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Journal of Soils and Sediments volume 21, pages 530–544(2021)

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Abstract

Purpose A recreational impoundment was constructed in the mid-19th century on the mudflats reclaimed from the Plym Estuary (SW England) following salt marsh removal and infilling with waste soils from local catchments. Restoration of the salt marsh was attempted about 25 years ago when a regulated tidal exchange system was installed in the embankment separating the impoundment from the estuary. Currently, the embankment is disintegrating with the potential loss of the impounded soils, of unknown composition, to the estuary.

Methods Cores were obtained from the impoundment and the adjoining estuary, sectioned, dried and analysed. The geochronology of the soils, and estuarine sediments, was established using gamma ray spectroscopy to determine the activities of fallout radionuclides, ^{137}Cs and ^{210}Pb. The concentrations of As, Co, Cr Cu, Fe, Mn, Ni, Pb, Rb, Sn, W and Zn in the core sections were determined by quantitative X-Ray Fluorescence spectrometry.

Results Below a shallow surface layer (>5 cm and post-1963) metal concentrations were high with several exceeding soil quality indices and enrichment factors (EFs) were elevated, in the sequence Sn>W≈As>Cu>Pb. Estimates of the total masses of particulate Sn, Pb, As and Cu available for down-estuary migration were significant.

Conclusions Given the ecotoxicological implications resulting from a loss of metal-contaminated soils into the estuary, a strategy for the future management of the impoundment is required. The conditions at this site are compared with ageing estuarine impoundments at other locations, where polluted sediments, or soils, could be vulnerable to release.

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Keywords: estuary; impoundment; managed realignment; contaminated soils; release

1 Introduction

Estuarine salt marshes and coastal wetlands have been impounded for more than two hundred years, mainly driven by a human need to increase the land available for alternative uses, such as agriculture, urban development and recreation (Gedan et al. 2009). Salt marshes are dependent on regular tidal intrusions to retain their geomorphology and fertility. Thus, impoundments may seriously impact the biogeochemical functioning of salt marshes, and their ecosystem value, particularly via interruption of natural supplies of sediments and plant propagules (Adam 2002). However, the growing imperatives introduced by climate change are causing an international re-assessment of the future for sea defences associated with the enclosure of salt marshes (Temmerman et al. 2013). Managed realignment involves the breaching, or complete removal, of impoundment barriers and, if required, the re-building of a new barrier landward (French 2006; Esteves 2011). This process promotes the incursion of estuarine water towards the foreshore, which may support the adventitious restoration of inter-tidal mud flats and salt marshes (Mazik et al. 2010; Mossman et al. 2012a; b). Also, it has been argued that barrier realignment forms a crucial part of an ecologically-based approach to utilising sea level rise positively leading to the re-establishment of salt marsh habitats that have a natural function in protecting coastlines (Temmerman et al. 2013). While managed realignment may have certain advantages, the potential recovery of the sediments, or soils, from impoundment can be uncertain. This is especially so where agriculture has taken place, inducing chemical and structural changes in the soil, leading to fluctuations in ecosystem biodiversity (Fernández et al. 2010; Spencer and Harvey 2012).

Regulated Tidal Exchange (RTE) is a modified form of managed realignment. Rather than completely removing the sea defences, a breach is made in an embankment, or a sea wall, coupled with the installation of a tide-gate, or strategically-placed culverts or weirs, to control the incursion of estuarine water into the impounded area (RSPB 2003; Esteves 2011). Consequently, tidal exchange between an impoundment and the estuary gives rise to

overlying waters whose physico-chemical composition varies with river flow and tidal elevation and the influx of estuarine suspended solids and plant debris may create, over several years, a viable, salt marsh habitat (e.g. Mossman et al. 2012b). RTE systems have been employed across the world (ABPmer 2017) from the USA (Anisfeld et al. 1999; Boyd and Sommerfield 2017) to China (Liang and Wong 2003; Gu et al. 2018). In the UK, RTEs have been created to sustain aquatic wildlife activity (Dixon et al. 2008; RSPB 2003; MMO 2019) and to revive salt marshes (Masselink et al. 2017). Managed realignment is common in Europe (Wolters et al. 2005), where embanked polders have been restored to tidal inundation (i.e. depolderisation) using a Controlled Reduced Tide (CRT) method (Beauchard et al. 2011), a modified form of RTE. , For example, the Polder de Sébastopol (Vendée, France) was reclaimed from the Atlantic coast in 1856 to support agriculture. In 1978 its embankments collapsed and were re-built in the CRT manner to foster the creation of an active salt marsh system (Esteves 2011).

However, the contamination status of impoundment soils or sediments, in terms of their metal content, has been assessed in a limited number of cases, even so some have elevated concentrations (Table 1). The Hayle Estuary impoundment (Cornwall, UK)

Table 1

was constructed in 1834, and fiited with a tide gate, has sediments highly impacted by inputs from metal mining (Rollinson et al. 2007; Aquatronics 2011). In the Scheldt Estuary (Lippenbroek, Belgium) a CRT was created by breaching the embankment of a polder to allow the incursion of estuarine water onto the metal-contaminated polder soils (Teuchies et al. 2012; 2013; Oosterlee et al. 2020). Furthermore, the potential release of metal-contaminated soils from ageing impoundments to the aquatic environment is exemplified by the scheme on the Blackwater Estuary (Essex, UK), where the failing barrier was manually breached in 1995 (Macleod et al. 1999; Emmerson et al. 2000; 2001).

Embankment failure illustrates the uncertainty associated with the long-term structural integrity of ageing sea defences enclosing estuarine and coastal impoundments. The

129 stability of all marine structures, and their associated coastal ecosystems, are currently
130 under enhanced environmental pressure from various factors associated with climate
131 change, such as sea level rise, the frequency of storm surges, increased wave activity and
132 highly variable river flows (Robins et al. 2016; Hanley et al. 2020). The durability of sea
133 defences is particularly important in cases where the impounded soils, or sediments, are
134 contaminated, which if released could impose near-term health risks to the surrounding
135 waters. In some respects, this proposed scenario is somewhat similar to the release, and
136 near-field dispersal, of contaminants from vulnerable, and poorly managed, coastal waste
137 repositories (e.g. Hübner et al. 2010; Pope et al. 2011; Njue et al. 2012; O'Shea et al. 2018).
138 Here we examine the soils of an impoundment with a failing embankment, which was
139 constructed about 170 years ago when environmental control on the use of contaminated
140 materials was not at today's standards (e.g.in the UK, the Control of Pollution Act, 1974).
141 Consequently, knowledge about the composition of soils in this ageing impoundment
142 requires urgent attention to ensure better long-term management should the embankment
143 finally breakdown. The aim of this study was to examine the elemental content of the soils in
144 an RTE impoundment located on the banks of an estuary and to assess the consequences
145 of their release to the estuary. The objectives of the study were: (1) to determine the
146 concentrations and spatial distributions of metal contaminants (As, Co, Cr Cu, Fe, Mn, Ni,
147 Pb, Rb, Sn, W and Zn), and their enrichment, in the soils of an estuarine impoundment; (2)
148 to evaluate the contaminant loadings and potential impact due to the release of particulate
149 metals to the estuary; (3) to consider potential management options for the containment, or
150 controlled release, of contaminated sediments at this site and elsewhere.
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2 Methods

2.1 Study area

The Blaxton Meadow impoundment is located on the upper Plym Estuary (Devon, England). The river rises 450 m above sea-level, its length is 32 km, the catchment area covers 79.2 km^2 and the River Plym is classed as having a good chemical status. The mean Plym river flow is 2.51 $m^3 s^{-1}$ with a 50% exceedance of 1.355 $m^3 s^{-1}$ and exceptional flow rates, >30 $m^3 s^{-1}$, were recorded in December 2000 and 2012 (Riverlevels.uk 2018). A significant tributary input arises from the Torry Brook, which has a mean flow of 0.77 $m^3 s^{-1}$. It passes via a functioning clay mine where, via industrial discharges, it may acquire elevated suspended solid concentrations that are likely deposited in the upper estuary. The mean springs and neaps tidal ranges at Plymouth are 4.73 m and 2.20 m, respectively.

FIGURE 1

The impoundment was constructed in 1852 to create a recreational area (Fig 1) for local inhabitants. The original salt marsh was removed and waste industrial solids were imported to create a level surface, which was raised slightly above high water neaps by the addition of a thin layer of soil. The source, or sources, of the particulate infill is not known. However, some of the material may have been sourced from the local catchments which are known for the extensive mining for metals from the early 17th century, including As, Cu, Pb, Sn and, more recently, W and the extraction of china clay (Jenkin, 2005). The impounded area covers an area of 5.5 ha and is fronted by a brick embankment (~450 m long and ~1.5 m high) (Fig. 1) built to completely exclude tidal intrusions from the estuary.

