with limited physical pollution prevention controls. In theory, any contamination from these 'historic landfills' (Mouser et al., 2005) and impacts on nearby coastal and estuarine environments was reduced through natural attenuation, relying on the dilution and dispersion capacity of tidal flushing, and adsorption and/or degradation in surrounding fine-grained sediments to reduce contaminant release to surrounding waters (Shukla and Rai, 2009).

In England alone, there are approximately 20,000 historic landfills (Cooper et al., 2012) constructed prior to the Control of Pollution Act (1974) and without any engineered waste management such as basal or side-wall engineering for leachate control enforced by the later European Union Council Directive (1999/31/EC). Of these 20,000 sites, at c. 1200 are located in tidal flood zone 3 with a 0.5% annual probability of coastal flooding, and many of these sites are within close proximity (< 100 m) to environmentally sensitive areas including sites of special scientific interest (SSSI), special protection areas (SPA), Ramsar sites, EU bathing water catchments and other protected areas (Brand, Spencer, O'Shea, & Lindsay, 2017). Fig. 1 shows the large numbers of historic landfills in the Thames Estuary, UK as an example,

but there are likely to be similar sites across the globe. Crucially, these historic landfill sites were also constructed prior to detailed and accurate assessments of the impact of climate change on the coastal environment. Recent predictions regarding sea level rise and the increased magnitude and frequency of storm events will enhance their future sensitivity and hence risk to surrounding habitats and potentially the wider environment. These habitats (saltmarshes and mudflats) are of global social, economic and ecological importance (Barbier et al., 2011) yet are in global decline and there is little understanding of the extent or potential impacts of this significant, yet currently under-investigated source of diffuse pollution in the coastal zone.

Previous research into historic landfills is very limited and has focused on natural attenuation within leachate plumes (Bjerg et al., 2011), leachate composition (Kjeldsen et al., 2002) and groundwater monitoring (Hubé et al., 2011). More recently, a small number of studies have examined contemporary releases of contamination to the environment due to continuing leachate production (Gooddy et al., 2014) and the release of eroded solid waste (Pope and Langston, 2011), demonstrating that historic landfills still have the potential to pollute many decades following site closure. However, very little attention has been given to the impacts of historic leachate production and whether, through natural attenuation, contaminants have been stored in surrounding sediments through e.g. precipitation in the anoxic sub-surface
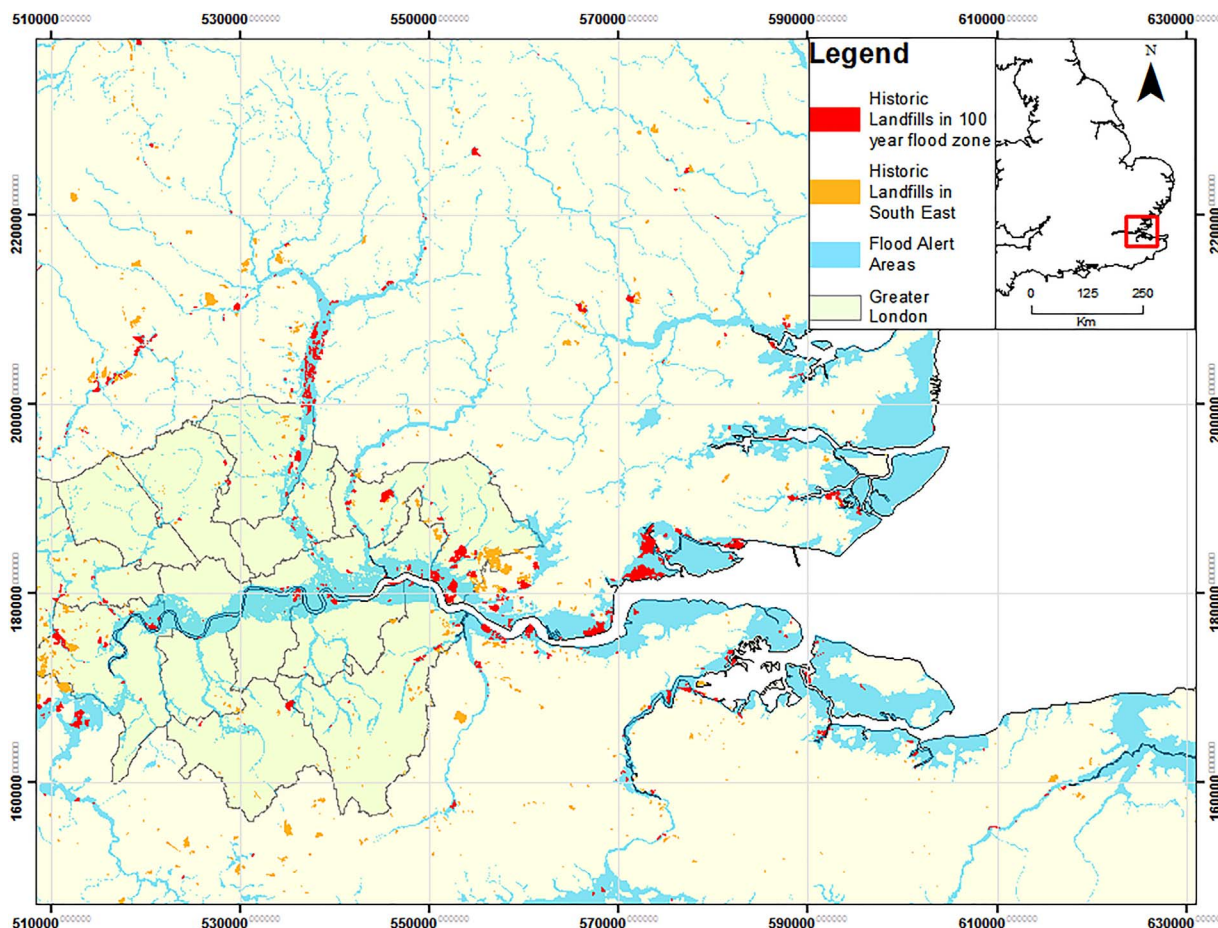
Fig. 1. Historic landfills within the Environment Agency flood alert area on the Thames Estuary, South East England (Environment Agency, 2010).
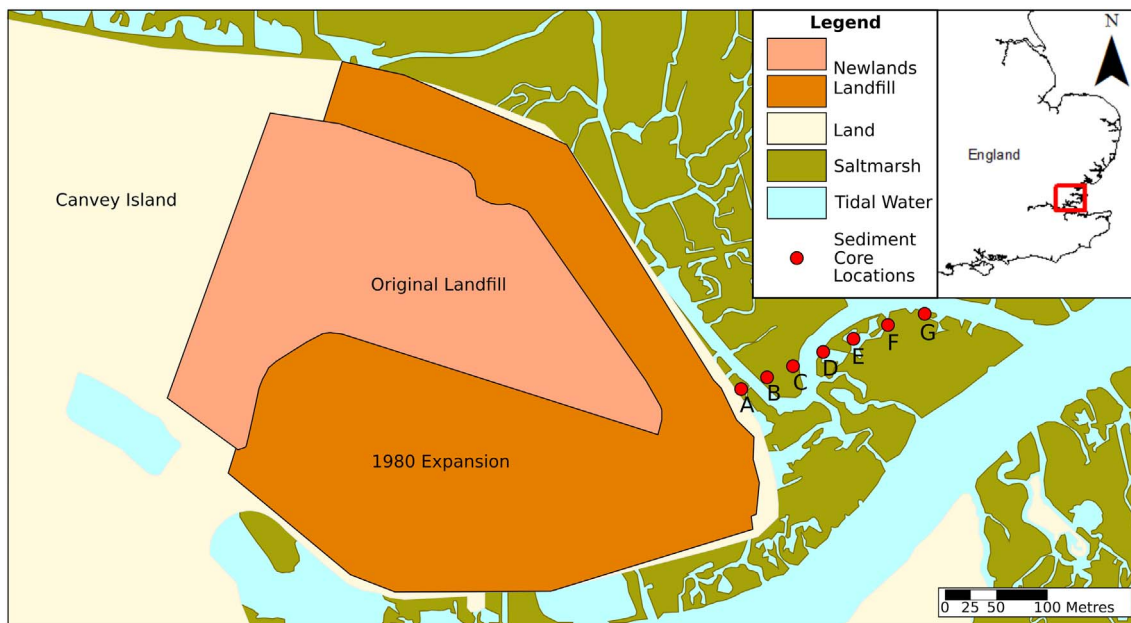

