The fate of contaminants and stable Pb isotopes in a changing estuarine environment: 20 years on.

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ABSTRACT.

Estuarine sediments provide an important sink for contaminants discharged into fluvial, estuarine and nearshore settings, and numerous authors have utilised this trapping function to assess historical contaminant loadings and contaminant breakdown/transformation processes. This paper examines the retention of elemental and isotopic sedimentary signatures in an industrialised estuarine system subject to a strongly upward sea-level trend, over a 20 year period. Two contrasting salt marsh sites (at Hythe and Hamble, part of the wider Southampton Water estuarine system, UK) were examined, which had been previously cored and analysed in the early 1990s. Much of the geochemical record of recent anthropogenic activity has been eroded and lost at the Hamble site. In contrast, radiometric, isotopic and elemental records of anthropogenic activity have been retained in the Hythe marsh, with ^{137}Cs and Cu depth profiles showing retention of input maxima related to fallout and local industrial discharges, respectively. Stable Pb isotope data show a broad degree of correspondence in cores analysed in 1994 and 2014 when plotted against sediment (radiometric) age, indicating the usefulness of isotopic data in retaining information on Pb sources and in disentangling Pb input histories. New ultrahigh precision, double-spike mass spectrometry stable Pb isotope data allow clearer discrimination of historical Pb input phases, and highlight within-estuary mixing and supply of reworked, secondary contamination from erosion of anthropogenically-labelled sediments elsewhere in the estuary.

Introduction.

Estuarine sediments provide an important sink for contaminants discharged into fluvial, estuarine and nearshore settings. Numerous authors have utilised this trapping function to reconstruct historical trends in contaminant input using undisturbed sediment cores from salt marshes, mudflats and other low-energy settings worldwide (e.g. *[1-9]*), allowing assessment of historical contaminant loadings, contaminant breakdown or transformation processes, early-diagenetic and other remobilisation processes, and the effectiveness of local contaminant reduction and management strategies. The derivation of contaminant chronologies or "pollution histories" using the records contained in estuarine sediment cores has been well-established as an approach for over 40 years. Such work however has generally involved one-off or short-term coring campaigns, with much less attention paid to how the contaminant signature retained in the sediments may change over longer time (decadal) scales, particularly under a predominant regime of rising sea-level. This is important firstly in understanding the "chemical taphonomy" (or retention/fossilisation) of estuarine contaminant signatures as a long-term environmental archive for monitoring purposes, whereby changes in water level and redox boundaries (e.g. under rising sea-level), organic matter breakdown, or water flow or leaching within the sediment column, may act to remobilise previously adsorbed or stabilised contaminants. In addition, due to regulatory changes, technological development and/or industrial decline, in many regions contaminant discharges are now significantly reduced over their previous (historical) levels, and estuarine sediments may act as an important secondary source of contaminant exposure to local ecosystems. Here, we examine the retention of heavy metal, radiometric and stable isotope contaminant signatures in two salt marsh systems from the highly developed and industrialised Southampton Water system, southern UK. Our earlier coring studies in the early 1990s (*[4,5,10]*)

showed the retention of distinct Cu, Pb and stable Pb isotope, and other heavy metal profiles in undisturbed (dated) salt marsh, mudflat and subtidal cores, which could be correlated with (a) historical discharges from the sizeable Esso oil refinery at Fawley and associated petrochemical industries, and (b) general industrial and urban activity around the wider estuarine system. In this study, we examine the retention of these geochemical and isotopic profiles 20 years on, following further coastal development and under a strongly upward regional sea-level trend (of 2 – 4 mm/y *[11,12]*), to assess the extent to which these temperate marsh sediments provide a long-term archive of contaminant inputs under changing physical, chemical and biological conditions. In particular, we utilise two new methods for assessing the timing, scale and source of anthropogenic inputs, previously applied in lacustrine sediments *[13]*: Non-destructive, high-resolution (200 μm scale) Itrax™ micro-X-ray fluorescence and microradiographic analysis *[14]*, to identify fine scale compositional change (e.g., seasonal contaminant inputs and sedimentary changes), validated against conventional wavelength dispersive X-ray fluorescence (WD-XRF); and high-precision double-spike lead isotope measurements, which offer *ca*. 10 times the precision of conventional single spike methods, to examine multisource inputs of lead *[15]*.

Study sites

Two salt marsh sites were sampled in 2014, which had been cored previously by the authors in the early 1990s (Figure 1). The first site was a mixed marsh system at Bunny Meadows in the Hamble estuary (the site of multiple cores reported in *[10]*), located seaward of a prominent sea-wall which prevents landward marsh expansion. A core was taken from a remnant and fragmented *Halimione portulacoides*-covered salt marsh stand, landward of an isolated *Spartina* sp.-dominated area, within 2-5 m of a previous core collected in 1993 (core 1, *[10]*). Much of the area seaward of the coring location was *Enteromorpha* sp. covered, with isolated mounds of former (eroded) saltmarsh present. The second site cored was an extensive *Spartina* sp. and *Halimione portulacoides*-dominated marsh system at Hythe, on the western shore of Southampton Water, 1 – 2 km NW of the chemical industrial complex and Esso oil refinery at Fawley *[5]*. A core was taken 9 m from the main creek edge, from a *Halimione portulacoides*-dominated marsh terrace, within 10 m of a core collected in 1992 (reported in *[5]*). Edge erosion is apparent at the seaward edge of the marsh and on creek banks, with prominent overwashed shell accumulations on the seaward cliffed edge of the marsh, although the coring site is apparently undisturbed.