In 1995 a sluice gate was installed in the embankment to allow the tidally-controlled incursion of estuarine water, fostering the formation of a wetland. However, the operation of the sluice was short-lived as it was vandalised repeatedly and it was only made fully operational in 2003 (Mossman et al. 2012a). Colonisation by species of salt-tolerant plants, mainly *Salicornia europaea*, occurred within two years of inundation of estuarine water

183 (RSPB 2003) and satellite images illustrate the time-dependent changes in the surface
184 composition (Supplementary Information 1), which have actively promoted the site as a
185 habitat for birds (RSPB 2003). Recently, the site owners, the National Trust, became
186 concerned about the integrity of the embankment which has become unstable, consequent
187 on tidal erosion and wave action. A technical report commissioned by the National Trust
188 (Ruston and Long 2015) considered the engineering options associated with the future of
189 the impoundment.

190 **2.2 Sample collection and processing**

191 Soil cores were collected in October 2017 (Fig. 1) from the impoundment, and a sediment
192 core from the Plym Estuary at low water, using a root corer with a barrel diameter of 8 cm.
193 After collection the cores were extruded from the core barrel, laid in plastic half pipes and
194 wrapped in polyethylene film. Impoundment cores were obtained to a depth where further
195 penetration was inhibited by a stony layer, typically between 30 cm and 40 cm. All cores
196 were stored immediately after collection in a cold room, at 4^{o}C.

197 Prior to quantitative analysis, initial screenings of elemental profiles were made on each
198 moist core, using a portable X-Ray Fluorescence instrument (Thermo Scientific Niton XL3t
199 GOLD+). Four sediment cores identified for complete analyses were numbered as Sites 1 to
200 4, together with the sediment core from the Plym Estuary. Analyses for As and Pb at mid-
201 depth were carried out on auxiliary cores A1 to A4 (Fig. 1). All cores were sectioned at 1 cm
202 intervals and stored in pre-weighed plastic petri dishes. The samples were weighed wet after
203 which they were frozen, then freeze-dried for 48 h and finally the dry weight was obtained.
204 Each dried core section was separated across a 2 mm plastic mesh sieve to remove coarse
205 particles.

206 **2.3 Gamma spectrometry**

207 To determine the activity concentrations of fallout radionuclides in the sieved sediment
208 sections they were packed into individual aluminium containers with sealable lids to inhibit

209 the escape of the gaseous decay product ^{222}Rn. Before measurement the samples were
210 incubated for a minimum of 24 days to allow attainment of secular equilibrium within the ^{238}U
211 decay scheme.
212 Activity concentrations (Bq kg^{-1}) of radionuclides were determined by gamma
213 spectroscopy using a High Purity Germanium (HPGe) coaxial planar detector (Type:
214 GMX50-83-LB-C-SMN-S; Ortec, UK), which had a full width-half maximum (FWHM) for the
215 1330 keV line of ^{60}Co of 1.76 keV and a relative efficiency of 25%. The gamma spectrometer
216 was calibrated using a natural soil, with low background activity, spiked with a radioactive
217 traceable standard solution (80717-669 supplied by Eckert & Ziegler Analytics, Georgia,
218 USA). The standard calibration relationships were derived using ORTEC GammaVision©
219 software. Samples were counted for a minimum of 80,000 s and their activities, in Bq kg^{-1},
220 returned with a 2-sigma counting error. Quality control runs were conducted regularly using
221 an IAEA world-wide proficiency test material, that is moss soil (IAEA-CU-2009-03), packed
222 and sealed in the same geometry as the samples (Supplementary Information 2; Table S.1).
223 The gamma energies of the target radionuclides were 46.5 keV for total $^{210}Pb_T$, 295 and 352
224 keV for ^{214}Pb and 661.6 keV ^{137}Cs. The unsupported component of ^{210}Pb ($^{210}Pb_{ex}$) was
225 estimated by subtracting the ^{226}Ra activity, which at radioactive equilibrium was determined
226 by the gamma emissions of ^{214}Pb i.e. $^{210}Pb_{ex} = {}^{210}Pb - {}^{214}Pb$.

227 **2.4 Wavelength-dispersive X-Ray fluorescence spectrometry**

228 Freeze-dried, sieved sediments (~10 g) were disaggregated prior to being milled for 3
229 minutes at 300 rpm in a Pulverisette 5 planetary ball mill (Fritsch, Germany) using agate
230 milling bowls and balls. Milled material was mixed with a polypropylene wax binding agent
231 (Ceridust 6050M, Clariant, Switzerland) at a ratio of 1:4 (binder:sample) prior to being
232 pressed into 40 mm diameter Al-backed pellets at 150 kN using a TP20 manual press
233 (Herzog, Germany).

The elemental contents of the samples were determined by wavelength dispersive X-Ray Fluorescence (WD-XRF) Spectrometry (Axios Max, PANalytical, Netherlands). The instrument was operated at 4 kW using a Rh target X-ray tube. During sequential elemental analysis, tube settings ranged from 25 kV, 160 mA for low atomic weight elements up to 60 kV, 66 mA for higher atomic weight elements. All analyses were carried out using the "Pro Trace" analysis application with results validated using a stream sediment certified reference material (NCS DC 73309). Measured values were generally within 10% of the certified values for the elements of interest (Supplementary Information 2; Table S.2). Repeatability of the procedure was determined by preparing 3 samples in triplicate with a relative standard deviation between replicates of <10%. Instrumental drift was assessed following internal quality control procedures using a multi-element glass sample.

2.5 Determination of acid-extractable elements

The soil sections of the core from Site 4, and sediment sections from the Plym core, were digested in 1M HCl (pH~0) to determine the potential "bioavailable" metals (Pope et al. 2011; Turner 2019). Approximately 0.2 g of dried sediment of each sample was accurately weighed, using a calibrated balance, into individual 50 mL glass beakers. Exactly 10 mL of 1M HCl was added to each beaker and the contents constantly agitated and allowed to digest for 2 h at room temperature. Afterwards 6 mL of the digest from each of the beakers was extracted using a calibrated pipette and transferred to 50 mL volumetric flasks, which were made up to the mark using Milli-Q water and the contents of the sealed flasks thoroughly mixed.

The digests were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) (iCAP RQ; Thermo Fisher Scientific, UK). The instrument was calibrated using multi-element standards prepared at an appropriate concentration range in the same matrix as the digested samples. Wash cycles, using 10% HNO_3, were performed between analyses to minimise contamination. After each batch of 10 analyses, a check sample was used to

monitor instrumental drift. Detection limits for the metals in the digests, defined as 3σ of the blank, were in the range 6-12 μg L^{-1} for all the metals.

3 Results and discussion

3.1 Fallout radionuclides

3.1.1 Depth profiles

The ^{137}Cs activities in the impoundment soils result from its atmospheric fallout from nuclear weapons testing, which began in the 1940s and reached a maximum in 1963 (Walling and He 2000). These events gave a well-defined peak in ^{137}Cs in each core (Fig 2: 1a to 4a), at approximately 5 cm depth, coincident with the 1963 testing maximum. Thus, the shallow top

FIGURE 2

layer of sediment was deposited post-1963. The ^{137}Cs inventories for Sites 1 to 4 are 1,473, 1,530, 1,127 and 1,177 Bq m^{-2}, respectively, values which compare well with the 2018 northern hemisphere decay corrected fallout of ^{137}Cs in annual precipitation (960 mm for SW England) of 1,460 Bq m^{-2} (Walling and He 2000). Our ^{137}Cs depth profiles are similar to those found in two Delaware Bay (USA) impoundments that were fitted with tide gates in the mid-1980s (Boyd and Sommerfield 2016). In the Delaware Bay case, the observed peaks in ^{137}Cs activities were also confined to the top 10 cm of the cores and the inventories were in the range 1,120-3,150 Bq m^{-2}.

The sediment core from the Plym Estuary comprised particulate matter that was a light grey in colour, likely arising from the supply of waste particulate solids emanating from commercial clay mining in the Plym catchment (Jenkin 2005). Compared to the impoundment soils, the estuarine sediment core had relatively low activities of ^{137}Cs in the near-surface sediments (Fig 2: Pa), typically <5 Bg kg^{-1}, and were below the minimum detectable activity after a depth of 13 cm. Thus, the low ^{137}Cs activities suggest the estuarine clay-like sediments had been excavated from below ground and released to the environment after the significant period of ^{137}Cs fallout about 50 years ago. Consequently, the ^{137}Cs

inventory for the Plym core was 180 Bq m^{-2}, which was approximately an order of magnitude lower inventory than the cores from the impoundment.

