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Reconstructing historical trends in metal input in heavily-disturbed, contaminated estuaries: studies from Bilbao, Southampton Water and Sicily

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Abstract

Estuaries may be important reservoirs for contaminants as they tend to act as sinks for fine, contaminant-reactive sediments, and, historically, they have acted as centres for industrial and urban development. Analysis of dated sediment cores from these areas may allow historical trends in heavy metal input to be reconstructed, and recent and historical inputs of metal contaminants to be compared. Undisturbed saltmarsh settings have been used widely in the reconstruction of historical trends in metal input as saltmarshes provide a stable, vegetated substrate of dominantly fine sediments, and are less prone to erosion and reworking than adjacent mudflat areas. In comparison, much less research on historical pollution trends has been undertaken at estuarine sites which are prone to severe local disturbance, such as intertidal areas which are routinely dredged or where sedimentary processes have been modified by human activities such as shipping, salt working, port activities, land claim etc. This paper assesses the usefulness of ^{210}Pb and ^{137}Cs dating, combined with geochemical studies, in reconstructing historical trends in heavy metal input and sediment accretion in 3 heavily-modified, industrialised estuarine areas in Europe: the Bilbao estuary (Spain), Southampton Water (UK), and the Mulinello estuary (Sicily). Of these sites, only a salt marsh core from the Mulinello estuary provides a high-resolution record of recent heavy metal inputs. In Southampton Water only a partial record of changing metal inputs over time is retained due to land-claim and possible early-diagenetic remobilisation, while at Bilbao the vertical distribution of heavy metals in intertidal flats is mainly controlled by input on reworked sediment particles and variations in sediment composition. Where ^{137}Cs and ^{210}Pb distributions with depth allow a chronology of sediment deposition to be established, and early-diagenetic remobilisation has been minimal, mudflat and saltmarsh cores from even the most heavily-disturbed estuarine sites can provide useful information on variations in historical contaminant input. When the sediments have been vigorously mixed or reworked, large-scale compositional variations are present, or significant early-diagenetic remobilisation has occurred, however, only general information on the scale of contamination can be obtained.

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1. Introduction

Estuaries may be important reservoirs for contaminants as they tend to act as sinks for fine, contaminant-reactive sediments, and, historically, they have acted as centres for industrial and urban development. Industrial and urban expansion around estuaries has commonly led to an increased input of heavy metals, a fraction of which sorb on to fine-grained suspended material and are subsequently deposited and buried in sub and intertidal mudflats and in saltmarshes. In many areas of western and southern Europe, however, the intensive industrialisation of estuarine areas has been followed by either economic decline or more efficient pollution control measures, hence older sediments may be far more contaminated than recent sediments (e.g. Pirrie et al., 1997; Cearreta et al., 2000). Reworking of contaminated sediments through natural physical, chemical and biological processes, however, and through anthropogenic activities such as dredging and land claim/abandonment means that even after cessation or reduction of discharge there is the potential for continued release of heavy metals into the biosphere. Analysis of sediment cores may allow recent and historical inputs of metal contaminants to estuarine areas to be compared, and, if the period of peak discharge is well-known, the extent of reworking of heavy metals may also be assessed. Those areas within estuaries that have the highest buried metal load, and which may release significant quantities of heavy metals if allowed to erode, may also be identified (e.g. Plater et al., 1998). The application of radiometric dating methods, particularly ^{210}Pb and ^{137}Cs dating, may allow sediment accumulation rates and mixing processes to be determined, and the rate and timing of historical and recent metal input to be calculated (e.g. Valette-Silver, 1993; Croudace and Cundy, 1995; Cundy and Croudace, 1996; Callaway et al., 1998). The reconstruction of historical trends in metal input using sediment cores has been undertaken along many estuaries and coasts (see Valette-Silver, 1993 for review), but is most effective where the sedimentological setting acts as an effective sink for contaminant-reactive fine sediments, and where erosion, reworking, and bioturbation are limited. Hence undisturbed saltmarshes have been used widely in the reconstruction of historical contaminant trends as these provide a stable, vegetated substrate of dominantly fine sediments, and are less prone to erosion and reworking than adjacent mudflat areas. In comparison, much less research on historical trends in metal input has been undertaken using sediments from intertidal estuarine areas which are prone to severe local disturbance, such as areas which are routinely dredged or where sedimentary processes have been heavily-modified by human activities such as shipping, salt working, port activities, land claim etc. These latter areas are often heavily contaminated by effluents from local industrial and urban centres, and information on the impacts of human activity on sedimentary processes, and the rate, magnitude and extent of metal input is particularly valuable. This paper therefore assesses the usefulness of ^{210}Pb and ^{137}Cs dating, combined with geochemical studies, in reconstructing historical trends in heavy metal input and sediment accretion at 3 heavily-disturbed, contaminated estuarine sites in Europe. At each site, in common with many European estuaries (e.g. Allen, 2000), historically-deposited sediments show elevated concentrations of a range of heavy metals, and natural sedimentary processes have been greatly modified by recent and historical dredging and land claim.

2. Study areas

2.1. Site 1: The Bilbao estuary, Spain

The Bilbao estuary (Fig. 1) is a partially-mixed system with tidal range of 4.6 m (spring tides) and 1.2 m (neap tides). The estuary is 15 km long and an average of 100 m wide, with channel depth ranging between 2 m (upper estuary) and 9 m (estuary mouth). The early industrial development of Bilbao occurred in the mid-19th century, due largely to the exploitation of local Fe ore. Since then, the Bilbao estuary (specifically, the tidal part of the Nervion river) has received effluent from a variety of industrial (including mineral sluicing) and urban sources. Large areas of the estuary have been reclaimed, and the present tidal channel has been isolated by dyking from much of its original intertidal area. The navigational channel of the estuary is continuously dredged, while historical capital dredging programmes may have significantly affected sediment dynamics in the estuary (e.g. Cearreta et al., 2000). At present, water and sediments from the Bilbao estuary have extremely low concentrations of dissolved O_2 and high organic matter and heavy metal content due to input of industrial and urban wastes (Irabien, 1993; Saiz-Salinas et al., 1996). The estuary is widely recognised as the most polluted coastal area of northern Spain (e.g. Cearreta et al., 2000), although environmental protection policies and improved waste treatment systems, combined with factory closures during recent periods of economic recession, have significantly reduced the input of heavy metals to the estuary.

2.2. Site 2: The Hamble estuary, Southampton Water, UK

The Hamble estuary is a mesotidal system on the eastern side of Southampton Water, southern England (Fig. 2). The Southampton Water area has undergone significant historical urban, industrial and leisure development.