Fig. 2. Newlands landfill site.

environment and/or sorption to fine-grained, organic rich saltmarsh sediments (Michalak and Kitanidis, 2002; Njue et al., 2012). Legacy sediment contamination has been identified as a significant cause of ecological deterioration in surface waters, yet the extent and magnitude of this potential diffuse pollution source surrounding historic landfills is poorly understood. Stores of legacy contaminants in surface and sub-surface sediments can be released to the water column due to a range of physical, chemical and biological processes, particularly associated with physical erosion and re-working of sediments (Spencer et al., 2003) and may present issues for stake holders and parties responsible

for the long term management of the historic landfills, and adjacent coast, sediments and natural habitats.

The aim of this study was to examine the long-term impact of an historic coastal landfill on sediment metal contamination in surrounding inter-tidal sediments. Sediment cores were collected from a saltmarsh adjacent to an historic landfill in the Thames Estuary, UK to determine the spatial extent, magnitude and behaviour of metal contamination in sediments and to understand whether historic release of metal-rich leachates is a significant source of metal contamination in the surrounding sediments. Additionally, the potential for this contamination to act as a secondary source of diffuse pollution within the aquatic environment was investigated.

2. Study site

A representative site (Newlands) was selected that is typical of historic landfills in low-lying coastal environments with no basal or side wall engineering, relying on attenuation by surrounding saltmarsh sediments for contaminant dilution, receiving both household and non-hazardous commercial waste and in proximity to a range of environmentally sensitive areas.

Newlands landfill is situated on the Thames Estuary in the UK (Fig. 2). The site was opened in 1954 and built on low-lying agricultural land that had previously been reclaimed from the sea. It was also designed as a flood defence raising the level of the saltmarsh to provide deflection and buffering of tidal storm surges in the Thames; a process known as 'landraise' (Gray, 1993). Throughout the 1970's and 1980's, the site was raised and extended and is now protected by rock armouring. The site closed in 1989, after receiving approximately 1,000,000 m^3 waste (Caulmert Limited, 2012) although there are no detailed records accounting for the nature and/or quantities of waste. The site was then capped and is now used as recreational parkland.

Immediately adjacent to the site to the north, east and south of the site are areas of intertidal saltmarsh which provide habitat for wildfowl and wading birds, and is classified as a SSSI (Benfleet and Southend Marshes), a SPA and is situated on an EU Water Framework Directive managed catchment (DEFRA, 2013).

3. Materials and methods

3.1. Sample collection

To explore the influence of historic leachate release from the landfill on the sediment geochemical environment, seven sediment cores were collected from the adjacent saltmarsh along an easily accessible transect perpendicular to the site boundary at 10 m intervals. The top 30 cm of sediment was collected using a 10 cm diameter polycarbonate pipe, and a Russian corer was used to collect deeper samples to minimise sediment compression (< 5%). The cores collected were between 200 and 440 cm long. Cores were wrapped in clear film, returned to the laboratory and stored at − 12 °C until required.

3.2. Laboratory methods

Sediment samples were taken from the frozen cores after discarding the outer layers to ensure no cross contamination. Samples were taken at 5 cm intervals for the top 1 m, then at 10 cm intervals below this depth. Samples were homogenised and split, with a sub-sample used for pH, particle size analysis and assessment of loss on ignition, whilst the other was freeze-dried for 24 h for metal analysis and sediment dating (Quevauviller and Donard, 1991). Due to large sample numbers some parameters were only measured on a sub-set of cores and used to identify general trends across the site (LOI and radiometric dating) and to identify suitable geochemical normalisers (grain size).

Trace and major element sediment concentrations were measured in all cores using a hotplate Aqua Regia extraction (Chen and Ma, 2001)

followed by ICP OES analysis (Varian Vista-Pro ICP OES). Percentage relative standard deviation for all analytes was < 5%, whilst accuracy was within 10% of certified reference values (Estuarine Sediment - LGC6137). pH was measured following the method of Rowell (1994), whilst percentage LOI (used as a proxy for organic matter content) was measured following ignition at 500° C for 4 h. Particle size was measured using a Beckman Coulter laser diffraction granulometer after digestion with H_2O_2 at 80 °C for complete removal of organic material (Di Stefano et al., 2010).

Freeze-dried samples from 0 to 30 cm depth were measured for both ^{210}Pb and ^{137}Cs to calculate sedimentation rates across the saltmarsh. Samples were counted on a Canberra well-type ultra-low background HPGe gamma ray spectrometer to determine the activities of ^{137}Cs, ^{210}Pb and other gamma emitters (Cundy et al., 2005). Detection limits depend on radionuclide gamma energy, count time and sample mass, but were typically ca. 15 Bq kg^{-1} for ^{210}Pb, and 3 Bq kg^{-1} for ^{137}Cs, for a 150,000 second count time.

