

**Geochemistry and related studies of Clyde estuary sediments**

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## Abstract

Around 200 words, intelligible without reference to the text or references

Geochemical and related studies have been made of near surface sediments from the Clyde estuary and adjoining areas, extending from Glasgow to the north and west as far as the Holy Loch. Multibeam echosounder, sidescan sonar and shallow seismic data, taken with core information indicate a shallow layer of modern sediment, often less than a metre thick, rests on earlier glacial and post-glacial sediments. The offshore Quaternary history can be aligned with onshore sequences with recognition of buried drumlins, settlement of muds from quieter water probably behind an ice-dam and later tidal delta deposits. The geochemistry of contaminants within the cores also indicates shallow contaminated sediments often resting on pristine pre-industrial deposits at depths less than 1 m. The distribution of different contaminants with depth in the sediment, such as Pb (and Pb isotopes), organics and radionuclides allow chronologies of contamination from different sources to be suggested. Dating was also attempted using microfossils, radiocarbon and  $^{210}\text{Pb}$  but with limited success. Some of the spatial distribution of contaminants in the surface sediments can be related to grain size effects. Contaminants are highest, both in absolute terms and in enrichment relative to the natural background, in the urban and inner estuary and in the Holy Loch reflecting the concentration of industrial activity.

## Key Words

150 characters max (words not already in title)

Contaminants, metals, organics, Pb isotopes, radionuclides, Quaternary history, Scotland, UK

Estuaries are important habitats for fish, shellfish, birds and mammals. They are also a focus of human activity encompassing urban and industrial development and recreation. Estuaries are both sources and sinks for sediments, although more commonly the latter in the UK because the large volumes of water introduced by the tides tend to outweigh the relatively modest riverine inputs (Dyer, 1997). Their sediment infill, and accompanying contaminants, can, however, include both fluvial and marine components.

Any contaminants in the sediments have the potential to harm the biota and thus to adversely affect both ecosystems and biodiversity. There have been relatively few detailed studies of estuarine contamination in the UK. This was recognised by an editorial in *Marine Pollution Bulletin*, which stated that, 'Truly appropriate, useful, research would involve the mapping of sediments and ..... development of contaminant inventories' (Pearce, 1997). The British Geological Survey set out to achieve this goal by initiating work in the Mersey Estuary (Ridgway et al., 2012). This was followed by studies in the Clyde Estuary.

The work goes some way towards addressing legislative requirements, such as the OSPAR aim for hazardous substances of 'achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances' (OSPAR, 2010) and achieving the goals of the EU Water Framework Directive (European Community, 2000). Contaminated sediments should be considered as part of river basin management plans under the Directive in order to achieve good ecological status and maintain ecosystem function. Contaminated sediment may also be relevant when meeting the European Habitats Directive and the Marine Strategy Framework Directive.

Climate change may affect the future disposition of contaminants in estuarine sediments, for example through sea level rise or the increased frequency of extreme weather events including storms and flooding.

Glasgow is a city that has been greatly affected by its industrial past. Situated along the lower River Clyde and upper Clyde estuary in the west of Scotland, it was once one of Europe's leading industrial centres, along with its outlying neighbouring towns further down the estuary, such as Dumbarton, Port Glasgow and Greenock. Coal mining, ship building, engineering and chemical industries have left their mark on the environment and the surrounding River Clyde.

Studies of the geochemistry of sediments from the Clyde Estuary were carried out in three phases from 2002 onwards. The first of these was funded by Glasgow City Council with support (ship time and logistics) from SEPA and the Glasgow Humane Society. This concentrated on the inner part of the estuary from the tidal limit in Glasgow downstream to Milton. The second phase in 2004 extended the study further down the estuary to Greenock. This was then continued westwards from Greenock to the Holy Loch in the third phase in 2007.

The aim of this paper is to summarise the estuarine contamination and related studies, providing some illustrative examples from the work and signpost more detailed publications that are available

## **1 Methods**

### **1.1 Sediment sampling**

Surface sediment and shallow sediment core samples were collected across the studied area. This sampling was supplemented by geophysical techniques to provide context on the spatial distribution of seabed features and sediment types and their disposition with depth, thus shedding light on the sedimentary history of the area.

Techniques varied according to the nature and accessibility of the areas studied. Sampling of the inner estuary commenced in October 2002 and was completed in February 2003. Samples were collected on three separate cruises, on which four different sampling methods were adopted according to the site conditions and the sampling platform:

1. Day Grab – Deployed from SEPA Research Vessel ‘Endrick II’
2. Gravity Corer - Deployed from ‘Endrick II’
3. Mackereth Piston Corer - Deployed from ‘Endrick II’ and BGS vessel ‘Big Buster’
4. Van Veen Grab - Deployed from ‘Endrick II’, ‘Big Buster’ and the Glasgow Humane Society vessel.

The grab samples provided surficial sediment to a depth of 10-20 cm; the smaller Van Veen grab sampled to 10 cm, whilst the larger Day grab obtained material to about 20 cm depth. The core samples enabled deeper material to be sampled, up to 76 cm depth for the gravity cores and 88 cm for the Mackereth corer. Sampling covered the area from the tidal limit to Milton.

Three sediment samples were collected from the upper estuary between Carmyle and Bogleshole, where access on foot, from the riverbank, was possible.

Intertidal areas between Milton and Greenock were sampled on foot from a small hovercraft at low water in June 2004. Surface samples were taken by hand trowel and shallow cores obtained by hammering polycarbonate tubing fitted with a core catcher into the sediment. The cores were capped and then extracted. In an attempt to obtain a more continuous record of sedimentation/contamination areas of salt marsh that were consistently present on a series of historical maps dating from 1863/4, 1899, 1922 and the present day were sampled by hand coring in 2006. The sites were selected by assessing the Ordnance Survey historical maps held by BGS in ArcGIS

Gravity cores and Shipek grabs were collected from Endrick II in the subtidal area NW of Greenock in March 2004.

The study was extended west of Greenock and into the Holy Loch in 2007 when sampling was by gravity corer and Craib corer (to recover undisturbed surface sediments) from the survey vessel Aora.

### **1.2 Sample handling**

Intertidal sites were photographed during collection of samples. Splits of samples for organic analysis, or duplicate cores, were frozen as soon as possible after sampling. Non-destructive testing of cores was undertaken first including gamma logging and X-ray photography and portable XRF analysis on selected cores. A subset of cores and all surface samples was then, spilt, photographed and logged before subsampling for further analysis.

Samples for geochemical analysis were sieved to < 2mm and freeze dried. Samples from the inner estuary were also subsampled at -150 µm to provide a direct comparison (and normalisation) with Clyde tributary sampling and analysis (Fordyce et al., 2004 and this volume).

### **1.3 Sample analysis**

Analysis during the first phase of work in the inner estuary was dictated by the requirements of Glasgow City Council and included inorganic and organic geochemistry, particle size and some engineering properties as well as some mineralogical estimation e.g. for asbestos content. Grain size analysis was carried out on these samples, and all those subsequently collected, by sieving and X-ray Sedigraph. Details of analytical methods are given in Jones et al. (2004).

Major and trace element determinations for sediment samples were carried out by a combination of wavelength-dispersive (WD) and energy dispersive (ED) X-ray fluorescence spectrometry of pressed powder pellets (Ingham and Vrebos, 1994). Mercury was analysed by Atomic Fluorescence Spectrometry following dissolution using aqua regia.

PCBs and organotins, and PDBE (flame retardants) on a small selection of samples, were analysed by GC-MS, and PAHs by HPLC, following solvent extraction (Vane et al., 2010; Vane et al., 2011; Vane et al., 2007).

Radionuclides were analysed on selected samples by gamma-ray spectrometry using an automated gamma core logger (NaI detector) for intact cores and Ge detectors for splits for dried sediment. Both detectors were housed in 10 cm Pb shields to reduce background radioactivity. Data were analysed using Canberra Genie 2000 software.

Pb isotopes were measured in a subset of cores by ICPMS (Vane et al., 2011).

Sequential extraction was used to determine the solid phase fractionation using the CISED method (Cave et al., 2004) as summarised in Figure 1.

The sequential extraction data (14 extracts per sample) from all 15 samples were analysed for the following elements: Al; As; B; Ba; Ca; Cd; Co; Cr; Cu; Fe; K; Li; Mg; Mn; Mo; Na; Ni; P; Pb; S; Se; Si; Sr; V and Zn. This data was assembled into a data matrix and processed to produce a single model consisting of a mixture of components common to all the sediment samples.

Mineralogy and petrology was examined on selected samples. The bulk and clay mineralogy was investigated by X-ray diffraction. Scanning electron microscopy was carried out on rough surfaces and resin-impregnated blocks. Phase/mineral identification was aided by qualitative observation of energy-dispersive X-ray spectra recorded simultaneously during SEM observation, using an Oxford Instruments INCA energy-dispersive X-ray microanalysis (EDXA) system.

### **1.4 Geophysics**

Shallow seismic reflection data were acquired with surface towed boomer systems. A single boomer line was run down the channel from slightly below the tidal limit at Glasgow Green to Greenock.

In the area NW of Greenock a Waverley 3000 Sidescan sonar and a BGS surface tow boomer were deployed over a grid of lines from the Endrick II.

During the hovercraft survey of the intertidal area between Milton and Greenock a C-Boom low voltage boomer was linked to the BGS Coda Da200 data acquisition system and Trac C + Trimble DGPS navigation. Geophysics was carried out around high water  $\pm$  about 2 hours.

In the Aora survey of 2007, west of Greenock, a grid of BGS surface towed boomer lines was acquired and a separate commercial multibeam survey was conducted over the whole of this area.

The coverage of the main geophysical methods is summarised in Figure 2.

## **2 Results**

### **2.1 Shallow seismic (boomer)**

The shallow seismic (boomer) data has been interpreted in light of previous studies on the glacial and post-glacial history of the area (Browne and McMillan, 1989; Fyfe et al., 1993; Jardine, 1980; Jardine, 1986; Peacock et al., 1978). However, this is constrained by abundant acoustic blanking believed to be caused by gas within muddy sediments. The worst affected areas being the finest sediments. The succession can be subdivided by a series of unconformities, the lowest of which is the bedrock.

Above the bedrock, a continuous mound-like reflector is interpreted as buried drumlins, analogous to those in the adjoining onshore areas, formed in a sub-glacial setting. These drumlins are not seen west of Greenock where the successions are thinner and of probable marginal glacial origin. The drumlins are overlain by acoustically transparent sediments, which in turn are draped by parallel layered deposits. The latter were probably deposited below floating sea or glacial ice, which blocked the estuary and hindered tidal flows.

Channels cut into the layered sediments, filled with probably muds, prograding westwards. These probably formed part of a tidal delta, built to the west of narrows at Duntocher, separating a large marine basin that existed to the south-east between about 15,000 and 11,500 years before present and the open sea to the west (Figure 3).

Erosion and infill of probable estuarine channels followed the delta progradation, most likely during the late Pleistocene or early Holocene.

This glacial and post-glacial history is harder to identify west of Greenock, where sediments are much thinner and more difficult to subdivide.