The activities of total ^{210}Pb were at a maximum near the soil surface with an approximate exponential decay down-core. The activities of total ^{210}Pb were in equilibrium with ^{214}Pb at a depth of approximately 10 cm for each impoundment core (Fig 2: 1b to 4b). The activities of ^{214}Pb, representing the activities of ^{226}Ra at equilibrium, are almost uniform with depth in each core, with activities centred about 50 Bq kg^{-1}. The estuarine core sections had total ^{210}Pb and ^{214}Pb activities with a similar range to those in the impoundment with a down-core exponential decay (Fig 2: Pb), importantly ^{214}Pb had a trend in common with the impoundment cores all having relatively constant and similar values. The inventories of all five cores were in the range 9,000 to 24,900 Bq m^{-2} which were significantly higher than the values (3,680-6,800 Bq m^{-2}) obtained in cores from an impoundment in the USA (Boyd and Sommerfield, 2016), indicating potential differences in ^{238}U sources of ^{222}Rn, the precursor of fallout ^{210}Pb.

3.1.2 Age-Depth Relationships

The ages of the soils, and sediments, in the core sections were assessed using the methodology described by Appleby (2001) and applied recently in our lab on lake sediments (Wynants et al. 2020). The constant rate of supply (CRS) model was used because of its inclusion of changes in the initial $^{210}Pb_{ex}$ activity and sedimentation rates. The age-depth relationship was estimated using 2018 as the starting date and the ages were calibrated against the maximum fallout of ^{137}Cs which occurred in 1963, 55 years previously. The age-depth relationships for the impoundment cores (Fig 2: 1c to 4c) had similar gradients indicating similar histories for the soils. However, the sedimentation rates were site-dependent in that Sites 1 and 2, close to the sluice gate (Fig 2: 1c; 2c), had similar increasing trends in sedimentation, in the range 0.10-0.80 kg m^{-2} $year^{-1}$. In contrast, the sedimentation at Sites 3 and 4 (Fig 2: 3c; 4c), both of which are set back from the tide gate,

was significantly lower and relatively constant typically 0.4 kg m^{-2} $year^{-1}$. The impoundment sedimentation rates were relatively low and were similar in value to those found in two impoundments in the Delaware Estuary (USA), where the mineral sedimentation accumulation rates were in the range 0.136-0.529 kg m^{-2} $year^{-1}$ (Boyd and Sommerfield 2016). However, the sedimentation rates in impoundments located on Long Island (USA) were higher and, based on the down-core distributions of ^{137}Cs fallout, were in the range 0.42 to 2.2 kg m^{-2} $year^{-1}$ (Anisfeld et al. 1999). Elevated sedimentation rates, estimated over several years, were also observed in the Scheldt Estuary where for a full tidal exchange (FTE) intertidal habitat they were 25 times higher than in a nearby partial exchange CRT system (Oosterlee et al. 2020).

The core from the Plym Estuary, consisting of cohesive sediment, had an age-depth relationship that was much steeper than those from the impoundment, reflecting on-going deposition within the estuary (Fig. 2: Pc). The sedimentation in the top 12 cm of the core was variable, in a range of 0.10-0.80 kg m^{-2} $year^{-1}$, with a peak about four decades ago (~1980), followed by a trough and then an increase over two decades to the present day.

3.2. Elemental concentrations

3.2.1 Mass dominant elements

The impoundment cores had significant differences between the total Fe, Mn and Rb concentrations compared to the core from the Plym Estuary (Fig 3). Thus, the total Fe concentrations in the soils of the impoundment were in a range of 22,900–46,500 mg kg^{-1} and the Fe concentrations below 5 cm were relatively constant throughout the depth, although there was some variability at depths >30 cm, especially at Sites 1 and 4 (Fig. 3a).

FIGURE 3

Manganese concentrations for impoundment cores were relatively uniform, covering a narrow range of 300–700 mg kg^{-1}, throughout the depth range 5-30 cm. However, small

peaks in the Mn concentrations were obtained in the upper ~5 cm and at >30 cm (Fig. 3b). The Rb concentrations in the impoundment soils were in the range 250-400 mg kg^{-1} and were relatively constant throughout the depth (Fig. 3c). The relatively high Rb concentrations are consistent with the Rb content of illite clay minerals (Köster, 1996), which, together with the light grey colour of the sediment, indicated a potential clay mineral input from mining in the Plym catchment.

In contrast, the Plym Estuary core had an irregular depth dependence of total Fe, Mn and Rb concentrations that were affected by significant fluctuations in concentration between 9 and 17 cm. The Plym Estuary core exhibited concentrations of Fe, in the range 15,500 to 38,200 mg kg^{-1} that were lower than those in the impoundment, except where a peak concentration occurred at 10.5 cm depth (Fig. 3a). Similarly, the concentrations of particulate Mn were relatively constant, except for a well-defined maximum concentration again at 10.5 cm depth (Fig. 3b). The Rb concentrations in the Plym were significantly higher than those in the impoundment and had a mean concentration of 430 ± 45 mg kg^{-1}, presumably because the clay-like sediment was finer and more cohesive than the soils from the impoundment.

The coherence in the depths and shapes of the maximum concentrations of Fe and Mn in the Plym core gave a strong positive statistical relationship between Fe and Mn throughout the core (R^2=0.756; $p<0.001$; n=25). This suggests that these redox-sensitive elements are involved in a common chemical process that created a redox boundary at approximately 11 cm, where dissolved species of Fe and Mn precipitate as ferromanganese oxides. The redox boundary is also associated with a notable decrease in particulate Rb concentrations between 11 and 15 cm. In this case, the Plym core has a strong negative statistical relationship between Fe and Rb (R^2=0.708; $p<0.001$; n=25). The reason for the inverse relationship between Fe and Rb is not clear unless the particulate Rb is exchangeable and is released to the dissolved phase by the chemical conditions induced by the formation of ferromanganese oxides.

3.2.2 Contaminant elements

The mean concentrations (±1 SD) of the contaminant elements in the Plym core and impoundment cores are summarised in Table 2. The group of elements consisting of Co, Cr, Ni, Pb and Sn have concentrations in the Plym core that are generally lower than those in

TABLE 2

the impoundment cores, whereas for As, Cu, W and Zn the concentrations of the Plym core overlap with the concentrations in the impoundment cores (Fig. 4). Cobalt (Fig. 4a) and Cr

FIGURE 4

(Fig. 4b) had soil concentrations that showed little variation with depth at each of the sites. Cobalt concentrations in the soils were low, although they varied somewhat with depth and Co at Site 2 decreased towards the surface. The concentrations of Cr increased from the surface to about 10 cm, after which all 4 sites were constant with depth. Nickel (Fig. 4c) also had relatively low concentrations in the impoundment soils with similar concentrations for cores from Sites 2 and 4 and slightly higher concentrations at Sites 1 and 3. The concentrations of Ni were constant from the surface to about 30 cm, after which they declined in each core. Lead concentrations (Fig. 4d) at Sites 2 and 4 were of similar magnitude and were uniform with depth, whereas Sites 1 and 3 had similar, elevated concentrations. Site 1 had a significant Pb peak at 30 cm. The Pb concentrations in the Plym Estuary profile were uniform ranging from 55-95 mg kg^{-1}. The additional cores A1 to A4 (Supplementary Information 3) had elevated Pb concentrations in the top 27 cm that were in the range 50-200 mg kg^{-1}. Tin concentrations in all impoundment cores (Fig. 4e) showed substantial variability and the concentrations were elevated, especially at Sites 2 and 3, where the maximum concentration was 810 mg kg^{-1}. There was little fluctuation in Sn concentrations the Plym Estuary core which were significantly lower than those from the impoundment.

408 The elements As, Cu, W and Zn had concentrations in the impoundment soils that
409 overlapped significantly with their concentrations in the Plym sediments. The depth-
410 dependences of As concentrations for Sites 1 and 2 were closely aligned (Fig. 4f) and at Site
411 4 As was higher in the upper layers and had a distinct As peak at ~40 cm depth. Arsenic in
412 the Plym sediments had minor variations in concentration with depth, which were confined to
413 a narrow range of 50 – 90 mg kg^{-1}. The As concentrations in the cores A1 to A4
414 (Supplementary Information 2) were mainly elevated and in the range 0-150 mg kg^{-1}.
415 Concentrations of Cu at Sites 1, 2 and 4 (Fig. 4g) were similar up to 30 cm, after which the
416 Cu concentrations exhibited a decreasing trend with depth, whereas the Cu concentrations
417 at Site 3 were elevated by comparison with the other sites. The Plym Estuary sediments up
418 to 10 cm depth had higher Cu concentrations than Sites 1, 2 and 4 after which the Plym
419 concentrations decreased with depth. The W concentrations in the impoundment soils (Fig.
420 4h), and the Plym Estuary sediments, cover a similar in range. However, impoundment Sites
421 1 and 4 show significant peaks at depth. The depth-distributions of Zn concentrations for
422 Sites 2 and 4 (Fig. 4i) were relatively uniform. In contrast, Sites 1 and 3 also showed a
423 similar trend but the concentrations for these cores were marginally higher. The Plym
424 Estuary core had variable concentrations of total Zn, together with a general trend of
425 decreasing concentrations up to 16 cm depth, after which the concentrations increased.