3.3. Data analysis

Prior to statistical analysis metal data were geochemically normalised to Li to compensate for grain size effects as Li showed the strongest relationship to < 63 μm fraction (R = 0.901, p < 0.01) for these sediments (Kersten and Smedes, 2002). Principal Component Analysis was performed using XLStat v2.01 on the entire dataset (normalised metal ratios, pH, LOI) using an orthogonal varimax rotation, to explore variability in metal sediment data and potential sources and/or behaviour of metals in the sediment (Quinn and Keough, 2002; Reid and Spencer, 2009). The Kaiser-Meyer-Olkin measure of sampling adequacy (measuring the ratio of squared correlation and squared partial correlation between variables) and the Bartlett's test of sphericity (measurement of inter-correlation) were used to demonstrate that the data were suitable for analysis. When interpreting PC loadings, values of > 0.6 were considered strong, however, values > 0.4 were also reported (Reid and Spencer, 2009). Enrichment factors (EFs) indicate the contribution of anthropogenic metals to the sediment load and were calculated by dividing the total metal concentration at a given depth (normalised to Li) by the geochemical background concentration (normalised to Li) (e.g. Çevik et al., 2009). A local natural geochemical background (Loska et al., 2004) was estimated by calculating the average metal concentration in the bottom 1 m of Core F, the deepest (4 m) core collected in this study, and assumes that this is pre-industrial, mineralogically similar sediment (whilst there is an increase in grain size at this depth, major element data suggest there is not a change in mineralogy).

4. Results

4.1. pH, % LOI and PSA

Median values for pH, % LOI and % < 63 μm for each sediment core are shown in Table 1 and Figs. 3, 4 and 5 and generally show little variation in pH, whilst % LOI and % < 63 μm is variable both between and within cores.

pH within the sediment cores ranged from 7.5 to 8.9 and increased with depth in all cores (except G), from a median of 7.7 within the top 1 m, to 8.5 at depth. Median core pH shows no trend with distance from the landfill.

Percentage LOI is highest in the surface sediments for all cores decreasing rapidly between 0 and 20 cm depth with a more gradual decrease to the base of the cores (Fig. 4). Values remain constant at depth. Median % LOI is higher at the landfill edge (9.1%) compared to cores within the middle (5%) and outer marsh (4%).

There is a clear grain size trend within each core, showing a shift from clayey silt near the sediment surface to silty sand at depth. Fig. 5 shows that grain size remains consistent in all cores in the top 70 cm,

Table 1
Median pH, % LOI and % < 63 µm for sediment cores.

	Core A			Core B			Core C			Core D		
	< 63 µm (%)	pH	LOI (%)	< 63 µm (%)	pH	LOI (%)	< 63 µm (%)	pH	LOI (%)	< 63 µm (%)	pH	LOI (%)
Median	n/a	8.7	9.1	73.2	8.0	n/a	n/a	8.5	5.1	77.5	8.2	n/a
Max	n/a	8.9	18.3	97.8	8.6	n/a	n/a	8.8	17.7	98.9	8.6	n/a
Min	n/a	7.9	4.7	12.6	7.6	n/a	n/a	7.5	2.9	26.5	7.5	n/a

	Core E			Core F			Core G		
	< 63 µm (%)	pH	LOI (%)	< 63 µm (%)	pH	LOI (%)	< 63 µm (%)	pH	LOI (%)
Median	31.3	8.4	n/a	n/a	8.3	4.9	n/a	8.3	6.2
Max	63.9	8.8	n/a	n/a	8.7	15.0	n/a	8.9	14.2
Min	4.6	7.6	n/a	n/a	7.5	1.1	n/a	7.7	1.2

before coarsening with depth, with a marked increase in the percentage of sandy grains at c. 1 m depth.

4.2. Major and trace element concentrations

A summary of major and trace element concentrations for cores A to G can be found in Table 2.

Generally, concentrations for the major elements Al (0.4–3.9%), Fe (0.8–6.1%), K (0.1–0.8%), Mg (0.3–1.4%) and Na (0.2–3.5%) show little variability between the cores, although median concentrations are all lowest in Core F. Calcium, however varies both between and within the cores (0.1–5%). Cobalt (9–12 mg kg^{-1}), Cr (41–54 mg kg^{-1}), Li (31–38 mg kg^{-1}) and Ni (25–35 mg kg^{-1}) show little variability in median concentration between cores. However, the trace metals more commonly associated with anthropogenic activity, such as Cu (4–74 mg kg^{-1}), Pb (4–205 mg kg^{-1}) and Zn (22–262 mg kg^{-1}) show higher variability. Manganese, Sr and V show highly variable concentrations between the sediment cores. None of the major or trace metals show clear trends with distance from the landfill.

Vertical distributions of normalised metal ratios (metal/Li) for sediment cores are plotted in Fig. 6 to 8. Aluminium (Al) and Magnesium (Mg) show little variation with depth in all cores, whilst, Fe fluctuates slightly throughout the vertical profiles. Potassium shows some fluctuation with depth in all cores, with cores D and F showing slightly higher levels towards the base. Sodium data are elevated at the very surface (0–5 cm) then either remain constant at depth or increase at depths greater than c. 100 cm. Manganese/Li (Fig. 7) is elevated in the upper 20–50 cm of sediment and increases slightly at the base of all cores, whilst Calcium/Li ratios (Fig. 8) drop rapidly in the first few centimetres of sediment and then increase at depth in all cores.
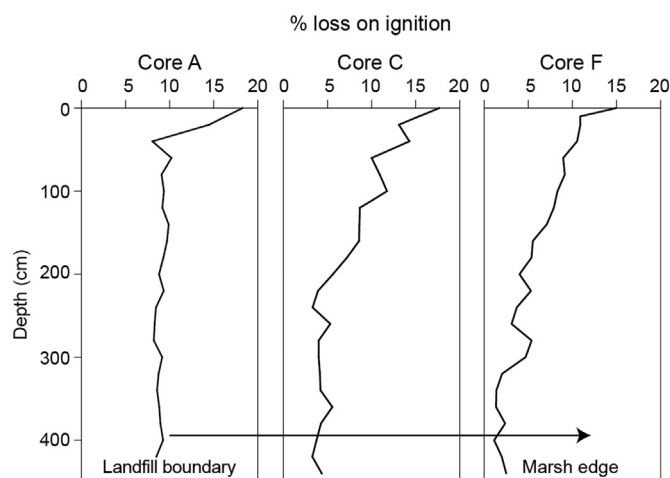

Fig. 4. LOI (%) within sediment cores.

