University of Strathclyde
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A Study of Potentially Toxic Elements in the Forth and Clyde Canal, Scotland, UK

by

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A thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

Signed:

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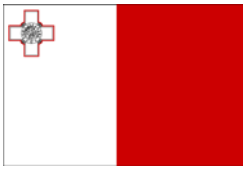

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Abstract

Canal sediments are an important geochemical indicator of the pollutant status of both the waterway itself and the surrounding area. In this study, sediment samples were collected from the Forth and Clyde Canal, Scotland, UK, and analysed for potentially toxic elements (PTE).

Pseudototal concentrations of As (5.54 – 219 mg/kg), Cd (< 0.000557 – 11.0 mg/kg), Cr (44.8 – 883 mg/kg), Cu (39.3 – 618 mg/kg), Fe (35.8 – 72.1 g/kg), Mn (720 – 4460 mg/kg), Ni (42.0 – 154 mg/kg), Pb (93.9 – 2740 mg/kg), Sn (5.36 – 122 mg/kg), and Zn (288 – 3640 mg/kg), measured by ICP-MS, were lower than those reported by British Waterways in 1992 but higher than relevant environmental quality standards, as was the Hg concentration (0.589 – 9.19 mg/kg) determined using CVAFS. The concentration of Fe was relatively constant, but an urban/rural divide was evident in the concentrations of the other analytes, indicting significant anthropogenic input, most likely due to runoff of contaminated urban soils. High levels of analytes at particular locations could often be attributed to historical industrial activities. For site-by-site comparisons, PTE concentrations were normalised to account for organic matter content.

The modified BCR sequential extraction was applied to fractionate the PTE content (except for Hg) and estimate their potential mobility. A risk assessment code calculation showed that the mobility order was: Cd/Mn/Zn>As/Fe/Pb>Cr/Cu>Ni>Sn. However, levels of Cd were generally low. The analyte of greatest concern was Pb with up to 1960 mg/kg released between the acid exchangeable and reducible fractions.

Concentrations of methylmercury (Me-Hg), monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) were measured using GC-ICP-MS. Levels of Me-Hg (3.44 – 14.1 μg/kg) were < 0.58% of the pseudototal Hg content. The likely source is *in situ* bacteria-mediated methylation of inorganic Hg. Organotin mean concentrations were low at 28.6 – 71.8, 48.7 – 113, and 48.2 – 189 μg/kg for MBT, DBT and TBT, respectively.

Table of Contents

1 Introduction

1.1 Why Study Canals?

Canal systems are of geochemical interest because they are a source of information about sources, transport and fate of potentially toxic elements (PTEs) in urban and rural environments. Surface water runoff carries substantial amounts of soil particles into freshwater canal systems. Particulate matter that is not light enough to remain suspended in the water will settle to the bottom of the canal, forming sediment that can act as a medium for dynamic sorption and desorption of PTEs, thus acting as both a sink for, and a source of, contamination.

Of particular interest are major canals that have been extant for long periods of time since their sediments may provide insight into both historical and current sources of PTEs; and canals that pass through areas with various land-uses allow comparisons to be made between types and levels of PTEs present in different locations.

The work described in this thesis is a detailed study of PTEs in the sediments of the Forth and Clyde Canal, Scotland, UK. The canal is more that 200 years old, extends 35 miles from the west coast to the east coast of the country, and passes through urban, sub-urban and rural areas. It has recently (2001) undergone redevelopment and been reopened for public use. These various factors make it an excellent system in which to study how anthropogenic activities affect PTE load and distribution in canal sediments.

1.2 The Study Area

1.2.1 Canals in Scotland

There exist three distinct man-made waterways in Scotland – the Caledonian Canal in the Highlands, the Crinan Canal in the West Highlands, and the Lowland Canal Network, which was made up of five segments: the Forth and Clyde Canal, which runs from Grangemouth to Bowling; the Glasgow Branch, which is a short side-branch of the Forth and Clyde Canal into central Glasgow; the Forth and Cart Canal, which was a short side-branch of the Forth and Clyde Canal that served as a

short cut to the River Clyde; the Monkland Canal, which ran through the eastern suburbs of Glasgow and connected with the terminus of the Glasgow Branch (known as Port Dundas); and the Glasgow and Edinburgh Union Canal (commonly referred to simply as the Union Canal), which connects with the Forth and Clyde Canal at Falkirk and runs towards central Edinburgh. For the best part of the late 1800s, the five canals of the Lowland canal network were interconnected. Nowadays, the Forth and Cart Canal has long been filled in, leaving no sign that it ever existed, while the Monkland Canal is in a non-navigable state as most of it has been filled in, except for two short segments. The rest of the canals reopened for public use at the turn of the century, albeit having had some modifications to their original route. Figure 1.1 shows the locations of the current waterways on a map of Scotland[1].

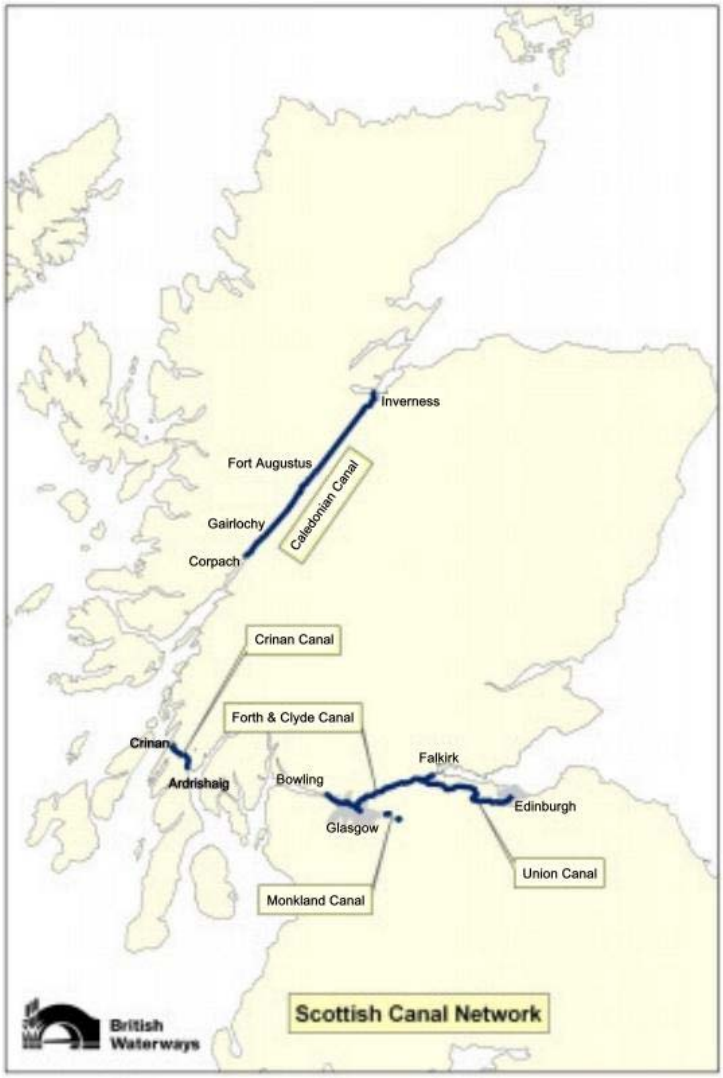

Figure 1.1 Present locations of man-made waterways in Scotland[1]

1.2.1.1 History of the Lowlands Canal Network

During the early years of the industrial revolution, an urgent need was felt for improvement of shipping to be able to cope with the ever increasing demands for transportation of goods and people at the time when road transport was still relying on horse-drawn cabs, and before the advent of the steam train and the rail network.

Man-made waterways were viewed as the solution at the time[1]. The Forth and Clyde Canal was constructed at the narrowest part of the Scottish Lowlands to provide a shorter, inland route for seagoing vessels between the Firth of Forth and the Firth of Clyde. The name of these two estuaries gave rise to its name.

Construction began on the 10th of June, 1768[2]. Works commenced from the River Carron in the town of Grangemouth on the Firth of Forth and moved westwards towards the village of Bowling on the Firth of Clyde[2], stretching 35 miles[3] and wide enough to accommodate the seagoing vessels of the time[4]. The Forth and Clyde Canal links Grangemouth, Falkirk, Bonnybridge, Castlecary, Twechar, Kirkintilloch, Lenzie, Maryhill (Glasgow), Clydebank and Bowling.

The Forth and Clyde Canal opened in 1790. It had 39 locks each of which were over 18 m long and nearly 6 m wide. An additional 3 mile branch to central Glasgow leading to the Port Dundas Basin from the Stockingfield Junction in Maryhill was also constructed at the same time[2].

The Monkland Canal's construction began in 1770 in the Eastern Glasgow Monklands district and surrounding suburbs to service the needs of that growing industrial area, and was joined with the Port Dundas Basin in 1793[5]. The Monkland Canal had numerous short side branches constructed to better service the local areas.

Construction on the Union Canal began in 1818 and concluded with its opening in 1822, ultimately providing a direct route between Glasgow and Edinburgh[4]. It was dug as a contour canal, spanning 32 miles[5], and therefore a characteristic was that it had no locks, except for a flight of 11 locks at the Falkirk Junction in Falkirk, where it met with the Forth and Clyde Canal.

The Forth and Cart Canal was a short canal which connected the Forth and Clyde Canal at Whitecrook with the River Clyde opposite the mouth of the River Cart. Construction of this 0.5 mile canal began in 1836 and it was opened in 1840.

This canal was intended to provide a short cut and thus avoid having to go through Bowling Basin, which was situated around 7 miles downstream on the River Clyde.

Timber, coal, clay and sand, and later even vehicles such as carts and railway wagons[2], were major cargoes transported from one side of Scotland to the other; there was also a regular passenger service[4]. Over three million tons of goods and 200,000 people are thought to have been transported per year in the mid-1800s along the Forth and Clyde Canal before its decline[1]. The transport facility and the presence of a fresh water source was the impetus for many industries to set up along the canal; these include, amongst others, dye and print works, whisky distilling, boat building, oil extraction, glass factories, a munitions factory, fertilizer manufacture, iron foundries, building material manufacture collieries, and leather tanning industries[1].

1.2.1.2 Demise of the Network

The introduction of the Glasgow to Edinburgh railway in 1842 caused the rapid downfall of the Forth and Clyde Canal and the Union Canal. The profitability of the canal network started to decline steadily by the end of the 19th Century following the expansion of the railway network in the 1860s[1], which proved to be a more convenient means of transport[4]. The development of the road network in the early 1900s dealt the canal its final blow[1].

The Union Canal was bought by the North British Railway Company in 1861, and in 1921 Port Hamilton and Port Hopetoun were sold to Edinburgh Council and filled in, leaving the Lochrin Basin as the new canal terminal at Edinburgh, while the Forth and Clyde Canal was bought by the Caledonian Railway in 1867[4].

The Forth and Cart Canal was short lived as it was closed in 1893 and quickly filled in, primarily to make way for the ever expanding rail network. The Union Canal was abandoned in the 1930s and had its connection with the Forth and Clyde Canal severed as the flight of 11 locks were filled in. The Monkland Canal was abandoned in 1942 after falling into disuse.

The Canal network was eventually taken over by the British Transport Commission following nationalisation of the waterways in 1948, and then passed onto the newly established British Waterways Board in 1962. As of the 1st January

1963[2], the waterways ceased to operate following a decree in Parliament which closed all rights of navigation[4]. Following its closure and years of disuse, the canals fell into a state of neglect with portions even being filled in and built over.

1.2.1.3 The Canal Network Today

Until the 2nd July 2012, British Waterways was responsible for the upkeep, maintenance and improvement of inland waterways and rivers in the whole of Great Britain. However, this statutory corporation owned by the UK Government has now ceased to exist and its responsibilities have been transferred to two newly created entities. Responsibility in England and Wales has been given to the Canal and River Trust charity[6], while all canals in Scotland are today under the authority of Scottish Canals, which is a public body of the Scottish Government[6].

In the 1990s, as part of the run up to the new millennium, the Millennium Commission secured sufficient funds for the rehabilitation and reconnection of the Forth and Clyde Canal and the Union Canal at the Falkirk Junction as part of the Millennium Link Project[4], for use by pleasure craft. The Forth and Clyde Canal was re-opened in 2001 providing coast-to-coast navigation, while the link with the Union Canal was opened in 2002, through the Falkirk Wheel, allowing once again navigation from the centre of Glasgow to the centre of Edinburgh[3]. The Falkirk Wheel could not be placed on the site of the original junction as this area was now built up. It was instead sited around a mile further to the west; this required the construction of an extension to the Union Canal that necessitated the installation of two, side by side, locks. The basin at the bottom of the Falkirk Wheel is higher than the Forth and Clyde Canal; they are connected through the Golden Jubilee Lock. All this is represented in the photograph displayed in Figure 1.2[7].

Figure 1.2 The new Falkirk Junction, with identification of the location of the former junction[7]

Rehabilitation of the Lochrin Basin area in Edinburgh is still ongoing since the restoration of the terminal of the Union Canal is combined with the regeneration of the whole area, where new buildings for offices and apartments are set to replace older ones, in a project called Edinburgh Quay[2].

The Monkland Canal is nowadays no longer available for navigation. Part the M8 motorway was built over much of the western section of the canal in the late 1970s[8], the reason being that the existence of the canal was a historical boundary to surrounding areas, thus problems arising from building this segment of the motorway were minimised by following on its contours[9]. Figure 1.3[10] depicts the route of the Monkland Canal and that of the M8/A8 road.

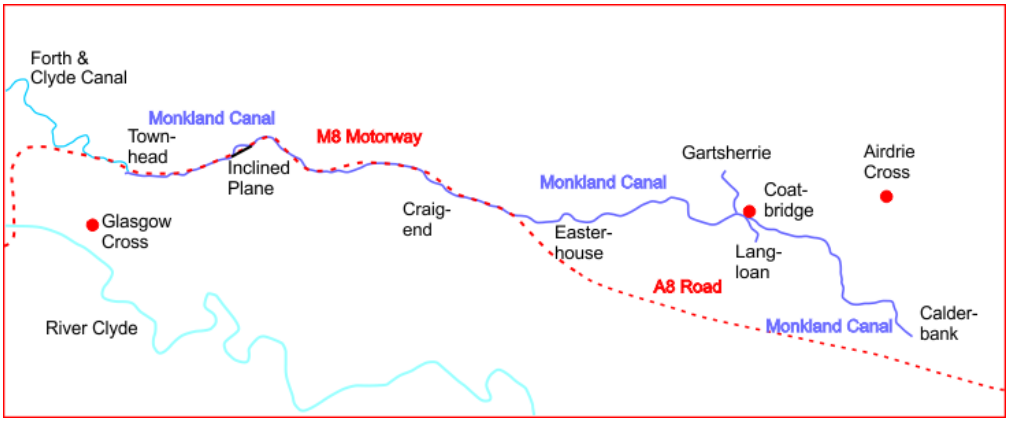

Figure 1.3 The Monkland Canal and M8/A8 road route diagram[10]

Although the M8/A8 road continued southwards west of Easterhouse, most of the eastern part of the Monkland Canal was filled in to make way for the redevelopment of the surrounding areas, leaving only two separate tracts which are still visible, in Coatbridge and Woodhall (east of Coatbridge). All the filled in sections had a set of twin culverts built and buried to ensure that the watercourse remained connected throughout[5].

In the western-most section, the Monkland Canal was filled in right to its junction with Port Dundas in the Glasgow Branch. As of 2012, although Port Dundas still exists, Spiers Wharf currently serves at the canal terminal as the entry to Port Dundas is partly filled in, allowing water to flow but too narrow for vessels to pass. The area is earmarked for redevelopment[3], but apparently there is an ongoing legal dispute regarding land ownership which needs to be settled first[11].

Another ongoing project called The Helix[12] is redesigning where the Forth and Clyde Canal joins the River Carron through the building of a new canal link at Grangemouth. This new segment will run along the River Carron eastwards, towards the wider Firth of Forth. This will improve access between the Forth Estuary and the Forth and Clyde Canal since the River Carron is tidal, precluding reliable access, and is also crossed by four bridges – this is a nuisance as facilities to raise or lower the mast of sailing boats are situated further downstream in the River Carron rather than at the Forth and Clyde Canal's terminus, as is the case at Bowling Basin. New boating facilities, including the ability to hoist and lower or raise masts onto sailing boats, will be installed at the new terminus being built and will help expand the east coast leisure, sailing and boating market[12]. Figure 1.4[13] is a photograph taken in October 2012 showing the progress of the project. The Forth and Clyde Canal can be seen at the far end, together with the new stretch of canal being dug along the south bank of the River Carron, whose terminus is before the first of the four bridges from the Firth of Forth.

Figure 1.4 A photograph showing the new canal stretch alongside the River Carron[13]

The network of Lowland canals that are presently navigable is outlined in Figure 1.5[14]. The canals are about 3 m deep. Scottish Canals aim at keeping a navigable depth of 2.2 m of water column above the sediment at the bottom[11]. The sediment has no long-term stratification since it is churned by the flow of boats above it as well as by dredging.

Figure 1.5 Map of the presently navigable Lowlands canal network[14]

1.2.2 The Forth and Clyde Canal and the Glasgow Branch

1.2.2.1 Water Supply

Maintaining navigability is not only achieved by keeping the sediment level at around 0.8 m through dredging, but necessitates that the water level is kept at around 2.2 m. Water is lost from the Forth and Clyde Canal primarily through the sea locks at either end since the canal is elevated above mean sea level. Other possible routes are through evaporation and pumping.

There exist specific points along the canal called feeder lades where water flow into the canal is regulated by Scottish Canals' personnel based on operational requirements.

The Monkland Canal's water supply is provided from three reservoirs (Hillend Reservoir, Black Loch and Lily Loch) near Coatbridge, and acts as a main water supplier to the Forth and Clyde Canal at Port Dundas to this day[5]. This is the reason why surface water along the Glasgow Branch appears to flow from Port Dundas towards the Stockingfield Junction rather than vice-versa, where it then flows westwards towards Bowling and ultimately out from the sea lock into the River Clyde.

Water is also supplied to the Forth and Clyde Canal from two purpose-built reservoirs near Kilsyth[5]; the Birkenburn Reservoir and the Townhead Reservoir, where the former feeds the latter, and from the latter the water is channelled through to the canal via a feeder lade at Craigmarloch[15]. This is the highest section of the canal above mean sea level and water flows either west or east from this location.

There are also small water feeders for the Forth and Clyde Canal at Lenzie and at Shirva, both close to Kirkintilloch, from natural streams in the vicinity[15].

Water is supplied to the Union Canal from Cobbinshaw Reservoir via the Murieston and Linhouse Waters, and then the River Almond. The canal feeder lade leaves the River Almond at Almondell and Calderwood Country Park in Midcalder and meets the Union Canal at Lin's Mill[16].

As this is the prime source of water to the canal, the direction of flow is determined here. As the water flowing eastwards meets a dead end at Lochrin Basin,

it flows back, creating a counter-current and hence a rather overall stale system. However, water flowing west is slow but constant because some is lost as it falls through the Falkirk Wheel into its basin, ultimately ending in the Forth and Clyde Canal through the Golden Jubilee lock.

1.2.2.2 Locks

The Forth and Clyde was initially constructed having 39 locks, whose numbering commenced from the east and progressively moved westwards. This was in line with the direction that the canal was built, and eventually as it was named. The layout of the canal is shown in Figure 1.6[17], listing lock numbers, names and landmarks the canal crosses along its route. It also indicates the location of the junction with the Union Canal and with the Glasgow Branch, as well as where the Monkland Canal and the Forth and Cart Canal were historically situated.

Nowadays, the locks commence from number 2, the present sea lock on the east coast. Originally, the terminus with the River Carron was situated further downstream and closer to the wider Firth of Forth; however, this section was filled in and built over after its closure. This is represented by the green line in Figure 1.6[17]. In the run up to its reopening in 2001, a new canal segment, termed the Carron Cut, was constructed to reconnect the canal with the river from the point it was severed. This involved also the movement of lock 3, which used to be in the straight section of the canal but is now ~200 m further to the east and round the bend into the Carron Cut. This is represented by the continuous blue line in Figure 1.6[17], whereas the dotted blue line outlines the new section that is being constructed as part of The Helix Project.

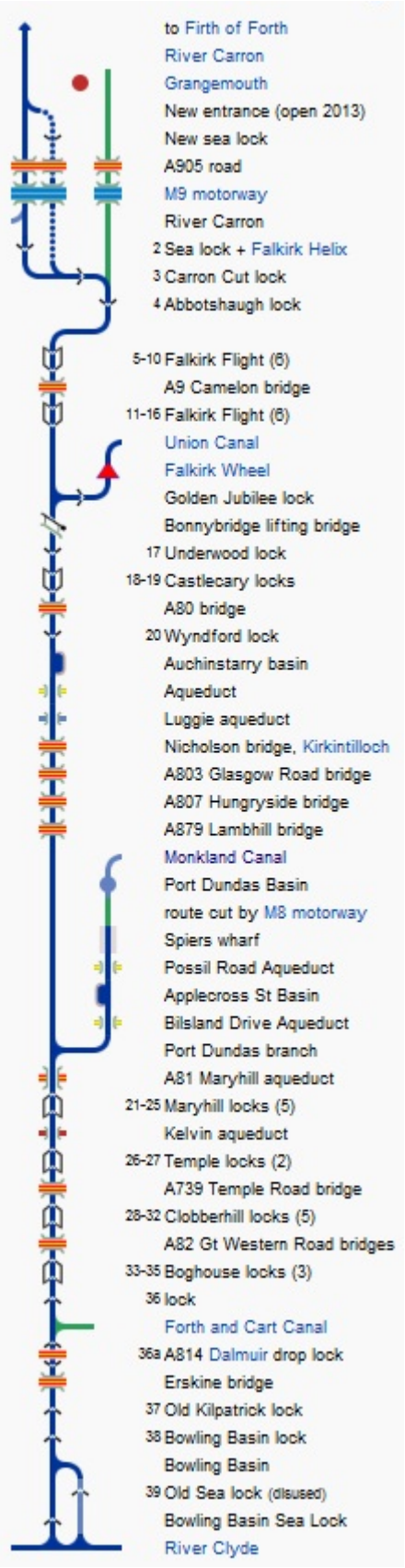

Figure 1.6 Schematic layout of the Forth and Clyde Canal and Glasgow Branch[17]

Figure 1.7[7] is a 1945 photograph showing the original route of the canal; the A905 Kerse Bridge was the only bridge crossing the River Carron at the time. Nowadays, this is crossed by the M9, a pedestrian bridge, the Kerse Bridge and yet another pedestrian bridge, as can be seen back in Figure 1.4[13].

Figure 1.7 Photograph from 1945 showing the original route of the east terminus of the Forth and Clyde Canal[7]

As other sections of the canal had roads built over on short bridges, some locks needed to be re-sited or built new prior to its reopening, to ensure there was enough headroom to enable passage of the vessels, without the need of modifying the road network. These are: lock 5 – moved ~300 m west; lock 7 – shifted just ~35 m west; lock 11 – moved ~150 m west; and lock 20 – moved ~150 m east. A new lock needed to be installed between lock 36 and 37 – the Dalmuir Drop Lock – and was numbered '36a'. This was necessary to lower the water level beneath the low A814 road bridge. At Bowling Basin, there used to be two operational sea locks, however nowadays only one is used, while the other has had its gates removed and serves as a berth where an old steamer is permanently moored.

The Glasgow Branch originally did not have any locks; however, it now has two that are situated between Spiers Wharf and Port Dundas. These were necessary to lower the water level of this short section of the canal due to the presence of a road bridge.

Lock Design

The lock gates stop at a wooden cill, which is a solid piece of timber, usually oak, laid horizontally at the base and acts like a doorstep. The timber's dimensions are approximately 300 mm (H) by 300 mm (W) by 6 m (L), the latter being the whole width of the lock. This timber is fixed to the bottom by long metal pins that are driven into a larger timber below that serves as the base of the lock. The gate is closed against the cill and the pressure of the water inside the lock or above the top gates pushes the gates against it, causing it to seal. The cill alleviates the pressure from the gates; in the absence of a cill, the gates would bear the full pressure of the water, causing leaks and ultimately structural damage to the gates. This permanent cill acts as a barrier to bottom sediment movement along a lock, while allowing only water and any suspended matter to flow through[15]. The cill and gates structure of a lock are shown in the photograph in Figure 1.8[18].

Figure 1.8 Photograph showing the cill and gates structure of a lock[18]

1.2.2.3 Possible Sources of Contamination

Pollutants can in principle enter the canal by three main routes; direct input from vessels, point source effluent discharges, and surface water runoff. Inputs from

vessels and effluent are now strictly regulated and so mainly historical, whereas soil runoff is an ongoing source of input.

Once introduced to the canal, the low volume of water present in the Forth and Clyde Canal as compared to the total area of walls and bottom sediment at any one segment of the canal, coupled with the slow water currents and flow rate, which is about 0.1 m/s[1], makes the surfaces an ideal sink for a wide array of chemical pollutants. The sediment acts as a sink and store for metals, and potentially other contaminants, which enter the canal.

The slow water flow contributes to a fairly high rate of sedimentation of autochthonous inputs. Suspended allochthonous input, particularly lighter particles, may travel some distance before depositing. Whereas natural rivers tend to have a rock bottom, man-made canals are cut through fields; hence the bottom is mostly covered in muddy sediment over a clay lining. The clay serves as an impermeable layer and was placed on purpose during the construction of the canal to prevent water loss through seepage into the surrounding ground[11]. These features enhance the cation exchange capacity (CEC) and the adsorption capabilities.

Anything that remains dissolved or suspended in the waters of the canal will eventually be washed out in the River Forth or the River Clyde, at the east and west ends, respectively.

Antifouling Paint

The canal has been and still is a sink for the various kinds of antifouling agents leaching from vessels' hulls that have been applied over the ages. Such input is deemed temporal and localised. First attempts at obtaining a suitable antifouling paint included mixtures of PTEs like As, Cd and Hg in paint. Later, pesticides were added. A breakthrough in effectiveness was obtained with tributyltin in the 1960s, and this was mass produced and widely popular. Presently-marketed antifouling paints typically are composed of a mixture of copper compounds and pesticides.

Any PTEs or compounds currently present in sediments are unlikely to be attributed to historical input due to intervening dredging operations. However, components in current antifouling paints may be present. These are expected to be

higher in ports and basins due to the longer residence time of berthed vessels as opposed to when they are simply passing through any stretch of canal.

Effluent Discharges

The advantages offered by the canal contributed to the fact that many industries flourished in the surrounding area over the years. Apart from its use in transportation and as a source of water, the canal was seen as a convenient sink for effluent discharge. Before the canal's closure in 1963, content of waste water effluent was unregulated[11].

Nowadays, Scottish Canals do not accept any form of industrial effluent discharge into the canal. Only surface water discharges are allowed[19]. However, they are aware of the existence of a number of historical domestic sewage discharge points which are still operative to date. The Scottish Environment Protection Agency, who are the regulators that grant licences for release of effluent into the water environment, including the canals, have advised that there are around 10 licensed discharges along the Forth and Clyde Canal, from houses, farms and stables situated mainly along the rural middle section where there is no sewage network. These empty directly into the canal or in a feeder lade that leads to the canal[20]. Discharge of anything other than domestic waste is not allowed. Any other effluent discharge source into the canal would be considered abusive and illegal. Such instances have been reported and action was taken[21].

Surface Runoff

The canal has numerous catchment areas. Some segments of the canal are elevated and are therefore not affected by this phenomenon. Those areas that lie at the bottom of an inclined plane are subject to direct input of surface runoff. Any surface water on adjacent land will trickle down towards the canal banks bringing in anything that can be carried along. Urban segments of the canal receive road dust as well as some soil, while rural segments receive primarily soil. Dust particles are typically small and may remain in suspension in the water for a considerably longer period of time than soil particles which typically clump and precipitate. Thus, the

canal is subject to heavy sedimentation from land soils, particularly in rural areas where there is more soil in the immediate vicinity of the banks.

The canal may also be subjected to indirect input from surface runoff through one of the feeder lades supplying water to the canal. This considerably increases the catchment surface area of the canal, whereby anything added to the water reservoirs or feeder lades may be transported into the canal.

1.2.2.4 Main Sources of Potentially Toxic Elements in Soils Adjacent to the Canal Network

The PTE content of the soil surrounding the catchment areas of the canal will be reflected in proximate sediment samples. This is because the greatest proportion of bottom arises from surface soil runoff. The industries that sprung up along the canal have left their mark on surrounding soils and beyond. It is logical to presume that rural and suburban areas with limited industrial past would have relatively less contaminated soils leading to lower levels of contamination entering adjacent waterways[22]. Rural areas with no industrial past may not necessarily be a reflection of natural background, such as soils originating from remote and pristine areas, due to water- or air-borne contamination and application of agrichemicals, but are likely to have the lowest PTE inputs.

The Glasgow Urban Conurbation

Glasgow is notorious for its heavy industrial past, from the very beginnings of the industrial revolution to its demise around 50 years ago. This has left its mark on contamination levels in soils, particularly those in the vicinity of where factories used to stand, but also at considerable distances away. The importation of raw materials and export of products, as well as any spillages or waste disposal, contributed to the contamination of soil in the industrial zones. Aerial emissions through the numerous stacks belching out unfiltered flue gas have caused contamination of soils situated further away through particle deposition. This process was affected by wind direction, wind speed, and rain.

Following the shift from the heavy industry to a more residential and business oriented approach in Glasgow, many regeneration and urban settlement programs

ensued in recent years. This included also projects which necessitated demolition of disused factories and landscaping. Much soil has been moved around, sometimes unwittingly spreading contamination. This has resulted in the presence of certain PTEs, in high levels, even in urban areas with no specific industrial history.

The recent (2012) survey of Glasgow soils published by the British Geological Survey outlined all the above mentioned scenarios[23]. These were proven through the extensive soil sampling and analysis survey carried out.

A recent major project commissioned by the European Commission (EC) was the EU URBSOIL project (Contract Number: EVK4-CT-2001-00053). Urban soil samples were collected from numerous sites at each of six major European cities: Aveiro (Portugal), Glasgow (UK), Ljubljana (Slovenia), Sevilla (Spain), Torino (Italy) and Uppsala (Sweden). The samples were analysed for their pseudototal (PT) Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn content using *aqua regia*[24] as well as using the revised Community Bureau of Reference (BCR) sequential extraction procedure[25], which is a widely applied protocol, to fractionate PTE content.

The authors report that substantial anthropogenic influence is present in Glasgow soils, especially particularly high levels of Cu, Pb and Zn, which are commonly associated with urban settings, as well as Cr and Ni, which are typically associated with point sources[22]. The PTE PT data will be discussed in further detail in Chapter 5.

Mercury Contamination from the Union Canal

Industries flourished along the Union Canal as they did along the Forth and Clyde Canal. Whereas other industries used various PTEs, the Nobel Westquarter Factory in Reddingmuirhead dealt with Hg. The factory operated between 1876 and 1968 and is estimated to have produced 73 million detonators, the main chemical constituent of which was mercury fulminate, $Hg(CNO)_2$[26].

The location of the detonator factory was within the outline drawn in Figure 1.9[27], which is a WWII aerial reconnaissance photograph taken by the Luftwaffe in 1941. The Union Canal can be clearly seen crossing the plant. The canal's water flows to the west at this point; the connection with the Forth and Clyde

Canal was originally about 2.5 miles west, and is now about 4 miles downstream at the Falkirk Wheel.

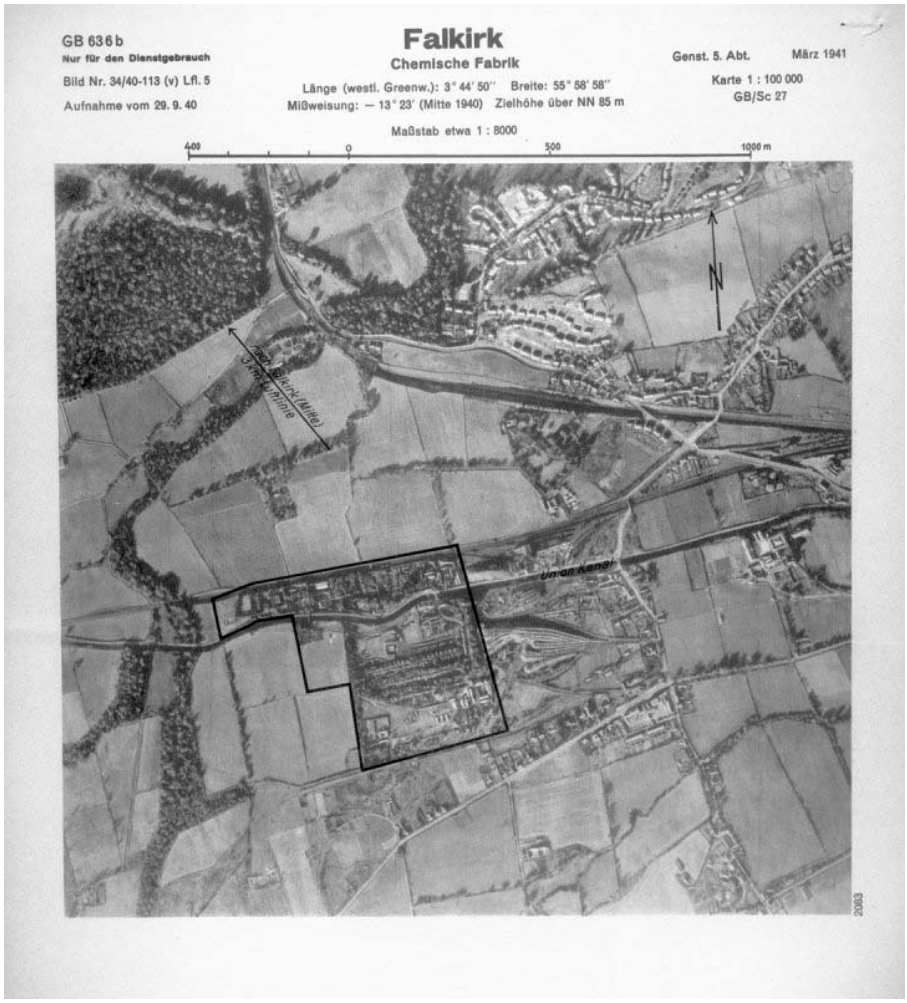

Figure 1.9 Photograph from 1941 showing the location of the Nobel Westquarter detonator factory in Reddingmuirhead[27]

In its early years, the factory was dedicated to building detonators only and used to purchase mercury fulminate from elsewhere. In the run up to the First and eventually Second World Wars, the production demands required that manufacturing of mercury fulminate be carried out on site to cut shipping time. Manufacture was estimated at around half a ton per day[28]. This is discussed further in Chapter 7.