426 **3.2.3 Evaluation of elemental distributions**

427 The concentrations of each element in the impoundment soils, and the Plym sediments, are
428 compared with their median concentrations obtained from analyses of 5,670 top soil samples
429 (15 cm depth, dried and mixed), collected from sites across England and Wales (Rawlins et
430 al. 2012). The sample collection avoided large urban areas and areas where the
431 concentrations of most elements may have been altered by processes such as the
432 atmospheric deposition of industrial contaminants or the release of waste solids. In our data
433 analyses the median soil concentration is preferred because it is a better measure of the

434 mid-point concentration because it reduces any bias that may be introduced into the mean
435 by the outliers, compared to the overall dataset.
436 The distributions of the elemental concentrations in the impoundment suggest the original
437 infilling with waste soils appears to have been applied in an uneven manner, as shown by
438 variability of downcore profiles, for example, Pb, Sn, As, Cu (Fig. 4). The comparisons
439 between the measured concentrations and the median elemental concentrations fall into
440 three groups. Firstly, only Mn (Fig. 3b) had concentrations in the impoundment samples that
441 were below the median values. Secondly, Co (Fig. 4a) and arguably Ni (Fig. 4c) had
442 impoundment concentrations that cohered with their median soil values. The third group
443 involves Fe (Fig. 3a), Rb (Fig. 3c), Pb, Sn, As, Cu, W and Zn (Fig. 4) all of which had
444 impoundment soil concentrations above, significantly so in some cases, the median value for
445 uncontaminated soils in England and Wales (Rawlins et al. 2012).
446 There are also questions as to the extent to which these elevated soil concentrations are
447 above what are considered to be the “normal background concentrations (NBC)” in UK soils
448 (Ander et al. 2013). The NBCs were determined from the analysis of >30,000 soil samples
449 from across the UK, where for As, Cu, Ni and Pb the NBCs were estimated as 32, 62, 42
450 and 180 mg kg^{-1}, respectively. Thus, the elemental concentrations in the impoundment cores
451 (Fig. 4) indicate that the NBCs for As and Cu were exceeded in each core, whereas our
452 measured concentrations of Pb at Site 3 were only ones elevated over the NBC value. The
453 NBC for Ni was not surpassed in any of the cores. Thus, a comparison of our data with the
454 NBC norms leads to the conclusion that As and Cu, and potentially Pb, are seriously
455 contaminated in the impoundment soils.
456 The ranges of total metal concentrations in the soils of the Blackwater Estuary managed
457 retreat site (UK) were lower than those recorded here (Table 1). The relatively low soil metal
458 concentrations at the Blackwater site were similar to those in the sediments of RTE
459 impoundments in Hong Kong (Liang and Wong 2003) and in the tidal flats of the Chongming
460 Dongtan impoundment, China (Ma et al. 2015). However, a polder restored to tidal influence,
461 in the Scheldt Estuary (Teuchies et al. 2013), had elevated metal concentrations in the soils

462 and the concentrations of Cr, Pb, Zn exceeded those found in the Plym impoundment (Table
463 1). An ageing impoundment in the Hayle Estuary, UK, which received inputs from the mining
464 industry had relatively low Sn concentrations, whereas As, Cr, Pb were similar in magnitude
465 to those in the Plym impoundment. However, the Cu and Zn concentrations in the Hayle
466 Estuary impoundment (Table 1) were significantly greater due to mining activity in the
467 catchment. In the lower Plym Estuary sedimentary metals in two cores from an inlet,
468 accommodating a boat yard, had concentrations of Cu, Pb and Zn that were generally higher
469 than those in our upper Plym core (Table 1), whereas Sn concentrations in the inlet cores
470 were lower by at least an order of magnitude (Takahashi et al. 2012). Towards the mouth of
471 the Plym Estuary sediments were found with elevated Pb concentrations, in the range 410-
472 500 mg kg^{-1} (Turner 2019).
473 It is also important to question whether the elemental concentrations released from
474 decaying coastal landfills (Hübner et al. 2010; Pope et al. 2011; O'Shea et al. 2018) were as
475 elevated as those recorded here. Total metal concentrations in foreshore sediments close to
476 these facilities are considerably lower than those in the Plym impoundment, with the possible
477 exception of Zn (Table 1). Sediments adjacent to a landfill had Cu and Pb concentrations
478 that were lower than those in the Plym impoundment, although the Zn concentrations were
479 comparable (Njue et al. 2012). In conclusion, metals in the soils/sediments found adjacent to
480 coastal landfills in the UK are relatively low compared to those in the Plym impoundment.

481 **3.2.4 Enrichment factors**

482 Estimations of elemental Enrichment Factors (EFs) require a normalising element which is
483 free from contamination in order to account for grain size and mineralogical differences in
484 the samples. Aluminium is usually adopted as the normalising element but it was not
485 measurable with our WD-XRF methodology. Thus, Rb concentrations were determined as a
486 geochemical proxy for the estimations of the EFs recently applied for marine solid phases
487 from Plymouth waters (Turner 2019). The EFs were estimated according to Equation 1:

$$EF = \frac{\left\{\frac{M}{Rb}\right\}}{\left\{\frac{M_{Ref}}{Rb_{Ref}}\right\}} \quad (1)$$

where M and Rb are the measured total concentrations of metal M and Rb in the soils and M_{Ref} and Rb_{Ref} are their total reference concentrations. To make a realistic assessment of the EFs, the total reference concentrations of the elements were taken as their median concentrations in the soils from England and Wales (Rawlins et al. 2012).

The general range of EFs vary from EF<1 indicating no enrichment, 1<EF<3 minor enrichment, 3<EF<5 moderately enriched, 5<EF<10 moderate to severe enrichment, 10<EF<25 severe enrichment to EF>25 very severe enrichment. Thus, the EFs estimated for the impoundment soils, and the Plym Estuary sediments, showed that several elements had no enrichment, EF<1, including Fe (range 0.13 to 0.32), Mn (range 0.14 to 0.19) and Co, Cr, Ni and Zn all have EF<0.6. In contrast, Sn had very severe enrichment in the

FIGURE 5

impoundment cores, whereas W was moderately enriched, As and Cu had minor to moderate enrichment and Pb was classed as not being enriched (Fig. 5). Thus, the EFs for metals in the impoundment soils were in the sequence Sn>W≈As>Cu>Pb>Co~Cr~Ni~Zn. The Plym sediment core had EFs lower than those in the impoundment, particularly for As, Cu and Pb where the EF≤1.

3.3 Implications of impoundment failure

3.3.1 Mobilisation of contaminated soils

Removal of some, or all, of the embankment may result in regular tidal flooding of the soils causing their intermittent remobilisation, coupled with their down-estuary transport. The elevated EFs raise concerns about the consequences of the estuarine re-distribution of metal contaminated soils. Thus, the inventories of the metals, I (g m^{-2}), in each core that

were available for dispersal from the impoundment were estimated by integrating the metal inventories of each core section, i, over the number of sections in the core, n:

$$I = \frac{1}{A}\sum_{i=1}^{i=n} c_i . m_i \quad (2)$$

where c_i is the metal concentration of the metal in section i, mg kg^{-1}, m_i is the mass of dried soil in section i, kg, and A is the area of the core barrel, m^2. The approximate total masses (tonnes) of each metal were obtained by multiplying the mean inventories over the total area of the impoundment, 55,000 m^2. The approximate total masses in the impoundment are in the sequence Sn>Pb~As~Zn (Table 3). A comparison of the inventories of metals in the

TABLE 3

Plym core with those in the impoundment shows that impoundment inventories are higher by a factor of two, and three for Sn. Clearly, the eroded impoundment soils may migrate down estuary while mixing with the pre-existing suspended sediment mobilised during tidal incursion, in which case some dilution could occur. Since the Plym Estuary is not protected under designated marine habitats policy, management options for remediation of the contaminated sediments needs to be considered (Chen et al. 2017). To avoid down-estuary contamination the soils could be removed by dredging and then disposed of at a designated offshore site. The UK Action Levels on dredged material (Table 4) provide a basis for decision-making on sediment disposal at sea (DEFRA 2003). Our mean soil concentrations

TABLE 4

for As, Cr, Cu and Pb are higher than criterion A1, whereas criterion A2 is only exceeded by the As concentrations at three sites and Cu concentrations at one site. Thus, the elevated values for As, and Cu, appear to preclude the possibility of sea disposal.