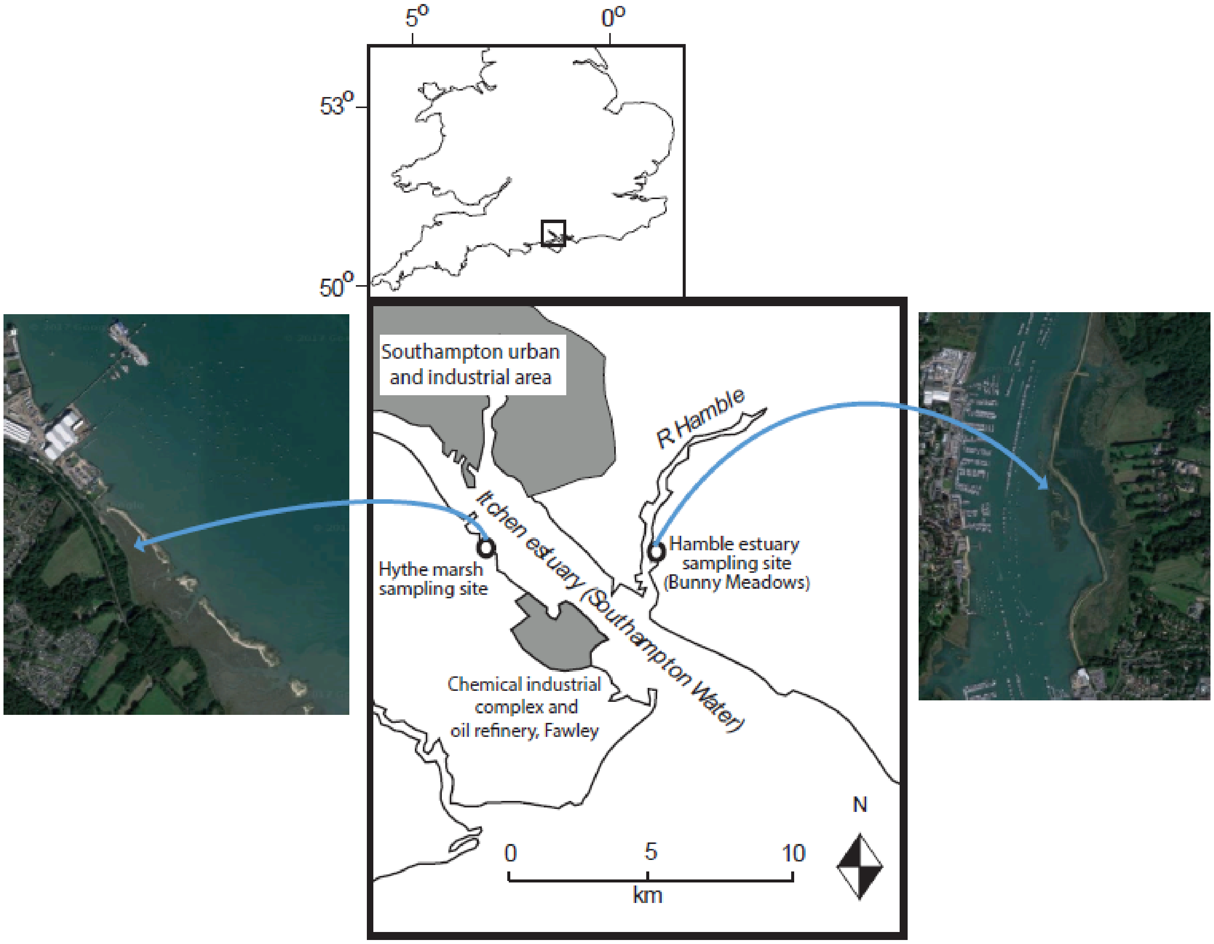


Figure 1. Study area: Southampton Water and the Hamble estuary, southern U.K. Aerial photographic images (source: google.co.uk, 2017) show detail of marsh areas sampled.

Materials and Methods.

Following field sampling, cores were returned to the laboratory and sliced vertically, and divided into 1cm or 2cm depth increments. Following drying, sediment sub-samples were analysed via XRF and digested for ICP-MS analysis. Radiochronology via ^{210}Pb and ^{137}Cs was used to determine sediment accumulation rates. ^{210}Pb activity was determined through the measurement of its granddaughter ^{210}Po using alpha spectrometry. The Constant Flux−Constant Sedimentation (CF:CS) model of ^{210}Pb dating used to determine sediment accumulation rates, where the sedimentation rate is calculated by plotting the natural logarithm of the unsupported ^{210}Pb activity against depth, and determining the least-squares fit. This model assumes that both the flux of unsupported ^{210}Pb to the sediment and the sedimentation rate are constant, which has been shown to provide a valid approximation to actual conditions in Southampton Water and surrounding marsh systems *[5,10]*. The ^{137}Cs activity of samples (sampled at 1 cm resolution) was determined using a Canberra well-type HPGe gamma-ray spectrometer (counting for 100000 s).

Cores collected in 2014, following vertical slicing, were cleaned and analysed using an Itrax^{TM} micro-XRF core scanner (step size 200 µm, counting time 30 s, Mo anode X-ray tube, XRF conditions 30 kV, 50 mA) in accordance with methods detailed in *[13]*. Cores were then sectioned at 1 cm intervals, sediment sub-samples freeze-dried, and subsequently analysed by WD-XRF using a Philips Magix-Pro WD-XRF fitted with a 4 kW Rh target X-ray tube. High precision stable Pb isotopic data were acquired using a Thermo Scientific NEPTUNE multicollector ICP-MS, using methods described in *[13]*. Instrumental mass bias was corrected using the SBL74 ^{207}Pb–^{204}Pb double spike developed at the University of Southampton. Precision of these measurements are nominally 0.1% relative *[15]*. Analytical methods for cores collected in the early 1990s are reported in full in earlier papers *[5,10]*, but in summary here: Major and trace elements were determined using a Philips PW1400 sequential X-ray fluorescence spectrometer system, and Pb isotopic abundances determined using a Fisons Elemental PQZ inductively-coupled plasma mass spectrometer (ICP/MS) following acid leaching and preconcentration on Dowex AG1-X8 resins.

Results and discussion.

Hamble estuary

The Hamble estuary site is now heavily-degraded and eroded from its earlier state and extent in the early 1990s (Figure 2). Cundy and Croudace *[10]* noted, based on ^{137}Cs and ^{210}Pb dating and analysis of Cu profiles in multiple (seven) cores, that in 1993 this marsh was vertically accreting at a rate exceeding local sea-level rise but that the surrounding mudflat areas were eroding. This trend has apparently continued leading to fragmentation and subsequent erosion/collapse of the marsh (Figure 2). Erosion of the former marsh surface is indicated by the presence of basal coarse deposits (flint pebbles and sands) encountered at *ca*. 30 cm depth in the 2014 core, which were not encountered in the earlier 1993 coring survey (where cores exceeding 40 cm core depth were collected), and most likely represent marsh basal deposits dating from an earlier (pre-20th century) period of land claim in the Hamble estuary *[6]*. Comparison of the vertical distribution of heavy metals in the 1993 versus 2014 cores (Figure 3, 1993 data show core 1 from *[10]*, the closest in location to the 2014 core) shows that while notable concentration maxima are present at depth for Cu (at -18cm) and Zn (at -23 cm) in the 1993 data, these are absent in the 2014 data. Cu in particular provides an effective estuary-wide geochemical "marker horizon" in Southampton Water and surrounding estuaries *[5,6,10]*, with its distribution with depth reflecting known inputs from local industrial activities. The main contributor of Cu into Southampton Water historically has been the Esso oil refinery at Fawley *[4]*, and while the discharge pattern of Cu is not known in detail, significant discharges of Cu into Southampton Water occurred following the development and expansion of the refinery from the 1950s. A program of effluent quality improvements was implemented in 1971, after which discharges reduced, leading to the presence of a single subsurface Cu concentration maximum in uniformly accreting marsh and mudflat deposits dating to 1970/1971, which has been used as a sediment dating tool to corroborate radiometric dates in the area (e.g. *[5]*). While Cu concentrations remain above local geogenic background in the upper sections of the 2014 core, a well-defined subsurface Cu maximum is not present. The vertical distribution of Pb also differs strongly between the two cores. Pb concentrations are generally higher in the 1993 core (Figure 3), showing sustained concentrations of > 100 ppm at depths below -15 cm. The 2014 core shows lower concentrations of Pb (although still above local geogenic background), with a single concentration maximum (of 96 ppm) at -15 cm depth. Zn concentrations are close to geogenic background throughout the 2014 core, indicating that Zn and Pb sources (or trapping processes) differ, shown also by an excursion in the Pb/Zn ratio (Figure 3). ^{210}Pb and ^{137}Cs show profiles typical of accreting, relatively undisturbed sediments in the 1993 core, with ^{210}Pb showing a quasi-exponential decline in activity with depth to near-constant activities (of 16-21 Bq/kg) at -19 cm depth which approximate supported ^{210}Pb activities. ^{137}Cs data show a broad subsurface activity maximum at -3 to -13 cm depth, with two peaks in activity at -3 to -5 cm, and -11 cm. The lower maximum likely correlates to the 1963 fallout maximum from above ground weapons testing *[10]*, with a contribution from fallout from the Chernobyl disaster (1986) in upper parts of the core *[5]*. In the 2014 core, ^{210}Pb shows a prominent near-surface maximum in activity, with a rapid decline with depth to supported activities at -3.5 cm, while ^{137}Cs has a relatively erratic profile, with consistently low ^{137}Cs activities (< 6 Bq/kg) periodically observed to -18 cm depth. The radiometric data, coupled with the lack of a Fawley-derived "marker" horizon for Cu (see above, even when coring to basal pebbles and sands), indicate erosion of the sediment column between 1993 and 2014 at this site. The ^{210}Pb surface activity maximum observed in the 2014 core presumably indicates temporary deposition of recent ^{210}Pb-labelled sediment at the sediment surface (similar to that observed in ^{210}Pb profiles from other (net) eroding settings *[6]*), while the residual ^{137}Cs activities are likely to represent a remnant of the deeper parts of the earlier ^{137}Cs profile recorded at the site. If so, this, and the loss of the Cu 1970/1971 concentration maximum, indicates *ca*. 20-25 cm of vertical sediment loss (Figure 3).