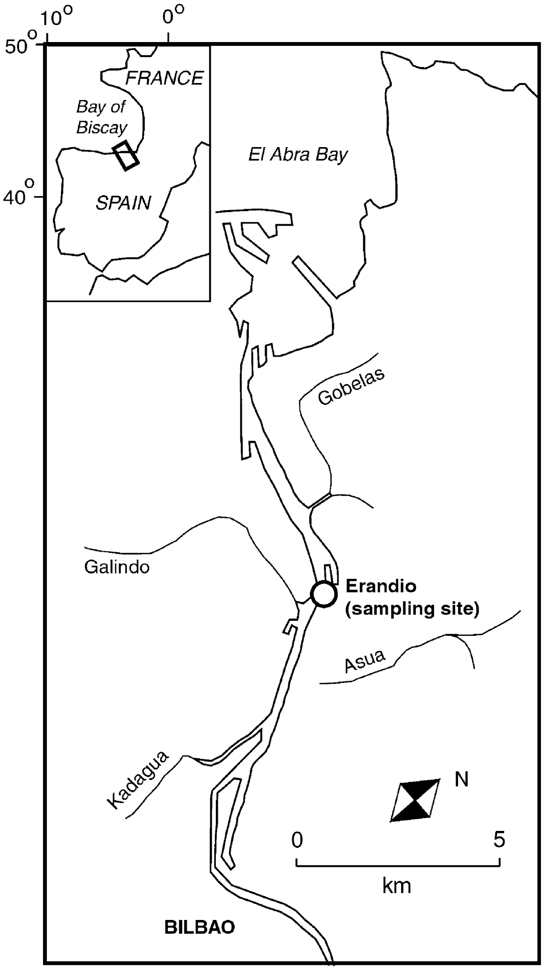

Fig. 1. The Bilbao estuary, Northern Spain. The site of the Erandio core is marked with an open circle.

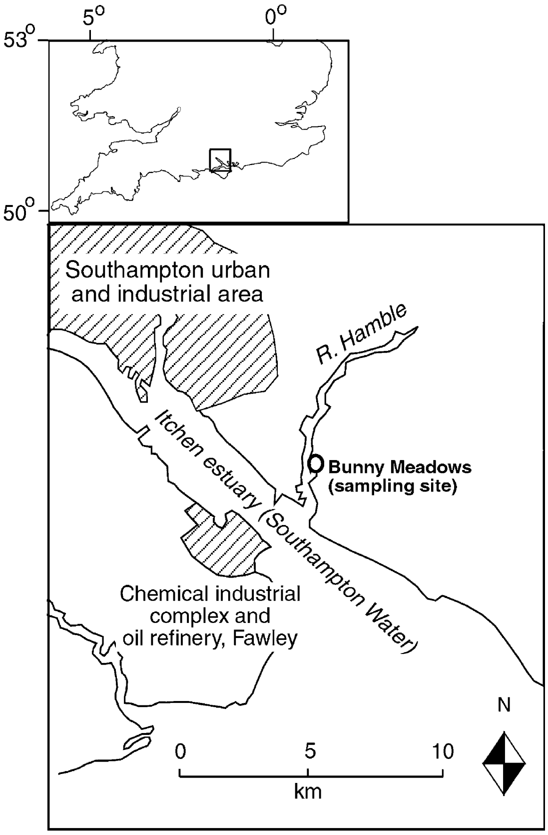

Fig. 2. The Hamble estuary, Southampton Water, UK. The site of the Bunny Meadows core is marked with an open circle.

Southampton has been a major port for several hundred years, and in the mid 20th century the dock area was expanded and the south-west bank of Southampton Water intensively developed for industry. At present, the area around Fawley contains the largest oil refinery in the UK and related industries that use the feedstock from the refinery. Following development and expansion in the early 1950s the refinery has been a major contributor of hydrocarbon (e.g. Dicks and Levell, 1989), Cu (Cundy and Croudace, 1995a) and (possibly) Pb pollution (Cundy and Croudace, 1995a) to Southampton Water, although effluent quality improvements since 1970 have led to marked reductions in discharge. Sediments labelled with contaminants derived from urban and industrial sources around Southampton Water are carried into the Hamble on the estuarine circulation (Cundy and Croudace, 1995a). The Hamble itself has undergone intensive development for recreational purposes, with the construction of 4 yachting marinas which have caused substantial loss of intertidal areas and high localised siltation rates following capital dredging works (Tosswell, 1984). Historical land-claim for agriculture has also taken place within the Hamble estuary, most noticeably at the Bunny Meadows site on the eastern side of the estuary. The site was abandoned in ca. 1930 and the sea-wall breached in a number of places, allowing (partial) regeneration of saltmarshes and mudflats.

2.3. Site 3: The Mulinello estuary, Sicily

The Mulinello estuary is a microtidal system which discharges into Augusta Bay, SE Sicily (Fig. 3). The original saltmarshes and intertidal flats of the estuary have been largely destroyed by historical salt workings (now disused) and recent (post-1970) port development. The coastline immediately south of the estuary has undergone intensive post-World War 2 industrial expansion, and by the late 1960s contained a number of (still active) oil refineries and related petrochemical industries. Degradation of water quality and high heavy metal concentrations have been recorded in the surrounding Augusta Bay (Magazzu et al., 1995; Castagna et al., 1985).

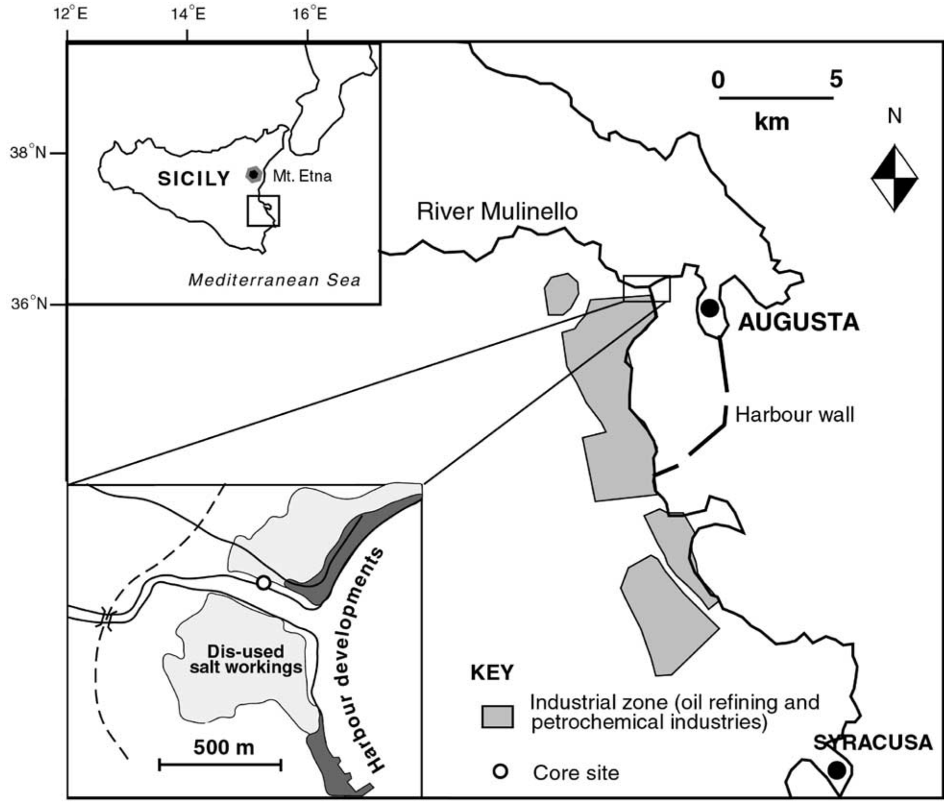

Fig. 3. The Mulinello estuary, Augusta Bay, Sicily. The coring site is marked with an open circle.