Given that off-shore disposal of the contaminated soils is highly unlikely, managed retreat may offer some advantages, especially if a new embankment installed further back. Encouraging the breach and removing more of the embankment to allow estuarine intrusion

536 would also contribute to better support the development of the salt marsh, with the protective
537 benefits that brings (Temmerman et al. 2013). The elevated concentrations of some metals
538 in the soils, implies their re-mobilisation presents an environmental risk, particularly to the
539 sediment dwelling biota down-estuary. However, capping and heightening the surface of the
540 impoundment using responsibly sourced sediments (e.g. clean dredged alluvial material)
541 may also provide additional protection, conditional on the interplay between the tidal
542 elevation and geomorphology (VanZomeren et al. 2018). Mobilisation of the contaminated
543 subsurface layer mixed with the uncontaminated alluvial material by water turbulence may
544 also produce particulate mixtures with overall lower elemental concentrations.

545 **3.3.2 Biological impact**

546 The potential biological impact of the total elemental concentrations in the soils may be
547 assessed by comparison with the threshold effect levels (TEL) and probable effect levels
548 (PEL) proposed by the Canadian Sediment Quality Guidelines (CCME 1995). The elements
549 of particular interest are As and Pb because the mean concentrations in all cores surpass
550 the value of the PEL (Table 4), whereas the PEL for Cu is only exceeded in Sites 3 and 4.
551 The PEL values for Cr and Zn are not exceeded in any of the cores. The extent to which tidal
552 inundation and wave action would mobilise contaminated sedimentary layers from the Plym
553 impoundment is unknown at present. However, the particulate metal contaminants released
554 from the impoundment, particularly As, and Pb, may migrate down-estuary, where they may
555 be taken up by biota. In mid-estuary there are significant beds of *Scrobicularia plana*, *Nereis*
556 *diversicolor* and *Littorea littorea* which, hitherto, contain relatively low metal concentrations in
557 their tissues (Langston et al. 2003).
558 While the fore-going assessment is based on the total metal concentrations, the potential
559 bioavailability of the elements was assessed using extractions by 1M HCl of the core
560 sections from Site 3. Thus, 82 ± 11% of Pb was released, 70 ± 10% of Cu, 44 ± 6% of As
561 and 12 ± 5% of Zn and less than 7% of Cr, W and Sn (Fig. 6a). Sn and W showed minimal

562 **FIGURE 6**

563 remobilisation with means of 2.4% and 0.76%, respectively. Not shown are the data for the
564 remobilisation of Mn and Fe, which had 0.3% and 13% remobilised, respectively. Cr and Sn
565 are tightly bound to the soils and not readily released by the extract. The sequence in the
566 percentage metal released by 1M HCl from the Plym sediment core (Fig. 6b) was generally
567 similar to the impoundment soils, where 36 ± 3% of As and 62 ± 4% of Cu were released.
568 However, more Zn (51.6 ± 4.2%) and slightly higher Cr (10.5 ± 1.5%) were mobilised. Our
569 metal bioavailability estimates are compared to those in foreshore sediments contaminated
570 by metal leakage from a coastal waste dump (Table 1), where Pope et al. (2011) found Cr,
571 Pb and Zn had similar 1M HCl bioavailability to the values found in this study, whereas As
572 and Cu both had lower values.

573 Of interest is the fate of soil particles with elevated particulate concentrations of toxins,
574 such as As, if they are repeatedly taken up by estuarine organisms. For example, the mean
575 total As concentration for soils from Site 3 was 177 mg kg^{-1}. Assuming the 1M HCl extract is
576 a good mimic of digestion by an organism, then 44% of As is removed during digestion in the
577 stomach. The imbibed particles are then excreted and they still contain a significant As
578 concentration, i.e. ~100 mg kg^{-1}. This particle concentration is still well above the PEL and
579 could, if taken up again by an organism, have a secondary effect.

580 In this study the contaminant metals Sn and W had elevated concentrations and EFs.
581 However, currently there are no international standards relating to their bioavailability in soils
582 or sediments. They both warrant further attention because of their potential toxicity. For
583 example, experiments involving Sn species showed they inhibited the growth of planktonic
584 cyanobacterium (Rüdel 2003). Sedimentary Sn also undergoes chemical reactions involving
585 formation of organo-compounds, such as methylated species (e.g. Me_nSnH_{4-n} where n=1-4),
586 which could evade the sediments and subsequently pass the water-atmosphere interface.
587 The chemical reactivity of Sn in estuarine sediments may, therefore, contribute to it being
588 lost to the atmosphere (Amouroux et al. 2000). For W, experiments involving low

589 concentrations of dissolved W resulted in a lower biomass production of the soil micro-
590 organisms *Bacilus subtilis* and *Pseudomonas fluorescence* and soils containing low metallic
591 W concentrations impaired the growth of rye grass (Strigul et al. 2005). The physico-
592 chemical form of W in the impoundment soils is not known, however its low bioavailability of
593 6.5% (Fig. 6) suggests that the health of the flora growing in the impoundment may be
594 largely unaffected by W.
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4 Conclusions

An impoundment, fitted with regulated tidal exchange, had elevated, and spatially-variable, elemental concentrations in the soils, resulting from the manner in which it was constructed in the mid-19th century. Concentrations of As, Pb and Cu in the impoundment soils were enhanced compared to the national background values in soils and Sn and W were elevated. On-going erosion of the ageing protective embankment, enhanced by climatic effects, may result in the tidal incursion of seawater. Along with the parlous state of the embankment, there are fundamental questions concerning the mobilisation of the contaminated soils and their potential impact on estuarine flora and fauna. An effective management strategy is required, including mitigation of the ecotoxicological damage arising from the uncontrolled release of particulate contaminants down-estuary.

Set in the international context the Plym impoundment is an example of many ageing impoundments in low-lying coastal zones, some containing contaminated soils, or sediments, that eventually could be vulnerable to re-mobilisation. Given the growing concern about the flood risk to low lying coastal areas, assessing the future management of coastal impoundments is an important issue and the effects of sea level rise and wave action on the stability impoundment barriers need further evaluation. Determining suitable management approaches to protect and preserve these coastal facilities is important, probably on a case by case basis. Consideration should be given to innovative, sustainable management approaches that will adapt to the long-term changes that man-made structures in estuaries are facing worldwide.

Acknowledgements The authors are grateful to members of staff of Saltram House Plymouth (National Trust), in particular Mr Tony Flux (National Trust Coast & Marine Adviser (SW)). All the chemical and radiological analyses were conducted in the ISO9001:2018 accredited Consolidated Radio-isotope Facility at the University of Plymouth. The authors thank Andrew Fisher for his assistance with the ICP-MS analyses and the Cartography Unit at the University of Plymouth. We are grateful to Dr Andrew Turner, University of Plymouth for his critical comments on an early version of this manuscript.

Funding The research did not receive any specific grant from any funding agency in the public, commercial or not-for-profit sectors.

Conflict of interest The authors confirm that they have no conflicts of interest.

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CAPTIONS TO FIGURES

Fig. 1 Location of Blaxton Meadow impoundment on the Plym Estuary, Plymouth, UK. The fully analysed cores are numbered 1 to 4, the Plym core (P) and the partially analysed mini-cores A1-A4 (Supplementary Information S.3). The thick white line defines the embankment undergoing decay and the position of the sluice gate is identified