Following rapid sedimentation during deglaciation the amount of sediment supplied to the Clyde Estuary would have been dramatically reduced with the onset of an interglacial climate and establishment of permanent boreal vegetation approximately 10 000 years ago. Man had no significant influence on the natural environment until the Iron Age which started in the Clyde Valley approximately 2 500 years ago. At this time the major areas of lowland forests were cleared to make way for agriculture and, possibly to a lesser extent, to service metalworking. This may have resulted in higher sediment input to offshore areas. Nevertheless, there is lower modern man-made and natural alluvial input to the offshore sediment compared to the colder periods of the Loch Lomond Stadial and the Windermere Interstadial. Over-deepened enclosed basins in the outer Firth of Clyde have trapped bedload sediment that would otherwise have been transported by tide and waves

from the open shelf in the northern Irish Sea into the Clyde estuary. Modern artificial embankments and dredging from Greenock east to the Port of Glasgow have confined much of the modern freshwater and tidal flow to the navigation channel adjacent to the more industrial south bank. Further east the main channel has been artificially constrained by embankments and dredging to the centre and north of the estuary.

An important sedimentary process in the intertidal environment arises when the seabed waves generated from prevailing winds interact with flooded seabed. High stress is put on the seabed when the wind blows over long fetches from the south and west and when winds have been funnelled to the east up the Clyde Valley by the configuration of the adjacent land. Interaction between waves and seabed has eroded the seabed and winnowed the seabed sediments. There is a prominent continuous beach complex that has been raised 8-10 m above Ordnance Datum on the northern flanks of the Clyde Estuary. There is not a raised beach on the southern shore. These observations suggest that wind-generated waves originating from the south and west have had a long term influence on the rate and sources of sediment input from the north shore of the Clyde Estuary to the offshore.

The net effects of regional natural environmental setting, long-term local uplift and artificial management now mean that the Clyde Estuary east of Greenock is an area of overall sediment bypass. There are probably smaller areas of shallow estuarine water, mud and sand flats and banks than would have been the case if the estuary had not been managed.

In the Outer Clyde Estuary the rugged topography might indicate a more active environment in which sediments at seabed are prone to movement during current maxima. It is unlikely, however, that there is significant net deposition of sediment at the present day, other than in the Loch Long Channel and other basins.

## **2.2 Surface sediments and shallow cores**

Seabed sediment maps have been compiled from the grain size analysis of the surface sediments or surface layers of core sample (Leslie et al., 2011) and are shown in Figure 4.

The middle part of the estuary downstream of Milton is predominantly sand, locally gravelly near the shore and becoming muddy towards Milton. In the vicinity of Greenock, and westwards from here, sandy mud is the main sediment type passing into mud in the deepest parts of Loch Long. There is a gravel component NW of Greenock and on the eastern edge of Loch Long and neighbouring patches of muddy sand.

Shallow cores ( $\leq 1.2$  m maximum depth) from east of Greenock were highly variable. The predominant sediment type was a yellowish-brown fine to medium sand. Clay, silt and gravel were also common. Several of the cores recovered along the southern shore of the estuary, between Langbank and Port Glasgow (695, 696, 697, 701 and 717; Figure 4), contained abundant shells and shell fragments (including *Turritella communis*, and *Mytilus edulis* [Common Mussel]). Of particular interest were cores collected towards the margins (680, 682, 684, 688, 697, 700, and 707) of the estuary which contained a laminated, pinkish-grey silty clay at their base. This is thought to be a basal clay of glacial origin which was deposited as ice retreated from the Clyde approximately 14 000 years ago. This silty clay is referred to as Unit 1 of the Clyde Beds by Jardine (1986). The clay was flocculated from plumes of glacial meltwater carried across more dense salt water (Peacock et al.,

1978). Each lamina appears to represent the suspension fraction of sub-aqueous sediment plumes discharged from the glacier margin (Peacock, 1975). The poor sorting has been caused by flocculation in a saline environment and the colour-banding is a result of the differences in proportions of glacially-derived Dalradian material from the Highlands, and locally-derived Old Red Sandstone material from the adjacent river catchments (Jardine, 1980)). This unit has subsequently been incised and eroded by the River Clyde (removing any evidence of Jardine's (1986) Unit 2), and then flooded and buried with modern fluvial and marine-derived sediments under sea level rise.

Coal and jet-black fragments were observed in nine of the cores (680, 691, 693, 694, 698, 703, 706, 707 and 712; Figure 4), at a maximum depth of 1.1 m with very thinly bedded (1 to 3 cm) gravel-sized coal fragments in core 706, down to a depth of 0.95 m. One possible source for the coal is spillage from the many coal barges that once transported the fuel along the Clyde. Core 717 was found to contain abundant oblate to spherical, sub-angular to well-rounded pebbles up to 3 cm in diameter. The presence of these pebbles may be due to the core's proximity to the active river channel which runs down the centre of the inner estuary and provides a higher transport threshold for the movement of coarser-grained material.

The cores from east of Greenock confirm the patchy and shallow nature of recent sediment in the Clyde Estuary with presumed glacial sediments very close to surface.

To the west of Greenock the cores were much more uniform very soft, black, silty, sandy, organic-rich mud, with common bleached shells and shell fragments and rare plant fragments, indicative of sediments deposited in a relatively low energy environment. Cores 745, 749 and 755 (Figure 4) were more varied with interlaminated and interbedded soft to firm black muds, dark yellowish brown fine to medium-grained sands and gravels. Core 755 also commonly contained angular and sub-angular coal clasts. All three cores lacked the shells or shell fragments typical of the sediments in this area. The cores were collected on an area of higher ground marked as spoil ground on the Admiralty Chart 1994 (Approaches to the River Clyde) and this would explain their heterogeneity. Core 739 was also collected in area marked as spoil ground and displays similar heterogeneity with chaotic interbedded muds and sands. Core 778, which was collected on the western edge of a north-south trending moraine also displays a chaotic heterogeneous sediment profile that would suggest it was collected in an area of dredge spoil, but it doesn't correspond with a marked area on the Admiralty Chart.

### **2.3 Multibeam**

The multibeam survey (Figure 5) is particularly revealing of surface features.

Glacial features such as moraines, depressions and scoured surfaces (bedrock outcroppings) are widespread. There is a landslip from the north shore of the Holy Loch and many pockmark-like natural features, probably reflecting the escape of gas that caused acoustic blanking on the boomer records. The trough south of Kilcreggan aligns with the Highland Boundary Fault. Man-made features include the area of dredge spoil dumping on the eastern side of Loch Long and some enigmatic triangular sets of 3 depressions near the east end of the area surveyed which might be the footprints of jack-up rigs (Leslie et al., 2011).

### **2.4 Dating and depositional environment of sediments**



A variety of approaches were used to try to date the sediments and shed light on their depositional environment.

Dating using  $^{210}\text{Pb}$  was attempted at SUERC but there was found to be too little unsupported  $^{210}\text{Pb}$ . Radiocarbon dating was also carried out on a few samples, although suitable material for dating was very sparse. Plant root material was obtained from two salt marsh cores within grey clay at 0.86 and 1.10 m depth respectively. The cores were chosen from areas where historical maps indicated salt marsh had been present on all editions from 1864 to the present day. The deeper material gave a date of  $235 \pm 30$  BP whilst the shallower material was dated at  $5960 \pm 30$  BP. Given that the clay is of likely glacial origin (section 2.2) this suggests significantly younger plants colonised the sediment over a wide period from the mid-Holocene onwards. A sample of wood and a bivalve shell from a depth of 1.33 m in core 787 (adjacent to 789 in Figure 4) gave ages of  $205 \pm 25$  and  $530 \pm 30$  respectively. The presence of  $^{137}\text{Cs}$  in the core below this depth, which was only introduced to the environment in significant amounts after about 1950, suggests that somewhat older material has been incorporated into more recent sediment.

Palynology and studies of diatoms were also carried out to try to date the sediments and provide information on their environment of deposition. Seven samples from cores 682 and 719 (Figure 4) were found to contain a mixture of allochthonous Carboniferous (mainly Westphalian) pollen and spores and a modern pollen/spore association typical of the local upland flora.

The three samples from core 719 were relatively uniform, and clearly derive from a single genetic unit. There is some evidence of marine influence via rare specimens of radiolaria, however the environment is clearly estuarine, as opposed to open marine, based on the palynoflora and the silicofossils present; the diatoms constitute a diverse assemblage of freshwater forms with a smaller number of salinity-tolerant forms. The dominant diatoms were alkaliphilous (occurring in waters with a pH of 7 and over) and beta-mesosaprobic (indicating a resistance to moderately polluted water).

Four samples were studied from core 682 (Figure 4). These proved considerably more variable, and there is a more marked marine influence. Thus this core may not represent a single genetic sedimentary unit. Samples from 0.10-0.15, 0.30-0.35 and 0.80-0.85 m depth proved relatively sparse palynologically. This is most probably a reflection of the winnowing of organic materials from the shallower samples, because they are rippled, very fine sand with occasional *Arenicola* casts. By contrast, the sample from 0.56-0.60 m depth proved extremely rich in allochthonous Carboniferous (chiefly Westphalian) spores. Dinoflagellate cysts (0.56-0.60 and 0.80-0.85 m depth) and unequivocally marine silicofossils (0.10-0.15 and 0.30-0.35 m depth) confirm a significant marine (tidal) influence at this locality. Core 682 was dominated by the same two diatom species as in core 719, but the assemblage lacked the diverse fresh water element and had a marked marine aspect with common *Navicula monilifera*, a species frequently associated with sandy substrates around the British Isles. This is consistent with core 682 being located some 3 km to seaward of core 719 (Figure 4). The downstream-upstream partitioning of marine indices in estuaries was not observed by Farr (1989) who has written the only study to date of the palynology of UK estuarine sediments.

## **2.5 Mineralogy and Petrology**

West of Greenock 31 samples from 7 sediment cores were investigated. The mineralogy was dominated by quartz (27.0-77.7%), albite (7.8-23.0%) and K-feldspar (4.8-12.6%) and the clay minerals: undifferentiated 'mica' (1.1-25.1%), kaolin group minerals (<0.5-11%) and chlorite (1.1-11.1%) with minor carbonates (mostly shell material), hematite, pyrite and smectite.

Trace quantities of heavy minerals (zircon, monazite, apatite, ilmenite, Fe- and Ti-oxides, barite) were seen with the SEM as well as well-preserved pyrite framboids. Anthropogenic components included spherical particles (20-200 µm across) resembling fly ash (composed of Al, Fe Si, O and trace Mg, K, Ti, Ca). Irregular patchy, <1 mm particles, with distinctive vesicular texture, composed of Al-rich silicate with trace amounts of Fe, Ti, K, are believed to be fragments of slag. Fly ash was seen in varying amounts in all the samples studied, slag in cores 720, 739 and 749 only. These are samples from the inner Holy Loch (720) and the two dredge spoil disposal grounds so perhaps their enhanced anthropogenic components are not surprising. Core 739 also contained abundant lithic clasts of siltstone and sandstone typical of Lower Carboniferous rocks bordering the Clyde Estuary east of Greenock, a likely input from dredging. Core 759 (in Gourrock Bay) had a negligible anthropogenic component but contained possible steel fragments.