3. Methodology

Sediment cores were collected using a hand-driven PVC coring tube. Samples were taken from areas of apparent sediment accretion, i.e. stable marsh surfaces (Hamble and Mulinello sites), or intertidal mudflats remote from known areas of continuous dredging activity (Bilbao). Locally, sites were chosen to avoid areas which were obviously eroding, or which had been trampled or received dumped material. Sediment compaction caused by the coring procedure was measured and was found to be negligible in all cases. On return to the laboratory cores were sliced open, described and X-radiographed, before being cut into 1 or 2 cm depth increments for further analysis. Sediments were dated using the ^{210}Pb and ^{137}Cs methods. The natural radionuclide ^{210}Pb has been extensively used in the dating of recent sediments. Dating is based on determination of the vertical distribution of unsupported ^{210}Pb (^{210}Pb$_{\text{excess}}$), or ^{210}Pb arising from atmospheric fallout, which then allows ages to be ascribed to sedimentary layers based on the known decay rate of ^{210}Pb (see Appleby and Oldfield, 1992 for synthesis of the ^{210}Pb method). ^{210}Pb activity was determined by a proxy method through alpha spectrometric measurement of its grand daughter nuclide ^{210}Po. The method employed was based on Flynn (1968), using double acid leaching of the sediment with ^{209}Po as an isotopic tracer and autodeposition of the Po isotopes in the leachate on to Ag discs. Detection limits were 1 Bq/kg. Dates were ascribed in the present study using the simple and CRS models of ^{210}Pb dating (e.g. Appleby and Oldfield, 1992). ^{137}Cs is an artificial radionuclide introduced to the study areas by atmospheric fallout from nuclear weapons testing and reactor accidents, and from authorised releases from nuclear facilities. It is well-established that, following its initial widespread release in 1984, marked maxima in the atmospheric deposition of ^{137}Cs occurred in 1958, 1963 (from nuclear weapons testing) and 1986 (from the Chernobyl accident). In favourable conditions, these periods of peak fallout, and in some locations the period of peak discharge from nuclear establishments, provide subsurface activity maxima in accumulating sediments and can be used to derive rates of sediment accumulation (e.g. Ritchie and McHenry, 1990; Cundy and Croudace, 1996). ^{137}Cs activities were determined by gamma spectrometry with Canberra HPGe well-type detectors. Errors were typically in the order of 4% (1σ), detection limits were 0.5 Bq/kg.

All samples were analysed using a PW1400 or PW1440 X-ray fluorescence spectrometer to obtain compositional data. Samples were oven or freeze-dried, pelletised for trace element determinations and fused for major element determinations. The methods used are well-established and are detailed in Croudace and Williams-Thorpe (1988). Precision is nominally 1% rsd for major elements and 5% rsd for trace elements. Accuracy was assessed by comparing a range of reference sample determinations (e.g. USGS MAG-1) with recommended values and was generally within 10% of the working values quoted in the literature. A Jeol scanning electron microscope with EDS and electron-backscatter detectors was also used to investigate hand-picked samples, which were set in resin blocks and polished prior to analysis.

4. Results

4.1. Site 1: The Bilbao estuary, Spain

A sediment core (50 cm in length) was taken from an intertidal flat in the middle estuary, near Erandio (Fig. 1), dated using ^{137}Cs and ^{210}Pb, and analysed for trace and heavy metals, and benthic foraminifera. Full details are given in Cearreta et al. (2000). X-radiography of the core showed no discernible bioturbation, with finely-laminated sediment present throughout core length. Surface sediments in the estuary have been observed to be anoxic (e.g. Urrutia, 1986), limiting infauna. This is consistent with benthic foraminiferal data: the foraminiferal standing crop is low, and the anoxic and highly polluted nature of the sediments does not allow benthic foraminifera to develop stable populations (Cearreta et al., 2000). A clear compositional change occurs in the core at −27 cm depth, from sandy mud (ca. 70% sediment <63 μm) to muddy sand (less than 20% sediment <63 μm). ^{137}Cs and ^{210}Pb distributions with depth are relatively erratic (Fig. 4), and there is a broad similarity between the profiles for ^{137}Cs, ^{210}Pb and the naturally-occurring radionuclide ^{40}K, which is an indicator of K-bearing mineral content (e.g. clays, feldspars). These radionuclides have different sources and input histories, and so similarity between the profiles indicates that the vertical distribution of ^{137}Cs and ^{210}Pb is controlled by input on reworked sediment particles and by variations in sediment composition, rather than by direct atmospheric fallout. Observed activities for each radionuclide are significantly lower in deeper, sandier sediments than in the overlying clay-rich sediments, indicating that each radionuclide is dominantly associated with the fine sediment fraction, as observed elsewhere (e.g. Cundy and Croudace, 1995b). Despite the anoxic characteristics of the estuarine water and sediment, and the chalcophilic nature of Pb, ^{210}Pb activity shows little correlation with S concentrations ($r^2 = 0.02$). Supported ^{210}Pb activities in mineralogically similar intertidal sediments from the nearby Plentzia estuary are typically 9 Bq/kg (Cearreta et al., 2002), indicating that ^{210}Pb$_{\text{excess}}$ is present throughout the cored depth of sediment. Hence, the entire 50 cm depth of sediment sampled has accreted in less than 120 a (normally taken as the time period over which ^{210}Pb$_{\text{excess}}$ decays to insignificant activities). The erratic nature of the ^{210}Pb profile, however, means that dating using this radionuclide is problematic, as no consistent decrease in activity with depth can be discerned. Dating using ^{137}Cs is similarly difficult—the ^{137}Cs activity vs. depth profile does not show clear subsurface maxima related to peak fallout from atmospheric weapons testing in 1963 or Chernobyl in 1986. ^{137}Cs is, however, present throughout the cored depth. In the absence of clear subsurface activity maxima that can be related to periods of maximum ^{137}Cs input, only a minimum sediment accumulation rate of 1 cm/a can be determined based on the premise that the entire sediment core is younger than 1954 (Fig. 4).

The heavy metals Zn, Cu and Pb, and As, show similar distributions with depth at each site (Fig. 4), indicating that they are derived from the same general source or that they have undergone similar post-depositional behaviour. The vertical distributions of Fe, Zn, Cu, Pb and As are similar to that of S, with co-incident maxima in concentration occurring at 7–13, 28–40 and 47–50 cm depth. This indicates possible association of heavy metals (and As) with sulphide phases. The concentrations of Fe, Mn, Cu, Pb, Zn and As are significantly higher in the lower part of the core, which is much coarser in grain size than overlying sediments. This contrasts with the radionuclide data, which show that ^{210}Pb, ^{137}Cs and ^{40}K are dominantly associated with fine-grained, shallower sediments (see above). Heavy metals and radionuclides have been observed in a large number of studies to be mainly associated with fine sediments (specifically clay minerals and associated Fe/Mn and organic coatings) which provide reactive sites for metal sorption (e.g. Grant and Middleton, 1990; Cundy and Croudace, 1995b). Hence, where fine sediments are interbedded with coarse sediments, as is the case in many saltmarshes and intertidal flats, much of the variation in metal concentration with depth may be caused by compositional variation (e.g. Cundy and Croudace, 1996). Often, normalisation to some proxy for fine-grained material (e.g. Al, Rb, Cs) is used to reduce the effect of varying grain size on measured metal concentration (e.g. Ackermann, 1980). SEM and microscopic studies of the lower part of the Erandio core, however, show the presence of coarse detrital smelting wastes and slags (Fig. 5), and compositional analysis indicates that these particles are rich in S and in a range of heavy metals (Ti, Cr, Fe, Zn). The elevated metal concentrations in the lower coarse layer are therefore caused mainly by the presence of detrital particles (i.e. mining and smelt products) rich in heavy