Figure 2. Photomontage of the Hamble coring site, showing erosion, fragmentation and collapse of the Hamble marsh between 1993 (lower photograph) and 2014 (upper photograph).

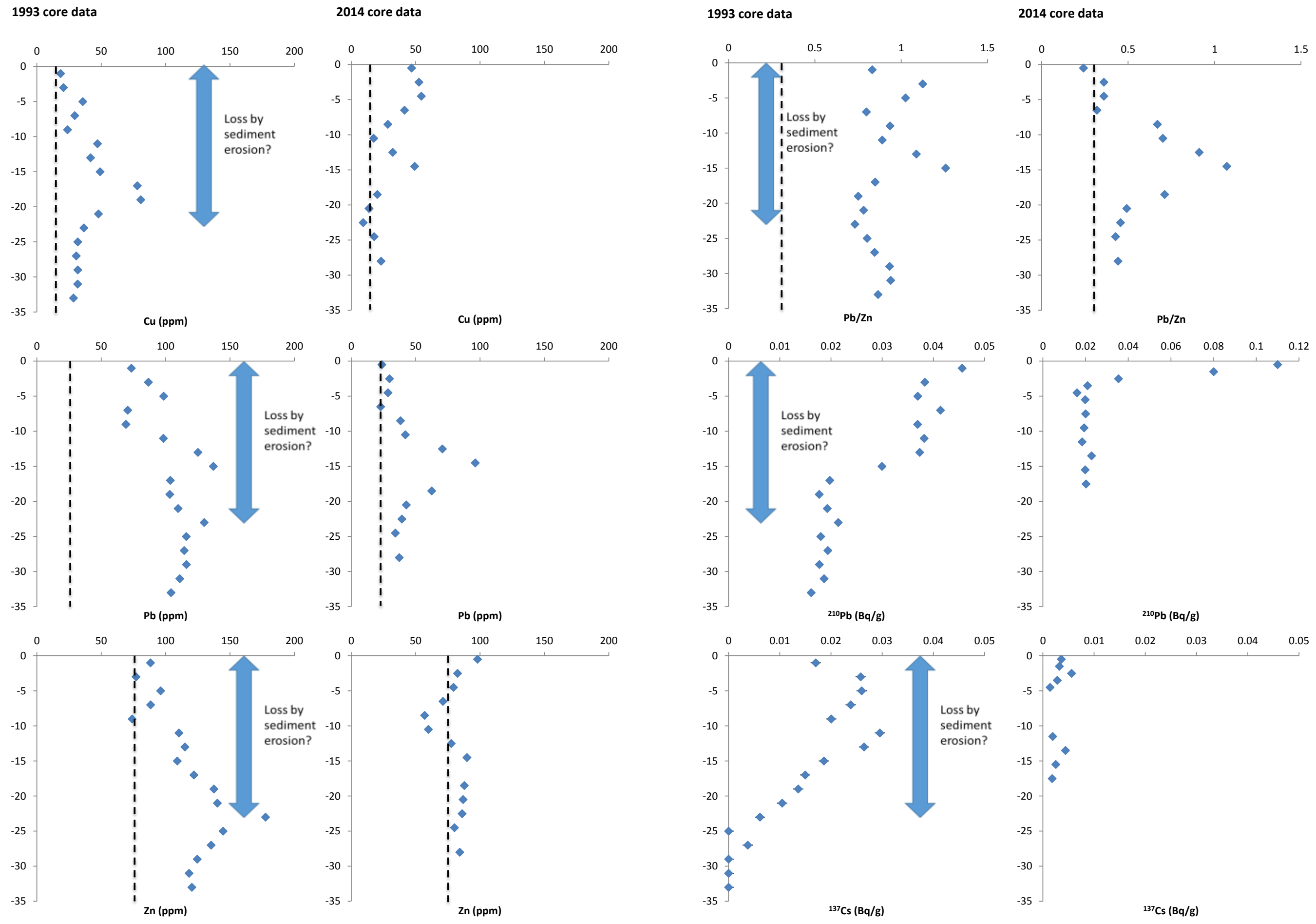


Figure 3. Cu, Pb, Zn, Pb/Zn, ^{210}Pb, and ^{137}Cs distribution with depth (cm, y axes) in Hamble estuary salt marsh, from 2014 coring (right graphs) and 1993 coring (left graphs). 1993 core data from *[10]* and *[19]*. Dashed vertical line on selected graphs shows geogenic background (or supported activity in the case of ^{210}Pb). Local geogenic background concentrations of Cu, Pb, Zn and Pb/Zn are derived from concentrations/ratios measured in mineralogically similar pre-industrial sediments from a subtidal core collected in the main Southampton Water navigation channel *[4]*).

Hythe, Southampton Water

Despite the edge erosion that is apparent at the seaward edge of the Hythe marsh and on creek banks, the area of marsh sampled shows little apparent change from its state when sampled in 1992, although (based on visual observations) the marsh has a greater coverage of *Halimione portulacoides* than previously (at the expense of *Spartina* sp.), possibly reflecting *Spartina* die-back (a phenomenon commonly observed in Southampton Water and in other UK south coast estuaries, e.g. *[16,17]*), slight sediment coarsening, or increased emergence of the marsh surface (with Cundy et al., noting in 1997 that marsh accretion here was 5+ mm/y, exceeding local sea-level rise *[5]*). Non-destructive high resolution Itrax^{TM} core scanning (Figure 4) of the 2014 Hythe core shows a clear vertical zonation in Fe and S (zonation in Mn data is less distinct), and clear maxima in Cu (in the upper, mottled, core section) and Zn (in the lower part of the core). The Itrax-derived Pb profile has a lower signal to noise ratio but records a broad subsurface Pb maximum at *ca*. -28cm depth. An increase in S concentration (and in S/Cl ratio in WD-XRF data, Figure 5, effectively normalising for possible increases in seawater derived-sulphate *[18]*) below -35 cm depth, a clear maximum in Fe concentration between -40 and -60 cm depth (most apparent in WD-XRF data, Figure 5), and the grey-black sediment coloration indicate the development of anoxic conditions at depth in the marsh, resulting in sulphate reduction and precipitation of Fe sulphides. S shows high variability in the Itrax data from lower core sections, with high S concentrations broadly correlating with distinct dark/black horizons in the core image, which represent zones of higher organic carbon content and enhanced sulphide mineral precipitation. Above this sulphate reduction zone, a layer of mottled red-brown sediment (with mottling caused by the presence of (partly-reduced) Fe/Mn oxides and oxyhydroxides) is present (Figure 4) and correlates with reduced Fe and Mn concentrations (most clearly in the WD-XRF data, Figure 5). This reflects a sediment zone subject to a fluctuating water table and periodic shifts from oxidising to reducing conditions during tidal inundation *[10]*. A similar redox zonation was observed by *[19]* and *[20]* in 1992 and 1995 core data from Hythe. Cl and Br data (Figure 4) show a general decline in intensity with depth, reflecting evaporative concentration of seawater-derived Cl and Br in near-surface sediments. Br however is also discharged into Southampton Water from local petrochemical industries which use feedstocks from the Fawley refinery, leading to enhancements in Br intensity in the upper core section above those of Cl (Figure 4). Despite the clear redox zonation in the Hythe 2014 core, there is little evidence for redox-driven migration of contaminants, with Cu and Pb maxima not correlating with apparent redox boundaries in the sediment core, and Pb stable isotope data showing no evidence for migration of Pb in the core (see below). Zn shows enrichment in the lower core sections, particularly around 25 – 50cm depth, above and within the proposed sulphate reduction zone. Two subsurface Zn maxima are resolved by the WD-XRF data (Figure 5), with the upper maximum coincident with the Pb maximum at -28 cm depth. Pb/Zn ratios (which have been used by a number of authors to assess heavy metal source and transport *[21,22]*) are variable with depth through the core, although ratios decline at the position of the lower Zn peak (-44 cm), indicating enhanced input or trapping of zinc over lead in this section of the core. While Cundy and Croudace *[10]* have argued that a fraction of the Pb and Zn supplied to local marshes is labile, it is unclear whether the Zn maximum at -44 cm depth is due to increased Zn input to the marsh, or to early diagenetic remobilisation and concentration by coprecipitation with Fe-sulphides in the sulphate reduction zone (Fe WD-XRF data also record a maximum at this depth, Figure 5). The near-surface decline in Pb/Zn ratio is likely due to reduction in input of Pb from leaded gasoline sources, discussed further below.