East of Greenock 50 samples from 14 sediment cores were studied petrographically and 63 samples (9 surface and 54 from 16 cores) by XRD. Quartz was the dominant mineral (25.3-85.5%) with the other main components being albite (6.0-15.7%), K-feldspar (2.4-9.7%), chlorite (1.2-16.0%), 'mica' (0.9-31.5%) and 'kaolin' (<0.5-16.1%). The prevalence of sandier sediments in the inner area is reflected by a generally higher proportion of quartz (median 77.3% compared with 44.1%) and lower medians for all other major minerals (summed median of 20.7% compared with 45.6% for the outer area).

Slag was frequently encountered in these samples and fly ash less commonly observed.

## **2.6 Geochemistry of surface sediments**

### **2.6.1 Inorganic**

The concentrations of Cu and Pb in the surface sediments range up to 206 and 370 mg kg<sup>-1</sup> respectively (Figure 6). However, it can be seen (by comparing Figure 4 and Figure 6) that much of the spatial variability can be related to grain size effects. These can be largely removed by normalising the data to an element such as aluminium (Figure 6b).

A measure of sediment quality can be evaluated by considering guideline values. However, these do not exist for marine sediments. OSPAR has suggested ....but...Guidelines do exist for soils and lake sediments. Sediment quality in the Clyde estuary was assessed using the Canadian freshwater sediment quality guidelines (MacDonald et al., 2000) to identify samples that exceeded the probable effect concentrations (PEC).

Highest concentrations of Cu occur in the urban area (up to 201mg/kg) and in the Holy Loch (up to 160mg/kg), while the highest concentrations of Pb occur in the inner estuary (up to 370mg/kg) and the urban estuary (up to 321mg/kg) (Figure 6). Sediment freshwater sediment quality guidelines (MacDonald et al., 2000) for Cr (111mg/kg), Ni (48.6mg/kg) and Pb (128mg/kg) were exceeded by 62%, 20% and 40% of the samples, respectively, while < 8% of the estuarine sediments exceeded the quality guidelines for As (33mg/kg), Cu (149mg/kg) and Zn (459mg/kg) (see Figure 7).

The natural background was modelled by calculating the average metal concentration of 15 samples, collected between 0.54 - 2.21m below the surface of the core sample 733, located in Holy Loch. Enrichment factors were calculated by comparing the analysed sediment metal concentration with the calculated natural background concentration.

Other elements such as cobalt, chromium, nickel, tin and zinc show similar element distribution patterns to copper and lead, with highest element concentrations occurring in the urban estuary, gradually decreasing to the middle estuary, where the lowest element concentrations were measured (Figure 6). The outer estuary samples show higher values again. This downstream pattern might be the result of grain size variations, as elevated concentrations correlate with muddy sea bed sediments (Figure 4). However, aluminium normalised distribution maps still display a similar pattern, suggesting that grain size variations are not the only influence on metal concentrations in the Clyde estuary (Figure 6).

Elevated metal concentrations in the urban estuary could reflect Glasgow's long history of urban and industrial developments. In central Glasgow, estuary sediments contain more than five times (classified as moderately severe enrichment, Birch and Davies, 2003) the natural level of chromium, copper and zinc, while enrichment factors for lead (EF = 11-16) and tin (EF = 18-26) are particularly high (classified as severe enrichment; Birch and Davies, 2003). Possible pollution sources might be docks, shipbuilding yards and roads (Figure 8).

In the Holy Loch, copper and zinc are enriched by a magnitude of at least five, while lead and tin have EFs between 11-12 and 18-25 respectively. Pollution of Holy Loch by trace metals has been confirmed previously to be severe but localised (Miller et al., 2000). Such elevated metal concentrations might still relate to the former US submarine base. The base was closed in 1992 and debris (mainly scrap metal) was cleaned up, but its impact on sediment quality in Holy Loch might still be present today.

### **2.6.2 Organic**

An assessment was made of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in surface sediments of the Inner Clyde Estuary from the tidal limit in Glasgow to Milton (Vane et al., 2007). Total PAH concentrations in the sediments ranged between 630 µg/kg and 23,711 µg/kg. This is broadly in line with values from earlier studies of UK estuaries including the Clyde, Tyne, Wear and Tees (Rogers, 2002; Woodhead et al., 1999). There was some correlation ( $r^2 = 0.56$ ) between the Total Organic Carbon (TOC) and the total PAH concentration of the sediments. Thus the coarser grained sands and gravel had lower TOC and total PAH (0.31–2.72% and 630–2615 µg/kg respectively) than the finer muddy sediments (3.98–6.15% and 11,701–23,711 µg/kg).

The relative abundances of the PAHs in the sediments suggest a predominantly pyrolytic origin, with a petrogenic component in the vicinity of an oil refinery at Yoker and from possible fuel spills near Upper Harbour, closer to the centre of Glasgow. The isomeric ratios suggest mainly liquid fuel combustion with a more limited input from coal combustion (Vane et al., 2007).

Total PCB concentrations ranged from 5.2 µg/kg to 129.9 µg/kg with a mean of 46.9 µg/kg. Again this is consistent with earlier work except for a value of 1822 µg/kg reported from Battery Park, Greenock (Edgar et al., 1999). Consensus based threshold effect concentrations (TEC) and probable

effect concentrations (PEC) provide a means of classifying sediments as toxic or non-toxic. These have been reported for total PCB concentrations in freshwater sediments as 59.8 lg/kg and 676 lg/kg, respectively (MacDonald et al., 2000). On this basis, seven sites fall below total PCB TEC, whereas, Lower Harbour, Merklands and King George V. Dock, lie between TEC and PEC.

## **2.7 Geochemistry of cores**

Assessment of a number of potential contaminants was examined with depth in the sediments using a selection of cores. These were chosen on the basis of initial screening of the sedimentology, automated gamma logging and selected analysis using portable XRF for a number of inorganic trace elements. The possible contaminants included inorganic and organic species, radionuclides and a study of lead isotopes.

In many cores a distinction could be made between uncontaminated sediment in the deeper portion of the core and a contaminated near surface zone; the former having lower concentrations of naturally-occurring components and an absence of anthropogenic substances. Knowing the chronology of human activity in the Clyde and its catchment, and the dates of introduction (and cessation of use) of different natural and anthropogenic materials, the age of the sediments and a history of contamination can be deduced. In general terms this supports the geophysical and sedimentological interpretation of a shallow surface layer of recent (sometimes contaminated) sediment sitting on uncontaminated sediment that may be of considerably earlier glacial or post-glacial origin. The surface layer ranges from less than 1 m in thickness to 2-3 m (or more) in places.

### **2.7.1 Inorganic**

Lead concentrations, measured in seven sediment cores from the Middle Clyde Estuary, ranged from 6 to 631 mg kg<sup>-1</sup>, while <sup>207</sup>/<sup>206</sup>Pb isotope ratios varied from 0.838–0.876 (Figure 13). These are indicative of various proportions of 'background', British ore/coal and Broken Hill type petrol/industrial lead. A chronology was established using published Pb isotope data for aerosol-derived Pb and applied to the cores (Vane et al., 2011). From the nineteenth century until about 1915 there was a fairly constant <sup>207</sup>/<sup>206</sup>Pb isotope ratio of about 0.855. After this the ratio increased markedly as industrial and petrol lead were used, reaching a peak of 0.893 in the 1980s, and declining thereafter as petrol lead was phased out. Core 4 (Figure 13) reflects all of these changes, suggesting the chronology is feasible for use with the sediment cores and that there has been continuous and fairly constant deposition over that period at that site. Other cores reach pre-industrial Pb signatures at depths of 40-70 cm although these were not attained at the base of core 4 despite this extending to a depth of nearly 1 m (Vane et al., 2011).

Similar patterns of higher concentrations of other inorganic contaminants in near surface layers and lower, and more consistent values at greater depth, are also apparent for other metals e.g. As, Cr, Cu, Hg, Ni, Sn and Zn, further suggesting a shallow contaminated zone overlies pre-industrial sediments with background levels of these elements.

### **2.7.2 Organic**

The concentrations of total petroleum hydrocarbons (TPHs), PAHs, PCBs, Pb and <sup>207</sup>/<sup>206</sup>Pb isotope ratios were measured in the same seven sediment cores from the middle Clyde estuary (Figure 13). Concentrations of TPHs ranged from 34 to 4386 mg kg<sup>-1</sup>, total PAHs from 19 to 16 163 µg kg<sup>-1</sup> and total PCBs between less than 4.3 to 1217 µg kg<sup>-1</sup> (Vane et al., 2011). Inventories, distributions and isomeric ratios of the organic pollutants were used to reconstruct pollutant histories.

Pre-Industrial Revolution and modern non-polluted sediments were characterized by low TPH and PAH values as well as high relative abundance of biogenic-sourced phenanthrene and naphthalene. The increasing industrialization of the Clyde gave rise to elevated PAH concentrations and PAH isomeric ratios characteristic of both grass/wood/coal and petroleum and petroleum combustion. PAHs had the longest history of any of the organic contaminants. Increasing TPH concentrations and a concomitant decline in PAHs mirrored the lessening of coal use and increasing reliance on petroleum fuels from about the 1950s. Thereafter, declining hydrocarbon pollution was followed by the onset (1950s), peak (1965–1977) and decline (post-1980s) in total PCB concentrations.

The concentrations of 16 polybrominated diphenyl ether (PBDE) congeners, a group of compounds used as flame retardants on a variety of products were determined in six short sediment cores from the Clyde Estuary (Figure 14) Vane et al., 2010 Total PBDE concentrations ranged from 1 to 2,645 µg/kg with an average of 287 µg/kg. Elevated total PBDE concentrations were seen in the uppermost 10 cm of four of the cores. Comparison of the down core PBDE profiles revealed that the increase was driven by the accumulation of deca-BDE. The increase in total PBDE concentrations and particularly the deca-BDE may possibly be ascribed to the use and subsequent disposal of electrical appliances such as televisions and computers. The concentrations of PBDE are similar to those reported from the Pearl River Estuary in China but appreciably higher than Scheldt Estuary and North Sea coastal sediments (Klamer et al., 2005; Mai et al., 2005).

### **2.7.3 Radionuclides**

The distribution of <sup>137</sup>Cs down five of the sediment cores from the middle estuary is also potentially informative of the contamination history (Figure 15). This radionuclide was not introduced into the environment prior to the advent of nuclear weapons and power generation. Peaks in the Clyde area can be ascribed to atmospheric weapons tests in the 1960s, the maximum discharges from Sellafield in the late 1970s (probably the most significant input to the Clyde) and the Chernobyl accident in 1986. The chronology from <sup>137</sup>Cs in cores 2 and 4 (700 and 718) is essentially in line with that from the Pb and organic components. However <sup>137</sup>Cs extends into sediments interpreted as 1915 or earlier from the Pb chronology suggesting either post-depositional redistribution of <sup>137</sup>Cs down these cores or that some reinterpretation of the chronology is needed. Core 5 (712) has <sup>137</sup>Cs-free sediment in the upper 30 cm suggesting the deposition of eroded sediment of probable pre-1950s age.

In addition to the middle estuary cores <sup>137</sup>Cs was measured by automated gamma logging in more than 20 cores from west of Greenock. This nuclide is absent in many of the cores below 30-60 cm depth indicating pre-1950s sediment. The largest peak in values in the Clyde Estuary sediments can probably be ascribed to Sellafield whilst a deeper, smaller peak seen in some cores may reflect weapons fallout, in the absence of modification by any significant sediment mixing, erosion or down-core redistribution. Pb isotope data suggests a number of cores possess a largely uninterrupted history of sedimentation. Occasionally cores have <sup>137</sup>Cs at much greater depths, with the maximum depth being achieved in core 787 at 1.7 m in an area of likely more rapid muddy sedimentation 'the deep' NW of Greenock.