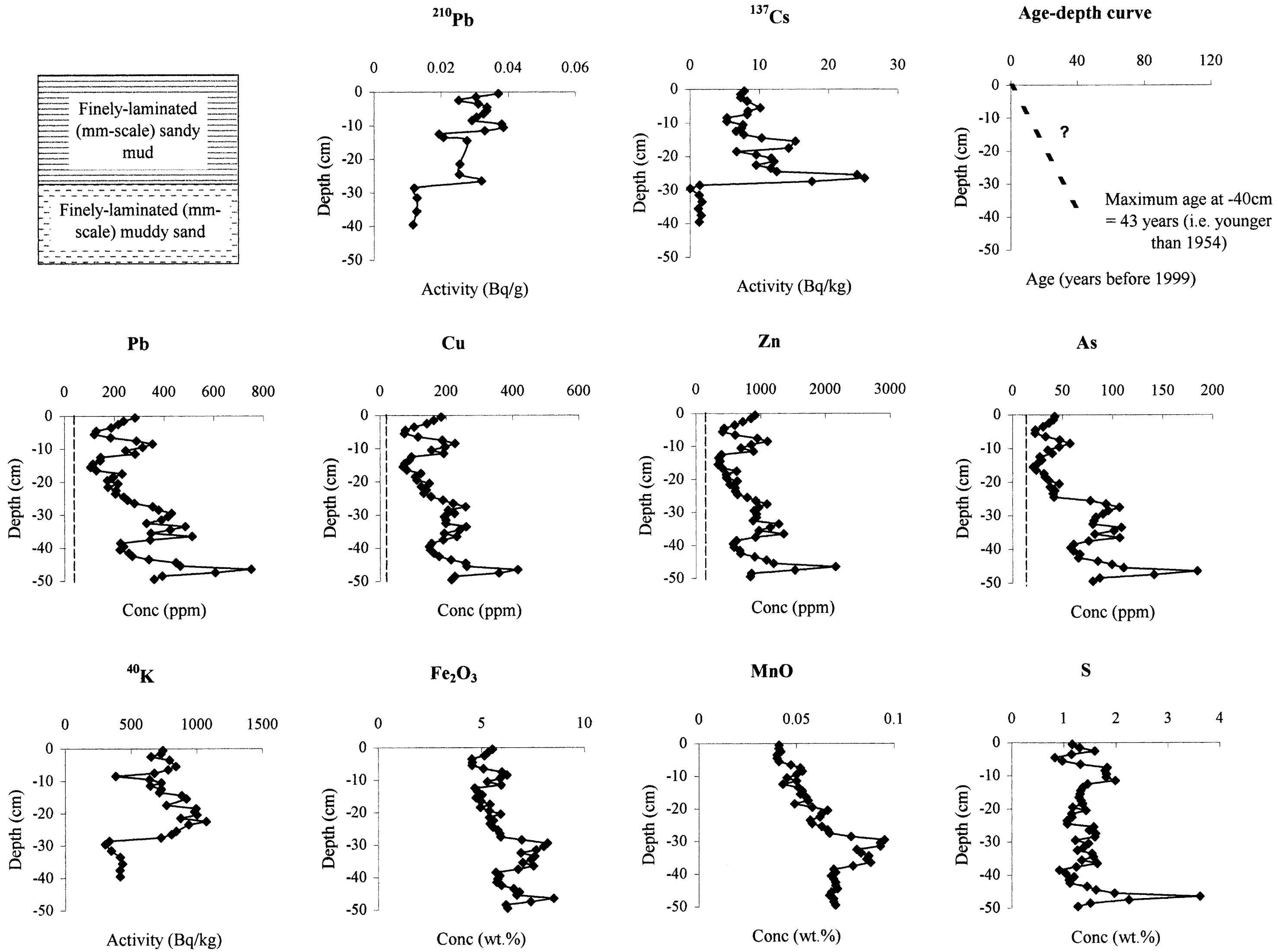

Fig. 4. Distribution of selected radionuclides and trace and major elements in the Erandio core, Bilbao estuary. An age-depth curve is also shown, based on ^{137}Cs and ^{210}Pb dating. The dotted vertical line on the graphs for Pb, Cu, Zn and As represent the pre-industrial geochemical background, determined using deep borehole samples (see Cearreta et al., 2000 for further details).

metals. Similar enrichments of heavy metals in coarse particles have been observed in other estuaries subject to inputs of mining and smelting wastes (e.g. Hughes, 1999). Due to the association of metals with coarse detrital slag and smelt products, normalisation to a clay content proxy is invalid at this site.

In general, the concentrations of Cu, Pb, Zn and As in the sediments analysed are greatly elevated ($>$ 10 times) above background concentrations (Fig. 4, determined from mineralogically-similar pre-industrial deposits, Cearreta et al., 2000). This is due to input of urban and industrial effluents and mining/smelt wastes since 1954 (the maximum age of the base of the core, based on ^{137}Cs dating). Historical trends in contaminant input cannot be determined using this sediment core however due to the lack of accurate dating control and the absence of clear subsurface maxima that can be related to periods of peak pollutant input. As illustrated by the similarity between the ^{137}Cs, ^{210}Pb and ^{40}K-depth profiles (see above) these sediments do not retain a record of discrete input events. Instead, the vertical distribution of radionuclides (and heavy metal contaminants) is largely controlled by input on reworked sediment particles and variations in sediment composition.

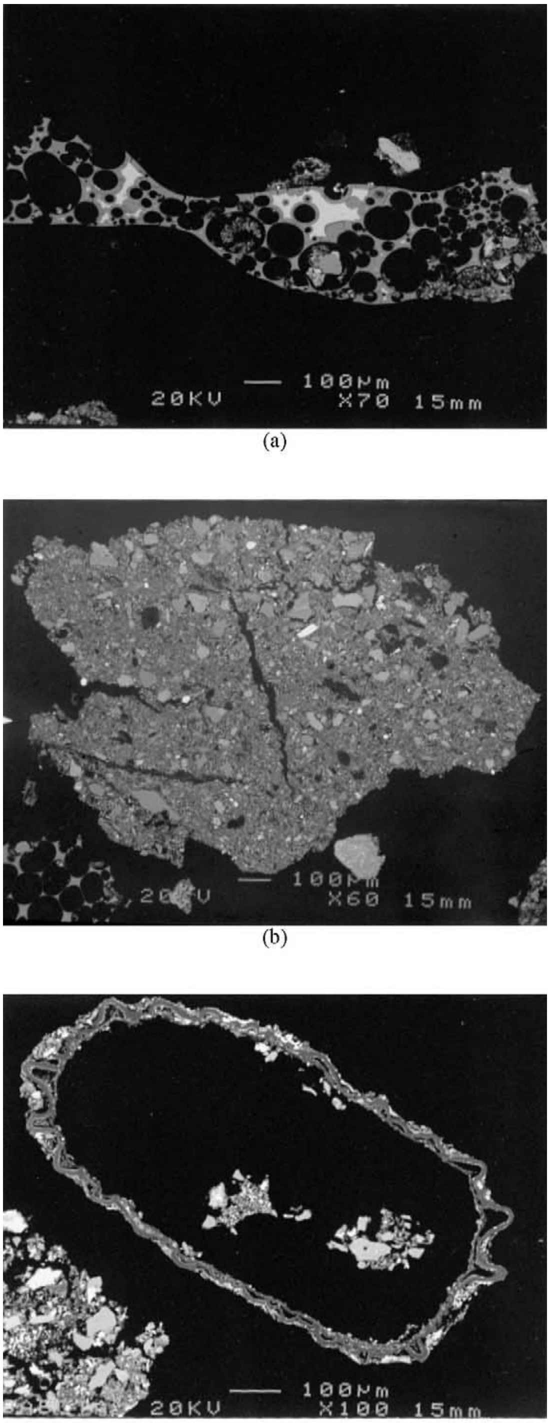

Fig. 5. SEM backscatter images of sand-sized material from the lower part of the Erandio core (at −47 cm depth); (a) shows a smelt product, (b) a complex sand-sized grain consisting of metal-rich particles (5– 40 μm size) contained in a silicate matrix, and (c) an anthropogenic particle rich in S, Fe, Cr, and Zn.