1.3 Soil Chemistry

1.3.1 Soil Composition

Soil is a very complex heterogeneous matrix, composed of packed particles and void spaces[29]. The soil particles are made of weathered minerals, typically containing inorganic solids such as clays, metal carbonates, phosphates, sulfates and (hydr)oxides (which comprise oxides, hydroxides and oxyhydroxides). Soils typically also contain a proportion of organic colloidal matter of detrital origin, as well as living organisms such as algae and bacteria[29].

Soil particles are classified according to a scale of fixed diameter ranges, given in BS EN ISO 14688-1:2002[30]. This classification is reproduced in Table 1.2. A soil that consists of particles of only one particle size range is called a basic soil. Existence of such soil is unnatural, unless it has been sieved. Natural soils are composite soils, *i.e.* consist of a mixture of two or more particle size ranges.

Table 1.1 Soil particle size fractions and relative grain types, as listed in BS EN ISO 14688-1:2002[30]

Soil type	Particle fraction	Particle sub-fraction	Particle size range (mm)
Very coarse soil	Large boulder	-	> 630
	Boulder	-	> 200 - 630
	Cobble	-	> 63 - 200
Coarse soil	Gravel > 2.0 – 63 mm	Coarse gravel	> 20 - 63
		Medium gravel	> 6.3 - 20
		Fine gravel	> 2.0 - 6.3
	Sand > 0.063 mm – 2.0 mm	Coarse sand	> 0.63 - 2.0
		Medium sand	> 0.2 - 0.63
		Fine sand	> 0.063 - 0.2
Fine soil	Silt > 0.002 mm – 0.063 mm	Coarse silt	> 0.02 - 0.063
		Medium silt	> 0.0063 - 0.02
		Fine silt	> 0.002 - 0.0063
	Clay	-	≤ 0.002

The finer the particles, the better they can pack together, leaving very small pore spaces. As particles grow bigger, so does the size of the empty spaces between them. Figure 1.10[31] illustrates this with the clay, silt and sand fractions.

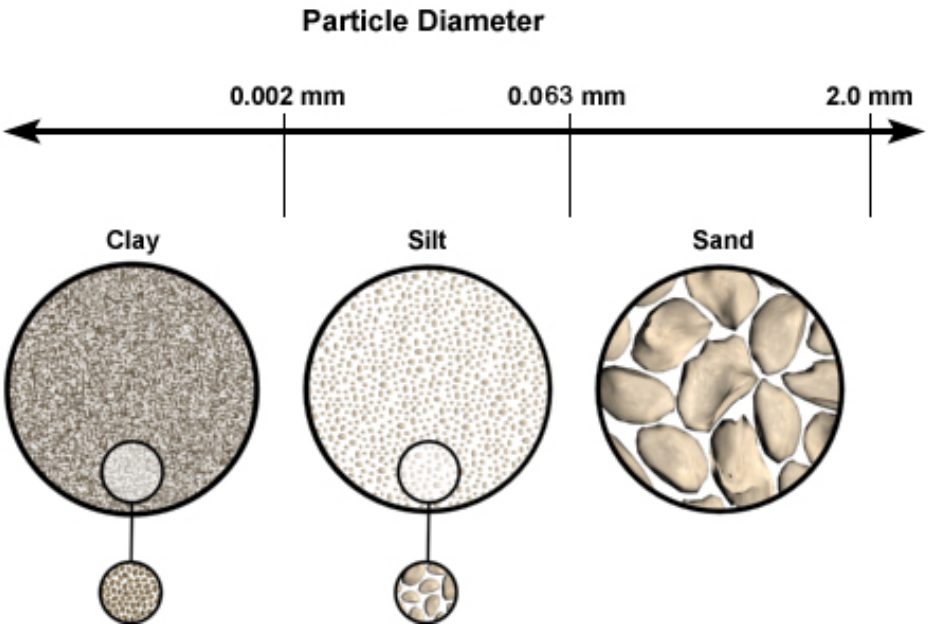

Figure 1.10 Illustration of the grain sizes, packing, and pore sizes of clay, silt and sand[31]

The particle size distribution (PSD) of a composite soil, in terms of the percentage composition of clay, silt and sand, is important in determining its texture. This is determined upon fitting each fraction's percentage composition into a chart known as the soil triangle, published by the United States Department of Agriculture (USDA)[32]. It has 12 categories of varying soil texture. A modified copy, which also depicts the PSD of each of the three fractions in the respective categories, is shown in Figure 1.11[33].

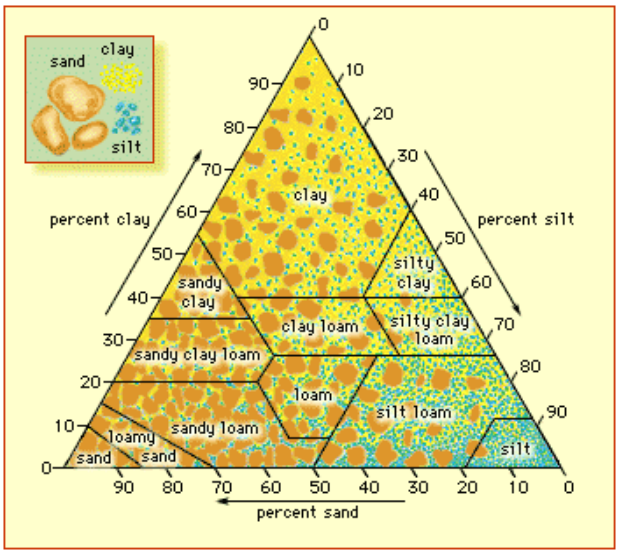

Figure 1.11 United States Department of Agriculture soil triangle used for determining soil texture[33]

There exists a UK variant of the soil triangle, issued by the Agricultural Development Advisory Service[34]. This chart has slightly different borders of each category and groups the clay loam and loam into one category, therefore having a total of 11 categories rather than 12.

Clay loam and loam are typically used in gardening and agriculture since the size of their pore spaces offers the right balance between drainage of excess water and long term retention of a proportion of the added water. This prolonged period of moisture content, as compared to flash flooding or drought, is a key factor affecting solute interaction reactions. This will be explained further in Section 1.3.2.

Sand consists of rounded grains of silica, whose size and structure do not offer much surface area for contact with water. Silt is considered to be the weathered product of sand, having the same granular structure albeit offering more surface area. The clay particle size fraction is the weathered product of silt, and offers the highest surface area amongst all fractions.

However, the clay fraction in the PSD pattern is not to be confused with clay minerals, which are a specific class of soil minerals and chemically distinct. The clay mineral particles are very small and have a flaky shape, making their available surface area for interaction with water and aqueous ions extremely high[35]. The clay mineral particles typically fall within the clay particle size fraction.

1.3.1.1 Clay Minerals

Clay minerals are known for their ability to effectively remove PTEs from solutions through sorption and cation exchange. Clays are composed of layers of aluminosilicate flat platelets, which are made up of sheets of tetrahedral units and sheets of octahedral units. Silicate tetrahedra are linked together by the sharing of three basal oxygen atoms and have their apex oxygen atoms all pointing in the same direction. The octahedral units contain two layers of oxygen atoms and hydroxyl groups surrounding the aluminium core. The relative number of oxygen atoms and hydroxyl groups varies between different clay types to satisfy the charge-balance criteria for the empirical structure[36-37].

There are many types of clay minerals. However, clays are subdivided into two main groups – the 1:1 clays and the 2:1 clays – reflecting the layout of their

structure[36-37]. The simplest clay structure is shown by the 1:1 clays. These clays have one octahedral sheet and one tetrahedral sheet. A common clay that has this arrangement is kaolinite [empirical formula - $Al_2Si_2O_5(OH)_4$]. Its structure is shown in Figure 1.12[36], where successive 1:1 layers are stacked above each other and held together by hydrogen bonds between the oxygen atoms in one layer and the hydroxyl groups in the next. Any aqueous ions from surrounding solutions are unable to enter between the layers due to the arrangement of the hydrogen bonds. Hence, this clay type has a relatively rigid structure.

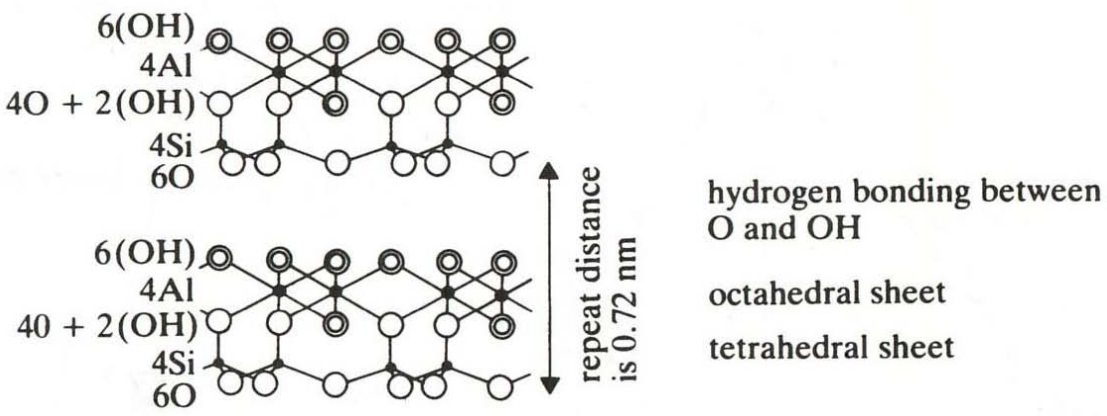

Figure 1.12 Lattice structure of kaolinite[36]

The 2:1 clay minerals consist of one octahedral sheet sandwiched between two tetrahedral sheets. A common clay with this arrangement is montmorillonite [empirical formula - $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$], whose structure is shown in Figure 1.13[36].

The oxygen atoms of one 2:1 layer always face the oxygen atoms of the next layer and therefore no hydrogen bonding can take place. Hence, the layers are not so strongly held together, and ions such as Na^+ and Ca^{2+}, and small molecules such as water, can enter between the layers. Montmorillonite is described as expanding clay because water can enter between the layers, causing the repeat distance to increase from 0.96 nm to 2.14 nm[36].

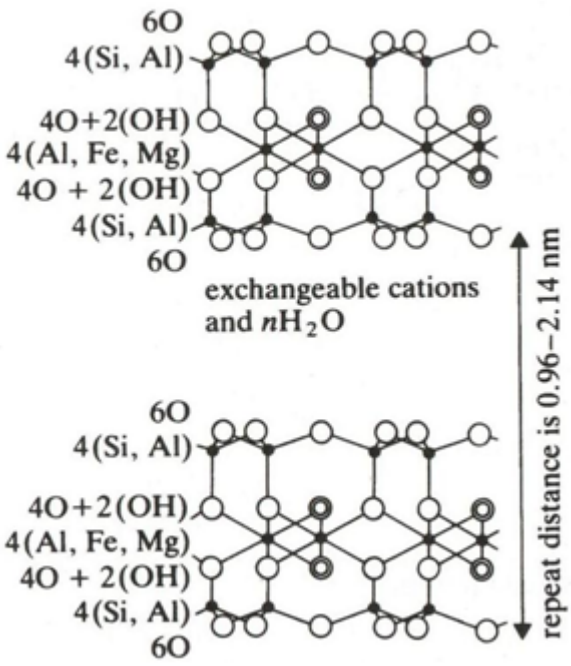

Figure 1.13 Lattice structure of montmorillonite[36]

Isomorphous Substitution

Isomorphous substitution is the replacement of one cation for another of similar ionic radius, within the lattice structure of the clay mineral, at the time of its formation. Typical examples include the replacement of Si^{4+} by Al^{3+} in the tetrahedral plane, and the replacement of Al^{3+} by ions such as Mg^{2+} and Fe^{2+} in the octahedral plane. This results in a net positive charge deficiency.

This is rarely observed in kaolinite, however it is very common in montmorillonite, so much so that it is rarely found in its empirical formula configuration. The final formula is dependent on the surrounding conditions present during mineral formation; replacement of up to 15% of Si^{4+} in the tetrahedral units, and up to 100% of Al^{3+} in the octahedral units, have been observed[36].

Cation Exchange

Aqueous cations are capable of sorbing onto surfaces of clay minerals in an exchangeable way (see Section 1.3.2). These reversible reactions take place to neutralize the unbalanced electrical charge within the mineral lattice structure caused by isomorphous substitution. Clay's capability of cation exchange is expressed as its CEC.

The 1:1 clays offer little capability for cation exchange for two reasons. The net negative charge of such clays is low since very little isomorphous substitution occurs during its formation. Also, their rigid structure offers only the external surfaces for sorption. The specific surface area of kaolinite is given as 5 – 40 m^2/g, whereas its theoretical CEC is given as 3 – 20 meq/100g[38].

The 2:1 clays offer a relatively higher capability for cation exchange. The higher proportion of isomorphous substitution causes these clays to have a higher net negative charge. Expanding clays such as montmorillonite also offer a very high surface area for sorption to occur. This is calculated at 700 – 800 m^2/g, while its theoretical CEC is given as 80 – 120 meq/100g[38].

1.3.1.2 Mineral (Hydr)oxides

Many primary minerals contain a high proportion of Fe. Other common elements include Mn and Al. The weathering of these minerals will initially cause fragmentation, increasing the surface area. These small fragments may react with H^+, causing the release of the cations. In oxic conditions, these cations will immediately oxidise. Iron is typically in the Fe^{3+} state, leading to the formation of $Fe(OH)_3$. This imparts the typical reddish-brown coloration of aerated soil. Anoxic soils will have a greater influence of Fe^{2+}, giving a more greyish colour to the soil.

As a consequence, the (hydr)oxides of iron, manganese and aluminium form a major component of oxic soil. The various oxygen and hydroxyl groups serve as surfaces for adsorption of other metal cations. This is further aided by the high surface area offered since these (hydr)oxides occur in the clay fraction of the PSD, and have an amorphous structure.

Reducing conditions, such as caused by waterlogging or a decrease in aeration due to an increase in particle compaction, will cause the breakdown of these (hydr)oxides and eventual release of the adsorbed cations.

1.3.1.3 Organic Matter

Any dead animals, material produced by living organisms such as manure, or plant matter that ends up in the soil, is referred to as organic material. Organic

material is unstable and will decompose naturally through macro and micro-organismic action.

The decomposition process will continue until the organic matter produced is stable, forming humus. Characterisation of such soil organic matter (SOM) would reveal amino acids, sugars, lipids, or aromatic oxidation products of plant matter such as lignin[39]. Other SOM may be formed after instances of fire or may be brought in through atmospheric deposition from anthropogenic emissions[39].

Organic matter is rich in C, H, N, O, P and S, amongst other elements. The heteroatoms present on these SOM compounds serve as ideal sites for sorption of aqueous metal cations when in contact with a solution. This typically occurs via chelation, where a metal cation forms two or more coordinate bonds with a polydentate ligand.

1.3.2 Interface Interactions

The interaction at the interface between the surface of soil particles and water present in pores will affect water retention and metal cation mobility between phases. Dry soils are brittle since the empty spaces between particles are filled with air. Addition of water will fill these pores. The infiltration rate of water into sandy soil will be higher than for silt and clay soils due to the lesser compaction of particles. Therefore, the amount of surface runoff during a rainfall event is low. However, the large pores also mean rapid drainage once wetting has ceased, making it unsuitable for long term water storage[31].

On the other hand, the infiltration of water into fine soils is a slow process due to the compaction of particles, and therefore there is an increased chance of having surface runoff during wetting, especially with higher clay content. However, water is retained for a far longer period of time than in the case of sandy soils since fine soils are unable to drain well[31].

Cohesion of soil particles together through bridging H-bonding with the water molecules makes wet fine soil stick together. This plasticity is exhibited to the greatest extent by clay soils, and decreases upon increasing particle size to a non-existent level with sandy soil.

Aqueous PTEs present in the waterlogged soil pores accumulate on the soil surfaces through sorption processes. There exist three possible types of sorption processes – adsorption, surface precipitation, and absorption[40]. Sorption is affected by the soil type and composition. Finer soils offer the greatest surface area, most contact time between the surface and the aqueous phase, as well as a larger solid:solution mass ratio[29]. The presence of a large number of (hydr)oxide groups in clay minerals and organic matter, as well as heteroatoms such as N and S in the latter, gives these two soil components a high bonding capacity[29, 40].

The soil pH is a very important factor in determining the extent of sorption since this will determine the surface charge[29]. High soil pH aids sorption of the aqueous PTE cations since the hydroxyl functional groups at the surfaces of soil particles would act as Lewis basis when deprotonated, by carrying a negative charge[29]. Hydroxyl-bearing groups include organic matter, the oxyhydroxy surface on the octahedral basal plane of 1:1 clays, the broken edges of clay minerals, and inorganic compounds bearing hydroxyl groups.

1.3.2.1 Adsorption

Adsorption of PTE cations onto the surfaces of soil particles may occur through physisorption, which involves the weak van der Waals forces, chemisorption, which involves strong covalent bonding, or via the mildly strong electrostatic (Coulomb) attraction[29]. Adsorption is a fast process, but limited to a surface phenomenon[41].

Upon contact with water, physisorption occurs between oxygen atoms in soil particles and aqueous cations[42]. Deprotonation of hydroxyl groups will lead to the formation of the double layer, which are two parallel layers of aqueous charged particles surrounding the soil particle[43]. Aqueous cations adsorb directly onto the negatively charged soil particles via electrostatic attraction and form the first layer – the stern plane. Other species may chemisorb permanently onto the surface. The second layer – the diffuse layer – is composed of ions attracted to the stern plane via electrostatic forces. This second layer is weakly associated with the stern layer. It is made of ions which are capable of moving in the aqueous phase should they be

influenced by a greater electrostatic attraction or following collisions caused by Brownian motion. The double layer formation is shown in Figure 1.14 [after [43]].

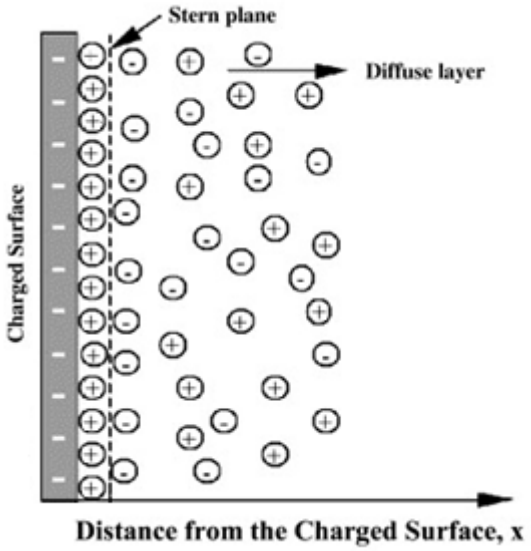

Figure 1.14 Formation of the double layer around the charged surface of a solid particle in water [after [43]]

Large anions – such as phosphate – present in the water can replace the surface hydroxyl functional groups. This results in the creation of a more negative surface charge[44]. Although the concentration of a PTE cation in the bulk of the solution may be lower than its solubility limit with respect to a particular salt, the same solubility limit may be exceeded close to the solid surface, leading to precipitation onto it[41].

1.3.2.2 Surface Precipitation

This surface precipitation occurs via heterogeneous nucleation and is a slow process, but is able to spread the growth of a new solid phase in a 3-dimensional manner[41]. This further increases the surface area available for sorption. Metal cations may form salts and precipitate as oxides, hydroxides, carbonates, sulfates and phosphates onto the solid surface. Therefore, surface precipitation is dependent on adsorption, which in itself is affected by the soil pH, as well as the amount of aqueous ions present in solution. For example, in calcareous soils, carbonates are expected to be the major salts precipitating. Sorption of PTEs onto a solid surface is a continuum between adsorption and surface precipitation.

1.3.2.3 Absorption

Absorption is the process whereby an adsorbed cation diffuses into the bulk of the sorbent particle. The cation may incorporate into the sorbent crystal lattice interstitially, that is, by settling in an existing hole in the lattice, or substitutionally, by replacing a cation in the lattice. Absorption is a slow process and may spread in a 2-dimensional or 3-dimensional manner, depending on the conditions in the lattice. The absorption phenomenon is generally limited to 2:1 clay minerals due to the lattice structure.

The extent of sorption of aqueous metal cations onto the surface of a particle is dependent on the various factors listed below:

- The sorption affinities of aqueous metal cations to their sorbent matrix are relative to the particle's surface moieties – greater PTE retention occurs at high soil pH due to deprotonation of the moieties[29] ;
- Competition between different PTEs[29];
- Concentration of the PTEs in solution[29];
- Contact time[29];
- The presence of organic and inorganic ligands in water may cause the release of PTEs bound to the soil particles. These ligands can be of natural organic origin, such as humic and fulvic acids, and/or of anthropogenic origin, such as nitrilotriacetic acid, ethylenediaminetetraacetic acid and polyphosphates[29]. Presence of anthropogenic ligands is typically associated with contamination of soils and presence of wastewater[29].

The dynamic sorption and desorption processes will ultimately affect the concentration of PTEs in soil and solution. The capability of soils to retain PTEs from waters is an important aspect for soil fertility in agriculture and soil contamination in the environment.

1.3.3 Sedimentation from Surface Runoff

Natural or anthropogenic disturbances to topsoil can easily result in soil runoff into a nearby watercourse. Similarly, urban lined segments of the canal are likely to receive a considerable load of dust and gravel. Particles entering a water

body are initially in suspension. The agitation caused by fast flowing waters, such as those in rivers, may prolong the residence time of these particles in the water column. This is the reason why rivers commonly have rocky beds. However, in canals where water flow rate is typically about 0.1 m/s[1], the particles settle out under gravity. This is the process of sedimentation, whose rate is directly proportional to the weight of the respective particles. Whereas heavier particles settle out quickly, lighter particles may remain suspended. Movement of particles may be further limited by the presence of reeds, bulky material illegally thrown in the canal, and locks.

During the sedimentation process, suspended particulate matter has the potential to act as a scavenger of dissolved PTEs, depending on the availability of sites available for sorption. The particulate matter that remains suspended will eventually be washed out into a wider water body, such as the sea, whereas the particles that settle out will retain these sorbed PTEs trapped in the bulk of the bottom sediment[45].

Apart from serving as scavenger, the runoff material entering the canal may bring in various organic or inorganic compounds. This is of particular importance in areas such as those lined by agricultural land, where the soil adjacent to the canal could be amended with various fertilizers and pesticides.

Immobile PTEs sorbed to sediment are not immediately available for uptake by a living organism. However, should any condition change, the sediment may act as a source through the release of a proportion of PTEs. These desorb and solvate, thus becoming mobile and potentially available for uptake by any organism. The extent of this ‘desorption capacity’ can be established through a series of sequential extraction steps, whereby the PTE content released upon application of different reagents of ever-increasing strength is measured. The proportion of the respective PTE which is released with the mildest reagent is considered the most potentially bioavailable, while the proportion that is hardest to extract is considered barely bioavailable. This will be discussed further in Chapter 6.

1.3.4 Sediment Dynamics

With the rather slow moving water currents, any material influx from runoff is likely to remain localised. Surface sediment is oxic due to the contact with dissolved oxygen present in the water body. The depth of this oxic layer largely depends on the particle size distribution of the sediment particles. Sediments with a high fine particle size fraction can compact together, effectively limiting the depth unto which dissolved oxygen in the water body may penetrate, creating a relatively shallow oxic layer. Underlying sediment is anoxic.

Microbial degradation of organic carbon to carbon dioxide during respiration may occur via different aerobic or anaerobic pathways. The preferred route would be the one which offers the highest energy gain[46]. The free energy gain from the different pathways is listed in Table 1.2[46].

Table 1.2 Free energy gain (represented as kJ/mol glucose) from mineralisation reactions of organic carbon (represented by CH_2O)[46]

Process	Reaction	Energy Gain (kJ/mol)
Oxic degradation	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-3190
Nitrification	$5\ CH_2O + 4\ NO_3^- \rightarrow CO_2 + 2\ N_2 + 4\ HCO_3^- + 3\ H_2O$	-2750
Mn reduction	$CH_2O + 3\ CO_2 + H_2O + 2\ MnO_2 \rightarrow 2\ Mn^{2+} + 4\ HCO_3^-$	-3090
Fe reduction	$CH_2O + 7\ CO_2 + 2\ Fe_2O_3 \rightarrow 4\ Fe^{2+} + 8\ HCO_3^-$	-1410
Sulfate reduction	$2\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2\ HCO_3^-$	-380
Methanogenesis	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	-350

However, in sediment, the selected mineralisation pathway is dependent upon the availability of the favourable electron acceptor. This results in a vertical zonation, as shown in Figure 1.15 [after [47]].

The respiration pathway of choice in the oxic layer is oxygen, being readily available and the most favourable in terms of energy gain. Upon increasing depth and oxygen depletion, nitrification becomes more common. As conditions become more anoxic, Mn and Fe reduction take over (Mn reduction is preferred initially due to the higher energy gain). Once Mn and Fe oxide reserves become depleted, sulfate reduction and ultimately methanogesis become increasingly predominant. The sulfate

reduction process gives the characteristic foul odour of hydrogen sulfide upon exposure following sampling. These reducing conditions will reduce all PTEs present.

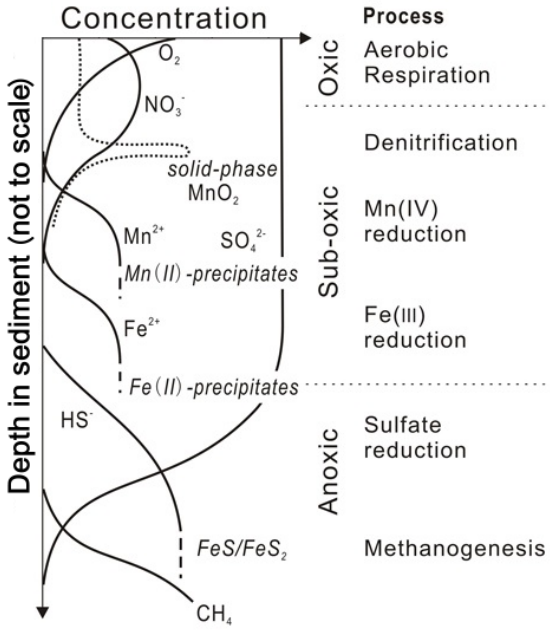

Figure 1.15 Redox zonation is sediments [after [47]]

The presence of benthic burrowing infauna would create some limited *in situ* churning[48]. However, churning of bottom sediments occurs mostly as a result of currents created by over passing vessels. Dredging operations also infer a similar effect. This churning will alter the redox conditions. It will result in spatial variance of the preferred respiration pathway at similar depths, but more importantly, resuspension of anoxic sediment will place reduced PTEs back in the water body. These PTEs are aqueous, and hence mobile. They can reoxidise and settle as particulates on the oxic surface sediment layer, ultimately completing the cycle. However, being mobile, some PTEs may be lost to other pathways, such as uptake by a living organism or adsorption onto a suspended particle and washed out to sea.

1.4 Aim of the Study

The overall aim of this thesis was to assess the environmental status of the Forth and Clyde Canal and Glasgow Branch. The selected study area was ideal since the extensive surrounding landscape has been impacted by varied inputs of contaminants throughout its history.

Specific objectives were:

- To carry out sediment sampling along the length of the canal (described in Chapter 3);
- To determine general characteristics of the sediment samples, *i.e.* moisture content, organic content, pH, and particles size distribution, (described in Chapter 4);
- To determine the PT PTE content of the samples and assess factors influencing their levels and distribution (described in Chapter 5);
- To determine the PTE content in respective fractions of the sediment samples following a sequential extraction protocol and assess their mobility and potential bioavailability (described in Chapter 6);
- To determine the PT Hg content of the sediment samples and assess factors influencing their levels and distribution (described in Chapter 7);
- To speciate the PT Hg content and determine the relative proportions of methylmercury (Me-Hg) and inorganic Hg (In-Hg) content of the sediment samples (described in Chapter 8).
- To determine the content of three organotin compounds; monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT), of the sediment samples (described in Chapter 9).

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2 Theory of Instrumental Techniques

2.1 Introduction

This chapter describes the instrumental techniques employed in this work. Three techniques have been used: inductively coupled plasma mass spectrometry (ICP-MS) for determination of 10 elements, namely As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn; atomic fluorescence spectroscopy (AFS) for determination of Hg; and gas chromatography (GC) coupled with ICP-MS for determination of Me-Hg and the organotin compounds MBT, DBT and TBT.

2.2 Inductively Coupled Plasma Mass Spectrometry

The ICP-MS technique is widely used due to its capability of providing very low limits of detection, potentially in the region of pg/g, for multi-element determination of metals and some non-metals[1].

The torch is a main component of the ICP instrument. It has three feeds of argon and is where the plasma is formed. A schematic diagram of the typical layout of an ICP-MS instrument is given in Figure 2.1[2].

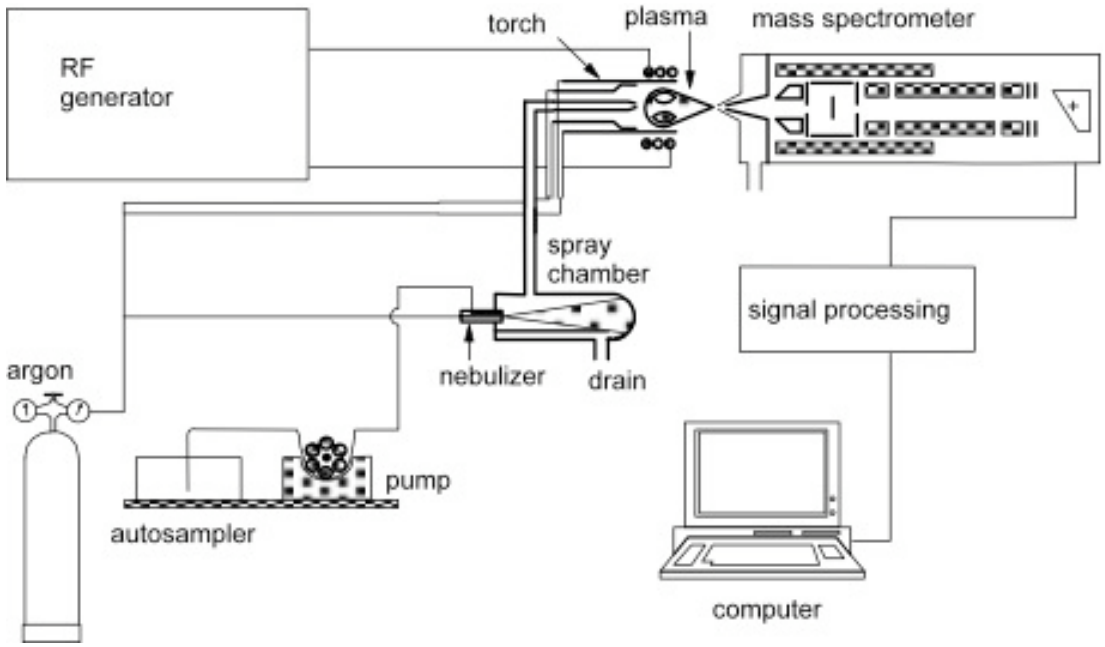

Figure 2.1 Schematic layout of an inductively coupled plasma mass spectrometer[2]

2.2.1 Sample Introduction

The plasma is used to disassociate, atomize, and most importantly, ultimately ionise a sample's elemental components. Ionisation can be achieved only if very small droplets of the sample are introduced into the plasma. Their size provides the very high surface area necessary for ionisation to occur. A sample is aspirated using a peristaltic pump. This pump ensures a constant flow of liquid, set typically at around 1 l/min, into a nebuliser[3]. As the liquid sample enters the nebulizer, it is met with an argon stream at a similar flow rate, creating an aerosol dispersion inside a spray chamber.

The layout of the spray chamber is such that it allows size-separation of the aerosol droplets formed by the nebuliser. Various commercially available configurations exist; the double-pass spray chamber is quite common[3]. The spray from the nebuliser is channelled straight through a tube, and as the aerosol exists at the far end, large droplets (typically > 10 μm diameter)[3] fall out under gravity into a drain while the smaller droplets remain suspended and flow, with the argon carrier gas present, in the bulk of the spray chamber (between the outer walls and the central tube's walls) and eventually into the inner cylinder of the torch. This layout also evens out the pulsed input of the sample caused by the peristaltic pump's action[3].

2.2.2 The Inductively Coupled Plasma Torch

A cross-section illustration of an ICP torch is shown in Figure 2.2 [after [4]]. The torch is composed of three concentric quartz cylinders and a water-cooled copper coil connected to a radio frequency (RF) generator at the top end of the torch.

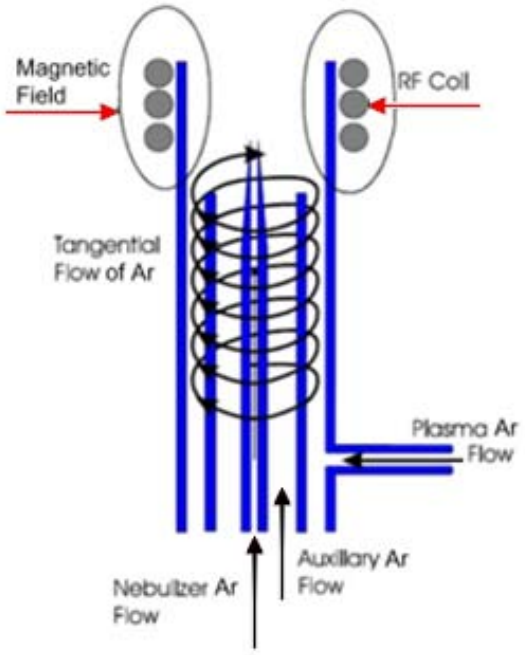

Figure 2.2 Cross-section of an inductively coupled plasma torch [after [4]]

A feed of argon flows through each of the three concentric cylinders of the torch. The gas flow rate through the outermost cylinder is typically between 15 and 20 l/min. This stream is used to feed the plasma as well as keeping the plasma away from the torch's sides. The gas flow rate through the intermediate cylinder is typically around 1 – 2 l/min, just slightly higher than the flow rate of the gas from the inner cylinder, which is usually around 1 l/min. The intermediate gas flow helps maintain the plasma, but is primarily present to avoid build-up of deposits around the nozzle of the central tube, through which flows the carrier gas and aerosol mixture derived from the spray chamber.