## **2.8 Solid Phase Fractionation of Potentially Harmful Elements**

Recent developments in sequential extraction methodologies and subsequent data processing have shown that simple mineral acid extractions combined with multivariate statistical analysis can

provide a powerful tool for examining the solid phase fractionation of potentially harmful elements in sediments (Santamaria-Fernández et al., 2006). This methodology has been applied to 15 sediment samples taken from the Clyde estuary (Figure 9).

The individual extraction profiles and chemical composition plots were examined to make a tentative assignment of the source of the geochemical component. The data processing identified 19 potential physico-chemical components in the 15 sediments studied. The extraction profiles for each component in each sediment sample are shown in Figure 10. The relative amounts of each component across all samples are summarised in Figure 11. The components are ordered by increasing difficulty of extraction. This gives a measure of the availability of the component and hence any potentially harmful elements associated with it. The fractionation of As, Cd, Cr, Pb and V between the geochemical components is shown in Figure 12.

As is mostly associated with Fe sulphides and Fe oxide geochemical components. Cd shows associations with a variety of geochemical sources including carbonates, alumino-silicates, Fe oxide and pore-water but is mostly concentrated in a Zn rich component. Cr is most strongly associated with an Fe sulphide with a high proportion of sulphur which indicates this is likely to be an amorphous sulphide film. V is associated with a component containing Na and K which is extracted with the acid containing hydrogen peroxide which oxidises organic matter. This information, combined with the fact that this component also contains B suggest this is derived from fuel oil residues which are known to contain V and borates are present as additives. Pb shows some associations with Fe oxides and sulphides but is mainly associated with a component that has high but variable Ca content but more clearly defined Al, Mg, Pb, P and Zn contributions (ca.1-15%). This component is higher in the samples from industrialised areas suggesting an anthropogenic source.

Can a spatial component be added???

### **3 Discussion and conclusions**

A consistent picture has emerged from the different components of this investigation. Most of the Clyde Estuary is not, with a few exceptions, an area of active modern sedimentation. Rather a thin veneer of recent contaminated sediment, mostly less than 1 m thick, rests on earlier material of glacial and post-glacial origin.

Within the near surface sediments depth profiles of different contaminants reveal a quite complex history of contamination through what has been termed by some the Anthropocene. There appears to be evidence of effects going back to the start of the industrial revolution, and perhaps beyond, to early forest clearance, mining and burning of fuel and smelting of ores. This reached an acme during Glasgow and Clydeside's heyday as an industrial powerhouse and has declined in more recent times.

A number of contaminants were first introduced during the 20th century, such as PCBs in the 1920s and <sup>137</sup>Cs in the 1950s. These reached a peak in the environment by the late 1970s or 1980s and, although persisting to the present day, have declined. The use of petroleum products replaced coal as the most important fuel over similar timescales and this is apparent in varying PAH patterns and through the increase, and subsequent cessation of the use of Pb as a petrol additive.

These changes have led to depth profiles of different contaminants that are sometimes quite consistent in the history they reveal and, at other times, can be somewhat contradictory and difficult to unravel. Thus there is not always perfect agreement between what depth profiles of Pb isotopes, organic contaminants and radionuclides appear to be telling us. These can perhaps be explained by imperfections in constructing a Pb chronology for estuarine sediments based on aerosol deposition data, the complexity of different sources of organic compounds such as PAHs and PCBs and their possible alteration over time, and the potential for redistribution of radionuclides such as  $^{137}\text{Cs}$  during diagenesis.

Depth profiles from the dredge spoil sites in Loch Long were, as might be expected, quite confused. The repeated disposal of sediment over time leading to a great deal of inhomogeneity, apparent in both the admixed sediments and their associated contaminants.

Whilst the majority of sites studied only revealed contaminated sediment to a depth ranging from a few tens of centimetres to a metre this was not true of all locations. Core 787 from 'the deep' off Greenock appears to have been a relatively rare site of greater deposition of muddy sediment in this seabed depression. Here  $^{137}\text{Cs}$  extends to a depth of some 1.7 m into the sediment.

As described earlier, the concentrations of certain elements exceed threshold or guideline values where they could give rise to potentially harmful environmental impacts. Such guideline or threshold values can be somewhat simplistic as they may not take account of natural levels of the substances or their bioavailability. Some of the guideline values developed by OSPAR for marine sediments can, for instance, span natural ranges. In other cases there are no guideline levels for marine sediments and those for freshwater sediments (discussed earlier) or soils might not be appropriate.

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## **Acknowledgements**



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Figure captions

Figure 1 CISED sequential extraction and chemometric data processing test methodology

Figure 2 track plots of boomer surveys and multibeam coverage in the Clyde Estuary.

Figure 3 Distribution of buried Late Glacial and Post Glacial sediment types interpreted from seismic facies in the Inner Clyde Estuary

Figure 4 Distribution of seabed sediments in the Clyde Estuary

Figure 5 a. Coloured and shaded relief (NW illumination) digital elevation model derived from multibeam echosounder data. b. interpretative map of bathymetry and surface features from multibeam and boomer data

Figure 6 Copper and lead distributions in the Clyde estuary. Shown are (a) the analysed values and (b) the values normalised to aluminium to address possible grain-size variations

Figure 7 Individual samples in the Clyde estuary that exceed the probable effect concentrations of the sediment quality guidelines for arsenic, chromium, copper, nickel, lead and zinc

Figure 8. Map showing the calculated enrichment factors (EFs) for samples that had: (i) EF > 5 for at least four elements; and (ii) major element concentrations similar to core sample 733 used to calculate the geological background. Also shown are current land use types as an indication for possible pollution sources

Figure 9 Locations of cores used for CISED sequential extraction study

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Figure 11 the relative contribution of each component in the CISED sequential extractions summarised as boxplots. The components are ordered by increasing difficulty of extraction

Figure 12 the fractionation of As, Cd, Cr, Pb and V between the geochemical components from the CISED sequential extractions

Figure 13 Location of samples and Organic contaminant depth profiles of sediments from Clyde estuary. TOC, total organic carbon; TPH, total petroleum hydrocarbons; PAH, polyaromatic hydrocarbons; PCB, polychlorinated biphenyls. Rationale for dates: 1750 =pre-industrial from  $^{207}/^{206}\text{Pb}$ ; 1915=peak coal production; 1954=onset of PCB production in UK; 1965–1977 =peak PCB production; 1985 from peak  $^{207}/^{206}\text{Pb}$  values. PCB concentration data not shown for core 7A due to interferences. Depth profiles for Pb (filled triangles) and  $^{207}/^{206}\text{Pb}$  (open diamonds). Note change in concentration scale for lower set of cores

Figure 14. Location of samples and depth profiles of PDBE in sediment cores from the Clyde Estuary

Figure 15 Depth profiles down cores for  $^{137}\text{Cs}$  in Clyde Estuary sediments (see Figure 4 for locations)

Figures

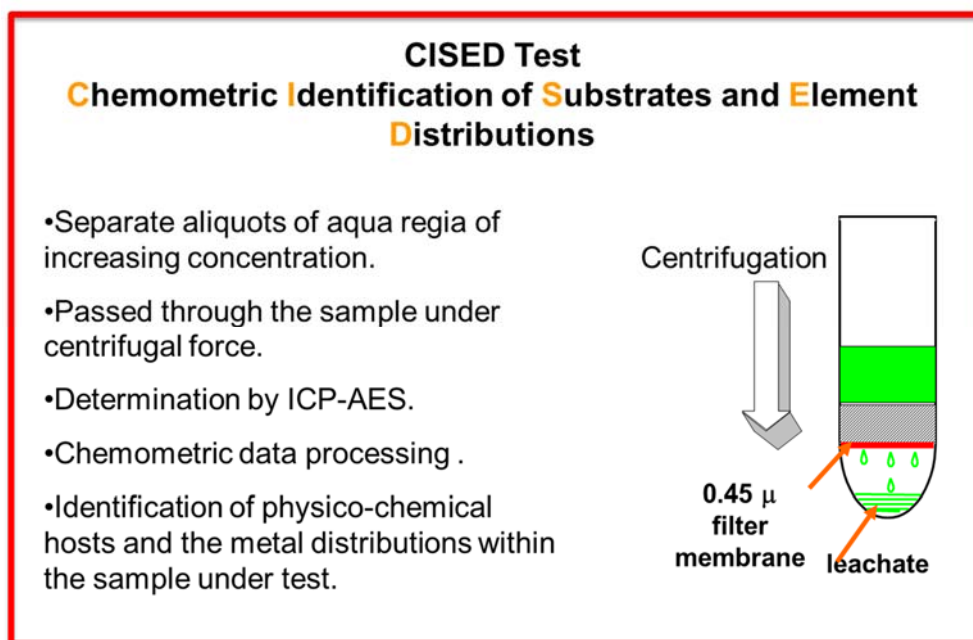


Figure 1 CISED sequential extraction and chemometric data processing test methodology

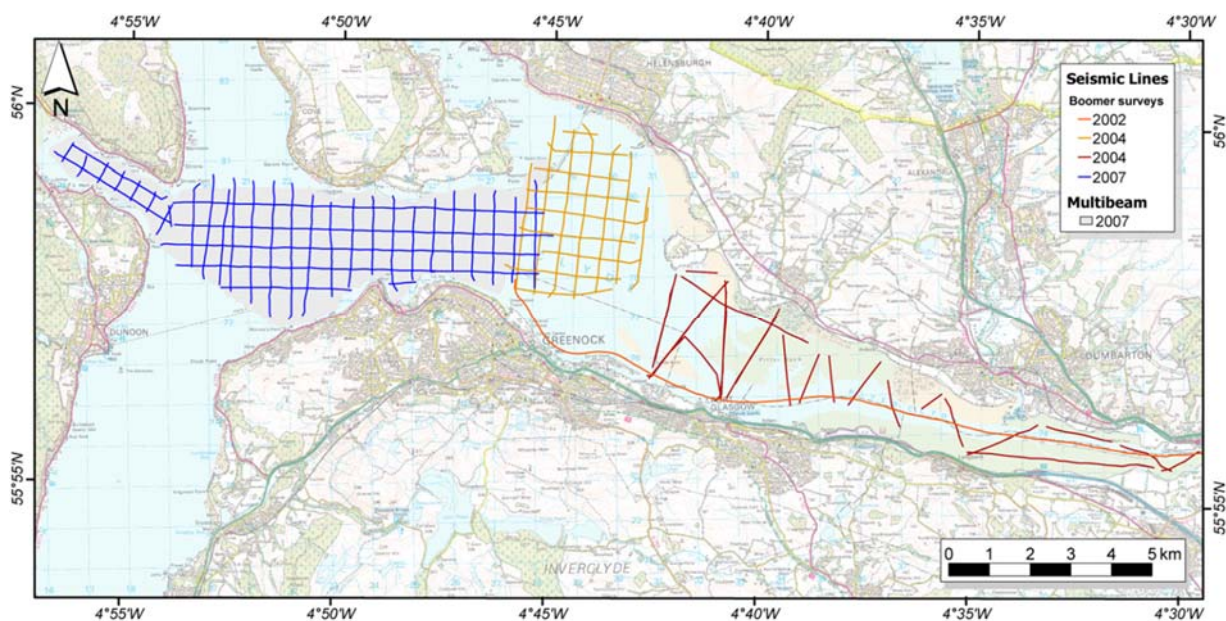


Figure 2 track plots of boomer surveys and multibeam coverage in the Clyde Estuary.