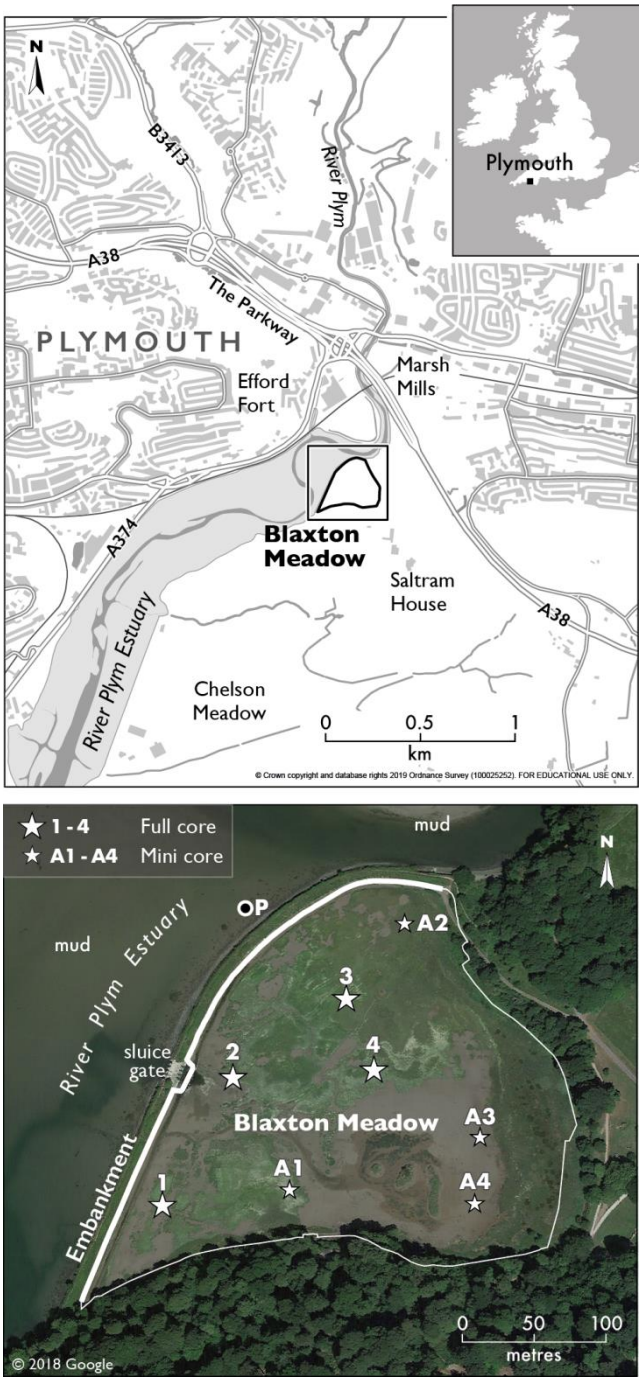
Fig. 2 Fallout radionuclide activities (Bq kg^{-1}) and the age-depth curve for the impoundment sites 1 to 4: (1a-4a) ^{137}Cs; (1b-4b) ^{210}Pb, ^{214}Pb; (1c-4c) age-depth (●) and the dashed line is the sedimentation rate. Fallout radionuclide activities and the age-depth curve for the Plym core: (Pa) ^{137}Cs, (Pb) ^{210}Pb, ^{214}Pb and (Pc) age-depth (●) and the dashed line is the sedimentation rate

Fig. 3 Particulate concentrations of elements in the Plym Estuary Core (✳) and the impoundment cores Site 1 (◆); Site 2 (●); Site 3 (x); Site 4 (x): (a) Fe (%); (b) Mn (mg kg^{-1}); (c) Rb (mg kg^{-1}). The vertical dashed lines are the median values for elements in soils from England and Wales (Rawlins et al., 2012)

Fig. 4 Particulate concentrations of elements (mg kg^{-1}) for the Plym Estuary core (✳) and the impoundment cores Site 1 (◆); Site 2 (●); Site 3 (x); Site 4 (x): (a) Cr; (b) Co; (c) Ni; (d) Cu; (e) Zn; (f) As; (g) Sn; (h) W; (i) Pb. The vertical dashed lines are the median values for elements in soils from England and Wales (Rawlins et al., 2012)

Fig. 5 Elemental Enrichment Factors (Mean ± 1σ) for sediments from the Plym Estuary core (■) and soils from the impoundment cores Site 1 (■); Site 2 (■); Site 3 (■); Site 4 (■)

Fig. 6 Percentage of total elements available to a 1 M HCl extraction of soil and sediment core sections (a) impoundment soil Core 3, (b) Plym Estuary sediment core. Pb (●); Cu (●); As (●); Zn (●); W (●); Sn (●); Cr (●)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B3413
River Plym
A38
The Parkway
PLYMOUTH
Efford
Fort
Marsh
Mills
Blaxton
Meadow
A374
Saltram
House
A38
River Plym Estuary
Chelson
Meadow
0
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km
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Plymouth
1 - 4 Full core
A1 - A4 Mini core
mud
N
OP
A2
mud
River Plym Estuary
3
sluice
gate
2
4
Blaxton Meadow
A3
A1
A4
1
Embankment
0
50
100
metres
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Figure 1

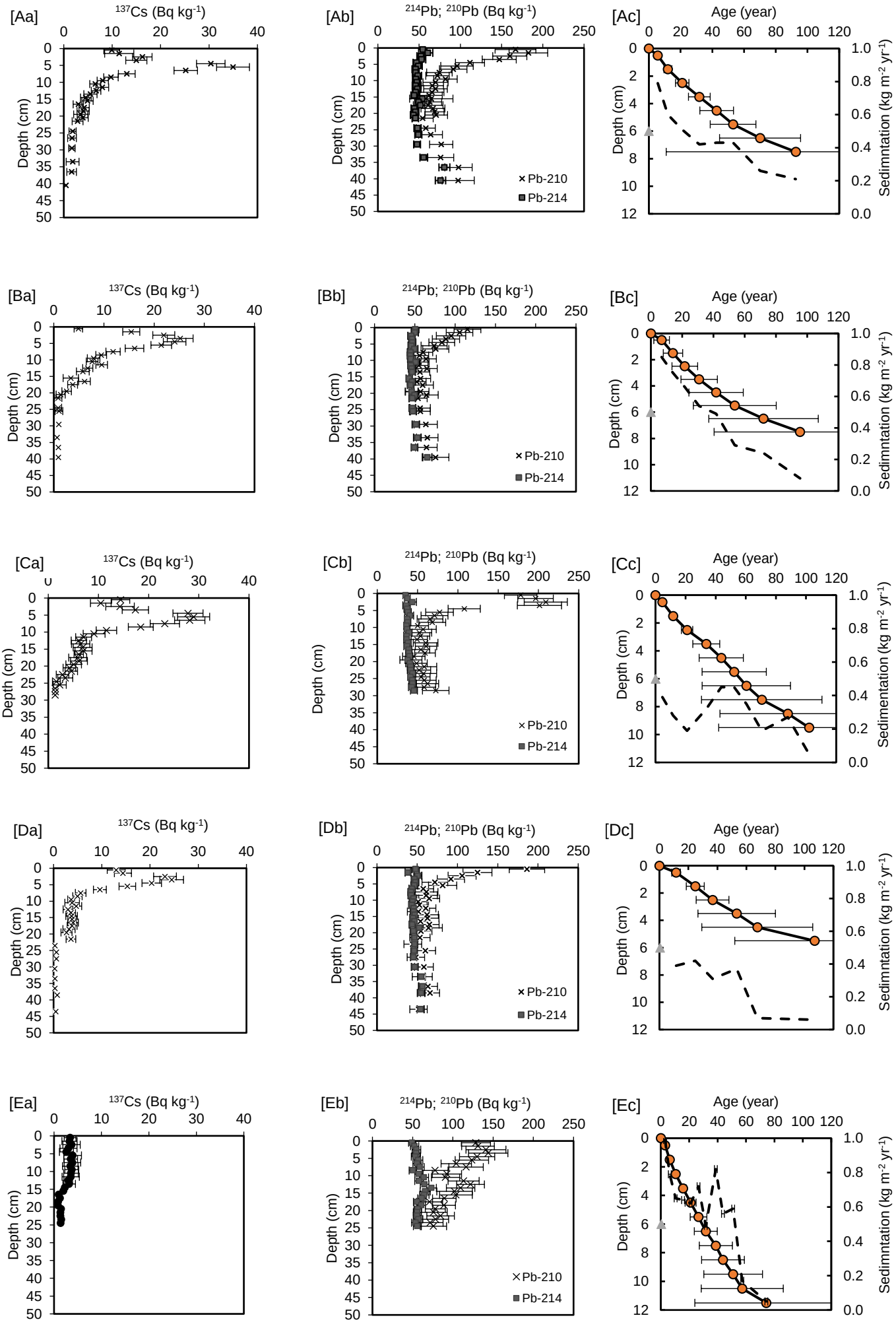
[Aa]
^{137}Cs (Bq kg^{-1})
Depth (cm)
[Ab]
^{214}Pb; ^{210}Pb (Bq kg^{-1})
Pb-210
Pb-214
[Ac]
Age (year)
Sedimntation (kg m^{-2} yr^{-1})
[Ba]
[Bb]
[Bc]
[Ca]
[Cb]
[Cc]
[Da]
[Db]
[Dc]
[Ea]
[Eb]
[Ec]