Generally, trace metals show more variability with depth with the exception of Co and V. Chromium, Ni, Cu, Pb and Zn show similar distributions in all cores with metal to Li ratios low at the sediment surface increasing to reach broad sub-surface peaks with maxima between 20 and 45 cm depth and then decreasing to low and constant values at depth (Fig. 9). Generally, metal/Li ratios below c. 180 cm depth are similar or lower than those in the surface sediments. However, in core A, collected closest to the landfill boundary, metal/Li ratios remain elevated at depth with respect to surface sediment values and this is most pronounced for Pb, then Cu and Zn (Fig. 10). In core G collected furthest from the landfill and at the boundary of the saltmarsh
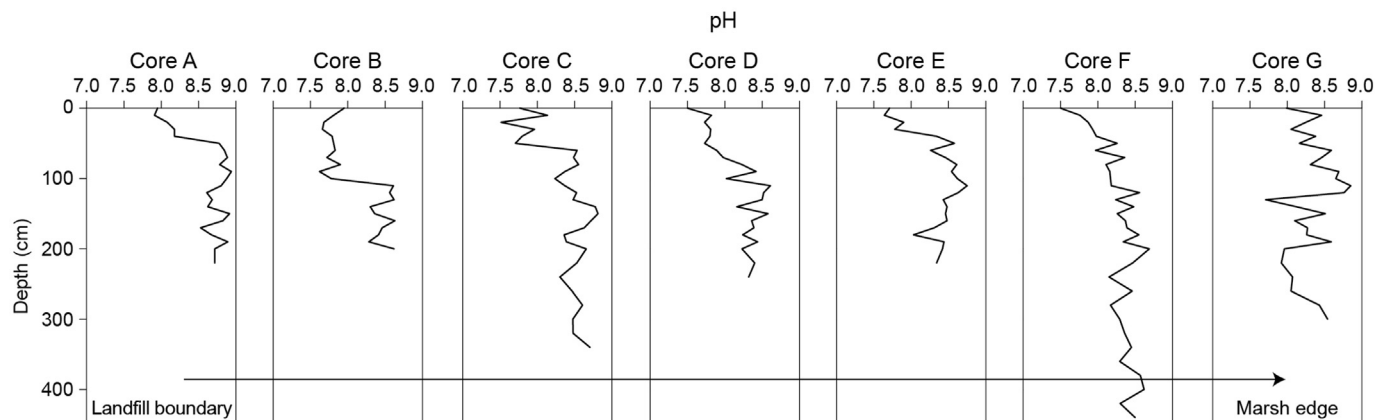

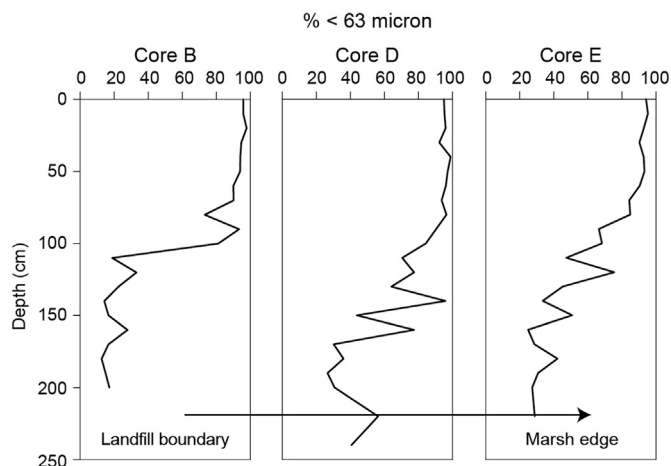
Fig. 3. Sediment core pH values.

Fig. 5. < 63 μm (%) fraction in sediment cores.

and open channel, metal/Li ratios peak close to the surface suggesting there has been some erosion or re-working of the sediment profile.

4.3. Sediment dating

Activities for ^{210}Pb were below detection in most sediment samples despite extended count times and hence data are not reported here. This irregular distribution with depth, at very low activities, reflects changes in sediment composition and/or limited ^{210}Pb supply, and so it was not possible to reliably date these sediments using ^{210}Pb. Vertical distributions of ^{137}Cs activity (normalised to Li) are shown in Fig. 11, for cores A, D and F. All three cores show a very broad sub-surface peak

centred at 10 or 15 cm depth and then decrease with depth.

4.4. Principal Component Analysis

Principal Component Analysis of the entire geochemical data set extracted 3 principal components (PCs) representing a cumulative variance of 77% (Table 3). Principal component 1, which accounts for the most variability in the data, has high positive loadings for Ca, Fe, K, Mg, Mn, Sr and V - elements associated with the lithogenic fraction. PC2 has high loadings for Cr, Cu, Pb and Zn, whilst PC3 has high negative loadings for Al and high positive loadings for Co and Ni. Exploration of scores for the PCs and a further PCA of individual sediment cores did not reveal any trends or different controlling factors with distance from the landfill site boundary.

4.5. Enrichment factors

Enrichment factors for Cu, Pb and Zn in cores A–G are given in Fig. 12. In cores B, C, D, E and F EFs are c. 1 in the surface sediments and have sub-surface maxima of c. 2 to 3 between 20 and 45 cm depth before decreasing back down to c. 1 or < 1 at depth. However, in core A, collected nearest the landfill boundary the EFs remain elevated throughout the core. This is most notable for Pb, Cu and Zn, with EFs for Pb and Cu > c. 1.5 throughout the entire core. In core G, collected from the marsh edge, surface sediments have high EFs suggesting that the deposits have been reworked and this core is not considered further.
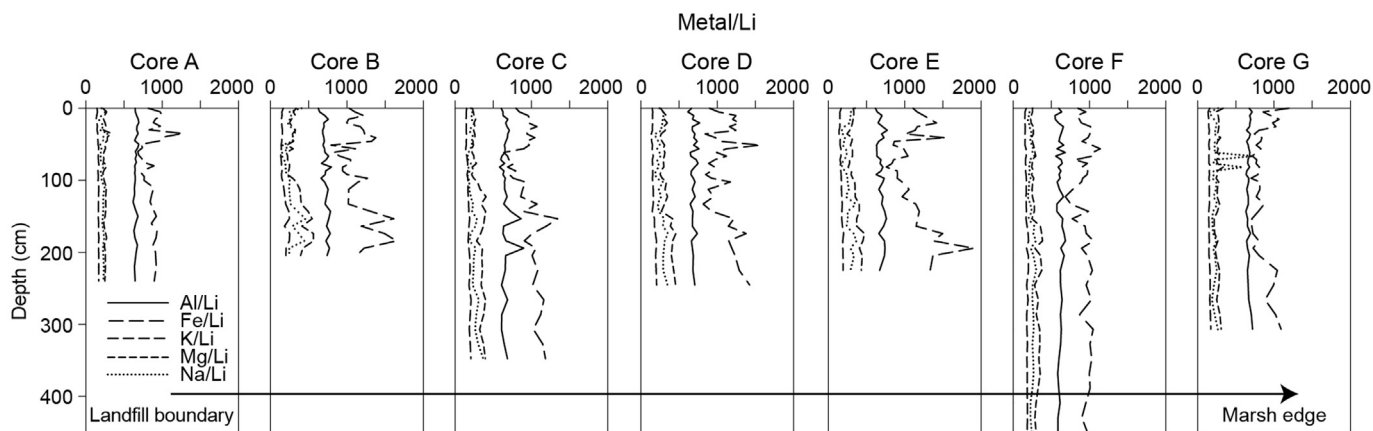
Table 2
Median sediment core concentrations of major and trace metals (ranges in parentheses).