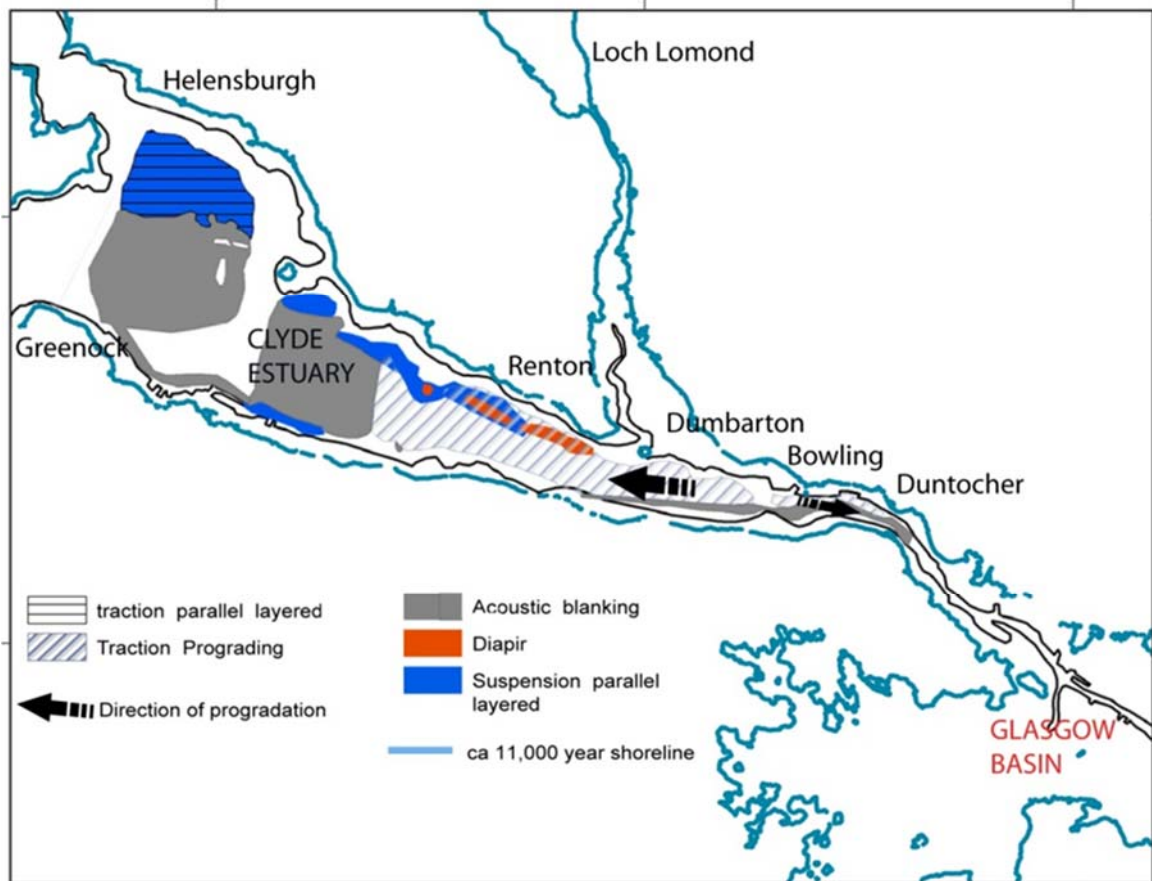


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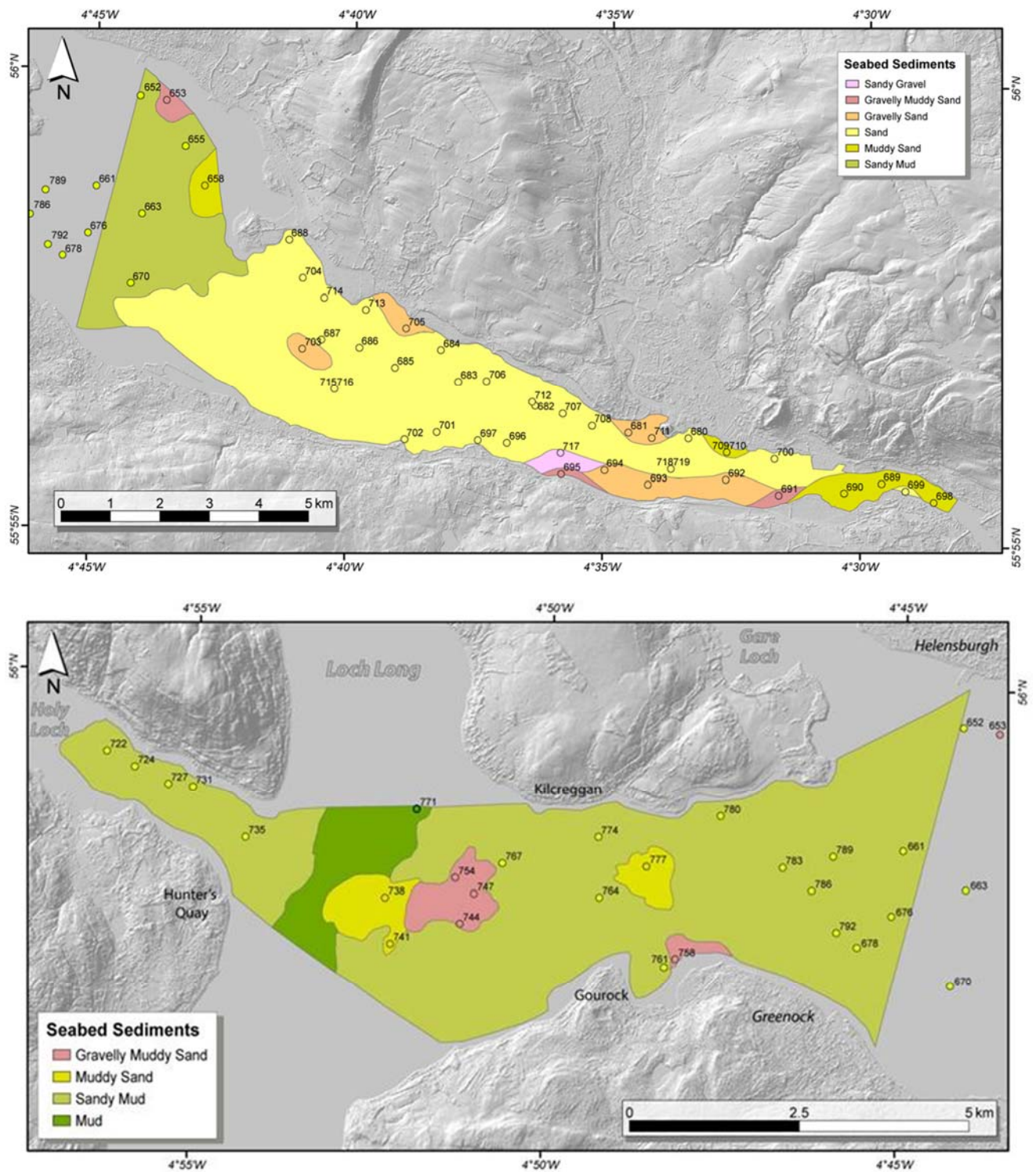