Figure 2

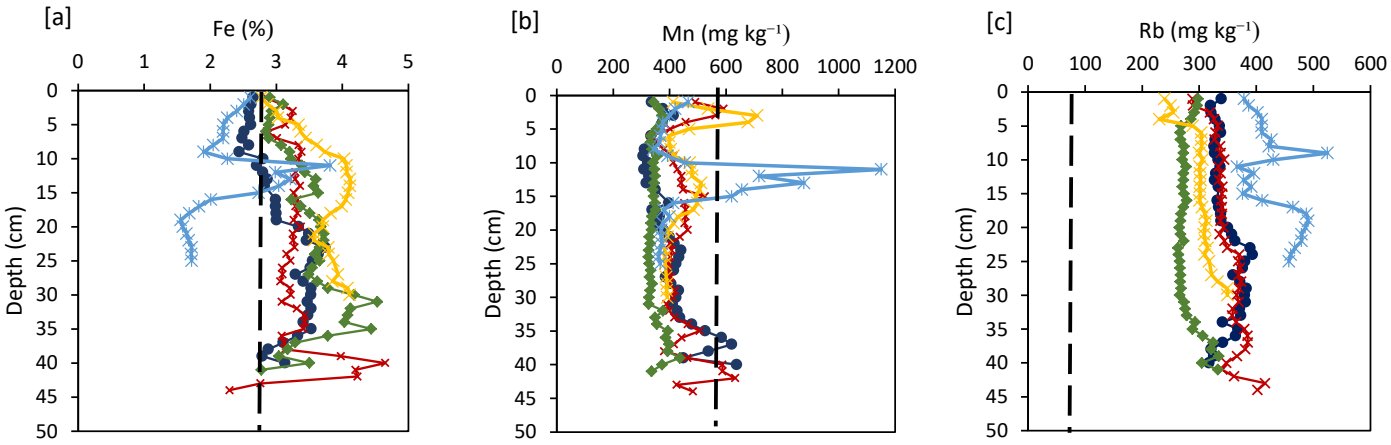

Figure 3

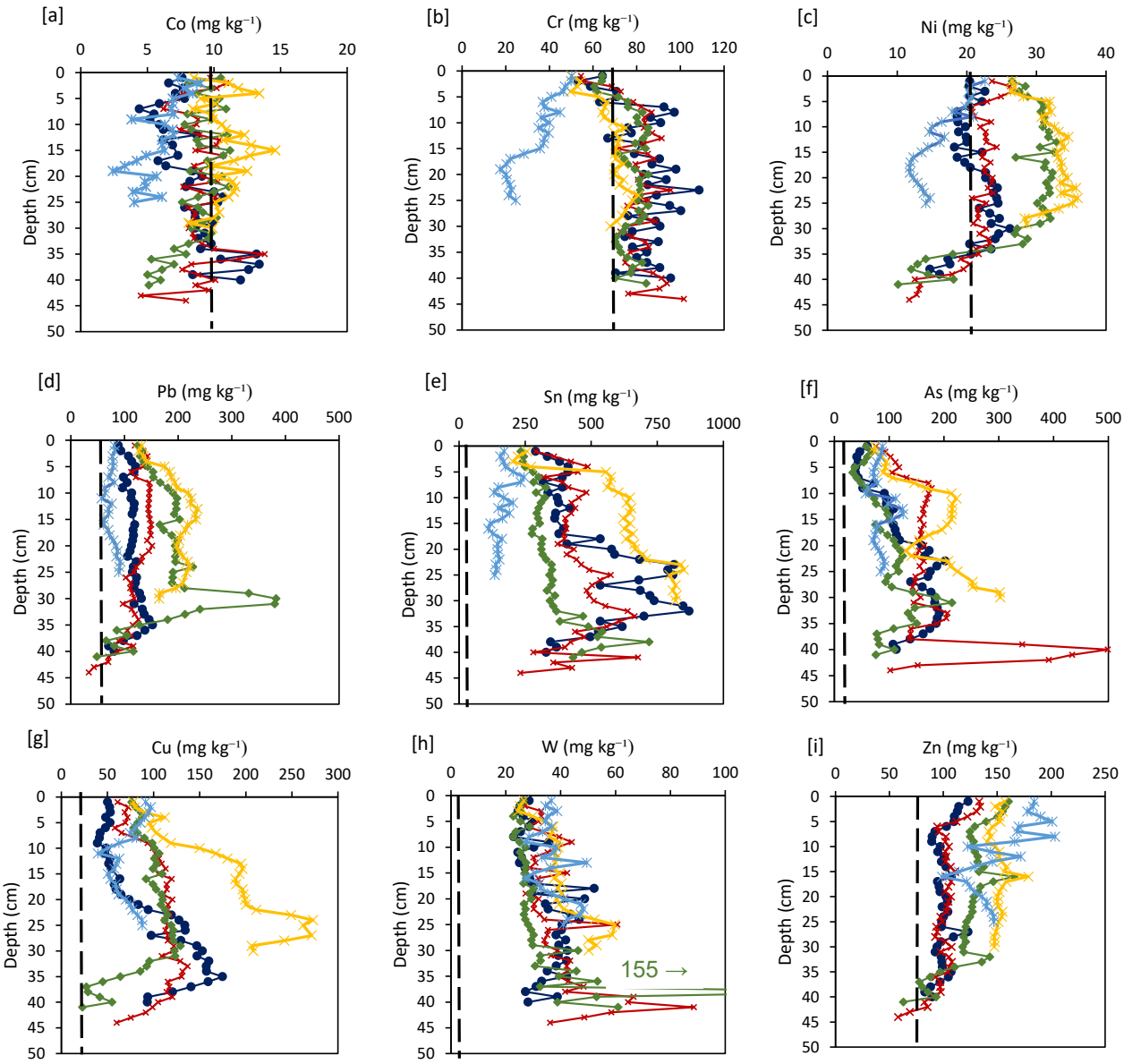
[a]
Co (mg kg⁻¹)
[b]
Cr (mg kg⁻¹)
[c]
Ni (mg kg⁻¹)
[d]
Pb (mg kg⁻¹)
[e]
Sn (mg kg⁻¹)
[f]
As (mg kg⁻¹)
[g]
Cu (mg kg⁻¹)
[h]
W (mg kg⁻¹)
155 →
[i]
Zn (mg kg⁻¹)
Depth (cm)