	A	B	C	D	E	F	G
%							
Al	2.3	2.5	2.5	2.6	2.1	1.9	3
	(1.8–3.9)	(0.4–3.8)	(0.6–3.7)	(0.6–3.5)	(0.6–3.4)	(0.7–2.7)	(1.3–3.6)
Ca	3.5	0.5	0.8	0.7	2.6	2.8	3
	(0.5–4.7)	(0.1–4.2)	(0.3–3.6)	(0.4–4.7)	(0.4–4.9)	(0.5–4.3)	(0.8–5.0)
Fe	3	4.2	3	3.8	3.1	2.8	3.5
	(2.2–4.9)	(0.8–5.1)	(1.0–5.1)	(1.1–6.1)	(1.4–6.0)	(1.1–4.3)	(2.4–4.6)
K	0.6	0.6	0.6	0.6	0.5	0.5	0.7
	(0.4–0.8)	(0.1–0.7)	(0.1–0.8)	(0.2–0.6)	(0.2–0.7)	(0.2–0.6)	(0.3–0.7)
Mg	0.9	1	1	1.1	1	0.9	1.1
	(0.7–1.3)	(0.3–1.3)	(0.3–1.2)	(0.4–1.3)	(0.4–1.2)	(0.4–1.1)	(0.7–1.4)
Na	0.8	0.8	0.7	0.9	0.7	0.7	1
	(0.6–1.2)	(0.2–1.3)	(0.2–1.1)	(0.3–1.1)	(0.3–1.1)	(0.3–1.0)	(0.5–3.5)
mg kg^{-1}							
Co	9	13	13	12	10	13	10
	(7–16)	(3–19)	(7–24)	(5–26)	(4–18)	(6–21)	(5–15)
Cr	47	54	44	52	41	43	52
	(36–91)	(9–86)	(7–89)	(15–80)	(12–72)	(18–82)	(24–82)
Cu	36	32	23	31	23	29	38
	(29–68)	(4–67)	(4–69)	(5–66)	(5–55)	(6–63)	(16–74)
Li	35	38	38	38	32	32	43
	(29–61)	(6–53)	(9–57)	(10–49)	(10–49)	(12–43)	(23–52)
Mn	270	336	175	253	205	247	270
	(207–1067)	(124–7052)	(143–1349)	(162–1718)	(153–1016)	(160–989)	(221–641)
Ni	30	37	26	36	30	29	33
	(25–54)	(8–49)	(3–57)	(10–69)	(10–45)	(12–48)	(15–42)
Pb	89	78	55	86	54	76	95
	(66–132)	(8–155)	(4–169)	(11–188)	(10–150)	(16–154)	(38–205)
Sr	89	57	55	57	65	71	80
	(43–169)	(34–96)	(31 − 123)	(39–127)	(49–115)	(50–132)	(50–124)
V	71	90	83	85	75	72	90
	(60–110)	(22 − 111)	(22–118)	(31–106)	(27–99)	(31 − 103)	(48–99)
Zn	134	113	98	127	86	90	119
	(88–202)	(27–181)	(22–205)	(33–261)	(29–193)	(28–260)	(54–262)

Fig. 6. Al, Fe, K, Mg and Na sediment concentrations (mg kg^{-1}) (normalised to Li).

5. Discussion

5.1. Spatial variability and sources of metals

Vertical profiles of major elements (Al, Fe, K, Mg and Na) normalised to Li are indicative of the lithogenic input to this saltmarsh. Generally, these major elements change little with depth except Fe and Mn, which are elevated in the top 20 to 50 cm of sediment and increase below 1 m. The diagenetic enhancement of Fe and Mn in saltmarsh sediments resulting in the mobilization of Fe and Mn species and precipitation in surface sediments, is well established (e.g. Zwolsman et al., 1993 and this indicates that the upper 20 to 50 cm of sediment are relatively oxic. Below 1 m depth Fe and Mn concentrations increase, due to possible co-precipitation with carbonates or sulphides (Dang et al., 2015). This may indicate either a change to more reducing conditions (Wang et al., 2015), or as this coincides with a shift from fine-grained silts to coarser sands, a change in the sedimentary regime and/or lithogenic source (Bai et al., 2011). An increase in pH, decrease in % LOI and decalcification are also indicative of the microbially-mediated decomposition of organic matter in these sediments following burial and are commonly observed in saltmarsh sediments (Spencer et al., 2003). Increases in Ca at depth in most cores are likely due to the re-precipitation of carbonate in increasingly alkaline conditions and/or co-precipitation with Mn at depth (Vranken et al., 1990; Dang et al., 2015).

Once normalised to account for grain size variations trace metals commonly associated with anthropogenic sources Cr, Cu, Pb and Zn (and to a lesser extent Ni) show typical pollution chronologies for urbanised, moderately contaminated estuaries (Li et al., 2000; Pope and Langston, 2011; Veerasingam et al., 2015). At depth metal

concentrations are low and indicative of pre-industrial background, concentrations increase with the onset of the Industrial Revolution and sub-surface maxima are likely to reflect increased urbanisation and industrialisation in the late 19th to mid-20th Century, before decreasing with the introduction of environmental regulation (Eades et al., 2002). Cobalt and V show little variation with depth suggesting that inputs to the estuary have varied little over time and are natural in origin. This is supported by the PCA where V tends to be associated with the lithogenic elements. Overall, PCA indicates that natural mineralogy is the main factor controlling metal variability in these sediments, however anthropogenic inputs are clearly important and probably associated with wide range of industrial activities.

Enrichment factors for Cu, Pb and Zn also support these broad pollution chronologies. An EF of one is indicative of minimum anthropogenic impact and metal concentrations that are at, or near, natural geochemical background. In cores B, C, D, E and F this suggests that both surface sediments and those below c. 45 cm depth have received relatively little anthropogenic enrichment.

However, in core A, collected nearest the landfill boundary the EFs remain elevated throughout the core. This is most notable for Pb, Cu and Zn, with EFs for Pb and Cu > c. 1.5 throughout the entire core. This suggests significant anthropogenic enrichment of these metals at depth, i.e. before the onset of industrialisation. Sediment dating enables the validation of this pollution chronology and provides an approximate time of deposition for those sediments anthropogenically enriched at the base of core A, closest to the landfill. Caesium-137 is an artificially produced radionuclide and was first globally distributed in 1954 due to atmospheric weapons testing. In the southeast UK, peaks in ^{137}Cs activity are frequently recorded in saltmarsh sediment cores due to the fallout maximum from peak atmospheric weapons testing in
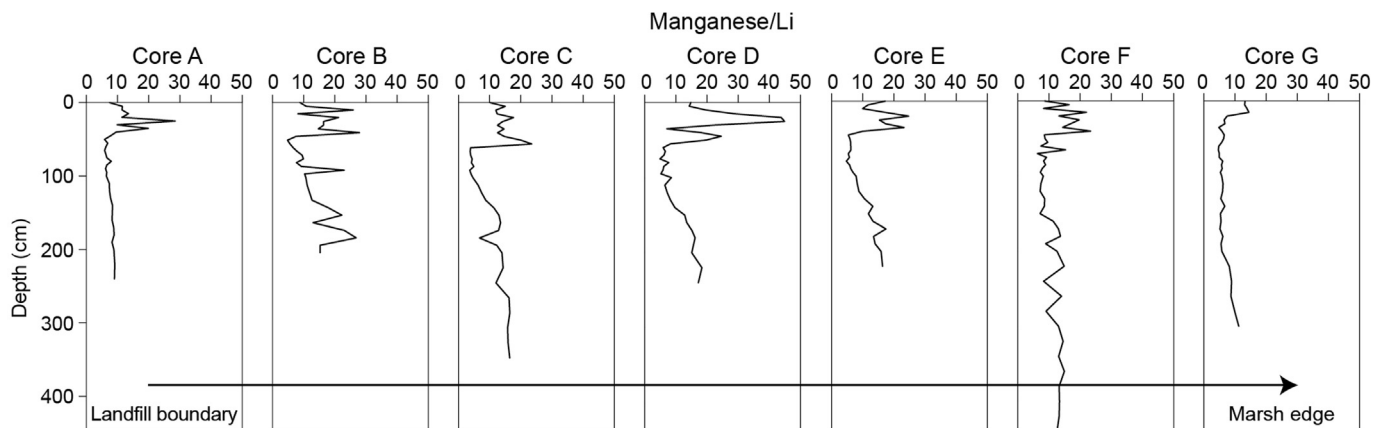