4.2. Site 2: The Hamble estuary, Southampton Water, UK

A 50 cm sediment core was retrieved from the northern part of the Bunny Meadows site in an area of former land-claim, dated using ^{210}Pb and ^{137}Cs, and analysed for trace and major elements. Sediments at the study site show a surface, root-rich layer grading into grey silty-clay, with some orange-brown mottling (Fig. 6). An organic-rich layer, with LOI^{450} values of up to 40%, occurs at −30 cm depth and extends over a distance of at least 50 m across the site. This organic-rich horizon is not as well-defined in the core analysed, but is still observable at −30 cm depth. Based on ^{210}Pb dating, the surface of this organic-rich layer corresponds to a date of ca. 1935 (Fig. 6, see below). Preliminary pollen data indicate a considerable increase in water meadow and cultivated pollen taxa in this horizon (authors unpublished data). Therefore, this layer is likely to be the land-claim surface, i.e. the land surface formed during the most recent phase of historical land-claim in the area, prior to seawall breaching in 1930. Below this organic-rich layer, sediments are grey-black, indicating presence of Fe-sulphides and consequently more reducing conditions than in the upper layers.

^{210}Pb shows a general exponential-type decline with depth, while ^{137}Cs shows a broad subsurface maximum between −5 and −20 cm depth (Fig. 6). For both radionuclides, observed activity maxima are not coincident with peaks in the redox-sensitive elements Fe, Mn and S, indicating little modification of radionuclide

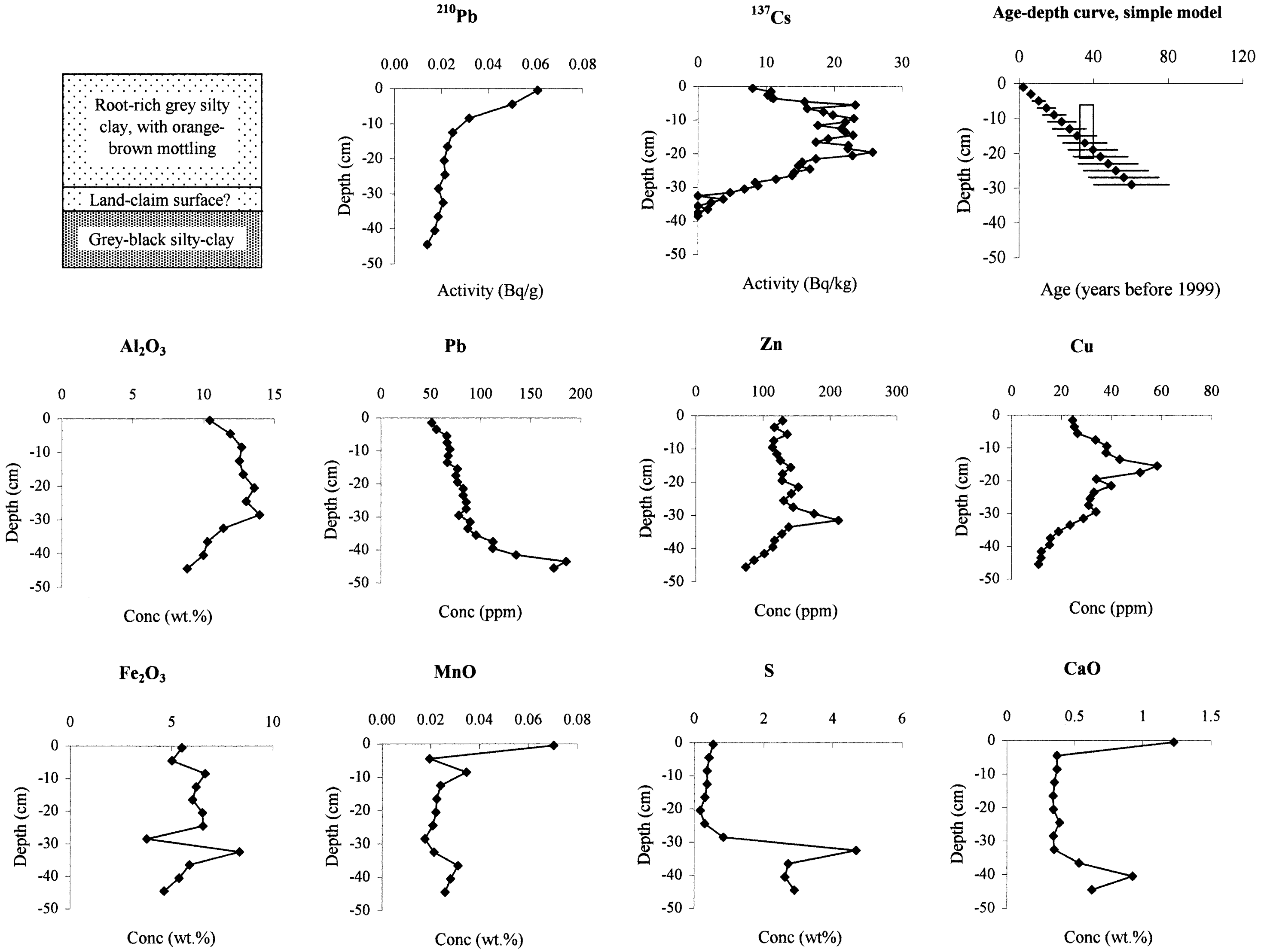

Fig. 6. Distribution of selected radionuclides and trace and major elements in the Bunny Meadows core, Southampton Water. An age–depth curve is also shown, based on ^{137}Cs and ^{210}Pb dating (the open rectangle represents the age derived from ^{137}Cs dating).

distributions by early-diagenetic processes. Based on the simple model of ^{210}Pb dating (Robbins, 1978), the sediment accumulation rate in the top 30 cm of the core (above the proposed land-claim surface) averages 4.8 mm/a (95% confidence interval = 3.5–7.2). This rate of accretion is slightly lower than those observed by Cundy and Croudace (1995a) using ^{210}Pb dating in non-reclaimed, open marshes near the Bunny Meadows site (5.2–8.4 mm/a), but is comparable to rates observed in other marshes around Southampton Water (e.g. Cundy and Croudace, 1996). Based on the ^{210}Pb -derived sediment accumulation rate, the broad subsurface ^{137}Cs maximum corresponds to an age range of 1957–1985. Peak input of ^{137}Cs occurred to the Hamble area in 1958–1963 (from atmospheric weapons testing). The Chernobyl incident in 1986 produced a much less significant input of ^{137}Cs to this area, while inputs from the COGEMA/La Hague and Sellafield nuclear facilities are not identifiable in Southampton Water sediments (e.g. Cundy et al., 1997). Hence, the broad age-range of the ^{137}Cs peak indicates either upward diffusion of ^{137}Cs through the sediments, or more likely, continued inputs of ^{137}Cs to the Bunny Meadows marsh due to reworking of ^{137}Cs-contaminated sediment from nearby intertidal areas which are clearly eroding (Cundy and Croudace, 1995a).