Figure 4 Distribution of seabed sediments in the Clyde Estuary

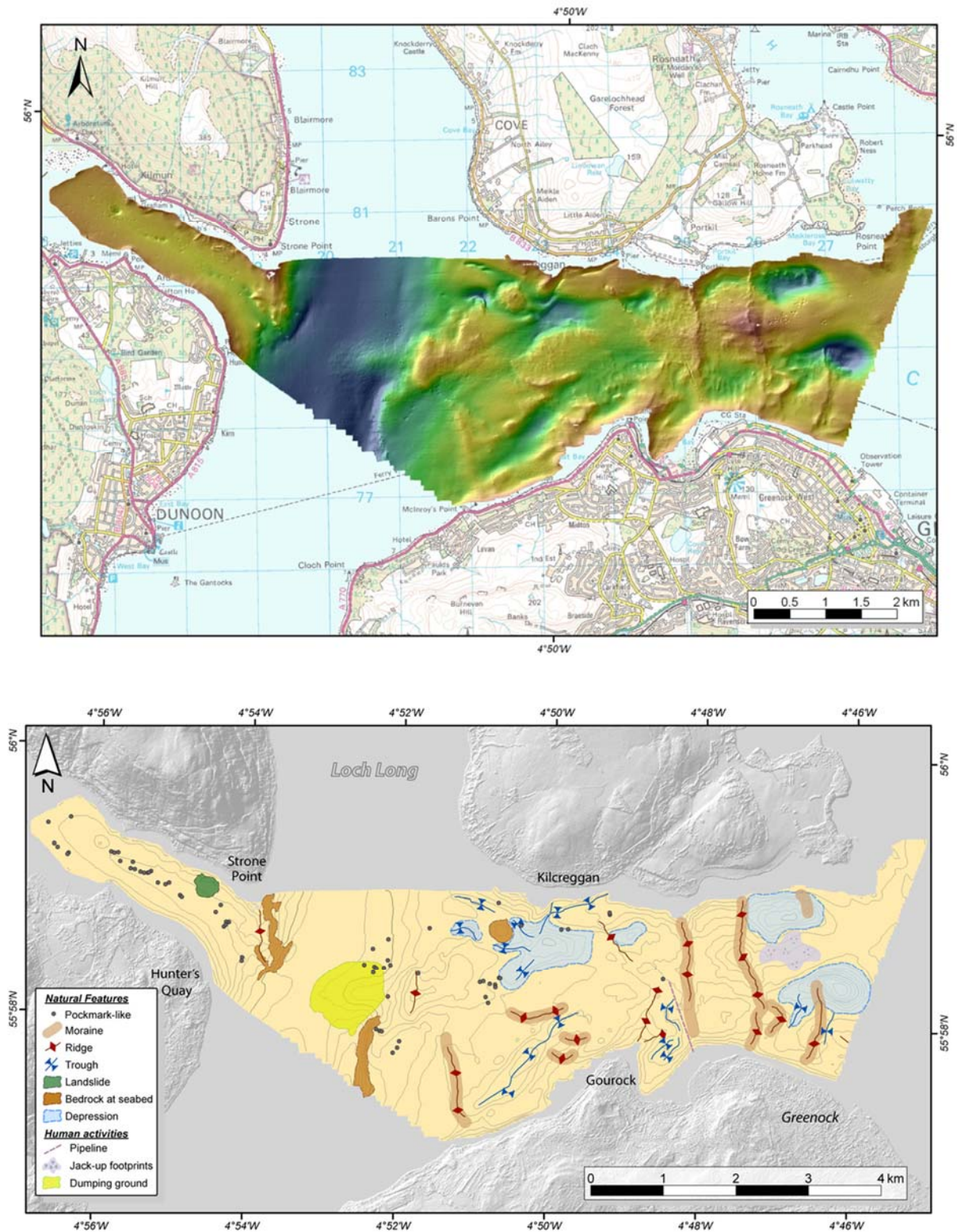


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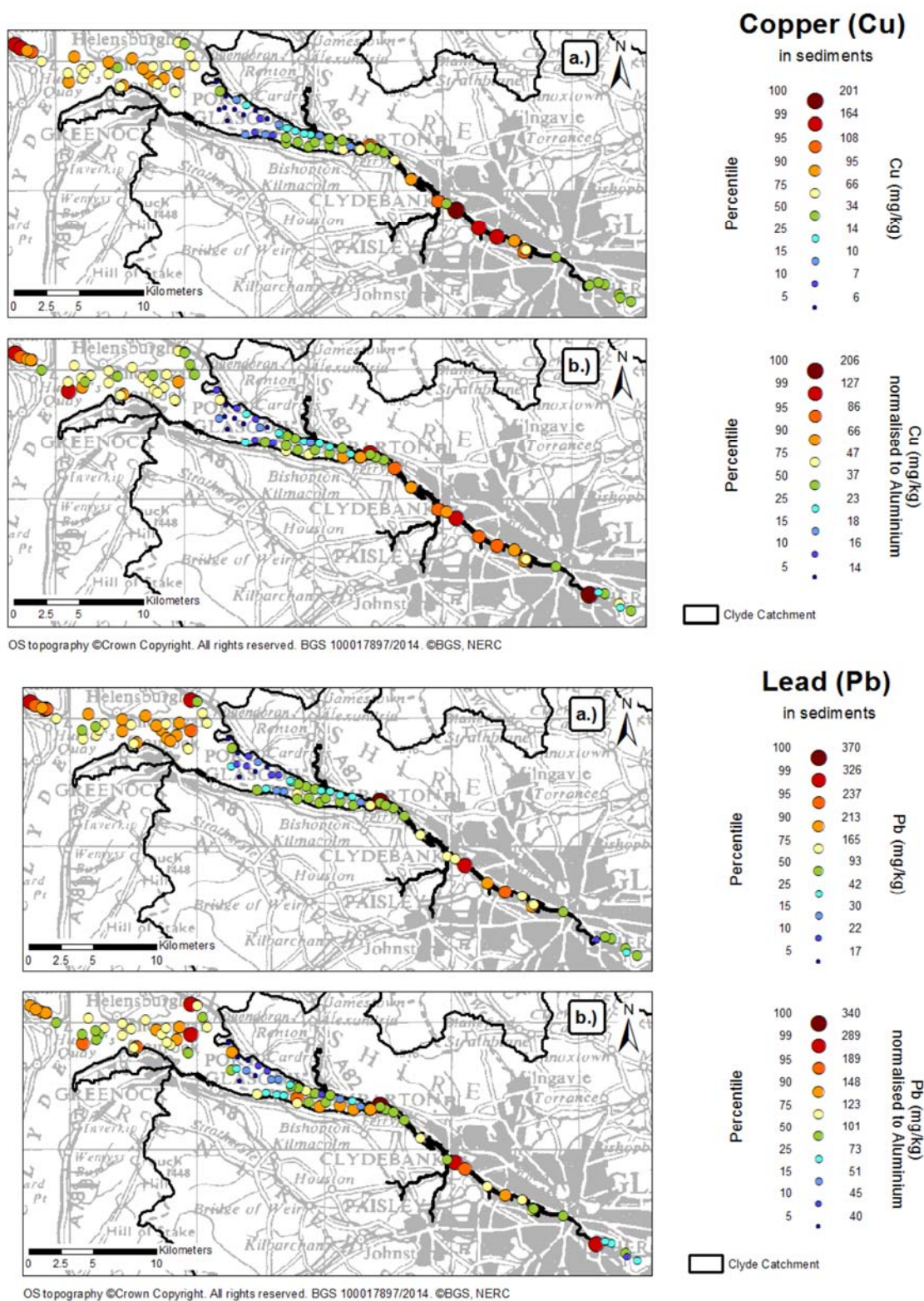


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### Exceeding Sediment Quality Guidelines

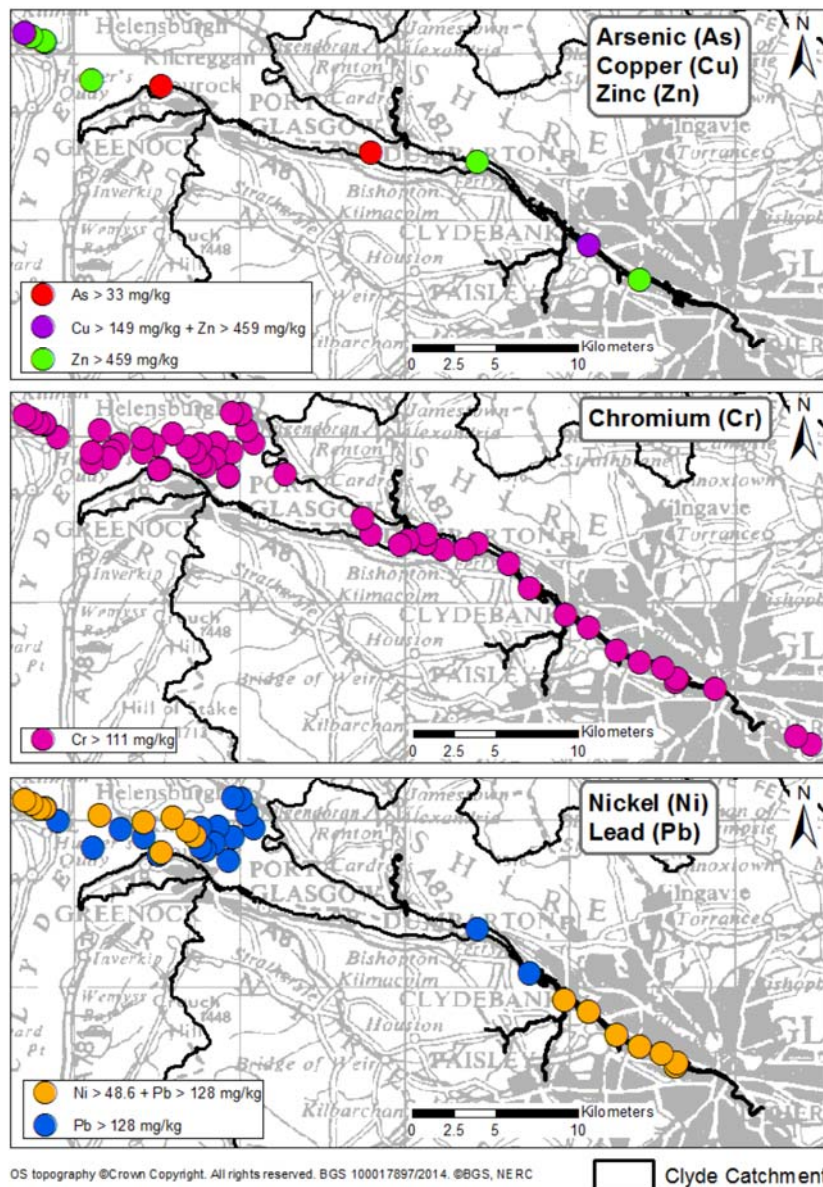


Figure 7 Individual samples in the Clyde estuary that exceed the probable effect concentrations of the sediment quality guidelines for arsenic, chromium, copper, nickel, lead and zinc



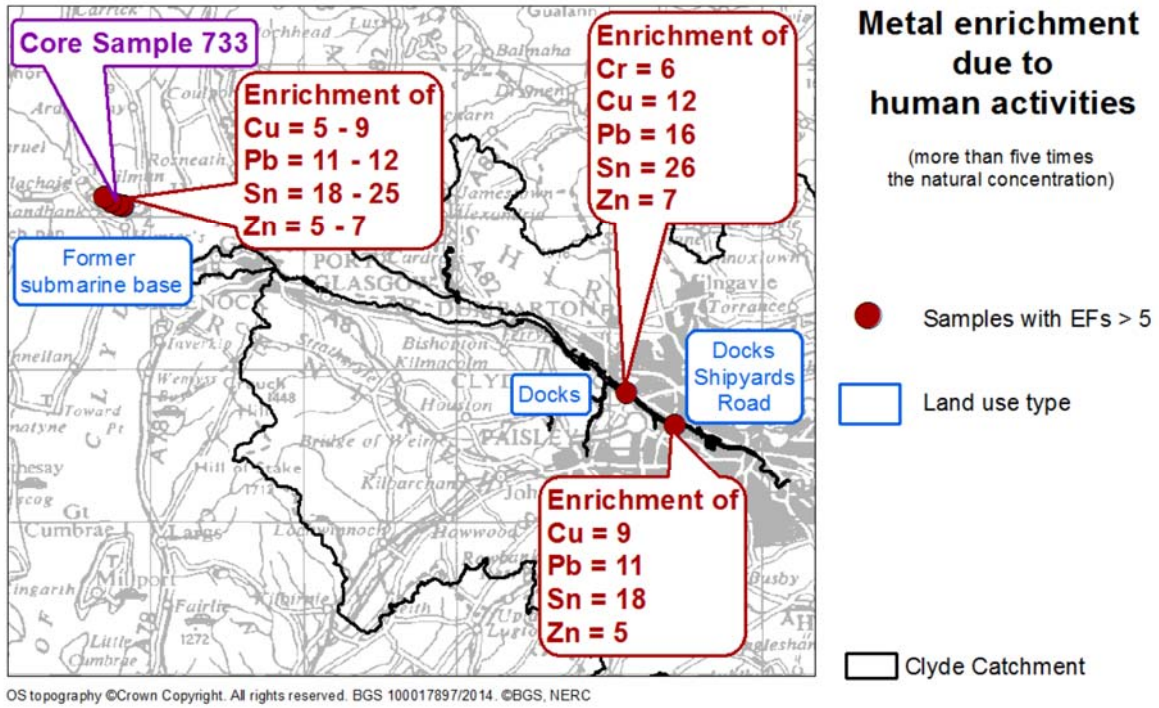


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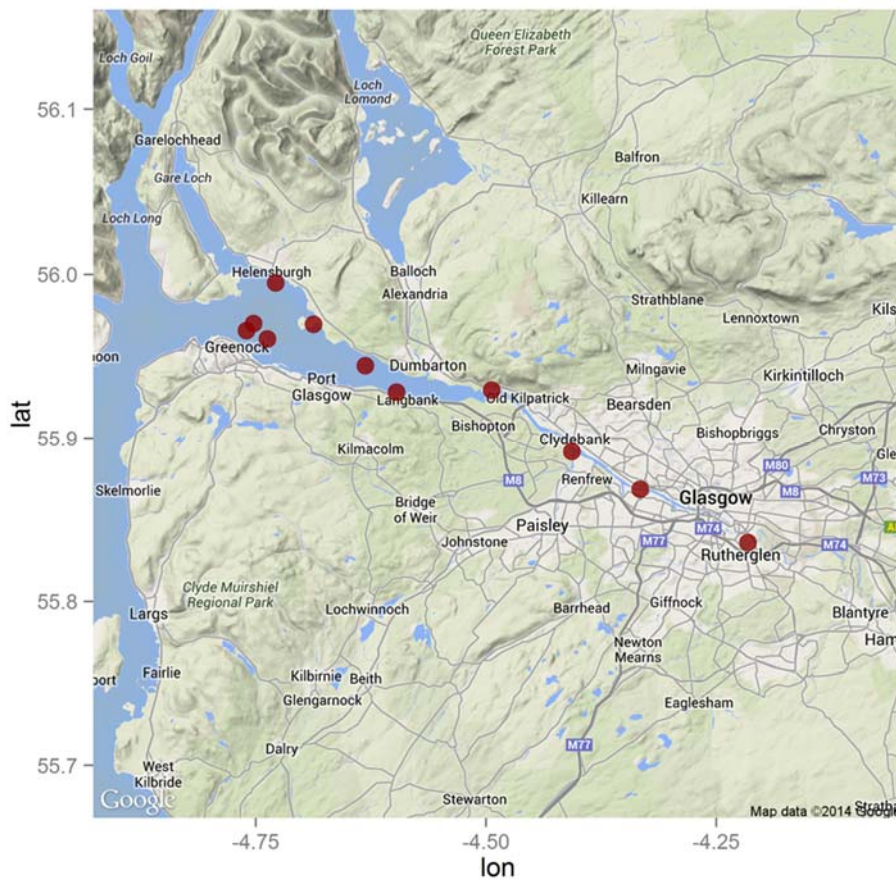