Fig. 7. Mn sediment concentrations (mg kg^{-1}) (normalised to Li).
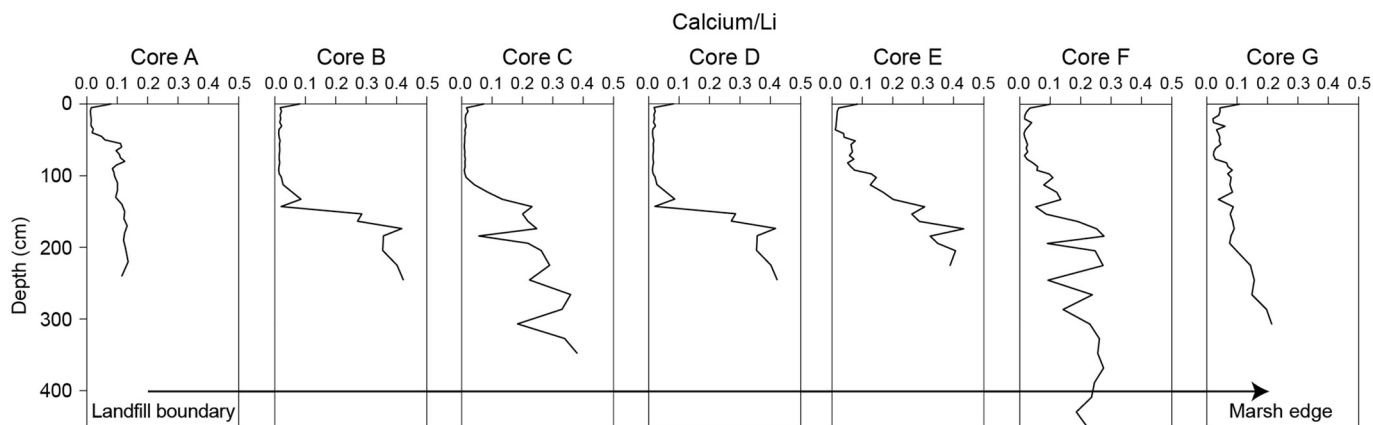
Fig. 8. Ca sediment concentrations (%) (normalised to Li).

1963 (Cundy et al., 1997; Spencer et al., 2003) and using this as a marker horizon the broad peak in activity at 10 cm (Core A and D) and 15 cm (Core F) depth generates a sedimentation rate of $2 \, mm \, a^{-1}$ ($\pm 0.5 \, mm \, a^{-1}$) at the landfill site boundary and $3 \, mm \, a^{-1}$ ($\pm 0.5 \, mm \, a^{-1}$) within the outer marsh. Extrapolation of these rates (assuming, to a first approximation, uniform sedimentation over time) dates the sub-surface Pb, Cu and Zn maxima (20–45 cm depth) at between 1788–1913 and 1863–1946 respectively. Significant industrial inputs to the Thames began in the late 18th and early 19th centuries with serious industrial pollution noted by the 1820s, and major water quality declines in both the 1850s and 1950s; water quality only began to improve from the 1960s onwards (Andrews, 1984; Vane et al., 2015). Therefore, these earlier dates (i.e. 1788–1913) probably pre-date peak industrial activity in the Thames. It is also possible that the ^{137}Cs peak observed represents elevated fallout from Chernobyl in 1986, with the 1963 peak not captured by our sampling strategy. This results in an estimated sedimentation rate of between $3.7 \, mm \, a^{-1}$ (Core A and D) and $5.6 \, mm \, a^{-1}$ (Core F) and dates the Pb, Cu and Zn sub-surface maxima between 1891–1959 and 1933–1979. However, SE England received little Chernobyl fallout. Caesium-137 is also highly mobile, and in these saline sediments could be remobilised both by the presence of competing Na^+ cations and NH_4^+ still being released from the historic landfill (Comans et al., 1989; Gooddy et al., 2014). Therefore, without corroboration from ^{210}Pb activities it is difficult to establish a robust pollution chronology. However, the estimated sedimentation rates are in broad agreement with those calculated locally in the outer Thames Estuary ($3.4 \, mm \, a^{-1}$) and southeast England (2.3 and $2 \, mm \, a^{-1}$) (Spencer et al., 2003; van der Wal and Pye, 2004; Spencer et al., 2008). Therefore, broad sub-surface maxima in the upper 50 cm of sediment are highly likely to represent anthropogenic activity

extending from the mid-19th to mid-20th Century. In Core A where sediments are enriched at depth, the range of sedimentation rates estimated above indicates these sediments were deposited between at least 270 and 500 years ago. This is prior to both the onset of industrial activity in the Thames and landfill construction therefore these sediments must have been contaminated post deposition and most probably by a contaminated leachate plume from the historic landfill. The evidence of this only extends to the core collected nearest the landfill, i.e. within c. 20 m.