When RF power, typically 1.2 – 1.3 kW[5], is applied to the load coil from the RF generator, an alternating electric current flows through the coil at the applied frequency, typically set between 27 and 50 MHz. The most common frequencies are 27 and 40 MHz since they are exclusively reserved for this purpose in order not to interfere with other frequencies used in communications[5]. An oscillating magnetic field is formed since the coil acts as a solenoid.

Some seed electrons are introduced near the tip of the torch with an electric spark. These electrons collide with argon gas coming from the torch, stripping them of an electron and forming argon cations, as shown in Equation 2.1[5].

Equation 2.1 Electron ionisation of an argon atom

$$Ar + e^- \rightarrow Ar^+ + 2e^-$$

These newly released electrons are accelerated backwards and forwards at the RF frequency in the magnetic field at the tip of the torch. This movement, coupled with the tangential flow of argon coming from the outermost cylinder of the torch, creates turbulence and causes further collisions with argon atoms which strip off further electrons. This is an inductively coupled plasma discharge, and is self-sustainable providing that a constant flow of argon and the RF are maintained to ensure the presence of the magnetic field[5].

Argon is used to create the plasma since its first ionization potential (1521 kJ/mol, 15.76 eV) is higher than that of all other elements except He, F, and Ne, but lower than the second ionisation potential of all these other elements. This ensures the formation of singly charged analyte cations. Having a MS detector, doubly charged cations are unwanted species as they complicate the mass spectrum.

Collision between argon atoms and electrons may occasionally produce metastable argon atoms, that is, atoms in a relatively stable excited state, rather than producing cations, as shown in Equation 2.2[5].

Equation 2.2 Electron excitation of argon

$$Ar + e^- \rightarrow Ar_m^* + e^-$$

Some electrons and Ar^+ will collide, also forming metastable argon atoms and releasing energy, as shown in Equation 2.3[5]. Following the principle of conservation of energy, the energy released, *hv*, is equivalent to the kinetic energy of the electron.

Equation 2.3 Radiative recombination of argon cations upon collision with electrons

$$Ar^+ + e^- \rightarrow Ar_m^* + hv$$

The flow rate of argon in the outer cylinder of the torch will determine the residence time of argon atoms in the plasma. Slower flows give longer residence times and hence hotter plasmas, but faster flows relatively cooler plasmas. The temperature of the plasma plays a key role in analyte ionisation, since this depends

on the ionisation energy of the respective elements. Those elements having ionisation energies < 8 eV are colloquially termed soft elements, whereas those having ionisation energies > 8 eV are conversely referred to as hard elements[6].

As the sample aerosol passes through the plasma core, analytes undergo a series of processes and convert from a solvated state to an ionised atomic state. Organic compounds decompose, whereas solvated metal salts desolvate as water molecules are stripped off. The solid state particles formed vaporize into the gaseous state with atoms in the ground state. These analyte atoms, denoted as M, become cations, M^+, through different routes. However, various other unwanted reactions also take place, particularly those involving formation of polyatomic species.

Collision with an electron typically strikes off one of the atom's outermost electrons, as shown in Equation 2.4[5].

Equation 2.4 Electron ionisation of an analyte atom

$$M + e^- \rightarrow M^+ + 2e^-$$

Occasionally, the atom's electron is not lost but the atom is elevated to a metastable excited state through absorption of some of the kinetic energy of the electron, as shown in Equation 2.5[5].

Equation 2.5 Electron excitation of an analyte atom

$$M + e^- \rightarrow M_m^* + e^-$$

A newly formed analyte cation may collide with an electron and recombine, forming an atom in a metastable excited state, as shown in Equation 2.6[5]. As before, the energy released, *hv*, is equivalent to the kinetic energy of the electron.

Equation 2.6 Radiative recombination of analyte cations upon collision with electrons

$$M^+ + e^- \rightarrow M_m^* + hv$$

Any metastable analyte atoms formed may be ionised upon absorption of an appropriate quantum of energy from their surroundings, as shown in Equation 2.7[5].

Equation 2.7 Ionisation of metastable analyte atoms

$$M_m^* + hv \rightarrow M^+ + e^-$$

Collision between an analyte atom and an argon cation may result in electron transfer, as shown in Equation 2.8[5]. Transfer does not happen in reverse due to argon's higher first ionization potential.

Equation 2.8 Charge transfer ionisation of an analyte atom

$$M + Ar^+ \rightarrow M^+ + Ar$$

Collision of an analyte atom with an argon atom in the excited state causes an energy transfer which is sufficient to ionise the analyte atom and release an electron. The argon atom is left in the ground state, with the surplus energy being transferred in the form of kinetic energy to the electron. This process is known as Penning ionisation, and is shown in Equation 2.9[5].

Equation 2.9 Penning ionisation with metastable argon atoms

$$M + Ar_m^* \rightarrow M^+ + Ar + e^-$$

The process of ionisation of analyte atoms is completed by the time they arrive in the analytical zone of the plasma, the location of which is shown in Figure 2.3[7]. This is normally around 1 – 2 cm away from the coil into the tail plume. The torch is placed such that this region is in contact with the sampling cone (described in Section 2.2.3); any closer to the coil and the background emission is very high. The energy release upon radiative recombination of argon cations and analyte cations with electrons, as well as the phenomenon of Bremsstrahlung, which is the release of energy upon changes in kinetic energies following close encounters between electrons and cations, create a continuum of background radiation[5]. This is highest in the region of greatest density of species, and hence close to the coil.

Collisions decrease upon moving away from the magnetic field created around the coil. Therefore, far away in the tail plume, temperatures decrease to such an extent that some metals may form refractory oxides.

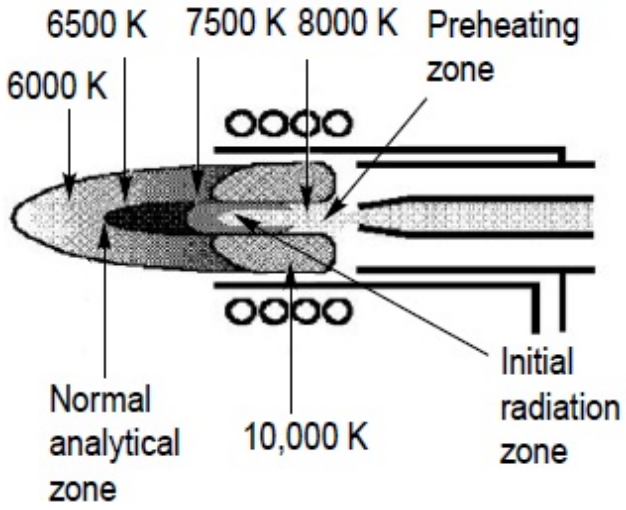

Figure 2.3 Temperature profile of the plasma's layout[7]

The degrees of first ionisation of elements for a plasma temperature of 7500 K and electron density of 10^{15} cm^{-3} have been calculated[8]. The degree of ionisation of argon was 0.04%, whereas that of most elements having their first ionization potential below 10 eV was close to 100%. Notable reductions in ionisation efficiency were observed in the metalloids group and the heavier transition metals in period 6 of the periodic table. The lowest was Hg with 38% ionisation[8].

The plasma is not in thermal equilibrium because the various reactions happening are not in equilibrium with one another. Thermal equilibrium implies that the temperature of all species - electrons, cations, and neutral species - is the same. However, the plasma is in local thermal equilibrium, meaning that all species have the same temperature in localised areas within the plasma. The elevated argon flow and turbulence maintain the high rate of collision, which lead to an efficient energy exchange between localised species[9].

2.2.3 Cones

The cones are the interface between the plasma and the MS. There are two cones; the one in contact with the plasma is the sampling cone, as mentioned earlier, whereas the other cone that is situated behind the sampling cone is the skimmer cone[10]. The sampling cone is water cooled to avoid overheating and melting, and is typically made of Ni or Pt because of their high thermal conductivity, relative resistance to corrosion, and robust nature[10]. The orifice of the sampling cone is

typically 1.00 mm, whereas that of the skimmer cone is slightly less, typically 0.75 mm[10].

The cones have two functions. The plasma is at atmospheric pressure, whereas the MS operates at a very low pressure. The small orifices enable the creation and maintenance of the low pressure in the MS through use of vacuum pumps. The difference in orifice diameters enables a gradual decrease in pressure as analyte cations flow through from the plasma into the mass analyser. The cones also focus the analyte stream into the mass analyser.

Samples having a dense matrix, typically anything above 0.1% of total dissolved solids (TDS), would clog the sampling or skimmer cones due to their small orifice[1]. Any samples having higher TDS levels need to be diluted.

2.2.4 Mass Spectrometry

Mass spectrometers work in vacuum and typically consist of three parts: an ionizer, a mass analyser, and a detector. The vacuum is necessary to avoid interferences caused by vapour analytes colliding with gases and loosing trajectory.

In ICP-MS, compounds exiting the ICP are already in a cationic form as they have been formed in the plasma and therefore no separate ionizer is required.

The quadrupole mass analyser is widely common and is composed of four parallel rods that have fixed DC and alternating RF potentials applied to them[11]. Incoming cations are channelled to the middle of the quadrupole; their motion will depend on the electric fields. The quadrupole works as a mass filter. Only ions of a particular *m/z* will have a stable trajectory and be able to pass through to the detector at a particular RF[12]. The instrument can scan over a *m/z* range by varying the RF to bring ions of different *m/z* into focus on the detector, thus form a mass spectrum. A schematic representation of a quadrupole is shown in Figure 2.4[12].

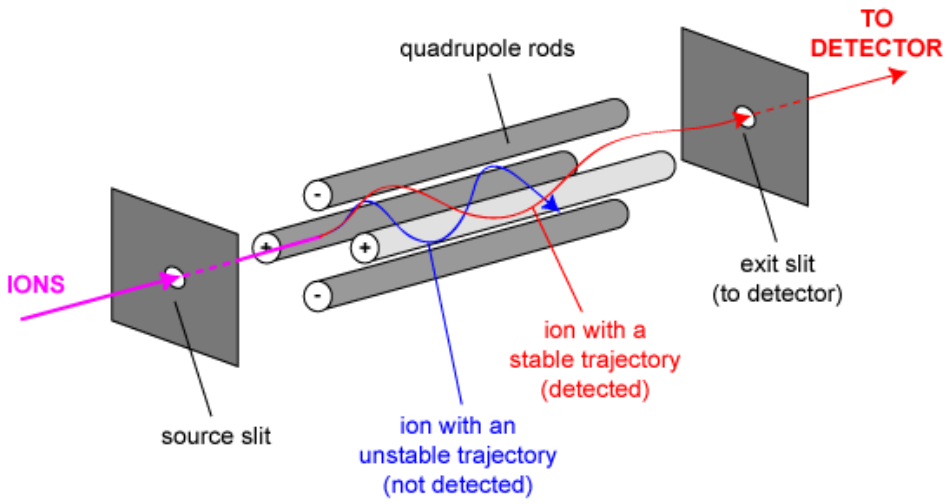

Figure 2.4 Schematic layout of a quadrupole mass analyser in MS[12]

Two opposite rods in the quadrupole have a positive potential, while the other opposite two rods have an equal negative potential[12], denoted as '+' and '-' in Figure 2.4. The positive potential is given by Equation 2.10 while the negative potential is given by Equation 2.11.

Equation 2.10 Positive potential of quadrupole rods

$$+(U + Vcos(\omega t))$$

Equation 2.11 Negative potential of quadrupole rods

$$-(U + Vcos(\omega t))$$

where:

U is the fixed potential

$Vcos(\omega t)$ is the applied RF;

V is the amplitude of the RF

ω is the frequency of the RF

t is the time

$cos(\omega t)$ represents the sinusoidal cycle of the applied potentials on the opposed pairs of rods with time

As ions travel along the central axis of the rods, they oscillate amongst the poles due to the applied potential. These oscillations result in complex ion trajectories dependent on the *m/z* of the ions at a particular RF, based on specific combinations of the potential *U*, the amplitude *V* and frequency ω of the RF. All other ions with *m/z* values that have unstable trajectories will either hit the quadrupole or exit the cavity between the rods and not be detected. This is depicted in Figure 2.4. The mass range and resolution of the instrument is determined by the length and diameter of the rods.

The MS can be set to perform a full scan, partial scan, or used in selected ion monitoring mode whereby the instrument 'jumps' from one selected mass to another, depending on whether the analyst is looking for particular analytes or is interested to know the full or partial composition of the sample. Reducing the scan range means that the overall scanning time is reduced. Also, as the mass spectrometer spends more time at a given mass, the signal-to-noise ratio is improved and the overall sensitivity of the instrument increases.

The detector converts the ion currents coming from the mass analyser into electrical signals and subsequently into a readable output form. The detector is offset from the quadrupole to minimize background from stray radiation and any incoming neutral species[13]. A schematic layout is shown in Figure 2.5[13].

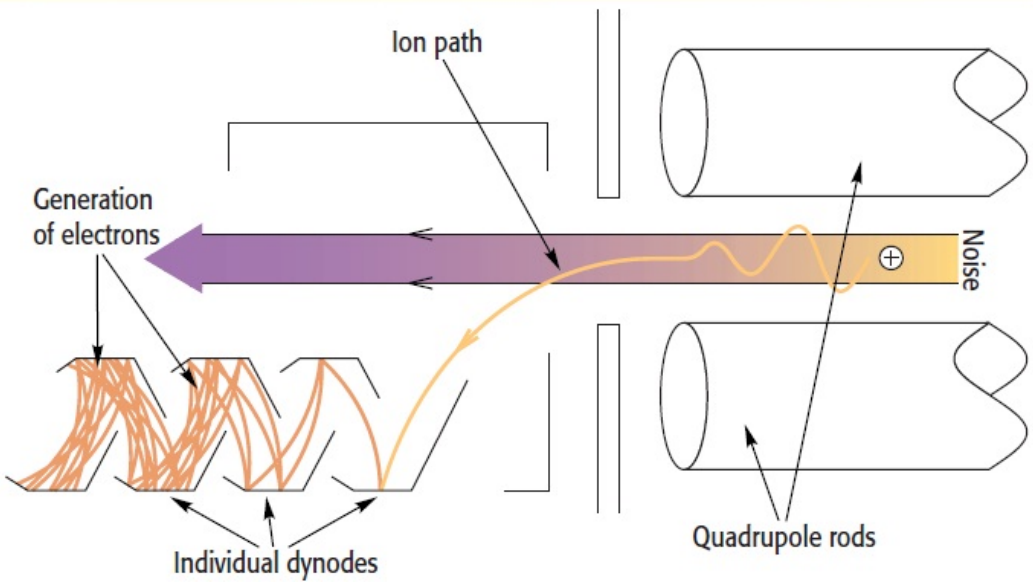

Figure 2.5 Schematic layout of an electron multiplier detector[13]

The dual-mode discrete-dynode electron multiplier is a common detector. This detector works on the principle of electron multiplication for amplification of signal. When a cation emerges from the quadrupole, it is attracted to a cathode, which is the first of a series of dynodes. This has a high negative voltage (around 1 - 3 kV)[14] which causes the deflected cation to accelerate towards it. Electrons are sputtered upon striking it. Being a discrete-dynode model, a series of distinct dynodes exist between the cathode and the anode, rather than a continuous dynode with varying potential. A dynode is an electrode whose charge is slightly more positive than that of the electrode preceding it. The dynodes are in a scale of ever increasing positive potential from the cathode culminating at the anode.

The released electrons from the cathode are accelerated towards the first dynode, triggering the release of more electrons as they hit the surface. This is termed secondary emission. Each electron released is accelerated towards the next dynode, causing a cascade effect of release of electrons, ultimately causing the amplification of the original signal, typically by a factor of one million by the time the electrons reach the anode[15].

Being dual-mode means that the detector has the ability to detect low signals in a pulse-counting mode as well as high signals in an analog mode, from different species coming from the same sample. The pulse-counting mode allows for high signal amplification to a threshold level, whereas the analog mode allows for less amplification since the incoming signal is already high. A schematic layout is shown in Figure 2.6[13].

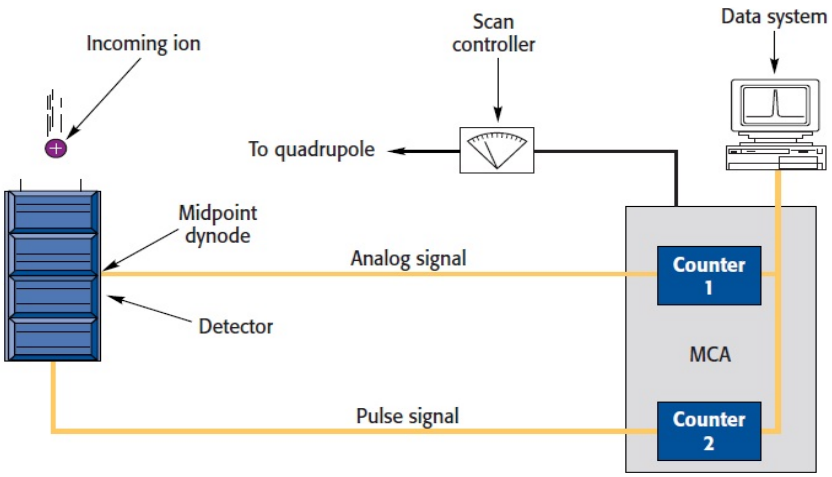

Figure 2.6 Schematic layout of a dual-mode detector[13]

When more than a threshold number of ions are detected at the midpoint dynode, the electron multiplication is terminated to prevent an overload and the detected signal is processed through the analog mode. Whenever this threshold is not met, the electron multiplication is allowed to proceed through the rest of the detector and is measured as a pulse-counting signal at the anode.

A pulse-counting calibration curve is typically linear up to 10^6 counts per second (CPS), whereby it is then terminated[13]. An analog calibration curve is typically linear between 10^4 and 10^9 CPS[13]. Anything less is allowed to be detected by the pulse-counting mode, while anything higher necessitates the dilution of the sample. Both linear fits are not continuous since the analog mode offers a lower CPS response to a similar cation signal. Both ranges are normalized by a cross calibration covering overlapping concentration levels, whereby the analog response is computationally modified and fitted over the pulse-counting calibration curve, offering a linear response over the entire detectable scale[13].

2.2.5 Quantification

Data obtained from mass spectrometry used in conjunction with ICP is represented as CPS at respective *m/z* ratios. The CPS values of analytes in a sample are fitted into a calibration curve obtained from CPS values of standard solutions.

2.2.6 Interference

The main interference experienced in ICP-MS is mass overlap. This occurs when a detected signal at a particular *m/z* in the mass spectrum is not solely due to the analyte ion, but also from unwanted cationic species formed in the plasma[16]. There are two sources of these unwanted cations, those originating from the plasma itself, namely ions of the isotopes of Ar, H, N, and O, and those coming from the sample solution, mainly ions of the isotopes of C, Ca, Cl, H, N, Na, O, P and S.

The presence of high concentrations of argon provides a variety of interfering species, notably Ar^+, causing detections at *m/z* 36, 38 and 40. Other common argon species formed and detected are argon dimers, Ar_2^+, argon oxide, ArO^+, and argon hydride, ArH^+. Their detection would occur at the *m/z* that corresponds to the sum of the isotope masses of the elements making up these species.

The presence of chloride in samples is a source of similar interference since it has the tendency to bind with most of the lighter elements, as well as forming $ArCl^+$ and ClO^+. Being a light atom, chlorine does not normally affect the heavier elements such as Cd, Sn and Pb. Various other polyatomic combinations exist, all of which are well documented. This results in a situation whereby interference is observed mainly in the region of *m/z* 45 – 80.

Some commercial ICP-MS instruments can come fitted with a reaction cell and/or a collision cell to minimize polyatomic cation interferences. These are found as a compartment between the cones and the MS, and can be switched on or off according to the user's preference. In a reaction cell, a reactive gas, typically hydrogen, is added to react with polyatomic cations and break them up. In a collision cell, helium, an inert gas, is added and disassociation of polyatomic cations occurs through collision. Some instruments have the facility of adding both H_2 and He simultaneously to have both reactive and collision mechanisms operative to reduce polyatomic cation interferences.

A typical quadrupole MS detects both the analyte and the interference species at a similar *m/z* ratio because it is unable to resolve small difference in atomic mass. Mass overlap interferences can be overcome with the use of high resolution magnetic sector mass spectrometers. These are able to distinguish *m/z* with a greater resolution. A selection of analyte species and important interferent species are listed in Table 2.1, along with their relative masses[16].

Table 2.1 Comparison of the masses of cationic analyte species and cationic interferent species[16]

Analyte		**Interferent**	
Cationic Species	**Mass (AMU)**	**Cationic Species**	**Mass (AMU)**
^{75}As	74.92160	$^{40}Ar^{35}Cl$	74.93123
^{52}Cr	52.94065	$^{37}Cl^{16}O$	52.96081
^{56}Fe	55.93494	$^{40}Ar^{16}O$	55.95729
^{40}Ca	39.96259	^{40}Ar	39.96238
^{87}Sr	86.90889	^{87}Rb	86.90918

2.3 Atomic Fluorescence Spectroscopy

2.3.1 The Quantum Theory

Atoms are normally in their ground state, as described by the Boltzmann distribution, whereby their electrons are orbiting the nucleus in an unexcited state, having a specific amount of baseline energy, E_0. An outer electron may absorb a photon of energy of the right amount, which causes it to become excited, and in doing so 'jump' to a higher energy level, having a total energy, E_1. This is the process of photo-excitation. After a short period of orbiting in the excited state, the electron emits that excess energy and 'falls' back to the ground state. Figure 2.7 [after [17]] depicts such an atomic energy level structure in an atom.

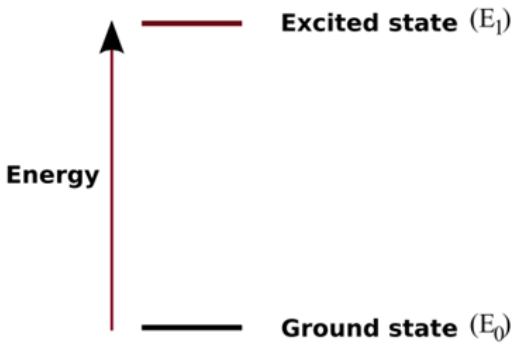

Figure 2.7 Atomic energy levels [after [17]]

The energy difference, ΔE, between the excited state, E_1, and the ground state, E_0, is given in Equation 2.12, where E_1 is always greater than E_0.

Equation 2.12 Energy difference between two states

$$\Delta E = E_1 - E_0$$

The ΔE determines the characteristic frequency of the photon of light required for the transition to occur, as shown in Equation 2.13.

Equation 2.13 Planck's equation

$$\Delta E = h\nu \quad \equiv \quad \Delta E = \frac{hc}{\lambda}$$

where:

ΔE is the energy difference between the ground state and excited state

h is Planck's constant; 6.26 x 10^{-34} Js

v is the frequency

c is the speed of light; 299,792,458 m/s

λ is the wavelength

The photon energy required for electron transition is unique to each element since the excited state of atoms is at a well-defined level. This leads to absorption or emission of specific frequencies, and hence line spectra.

Assuming there is a group of N atoms capable of being in the ground state, N_1, and in the excited state, N_2, which are in thermal equilibrium, then the ratio of the number of atoms in each state is given by the Boltzmann equation in Equation 2.14.

Equation 2.14 Boltzmann equation

$$\frac{N_2}{N_1} = e^{\frac{-(E_2-E_1)}{kT}}$$

where:

T is the thermodynamic temperature of the group of atoms

k is the Boltzmann's constant, 1.380 x 10^{-23} J/K

In visible light ($v \approx 5\text{x}10^{14}$ Hz), ΔE is calculated at ~2.07 eV. At room temperature ($T \approx 300$ K), the kT portion of the Boltzmann distribution equation is calculated at ~0.026 eV. Thus, since $E_2 - E_1 \gg kT$, the exponential in Equation 2.14 is a large negative number, signifying that N_2/N_1 is very small; hence there are almost no atoms in the excited state, but rather all are in the ground state when in thermal equilibrium at room temperature. As the temperature, T, increases, the number of electrons in the excited state increases.

2.3.2 Principles of Atomic Fluorescence

Atomic fluorescence spectroscopy is an analytical technique based on optical absorption and emission, hence fluorescence, from vapour phase atoms within an atom reservoir that have been excited to a higher energy level by absorption of radiation of a specific wavelength that is characteristic of the element of interest, emitted by a suitable primary source.

The AFS technique is particularly sensitive for the determination of metals such as Cd and Hg and metalloids of Group 14, 15 and 16[18-19]. These elements do not atomise fully in the plasma when analysing by ICP-MS, making the latter technique unable to offer very low limits of detection (LODs). Most of these elements are analysed by AFS using a hydride generator, where the dissolved analytes are reduced to their volatile hydrides. However, Hg is preferentially determined using a cold vapour method, CVAFS, rather than the hydride generation method. The sample solution is mixed and reacted with a reductant such as tin (II) chloride before introduction into the atom reservoir to generate elemental mercury (Hg^0) from its compounds, through the reaction in Equation 2.15.

Equation 2.15 Reduction of mercury (II) with tin (II)

$$Sn^{2+} + Hg^{2+} \rightarrow Hg^0 + Sn^{4+}$$

The cold vapour technique is possible only with mercury as it is the only element to have a large enough vapour pressure (0.0016 mbar at 20 ºC)[19] at ambient temperature that sustains it being volatilized. The Hg vapour and the remaining solution separate in a gas/liquid separator where any liquid is taken to waste, while the gas is transported with an argon stream into the atom reservoir. It is dried on the way to avoid water condensation. The CVAFS atom reservoir is an unheated glass tube with quartz windows[20]. Light from the line source is focused through the tube. This is unhindered by the windows since quartz is transparent to UV light.

2.3.2.1 Line Source

Measurements by AFS are in the UV/VIS range[19]. A line source such as a hollow cathode lamp (HCL) is a widely used primary source. The shape and

configuration of the HCL helps to focus the radiation into the optical path of the instrument. Hollow cathode lamps get their name from the cup-shaped cathode, which is made from (or coated with) a particular metal[21], as shown in Figure 2.8 [after [21]]. The anode is typically made of tungsten. A different lamp exists for every element that can be determined by spectroscopy, although some manufacturers produce multi-element lamps whose cathode consists of alloys of metals having similar melting points. Should elements with different melting points be used, the more volatile element would be lost first, resulting in rapid degeneration of the cathode. The lamp is filled with an inert gas, usually argon or neon, though the latter is preferred as it gives a higher spectral output[21]. The pressure inside the lamp is typically between 100 - 200 Pa.

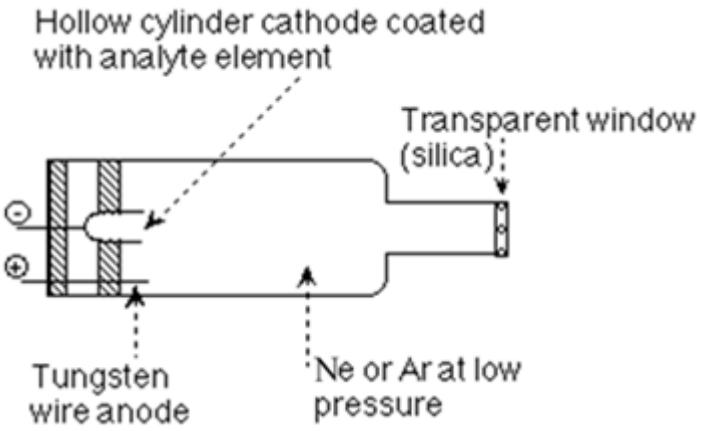

Figure 2.8 Schematic diagram of a hollow cathode lamp [after [21]]

Upon applying the current, the electric discharge ionizes the inert gas atoms, which are accelerated into the cathode and sputter element atoms into the gas phase. Collisions of these element gas atoms with other gas atoms or electrons excite the element atoms to higher energy levels, which decay to lower levels by emitting light having the characteristic line spectra of that element.

The emission spectrum of the cathode element includes a number of intense, sharp lines called resonance lines[19]. Intensity of these resonance lines is proportional to the applied current. The optimum current is specified by the manufacturer, and any variation will directly influence the number of photons released from the lamp. This

will in turn affect the detection response and is therefore an important operational parameter.

The HCL is a preferred option over a continuum light source as it emits specific line spectra. This avoids the possibility of having non-analyte components of the sample absorbing and fluorescing line spectra which may overlap that of the analyte of interest, and hence be detected too. This is particularly important when having elements that have close or partially overlapping line spectra, such as As/Cd, Co/In, Co/Hg, Fe/Mn and Ni/Sn, as well as to avoid overlapping spectra from molecular species within the sample matrix.

Mercury atoms in the ground state, absorb and emit radiation at 253.7 nm. An instrument with a permanent configuration for Hg determination using a line source does not need a monochromator because the radiation emitted is particular to the element of interest only. Only a filter is installed before the detector to eliminate the interference from ambient light[19].

2.3.2.2 Detector

The fluorescent radiation exiting the filter is channelled onto the photomultiplier tube (PMT) detector. A PMT consists of a glass tube with a photocathode, a focusing electrode, several dynodes and an anode, all under vacuum, and laid out as shown in the schematic representation in Figure 2.9 [after [22]].

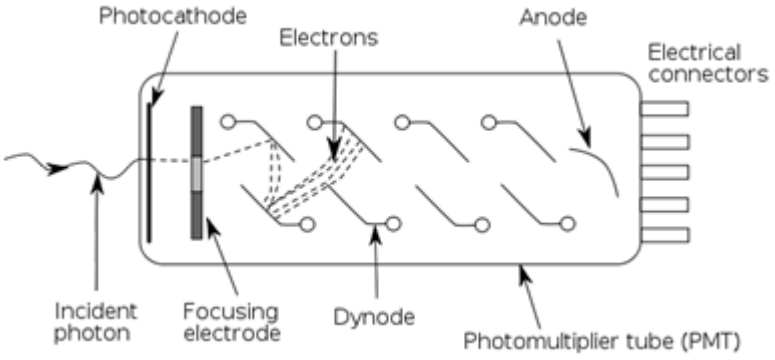

Figure 2.9 Schematic diagram of a photomultiplier tube [after [22]]

Fluorescent photons incoming from the instrument strike the photocathode, causing the release of electrons through a photoelectric effect. These electrons are directed by the focusing electrode toward the closest of a series of dynodes, causing

an amplification of the original signal similar to that which occurs in the mass spectrometer electron multiplier detector[15]. The output from the detector is suitably amplified and displayed on a readout device, typically an onboard meter or through software on a computer.

2.3.2.3 Interferences

Like other spectroscopic techniques, AFS faces two major types of interferences; spectral and chemical.

Spectral Interference

Spectral interference caused by overlapping spectral lines from molecular species in the sample matrix is avoided in CVAFS since the instrument has the advantage of precluding any molecular species from reaching the atom reservoir[19].

Since the incident and emitted photons have the same wavelength, the detector in a CVAFS instrument is always placed in a direction perpendicular to that of the incident radiation being emitted from the lamp to avoid detecting incident light. Only fluorescent lines from the analyte atoms are detected since these are emitted radially. This has the advantage over atomic absorption spectroscopy of decreasing the background light, greatly improving the instrument's sensitivity.

Chemical Interference

This type of interference is typically associated with any possible chemical reactions between the analyte and other components in the sample matrix that may preclude the formation of free atoms, which are necessary for accurate analyte quantification by AFS.

In CVAFS, interference may be caused by substances in the sample matrix that hinder the reduction of mercury and its eventual formation of vaporized atoms[19].

2.3.2.4 Quantification

Quantitative analysis using AFS can be carried out by comparing the signal obtained from an unknown against those given by a standard calibration plot, similar

to other spectrometric methods. Whenever reasonably possible, it is advisable that standard solutions are reagent-matched.

At low concentrations of an analyte, fluorescence intensity is directly proportional to the concentration[18, 23]. At higher concentrations, self absorption may occur whereby some fluorescence emission will be absorbed by atoms in the ground state, causing a lowering in the intensity of the perceived emitted radiation.

When analysing solutions with very low levels of mercury, a purge and trap system may be used whereby mercury vapour generated is purged with argon as usual but is trapped on a gold gauze prior to reaching the atom reservoir[18, 23]. This serves as a pre-concentration method. The gauze is then heated to release the trapped mercury, which will continue into the quartz cell for analysis[18, 23].

The determination of mercury via reduction with tin is only effective on mercury ions. Any organomercury will remain trapped and will be washed out as waste in the gas/liquid separator[19]. Therefore, if the total mercury content is to be determined, rather than just the inorganic content, the mercury needs to be released from the organic species, either by pre-oxidation with potassium permanganate, by displacement with a similar cation such as cadmium, or by digestion with *aqua regia.*

A drawback with measuring fluorescence emission exists whereby atoms in the excited state relax back to the ground state through a non-fluorescence route. This process is called quenching[19]. Excited analyte atoms may collide with other species in the atom reservoir, transferring their electronic energy to the translational, vibrational or rotational energy of the colliding species. This effect is mostly perceived when the analyte concentration is high[19].

2.4 Gas Chromatography

Gas chromatography enables the separation of a wide array of organic compounds present in a sample. Like all other chromatographic techniques, a stationary and a mobile phase are required. The stationary phase consists of a packed column where the solid material itself is the stationary phase, or where there is a support material that is coated with a liquid, high boiling point polymer, which serves as the stationary phase. Capillary columns are the most commonly used, where the stationary phase coats the walls of a very long, small-diameter tube. The

mobile phase is an inert gas, typically helium, which carries the analytes in a sample from the injection port through the column and out into a detector.