Figure 9 Locations of cores used for CISED sequential extraction study

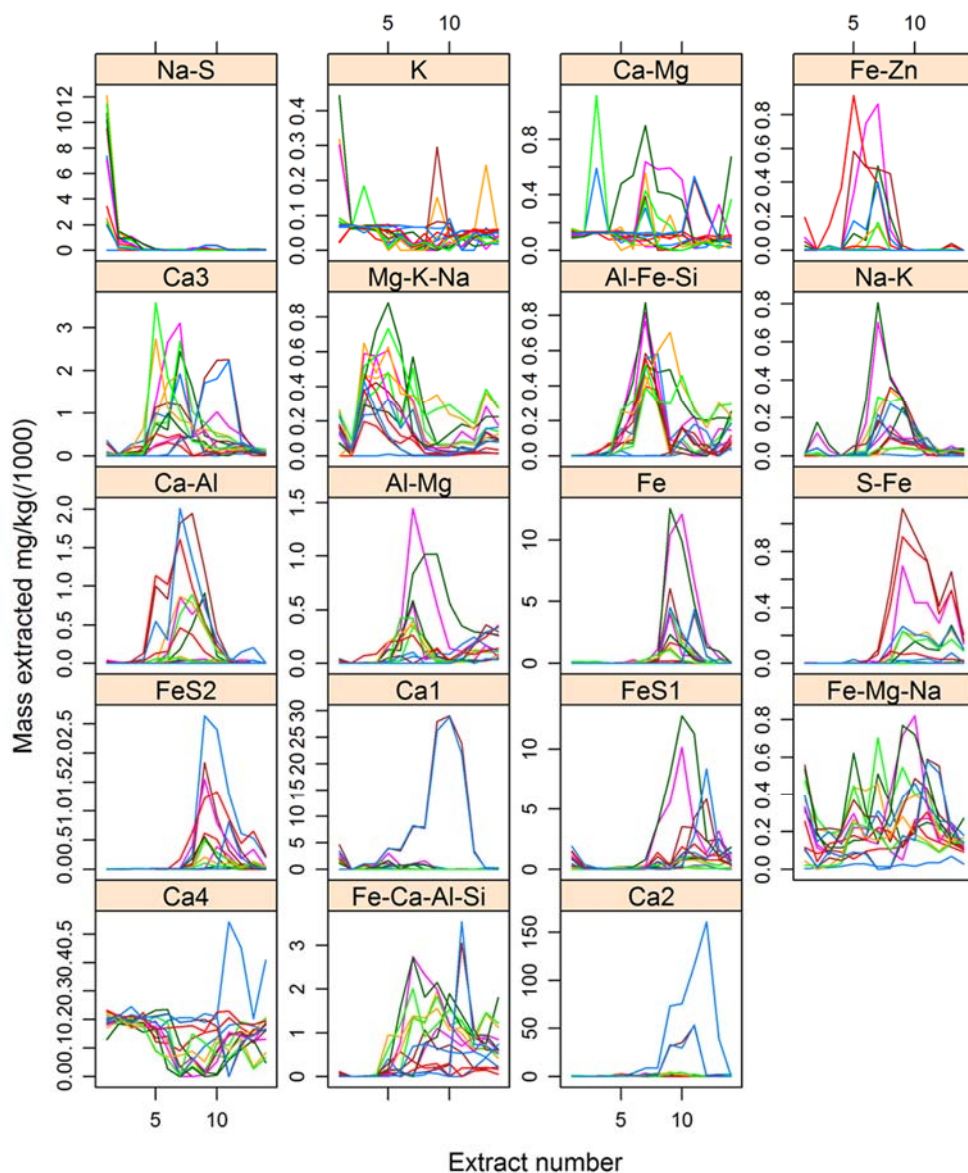


Figure 10 CISED sequential extraction profiles for each component in each sediment sample. The components are ordered by increasing difficulty of extraction

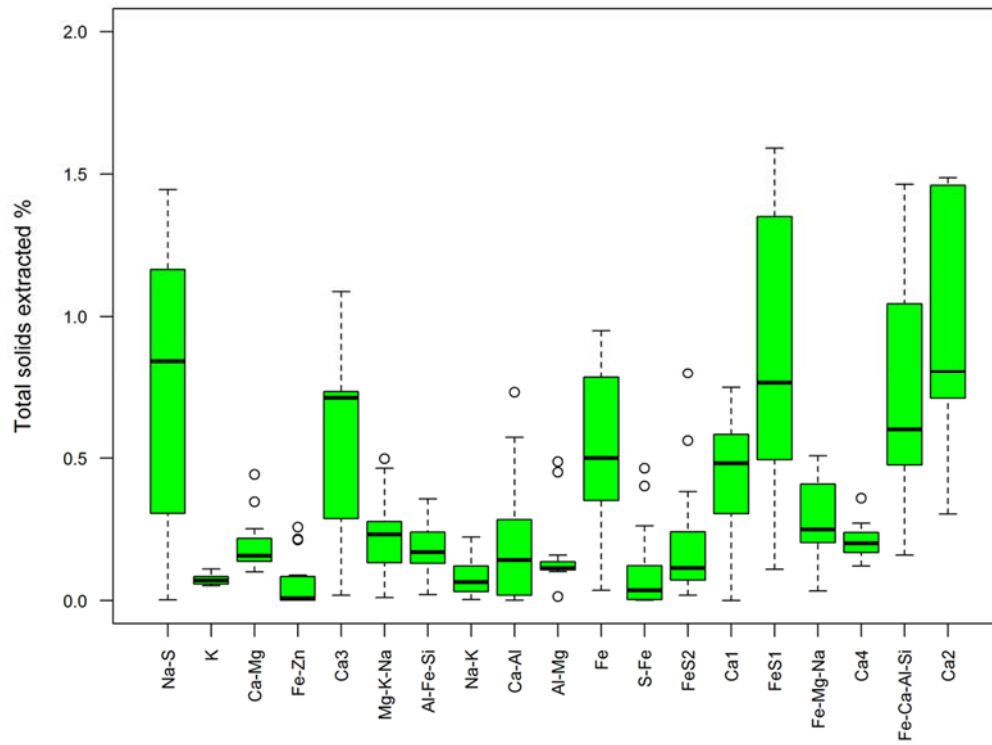


Figure 11 the relative contribution of each component in the CISED sequential extractions summarised as boxplots. The components are ordered by increasing difficulty of extraction