Figure 4

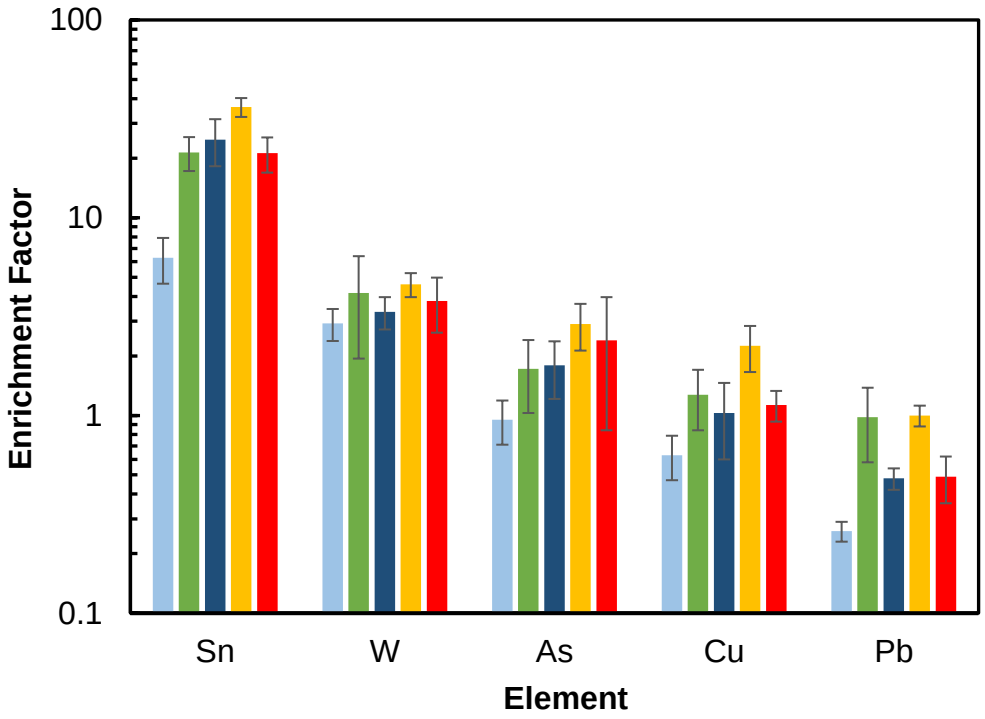

Figure 5

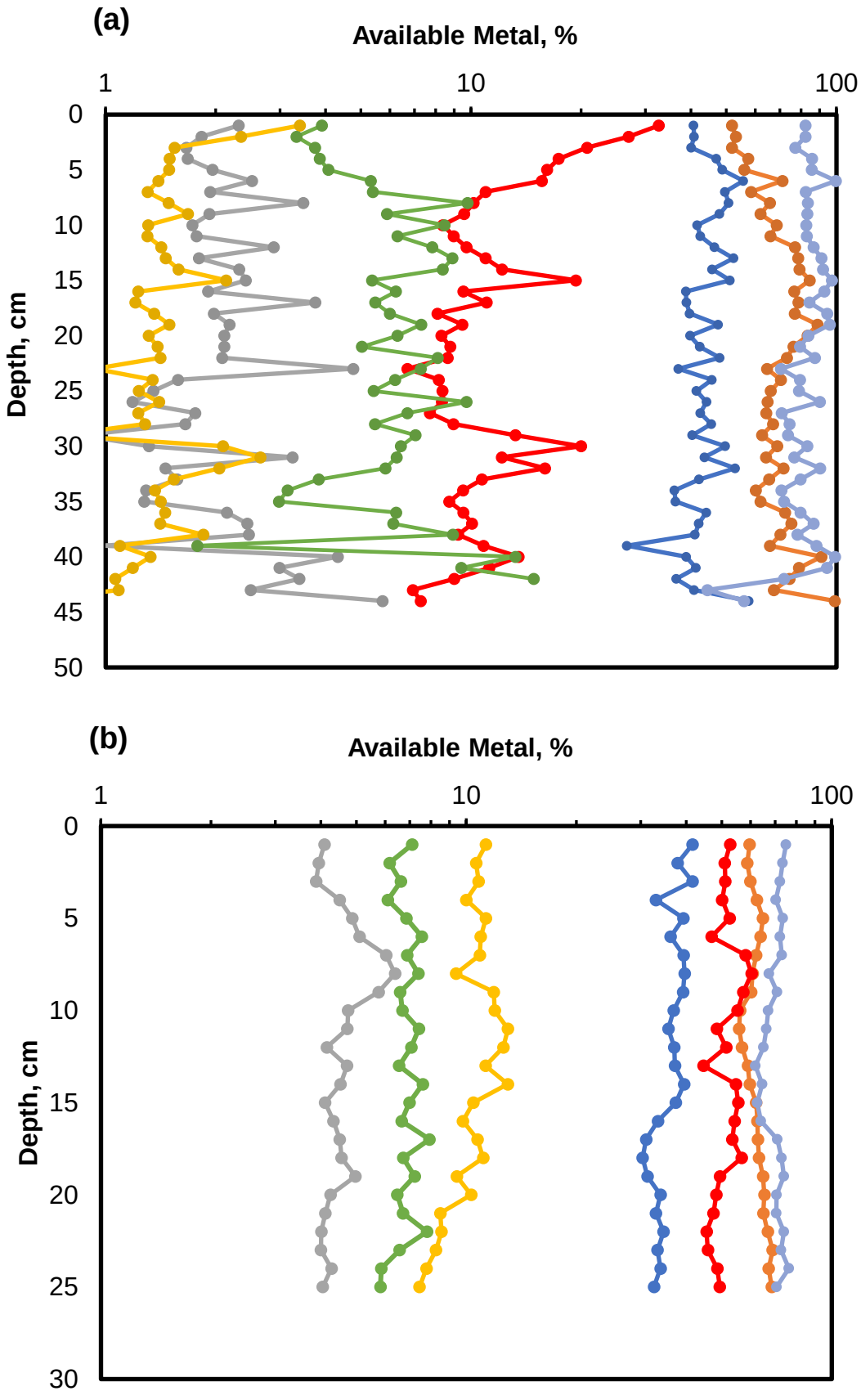
(a)
Available Metal, %
1
10
100
0
5
10
15
20
25
30
35
40
45
50
Depth, cm
(b)
Available Metal, %
1
10
100
0
5
10
15
20
25
30
Depth, cm

Figure 6

Table 1 Range of concentrations of total metals in the soils and sediments (mg kg^{-1}) of impoundments, including polders, and examples of intertidal sediments impacted by metal leakage from landfills. The values in brackets are the ranges of percentage metal concentrations available to a 1M HCl extraction of solid phases.

Site (Area hectares)	Soil or Sediment Concentration, mg kg^{-1}						Reference
	As	Cr	Cu	Pb	Sn	Zn	
Impoundment Soils and Sediments							
Blackwater Estuary, UK Soils (44 ha)	---	38-65	16-28	15-104	---	59-87	Macleod et al 1999
Mai Po, Hong Kong Sediments (1500 ha)	---	11-46	19-87	17-91	---	56-328	Liang & Wong 2003
Hayle Estuary, UK Sediments (6 ha)	211-596	68-167	535-1,510	83-214	70-166	386-911	Aquatronics 2011
Scheldt Estuary, Belgium Polder Soils (8 ha)	10.7-57.1	48.2-710	29.8-173	64.2-323	---	308-1,640	Teuchies et al 2013
Yangtze Estuary, China Soils (1858 ha)	---	55-77	26-48	23-37	---	90-125	Ma et al 2015
Plym Estuary, UK Soils (5.5 ha)	33-505 (36-58%)	50-109 (0.6-2.7%)	7-175 (52-99%)	34-380 (44-97%)	231-871 (0.9-5%)	58-166 (7-33%)	This Work
Intertidal Sediments impacted by decaying landfills							
Christchurch Harbour, UK	0.34-13	3.3-54	4.4-34	4.7-61	0.1-2.3	10-170	Hübner et al 2010
Lyme Bay, UK	3.6-10 (3.3-42%)	10-22 (0.1-5.0%)	11-64 (13-32%)	14-153 (25-63%)	---	41-278 (10-38%)	Pope et al 2011
Thames Estuary, UK	---	7-91	4-74	8-205	---	22-262	O'Shea et al 2018

Table 2 Mean (±1 SD) metal concentrations in the Plym Estuary core sediments and the impoundment soil cores from sites 1-4. The sequence of the elements is organised to cohere with the sequence in Fig. 4.

Location	Sedimentary Metal Concentrations, mg kg^{-1}								
	Co	**Cr**	**Ni**	**Pb**	**Sn**	**As**	**Cu**	**W**	**Zn**
Plym Estuary	5.9 ± 1.6	33.4 ± 10.3	16.0 ± 3.4	76.1 ± 9.8	161 ± 33	84.9 ± 17.1	71.6 ± 15.9	37.0 ± 6.4	152 ± 28
Impoundment									
Site 1	8.8 ± 1.7	79.0 ± 4.8	27.4 ± 6.5	180 ± 69	354 ± 98	97 ± 39	92 ± 38	35.2 ± 22.2	124 ± 23
Site 2	8.5 ± 2.3	84.6 ±10.0	21.1 ± 2.7	115 ± 16	517 ± 175	126 ± 54	93 ± 45	34.9 ± 7.6	101 ± 8.8
Site 3	10.8 ± 1.5	68.2 ± 7.9	32.0 ± 2.7	196 ± 31	623 ± 180	177 ± 65	175 ± 59	40.2 ± 8.8	152 ± 7.0
Site 4	8.8 ± 1.6	83.0 ± 6.8	21.3 ± 3.5	121 ± 28	450 ± 94	174 ± 85	103 ± 22	70.0 ± 12.5	101 ± 14

Table 3 Inventories, g m^{-2}, of elements for each core. Total inventories estimated assuming the mean inventory is representative over the area of the impoundment, 5.5 ha.

Site	Elemental Inventories, g m^{-2}						
	As	Cu	Pb	Sn	Cr	W	Zn
Plym Estuary Core	27	22	24	52	11	11	47
Impoundment Cores							
1	21	26	46	77	20	6.8	34
2	42	27	43	185	32	13	40
3	52	55	63	195	21	12	46
4	53	36	48	127	29	12	37
Inventory Mean	42	36	50	146	26	11	39
Total, t	2.3	2.0	2.8	8.0	1.4	0.6	2.2

Table 4 DEFRA (2003) action level guidelines (A1=disposal at sea and A2=no disposal at sea) for disposal of dredged material at sea, and concentration ranges of impoundment sediment cores. CSQG criteria (CCME, 1995), where less than the TEL=the minimal concentration below which adverse effects rarely occur; between the TEL and PEL=the concentration range within which adverse effects occasionally occur; above the PEL=concentration above which adverse effects frequently occur. All concentrations are in mg kg^{-1} (dry weights).

Metal	Contaminant Criteria, mg kg^{-1}				Mean Metal Concentrations (±1σ), mg kg^{-1}			
	DEFRA		CSQG					
	A1	A2	TEL	PEL	Site 1	Site 2	Site 3	Site 4
As	20	100	7.24	41.6	97 ± 39	126 ± 54	177 ± 65	174 ± 85
Cr	40	400	52.3	160	79 ± 4.8	85 ± 10	68 ± 7.9	83 ± 6.8
Cu	40	400	18.7	108	92 ± 28	93 ± 45	175 ± 59	103 ± 22
Pb	50	500	30.2	112	180 ± 69	115 ± 16	196 ± 31	121 ± 28
Zn	130	800	124	271	124 ± 23	101 ± 8.8	152 ± 7.0	101 ± 14