The reason why different compounds can be separated along the column is the interaction of the compound with the stationary phase. This follows the "like dissolves like" rule. The stronger the interaction between the analyte and the stationary phase, the longer the compound remains adsorbed to the stationary phase, whilst, conversely, loosely bound molecules elute quickly. The time it takes for an analyte to go through the column is referred to as the retention time, and this time is repeatable if a similar column and operating conditions are used.

A simplistic layout of a GC is shown in Figure 2.10 [after [24]]. The GC operates at a pressure of about 760 torr[25]. The column temperature affects the retention time of analytes since an analyte which boils at a temperature higher than the column temperature would not vaporize or may condense if the column temperature is set similar to its boiling point. Knowledge of the boiling point of the target analytes is essential to set the column at an appropriate temperature.

Solution samples are injected into the GC. The sample is vaporized upon heating to boiling point in the oven chamber. Typical solvents employed as mobile phases in normal phase chromatography are isooctane and hexane, being non-polar and volatile. The analytes adsorb onto the stationary phase surface as they flow through. The strength of the bond formed depends on the kind of interactions that occur. Organometallic compounds are polar organic compounds. When injected into a non-polar fused silica capillary column, the analytes will form long range dipole-dipole bonds, the strength of which depends on the polarity of the respective analytes; the higher the polarity, the stronger the bonds. The non-polar organic solvent interacts through induced dipole forces, which are weaker than permanent dipole forces, hence the reason why the solvent elutes first. It is important not to introduce any ionic compounds as these will form permanent, strong, short range ionic bonds with the oxygen present in the column, leading to a deterioration in the separation capabilities of the column. The continuous flow of carrier gas ensures that the analytes do not stick permanently to the stationary phase. The separated substances emerge from the end of the column and flow into the detector.

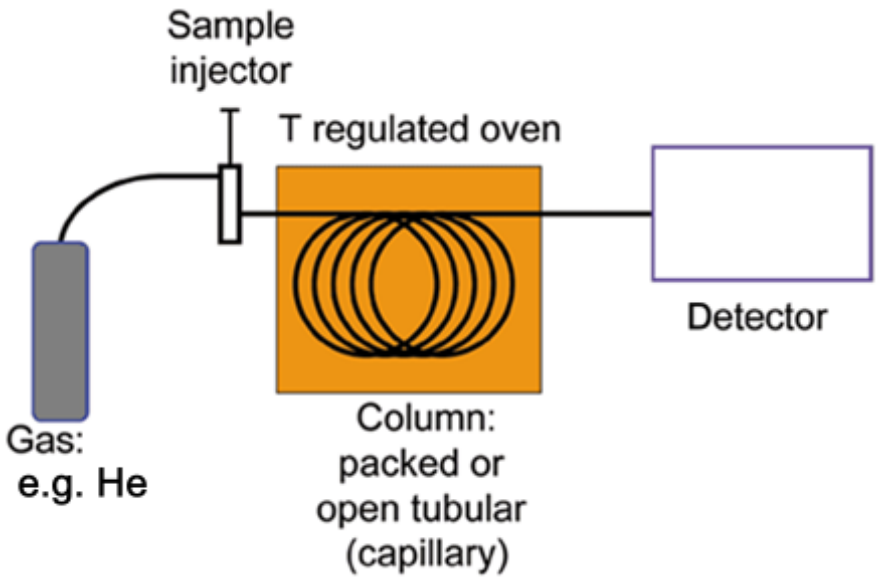

Figure 2.10 Schematic diagram of a typical GC instrument [after [24]]

Common GC columns used for normal phase chromatography are those in which the stationary phase has been chemically bonded to fused silica. One such column is the Rtx®-1 capillary column, which is 30 m long, has an internal diameter of 0.59 mm, a film diameter of 1 μm, is non-polar and composed of Crossbond® 100% polydimethylsiloxane. A monomeric unit is shown in Figure 2.11[26].

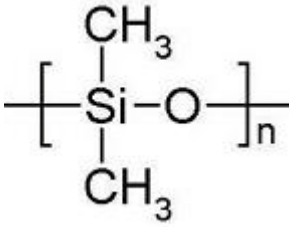

Figure 2.11 Chemical structure of the 100% polydimethylsiloxane polymer units[26]

Gas chromatography coupled with ICP-MS offers the detection capabilities of a mass spectrometer together with the added sensitivity and ability to perform elemental analysis inferred by ICP. A schematic diagram of a typical GC-ICP-MS interface is shown in Figure 2.12[27].

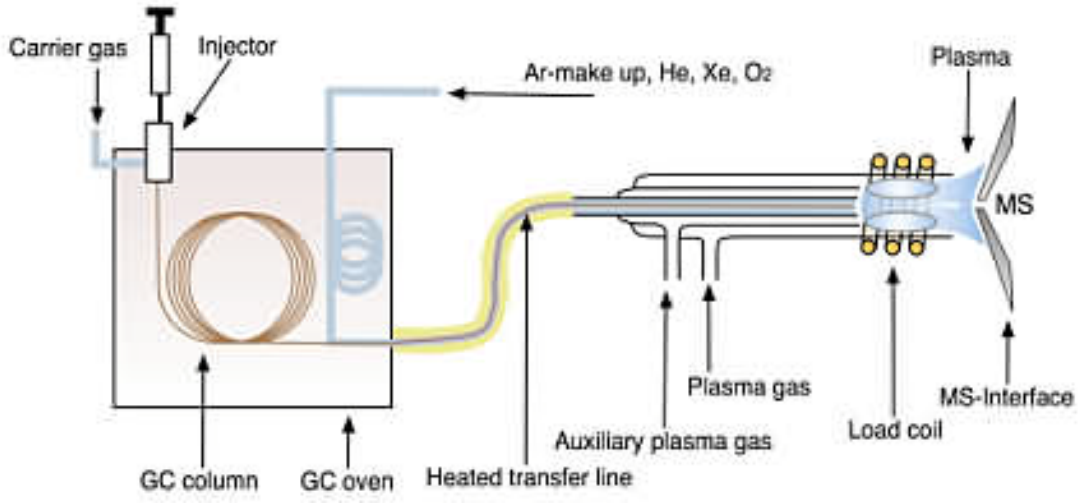

Figure 2.12 The GC-ICP-MS hyphenation[27]

The analytes elute from the GC column as concentrated quasi-matrix-free species in gaseous form. A transfer line is connected from the outlet of the GC column to the inner cylinder of the ICP torch. Several commercially available GC-ICP transfer lines are available. The interface is held at 250 to 280 °C to ensure that any organic compounds remain volatile. Due to the elevated temperatures, the material in the interface is commonly made of fused silica-lined stainless steel tubing to avoid reactions[25]. The line is encapsulated in an insulating material to reduce heat losses from the steel capillary's surfaces. The uniformity in layout prevents formation of any cold spots along the line.

The carrier gas mixture is added at the point where the GC column is connected to the transfer line to transport the eluent to the ICP torch. This gas mixture must be pre-heated to avoid condensation through cooling. This also brings the speed of the gas flow from the capillary GC column, which is 1 to 2 ml/min, to that needed for ICP, which is around 1 l/min for the torch's inner cylinder. Argon is the main component of the carrier gas. Other components include oxygen and xenon. Oxygen is recommended to prevent deposition of carbon on the sampling cone, arising from the decomposition of the organic components in the sample, through formation of CO_2[28]. Xenon provides a continuous signal which allows for an easy optimization of the operational parameters[29].

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3 Sample Collection and Methodologies

3.1 Sampling

Permission for access was sought from British Waterways (now Scottish Canals) prior to every sampling session. An initial risk assessment was completed and all necessary precautions on site were taken every time, including wearing personal protective equipment (PPE) consisting of a life-jacket, high visibility vest and gloves.

A stainless steel bucket was tied to 10 m of rope, and sediment samples were collected by throwing the bucket from the bank into the water across the width of the canal, allowing it to sink to the bottom and pulling back steadily. Once collected, the surface water was decanted back into the canal while the sediment was examined for the presence of unwanted large objects like plastic, pebbles and weeds which may have also been collected. These were removed and the sediment at the bottom was poured into appropriately labelled 500 ml wide neck new sample bottles and taken back to the laboratory. Top layer sediment was thus collected along a perpendicular transect to the canal at each site.

The whole length of the Forth and Clyde Canal and the Glasgow Branch was subdivided into approximately 2 km intervals to designate sampling locations. This was done using the British grid reference system on Ordnance Survey Landranger Maps[1-2], from which the exact sampling locations' coordinates were determined. Initial sampling was carried out in 2010. The sampling dates and relevant details are listed in Table 3.1 and Table 3.2 while locations are depicted in Figure 3.1 [after [3]].

Twenty four samples (labelled 5 – 28) were collected along the Forth and Clyde Canal and another two samples (labelled SFJ and BW) were collected along the Glasgow Branch. Harbour areas were sampled separately; four samples were collected within 50 m intervals at Bowling Basin (labelled 1 – 4), while one sample (labelled PD) was collected from Port Dundas at the end of the Glasgow Branch. No sediment was retrieved at sites 3 and 5 where samples were solely composed of numerous small gastropods, mainly snails but also a few bivalves (see Figure 3.2).

Table 3.1 Initial Forth and Clyde Canal sediment sampling details

Sample	Sampling Date	Location	Grid Letter	Easting	Northing
1	13/07/2010	Bowling Harbour centre leading to River Clyde	NS	450	735
2	13/07/2010	Bowling Harbour opposite British Waterways Office	NS	450	735
3	13/07/2010	Bowling Basin before strait to Harbour	NS	451	735
4	13/07/2010	Bowling Basin after Lock 38	NS	451	735
5	13/07/2010	Before Lock 38 leading to Bowling Basin	NS	453	735
6	13/07/2010	Beneath Erskine Bridge in Old Kilpatrick	NS	466	725
7	13/07/2010	Close to Dumbarton Rd North of Dalmuir Drop Lock 36a	NS	485	712
8	13/07/2010	Opposite Lidl car park in Clydebank Shopping Centre	NS	503	704
9	13/07/2010	Close to Lock 35 in Old Drumchapel	NS	519	699
10	13/07/2010	Close to footbridge leading to Westerton Rail Station	NS	539	703
11	11/10/2010	Close to Clevenden Rd bridge opposite Kelvindale Rail Station	NS	556	690
12	11/10/2010	500m East of Stockingfield Junction	NS	575	690
13	11/10/2010	Close to Balmuildy Rd bridge crossing the canal	NS	605	716
14	11/10/2010	Close to Kirkintilloch Rd (A803) bridge crossing the canal	NS	633	730
15	11/10/2010	Close to New Lairdsland Rd (A8006) bridge crossing the canal	NS	655	738
16	11/10/2010	On top of B8023 – Auchendavie Rd connecting tunnel	NS	673	748
17	12/10/2010	Close to Main St. bridge crossing the canal at Twechar	NS	699	758

18	12/10/2010	Close to the B802 bridge crossing the canal at Auchinstarry	NS	720	769
19	12/10/2010	Close to bridge of rural road connecting Kilsyth and Dullatur	NS	737	774
20	12/10/2010	At end of footpath opposite Kelvinhead Rd. leading to Banton	NS	758	782
21	12/10/2010	Close to Wyndford Lock 20 before entering Banknock	NS	776	787
22	12/10/2010	Close to Underwood Lock 17 before entering Bonnybridge	NS	806	790
23	12/10/2010	Close to the Bonnybridge Lifting Bridge	NS	824	801
24	28/07/2010	West of Junction to Falkirk Wheel	NS	850	803
25	28/07/2010	East of Junction to Falkirk Wheel	NS	854	802
26	28/07/2010	Close to Lock 16 in Camelon, Falkirk	NS	867	800
27	28/07/2010	Close to Lock 5 in Bainsford, Falkirk	NS	886	810
28	28/07/2010	Close to Harbour leading to River Carron near Grangemouth	NS	906	819

Table 3.2 Initial Glasgow Branch sediment sampling details

Sample	Sampling Date	Location	Grid Letter	Easting	Northing
SFJ	13/10/2010	Close to Ruchill St. bridge crossing the Glasgow Branch of the canal	NS	572	688
BW	13/10/2010	Opposite British Waterways Head Office on Glasgow Branch	NS	586	671
PD	13/10/2010	Furthest point South at Port Dundas	NS	595	667

Figure 3.1 Sampling locations along the Forth and Clyde Canal and Glasgow Branch [after [3]]

Sampling locations along the Forth and Clyde Canal are numbered 1 to 28

Sampling locations along the Glasgow Branch are labelled SFJ (Stockingfield Junction), BW (British Waterways), and PD (Port Dundas)

Figure 3.2 Gastropods collected at sites 3 and 5, compared to scale with a penny

With reference to Figure 3.1, the samples can be grouped together based on similarities in locations where they were obtained. Sampling sites 1 – 4 of the Forth and Clyde Canal are in a harbour area, while the canal stretch can be divided into 3 segments. Sites 5 – 12 are considered to be in an urban area, sites 13 – 23 in a rural area, with sites 24 – 28 being in a suburban area. The three sampling sites of the Glasgow Branch are considered urban inner city, with PD being also a harbour area.

At the time of sampling, these gastropods were noticed to be live. The species of bivalves could not be determined, in part due to the limited number of specimens collected. However, the snails appeared to be *Lymnaea peregra* (Müller, 1774). This is a rather common freshwater snail species in Britain. Hence, their origin is not from terrestrial soil runoff. Also, these snails were found in great numbers. This implied that the sediment dynamics in the respective areas are rather low-key, providing a stable environment which enabled the species to acclimatize and grow in population.

3.2 Sample Preparation

All analysis was carried out on air-dried samples. The samples were spread in separate aluminium containers and once dry, large items like leaves, twigs and stones were removed. Each sample was sieved through a 2 mm stainless steel mesh [Fisherbrand, Fisher Scientific UK Ltd., Loughborough, UK] before storage in amber glass bottles in a refrigerator.

3.3 Analytical Methods Employed

Since all samples were analysed as air-dried, their residual moisture content had to be determined for calculation purposes. Organic matter (OM) content was estimated using the loss on ignition (LOI) test, which can be performed as a continuation of the moisture content test. The pH and the PSD of the sieved (< 2 mm) samples were also determined at a later stage. All these tests, which summarise the general characteristics of the samples, are described in Chapter 4.

The original 31 samples (29 of sediment and 2 of gastropods) collected were left to air dry in an oven set at 30 ºC for a few days and analysed for PT content of 10 elements; As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn. The method and results of this exercise are described in Chapter 5. Very little of sample 25 remained after this test and so another sample from site 25 was collected on 23/03/2012; this was termed 25R (where R stands for re-sampled). This new sample was air-dried as described above and had the PT content of the aforementioned 10 PTEs determined.

After the PT content analysis, the 29 sediment samples (consisting of 28 original samples and the newer sample 25R instead of sample 25) were subjected to sequential extraction following the modified BCR technique – the gastropod samples from sites 3 and 5 were omitted. This is described in Chapter 6.

The original 29 sediment samples were screened for their PT content of Hg. The nine sites that were deemed the most interesting based on their location and PT Hg concentration were 15, 19, 24, 25, 26, 27, SFJ, BW, and PD. These were re-sampled on 01/08/2012, paying special attention to the requirements associated

with collecting and storing samples destined for Hg analysis. The nine fresh samples were collected in glass bottles and air-dried on a bench top for several days before being taken for quantitative analysis. This is described in Chapter 7.

These nine new sediment samples were also analysed for Me-Hg (described in Chapter 8) and three organotin compounds; MBT, DBT and TBT (described in Chapter 9).

3.4 General Laboratory Procedures

All materials were used without further purification. All glassware used in this study was thoroughly cleaned by soaking overnight in a 5% nitric acid (v/v) bath (65%, GPR, Sigma-Aldrich® Company Ltd., Dorset, UK), after which it was rinsed and air dried. Final washings of glassware and preparation of solutions were done using deionised (Millipore Milli-Q) water.

General health and safety practices, such as wearing PPE at all times and using the fume-cupboards when necessary, were strictly adhered to. Risk and safety statements of all reagents used were noted before use and appropriate control of substances hazardous to health forms for procedures that were to be followed were drawn up, unless already available, in which case they were read thoroughly and signed afterwards.

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4 General Characteristics of the Sediment Samples

4.1 Introduction

The basic general characteristics tests that have been carried out on the samples are included in this Chapter. The determination of the % moisture content and the estimation of the % organic matter with the loss on ignition test were carried out on all samples. The pH and PSD tests were carried out on sediment samples only. The pH was determined on all the original sediment samples (except 25), sample 25R, and the nine new samples, whereas the PSD was determined only on the original sediment samples (except 25) and sample 25R.

4.2 Determination of Moisture Content and Organic Content

4.2.1 Introduction

Samples are preferentially left to air dry at room temperature before being processed. This has two advantages. Should samples be analysed wet, considerable variation in test sub-sample masses would be expected due to the uncertainty in the water content[1]. Secondly, through air drying, as opposed to exposure to heat, volatile PTEs or organic compounds are not lost from the sample[2].

However, an air dried sample would still have a small moisture content[2]. The quantity of residual moisture is dependent on the sample texture and constituents. Therefore, this varies between samples and should be determined so as to correct for it and compare all analysis results on a dry weight basis.

As outlined in Chapter 1, organic matter is a bulk component of soil, and also of sediment following surface runoff and sedimentation in a water body. The OM plays a major role in retaining PTEs in an exchangeable form, as well as supplying organic compounds in solution that may act as chelating agents towards dissolved PTEs.

The OM content of a sediment sample is commonly estimated using the LOI method. This is a fast and inexpensive gravimetric technique based on the fact that

the OM content is oxidised to carbon dioxide and water vapour at 500 – 550 ºC, leaving ash residue. Higher temperatures should be avoided since carbonates will decompose to carbon dioxide and metal oxide at around 900 – 1000 ºC[3].

The test should be carried out on a dry sample to avoid inaccuracies created by the presence of moisture. The weight loss of a dry sample following LOI is proportional to the amount of organic carbon present. This was shown to correlate closely with organic carbon content in lake sediments determined using chromatography[4].

4.2.2 Experimental

4.2.2.1 Equipment

i. 4-digit weighing balance [AE200, Mettler, Leicester, UK]
ii. Desiccator with silica gel as desiccant
iii. Oven [Memmert GmbH + Co. KG, Camlab Ltd., Cambridge, UK]
iv. Muffle furnace [Box Furnace, Elite Thermal Systems Ltd., Market Harborough, UK]

4.2.2.2 Analytical Method

The moisture content test was carried out following BS EN 12880:2000[5]. One gram of each air dried and sieved (< 2 mm) sample was accurately weighed in a pre-weighed ceramic crucible. The sample was placed in an oven at 110 ºC for 24 hr. It was then removed and placed in a desiccator and allowed to cool for a few hours, after which it was accurately weighed. The latter procedure was repeated until a constant mass was obtained. The difference in mass obtained before and after the drying process was used to calculate the % mass lost, which was equivalent to the % moisture content.

The residue from the moisture content determination was used for the LOI test, as described in BS EN 12879:2000[6]. The sample was placed in a furnace preset with the following programme: temperature ramp set at 10 ºC/min until reaching 550 ºC, then hold at 550 ºC for 8 h, followed by a cooling down period. When the temperature reached 110 ºC, the crucible was removed, placed in a desiccator to avoid absorption of atmospheric moisture and allowed to cool for a few hours, after

which it was accurately weighed. The latter procedure was repeated until a constant mass was obtained. The difference in mass obtained before and after the ignition process was used to calculate the % mass lost, which was an estimate of the OM content.

4.2.3 Results and Discussion

Results obtained for % moisture and LOI in the original 31 samples collected from the Forth and Clyde Canal and the Glasgow Branch, together with sample 25R, are shown in Table 4.1. Both parameters were also measured for the nine new samples that were collected for the Hg, methyl-Hg and organotin analysis. These results are shown in Table 4.2.

Table 4.1 % Moisture and % organic matter content of the original 31 samples, as well as sample 25R, collected from the Forth and Clyde Canal and Glasgow Branch

Sampling Site	% Moisture Content (110 °C)	% Organic Matter Content (550 °C)
1	5.21	24.5
2	3.44	16.4
3	41.2	13.3
4	5.14	24.8
5	39.6	13.8
6	4.05	20.3
7	2.02	9.49
8	2.93	11.3
9	3.47	16.9
10	6.06	28.3
11	3.00	16.1
12	3.86	22.3
13	3.92	19.1
14	4.27	18.8
15	3.91	25.1
16	4.28	18.3
17	4.16	24.7
18	3.12	19.5
19	4.83	26.7
20	3.65	17.5
21	4.95	24.4
22	5.50	27.6
23	2.67	13.7
24	4.34	15.5
25	4.39	23.0
25R	4.28	23.4
26	4.50	14.8
27	4.93	20.7
28	3.50	11.6
SFJ	4.07	23.2
BW	3.32	19.1
PD	6.17	28.5

Table 4.2 % Moisture and % organic matter content of the nine new sediment samples

Sampling Site	% Moisture Content (110 ºC)	% Organic Matter Content (550 ºC)
15	4.56	22.3
19	6.29	23.7
24	5.73	21.7
25	4.59	17.9
26	4.58	16.8
27	5.68	23.7
SFJ	5.31	23.0
BW	4.22	17.1
PD	7.97	29.1

The moisture content of both gastropod samples (3 and 5) was far greater than that of sediment samples at 41.2% and 39.6%, respectively. This was expected since the samples were live organisms. On the other hand, their OM content was less than the average of the sediment samples. This was because their dry body mass, excluding their carbonate shell (that does not decompose at 550 ºC), is very small.

The % moisture content of all sediment samples in Table 4.1 and Table 4.2 was quite constant, averaging at 4.93%. The difference in the % moisture content between the original samples and the analogous ones in the nine new samples was less than 1.5%. This implies that the constituents of the sediment samples were fairly similar along the whole stretch of canal and that they did not change markedly over the *ca.* 1.5 year period between sampling sessions (where resampled).

Samples 7 – 11 are located in the Greater Glasgow area. The input of surface runoff in the urban area was expected to contain proportionally the lowest amount of soil and the highest amount of roadside dust. The composition of dust makes it unable to contain as much residual moisture as soil after air drying. With the exception of sample 10, the results obtained appear to support this.

This same trend was observed with the % OM content, whereby samples 7, 8, 9 and 11 were amongst the samples that had the lowest amount – ranging between 9.49% and 16.9%. The average % OM of all samples was 20.5%. Sample 10 was one of the samples which had the highest % OM content – at 28.3% – suggesting a greater soil input at this location compared to its adjacent sampled sites.

Other locations with low % OM content were samples 23, 24, 26 and 28. Sample 23, which also had low % moisture content, was collected from the town

centre of Bonnybridge. This may be the reason behind the similarity of the results with those from other urban areas. As for samples 24 – 28, these were collected from sub-urban areas.

The LOI values obtained are unlikely to have been effected by decomposition of carbonate. The sediment samples appear to have little carbonate content. This is corroborated by the pH values obtained, which were all acidic (see Section 4.3).

4.3 Measurement of pH

4.3.1 Introduction

Sediment samples may be acidic or basic depending on the type of soil received from surface runoff. Acidic sediment is rich in organic matter whereas basic sediment will contain carbonate. In the environment, the pH of the solution that comes in contact with the sediment determines the number of negatively charged surface sites available on the sediment for adsorption of PTE cations. A negative correlation between soil pH and PTE mobility and bioavailability typically exists. A low pH will increase cation solubility from sediment surfaces and maintain the aqueous cations in a solvated state.

Natural waters typically have a pH which is near neutral. However, aqueous cations may still adsorb onto surfaces through cation exchange with H^+ ions. The release of these H^+ ions will determine the pH of the surrounding solution. There are different ways of measuring the pH of a sediment sample[7-8]. The two most common methods involve the preparation of a 1 : 5 mixture of sediment : distilled water or of sediment : dilute calcium chloride solution, followed by pH measurement on the solution with a calibrated pH meter.

When a sediment sample is diluted with distilled water, most of the H^+ ions tend to remain adsorbed onto the clay minerals and organic matter and are not released into solution. The dilute calcium chloride solution provides Ca^{2+} ions which are able to replace some of the adsorbed H^+ ions. This greater release of H^+ ions causes a further lowering of the pH of the solution, typically by 0.8 units when compared to using the distilled water method[8]. Therefore, it is important to note which method was used and compare results derived from similar methods to avoid method induced discrepancies. The dilute $CaCl_2$ solution method is the preferred

method since it gives more consistent results than when using distilled water[8] and offers a closer resemblance to a natural situation.

4.3.2 Experimental

4.3.2.1 Equipment

i. Centrifuge tubes (50 mL, polypropylene) [Fisherbrand, Fisher Scientific UK Ltd., Loughborough, UK]

ii. Calibrated pH meter [Jenway 3505 pH Meter, Bibby Scientific Limited, Staffordshire, UK] with probe [BDH Gelplas Ag/AgCl/Sat. KCl reference electrode, VWR International Limited, Leicestershire, UK] and pH 4 and 7 calibration buffer solutions [Solutrate, Fisher Scientific UK Ltd., Loughborough, UK]

iii. End-over-end mechanical shaker [GFL® 3040, GFL Gesellschaft für Labortechnik mbH, Burgwedel, Germany]

4.3.2.2 Reagents

i. Calcium chloride anhydrous
(Laboratory Reagent, Fisher Scientific UK Ltd., Loughborough, UK)

4.3.2.3 Analytical Method

The gastropod samples from sites 3 and 5 were omitted from this study due to unsuitability of the matrix. The determination of pH of the sediment was carried out following BS ISO 10390:2005[7].

At least 5 ml of each air dried, sieved (< 2 mm) sample were transferred using a spoon into a 50 ml centrifuge tube, followed by 25 ml of 0.01 mol/l calcium chloride solution. The tube was tightly capped and placed in the end-over-end mechanical shaker for 60 min ± 10 min, after which it was removed and left to stand for at least 1 hour, but not longer than 3 hours. The solution was then stirred manually and the pH was measured in the suspension at 20 ± 2 ºC immediately after, using a calibrated pH meter. The pH was noted after the digital readout on the pH meter had stabilized.

4.3.3 Results and Discussion

The measured pH values of the original sediment samples (excluding sample 25, but including sample 25R) collected from the Forth and Clyde Canal and the Glasgow Branch, and of the nine new samples, are listed in Table 4.3.

Table 4.3 pH values of the original sediment samples (excluding 25, but including 25R) and the nine new sediment samples

Sampling Site	pH (original sediment samples)	pH (nine new sediment samples)
1	5.90	-
2	6.05	-
4	6.02	-
6	6.14	-
7	6.34	-
8	6.34	-
9	6.18	-
10	6.33	-
11	6.43	-
12	5.88	-
13	5.50	-
14	5.23	-
15	5.13	5.80
16	5.64	-
17	5.70	-
18	5.79	-
19	4.88	5.79
20	5.33	-
21	5.94	-
22	5.02	-
23	5.66	-
24	5.87	5.69
25	-	5.37
25R	5.85	-
26	5.83	5.51
27	6.06	5.83
28	6.38	-
SFJ	6.19	6.20
BW	6.20	6.23
PD	6.36	6.55

The $CaCl_2$ solution has a pH of around 7. Therefore, the resulting acidic pH of the sediment slurry is a product of the effect exerted by the aqueous cations present in solution on soil minerals. The pH values obtained may be compared to each other since the concentration of calcium chloride solution used was similar throughout.

The urban/rural divide of the canal system is evidenced from the results obtained. In the original set of samples, the urban sediments – 1 to 12 – and sub-urban sediments – 27 and 28 – of the Forth and Clyde Canal, as well as the three sediments of the Glasgow Branch, all had pH around or greater than 6. The more rural samples – 13 to 26 – had pH less than 6. Rural samples are expected to receive a greater proportional load of organic matter, particularly soil and dead foliage. Sediments from urban areas tend to have a lesser proportion due to the relative lower amount of soil and plant matter surrounding the canal.

The only samples that show a marked difference in sediment pH between the older nine sediment samples and the new analogous ones (over the *ca.* 1.5 year period) are those originating from rural sites – 15 and 19. The content of runoff that forms the top layer of sediments in rural areas is expected to vary widely, possibly due to the variation in organic matter content. In urban areas, the variation is expected to be low and the amount is constant. The observed results may reflect a real difference between the two sets of samples because of the length of time that has passed. However, this cannot be claimed with certainty since replicate measurements on the same sediment samples were not carried out, and therefore, the repeatability is not known.

4.4 Particle Size Distribution

4.4.1 Introduction

The PSD of a granular sample gives an indication of its properties. Samples with a high surface area may participate better in chemical reactions, therefore exhibiting a higher reactivity. Different methods exist for determination of the PSD.

Each method exploits a different physical property. The most appropriate method should be selected based on the type of sample available.

A sophisticated technique that makes use of the light-scattering properties of the sample is described in BS ISO 13320:2009[9]. It requires an expensive instrument but is easy to perform. This method is applicable to particle size ranges from around 0.1 μm to 3 mm. However, it assumes that all particles are spherical. This is generally in conflict with the real shape of constituents in the clay fraction of soils and sediments, since clay particles, organic matter, and Fe/Mn (hydr)oxides are amorphous.

Sieving is a relatively cheap and common approach. It is described in BS 410-2:2000 (equivalent to ISO 3310-2:1999)[10]. A set of sieves are fitted on top of each other, arranged in a scale of ever decreasing mesh pore size, and through mechanical shaking, the finer particles will fall through and settle in the appropriate sieve. This method is suitable for particle sizes that range from 200 mm down to 63 μm. Therefore, while being ideal for the coarser fractions, any particles having a diameter of < 63 μm will be collected together in the bottom pan.

Another method is the sedimentation technique. This is based upon the terminal velocity acquired by particles as they fall in a fluid by their own weight due to the gravitational pull. This method is documented in ASTM D422 – 63 (Reapproved 2007)[11]. It is suitable only for particles with sizes between 75 μm and 1 μm. Larger particles are too heavy and fall to the bottom of the fluid right away, whereas smaller particles will be affected by Brownian motion and will remain in suspension for a considerable length of time.

The sedimentation technique is a cheap, quick and simple experiment. The method makes use of a hydrometer, which is an instrument made of glass and consists of a cylindrical stem and a weighted bulb to maintain it upright. When a hydrometer is suspended in a water column, it will settle at a point of neutral buoyancy. The stem has graduations, which for an ASTM 152H hydrometer, range from 0 g/l (at the top of the stem) to 60 g/l (at the base of the stem, near the bulb). The value which would be aligned to the bottom of the meniscus which forms around the stem will indicate the density of the water. Density is a factor of temperature *T*, and so *T* should be noted with each hydrometer reading.

The lower the density of the substance, the farther the hydrometer will sink. Whereas the density of water at room temperature would be slightly less than 1 g/l, the density of a sediment/water suspension would be considerably higher. By measuring both such suspensions, the hydrometer method is able to give the relative density (specific gravity) of a sediment/water suspension with respect to its blank solution. The specific gravity of the suspension is measured at a depth *L* in the water column. The depth *L* is called the effective depth, and is measured from the bottom of the meniscus around the stem to the centre of the hydrometer bulb. Therefore, fixed lengths of *L* exist for each hydrometer reading between 0 and 60 g/l. These are given in the standard method[11].

There are three types of corrections that should be applied to hydrometer readings:

Meniscus Correction

The reading on the stem should be taken at the bottom of the meniscus; however, in practice this is only possible on a blank solution since the stem's graduations would be obscured by the dark brown colour of the suspension. Therefore, a reading on the top of the meniscus is taken in the blank too, and the difference (between the top and the bottom) is measured. This value should be subtracted from hydrometer readings in suspensions, which are taken at the top of the meniscus.

Temperature Correction

Since the density of a fluid is a function of temperature, and since the hydrometer is calibrated at 20 ºC, any hydrometer readings taken at a different solution temperature will induce errors as a result of the variance of density. Measurements are ideally taken in a controlled environment at 20 ºC, or else an appropriate correction factor is applied to the hydrometer reading. The discrepancy is determined by taking a reading of the blank set at 20 ºC in a water bath and a reading of the blank at the operating (room) temperature.

Zero Correction

The hydrometer reading of a test solution should always be followed by a reading from a blank solution at the same temperature. The hydrometer reading from the test solution should be blank corrected. The blank should be made up of the same constituents of the suspension solution (*i.e.* same amounts of water and dispersing agent, which is added to aid in the deflocculation of the particles), but without addition of sediment sample.

Once a sediment/water suspension is prepared (time $t = 0$), particles will start to settle out. Through calculations described in the standard method[11], when a hydrometer reading is taken at time *t*, the largest diameter of the particles still in suspension (at depth *L*) at that time *t* could be calculated. It has been established[11] that sand particles (75 μm – 63 μm) settle within the first 30 s, while all silt particles (< 63 μm – 2 μm) would have settled by $t = 250$ min, thereafter leaving only clay particles in suspension.

Since the hydrometer reading is a measure of the specific gravity of the suspension (at depth *L*) at time t, the corrected hydrometer reading could be used to calculate the percentage of suspended particles.

4.4.2 Experimental

4.4.2.1 Equipment

i. 4-digit weighing balance [AE200, Mettler, Leicester, UK]
ii. Stainless steel sieve (63 μm aperture) [Fisherbrand, Fisher Scientific UK Ltd., Loughborough, UK]
iii. Borosilicate glass measuring cylinders (capacity 1 l) [Fisherbrand, Fisher Scientific UK Ltd., Loughborough, UK]
iv. Thermometer [THL-210-110E, A. Gallenkamp and Co. Ltd., London, UK]
v. Hydrometer [ASTM E100 152H, S. Brannan and Sons Ltd., Cumbria, UK]

4.4.2.2 Reagents

i. Sodium hexametaphosphate, powder form
(Laboratory Reagent, Fisher Scientific UK Ltd., Loughborough, UK)

4.4.2.3 Analytical Method

The PSD test was carried out following an adapted version of ASTM D422 – 63 (Reapproved 2007)[11]. About 100 g of the air-dried, sieved (< 2 mm), sediment sample were accurately weighed (recorded to ± 0.01 g accuracy) and sieved through a 63 μm sieve. With reference to the particle size classification table[12], the proportion of sample retained on the 63 μm sieve was the sand fraction. This was collected and weighed accurately. Care was taken to ensure that at least 50 g of sample had passed through the 63 μm sieve. This contained the silt (63 μm – > 2 μm) and clay (≤ 2 μm) fractions.