5.2. Contaminant legacy from historic landfills

Here, historic landfills are defined as those without basal or side linings and which were built on fine-grained inter-tidal sediments such that natural attenuation – through e.g. sorption and biodegradation – reduces the impact of contamination to environmental receptors. Hence, the magnitude of contaminants is reduced through the slow release of leachate into surrounding sediments, relying on the dilution and dispersion capacity of the surrounding saturated and unsaturated zones (Shukla and Rai, 2009). Contaminated leachate released from the landfill initially migrates through the groundwater via advection and dispersion (McCarthy and Zachara, 1989), physically dispersing the contaminants (Njue et al., 2012), but not reducing the contaminant load available to sensitive environmental receptors. This legacy of contamination is clearly present in the sediments surrounding the Newlands Historic Landfill, and is confined to a zone that extends < 20 m from the landfill boundary and persists for at least two decades following site closure. This confined zone of contamination, may either be due to the efficiency with which these fine-grained sediments have attenuated metal concentration from the leachate, or post-depositional
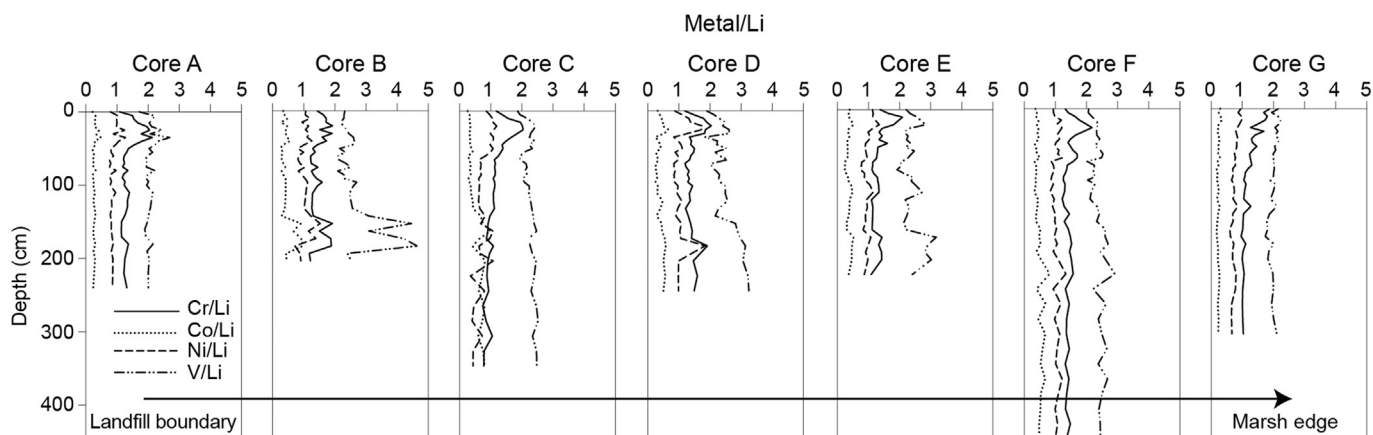

Fig. 9. Cr, Co, Ni and V sediment concentrations (mg kg^{-1}) (normalised to Li).
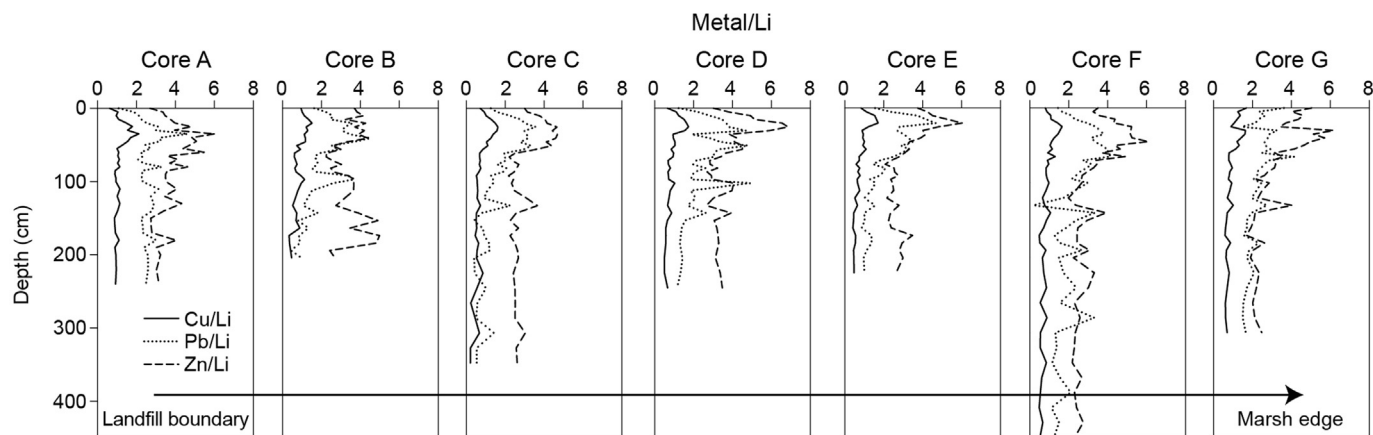
Fig. 10. Cu, Pb and Zn sediment concentrations (mg kg^{-1}) (normalised to Li).
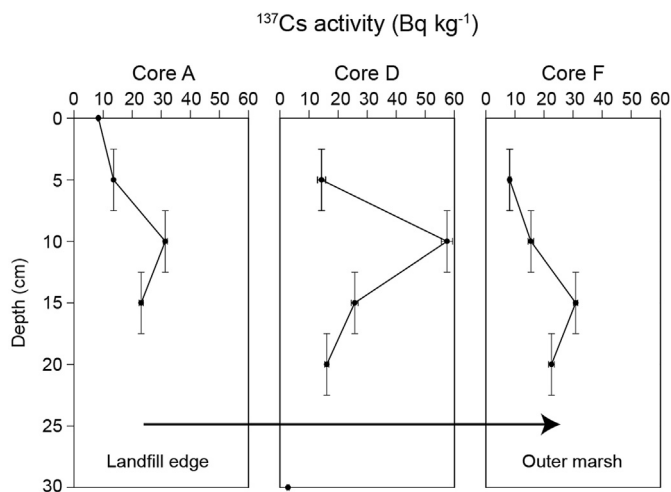

Fig. 11. Cs activity for three sediment cores (normalised to Li). Vertical error bars represent uncertainty with depth, horizontal error bars indicate Cs/Li error.

Table 3
Principal Component Analysis factor loading tables for the whole dataset. Significant (> 0.6) loadings are shown in bold.

	PC1	PC2	PC3
pH	0.093	**−0.624**	−0.121
Al/Li	0.449	0.119	**−0.805**
Ca/Li	**0.825**	−0.476	0.111
Co/Li	0.451	−0.109	**0.783**
Cr/Li	0.325	**0.808**	−0.164
Cu/Li	−0.271	**0.863**	0.03
Fe/Li	**0.813**	0.279	−0.307
K/Li	**0.832**	−0.403	0.043
Mg/Li	**0.928**	−0.12	−0.131
Mn/Li	**0.607**	0.507	0.149
Na/Li	**0.613**	0.076	0.176
Ni/Li	0.095	0.462	**0.774**
Pb/Li	−0.314	**0.805**	−0.009
Sr/Li	**0.813**	−0.432	0.212
V/Li	**0.885**	0.151	−0.062
Zn/Li	0.147	**0.85**	0.017
Cumulative variance (%)	36	64	77

erosion and inundation. This research focussed on the examination of metals in the surrounding sediment. Metal-rich leachates would have been produced in the short 'acetogenic' phase of waste degradation where acetogens convert carboxylic acids into acetic acid, which along with chloride, ammonium and phosphate ions increase the mobility of metal ions (Williams, 2005). This stage has ceased, as contemporary pH data do not show acidic conditions and contemporary release of metal-rich leachates under current biogeochemical scenarios is unlikely. However, it is also possible that this zone of contamination contains elevated concentrations of ammonia (Gooddy et al., 2014) and organic and emerging contaminants not examined here (Andrews et al., 2012).