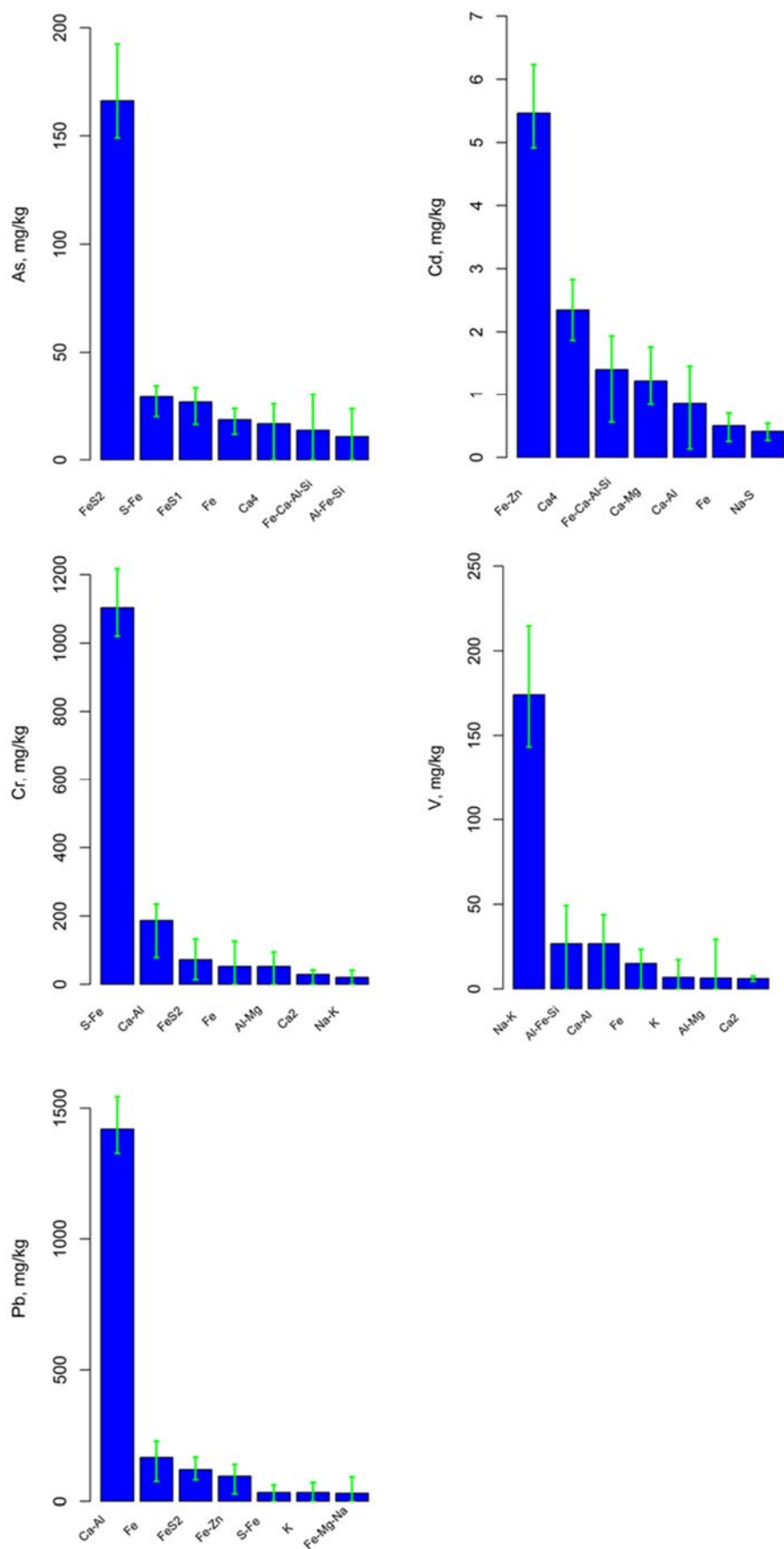


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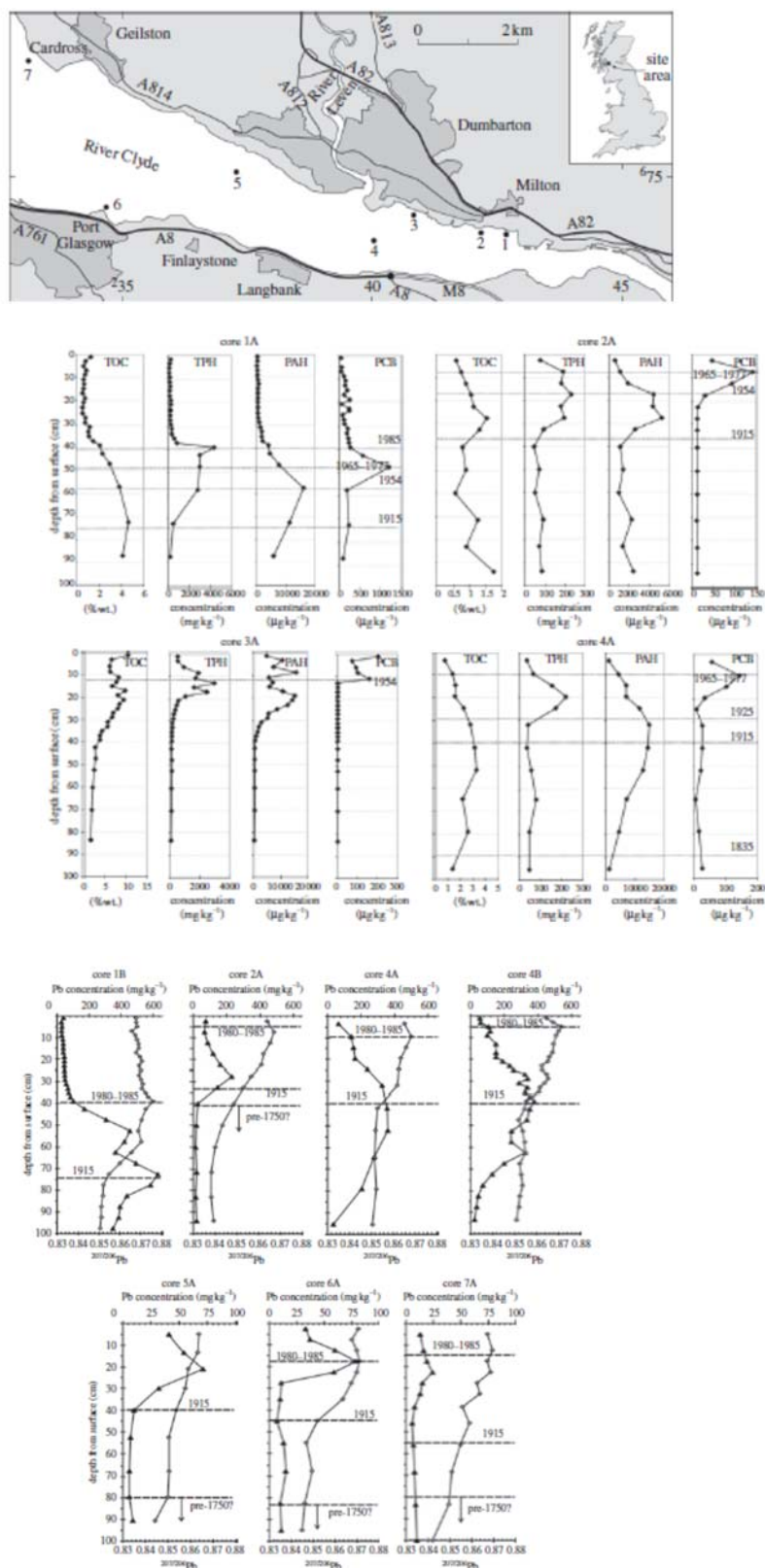


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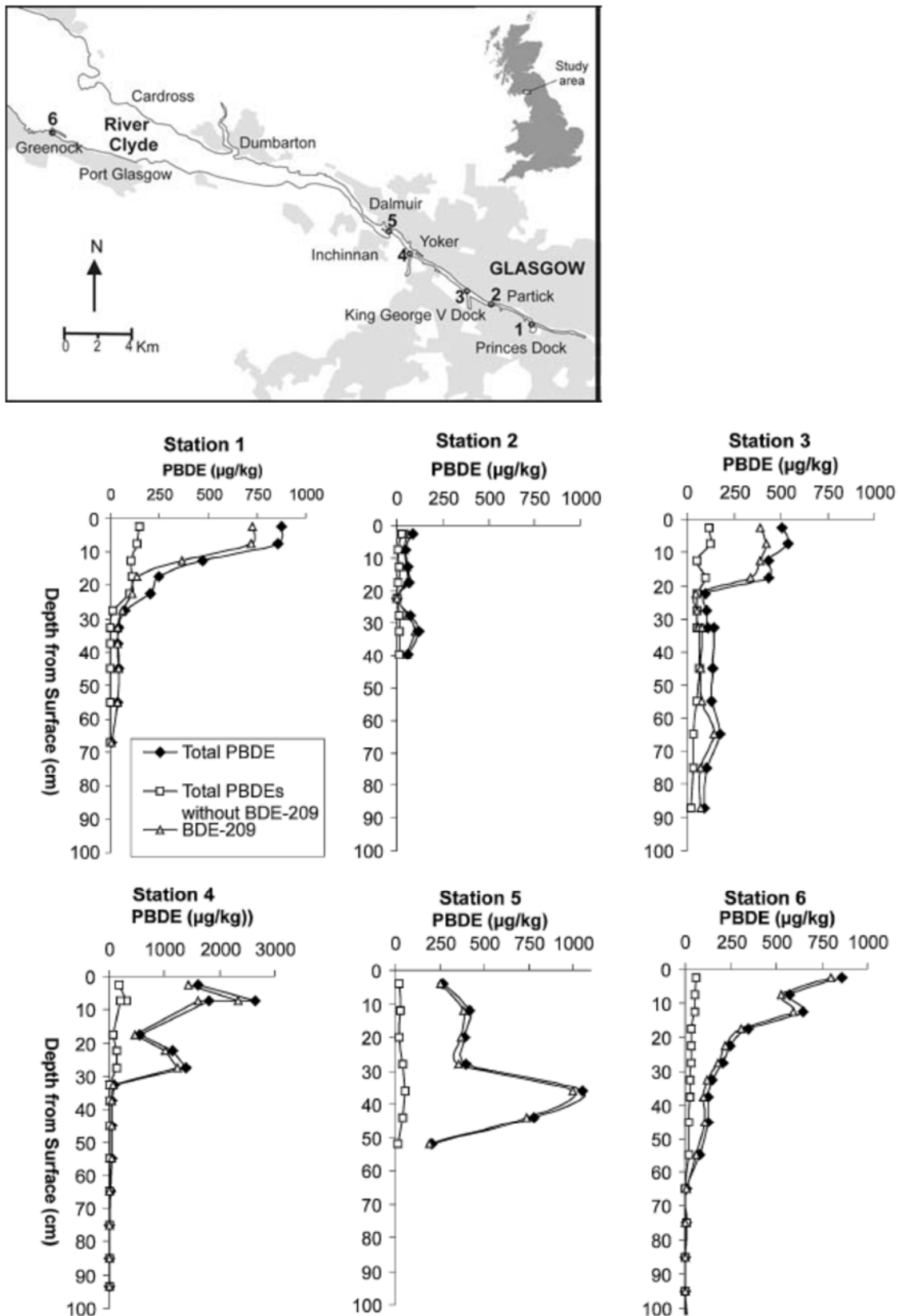


Figure 14. Location of samples and depth profiles of PBDE in sediment cores from the Clyde Estuary Vane et al 2010

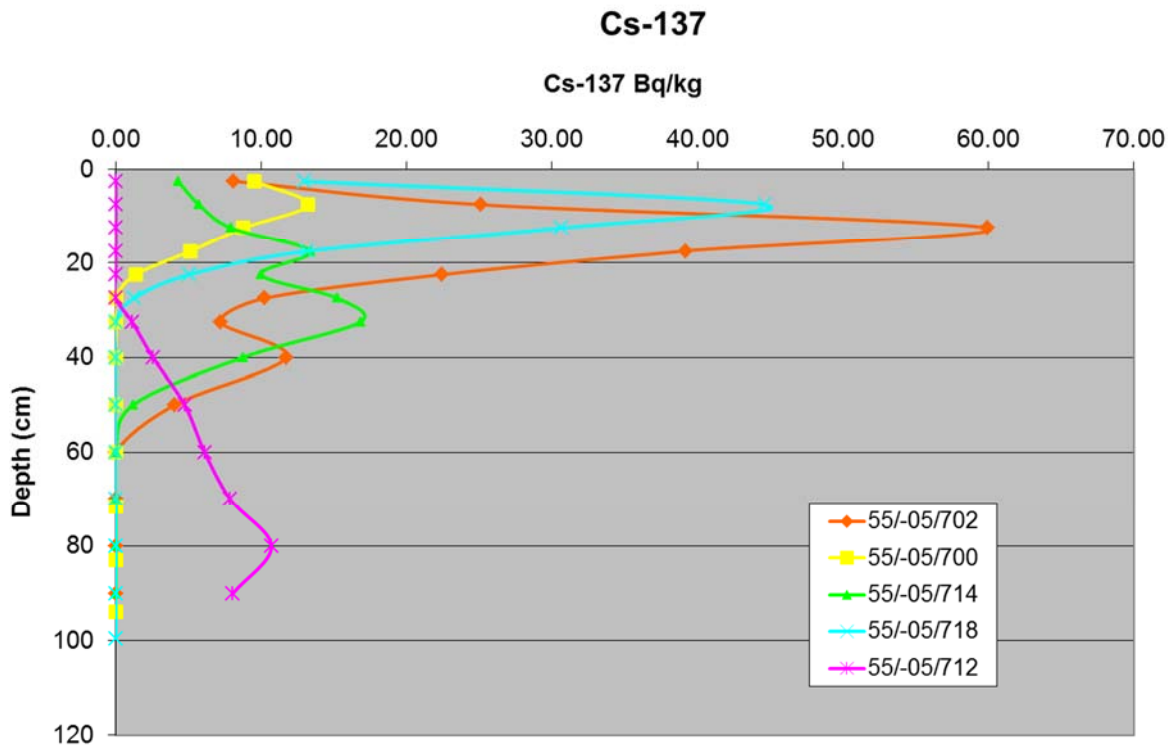


Figure 15 Depth profiles down cores for <sup>137</sup>Cs in Clyde Estuary sediments (see Figure 4 for locations)

***Jones et al., 2019 in Earth and Environmental Science Transactions of the Royal Society of Edinburgh. 108 (2-3). 269-288.***

Tables (on separate pages)