Whereas the distribution of particle sizes > 63 μm was determined by sieving, the PSD of smaller particles was determined by a sedimentation process, using an appropriate hydrometer.

A *dispersing solution* was prepared by dissolving 40 g of $Na_6(PO_3)_6$ in deionised water, and making it up to the 1 l mark. This was prepared fresh before every use since in acidic conditions, caused by dissolution of atmospheric CO_2, the salt will hydrolyze to the orthophosphate form, which has less dispersive action than the hexamethaphosphate form. A blank solution was prepared by mixing 125 ml of the dispersing solution with 875 ml of deionised water in a 1 l measuring cylinder.

The sieved (< 63 μm) sediment fraction was transferred to another 1 l measuring cylinder, together with 125 ml of dispersing solution. This was allowed to soak for 16 h. Once this time elapsed, 500 ml of deionised water were added. The solution was shaken vigorously for 1 minute, after which the suspension was made up to the 1 l mark with deionised water.

A water bath was set up and maintained at 20 ºC. The blank cylinder and the test cylinder were placed and kept in the water bath to equilibrate with this set temperature. The hydrometer used came calibrated at 20 ºC, and therefore this avoided the need to correct for temperature-induced variances.

Once the temperature of the blank and test solution were 20 ºC, the test cylinder was shaken once more to re-suspend the particles, making sure no sediment remained at the bottom, and placed back in the water bath. The time *t* was noted. Since the samples were sieved to 63 μm, no sand particles were introduced. Therefore, there was no need to take a reading at t = 30 s.

A hydrometer reading was taken at time t = 250 min. The hydrometer was inserted into the test cylinder and 30 s allowed for it to stabilize and immobilise before taking the reading. The reading was taken at the top of the meniscus formed around the stem. The hydrometer was removed after the reading, washed clean, and inserted in the blank cylinder. After allowing 30 s, a reading was then taken at the top of the meniscus too, after which the hydrometer was removed and wiped dry. After each hydrometer reading, the temperature was also checked to ensure that the solution were still at 20 ºC.

Following the application of the meniscus and zero correction, the corrected hydrometer reading was used to calculate the % clay fraction in suspension. The % silt content was calculated by difference.

4.4.3 Results and Discussion

Following a visual inspection at the time of sampling, samples 7 and 24 appeared to contain some of the canal's clay lining. This was evidenced as light brown streaks amongst the dark brown sediment. The remaining samples appeared similar in their dark coloration.

A quick, manual sediment texture test indicated that no sample contained a high proportion of particles in the sand fraction since samples were not gritty, but were rather more like a smooth paste.

The determined sand, silt and clay fractions of the sediment samples are listed in Table 4.4. The table also lists the relative soil texture based on the descriptions as given by the USDA soil texture triangle[13], even though these samples are sediments and not soils. This is justifiable since the main source of sediments is soil runoff.

Table 4.4 Particle size distribution of the Forth and Clyde Canal and Glasgow Branch sediment samples (< 2 mm)

Sampling Site	% Sand	% Silt	% Clay
1	15	58	27
2	13	61	26
4	17	54	29
6	19	58	23
7	14	44	42
8	13	58	29
9	18	63	19
10	20	57	23
11	12	68	20
12	15	62	23
13	16	60	24
14	18	54	28
15	17	55	28
16	13	55	32
17	15	59	26
18	14	57	29
19	22	47	31
20	18	49	33
21	13	56	31
22	18	52	30
23	16	59	25
24	15	38	47
25R	15	54	31
26	13	58	29
27	17	59	24
28	20	57	23
SFJ	20	56	24
BW	19	61	20
PD	26	56	18

The presence of clay minerals, which fall within the clay fraction of the PSD, possibly influenced the texture result of samples 7 and 24. The fact that some clay canal lining was collected with the sampling method employed signified that the layer of sediment present at these two sites was quite thin.

Overall, all samples had a high proportion of silt. Considering that the major source of influx contributing to bottom sediment is soil runoff, the PSD of the sediment samples did not reflect the fact that soil typically has a substantial

proportion of particles in the clay fraction due to the presence of OM, clay minerals and Fe/Mn (hydr)oxides. The typical PSD of soil from central Scotland is loam/clay loam[14]. The reason for this may be that once soil runoff enters the canal, the lighter fraction may be prevented from settling out in its entirety. These particles may remain in suspension due to the turbulence caused by the water current. Slightly larger particles that will fall to the bottom may be resuspended with the drag created by propellers of passing vessels. Suspended particles will eventually be washed out to sea.

The rural areas are expected to receive higher amounts of soil runoff as compared to urban areas. This difference appears slightly evident in that samples from rural areas had slightly more particles in the clay fraction. The determined texture of all sediment samples confirmed that the % sand content was low overall. High quantities of particles in the sand fraction are not common with UK soils and in fresh water canal sediments. High sand content is typical of sediments in marine coastal areas, which receive runoff from weathering rocks. The highest sand result recorded was at PD. This may be coming from roadside dust due to the substantial anthropogenic influence in this industrial area.

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5 Pseudototal Potentially Toxic Element Contents in Sediments of the Forth and Clyde Canal

5.1 Introduction

Pseudototal digestion with *aqua regia* is widely used to measure concentrations of PTEs in sediment samples. Unlike HF, the reagent does not liberate metals bound in the lattice structure of primary silicates. Nor does it fractionate the metal content into operationally-defined species with different liabilities, as does sequential extraction (see Chapter 6). Hence, no information on metal binding forms or current mobility, bioavailability and potential toxicity is obtained. However, its rapidity and relative simplicity make it a useful approach for initial determination of maximum concentrations of potentially mobile PTEs present.

5.1.1 Potentially Toxic Elements in Canal Systems

A common feature of canals is that they are, at least in part, artificial waterways. A canal typically connects one shipping lane or port to another or else ends at an inland terminal. The former type of canals are used as shorter, faster, inland maritime routes, while the latter are used to service the needs of a particular industrial centre and the surrounding communities.

Some transit canals such as the Suez Canal and the Panama Canal form part of the major shipping routes of the world. Their strategic location means that they have been modified, and will continue to be, in order to be able to accommodate modern sized ships. However, many of the older and smaller types of canals have long ceased to serve their original purpose. Those canals that ended at an inland terminal have lost out to competition with other means of transport such as trains or lorries for delivery of supplies, while other transit canals have become too small for the size of modern vessels. Whilst some of these canals became derelict and were later infilled, others have been regenerated and reopened for use by pleasure craft.

Canals that cut through urban and rural areas can serve as a convenient indicator of the status of contamination of the surrounding areas through monitoring of the bottom sediment. This is because the major component of the sediment originates from surface soil runoff from along the banks of the canal. Since water flow rates in canals are typically a few centimetres per second, the heavier particles will precipitate in the proximity of their entry point.

Sediment can move along the canal by resuspension caused by the currents created by the propellers of passing vessels, but the distance travelled is likely to be rather short since the heavy particles tend to settle back quickly. However, the extent of sediment movement is dependent on the shipping traffic flow. Lighter particles directly inputted or generated by the churning of passing vessels will travel with the water flow for a considerable distance before precipitating, or may even be eventually washed out of the canal into the open water.

The presence of a lock acts as a physical barrier. Hence, although it is plausible that the lighter, suspended particles pass through locks, it is unlikely that the bulk of sediment does so. This physical barrier limits mobility, therefore supporting the hypothesis that there is correlation between the physical and chemical properties of the sediment and those of the surrounding soil. Sediment in sea level canals may also contain a proportion of marine material that is transported in with currents created by incoming vessels[1]. Canals that are elevated from sea-level are separated with a sea lock and therefore sediments would be expected to be primarily composed of surface soil runoff.

The urban/rural divide and the origin of sediment were particularly noticeable factors in studies carried out on the Delft Canal in The Netherlands[1-2]. Delft is a city situated in the Dutch countryside and has urban canals that are connected with the network of Dutch canals that eventually lead out to the North Sea. The PTE levels in sediment from inner city urban stretches of the canal were significantly higher than levels determined in sediment originating in rural areas just outside the city. Table 5.1 lists the respective PTE ranges determined in the 18 urban sediment samples and 33 rural sediment samples collected[1]. The general trend observed with all PTEs, with the exception of As, was that the concentration range of the samples collected from the rural area were lower than those from the urban area.

Table 5.1 Potentially toxic element (PTE) concentrations in urban and rural sediment collected from the Delft Canal, The Netherlands[1]

PTE	Urban Sediment (mg/kg)	Rural Sediment (mg/kg)
As	8.0 – 44.0	3.0 – 65.0
Cd	0.27 – 4.30	0.20 – 3.0
Cr	10.0 – 140	7.0 – 44.0
Cu	120 – 630	5.0 – 350
Ni	10.0 – 80.0	7.0 – 37.0
Pb	165 – 2500	0.26 – 250
Zn	360 – 2000	50.0 – 1650

The PTE levels determined were compared with the environmental quality standards (EQS) categories given by the Dutch system of sediment pollution classes for quality assessment. There are four classes, and their values are given in Table 5.2[3]. The class limits are defined for a standard sediment having 10% organic matter and 25% clay contents. Correction factors are applied to the results obtained wherever non-standard sediment composition was determined. This is done to take into account the stronger, semi-permanent binding capacity of organic-rich, muddy sediments. Sediments with concentrations in Class 3 or higher are considered of unacceptable quality and are required to undergo remediation through dredging and safe disposal.

Table 5.2 Sediment pollution classification system used in The Netherlands for potentially toxic elements (PTEs)[1]

PTE	Class 1 (mg/kg) (unpolluted)	Class 2 (mg/kg) (slightly polluted)	Class 3 (mg/kg) (moderately polluted)	Class 4 (mg/kg) (very polluted)
As	< 55			> 55
Cd	< 2	2 – 7.5	7.5 – 12	> 12
Cr	< 380			> 380
Cu	< 35	35 – 90	90 – 190	> 190
Ni	< 35	35 – 45	45 – 210	> 210
Pb	< 530			> 530
Zn	< 480	480 – 720		> 720

All As levels in the urban samples fell within Class 1, whereas some of the rural samples surpassed that limit. Only traces of Cd were detected in both regions, and both had some samples that surpassed Class 1 but not Class 2. The top end of the urban range was slightly higher than that of the rural area, but the overall low levels observed reflected the lack of specific Cd-related industries in the area. Chromium levels were as much as 3 times higher in the urban area than the rural area, but all results fell within Class 1. In the urban canal sediments, Cu concentration was determined to be in either class 3 or 4. The rural content ranged across all four classes. The rural range of Ni fell within Class 1 and 2, while the urban range spanned Class 1 to 3. The rural range of Pb was entirely within Class 1 whereas a proportion of urban sediments fell in Class 4. The urban concentration range of Zn was higher than that in the rural area, although both areas had levels which ranged from Class 1 to Class 4.

Overall, 17 out of the 18 inner city sediments were in class 3 or 4. In contrast, only 11 out of the 33 sediments in the outer city stations fell into these classes, with the reason attributed to elevated Cu levels. Cadmium, Cr and Ni are mainly of anthropogenic origin in the area studied, and therefore the low levels observed in the rural environment were expected. On the other hand, the lower end of the rural concentration range is elevated for Cu, Pb and Zn since they are widespread general pollutants.

In another study[2] involving 200 stations in the urban and rural Delft canals, 95% of sediment samples from the inner city canals fell within Class 3 and 4, in contrast to only around 45% of the outer city samples, where in general, concentration ranges were 2 – 10 times lower than in the inner city.

Inner city canals were found to be particularly high in Cu, Pb and Zn. The extent of contamination determined was such that it was improbable that it originated fully from local pollution sources. Results have shown that 65 – 85% of sediments present were imported from the Rijn-Schie canal. This canal connects the river Rhine and the Delft inner city canals, having five connections, all of which are level, with the latter. Results reported indicated some common sources between suspended solids found in the river Rhine and the sediment in the Delft inner city canal[2].

Shipping traffic was found to play a significant role in the movement of

sediments[2]. This was determined from a mathematical model that took into consideration the shear stress exerted by a vessel's propellers on the sediment bed and also the hydrodynamic phenomenon of water drawdown during passage of a vessel of uniform size and weight in a canal of fixed water column height and sediment characteristics. The key variable was the vessel's velocity; increase in speed gave rise to a near exponential increase in sediment resuspension. With the Delft inner city canals having a water flow of around 5 cm/s, redeposition or extent of movement is dependent on shipping traffic[2]. Sediment movement could be reduced through measures aiming at reducing vessel speeds.

Non-agitated waters lead to a high sedimentation rate and very low mixing through the lack of resuspension. This leads to the formation of a rather thick layer of anoxic, reduced sediment. Such sediments serve as important sinks for PTEs, but when there is a change in conditions such as pH and redox potential, the sediments can then act as sources of PTEs[4]. Situations when sediments can become sources are through dredging and land disposal, through *in situ* water column height reduction, or through sediment resuspension. Contact with atmospheric oxygen or dissolved oxygen will cause oxidation, affecting the redox potential.

The extent of release of PTEs depends on how they are found bound with the sediment matrix, with loosely bound elements being the most mobile and hence potentially bioavailable. This topic will be dealt with separately in Chapter 6.

Table 5.3 lists sediment PT values from studies carried out on canals around the world. It is interesting to note that while only a few included Fe and Mn in their studies, none of these authors measured PT Sn content. The fact that the levels of Fe and Mn are high in common soil minerals reduces their usefulness in monitoring of anthropogenic inputs. Nevertheless, the determination of high levels of Fe serves as a good indicator for the fact that the major source of that sediment could be from surface soil runoff.

There exist numerous other studies that make use of the PT test but have not worked on canal sediments. The PT content of a small selection of these is listed in Table 5.4. In other studies, authors have opted for measuring the total content (using HF) rather than the PT content – some also on canal sediments. A selection is also included in Table 5.4.

Table 5.3 Pseudototal content results obtained from various studies on canal sediments around the world [a, b]

Location	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Woolston Canal, Warrington, UK[4]	145	-	1315	887	-	-	102	1887	4858
Woolston Canal, Warrington, UK[5]	420	20	980	740	-	-	-	1445	4285
Shropshire Union Canal - S. Staffordshire, UK[6]	-	1.82	59.45	56.6	6575	-	27.01	16	235
Grand Union Canal - S. of Milton Keynes, UK[6]	-	< 1	38	56.6	-	-	30.25	49	202
Canal near Milton Keynes, UK[7]	7.6 (1.0)	1.14 (0.50)	31.5 (2.8)	20.6 (1.8)	20953 (1707)	-	48.4 (11.5)	43.2 (0.9)	139 (17)
Caland Canal, The Netherlands[8]	-	0.6 - 1.8	-	20.0 - 40.0	-	-	9.0 - 20.0	40 - 60	120 - 190
Begej Canal, Romania[9]	-	0.88 - 66	< 1 - 800	42 - 940	2300 - 31000	190 - 790	40 - 100	28 - 680	100 - 1770
Great Backi Canal, Serbia[10]	63.9	-	1335	-	-	-	-	-	-
Indiana Harbour Canal, USA[11]	18	4.2	210	75	18000	850	-	860	820
Jamshoro districts canals, Sindh, Pakistan[12]	13.0 - 19.5	-	-	-	-	-	-	-	-

[a] all values in mg/kg

[b] values in parenthesis refer to standard deviation (± mg/kg), where available

Table 5.4 Pseudototal (PT) or total (T) content results obtained from various studies on sediments from freshwater systems around the world [a, b]

Method	Location	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
PT	Mai Po estuary, Hong Kong[13]	1.1 - 1.4	20 - 74.6	51.1 - 87.4	385 - 3328	-	43.9 - 86.9	68.7 - 220	130 - 308
PT	Carska Bara wetlands, Serbia[14]	50.9 (3.4)	615 (60)	590 (25)	-	-	698 (33)	2080 (53)	1370 (110)
PT	Barcelona Harbour, Spain[15]	0.43 (0.01) - 2.76 (0.07)	38.8 - 110 (21)	70.6 (0.1) - 531 (2)	224000 (600) - 297000 (50)	255 (1) - 472 (3)	18.3 (1.0) - 34.3 (0.1)	123 (3) - 589 (3)	183 (1) - 1133 (3)
PT	Akyatan Lagoon, Turkey[16]	-	54 - 102	-	-	-	-	-	-
T	U-Tapao Canal, Songkhla, Thailand[17]	-	-	12.4 - 28.2	25.2 - 42.0	0.2 - 0.5	-	16.7 - 43.1	48.6 - 123
T	Suez Canal, Egypt[18]	1.45 - 3.06	28.1 - 104	-	4550 - 5695	485 - 245	14.2 - 54.2	20.3 - 95.3	20.7 - 176
T	Grand Canal, Hangzhou - Beijing, China[19]	3.5	103	196	-	-	-	133	1257
T	River Asopos estuary in S. Evoikos Gulf, Greece[20]	0.095 - 0.652	247 - 404	11.4 - 43	1.93% - 5.23%	331 - 552	246 - 698	7.29 - 36.7	39.5 - 129

[a] all values in mg/kg, except where noted otherwise

[b] values in parenthesis refer to standard deviation (± mg/kg), where available

With reference to Table 5.3, the Woolston Canal studies[4-5] show that the sediment contained high quantities of PTEs that are generally associated with direct anthropogenic input, such as As, Cd, Cr and Ni, as well as general urban pollutants such as Cu, Pb and Zn. It is important to note that this is a derelict canal – the only one amongst the canals listed in the table. Therefore, it is likely that it is not dredged and continues to receive surface soil runoff. It may also be prone to sporadic input from illicit discharges.

The Shropshire Union Canal, the Grand Union Canal, as well as the unnamed canal near Milton Keynes (which is likely to be the Grand Union Canal) are British canals that are open to the general public for use by pleasure craft. With the exception of Fe, the levels of all determined PTEs are low. The areas through which most of these canals pass are rural. This may have an effect on the detected levels since the anthropogenic impact would be relatively low. Unfortunately, nothing is known about the periodicity of sediment dredging to ensure navigability, however, if and when this occurs, this may also have an influence on the levels determined.

The Caland Canal[8] also has low PTE levels. The study on the Begej Canal[9] revealed considerable variation between levels of all PTEs. This canal passes through urban and rural areas. Soil runoff appears to be a main source of PTEs, particularly along urban stretches. However, levels of certain PTEs appear to be augmented by point sources at specific sites.

The study on the Great Backi Canal[10] reveals that there exist sources of As and especially of Cr since the levels are substantially high. The Indiana Harbour Canal study[11] points to the presence of a Cr source too. The presence of high levels of Fe and elevated quantities of Pb and Zn indicates that the surrounding soil, which is contributing to the sediment from runoff, is widely contaminated with these latter elements. Arsenic levels in the Jamshoro districts canals[12] indicate a generic presence of this PTE.

With reference to Table 5.4, none of the PTEs had PT content which indicated significant anthropogenic influence in the estuary[13] study. In contrast, the wetlands[14] study area appears to be a catchment for contaminated land. The levels of Cd are much higher than natural background levels, which are typically around the

1 – 2 mg/kg. All the other listed studies had Cd levels which were more than 10-fold lower. Levels of Cr and Ni, which are generally associated with anthropogenic sources, were also high. This implies the presence of different point sources. Levels of the general urban pollutants Cu, Pb and Zn were high too; an indication that the surrounding urbanized area is widely contaminated.

Sediment in a harbour area may have a long residence time due to the location being sheltered, leading to a comparatively increased exposure contact time. The high PTE content of Cu, Pb and Zn seen in the harbour study[15] may be attributed to this. Levels of Fe and Mn are characteristically high, but more importantly, there appears to be a point source for Cr. This was implied about the Turkish lagoon study[16] too.

The total content of PTEs in sediments of the U-Tapao[17] and Suez[18] canals were considerably lower than the PT content in other canals listed in Table 5.3. Levels of PTEs measured in the Grand Canal[19] showed elevated levels of Cu, Pb and Zn. A point source of Cr may be present, but not of Cd. The Greek estuary[20] study has shown the greater presence of anthropogenic elements such as Cr and Ni, denoting the presence of point sources. Interestingly, levels of Cu, Pb and Zn were low; hence, the observed results may be a result of limited but specific industrial activity.

5.1.2 Environmental Quality Standards for Potentially Toxic Elements

Specific concentration limit values of PTEs in the environment are laid down in legislation for the protection of ecosystems and ultimately human health.

A PTE is able to exert its toxic effects only when it is in a bioavailable form to living organisms. The reason why, so far, there are no legislated EQS values for sediments in the UK or the EU, but only guideline values, lies in the fact that PTEs in sediment are not directly bioavailable *in situ*. However, there exist EQS values for waters – a landmark of which is the EU Water Framework Directive (WFD)[21] – since aqueous PTEs may travel long distances with water and are in a form that may be easy to take up by an organism.

The WFD recognises the fact that sediment is a sink of various substances and, should environmental conditions change *in situ*, becomes a potential source of

PTEs in the aquatic environment. Its Daughter Directive, 2008/105/EC[22], called for Member States to establish EQS values for sediment (and/or biota) at national level.

Different countries around the world have established a set of sediment EQS values for their own use. In the UK, the Centre for Environment, Fisheries and Aquaculture Science (CEFAS), which is an executive agency of the Department for Environment, Food and Rural Affairs (DEFRA), is responsible for issuing sediment EQS values. There are two Action Level (AL) categories, and these are used as part of a wider assessment process into how to dispose of dredge sediment. These values are not legally binding but only guidelines, and CEFAS is tasked with revising them to reflect latest environmental data. Original and recently revised (2004) guideline EQS values available for PTEs are listed in Table 5.5[23]. Values refer to PT metal content.

Table 5.5 Pre-2004 and post-2004 Guideline Action Level values established by CEFAS for potentially toxic elements (PTEs) in sediments[23]

PTE	Action Level 1 (pre-2004) mg/kg	Action Level 2 (pre-2004) mg/kg	Action Level 1 (post-2004) mg/kg	Action Level 2 (post-2004) mg/kg
As	20	50 – 100	20	70
Cd	0.4	2	0.4	4
Cr	40	400	50	370
Cu	40	400	30	300
Ni	20	200	30	150
Pb	50	500	50	400
Zn	130	800	130	600

All values refer to dry weight

With respect to the individual parameters, where concentration is below AL 1, the sediment is generally considered safe for disposal at sea. Conversely, when concentration is above AL 2, the dredged material is considered unsuitable for disposal at sea. Whenever concentration falls between AL 1 and 2, further testing is typically carried out and a final decision is reached based also on other considerations.

The EQS values for AL 1 were derived from typical background sediment levels, whereas values for AL 2 were based largely on ecotoxicological data obtained from the USA[23]. The existing EQS values were revised in 2004 in line with more recent ecotoxicological data derived from peer reviewed literature. The changes included a reduction in values for copper, and an increase in the value for chromium and nickel for AL 1.

In general, sediment *in situ* is left undisturbed unless otherwise necessary to remove obstructions to navigation. Whenever sediment is dredged, the responsible authority follows a defined protocol to dispose of the sediment in the best possible manner.

5.2 Aim

The aim of the work presented in this chapter was to determine the PT content of 10 PTEs; As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn, in the canal sediments.

5.3 Experimental

5.3.1 Equipment

i. 4-digit weighing balance [AE200, Mettler, Leicester, UK]
ii. Microwave with associated high pressure vessels [MARSXpress™ High-Throughput Microwave Reaction System, CEM Microwave Technology Ltd., Buckingham, UK]
iii. Filter paper [Fisherbrand QL 100 (cellulose, 110 mm), Fisher Scientific UK Ltd., Loughborough, UK]
iv. Inductively Coupled Plasma – Mass Spectrometer [7700x Series ICP-MS, Agilent Technologies UK Ltd., Wokingham, UK], complete with auto-sampler [ASX-500 series ICP-MS auto-sampler, Agilent Technologies UK Ltd., Wokingham, UK]

5.3.2 Reagents

i. Hydrochloric Acid
(30% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

ii. Nitric Acid
(65% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

iii. Standard Solutions for ICP-MS: Multi-Element Calibration Standard 2A, containing: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn.
(10 mg/l, matrix 5% HNO_3, Crawford Scientific™ Ltd., Strathaven, UK)

iv. Standard Solutions for ICP-MS: Multi-Element Calibration Standard 3, containing: Au, Hf, Ir, Pd, Pt, Rh, Ru, Te, Sn.
(10 mg/l matrix, 10% HCl / 1% HNO_3, Crawford Scientific™ Ltd., Strathaven, UK)

v. *Basic Rinse* for ICP-MS: the stock solution is composed of a mixture of:
2.5 g EDTA, acid form
(Sigma-Aldrich® Company Ltd., Dorset, UK)
0.2 g Triton™ X-100
(Sigma-Aldrich® Company Ltd., Dorset, UK)
15 g ammonium hydroxide
(Sigma-Aldrich® Company Ltd., Dorset, UK)
20 g hydrogen peroxide
(Sigma-Aldrich® Company Ltd., Dorset, UK)
This is made up to 250 ml with deionised water and kept refrigerated. A 1:10 dilution is prepared to serve as the actual *basic rinse* solution.

5.3.3 Analytical Method

Sample digestion and analysis was carried out in triplicate for all determinations. The blank was treated similarly to the sample solutions, but without addition of any sediment. This procedure was applied to all initial 31 samples as well as sample 25R. Samples 3 and 5, which were the gastropods, were treated similarly to the sediment samples.

5.3.3.1 Sample Digestion

Aqua Regia Digestion

Using the cone and quarter technique, about 1 g of oven dried (at 30 ºC) sediment was accurately weighed and placed in a clean high pressure microwave vessel followed by 20 ml of *aqua regia* (prepared as 3 HCl : 1 HNO_3). This was left for 24 hours in a fume hood to allow for any vigorous reaction to take place, after capping loosely with the vent plug to allow CO_2 to escape, but avoiding airborne dust from depositing in the vessel.

Microwave-Assisted Digestion

After the 24 hour period, the screw cap was tightly secured and the microwave vessel was fitted in the microwave's carousel. The carousel could hold up to 40 high pressure vessels per run; each location in the carousel had an assigned number for identification. The respective position of every vessel was noted, and the carousel was placed in the MARSXpress™ microwave. As per manufacturer's requirements, a minimum of six vessels had to be placed in the carousel at any one time for operation; 'dummy' samples were occasionally included when the number of sample replicates and blanks was less than six. Vessels were positioned symmetrically in the carousel to distribute the heat absorbance capacity.

The appropriate program was input and stored in the microwave for future use. The typical settings used are outlined in Table 5.6[24].

Table 5.6 Microwave digestion program settings[24]

Microwave Parameter	Condition
Power	1600 W [a]
% Power	100
Temperature ramp time	10 minutes
Temperature control	160 ºC
Hold time	20 minutes

[a] Power reduced to 800 W for 6 – 11 vessels or 1200 W for 12 – 17 vessels

After completion of the 30 minute run, the microwave automatically proceeded to a cooling period. The carousel was then removed and placed on a bench

top and each vessel was removed and placed in a fume cupboard for 24 hours to allow cooling to room temperature. Once cool, each vessel was opened with care, in the fume cupboard, and with the top facing away from the analyst in case any *aqua regia* spurted upon opening due to some residual vapour pressure. The contents of each vessel were filtered through a fluted filter paper and collected in a 100 ml volumetric flask. The vessel was washed several times with deionised water and the contents passed through the filter and collected in the same flask and made up to the mark to produce a 20% *aqua regia* solution. One ml from this solution was taken and diluted 10-fold with deionised water to give a 10 ml, 2%, *aqua regia* solution. This was stored at 4 ºC until taken for analysis by ICP-MS.

5.3.3.2 Potentially Toxic Element Determination using Inductively Coupled Plasma Mass Spectrometry

Preparation of Standards

A set of mixed standard solutions with concentrations 10, 100, 200 and 400 µg/l were prepared from the respective 10 mg/l multi-element commercial standards. Standard solutions were prepared in 2% *aqua regia* to reagent match the sample digests. A blank solution of 2% *aqua regia* was also prepared to use as the 0 µg/l 'standard'.

Operating Conditions

The concentrations of the most abundant isotopes of the 10 elements of interest were determined in each standard, sample replicate and blank, with the ICP-MS. These were ^{75}As, ^{111}Cd, ^{114}Cd, ^{52}Cr, ^{53}Cr, ^{63}Cu, ^{65}Cu, ^{56}Fe, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{118}Sn, ^{64}Zn, and ^{66}Zn. Indium (^{115}In) was used as an internal standard. The instrument operating conditions are listed in Table 5.7.

Table 5.7 Agilent 7700x inductively coupled plasma mass spectrometry (ICP-MS) operating conditions

ICP-MS Parameters	Condition
RF Power	1600 W
Carrier Gas (Argon)	0.59 l/min
Dilution Mode (HMI [a])	ON: Ultra Robust – Level: Low
Makeup Gas (Argon)	0.34 l/min
MicroMist Nebulizer Pump	0.1 rps [b] (≡ 333 ml/min)
Collision Mode	OFF [c] / ON [d] @ 4.3 ml/min He

[a] HMI = High Matrix Interface; [b] rps = revolution per second, where rps = ml/min x 0.0003; [c] Collision Mode was OFF for As, Cr, Cu, Fe, Mn, Ni, and Zn; [d] Collision Mode was ON for Cd, Pb, and Sn

Measurement

Measurement using ICP-MS followed a set sequence using an auto-sampler. Five replicate readings were taken for every measurement of standard, sample or blank.

The auto-sampler probe was set to perform a wash protocol as advised by the manufacturer, prior to aspirating any of the test solutions. The probe, from rest position, went into pot 1, containing the *basic rinse*, then into pot 2, containing 2% HNO_3, and finally into pot 3, containing a blank solution of the samples reagent (2% *aqua regia* in the case of PT PTE determination), before proceeding to a test vial in the rack. This was necessary to ensure thorough cleaning of the tubing, thus avoiding memory effects.

The analysis sequence was as follows:

- Standards' blank – which served as an initial washing solution
- The same standards' blank – which served as the 0 µg/l 'standard'
- Standard solutions in ascending order: 10, 100, 200, 400 µg/l
- Check standard; 100 µg/l
- Samples' blank
- Sample solutions

After every 9 sample solutions, which correspond to 3 test portions of 3 samples each, the check standard was re-run, followed by the samples' blank. The

purpose of the check standard was to monitor for any instrumental drift, while the blank which followed was run to extend the washing program and avoid memory effects on the next test sample that followed in the sequence. Wherever the drift was observed to exceed ± 10% of the concentration of the check standard, the sequence was halted and a fresh calibration was run, after which the sequence was continued at the point of the first test sample after the last known acceptable test standard run.

Other standards of higher concentration were inserted into the sequence as necessary to ensure sample solutions always fell within the calibration range.

5.4 Results and Discussion

5.4.1 Limits of Detection

The LOD is a measure of the minimum amount of an analyte that can typically be determined analytically with over 95% confidence limit. For determination of an instrument's LOD, it is generally accepted that the detected signal must be at least three times greater than the instrument's background noise levels for it to be attributed with certainty to the analyte. This noise level can be determined by measuring the blank for a particular analyte, and the LOD is generally calculated by multiplying the positive standard deviation (SD) value obtained from 10 readings of the blank by three, and dividing the sum obtained by the gradient from a calibration curve obtained using standard solutions of varying concentrations of the analyte of interest, as shown in Equation 5.1.

Equation 5.1 The equation for calculation of the instrumental limit of detection of an analyte

$$LOD = \frac{3(SD)}{m}$$

where:

SD is the standard deviation

m is the gradient of the calibration curve

Since the level of background noise is dependent on instrumental conditions as well as the sample matrix, the instrumental LODs of every analyte should be determined prior to every analysis.

Since analysis on the ICP-MS was carried out on various instances during the course of this work, various LODs have been obtained. However, these were found to be always similar when the blank was uncontaminated and the instrument worked optimally. A set of typical LODs given by the ICP-MS instrument are listed in Table 5.8.

Table 5.8 A set of instrumental limits of detection (µg/l) obtained for the isotopes of the potentially toxic elements (PTEs) determined using inductively coupled plasma mass spectrometry

PTE Isotope	Limit of Detection (µg/l)
^{75}As	0.0555
^{111}Cd	0.0207
^{114}Cd	0.0350
^{52}Cr	0.109
^{53}Cr	0.140
^{63}Cu	0.662
^{65}Cu	0.350
^{56}Fe	1.17
^{57}Fe	3.43
^{55}Mn	0.245
^{60}Ni	0.148
^{206}Pb	0.216
^{207}Pb	0.275
^{208}Pb	0.153
^{118}Sn	0.287
^{64}Zn	0.548
^{66}Zn	0.976

Matrix: 2% a*qua regia*

The instrumental LODs are not the same for the different elements and their isotopes. The LOD is relative to the instrument's sensitivity towards the element. The presence of the element in the blank will result in an increased LOD. Instrumental LODs were used to calculate procedural LOD values. These are listed in Table 5.9.

Table 5.9 A set of procedural limits of detection (LODs, μg/kg) for determination of potentially toxic elements (PTEs) in sediment, calculated from the instrumental LODs listed in Table 5.8

PTE	Limit of Detection (μg/kg)
As	1.11
Cd	0.557
Cr	2.49
Cu	10.1
Fe	46.0
Mn	4.9
Ni	2.96
Pb	4.29
Sn	5.74
Zn	15.2

These procedural LODs are the actual PTE concentrations that could be detected in sediment samples with the digestion method used.

5.4.2 Quality Control

The performance of the method was assessed using a certified reference material (CRM); BCR®-143R – Sewage Sludge Amended Soil[25]. This CRM is marketed by the Institute for Reference Materials and Measurements (IRMM), which is one of the seven institutes of the Joint Research Centre (JRC) of the EC. Analysis was carried out in triplicate and the concentrations of PTEs obtained are listed in Table 5.10, together with reference values and percentage recovery.