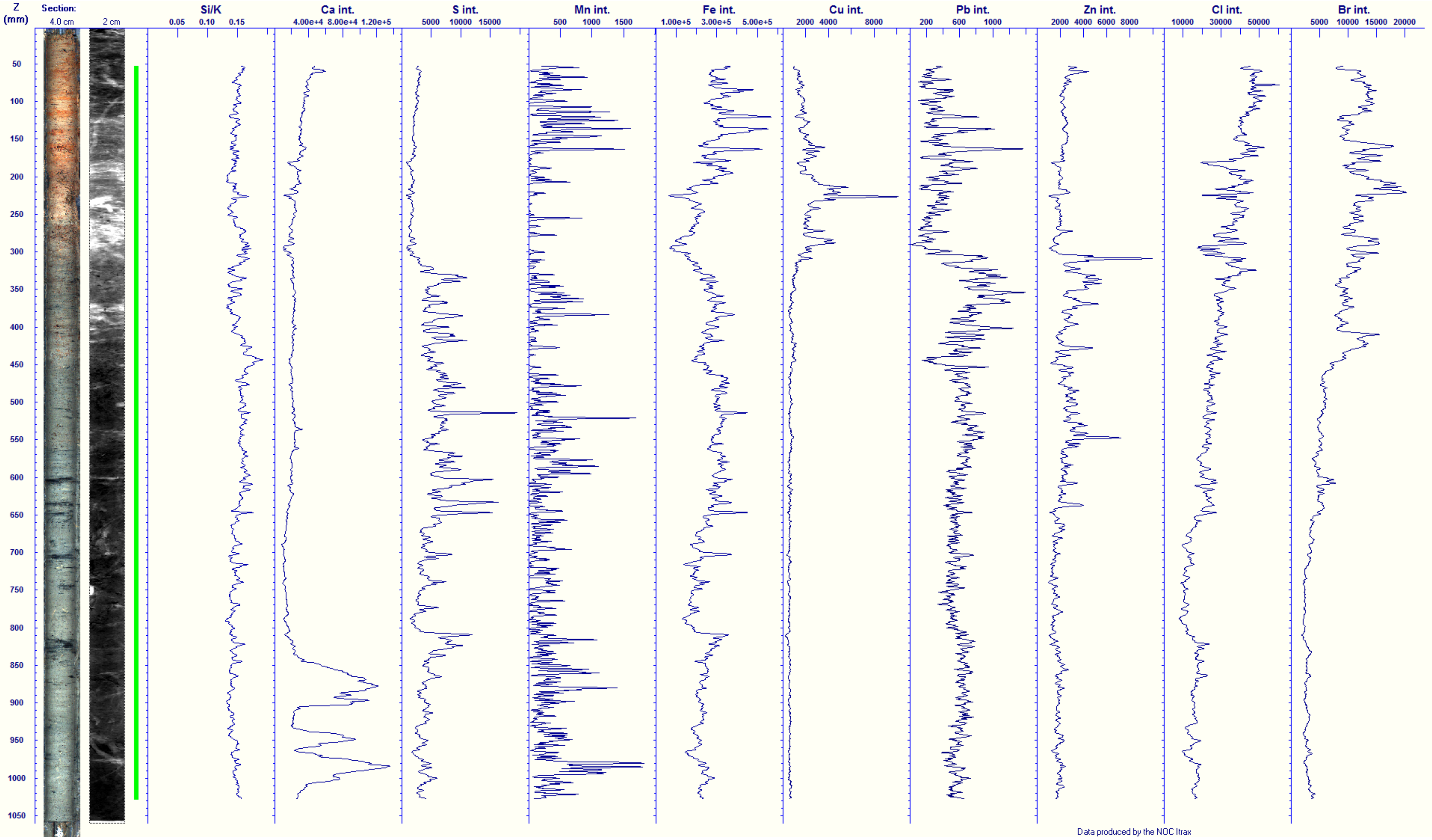
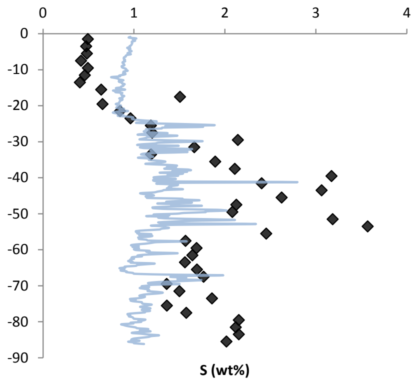
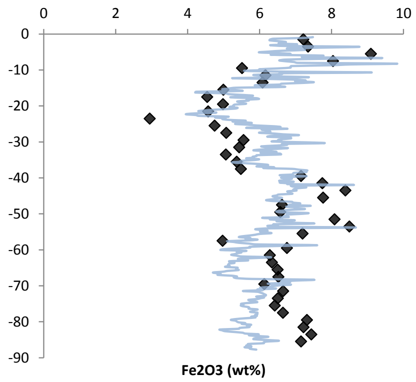
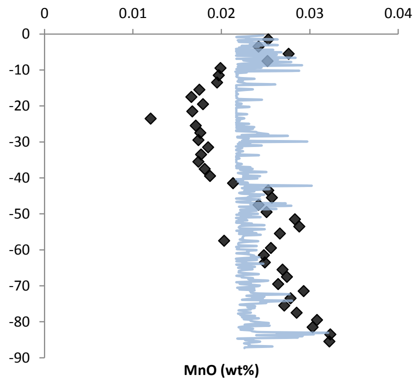


Figure 4. Non-destructive Itrax^{TM} core scanning data, showing elemental response (counts) with depth for major and trace elements in the Hythe 2014 salt marsh core. Left image shows colour photographic scan of the core – note clear colour change from orange-red to grey-black at -30 cm depth. X-radiograph of core is also shown. See text for discussion.