The heavy metals Pb, Cu and Zn show markedly different distributions with depth (Fig. 6). Lead shows a maximum concentration of 185 ppm at −43 cm depth, declining towards the saltmarsh surface, while Zn shows minimum concentrations at −43 cm but a pronounced maximum in concentration (213 ppm) at −31 cm. Copper shows a maximum in concentration at −15 cm. The concentrations of each element throughout the core are significantly higher than local background concentrations (observed in mineralogically-similar, local, pre-industrial sediments, where Pb = 24 ppm, Cu = 15 ppm, and Zn = 74 ppm, Croudace and Cundy, 1995). The variations in metal concentration are not an artefact of varying grain size, as they are still present after normalising to Al (a reliable grain-size indicator in sediments from this area, Cundy and Croudace, 1996), but may be partly due to early-diagenetic processes. The reported extent of early-diagenetic remobilisation in saltmarshes varies significantly between sites. Many authors report little remobilisation, allowing reconstruction of contaminant trends (e.g. Bricker, 1993; Cundy *et al.,* 1997, 1998; Lee and Cundy, 2001), whereas Zwolsman et al. (1993) and Cundy and Croudace (1996) report significant modification of elemental distributions in some saltmarshes via early-diagenesis. The radionuclides used for dating may also be mobilised under some environmental conditions (e.g. ^{137}Cs— Sholkovitz et al., 1983; Cochran et al., 1998, ^{210}Pb—see Urban et al., 1990), although this is not apparent in the sediments examined here. In the Hamble core, S shows a pronounced increase below −30 cm depth, at the elevation of the proposed land-claim surface and corresponding to the colour change to grey-black observed in the cored sediments. High S/Cl ratios (greater than 3) below −30 cm depth indicate enrichment of S by early-diagenetic processes, due to the precipitation of insoluble metal sulphides following bacterially-mediated SO_4^{2-}-reduction (e.g. Pye et al., 1997). Calcium, and to a lesser extent Fe, are also enriched in these deeper sediments. The increase in Ca may be due to secondary carbonate mineral formation, following the increase in alkalinity caused by SO_4^{2-}-reduction reactions (e.g. Pye et al., 1997; Zwolsman et al., 1993) while the increase in Fe is most likely due to (co)precipitation as Fe-sulphides or Fe-carbonates. Zinc (and Ni, not shown) shows a near co-incident peak in concentration at the depth where S begins to strongly increase, indicating (co)precipitation of Zn with sulphides. Lead shows greatest enrichment in sediments at the base of the core, significantly below the peaks in the other heavy metals. Lead concentrations then show a progressive decline towards the sediment surface. The peak in Pb at the base of the core pre-dates the period of major industrial expansion in Southampton Water, and is not consistent with Pb profiles observed elsewhere in Southampton Water (e.g. Cundy and Croudace, 1995a; Cundy et al., 1997). Its position in the SO_4^{2-}-reduction zone indicates that the peak may have an early-diagenetic rather than anthropogenic origin, although without Pb isotopic and/or sequential extraction studies it is difficult to confirm this. On the basis of the solid phase geochemical data it appears that temporal trends in Pb and Zn input cannot be reliably reconstructed using this core as the profiles of both metals may have been significantly affected by early-diagenetic processes. In contrast, the maximum in Cu concentration at −15 cm depth is not co-incident with any peaks in redox-sensitive elements (S, Mn, Fe) (Fig. 6). The main anthropogenic contributor of Cu to Southampton Water has been the refinery at Fawley, which has used Cu in several treatment processes. Significant discharges of Cu into Southampton Water occurred following the development and expansion of the refinery in the 1950s. The Cu peak observed here at −15 cm depth dates to ca. 1968 (based on the ^{210}Pb-derived sediment accumulation rate of 4.8 mm/a), corresponding to the period of peak Cu output from Fawley. This peak, and the subsequent decline in Cu at shallower depths caused by reduced Cu inputs after 1970, is consistent with Cu profiles observed by Cundy and Croudace (1995a) in nearby open, non-reclaimed saltmarshes. Hence, the salt marsh core from the Bunny Meadows site provides a partial record of changing Cu inputs over time, despite major sedimentary changes following seawall abandonment in 1930, and possible modification of other elemental profiles by early-diagenetic processes.

4.3. Site 3: The Mulinello estuary, Sicily

A sediment core was collected from a small channel-side saltmarsh, adjacent to the recently-constructed port access road, dated via ^{210}Pb and ^{137}Cs, and analysed for heavy metal, pollen and diatom content. Full details are given in Cundy et al. (1998). The ^{210}Pb$_{excess}$ activity distribution with depth at this site indicates considerable variation in sediment accretion over time i.e. rather than showing an approximately exponential decline with depth, there is an abrupt decrease in ^{210}Pb$_{excess}$ activity at -9 cm, with an increase in activity between -11 and -15 cm (Fig. 7). An age-depth curve calculated using the CRS (Constant Rate of Supply, Goldberg, 1963) model of ^{210}Pb dating indicates an initial accretion rate of ca. 0.7 mm/a (over the period ca. 1880 to 1940) increasing to 4.3 mm/a over the period ca. 1945–1965. The errors in the age depth curve over this period mean that sediment accretion could have been more rapid than this, although it is unlikely that sedimentation was instantaneous (due, for example, to direct dumping of material on the marsh surface) due to the well-defined shape of the ^{137}Cs peak in this section of the core (Fig. 7). A distinct maximum in ^{137}Cs activity occurs at 13–15 cm depth, most likely derived from the 1963 period of peak fallout from atmospheric weapons testing (NB the remote position of Sicily relative to the Chernobyl releases in 1986, and the rapid drop in activity to zero below this peak indicate a weapons testing, rather than a Chernobyl, source). There is a discrepancy between the ^{137}Cs-derived age and the ^{210}Pb-derived age over this section of the core (1963 via ^{137}Cs and ca. 1950 via ^{210}Pb), which is most likely due to variations in sediment source and composition influencing both the flux of ^{210}Pb$_{excess}$ to the marsh and the supported ^{210}Pb activity (both of which may slightly affect ages given by the CRS model—see Cundy et al., 1998 for full discussion). Despite this discrepancy, the age-depth curve clearly shows considerable variation in sediment accumulation rate. Post-1965 (i.e. above -9 cm, based on the ^{210}Pb date) the average sediment accumulation rate decreased to 3.4 mm/a, and has shown little variation between 1965 and present, even though this has been a period of extensive local port and industrial development (Mountjoy, 1970). In particular, road construction and port development has taken place at the rear of the marsh within the last decade, although this seems to have had little effect on sedimentation.