Table 5.10 Concentration (mg/kg), standard deviation (SD, ± mg/kg), relative SD (% RSD), and calculated % recovery of PTEs with respect to BCR®-143R certified values[25], for pseudototal content determination

PTE	Notation	BCR®-143R		Found Value [a]			% Recovery
		mg/kg	± mg/kg	mg/kg	± mg/kg	% RSD	
Cd	CV	72	1.8	78.8	3.6	4.57	109
Cr	CV	426	12	488	26	5.33	115
Cu	IV	128	7	134	7	5.22	105
Fe	AMI	19580	-	28300	1170	4.13	144
Mn	CV	858	11	979	45	4.60	114
Ni	CV	296	4	314	14	4.46	106
Pb	CV	174	5	193	8	4.15	111
Zn	CV	1063	16	1090	43	3.94	103

The notations, which were taken from the material's certificate, are defined as follows:

CV = Certified Value, IV = Indicative Value, AMI = Additional Material Information

[a] Results represent mean ± 1 SD, n=3

% Recovery values calculated from results and exclude SD values

The percentage recoveries of Cd, Cr, Mn, Ni, Pb and Zn were within +15% of the certified values. The % relative SD (RSD) of each of these six elements from the three replicate samples average 5%, signifying satisfactory precision. The given value for Cu was indicative rather than certified. Nonetheless, the result obtained was less than 5% higher than the given value. The only exception was Fe, where the amount recovered was nearly one and a half times the listed quantity. However, in the certificate, the amount of Fe was not even an indicative value, but only additional information. It may therefore be subject to considerable uncertainty.

5.4.3 Gastropods

The respective PTE PT concentrations (mg/kg) and SD (± mg/kg) determined in the gastropods at sites 3 and 5 are represented in Figure 5.1. The actual data values are listed in Table A.1 and Table A.2 in the Appendix.

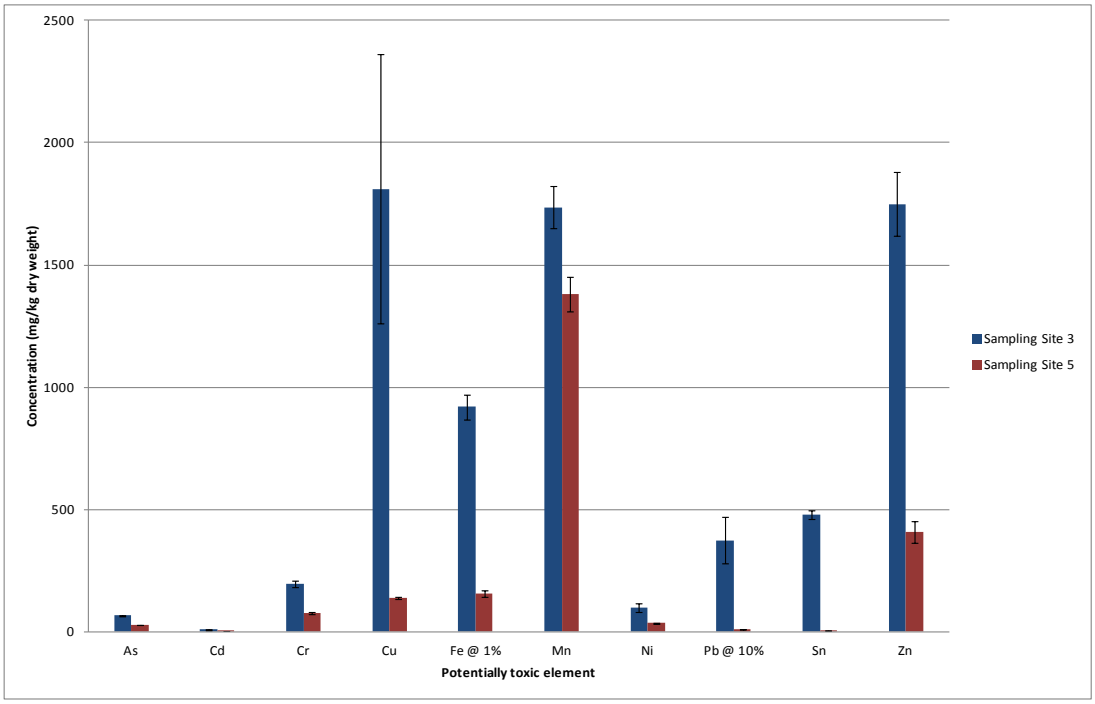

Figure 5.1 Respective potentially toxic element concentrations in gastropods from site 3 and 5 in the Forth and Clyde Canal (Error bars represent mean ± 1 standard deviation, n=3)

It is evident that PTE levels in the gastropods collected at site 3 are much higher than those determined in gastropods from site 5, even though they were only around 150 m apart. While site 5 is in the canal and hence in a passage way, site 3 is in the basin. Both sites are separated by the Bowling Basin lock (lock 38). The canal is at an elevated level at site 5, inhibiting possible movement of gastropods from site 3 to site 5. The number of vessels at site 3 is by far greater than at site 5 – as is their residence time. It appears that gastropods at site 3 are substantially exposed to PTEs from anthropogenic sources, and this is likely to have led to bioaccumulation. Nevertheless, these gastropods appear to be able to tolerate these PTE levels since they are of waterborne origin and were found live at the time of sampling.

5.4.4 Sediments

The PTE PT concentration (mg/kg) and SD (± mg/kg) results obtained in all sediment samples (except 25R) are represented in Figure 5.2 to Figure 5.11. The revised (2004) CEFAS Guideline ALs 1 and 2 are superimposed on these figures in the form of transverse lines, where available. There exist no ALs for Fe, Mn and Sn. The actual data values are listed in Table A.3 and Table A.4 in the Appendix.

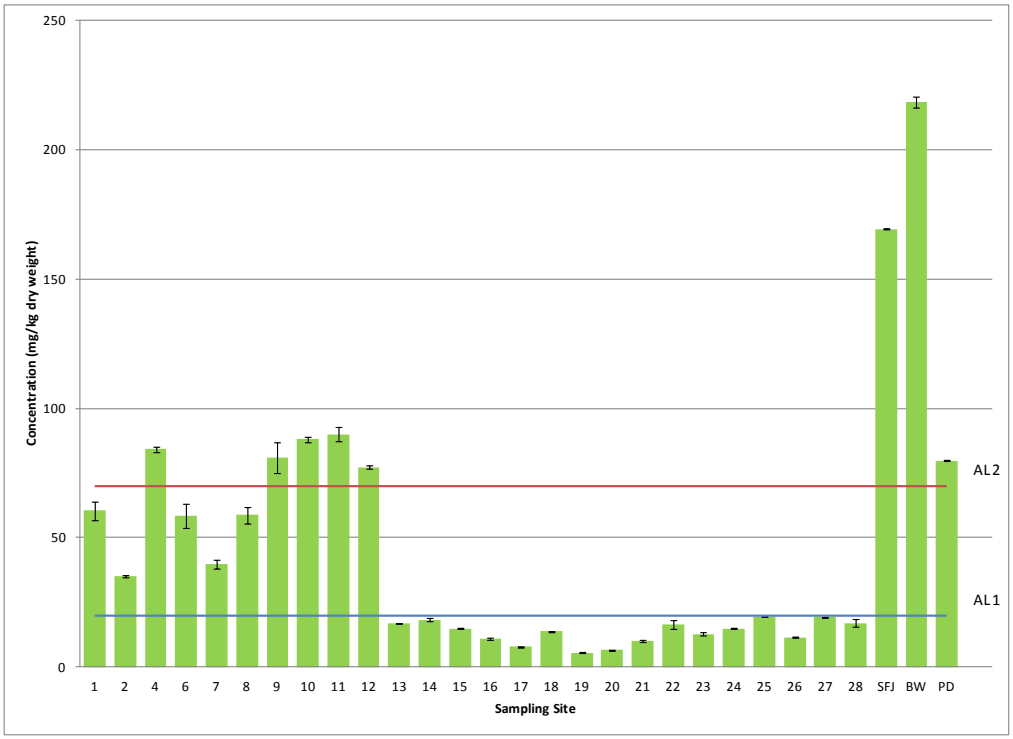

Figure 5.2 Arsenic pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch with superimposed CEFAS's Revised (2004) Guideline Action Levels[23] (Error bars represent mean ± 1 standard deviation, n=3)

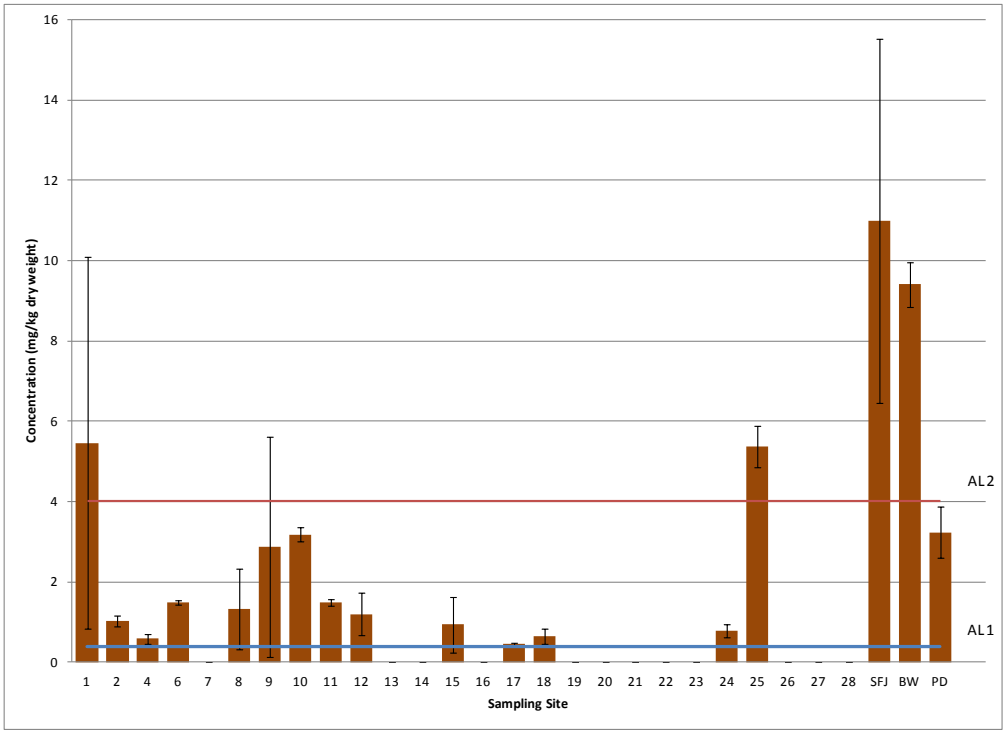

Figure 5.3 Cadmium pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch with superimposed CEFAS's Revised (2004) Guideline Action Levels[23] (Error bars represent mean ± 1 standard deviation, n=3)

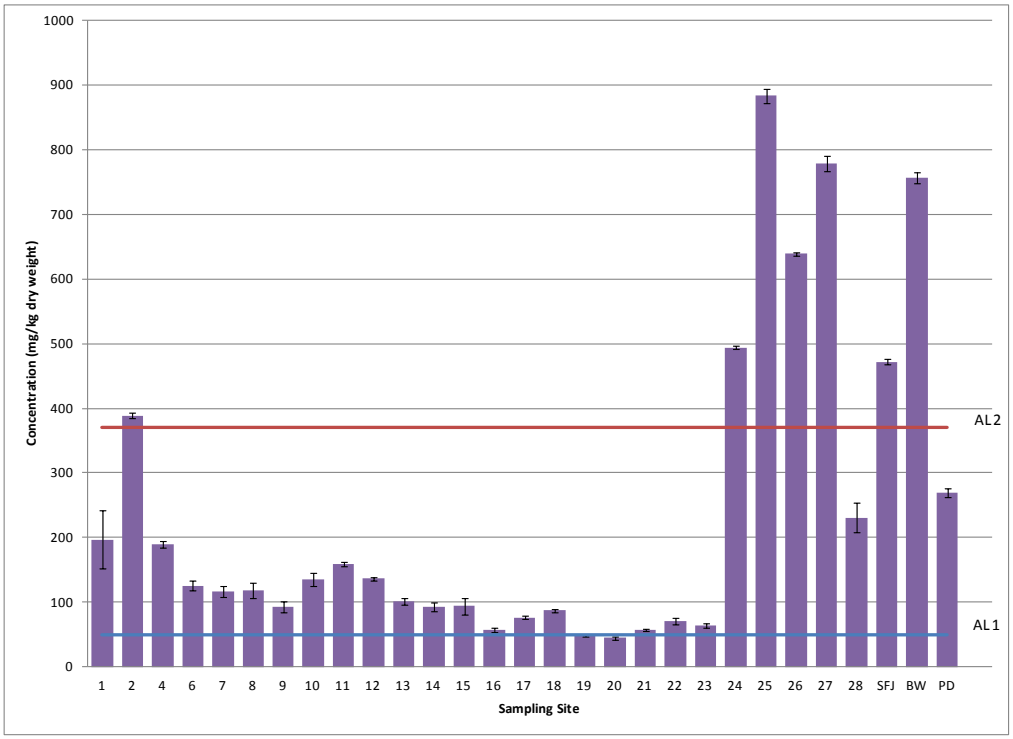

Figure 5.4 Chromium pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch with superimposed CEFAS's Revised (2004) Guideline Action Levels[23] (Error bars represent mean ± 1 standard deviation, n=3)

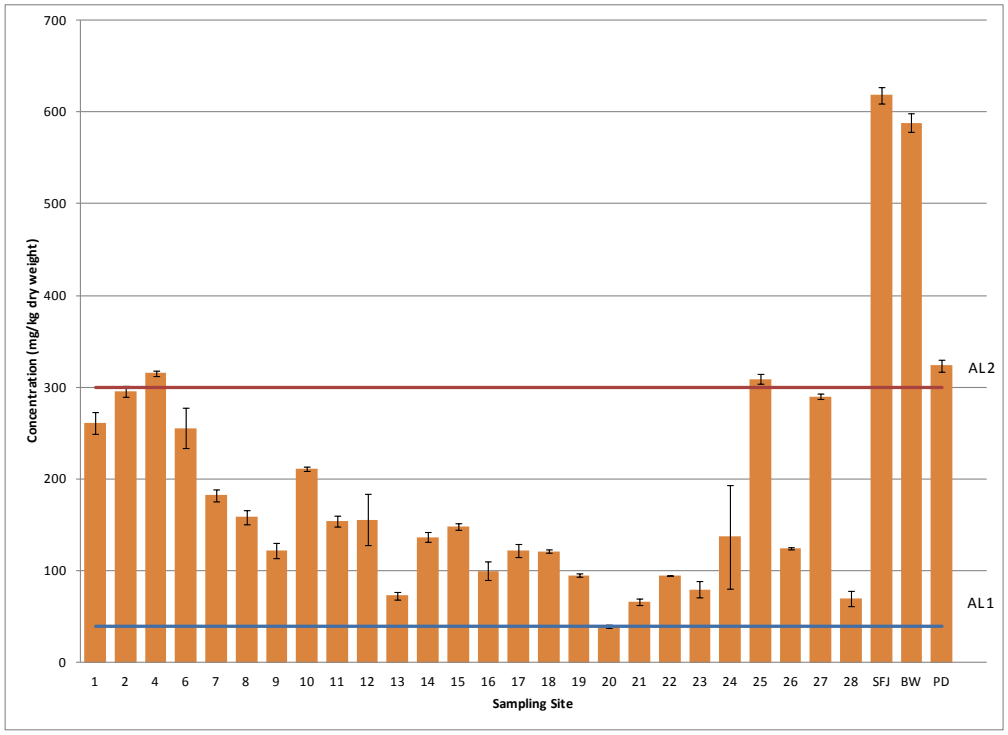

Figure 5.5 Copper pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch with superimposed CEFAS's Revised (2004) Guideline Action Levels[23] (Error bars represent mean ± 1 standard deviation, n=3)

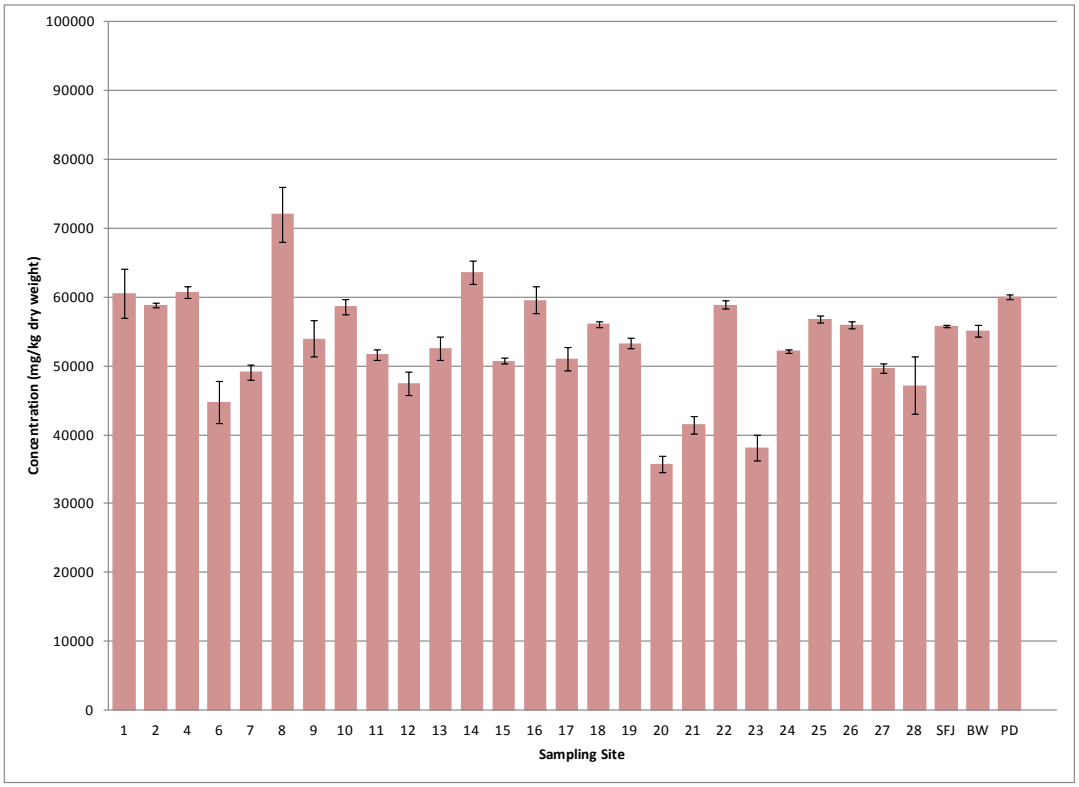

Figure 5.6 Iron pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

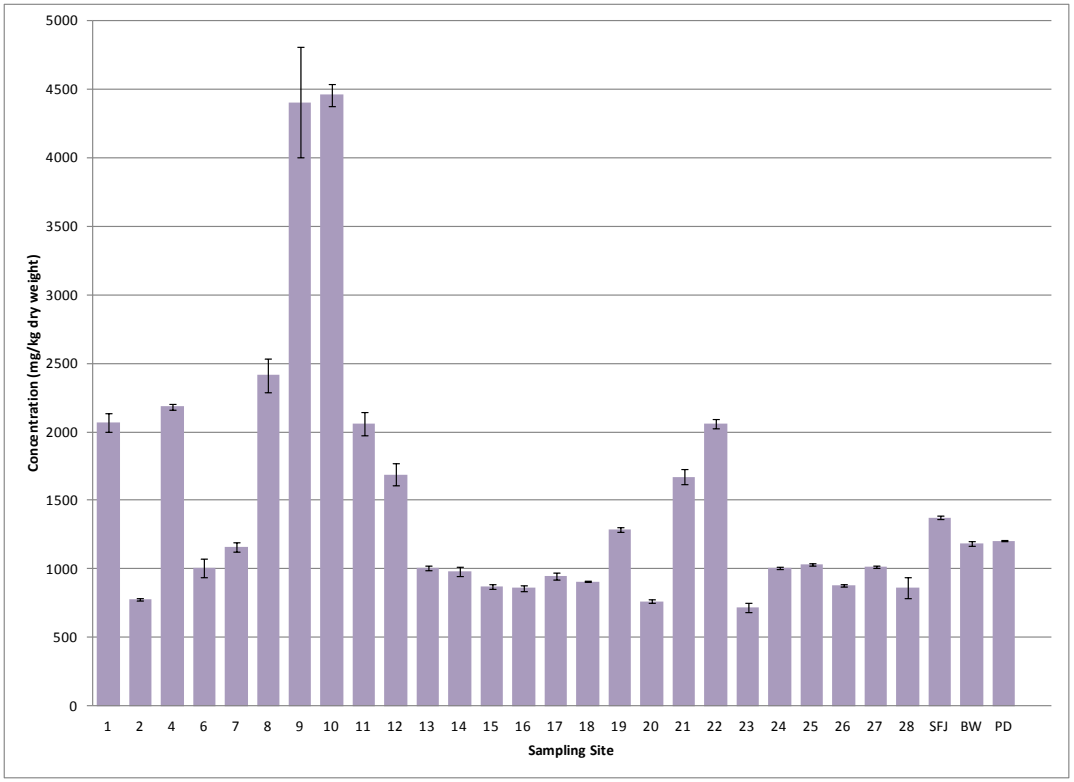

Figure 5.7 Manganese pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

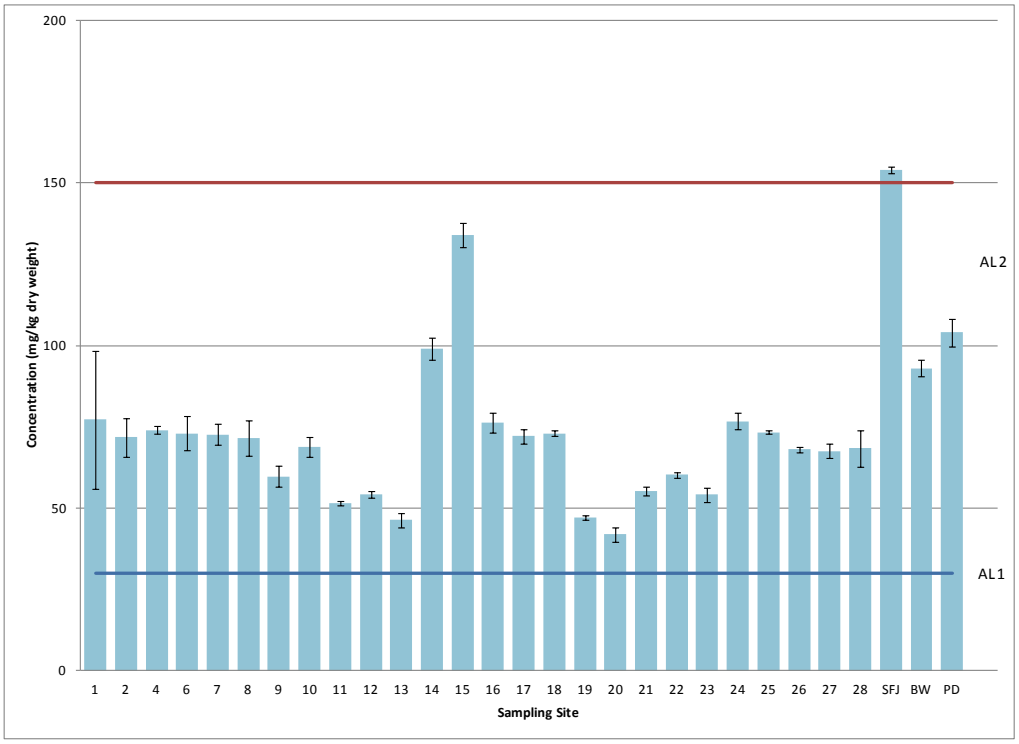

Figure 5.8 Nickel pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch with superimposed CEFAS's Revised (2004) Guideline Action Levels[23] (Error bars represent mean ± 1 standard deviation, n=3)

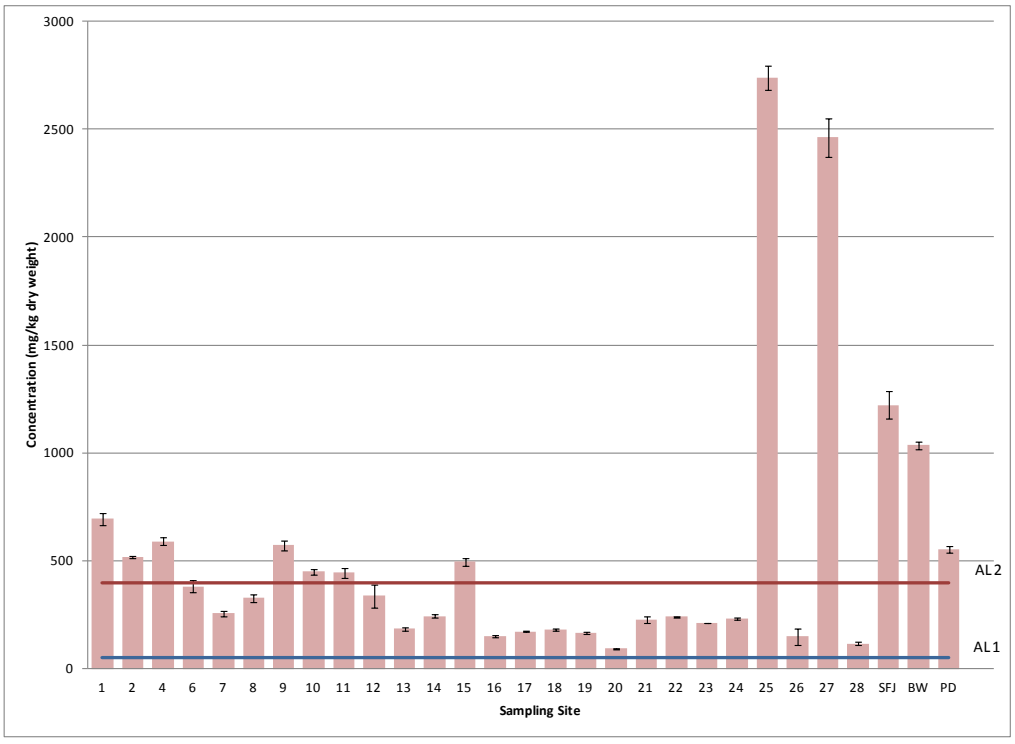

Figure 5.9 Lead pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch with superimposed CEFAS's Revised (2004) Guideline Action Levels[23] (Error bars represent mean ± 1 standard deviation, n=3)

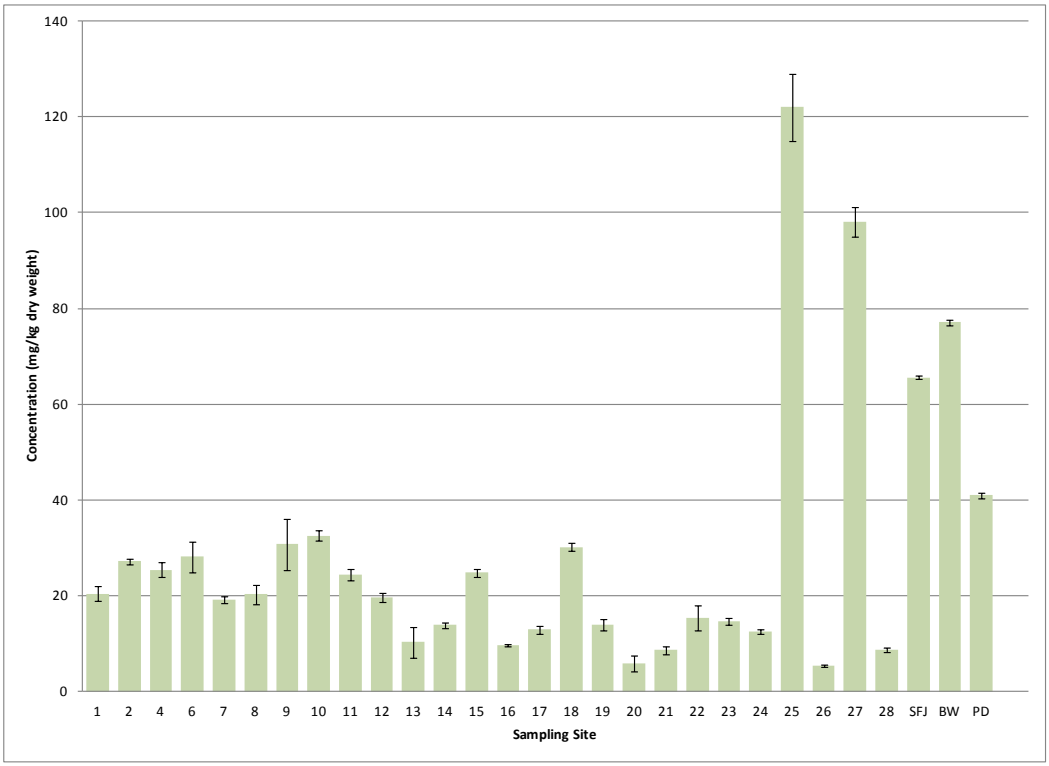

Figure 5.10 Tin pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

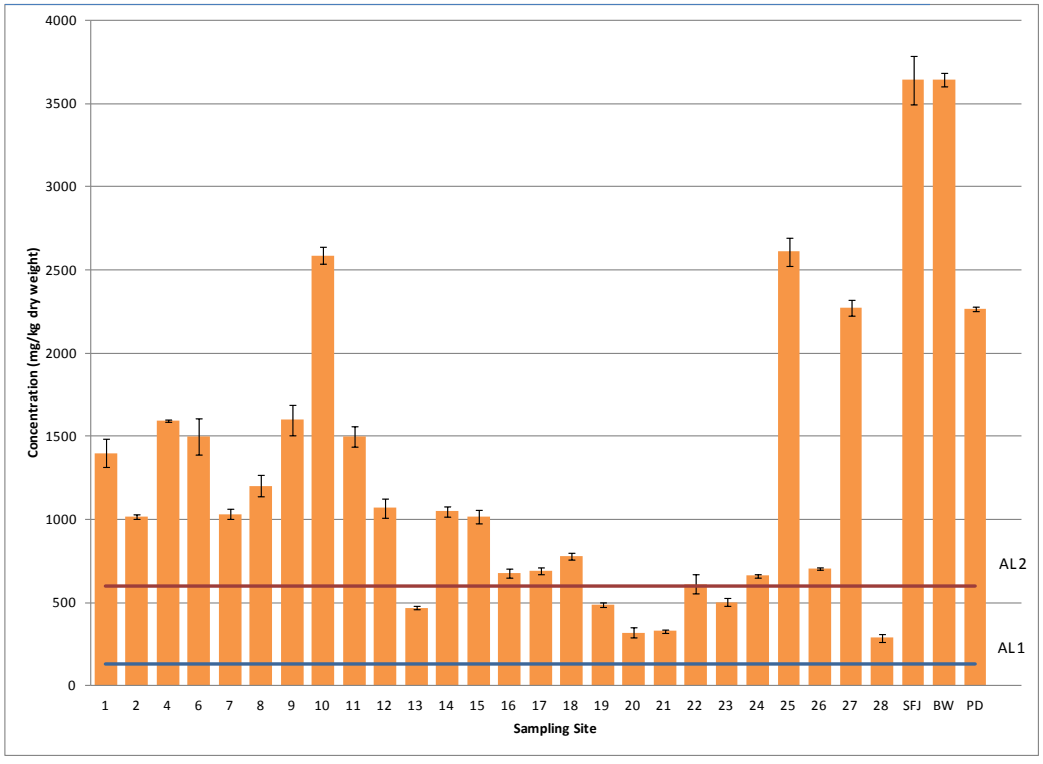

Figure 5.11 Zinc pseudototal concentration in sediment from the Forth and Clyde Canal and Glasgow Branch with superimposed CEFAS's Revised (2004) Guideline Action Levels[23] (Error bars represent mean ± 1 standard deviation, n=3)

A site by site comparison of the observed PTE concentrations may not necessarily be solely a reflection of the PTE input at the respective sites. This is because of the variation in the retention capability of the sediment, which is dependent on the sediment's composition, particularly the organic matter content. Therefore, the PT content data should be normalised first. One way of doing this is to divide each PTE's PT concentration by the organic matter content determined in the respective samples (see Table 4.1). These ratios are given in Table 5.11; Cd has been omitted due to the very low levels determined.

Table 5.11 Ratio of PTE PT concentration with respect to the organic matter content in each sediment sample

Sampling Site	As	Cr	Cu	Fe	Mn	Ni	Pb	Sn	Zn
1	2.47	8.05	10.7	2470	84.4	3.15	28.3	0.836	57.1
2	2.14	23.7	18.0	3590	47.3	4.38	31.6	1.66	62.0
4	3.39	7.66	12.7	2450	88.1	2.99	23.8	1.03	64.3
6	2.88	6.19	12.6	2530	49.8	3.60	18.8	1.39	73.9
7	4.19	12.3	19.2	5180	122	7.66	27.1	2.02	109
8	5.19	10.5	14.0	6378	214	6.34	29.0	1.79	106
9	4.78	5.53	7.22	3190	261	3.54	33.9	1.82	94.6
10	3.11	4.77	7.45	2070	157	2.43	15.9	1.15	91.4
11	5.59	9.90	9.57	3210	128	3.20	27.7	1.51	93.1
12	3.47	6.12	6.99	2130	75.8	2.43	15.1	0.881	47.9
13	0.882	5.28	3.84	2750	52.8	2.42	9.69	0.539	24.6
14	0.971	4.94	7.28	3380	52.2	5.27	13.0	0.740	55.7
15	0.595	3.75	5.92	2020	34.8	5.34	19.7	0.988	40.5
16	0.591	3.14	5.46	3250	47.0	4.16	8.30	0.535	37.0
17	0.315	3.11	4.95	2070	38.5	2.92	6.99	0.523	28.0
18	0.702	4.48	6.21	2880	46.5	3.74	9.41	1.55	39.9
19	0.207	1.82	3.56	2000	48.2	1.76	6.28	0.524	18.2
20	0.372	2.56	2.25	2050	43.8	2.40	5.37	0.331	18.2
21	0.412	2.34	2.72	1920	68.6	2.26	9.29	0.354	13.5
22	0.596	2.56	3.44	2130	74.5	2.18	8.73	0.556	22.2
23	0.936	4.69	5.79	3180	52.6	3.95	15.5	1.07	36.7
24	0.963	31.9	8.86	3370	65.2	4.94	15.1	0.813	42.6
25	0.849	38.4	13.4	2470	44.6	3.19	119	5.29	113
26	0.780	43.2	8.41	3780	59.5	4.60	10.1	0.362	47.5
27	0.929	37.6	14.0	2670	49.2	3.27	119	4.74	110
28	1.46	19.9	6.03	4220	74.7	5.90	10.2	0.746	24.8
SFJ	7.30	20.3	26.6	2400	59.2	6.64	52.7	2.83	157
BW	11.4	39.6	30.8	2890	62.1	4.87	54.3	4.03	191
PD	2.80	9.47	11.3	2110	42.3	3.65	19.4	1.44	79.6

Comparison of respective PTEs using these ratios gives a more appropriate representation of the relative levels between samples.