0 1 2 3 4
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
S (wt%)


0 2 4 6 8 10
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
Fe2O3 (wt%)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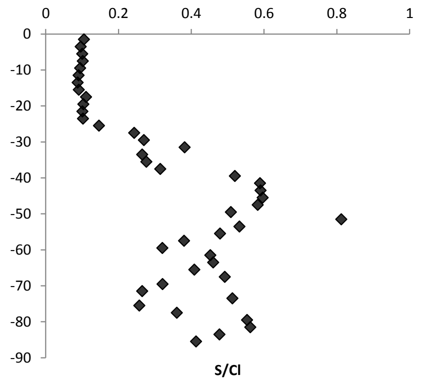
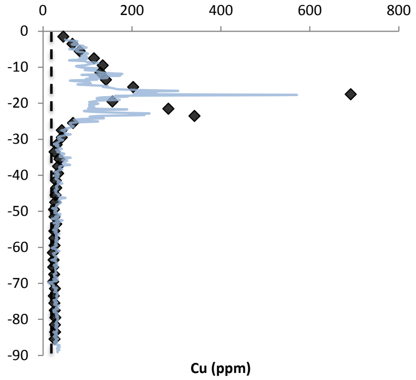
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
MnO (wt%)


0 0.2 0.4 0.6 0.8 1
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
S/Cl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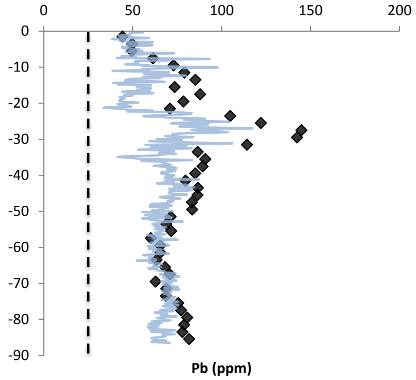
Cu (ppm)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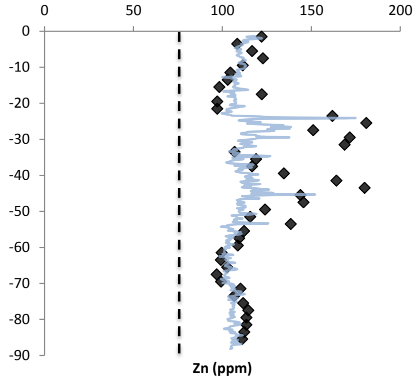
Pb (ppm)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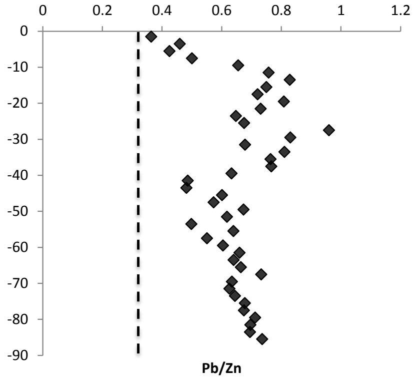
Zn (ppm)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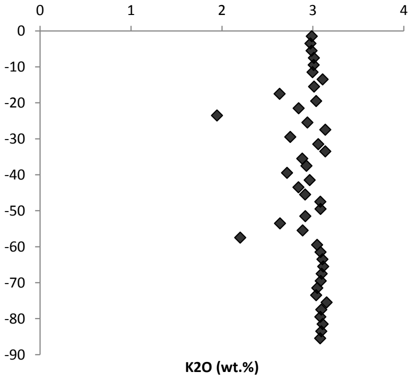
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
Pb/Zn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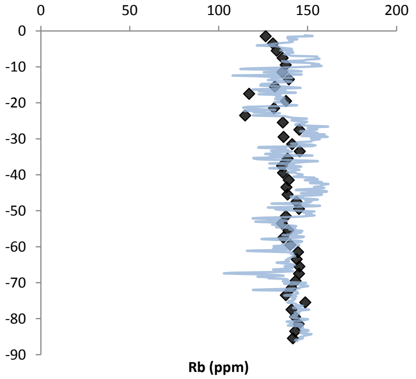
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
K2O (wt.%)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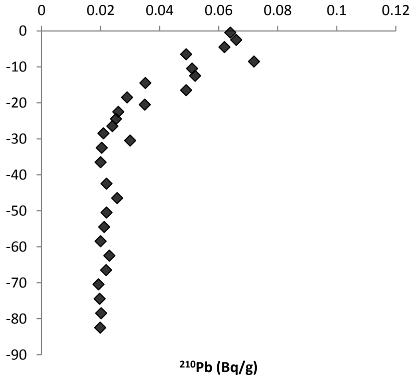
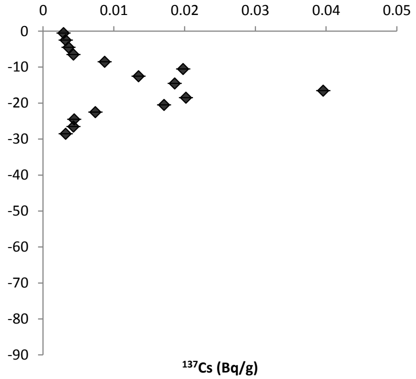
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
Rb (ppm)


0 0.02 0.04 0.06 0.08 0.1 0.12
0 -10 -20 -30 -40 -50 -60 -70 -80 -90
^{210}Pb (Bq/g)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0 -10 -20 -30 -40 -50 -60 -70 -80 -90
^{137}Cs (Bq/g)

Figure 5. S, Fe_2O_3, MnO, S/Cl, Cu, Pb, Zn, Pb/Zn, Rb, K_2O, ^{210}Pb, and ^{137}Cs distribution with depth (cm, y axes) in the Hythe salt marsh core (Southampton Water), from 2014 coring. Itrax^{TM} count data (smoothed, 5 point average) are also shown for comparison for selected elements. Dashed vertical line on selected graphs shows geogenic background (or supported activity in the case of ^{210}Pb). Local geogenic background concentrations of Cu, Pb, Zn and Pb/Zn are derived from concentrations/ratios measured in mineralogically similar pre-industrial sediments from a subtidal core collected in the main Southampton Water navigation channel *[4]*).

The Itrax produces elemental data in counts but numerous studies (e.g. *[13]*) have shown that these data correlate well with quantitative analytical data (e.g., ICP-OES or WD-XRF), and indeed similar trends in heavy metal profile are apparent here in the bulk geochemical (WD-XRF) data (Figure 5) using 1 cm subsamples. The Itrax micro-XRF core scanner however provides continuous, non-destructive, high-resolution elemental profile data, and the high frequency compositional changes identified using the Itrax are often missed when using lower resolution bulk subsamples. In this case, Cu in particular (while still showing a similar trend to that identified using WD-XRF) shows a highly "spiked" profile in the Itrax scanning data. It is likely that the Cu released to Southampton Water from the Fawley refinery was continuously output with an occasional spike *[23]*, and this, coupled with possible seasonal or spring/neap tidal variations in inwash of Cu-labelled sediment, is recorded in the Itrax data. The WD-XRF data (at lower sampling resolution) tends to "smooth out" or integrate the Cu profile and lose this temporal detail. Similarly, Si/K ratios in the Itrax data can be used to assess (at high resolution) down core compositional changes, particularly in the clay sediment fraction. The Si/K Itrax data show regular small-scale fluctuations down the core, which may relate to slight seasonal or tidally-induced fluctuations in clay composition or input, although these fluctuations occur around a broadly uniform intensity ratio (of 0.15) with depth. WD-XRF concentrations of Rb, commonly used as an indicator of clay content in estuarine sediments *[24-26]*, are also relatively constant with depth, indicating minimal variation over the cm-scale in bulk sediment composition in the sampled core section.