Heavy metals are not enriched in near-surface sediments (Fig. 7), despite rapid industrial expansion in Augusta Bay since 1965. This indicates limited inwash of contaminated sediments from Augusta Bay, an idea that is consistent with a lack of marine planktonic forms in diatom assemblages from this site (Cundy et al., 1998). With the exception of Pb, maximum fluxes of heavy metals (including those characteristic of refinery/petrochemical industry effluent such as Cu, Ni and Zn) occur over the period ca. 1945–1965, before major industrialisation. The strong similarity between the vertical distribution of these heavy metals and those of TiO_2, Fe_2O_3 and MnO (which, in this area, are likely to be dominantly detrital, rather than anthropogenic) indicates that the increased flux is due to a change in detrital input, rather than pollution. A change in sedimentation over this period is supported by palynological data, which indicate a collapse in local halophytic vegetation and an increase in terrestrial, mainly catchment-area, taxa (Cundy et al., 1998). The most likely cause of this change in pollen types was inundation by sediment-laden fresh water from the adjacent channel of the Mulinello, possibly due to flooding from contemporaneous storm events (Cundy et al., 1998). The marked change in heavy metal flux over this period may be a result of increased input of heavy metal-rich alluvial deposits, derived from basic igneous and volcanic sequences in the Mulinello catchment. In contrast, total Pb flux shows little relationship with TiO_2, Fe_2O_3 or MnO, increasing from 1 mg/cm^2/a to 20 μg/cm^2/a between 1950 and 1970, with a slight decrease to 14 μg/cm^2/a at the sediment surface. The increased Pb flux is probably due to increased road traffic following industrial and port construction, and is comparable to fluxes observed in other industrialised coastal areas (e.g. Bricker, 1993; Cundy et al., 1997; Lee and Cundy, 2001).

Despite extensive modification of saltmarshes and intertidal areas in the Mulinello by historical salt working, recent port development and road construction around the study site, the small channel-side marsh area sampled provides an excellent record of changing heavy metal inputs and vegetational changes over the last ca. 100 a. The interpretation of environmental changes at this site, however, is made significantly easier by using a range of environmental indicators, i.e. combining radiometric, geochemical and palynological/microfossil analyses.

5. Discussion

While undisturbed saltmarsh environments and subtidal areas have typically been used to reconstruct historical pollution trends in estuaries, one of the above examples (the Mulinello estuary) shows that excellent records may be obtained for some contaminants using heavily-disturbed intertidal sites—in the case of the Mulinello despite major sedimentary changes associated with salt working and extensive recent port development and land claim. At the other sites, though, past trends in contaminant input cannot be accurately reconstructed. This is due to possible early-diagenetic remobilisation and the effects of land claim/abandonment (in Southampton

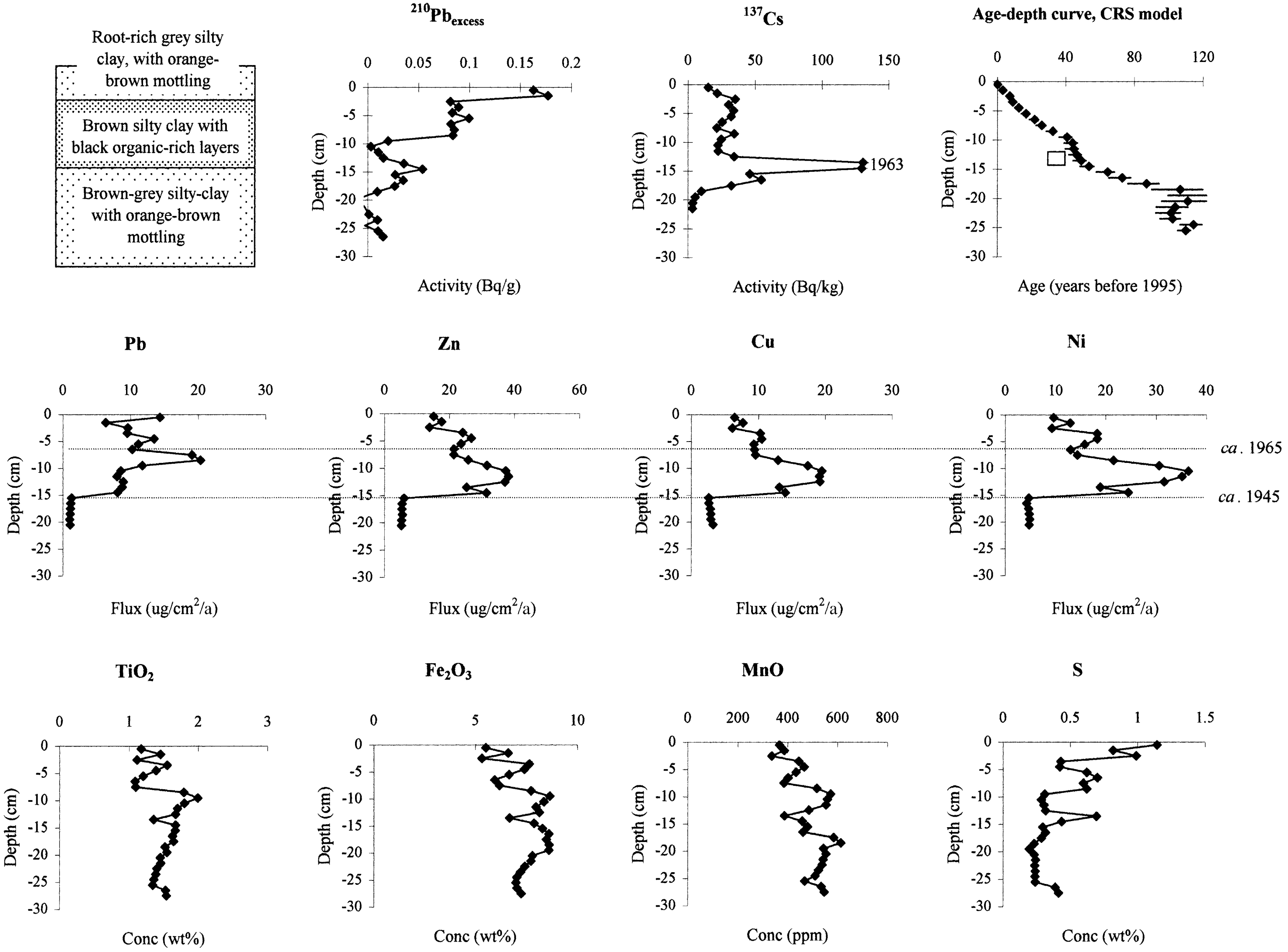

Fig. 7. Distribution of selected radionuclides and trace and major elements in the Mulinello salt marsh, Augusta Bay. An age-depth curve is also shown, based on ^{137}Cs and ^{210}Pb dating (the open rectangle represents the age derived from ^{137}Cs dating).

Table 1
Types of ^{210}Pb and ^{137}Cs profile observed in estuarine, coastal and nearshore sediments, and their relationship to site characteristics

Geochemical profile type	Site type	Examples	Causes
Ideal	Salt marshes, subtidal sediments and intertidal flats with a relatively uniform fine-grained composition.	Southampton Water (Cundy et al., 1997), Tees estuary (Plater et al., 1998).	Constant sediment accumulation rate of > ca. 3 mm/a, limited mixing and bioturbation.
Smoothed (*e.g. site 2, Hamble estuary, Southampton Water*)		Forth estuary (MacKenzie et al., 1994), Severn estuary (French et al., 1994), Poole harbour (Cundy and Croudace, 1996), Tees estuary (Plater et al., 1998), Humber estuary (Lee and Cundy, 2001).	Pre-depositional and post-depositional mixing (the former through marine, riverine or in-estuary mixing, the latter through physical mixing and bioturbation).
Interrupted/truncated (e.g. *site 3, Mulinello estuary*)	Sites subject to tsunami, storm surges, river flooding, dredging, historical land-claim, clay digging etc.	Southampton Water (Croudace and Cundy, 1995), Aegean Sea (Dominey-Howes et al., 2000), Isle of Sylt (Kirchner and Ehlers, 1998).	Rapid changes in sediment supply and/or energy conditions.
Erosional /non-accreting	Eroding intertidal and subtidal areas; continuously dredged sites; areas of no net accretion	Severn estuary (Kirby and Parker, 1980), Southampton Water (Cundy and Croudace, 1995a).	Prolonged sediment erosion or sediment removal, or no net vertical accretion.
Linear/erratic (*e.g. site 1, Bilbao estuary*)	Sites subject intense mixing and resuspension or clay/bait digging; intertidal and subtidal flats with sand and clay intercalations; immature, rapidly accreting salt marsh environments.	Severn estuary (Kirby and Parker, 1980), Ganges delta (Goodbred and Kuehl, 1998), subtidal Rhone delta (Radakovitch et al., 1999), Humber estuary (Andersen et al., 2000), Dollard estuary (Andersen et al., 2000).	Vigorous mixing and reworking; large-scale compositional variations; extremely rapid sediment accumulation rates (cms/a).