Arsenic

A mean level of 10 mg/kg As has been attributed to uncontaminated soils[26]. The presence of higher levels of As in the environment is attributed primarily to anthropogenic sources. Sites 1 – 12 and the Glasgow Branch are within an urban area and the levels of As determined were considerably higher than any site eastwards from site 13. The greatest amount of As was determined along the Glasgow Branch, which historically was a heavy industrialised area. All 13 urban sediment samples had concentrations above AL 1, eight of which were also above AL 2. Sites 13 to 28 of the Forth and Clyde Canal had sediment with a concentration of As that was below AL 1.

Fairly similar distribution ratios were obtained from the normalised values for the urban group and the rural group of the Forth and Clyde Canal sediments, with those of the urban group being higher. This signified that the low PT content determined in samples 2 and 7 was due to the sediment having relatively less OM content than the others and not because of limited input. The widespread distribution was likely aided by aerial emissions from stacks.

In contrast, the low levels determined in the rural samples are due to limited input. The urban/rural divide at sites 12/13 is prominent as the decrease in As concentration observed upon crossing the boundary from the urban area into the rural zone is marked. There appears to be limited input from the Falkirk Wheel Junction (site 25) and the sub-urban area at the east end of the canal (sites 26 – 28).

The normalised values have shown that high As content determined in the Glasgow Branch samples was due to high input, however, the perceived high As content in sample PD was mainly a result of the relatively higher OM content.

Cadmium

Natural occurrence of Cd in soil is typically < 1 mg/kg[26]. Where detected in higher levels, it is typically attributed to anthropogenic origin. Cadmium is commonly associated with Zn. Levels determined were low throughout the whole

stretch of canal, with many sites having concentrations below the limit of detection of the ICP-MS, with others just above it. This is reflected in the wide SD obtained from the replicates analysed in some of the samples. Nevertheless, wherever detected, Cd levels were above AL 1; this benchmark is set very low due to the element's high toxicity. Only three samples (25, SFJ, and BW) had concentrations which were clearly above AL 2.

Chromium

Chromium is commonly found in soils at a mean level of 100 mg/kg[26] and its commercial uses are typically associated with iron and tanning industries. All sites, except 19 and 20, had levels of Cr which were above AL 1. Seven sites had levels which surpassed AL 2.

The Cr concentration determined at site 2 was twice that observed at sites 1 and 4. This was coupled by the fact that sample 2 had comparatively less OM content than samples 1 and 4. Since site 2 was only 50 m away from site 1 and 125 m away from site 4, the higher result at site 2 seems to be caused by a very localised source. This could be attributed to the presence of a considerable number of moored boats, particularly near site 2 as compared with site 1 and 4, which may have Cr-based pigment in their paintwork.

The urban area samples (sites 6 – 12) appear to have slightly lower Cr levels than in Bowling Basin (excluding site 2) but slightly more Cr than the rural area samples (sites 13 – 23). Substantial contamination was observed in the Glasgow Branch. Historical maps show the presence of an iron works, chemical works, colour works, and a foundry in the vicinity of site SFJ, a tannery and a foundry near site BW, and a foundry and coal storage areas situated around Port Dundas. The tannery's existence is likely to be the major cause for the high levels of Cr still detected at site BW. Chromium is involved in all the other industries mentioned, and the level of contamination in the surrounding soil is likely to be proportional to the number of factories present in the respective areas. The direction of water flow at site BW is towards SFJ, and thus some sediment, particularly that in suspension after churning by passing vessels, may contribute to the higher Cr concentration detected at SFJ.

Substantially high results were obtained in the sub-urban area (sites 24 – 28) of the Forth and Clyde Canal. Historical data available revealed the presence of several acres of ironstone pits on the south bank of site 24. The presence of Cr in soils derived from ironstone is elevated[27]. Recent [Google Earth, 2009] aerial photography of that area showed patches of land that support no vegetation, suggesting that contamination is still present. Contaminated sediment may be transported downstream from site 24 towards site 25, however, the Cr levels here imply the presence of a localised source. This is possibly soil runoff from the south bank where the Lime Wharf Chemical Works once stood.

At site 26, the south bank was historically industrialised and was lined with alum works, Camelon Chemical Works, iron works and foundries, and in the vicinity, the Camelon Colliery with associated coal pits. The Falkirk Iron Works was spread over 2 hectares of land on the south bank of site 27. On the north bank were the Castlelaurie Iron Works, and adjacent to it the Castlelaurie Acid Works. Various other industries were situated in the vicinity along the canal, including Burbank Iron Foundry, Gowanbank Iron Foundry, and a chemical works.

Historical data for the area surrounding site 28 does not reveal the presence of any industries in the vicinity, possibly since this stretch was only constructed prior to the canal's reopening in 2001 – most industries were built along the canal banks as it served as a source of water, for transportation purposes, and for effluent discharge. The determined Cr concentration was fairly similar to that of site 1 and 4. However, upon taking into account the OM content, the normalised values denote a similarity with sample 2 since both these samples had low OM content. Similarly, vessels' paintwork could be a likely source due to this site's proximity to the canal terminal harbour. Some Cr may also be coming from contaminated sediment transported downstream.

Copper

Copper is found naturally in soils in levels typically 20 – 30 mg/kg[26] but is also a widespread general urban pollutant due to its various commercial uses. Five sites had Cu levels that surpassed AL 2, while the remaining 24 sites had levels between AL 1 and AL 2. Common sources of Cu include abrasion of copper particles

from high voltage electricity wires, corrosion from water network pipes, and through soil runoff, where Cu is a common fodder additive[2]. Copper is a main ingredient in modern antifouling paint.

Within the Bowling Basin samples, the normalised value of Cu in sample 2 was higher than that of sample 1 and 4, whereas its OM content was comparatively lower. This entailed the presence of a point source. Similarly as with Cr, this could be attributed to the presence of numerous moored boats near site 2, as compared with site 1 and 4.

An urban/rural divide at site 12/13 is evident from the normalised values, although some rural samples such as 14, 24 and 26 had a level of Cu input which was similar to that of some urban samples. The exceptionally high Cu levels determined in sample 25 and 27 may be attributed to a local point source.

The normalised values showed that high Cu content determined in the Glasgow Branch samples was due to high input, although similarly to As, the perceived high Cu level in sample PD was mainly a result of the relatively higher OM content.

Iron

The Fe concentration determined in all samples is by far the highest of all the elements measured since substantial amounts of Fe are found naturally in soil. Levels obtained do not show a divide between urban and rural zones, but rather a more or less equal distribution. This may be due to a counterbalance effect - urban soils contain more Fe but there is less soil runoff, whereas in rural areas, the Fe content is comparatively less but the runoff soil quantity is considerably greater. Various iron works, steel works and foundries lined the canal in urban areas, where it is likely that they have contaminated the surrounding soil with Fe too. It is likely that the amount of Fe of anthropogenic origin is proportionally far smaller than that of natural origin, and therefore, any such contribution is insignificant.

Manganese

The presence of Mn is also widespread in soil, with levels typically up to several thousand mg/kg[26]. However, quantities are far less than those of Fe. Within

Bowling Basin, the low levels of Mn determined at site 2 may be because of the relatively lower OM content, compared to samples 1 and 4. Sample 7 appears to have a similar load of Mn as the other urban samples (8 – 12), but the determined Mn content was lower due to a lower OM content. Input levels of Mn in the Glasgow Branch were lower than in the Forth and Clyde Canal urban samples.

The higher Mn content determined in sample 19 appears only to be a result of high OM content in the sample, and hence the input load is similar to the rural samples. Conversely, the peaks at site 21 and 22 seem to point to some localised input. The normalised value of sample 28 denotes that there is considerably higher input of Mn at this site, but this is not perceived due to the low OM content.

Nickel

The concentration of Ni appears fairly evenly distributed along the Forth and Clyde Canal. The equal distribution comes from the fact that the surrounding soil has a natural background level of Ni, which is typically around 40 mg/kg[26]. All samples had levels which were between AL 1 and AL 2, with the exception of site SFJ which was just slightly higher than the AL 2 benchmark.

Historical data shows the presence of a Nickel Works in the vicinity of site 15. It is likely that sediment originating near site 15 may have been transported downstream towards site 14. Further transportation downstream is not evidenced since Ni levels at site 13 were comparable to background.

The three Glasgow Branch samples are presumed to have Ni contribution from local sources. The heavy industrialisation of this area would have invariably included Ni. Nickel was commonly used in corrosion-resistant plating for iron works and as part of an alloy mixture in the production of steel. Nickel was commonly used to give a green tint in glass, and historical maps show the presence of numerous glass works near SFJ.

Lead

Natural levels of Pb are typically 10 – 30 μg/kg[26]. However, Pb is considered a general urban pollutant since its distribution due to anthropogenic sources, such as through the use of leaded petrol until a few years ago, has been widespread. In fact at

all sites, the levels determined where higher than AL 1. This is evidenced further by the observed urban/rural divide, where concentration levels of Pb in the urban segment (sites 1 – 12) appear to be roughly double the concentration of those sites in the rural segment of the canal (sites 13 – 28). Notable exceptions are site 15, 25 and 27. These three sites, together with nine others from the urban area, had concentrations above AL 2. Localised point sources contribute to the Pb input in these areas, as well as in the Glasgow Branch. Historical maps show the presence of industries in the vicinity of these sites, notably iron works and foundries, which appear to have contaminated the surrounding soil, as well as a lead works just opposite site SFJ. The use of red lead paint in iron works was common. The perceived high Pb level in sample PD was mainly a result of the relatively higher OM content.

Tin

The Sn results show a great similarity in distribution pattern to the Pb results, particularly where the latter is found at exceptionally high levels, such as at sites 25 and 27, as well as in the Glasgow Branch. Industrial uses of Sn include tin plating of iron or steel, as an alloy component of bronze, which is typically 12% Sn with a copper bulk, and as an alloy component of solder, typically 60/40 Sn/Pb.

A proportion of tin present may be from TBT-based antifouling paint. The historical presence is presumed to be minimal since the canal was closed for navigation in 1963, shortly after TBT-based paint was put on the market. This product is now completely banned from sale, however, some boat owners may still have old stocks and occasionally apply it, illegally. This may be a potential current source of TBT and its degradation products.

Zinc

Zinc is found naturally in soils, typically ranging between 10 and 300 mg/kg[26]. Like Cu, Zn has various commercial uses making it also a widespread general urban pollutant, commonly a result of corrosion of Zn-containing materials[2]. Both elements are commonly found associated together in industries. The Zn results show great resemblance with the distribution pattern of Cu, such as the peaks

observed at site 10 and the Glasgow Branch in the urban area, and sites 14, 15, 25 and 27 in the rural area, which are attributed to point sources.

The urban/rural divide at sites 12/13 is also evident, with levels in the rural area roughly half those in the urban area. Six sites had Zn levels between AL 1 and AL 2. All of the remaining 23 sites had concentrations that surpassed AL 2.

5.4.4.1 Pearson's Product-Moment Correlation Coefficient

This statistical test, developed by Karl Pearson, is a measure of the extent of correlation between two variables, expressed through a coefficient scale ranging from 1 to -1. A perfectly directly proportional relationship whereby both variables either increase or decrease together would give a value of 1. Conversely, a perfectly inversely proportional relationship whereby one variable increases as the other decreases, would give a value of -1. A value of 0 implies that there is no linear correlation whatsoever between the two variables.

In the current work, the test was used to determine whether there existed correlations between nine of the 10 elements analysed in the 29 sediment samples collected – Cd was left out because of the very low amounts detected throughout, making it unsuitable for any comparisons and correlations. The correlation coefficients obtained are given in Table 5.12.

Due to the observed general concentration difference between samples collected from urban areas and those collected from rural areas, the samples were then separated into two groups. The urban group consisted of samples 1, 2, 4, 6 – 12, 24 – 28, and the three samples from the Glasgow Branch. The rural group consisted of samples 13 – 23. The respective Pearson's correlation coefficients obtained for these two groups are given in Table 5.13.

Table 5.12 Pearson's correlation coefficients of the 29 sampling sites along the Forth and Clyde Canal and Glasgow Branch

	As	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Sn**	**Zn**
As		0.41	0.85	0.21	0.33	0.44	0.38	0.54	0.87
Cr			0.64	0.18	-0.18	0.32	0.73	0.74	0.60
Cu				0.30	0.02	0.66	0.62	0.73	0.91
Fe					0.27	0.32	0.20	0.21	0.31
Mn						-0.14	0.05	0.05	0.29
Ni							0.35	0.41	0.59
Pb								0.95	0.70
Sn									0.82
Zn									

Table 5.13 Pearson's correlation coefficients of urban and rural sites along the Forth and Clyde Canal and Glasgow Branch

Urban / Rural	As	Cr	Cu	Fe	Mn	Ni	Pb	Sn	Zn
As		0.82	0.43	0.57	0.10	0.45	0.46	0.38	0.59
Cr	0.20		0.62	0.47	-0.19	0.56	0.51	0.54	0.67
Cu	0.81	0.52		0.66	-0.13	0.86	0.63	0.70	0.94
Fe	0.07	0.05	0.17		0.26	0.40	0.17	0.33	0.63
Mn	0.20	-0.43	-0.18	0.21		-0.23	0.07	-0.15	-0.25
Ni	0.56	0.36	0.82	0.20	-0.22		0.82	0.56	0.91
Pb	0.24	0.68	0.54	0.14	-0.08	0.34		0.51	0.63
Sn	0.44	0.70	0.68	0.11	-0.07	0.44	0.95		0.65
Zn	0.83	0.46	0.88	0.18	0.17	0.68	0.64	0.80	

Left section shows correlation coefficients of urban sites; Forth and Clyde Canal sites 1, 2, 4, 6 – 12 and 24 – 28, and the three Glasgow Branch sites

Right section shows correlation coefficients of rural sites; Forth and Clyde Canal sites 13 – 23

Iron and Mn appeared to have the lowest correlations with all the other measured PTEs, in the grouped as well as in the separate urban/rural scenarios. Coefficients generally did not surpass 0.5, with exception of As/Fe (0.57), Cu/Fe (0.66) and Fe/Zn (0.63) in the rural environment. The reasons behind these observed correlation coefficients may be the fact that natural As has a tendency of being found bound with (hydr)oxides of Fe; and that Cu, Fe and Zn all occur naturally and are relatively abundant.

From Table 5.12, the highest correlations observed were As/Cu (0.85), As/Zn (0.87), Cu/Zn (0.91) and Pb/Sn (0.95). Upon separation into urban and rural scenarios, the correlations for these pairs in the urban scenario were As/Cu (0.81), As/Zn (0.83), Cu/Zn (0.88) and Pb/Sn (0.95), whereas the rural correlations observed were As/Cu (0.43), As/Zn (0.59), Cu/Zn (0.94) and Pb/Sn (0.51).

Copper and Zn are naturally common but also widespread general urban pollutants. From the listed pairs, only Cu/Zn have a strong correlation in rural samples as well as in urban samples, denoting their geogenic occurrence. The urban anthropogenic contribution of Cu and Zn appears to have been unequal, creating a localised bias and imbalance in the background ratios, causing a shift from the natural Cu/Zn abundance ratio. This is seen as a slight decrease in the urban coefficient when compared to the rural coefficient.

Correlations involving As with Cu and Zn are high only in urban samples. The results show that there is considerable As of anthropogenic origin in urban samples, since As is not naturally abundant, and that the contamination is widespread, rather than limited only to localised point sources.

The urban Pb/Sn coefficient of 0.95 signifies that the distribution of one element is similar to the other. This is corroborated by the fact that both elements were present in high concentration in sites 25, 27 and all three sites of the Glasgow Branch.

Nickel showed a high correlation with Cu, Pb and Zn in rural samples, where coefficients obtained were Cu/Ni (0.86), Ni/Pb (0.82) and Ni/Zn (0.91). This is likely to have been caused by the common peaks at sites 14 and 15. Coefficients of the same pairs in urban samples were lower; Cu/Ni (0.82), Ni/Pb (0.34) and Ni/Zn (0.68). The distribution pattern of Ni in the remaining samples of the Forth and

Clyde Canal and Glasgow Branch did not resemble the pattern of any of the other PTEs. This was reflected by Ni not showing any strong correlation with any other PTE.

Arsenic and Cr have also shown a positive correlation (0.82) in rural samples only. This may have been due to the fairly similar (low) concentrations and distribution pattern obtained in the rural samples. Conversely, the correlation in urban samples was quite low (0.20), denoting that anthropogenic sources for these two PTEs are not related. The respective distribution patterns in urban samples do not show any marked similarities. In fact, As contamination is common via aerial stack emissions whereas Cr contamination is usually more restricted to localised point sources.

5.4.4.2 Change in Potentially Toxic Element Concentration in Sediment over Time

A second sediment sample from site 25 was collected nearly 20 months after the first and termed sample 25R. This was necessary because the original sample ran out, but provided a useful opportunity to compare PTE levels at the same location over time. Site 25 is of particular interest since it is situated less than 100 m downstream from the junction with the Golden Jubilee Lock. It is therefore a relatively more dynamic point than most of the other sampling sites. The PT content of PTEs determined in both samples is listed in Table 5.14.

Table 5.14 Potentially toxic element (PTE) concentration (mg/kg) and standard deviation (± mg/kg) at site 25 of the Forth and Clyde Canal in the span of a 20 month difference

Sample	**25**		**25R**	
Sampling Date	**28/07/2010**		**23/03/2012**	
PTE	**mg/kg**	**± mg/kg**	**mg/kg**	**± mg/kg**
As	19.5	0.3	8.86	0.71
Cd	5.37	0.51	0.24	0.01
Cr	883	11	78.0	7.8
Cu	309	5	71.1	3.4
Fe	56800	521	48800	2740
Mn	1030	8	689	43
Ni	73.4	0.6	53.9	2.6
Pb	2740	56	77.5	7.2
Sn	122	7	5.59	0.07
Zn	2610	86	291	9

There appears to be a reduction in concentration of all PTEs over time, albeit some more than others, particularly Cu, Cr, Pb and Zn. However, there are a number of considerations that should be taken into account. Most importantly, these results reflect a single sample taken during each sampling session, and therefore, the respective results may be liable to a considerable sampling uncertainty.

Also, the change in sediment PTE content is effected by the sedimentation rate and dredging, necessary to ensure continued navigability. Unfortunately, neither the sedimentation rate nor the periodicity of dredging of the canal sediments is known. The latter is done by a contractor through public tender, although Scottish Canals were not aware of any recent dredging operation in the last few years[28]. In any case, the residence time of the top layer sediment from which the respective samples were taken is not known. Since PTEs adsorb to the surface of the sediment – and allowing for the fact that there might be a proportion of churning by currents created by the passing vessels – the PTE concentration in the top layer of sediment is proportional to the time spent *in situ*. Upon dredging or through sedimentation, and to a certain extent also churning, a new top layer is formed. Hence the fact that at face value, the PTE levels appear higher in the 2010 sample throughout, does not necessarily mean that there was higher input of PTEs at that time over the more recent instance.

Comparison may be drawn between the current work and the survey carried out by British Waterways in 1992[29]. A site by site comparison is not possible since each study used different sampling sites. However, the minimum/maximum range along both the Forth and Clyde Canal and the Glasgow Branch may be compared. As the British Waterways survey encompassed only sediment samples, results from the gastropod samples are omitted.

Twenty-seven samples were collected as part of the 1992 survey[29]. Levels of Cd, Cr, Cu, Pb, Sn and Zn in sample 27 were markedly higher than the general range obtained in the other 26 samples. Site 27 was roughly where the current study's samples 27/28 were taken. The British Waterways survey also revealed an urban/rural divide in the PTE levels, somewhat similar to that observed in this work. The minimum and maximum concentrations obtained in the 1992 and the current

project (2010) are listed in Table 5.15. The British Waterways' Forth and Clyde Canal range denotes results from sample 1 to 26, with the result from sample 27 in parenthesis where it falls outside the stated range. Sample 25R from the current work is omitted from the Forth and Clyde Canal range listed in order to keep the comparison limited to one temporal period.

Table 5.15 Potentially toxic element (PTE) concentration range (mg/kg) in the Forth and Clyde Canal and the Glasgow Branch in the British Waterways survey (1992)[29] and this survey (2010)

Canal		**Forth and Clyde**			**Glasgow Branch**	
Survey		**BW 1992[29]**	**2010**		**BW 1992[29]**	**2010**
PTE		**mg/kg**	**mg/kg**		**mg/kg**	**mg/kg**
As		9 – 98.2	5.54 – 90.0		140 – 873	79.7 – 219
Cd		0 – 5 (21)	0.451 – 5.46		5 – 8	3.23 – 11.0
Cr		34 – 205 (4011)	44.8 – 883		454 – 1294	270 – 756
Cu		26 – 293 (451)	39.3 – 315		334 – 1357	323 – 618
Fe		-	35800 – 72100		-	55100 – 60100
Mn		-	720 – 4460		-	1190 – 1370
Ni		38 – 152	42.0 – 134		81 – 93	93.1 – 154
Pb		22 – 1008 (8275)	93.9 – 2737		777 – 1358	553 – 1220
Sn		9.7 – 60.7 (278)	5.36 – 122		61.9 – 124	41.0 – 77.1
Zn		154 – 2869 (6671)	288 – 2610		1762 – 3627	2270 – 3640

British Waterways did not measure Fe and Mn. The 1992 survey[29] took place on sediment which was *in situ* for a considerable length of time since the canal was not open to navigation at that time, so there were no dredging operations.

The concentration ranges of As, Cd, Cu and Ni in the Forth and Clyde Canal were fairly similar in the 1992 and 2010 surveys. This implies that the source of these PTEs has remained constant, typical of input via soil runoff.

Levels of Cr appear to have increased considerably. This is due to the high levels determined between samples 24 and 28, and the Glasgow Branch. The junction with the Union Canal at the Falkirk Wheel, which occurs near site 24, may be acting as a new source of Cr into the Forth and Clyde Canal. This connection did not exist in 1992.

Levels of Pb and Sn appear to have increased, although the top of the respective ranges of the current work (2010) are influenced by the exceptionally high results for samples 25 and 27. Sample 25R has shown that levels of Pb and Sn at this

location have varied considerably. Excluding samples 25 and 27, which are likely a reflection of localised, temporal, point source input, the next highest Pb level was 694 mg/kg at site 1 in Bowling Basin, while the next highest Sn level was 32.5 mg/kg at site 10. Both these levels are considerably lower than the maximum reported in the 1992 survey. Whereas the Sn levels are relatively low, the considerable decrease in Pb content may be a reflection of a general decrease in topsoil Pb contamination, which used to happen via aerial deposition. The decrease may be reflecting an improvement in general environmental health as a result of the phasing-out of leaded petrol, which happened on 1st January 2000 as a consequence of EC Directive 98/70/EC[30].

The levels of Zn in the 2010 survey were close to those reported in the 1992 survey. Levels at the lower end of the scale increased, whereas at the higher end have decreased. This implies a stable and continuous source of Zn, typical of input via soil runoff.

Slightly different trends were observed in the Glasgow Branch. Considerable landscaping work has been carried out around the Glasgow Branch prior to its reopening. This involved shifting, removal and replacing of terrain at the banks of the canal. This is evidenced by the substantial lowering in levels of PTEs common in anthropogenic sources such as Cr, which was present in high levels due to the historical presence of a tanning industry, as well as others such as As, Pb and Sn. This rehabilitation has also resulted in a decrease in Cu levels. It is likely that there was a historical anthropogenic contribution in urban Cu levels, but the current levels reflect the geogenic occurrence of Cu in soil. The concentration range of Ni remained similar, further sustaining the hypothesis that the Ni present is of geogenic origin and that it was not commonly used. Zinc levels appear to have remained similar, denoting the geogenic occurrence in soil.

5.4.4.3 Comparison with Potentially Toxic Element Concentrations Determined in Glasgow Soils as part of the URBSOIL Project[31]

An interesting comparison to make is between the PT data obtained for Glasgow soils during the URBSOIL Project[31] and the PT data obtained from the sediment samples collected within the stretch of canal that passes through the Greater

Glasgow area, that is, samples 6 – 12 of the Forth and Clyde Canal and the three samples of the Glasgow Branch.

The URBSOIL Project focused on eight PTEs in soils: Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The concentrations determined are shown in Table 5.16. Analysis for As and Sn was beyond the scope and, although the project did attempt to measure Cd, the levels determined were close to procedural LODs. The very low levels of PT Cd content detected in the sediment samples mirrored the outcome of the Glasgow soils' PT analysis. It is evident that historical industries in the area did not make use of Cd.

Table 5.16 Pseudototal (PT) concentrations (mg/kg) of potentially toxic elements (PTEs) determined in Glasgow Soils as part of the URBSOIL Project[31]

PTE	PT concentration (mg/kg)
Cr	22.0 – 143
Cu	18.3 – 194
Fe	17100 – 40400
Mn	94.0 – 894
Ni	20.9 – 131
Pb	38.0 – 618
Zn	67.0 – 621

The canal sediments had higher quantities of PTEs than soils throughout the urban section. The soil in the vicinity of the canal where sediment samples were collected may have had higher concentrations than determined in the soil samples collected and analysed. The higher PTE content in sediments may also be attributed to accumulation *in situ*.

5.4.4.4 Comparison with other Canal Systems

An analogy can be drawn between the urban/rural divide seen in the Forth and Clyde Canal and the contamination of the sediments in the inner/outer Delft canals[7]. A drastic drop in PTE concentrations was observed in both instances when moving away from urban areas and into rural ones, denoting the significant anthropogenic influence in urban lined segments of canals. This is particularly

evident with elements such as Cd, Ni and Cr which are attributed to point sources from particular industries. The widespread contamination of Cu, Pb and Zn, which contributed to elevated baseline levels in rural areas, is also a common factor in both studies. Whereas movement of sediment is indeed possible due to the resuspension caused by passing vessels as observed in the Delft Canal study, the locks present in the Forth and Clyde Canal appear to be an effective barrier to this movement.

With reference to the various studies carried out and outlined in Table 5.3, it is evident that the level of contamination in the Forth and Clyde Canal and Glasgow Branch, particularly along its urban segments, is generally far greater than many other canals elsewhere, with the exception of the Woolston Canal[4], which is derelict and stagnant. Few are the (operational) canals which run across the centre of a city such as Glasgow, which spent 200 years as one of the major industrial hubs in the western world, and although nowadays industrial activity has subsided, it remains an active metropolitan city.

5.4.5 Sediment Dredging Management

Scottish Canals are responsible to ensure navigability by engaging contractors to perform sediment dredging and assess the best option for its disposal[32]. The PTE content of the dredged sediment determines its disposal route. Scottish Canals would rather have it disposed of at sea[28]. This is a cheaper option than disposal at landfill.

For disposal at sea, Scottish Canals would need to apply and obtain a permit from Marine Scotland. Marine Scotland is a body of the Scottish Government and was set up under the Marine (Scotland) Act 2010. Marine Scotland does not have legislative remit on canals, and as such would not be involved in licensing any sediment removal or movement operations, except for dredging operations outside a sea lock since its remit is confined to the management of the marine environment.

The decision to grant a license for sea disposal of dredged material at a pre-assigned site is based on a number of factors, most important of which is comparison of dredge contaminant content with CEFAS's revised ALs[33]. Marine Scotland pursues also other methods such as bioassays, historical data and insight relating to the earmarked disposal site. This is regarded as a 'weight of evidence' approach to

environmental management of sediments where various data concerning potential ecological impact is considered before deciding on the fate of dredged material[23].

Various countries have set their own sediment guideline values. Marine Scotland often refer to some of these[33], together with those set by CEFAS, to provide additional benchmarks against which to evaluate the sediment quality to be deposited in the marine environment.

Reference is often made to the 1992 Convention for the Protection of the Marine Environment of the North-East Atlantic (the OSPAR Convention)[23], which was signed by 15 countries – the Contracting Parties (Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom) - ratified also by Portugal, and approved by Spain and the European Community. The national sediment guideline ALs employed by the environment agencies of the contracting parties for assessment of disposal at sea of dredged material have been grouped to form minimum/maximum ranges. These are listed in Table 5.17[23]. Sweden employs a different approach to that of ALs, and thus its values have not been considered and included.

Table 5.17 Potentially toxic element (PTE) Guideline Action Level range (minimum/maximum) values of OSPAR Contracting Parties, except Sweden[23]

PTE	Action Level 1 Range (mg/kg)	Action Level 2 Range (mg/kg)
As	20 – 80	29 – 1000
Cd	0.4 – 2.5	2.4 – 10
Cr	40 – 300	120 – 5000
Cu	20 – 150	60 – 1500
Ni	20 – 130	45 – 1500
Pb	50 – 120	110 – 1500
Zn	130 – 700	365 – 10000

All values refer to dry weight

Marine Scotland advised[33] that it commonly uses the EQS values set by The Netherlands and Canada as benchmarks too. Dutch EQS values have been listed in

Table 5.2, where their Class 1 and 2 are equivalent to the UK's AL 1 and AL 2 respectively, while the Canadian ALs are listed in Table 5.18[34] .

Table 5.18 Canadian environmental quality standard values for potentially toxic elements (PTEs)[34]

PTE	Threshold Effect Level (TEL) [a] (mg/kg)	Probable Effect Level (PEL) [b] (mg/kg)
As	7.24	41.6
Cd	0.700	4.20
Cr	52.3	160
Cu	18.7	108
Ni	15.9	42.8
Pb	30.2	112
Zn	124	271

[a] Canadian TEL values are analogous to CEFAS's Guideline Action Level 1

[b] Canadian PEL values are analogous to CEFAS's Guideline Action Level 2

None of the 29 sediment samples collected in this study can be classed as below CEFAS's revised (2004) AL 1. The sediment at six sites, namely 13, 19, 20, 21, 23 and 28, have all their PTE levels between AL 1 and AL 2. The remaining 23 sites have at least one of the measured PTEs that surpassed AL 2. In a hypothetical scenario of having to dispose of dredged sediment having the PTE content determined in this study, disposal at sea for dredged material from these 23 sites is likely to be prohibited.

Whenever permission for sea disposal is not granted, sediment would have to be disposed of on land. A recent procedure followed when needing to dispose of sediment heavily contaminated with Hg was of having the sediment solidified on site, through mixture with some agents, the nature of which is commercially sensitive and undisclosed[35]. This facilitated the transportation and served as a binding agent for PTEs, therefore avoiding leaching. This sediment was transported to a hazardous landfill. Such licensed engineered landfills have a protective lining to prevent leaching of PTEs back into watercourses.

Since disposal at a landfill is expensive, both in terms of outright cost and carbon footprint due to transportation, Scottish Canals are currently exploring other possibilities[28]. One such option is that of placing the sediment on the banks close to

where it was dredged. However, although this is a low cost option, it is likely that the material will eventually re-enter the canal through soil runoff.

5.5 Conclusion

The PT concentration of As, Cd, Cr, Cu, Fe, Mn, Pb, Ni, Sn and Zn were determined using a microwave-assisted *aqua regia* digestion followed by analysis with ICP-MS. The high levels of Fe (ca. 50 g/kg) and the even distribution indicated that soil runoff was a primary source of sediment in the canal. The distribution of the other PTEs along the canal revealed a clear urban/rural divide in sediment concentration levels. The heavy industrial past of Glasgow appears to have contaminated the urban soils. This was inferred by comparison with the PTE levels obtained in rural samples, where they were likely to be less contaminated, offering a greater resemblance to natural geogenic content. The organic matter content of samples had to be taken into account for appropriate comparisons of PTE PT content between samples to be able to relate whether perceived levels at respective sites were due to the input load or retention capability of the sediment.

Any Fe from anthropogenic contribution is likely masked by the high levels of geogenic Fe present. Conversely, levels of Cd were very low, denoting that former industries in the area did not make use of this PTE. The distribution pattern of As and Pb showed a widespread contamination over the urban area. This is typical since their dispersion generally occurred via aerial deposition. Notably higher levels of Cr and Ni, such as in sample BW for Cr and sample 15 for Ni, were typically found near former industries that made specific use of them. Natural occurrence of Cu, Mn and Zn is widespread; however, anthropogenic contribution in urban sediments was evidenced by an increase in overall levels. Presence of Sn was generally low, although some notable high levels were noted in samples 25, 27 and the Glasgow Branch, indicating localised point sources.

The PTE levels in the gastropods collected at site 3 were much higher than those determined in gastropods from site 5. These were only about 150 m apart, but separated by a lock. Gastropods at site 3 are likely to be exposed to greater quantities of PTEs since they are in a harbour, whereas gastropods at site 5 are in a passage way. The lock appears to be acting as an effective barrier for movement, and the results point to the possibility of bioaccumulation in gastropods at site 3. The fact

that they were waterborne species and live at the time of sampling implies that they have adapted to withstand these PTE levels.

The Pearson's correlation coefficient statistical test was used to determine any strong correlations between PTEs present. The high correlation of Cu/Zn in both urban (0.88) and rural (0.94) scenarios reflects the fact that they are naturally abundant but also widespread general urban pollutants. High correlations of As with Cu (0.81) and Zn (0.83) were determined only in the urban samples because the widespread distribution of As was limited only to the urban samples.