^{210}Pb (Figure 5) shows a broadly exponential decline in activity with depth in the 2014 core to supported activities of *ca*. 20 Bq/kg, at 30 cm depth. Applying the Constant Flux : Constant Sedimentation (CF:CS) model of ^{210}Pb dating indicates a sediment accumulation rate of 2.9

mm/y (range 2.2 – 4.0 mm/y at 95% confidence). ^{137}Cs data (also Figure 5) show a broad subsurface activity maximum at -17 cm depth, similar to the profile observed previously in 1992 (Figure 6). Ascribing this subsurface maximum in ^{137}Cs activity to the 1963 peak fallout from atmospheric weapons testing *[5]* indicates a sediment accumulation rate of 3.3 mm/y (i.e. 17 cm deposition in 51 years), in good agreement with the ^{210}Pb-estimated rate. A subsidiary peak in activity at -10 cm depth can tentatively be attributed to 1986 fallout from Chernobyl. If this activity peak is indeed real (rather than being an effect of slight sediment compositional variability) then this indicates a sediment accumulation rate of 3.6mm/y (i.e. 10 cm in 28 years). If the Cu maximum observed in the 2014 core is assumed to correlate to the 1970/1971 discharge maximum from nearby Esso refinery at Fawley *[5,6,10]*, this indicates a sediment accumulation rate of 3.6-4.0 mm/y, at the upper range of the ^{210}Pb and ^{137}Cs dates. These rates are slightly lower than those calculated in the 1992 core data, which indicate rates of 5-6 mm/y, but are more similar to that of 4.3 mm/y recorded by *[20]* and reported in *[5]*, suggesting that this apparent change in accumulation rate is dominantly an effect of in-site heterogeneity (see also *[10]*), although marsh emergence and consequent reduction in sediment supply could also be a factor in reducing sedimentation rates here from those calculated in 1992.

In 1992 core data (Figure 6), maximum Cu concentrations were 320 ppm, lower than those measured in 2014, although Cu concentration does vary significantly across the Hythe marsh and surrounding sedimentary environments due to site heterogeneity, varying sediment composition and supply routes, and distances from the Fawley outfall point *[20]*. Maximum copper concentrations have been observed in subtidal sediments adjacent to Fawley by Croudace and Cundy *[4]* (1022 ppm), which are over 50 times the background level (of 15 ppm, in local pre-/early Industrial Holocene sediment) and over an order of magnitude higher than those observed in nearby relatively uncontaminated systems. Concentrations of Zn in the 2014 data are similar to those observed previously *[19]*. Pb is discussed below.

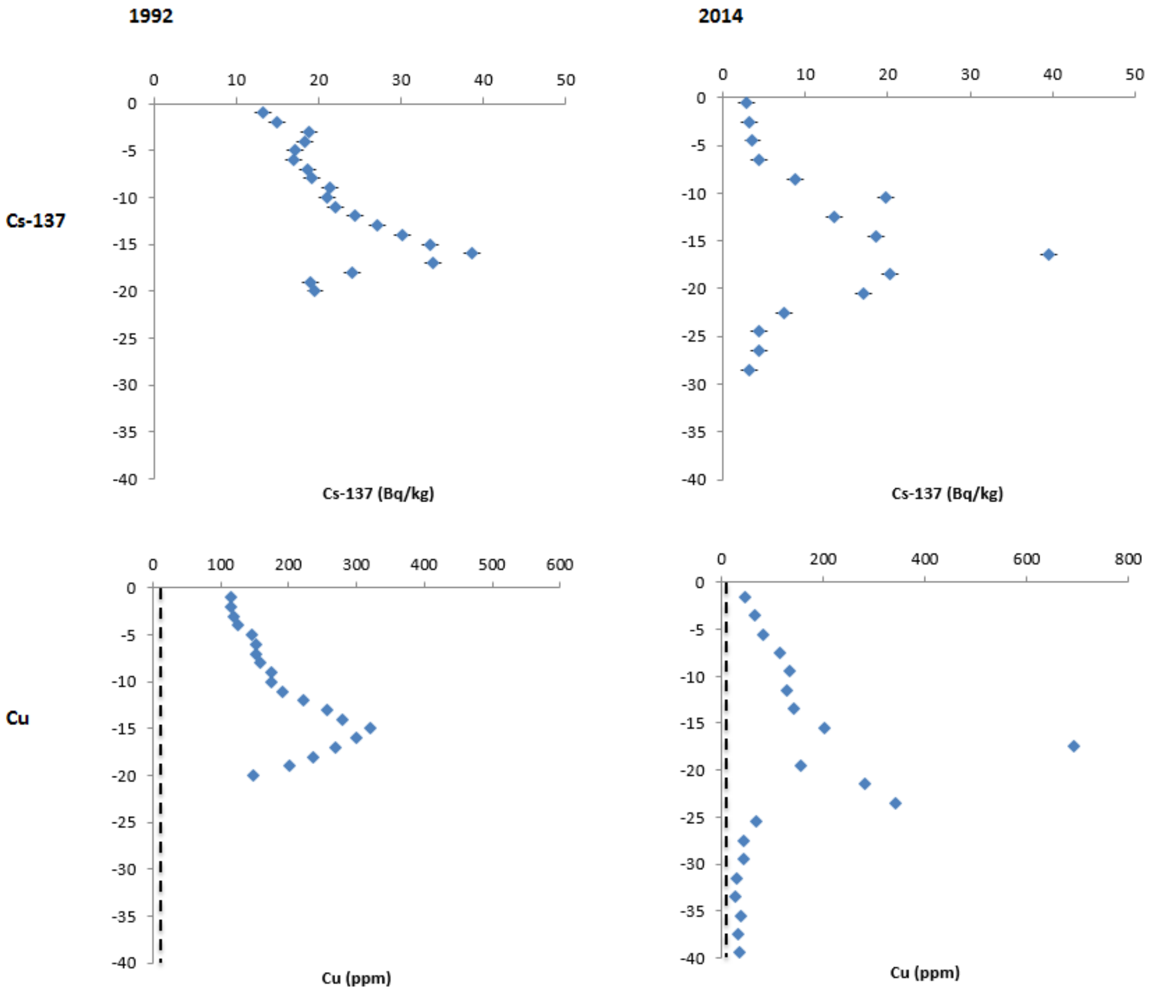

Figure 6. Comparison between 1992 and 2014 salt marsh core data (Hythe) for ^{137}Cs and Cu sediment "marker" horizons. 1992 core data from *[5]* and *[19]*. Y-axes show depth in cm. Dashed vertical line on Cu vs. depth graphs shows geogenic background, derived from concentrations measured in mineralogically similar pre-industrial sediments from a subtidal core collected in the main Southampton Water navigation channel *[4]*). See text for discussion.

Pb and stable Pb isotope data - Hythe.