5.3. Magnitude of legacy contamination

Maximum sediment core concentrations for anthropogenic metals exhibit similar concentrations to other industrialised estuaries (Benninger et al., 1979; Li et al., 2000; Veerasingam et al., 2015) although Pb concentrations are significantly elevated (Table 4). To consider potential ecological impacts, sediment metal concentrations were compared to sediment quality guidelines (Buchman, 2008). Median core metal concentrations generally exceed the probable effects level (PEL) above which there is a potential for ecological harm, with the exception of Zn and majority of samples from within the saltmarsh exhibit contamination above the threshold effects level (TEL) and PEL, and could therefore pose an environmental hazard and the sediments at depth in proximity to the landfill site present an additional source of contamination.

Although Pb and Zn concentrations in sediments surrounding the landfill are not particularly high compared to other areas of contaminated sediment within the Thames (Pope and Langston, 2011), the saltmarsh is situated within the Environment Agency's flood zone 2 (Environment Agency, 2010) and whilst the landfill boundary is protected, the fronting saltmarsh is not and erosion under scenarios of climate change and sea level rise could result in the release of this contaminated material to the coastal environment. The volume of sediment contaminated by the landfill can be estimated from the length of the site boundary facing the Thames (c. 1000 m), and extends no > 15 m from the site boundary between a depth of 1 to 2 m. Using an average wet bulk density for the sediment of 0.54 g cm^{-3} (Tempest et al., 2014), and average Cu, Pb and Zn concentrations of 32, 80 and 110 mg kg^{-1} respectively, an estimated 480 kg of Cu, 1200 kg of Pb and 1650 kg of Zn could be released as secondary diffuse pollution from Newlands historic landfill were these sediments to erode. Individually, this is arguably not a significant load, however there are 50 historic coastal landfills in the Thames Estuary, 4000 around the UK coast (Cooper et al., 2012) and many more both documented and undocumented around the world. If similar legacy sediment
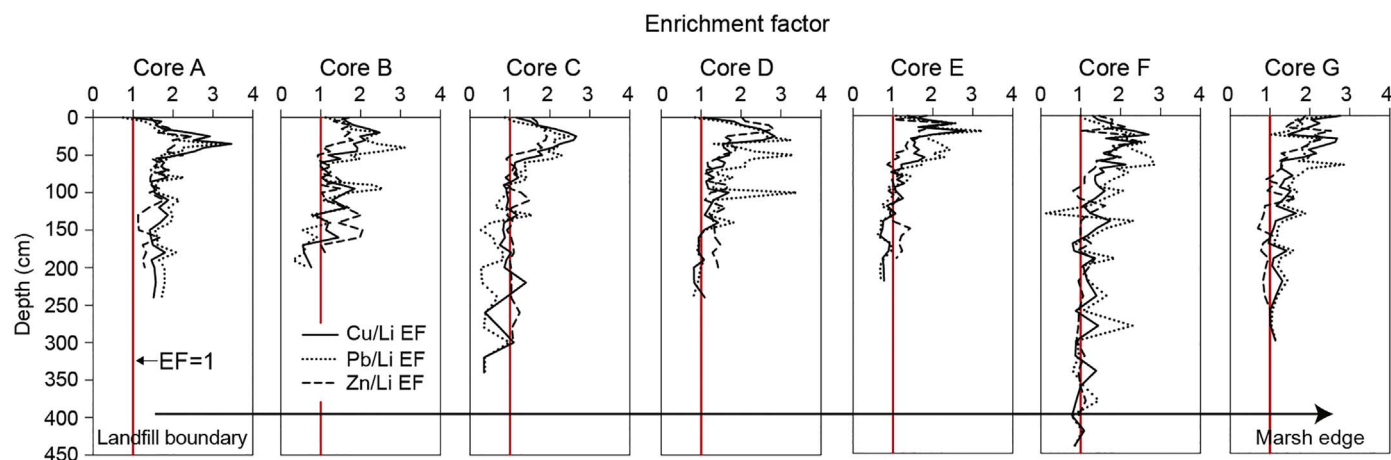
mobility. Whilst this volume of contaminated sediment is relatively small compared to the overall volume of sediment in the Thames Estuary it represents a potential future source of diffuse pollution in the context of rising sea level and increased coastal erosion and storm surges. Particularly as the legacy contaminated sediment extends beyond the engineered coastal defences protecting the landfill from

Enrichment factor

Fig. 12. Cu, Pb and Zn Enrichment factors (red reference line at EF = 1).

Table 4
Maximum sediment core concentrations from other industry impacted estuaries.

	Co	Cu	Ni	Pb	Zn
	mg kg^{-1}				
Pearl Estuary[a]	20.5	74.3	91	99	332
This study (Thames)	26	74	69	205	262
Long Island[b]		96		52	194
Mandovi[c]	29	58		28	71

[a] Li et al. (2000).
[b] Benninger et al. (1979).
[c] Veerasingam et al. (2015).

contamination is present at all these sites this represents a significant potential source of diffuse pollution that has previously been un-recognised and may contribute to surface waters failing good ecological status. Where historic landfill sites contain hazardous waste or low-grade nuclear waste contaminant concentrations may be more significant. Currently, this pollution source is not considered within shoreline management plans and is not formally classified as contaminated land under part IIa of the Environmental Protection Act and as such is not considered within Environmental Impact Assessments (DCLG, 2015). This also has consequences for those responsible for the long-term management of historic coastal landfills including landfill managers and local government who have a duty of care to protect the adjacent aquatic environment.

6. Summary

Vertical sediment cores collected from an inter-tidal saltmarsh adjacent to a historic coastal landfill in the Thames Estuary show typical pollution chronologies with broad peaks in the anthropogenic metals, Cu, Pb and Zn that correspond to industrial activity in the Thames Estuary. At depths below approximately 1 m sediment metal concentrations generally reach local geochemical background levels with enrichment factors of approximately 1. However, sediments collected closest to the landfill boundary sediments are enriched in the anthropogenic metals at depth and preliminary sediment dating using ^{137}Cs suggests that these sediments were deposited at least 270 years ago, pre-dating the onset of industrial activity in the Thames. Therefore, these sediments must have been enriched with anthropogenic metals post-deposition and this is most likely to be the result of the natural attenuation of historic metal-rich leachates from the landfill. These sediments are moderately contaminated and generally metal concentrations exceed the Canadian Sediment Quality Guideline PELs suggesting that if released they would cause significant ecological

impact. These sediments extend beyond current coastal defences and could release up to 480 kg of Cu, 1200 kg of Pb and 1650 kg of Zn to the Thames Estuary. Whilst the potential contaminant loads associated with one historic landfill may not be significant, the large numbers of historic coastal landfills within the UK (c. 4000) and globally represent a significant un-recognised and un-quantified source of diffuse pollution that is currently not considered within coastal planning and may contribute to poor estuarine water quality and poor ecological status.

Contributions

FTO'S carried out the research and performed all analysis, data collection and interpretation. KLS conceived the overall project and contributed to data interpretation. FTO'S and KLS wrote the manuscript. ABC carried out sediment dating, helped interpret pollution chronology data and edited the manuscript.

Acknowledgements

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