See text for discussion.

Water), and sediment reworking and large-scale variability in sediment composition over time (in the Bilbao estuary).

The vertical distribution of ^{210}Pb and ^{137}Cs observed at the sites discussed here, and at other estuarine sites, can be grouped according to profile shape (Table 1). "Ideal" profiles are those in which the ^{210}Pb$_{\text{excess}}$ activity vs. depth distribution approximates to an exponential curve (allowing its solution by the simple model of ^{210}Pb dating, i.e. there has been a constant influx of ^{210}Pb and a constant sediment accumulation rate), and the ^{137}Cs activity vs. depth distribution shows distinct peaks in activity corresponding to periods of peak ^{137}Cs fallout or discharge. In the sites discussed above these peaks correspond to 1963 (maximum fallout from above-ground weapons testing) and 1986 (the Chernobyl accident). Provided that a small sampling increment (1 cm or less) is used, these peak inputs can be clearly distinguished as subsurface maxima in accreting sediments. These "ideal" profiles may be observed in laminated (non-bioturbated) subtidal sediments and in saltmarsh settings where accretion rates are $>$ 3 mm/a and bioturbation is minimal (Valette-Silver, 1993), and allow a high-resolution chronology of contaminant inputs to be determined (e.g. Cundy et al., 1997; Plater et al., 1998). Slightly more active sediment mixing (either within the estuary before deposition, or after deposition via bioturbation or physical mixing) may give a "smoothed" profile, where subsurface ^{137}Cs maxima are broadened (e.g. the Southampton Water site in the present study), and the heavy metal distribution with depth represents a time-integrated record of metal inputs. These profiles have been observed in saltmarsh, mudflat and subtidal settings which have relatively uniform sediment composition (e.g. MacKenzie et al., 1994; French et al., 1994; Cundy and Croudace, 1996; Plater et al., 1998; Lee and Cundy, 2001), and provide useful information on general contaminant loading in estuaries and its variation over time. Rapid changes in energy conditions within an estuary, either naturally (through tsunami, storm surges, river flooding events etc.) or through anthropogenic activity (dredging, historical land claim/abandonment) may give rise to an interrupted or truncated profile, as at the Mulinello estuary, Sicily (see also Croudace and Cundy, 1995; Kirchner and Ehlers, 1998; Dominey-Howes et al., 2000). Changes in sediment accumulation rate caused by rapid addition or removal of sediment produce inflections in the ^{210}Pb$_{\text{excess}}$ profile, and can be identified through the use of ^{210}Pb dating models such as the CIC and CRS models (e.g. Appleby and Oldfield, 1992). Variable sediment accumulation rates, however, may produce a complex distribution of ^{137}Cs and metal contaminants with depth. For example, a maximum in heavy metal concentration may simply be due to a slower sediment accumulation rate, rather than an increase in pollutant discharge. Hence, in any area where the rate of sediment accumulation has varied significantly over time, the use of concentration or activity data alone may be misleading. This effect is removed by calculating fluxes, which take into account variations in sediment accumulation rate (e.g. Croudace and Cundy, 1995). Once fluxes, rather than concentration data, are considered, settings subject to changing energy conditions/sediment accumulation rates may retain a high-resolution record of environmental change and changes in metal loading over time.

An extreme case of an interrupted or truncated profile is produced where prolonged erosion or repeated dredging has completely removed recent sediments, exposing older deposits (an erosional/non-accreting profile, Table 1). At these sites, ^{137}Cs and ^{210}Pb$_{\text{excess}}$ may be absent, or present only at the sediment surface, with a rapid decline to zero activity within the top few cms (e.g. Kirby and Parker, 1980; Cundy and Croudace, 1995a). The same profile may be observed at sites where there is no net sediment accretion, i.e. at locations where the rate of vertical accretion is equal to the rate of erosion, such as intertidal sites where a resistant, older, eroded surface is periodically covered and uncovered by tidally-supplied sediment. The lack of sediment accumulation means that it is not possible to examine recent trends in contaminant input using these sites.

Finally, vigorous mixing and reworking of sediments, extremely rapid accretion rates, or large-scale compositional variability (or a combination of these) may produce "linear" or "erratic" profiles, such as those observed in the Bilbao estuary (see also examples in Kirby and Parker, 1980; Goodbred and Kuehl, 1998; Radakovitch et al., 1999; Andersen et al., 2000). The ^{137}Cs and ^{210}Pb distributions with depth may be similar in each sediment core, and also show a good correlation with grain size proxies such as ^{40}K. At these sites, the vertical distribution of ^{137}Cs and ^{210}Pb (and heavy metal pollutants) is controlled by input on reworked sediment particles and by variations in sediment composition, rather than by atmospheric fallout. The extent to which recent environmental changes and historical contaminant input can be reconstructed at these sites is limited. Sediments may be dated as pre- or post-1954 (the date of first widespread release of ^{137}Cs in the northern hemisphere) on the basis of presence or absence of ^{137}Cs, but the lack of clear subsurface maxima in ^{137}Cs activity and the lack of decline of ^{210}Pb with depth preclude more accurate dating of the sediment sequence.

6. Conclusions

When ^{137}Cs and ^{210}Pb distributions with depth allow a chronology of sediment deposition to be established, and early-diagenetic remobilisation has been minimal, mudflat and saltmarsh cores from even the most heavily-disturbed estuarine sites can provide useful information on historical contaminant input. For example, analysis of a core from the Mulinello estuary, Sicily, allowed a high-resolution reconstruction of temporal changes in heavy metal input to be made, despite major sedimentary changes associated with salt working and extensive recent port development and land-claim. Using geochemical analyses in combination with other environmental reconstruction techniques, such as pollen analysis, foraminiferal analysis etc. can considerably improve the interpretation of the sedimentary record at these sites. As illustrated by the Bilbao study, the use of mineralogical and SEM studies in combination with bulk geochemical analysis is particularly important in assessing whether metal input is via wash-in of detrital material, dumping of slag products or sorption onto fine-grained suspended material, and so whether metals are present in a form that is susceptible to physical or chemical reworking. The use of ^{137}Cs and ^{210}Pb in combination, alongside other independent dating techniques where possible, is also advisable to confirm dates and fully assess sediment accumulation, mixing and erosion processes. Where sediments have been vigorously mixed or reworked, large-scale compositional variations are present, or significant early-diagenetic remobilisation has occurred, however, only limited information on the general scale of contamination can be obtained using intertidal sedimentary records.

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