Pb data in the 2014 core (Figure 4 and 5) show a prominent concentration maximum at -28 cm depth, with Pb concentrations of up to 145 ppm (compared to a local geogenic background of *ca.* 24 ppm). In 1992 core data (reported in *[5]*), Pb concentrations show less variability with depth, ranging from 80 to 100 ppm with a broad concentration maximum at 15 cm depth. Cundy et al., *[5]* note that the temporal input of Pb recorded at Hythe and in other local salt marshes does not reflect atmospheric pollutant input but instead reflects a more complex, mixed marine / atmospheric input from multiple sources. In these situations, stable Pb isotope ratios provide an additional means of Pb source discrimination and have been applied successfully in a range of sedimentary/environmental settings (e.g. *[27–34]*). Ultrahigh precision, double-spike mass spectrometry stable Pb isotope data for the 2014 Hythe core (Figure 7) show a gradual reduction in ^{206}Pb/^{207}Pb ratio from core base upwards (consistent with studies from other sedimentary settings in the UK (e.g. *[28,35]*), from *ca.* 1.18 (a typical value for Southampton Water pre-industrial sediments or Pb derived from coal-burning, *[4,36]*) to 1.13 or less. This reflects increasing use of alkyllead gasoline additives from the 1920s onwards, which in the UK mostly used a mixture of “ancient” (in terms of isotopic composition) Australian (^{206}Pb/^{207}Pb = 1.04) and Canadian (^{206}Pb/^{207}Pb = 1.16) Precambrian ores, with varying amounts of U.S. Mississippi Valley Pb ores (^{206}Pb/^{207}Pb = 1.38) *[5]*, coupled with local industrial inputs of Pb (derived, at least partly, from the same Pb ore sources). ^{206}Pb/^{207}Pb data in the 2014 core plot on a mixing line between a coal-burning/inherent detrital lead end-member (^{206}Pb/^{207}Pb = 1.18) and a UK leaded gasoline end-member (*[37]*, Figure 8) when plotted against the ^{206}Pb/^{208}Pb ratio in the same samples. Values for refuse incinerator fly ashes (France, *[37]*), which have been proposed as an approximation for industrially-derived Pb in the Southampton region *[5]*, are also shown for comparison. The concentration maximum for Pb at -28 cm depth corresponds to a sharp reduction in the ^{206}Pb/^{207}Pb isotopic ratio to 1.12 (confirmed by repeat analysis), closer to the leaded gasoline end-member. Based on radiometric dating for the core, this "event" dates to the mid to late 1930s or early 1940s (Figure 7), a period of significant urban and industrial expansion in the Southampton area, and of intense military activity associated with WW2. An increase in ^{206}Pb/^{207}Pb can be observed toward the top of the core, from -10 cm to the sediment surface, reflecting the phase-out of leaded gasoline between 1986 (the date of introduction of unleaded gasoline in the UK) and 2000 (when leaded gasoline was banned in the EU). These dates are consistent with sediment accumulation rates observed in the core, and the inflection in the ^{206}Pb/^{207}Pb profile to more radiogenic values also correlates with the apparent 1986 Chernobyl-derived activity maximum observed in the ^{137}Cs data at -10 cm depth. Stable Pb isotopes were not measured in the core collected in 1992, but data are available for two nearby (i.e. retrieved from within 100-200 m of the 2014 sampling location) cores from the Hythe marsh collected by Lewis in 1994 *[20]*. Data from both of these cores are plotted here to assess uniformity of the stable Pb isotope data across the Hythe marsh, and over time. The stable Pb isotope data show a broad degree of correspondence between the cores (Figure 7), despite: (a) the lower precision on the earlier data; (b) likely within-site heterogeneity; (c) differences in the stable Pb profile; and (d) the 20 year difference in sampling date. This correspondence is stronger when the stable isotope data are plotted against sediment age rather than depth (Figure 7, lower graphs), although the lower precision data from the 1994 cores do not record the sharp nature of the reduction in the ^{206}Pb/^{207}Pb isotopic ratio to less radiogenic values (1.12) observed at -28 cm depth in the 2014 core. In addition the older cores, being sampled earlier and within the phase-out period of leaded gasoline, do not show as significant a rise in $^{206}Pb/^{207}Pb$ ratios to more radiogenic values towards the sediment surface.

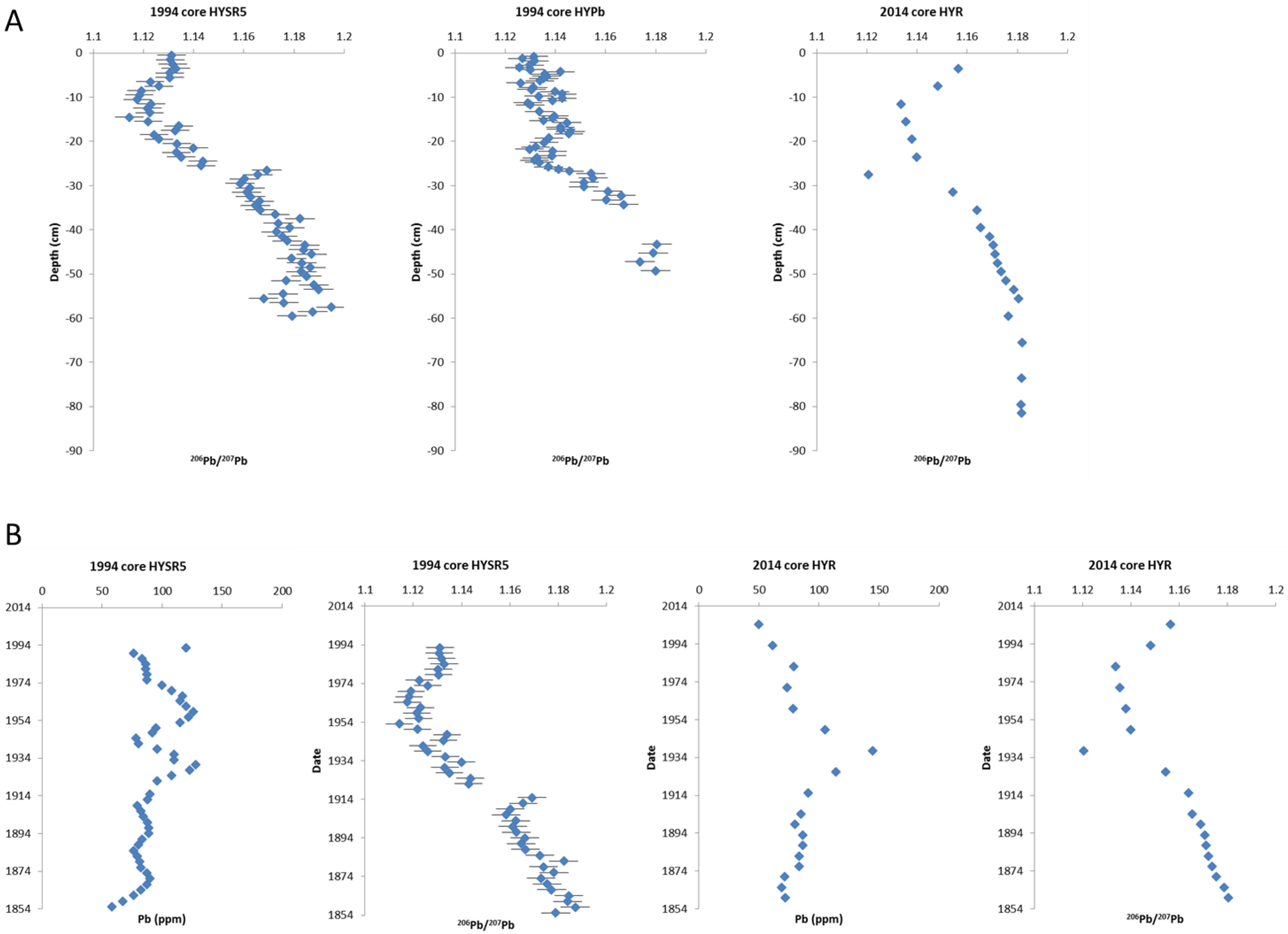
A
1994 core HYSR5
1994 core HYPb
2014 core HYR
1.1
1.12
1.14
1.16
1.18
1.2
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Depth (cm)
^{206}Pb/^{207}Pb
B
1994 core HYSR5
1994 core HYSR5
2014 core HYR
2014 core HYR
0
50
100
150
200
2014
1994
1974
1954
1934
1914
1894
1874
1854
Date
Pb (ppm)
^{206}Pb/^{207}Pb

Figure 7. A. Comparison of $^{206}Pb/^{207}Pb$ distribution with depth for 1994 Hythe core data (HYSR5 and HYPb, *[20]*) and 2014 Hythe core. Error bars on 2014 data are smaller than the diamond marker symbols used. Larger error bars on 1994 data reflect lower analytical precision on an earlier generation ICPMS instrument and single spike method. B. Pb and $^{206}Pb/^{207}Pb$ distributions versus calendar year (derived from ^{210}Pb and ^{137}Cs dating, see text for discussion) in 1994 and 2014 Hythe salt marsh cores.

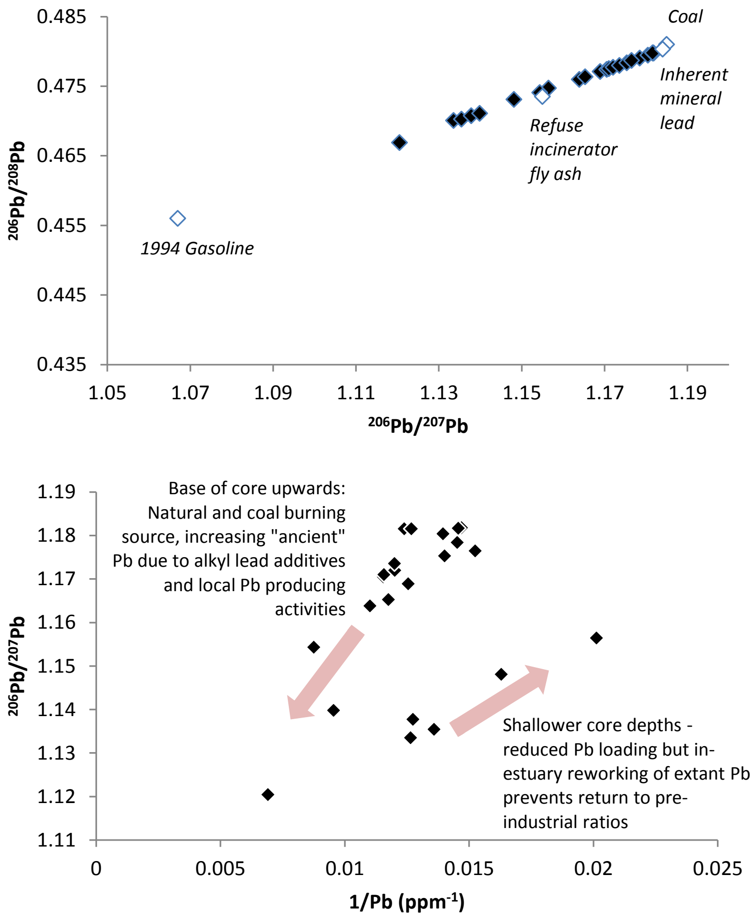

Figure 8. ^{206}Pb/^{207}Pb vs. ^{206}Pb/^{208}Pb for Hythe 2014 salt marsh data. Note plotting of data points on a mixing line between leaded gasoline and mixed local detrital / coal burning-derived Pb, approximating a two end-member mixing model. Open diamonds (from bottom left to top right of diagram) show stable Pb isotope ratios measured for: gasoline and refuse incinerator fly ash, from Monna et al., *[37]*, inherent mineral lead (taken as approximate to that of preindustrial deposits from Fawley, Southampton Water, from *[4]*) and coal, after Sugden et al., *[36]*. Lower graph shows ^{206}Pb/^{207}Pb ratio plotted against stable Pb (ppm) (as 1/Pb) for the Hythe salt marsh core. Arrows show direction of decreasing depth in the core.

Retention of the anthropogenic geochemical record.

Much of the geochemical record of recent anthropogenic activity has been eroded and lost at the Hamble marsh site, due to marsh fragmentation and erosion over the 20 year period since 1992. The contaminants within this marsh have been reworked into the wider estuarine system, and either subsequently trapped in surrounding accreting sedimentary systems or discharged to sea. In contrast, radiometric, isotopic and elemental records of anthropogenic activity have been preserved at Hythe, despite vertical marsh accretion, ongoing breakdown or leaching of labile sediment fractions (e.g. labile or easily degradable organic matter components, colloidal material etc), and upward migration of the water table (and consequently redox boundaries) under the strongly upward sea-level trend. ^{137}Cs and Cu depth profiles in particular (Figure 6) show clear retention of 1963 and 1970/71 input maxima (respectively) between the 1992 and 2014 sampling, which occur at slightly greater depths in the 2014 core due to marsh accumulation / sediment burial over the intervening time period. ^{137}Cs present in the marsh and the wider estuary has also undergone radioactive decay (where $t_{1/2}$ for ^{137}Cs = 30 years) over the 1992 to 2014 period, although this is not apparent when comparing the 1992 and 2014 cores due to within-site heterogeneity in the specific activity of the ^{137}Cs 1963 fallout maximum. While elemental Pb data are not as clearly comparable between cores, stable Pb isotope data show a good degree of correspondence in 1994 and 2014 cores when plotted against sediment age, indicating the usefulness of isotopic data in preserving information on Pb sources and disentangling Pb input histories, even in relatively complex estuarine settings. The ultrahigh precision stable Pb isotope data from the 2014 core however highlight:

(a) that the early to mid-20th century decline in ^{206}Pb/^{207}Pb stable isotope ratio towards less radiogenic values was more rapid and pronounced than previously reported for this site (in *[20]*), and so records a more abrupt input of isotopically "old" lead. Given uncertainties in core dating, the abrupt nature of the decrease in $^{206}Pb/^{207}Pb$ at -28 cm depth towards the UK gasoline end-member (Figure 8) indicates that it is likely to be derived from WW2-associated military/industrial activity rather than gradual industrialisation. There is no evidence in sediment samples or X-ray images (e.g. figure 4) of presence of lead shot from hunting or wildfowling activity; and

(b) the importance of within-estuary mixing and supply of reworked, secondary contamination from erosion and redistribution of extant, anthropogenically-labelled, sediments. Plotting 1/Pb against $^{206}Pb/^{207}Pb$ ratio (Figure 8) clearly shows a reduced Pb loading in more recent, near-surface sediments in the 2014 core (right of diagram), but in-estuary reworking of extant Pb, coupled with (relatively minor) continued inputs of industrial Pb, prevents stable Pb isotope ($^{206}Pb/^{207}Pb$) ratios increasing to values characteristic of local background or coal-burning sources. This reworking is not as immediately apparent for other contaminants such as Cu and ^{137}Cs, but tends to produce a peak broadening effect, as observed clearly for ^{137}Cs in the Hamble marshes *[6]*. Near-surface Cu concentration in the 2014 Hythe core is *ca*. 50 ppm, significantly higher than Cu concentrations in nearby uncontaminated estuaries and in mineralogically similar pre-industrial deposits from Southampton Water (*ca*. 15 ppm), indicating continued Cu inputs through reworking of extant Cu-labelled sediments in the wider estuarine system, from subtidal and eroding intertidal areas.

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