A high urban Pb/Sn coefficient (0.95) reflected the fact that the distribution pattern of Sn was similar to that of Pb. High correlations of Ni in rural samples were Cu/Ni (0.86), Ni/Pb (0.82) and Ni/Zn (0.91). This is likely a result of the common peaks at sites 14 and 15. A high correlation of As/Cr (0.82) in rural samples may be due to the similarly low concentrations and distribution pattern.

The generally low correlations of Fe and Mn with all other PTEs may be due to the high quantities present. A moderate correlation could be present between As and Fe in urban sediments; As has a tendency of being found bound with Fe (hydr)oxides.

Upon comparison with the PT data obtained from Glasgow Soils as part of the URBSOIL project[31], it was evident that the urban canal sediments had higher quantities of PTEs. The reason for this could be that the soil in the vicinity of the canal where sediment samples were collected may have had higher concentrations than determined in the soil samples that were collected and analysed. Also, the higher PTE content in sediments may be a result of accumulation *in situ*.

The general trend observed was that present PTE levels were lower than those determined by British Waterways in the survey they conducted in 1992[29]. The higher levels then may have been a result of *in situ* accumulation since the canal laid derelict at the time. However, the extensive dredging carried out prior to the canal's reopening, as well as routine dredging necessary to ensure a continuous navigable depth is likely the cause for the generally lower PTE levels that were determined. However, the general current status implies that there still is considerable input of PTEs as a result of substantially contaminated urban soils. Present determined levels were generally higher than relevant EQS values.

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6 Sequential Extraction of Potentially Toxic Elements in Sediments of the Forth and Clyde Canal

6.1 Introduction

This chapter describes the application of sequential extraction to fractionate the PTE content in canal sediments. Sequential extraction offers a better insight than pseudototal digestion into the behaviour of PTEs in environmental samples through assessing their potential mobility. This offers the ability to deduce the potential risks that the environment, and particularly biota, may be exposed to. The approach has become widely adopted in recent years.

6.1.1 Sequential Extraction

Sequential extraction involves the application of a series of reagents of increasing vigour in a stepwise manner to the residue left following each preceding step. This allows for the extractable metal content to be sub-divided based on the reagents used to extract the sample, in a process termed operational speciation[1]. The PTEs that are most loosely bound to the sample matrix are extracted with the least vigorous reagent. These have the greatest potential mobility, as opposed to the PTEs that are more strongly held.

Sequential extraction can only indicate the potential and not the actual mobility of PTEs bound to the matrix. Whether mobilization actually occurs – or the extent to which it occurs – in the environment is dependant also on other factors. Although PTEs may be released from the solid matrix, the pH and redox potential of the aqueous solution they are transferred into, as well as the presence of other chemical species, will determine whether they remain solvated or precipitate. The presence of suspended particles will offer surfaces for re-adsorption.

The potential PTE mobility information gathered after sequential extraction is typically used to infer the potential bioavailability. Bioavailability has been defined as the “degree to which chemicals present in the soil may be absorbed or metabolized

by a human or ecological receptor or are available for interaction with biological systems"[2]. The fact that PTEs are mobile does not necessarily mean that they are bioavailable because the uptake of PTEs by an organism is dependent also on having the correct physical, chemical and physiological conditions[3]. The potential bioavailability information deduced from sequential extraction serves also as an indicator of the potential toxicity and holistic environmental impact.

6.1.2 History of the Sequential Extraction Approach

The first recognised sequential extraction protocol can be traced back to that devised by Tessier *et al.* in 1979[4]. They proposed a five-stage sequential extraction procedure to fractionate Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in river sediments. The protocol, with the reagents used and the respective targets, is listed in Table 6.1[4].

Table 6.1 The sequential extraction protocol devised by Tessier *et al.* (1979)[4]

Step	Reagent	Fraction label and target phase(s)
1	1.0 mol/l $MgCl_2$ at pH 7.0	Exchangeable
2	1.0 mol/l CH_3COONa adjusted to pH 5 with CH_3COOH	Bound to carbonates
3	0.04 mol/l $NH_2OH{\cdot}HCl$ in 25% CH_3COOH (96 °C)	Bound to Fe-Mn oxides
4	HNO_3/H_2O_2 (85 °C), followed by 3.2 mol/l CH_3COONH_4 in 20% HNO_3	Bound to organic matter and sulfides
5	$HClO_4$/HF	Residual

The authors reported that the reagents used were selected on the basis of their ability to remove PTEs by exchange processes from, or dissolution of, the specific target phase. The notion of having nominal target phases, rather than specific target phases, came later when authors realised that the sequential extraction of a PTE is operationally defined, *i.e.*, the fraction a metal is determined in, is dependent on the reagent used[5].

Many researchers modified Tessier *et al.*'s[4] protocol to their needs and widened the scope from sediment to other substrates. These include Gibson and Farmer (1986)[6]; Miller *et al.* (1986)[7] and Oughton *et al.* (1992)[8], among many others.

The use of sequential extraction in publications has seen an exponential growth since 1990[3]. Results reported from the different protocols could not be compared to each other since the different procedures make use of their own number

of steps, reagents, conditions and targets. Also, the definition of which fraction(s) is/are mobile is subjective and wide[3].

Harmonization of sequential extraction procedures was necessary, and the Community Bureau of Reference of the Commission of the European Communities (BCR) – later superseded by the Standards, Measurement and Testing Programme – embarked on a project that led to the development of the three-step BCR protocol[9-10]. The differences with respect to Tessier *et al.*'s protocol[4] are that their Step 1 and 2 were combined, together with other slight modifications to concentrations and reaction conditions. The original BCR protocol is listed in Table 6.2[9]. Another aim of the project was to produce a CRM – coded lake sediment BCR CRM 601 – with certified extractable metal content with this protocol[11]. This was an important step towards improving quality control.

It later became evident that Step 2 of the original BCR procedure revealed inconsistencies in the results reported by various authors [for example [12]]. This led to a re-evaluation of this step[13], and a modified protocol was later recommended[5, 13-14]. The differences between the original and the modified protocol are that the concentration of hydroxylammonium chloride in Step 2 was increased, while the pH was lowered. The reproducibility of results increased, possibly due to a more efficient dissolution of the iron (hydr)oxide reducible fraction[15]. This has also led Pb to be mainly extracted in Step 2, as opposed to Step 3 in the original BCR procedure, and an overall increase in the amount of metal extracted[5]. Another recommendation made was that the speed of centrifugation should be increased from 1500 to 3000 g[13]. The modified BCR protocol is listed in Table 6.3[5].

An additional 4th Step – *aqua regia* digestion of the residue from Step 3 – was recommended, although not in the official modified BCR protocol. This serves as a measure of the residual fraction. The summation of all four steps should add up to the PT content (see Chapter 5). This may serve as a quality control.

Table 6.2 Original BCR protocol[9]

Step	Reagent	Fraction label	Nominal target phase(s)
1	0.11 mol/l CH_3COOH	Exchangeable, water- and acid-soluble	Soluble species, carbonates, cation exchange sites
2	0.1 mol/l $NH_2OH{\cdot}HCl$ at pH 2	Reducible	Fe and Mn (hydr)oxides
3	H_2O_2 (85 ^oC), followed by 1.0 mol/l CH_3COONH_4	Oxidisable	Organic matter and sulfides

Table 6.3 Modified BCR protocol[5]

Step	Reagent	Fraction label	Nominal target phase(s)
1	0.11 mol/l CH_3COOH	Exchangeable, water- and acid-soluble	Soluble species, carbonates, cation exchange sites
2	0.5 mol/l $NH_2OH{\cdot}HCl$ at pH 1.5	Reducible	Fe and Mn (hydr)oxides
3	H_2O_2 (85 ^oC), followed by 1.0 mol/l CH_3COONH_4	Oxidisable	Organic matter and sulfides
4[a]	*Aqua regia* (prepared as 3 HCl : 1 HNO_3)	Residual	

[a] Not part of the modified BCR protocol, however, it is recommended as a means for quality control - the sum of a PTE's concentration from Steps 1–4 should be equal to that given by a pseudototal content determination using *aqua regia*[14]

6.1.3 Applicability of the BCR Procedure

Numerous publications have made use of the modified BCR procedure in recent years. Although the original scope was the analysis of sediments, the BCR procedure has been applied successfully to other matrices[3], such as to soil (including agricultural soils[16], soils amended with organic wastes[17], rhizosphere soils[18], urban soils[19], forest soils[20], and industrial contaminated soils[21]); road particulates[22]; mine spoil[23]; sewage sludge[24]; incinerator fly ash[25]; medical waste fly ash[26]; airborne particulate matter[27]; electric arc furnace dust[28]; gas pipeline corrosion products[29]; and compost[30].

The adoption of this sort of *standard* sequential extraction protocol by researchers offers two main advantages – the results obtained in different studies can be compared, providing that no alterations have been introduced, and the availability of CRMs (such as BCR®-601 and BCR®-701 for sediment analysis) enables researches to validate their analysis by subjecting a CRM sample to the procedure alongside test samples.

There are conflicting opinions about the reliability of the results given by the BCR protocol for operational speciation of certain PTEs such as As, Sn and Hg, due to their different chemistry from that of transition metals[3]. However, various studies have attempted to apply it to As. It has been reported that the highest amount of As was extracted in Step 2, followed closely by Step 4. The amounts of As extracted in Step 1 and 3 were typically minimal[15, 31-32]. Arsenic is present mainly as ferric arsenate in soils or sediments[31]. Arsenic has a particular affinity for bonding with Al, Cd and Fe[33]. Some As may be found bound to organic compounds[32].

Like As, the chemistry and behaviour of Sn is not like transition elements, and as such, the BCR approach is rarely applied. However, where determined, results typically have showed that Sn was mainly extracted in Step 4, with minimal amounts extracted in Steps 1, 2 and 3[34-35].

Mercury is seldom analysed with this protocol since most of the Hg is believed to volatilise when the solution is heated at 85 °C during Step 3 to reduce the volume to a few ml[36].

6.1.4 Application of the BCR Procedure to Sediments

The importance of studying canal sediments stems from the fact that sediments act as sinks and sources of PTEs. The fact that sediments act as a sink may serve as a good indicator for anthropogenic influence in the surroundings. The fact that sediments may act as sources of PTEs should environmental conditions change[37] greatly increases the importance of studying such systems as bound metals may be remobilised.

The modified BCR procedure has been applied by various authors to sediment from different origins such as marine[38], estuarine[39] and lagoon[40]. A study on sediment from drainage and irrigation water supply canals[41] – located south of the River Po in Italy – serving agricultural and/or industrial activities, revealed that samples from intensively industrialized areas had higher PTE concentrations and a different fractionation pattern from samples collected in remote and rural areas. Relatively greater quantities of all the PTEs determined – As, Cd, Cr, Hg, Ni, Pb, and Zn – were extracted in the initial steps of the modified BCR procedure in sediment adjacent to industrial areas compared to rural samples, where a greater relative quantity was extracted in the later Steps 3 and 4.

Another study, on sediments from Barcelona Harbour[42], showed that from six samples collected, the highest PTE concentrations were determined in a sample collected adjacent to an urban discharge point. Similarly to the study of the canals south of the River Po, the anthropogenic PTE input received by the sample collected near the urban discharge point was found bound in the more mobile fractions. In general, the most mobile PTE was Cd, followed by Zn. Both were extracted mainly in Step 1. Lead was extracted mainly in Step 2, followed by Cu which was roughly equally distributed between Step 2 and 3. The greatest amounts of Ni were extracted in Step 3, followed by Cr, which was mainly extracted in Step 3 alone.

It has also been shown[43] that oxidation of anoxic sediments – which *in situ* may easily occur through churning of the top layer sediment by passing vessels – causes some redistribution of Cr, Cu, Fe, Ni, Pb and Zn from residual or oxidisable phases to more mobile phases, particularly the reducible phase. This may be due to scavenging by iron (hydr)oxides, which form readily upon oxidation[43]. However, there are contrasting opinions about the effect on the mobility of As and Cd[43].

6.1.4.1 Glasgow URBSOIL BCR Data[19]

The fractionation pattern of the Glasgow soils obtained using the modified BCR procedure as part of the URBSOIL Project[19] is of particular relevance for this study as it may serve for indicative comparison purposes with the sediment samples collected from the urban section of the canal. The general fractionation pattern of the seven PTEs determined in Glasgow soil samples are shown in Figure 6.1.

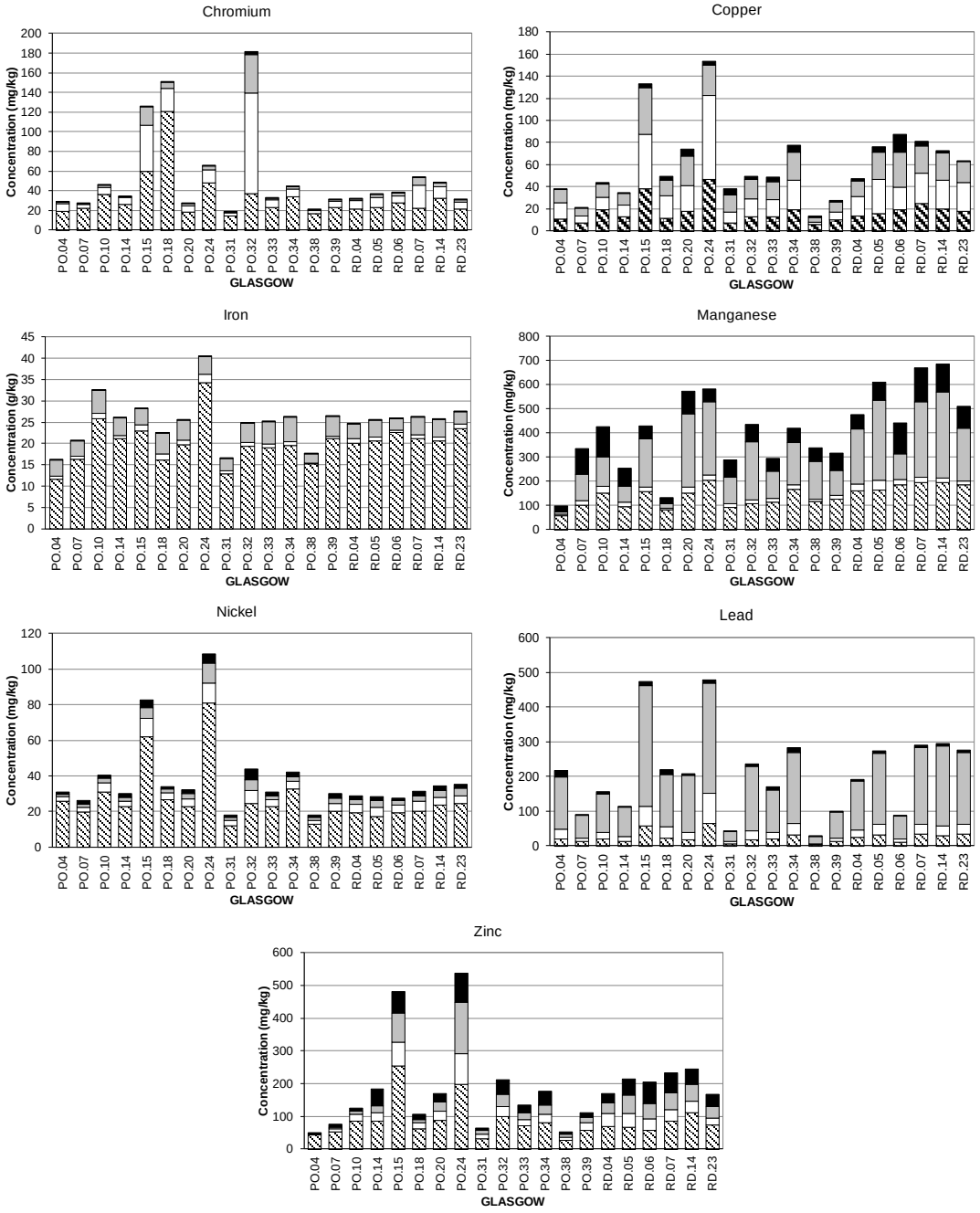

Figure 6.1 Fractionation pattern of the Glasgow URBSOIL soils[19]

Chromium, at most sites, together with Fe and Ni were found mainly in with the residual phase. Copper was associated mainly with the reducible fraction, although considerable quantities were also determined in the oxidisable and residual fractions. Manganese and Pb were mainly associated with the reducible fraction, whilst zinc was found in all four sequential extracts.

6.2 Aim

The aim of this work was to fractionate the PT content of the PTEs determined in sediments in Chapter 5 in order to obtain a better insight into their potential mobility, and to attempt to identify the anthropogenic influence, particularly in urban sections of the canal. Determination of Hg was not attempted due to the volatility concerns during Step 3.

6.3 Experimental

6.3.1 Equipment

i. 4-digit weighing balance [AE200, Mettler, Leicester, UK]
ii. Centrifuge tubes (50 ml, polypropylene) [Fisherbrand®, Fisher Scientific UK Ltd., Loughborough, UK]
iii. Calibrated pH meter [Jenway 3505 pH Meter, Bibby Scientific Limited, Staffordshire, UK] with probe [BDH Gelplas Ag/AgCl/Sat. KCl reference electrode, VWR International Limited, Leicestershire, UK] and pH 4 and 7 calibration buffer solutions [Solutrate, Fisher Scientific UK Ltd., Loughborough, UK]
iv. End-over-end mechanical shaker [GFL® 3040, GFL Gesellschaft für Labortechnik mbH, Burgwedel, Germany]
v. Centrifuge [ALC 4237 CENTRIFUGE]
vi. Filter paper [Fisher Brand QL 100 (cellulose, 110 mm), Fisher Scientific UK Ltd., Loughborough, UK]
vii. Microwave with associated high pressure vessels [MARSXpress™ High-Throughput Microwave Reaction System, CEM Microwave Technology Ltd., Buckingham, UK]

viii. Inductively Coupled Plasma – Mass Spectrometer [7700x Series ICP-MS, Agilent Technologies UK Ltd., Wokingham, UK], complete with auto-sampler [ASX-500 series ICP-MS auto-sampler, Agilent Technologies UK Ltd., Wokingham, UK]

6.3.2 Reagents

i. Glacial acetic acid
(≥ 99.0% *Trace*SELECT® Ultra, Sigma-Aldrich® Company Ltd., Dorset, UK)

ii. Hydroxylammonium chloride
(99.0+%, CertiFied AR®, Fisher Scientific UK Ltd., Loughborough, UK)

iii. Ammonium acetate
(99.0+%, CertiFied AR®, Fisher Scientific UK Ltd., Loughborough, UK)

iv. Hydrogen peroxide
(About 30% (v/v), AnalaR NORMAPUR® BDH Prolabo – VWR International, Lutterworth, UK)

v. Hydrochloric acid
(30% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

vi. Nitric acid
(65% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

vii. Standard Solutions for ICP-MS: Multi-Element Calibration Standard 2A, containing: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn.
(10 mg/l, matrix 5% HNO_3, Crawford Scientific™ Ltd., Strathaven, UK)

viii. Standard Solutions for ICP-MS: Multi-Element Calibration Standard 3, containing: Au, Hf, Ir, Pd, Pt, Rh, Ru, Te, Sn.
(10 mg/l matrix, 10% HCl / 1% HNO_3, Crawford Scientific™ Ltd., Strathaven, UK)

ix. *Basic Rinse* for ICP-MS: the stock solution is composed of a mixture of:
2.5 g EDTA, acid form
(Sigma-Aldrich® Company Ltd., Dorset, UK)
0.2 g Triton™ X-100
(Sigma-Aldrich® Company Ltd., Dorset, UK)

15 g ammonium hydroxide

(Sigma-Aldrich® Company Ltd., Dorset, UK)

20 g hydrogen peroxide

(Sigma-Aldrich® Company Ltd., Dorset, UK)

This is made up to 250 ml with de-ionised water and kept refrigerated. A 1:10 dilution is prepared to serve as the actual *basic rinse* solution.

6.3.3 Analytical Method

Sample digestion and analysis was carried out in triplicate for all determinations. The blank was treated similarly to the sample solutions, but without addition of any sediment. This procedure was applied to the 29 sediment samples, composed of 28 original samples and sample 25R, which replaced sample 25. The gastropod samples from sites 3 and 5 were omitted from this study since this procedure was aimed at studying the mobility of PTEs in sediment.

6.3.3.1 Sequential Extraction of Potentially Toxic Elements using the Modified BCR Technique

The oven dried (at 30 ºC) sediment samples were sequentially extracted following the three-step method described by Rauret *et al.*[5] known as the modified BCR technique. An additional 4th step was carried out on the residue from the modified BCR method's Step 3, following the procedure already outlined in Chapter 5 (Section 5.3.3.1).

Preparation of Solutions

Solution A is 0.11 mol/l acetic acid, CH_3COOH

A 0.43 mol/l acetic acid solution was prepared by addition of 25 ± 0.2 ml glacial acetic acid to a 1 l volumetric flask and making up to the mark with de-ionised water. This solution was diluted four-fold by transferring 250 ml to a new 1 l volumetric flask and making up to the mark, producing a 0.11 mol/l solution.

Solution B is 0.5 mol/l hydroxylammonium chloride, $NH_2OH \cdot HCl$

A solution made of accurately weighed 34.75 g hydroxylammonium chloride in 400 ml deionised water was prepared in a beaker. This was transferred into a 1 l volumetric flask. The beaker was washed, with the resulting washings being transferred also to the volumetric flask. By means of a calibrated pipette, 25 ml of 2 mol/l HNO_3 were added to the volumetric flask, which was then made up to the mark with deionised water. The solution was prepared freshly on the day of use since it is unstable.

Solution C is 300 mg/g (30%), 8.8 mol/l (100 vol) of hydrogen peroxide, H_2O_2

This solution was purchased and used as is.

Solution D is 1 mol/l ammonium acetate, CH_3COONH_4

In a beaker, 77.08 g of ammonium acetate were accurately weighed and mixed with 900 ml of deionised water. The pH of solution was adjusted to 2.0 ± 0.1 using concentrated HNO_3. This solution was then transferred into a 1 l volumetric flask. The beaker was washed, with the resulting washings being transferred also to the volumetric flask. This was made up to the mark with deionised water.

Sequential Extraction Procedure

Step 1

One gram of sediment sample was accurately weighed in a 100 ml centrifuge tube, followed by the addition of 40 ml of solution A. The cap was secured and the tube placed in an end-over-end shaker for 16 h at 22 ± 5 ºC. Care was taken to ensure no delay between addition of the extractant solution and the commencement of the shaking process.

Following extraction, the tube was placed in a centrifuge at 3000 g for 20 min. The supernatant solution was then decanted into a clean vial. This was labelled and placed in a refrigerator at 4 ºC until taken for analysis by ICP-MS.

The residue was washed with 20 ml of deionised water, followed by end-over-end shaking for 15 min and centrifuging at 3000 g for 20 min. The supernatant

was decanted and discarded, while the solid residue was retained in the same tube and taken for Step 2.

Step 2

Forty ml of freshly prepared solution B were added to the solid residue from Step 1. The cap was secured and the solid was resuspended by manual shaking. The tube was placed in an end-over-end shaker for 16 h at 22 ± 5 ºC. Care was taken to ensure no delay between manual resuspension and the commencement of the shaking process.

Following extraction, the tube was placed in a centrifuge at 3000 g for 20 min. The supernatant solution was then decanted into a clean vial. This was labelled and placed in a refrigerator at 4 ºC until taken for analysis by ICP-MS.

The residue was washed with 20 ml of de-ionised water, followed by end-over-end shaking for 15 min and centrifuging at 3000 g for 20 min. The supernatant was decanted and discarded, while the solid residue was retained in the same tube and taken for Step 3.

Step 3

Ten ml of solution C were added to the solid residue from Step 2 carefully and in small aliquots to avoid losses following possible violent reaction. The tube was loosely capped and allowed to digest at room temperature for 1 h with occasional manual shaking. The digestion was continued in a water bath. Care was taken to increase the water bath temperature gradually from room temperature with the tube inside to avoid thermal shocks which would have caused a vigorous reaction and losses. Digestion was allowed for 1 h at 85 ± 2 ºC, after which the cap was removed and the solution was allowed to reduce to < 3 ml volume.

A further 10 ml aliquot of solution C was then added. The tube was loosely capped and allowed to digest at 85 ± 2 ºC for 1 h. The cap was then removed and the solution was allowed to reduce to about 1 ml, making sure to avoid complete dryness.

Fifty ml of solution D were then added to the cool moist residue. The cap was secured and the solid was resuspended by manual shaking. The tube was placed in an

end-over-end shaker for 16 h at 22 ± 5 ºC. Care was taken to ensure no delay between manual resuspension and the commencement of the shaking process.

Following extraction, the tube was placed in a centrifuge at 3000 g for 20 min. The supernatant solution was then decanted into a clean vial. This was labelled and placed in a refrigerator at 4 ºC until taken for analysis by ICP-MS.

The residue was washed with 20 ml of de-ionised water, followed by end-over-end shaking for 15 min and centrifuging at 3000 g for 20 min. The supernatant was decanted and discarded, while the solid residue was retained in the same tube and taken for Step 4.

Step 4

Twenty ml of *aqua regia* (prepared as 3 HCl : 1 HNO_3) were used to transfer the residue from Step 3 in the centrifuge tube to a clean high pressure microwave vessel, taking care to minimalise losses as much as possible. This was left for 24 h in a fume hood to allow for any vigorous reaction to take place, after capping loosely with the vent plug to allow CO_2 to escape, but avoiding airborne dust from depositing in the vessel. After the 24 h period, the screw cap was tightly secured and the microwave vessel was fitted in the microwave's carousel. The microwave-assisted digestion followed the procedure already outlined in Chapter 5 (Section 5.2.3.1).

6.3.3.2 Determination of Potentially Toxic Elements using Inductively Coupled Plasma Mass Spectrometry

Preparation of Standards

A set of mixed standard solutions with analyte concentrations 10, 100, 200 and 400 µg/l were prepared from the respective 10 mg/l multi-element commercial standards. Different sets of standard solutions were prepared in 0.11 mol/l acetic acid, 0.5 mol/l hydroxylammonium chloride, 1 mol/l ammonium acetate, and 2% *aqua regia* – each to be used with the analogous sample extracts, for reagent matching purposes. A blank solution of each of the 4 reagent matrices was also prepared to use as the respective set's 0 µg/l 'standard'.

Operating Conditions

The concentrations of the most abundant isotopes of the 10 elements of interest were determined in each standard, sample replicate and blank, with the ICP-MS. These were ^{75}As, ^{111}Cd, ^{114}Cd, ^{52}Cr, ^{53}Cr, ^{63}Cu, ^{65}Cu, ^{56}Fe, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{118}Sn, ^{64}Zn, and ^{66}Zn. Indium (^{115}In) was used as an internal standard. The instrument operating conditions are listed in Table 6.4.

Measurement

Measurement using ICP-MS followed the same procedure already outlined in Chapter 5 (Section 5.2.3.2), making sure that the blanks and standards of the same reagent matrix as the samples being analysed were used.

Table 6.4 Agilent 7700x inductively coupled plasma – mass spectrometry (ICP-MS) operating conditions

Matrix	**0.11 mol/l CH_3COOH**	**0.5 mol/l $NH_2OH{\cdot}HCl$**	**1 mol/l CH_3COONH_4**	**2% a*qua regia***
ICP-MS Parameters	**Condition**	**Condition**	**Condition**	**Condition**
RF Power	1600 W	1600 W	1600 W	1600 W
Carrier Gas (Argon)	0.59 l/min	0.59 l/min	0.59 l/min	0.59 l/min
Dilution Mode (HMI [a])	ON: Ultra Robust – Level: Low	ON: Ultra Robust – Level: High	ON: Ultra Robust – Level: High	ON: Ultra Robust – Level: Low
Makeup Gas (Argon)	0.34 l/min	0.34 l/min	0.34 l/min	0.34 l/min
MicroMist Nebulizer Pump	0.1 rps [b] (≡ 333 ml/min)	0.1 rps [b] (≡ 333 ml/min)	0.1 rps [b] (≡ 333 ml/min)	0.1 rps [b] (≡ 333 ml/min)
Collision Mode	OFF [c] / ON [d] @ 4.3 ml/min He	OFF [c] / ON [d] @ 4.3 ml/min He	OFF [c] / ON [d] @ 4.3 ml/min He	OFF [c] / ON [d] @ 4.3 ml/min He

[a] HMI = High Matrix Interface; [b] rps = revolution per second, where rps = ml/min x 0.0003; [c] Collision Mode was OFF for As, Cr, Cu, Fe, Mn, Ni, and Zn; [d] Collision Mode was ON for Cd, Pb, and Sn

6.4 Results and Discussion

6.4.1 Limits of Detection

The LODs of each analyte in the respective matrix were determined following the procedure outlined in Chapter 5 (Section 5.3.1). Analysis on the ICP-MS was carried out on various instances during the course of this work and various LODs were obtained. However, these were found to be always similar when the blank was uncontaminated and the instrument worked optimally. A set of typical LODs given by the instrument are listed in Table 6.5.

Table 6.5 A set of instrumental limits of detection (µg/l) obtained for the isotopes of the potentially toxic elements (PTEs) determined in each BCR Step matrix using inductively coupled plasma mass spectrometry

PTE	**Limit of Detection (µg/l)**		
Isotope	**0.11 M CH_3COOH**	**0.5 M $NH_2OH{\cdot}HCl$**	**1 M CH_3COONH_4**
^{75}As	0.0212	0.0898	0.0162
^{111}Cd	0.0151	0.0959	0.0226
^{114}Cd	0.0186	0.115	0.0157
^{52}Cr	0.0285	0.0362	0.0499
^{53}Cr	0.0816	0.191	0.0833
^{63}Cu	0.349	5.11	0.172
^{65}Cu	0.484	10.4	0.218
^{56}Fe	1.23	7.18	0.982
^{57}Fe	4.21	289	4.80
^{55}Mn	0.186	11.5	0.172
^{60}Ni	0.126	12.8	0.0825
^{206}Pb	0.182	5.67	0.196
^{207}Pb	0.211	6.89	0.262
^{208}Pb	0.134	2.77	0.147
^{118}Sn	1.59	3.46	0.170
^{64}Zn	0.593	18.9	0.538
^{66}Zn	1.24	31.9	1.20

The instrumental LODs of the PTEs in acetic acid and ammonium acetate were fairly similar, with the exception of Sn, which was about 10 times higher in

acetic acid. Comparison with the procedural LODs of PTEs in *aqua regia* (see Table 5.9) shows that these limits are quite similar to those in acetic acid (except Sn) and ammonium acetate.

The PTE procedural LODs of Cu, Fe, Mn, Ni, Pb and Zn in hydroxylammonium chloride were considerably higher than those given in acetic acid, ammonium acetate and *aqua regia*. The LODs of Fe and Zn were substantially higher in this matrix.

Problems were often encountered when using this matrix at this concentration since crystals formed around the ICP-MS cone aperture, eventually causing the flow rate to diminish. The cones required cleaning after prolonged use. This may explain the relatively high LODs obtained. The high levels of PTEs present in some sediment samples necessitated that the extracts be diluted to fall within the calibration range. These were diluted using 2% HNO_3, and so the crystallisation problems were averted.

Instrumental LODs were used to calculate procedural LOD values, the actual PTE concentration that could be detected in sediment samples with the extraction method used. Procedural LODs are listed in Table 6.6.

Table 6.6 A set of procedural limits of detection (LODs, µg/kg) for determination of potentially toxic elements (PTEs) in sediment, calculated from the instrumental LODs listed in Table 6.5

PTE	**Limit of Detection (µg/kg)**		
	0.11 M CH_3COOH	**0.5 M $NH_2OH{\cdot}HCl$**	**1 M CH_3COONH_4**
As	0.848	3.59	0.810
Cd	0.674	4.22	0.958
Cr	2.20	4.54	3.33
Cu	16.7	310	9.75
Fe	109	5920	145
Mn	7.44	460	8.60
Ni	5.04	512	4.13
Pb	7.03	204	10.1
Sn	63.6	138	8.50
Zn	36.7	1020	43.5

6.4.2 Quality Control

The performance of the method was assessed using a CRM; BCR®-701 – Sediment[44]. Analysis was carried out in triplicate and the concentrations of PTEs obtained are listed in Table 6.7, together with reference values and percentage recovery.

Table 6.7 Potentially toxic element (PTE) concentration (mg/kg), standard deviation (SD, ± mg/kg), relative SD (% RSD), and calculated % recovery with respect to BCR®-701 values[44], at each step of the modified BCR procedure[5]

		Step 1				Step 2				Step 3			
PTE		**mg/kg**	**± mg/kg**	**% RSD**	**% Recovery**	**mg/kg**	**± mg/kg**	**% RSD**	**% Recovery**	**mg/kg**	**± µg/kg**	**% RSD**	**% Recovery**
Cd	BCR®-701	7.34	0.35	-	-	3.77	0.28	-	-	0.27	0.06	-	-
	Found Values	6.82	0.07	1.03	92.9	3.59	0.06	1.67	95.2	0.204	0.008	3.92	75.6
Cr	BCR®-701	2.26	0.16	-	-	45.7	2.0	-	-	143	7	-	-
	Found Values	2.07	0.10	4.83	91.6	45.5	2.2	4.84	99.6	147	2	1.36	103
Cu	BCR®-701	49.3	1.7	-	-	124	3	-	-	55.2	4.0	-	-
	Found Values	43.3	2.1	4.85	87.8	122	5	4.10	98.4	55.3	1.2	2.17	100
Ni	BCR®-701	15.4	0.9	-	-	26.6	1.3	-	-	15.3	0.9	-	-
	Found Values	13.6	0.6	4.41	88.3	26.2	1.2	4.58	98.5	14.7	0.2	1.36	96.1
Pb	BCR®-701	3.18	0.21	-	-	126	3	-	-	9.3	2.0	-	-
	Found Values	3.05	0.02	0.66	95.9	124	2	1.61	98.4	8.36	0.08	0.96	89.9
Zn	BCR®-701	205	6	-	-	114	5	-	-	45.7	4.0	-	-
	Found Values	185	8	4.32	90.2	106	5	4.72	93.0	41.7	0.8	1.92	91.3

Results represent mean ± 1 SD, n=3

% Recovery values calculated from results and exclude SD values

Replicate analysis of the CRM showed good accuracy where the percentage recoveries of Cd, Cr, Cu, Ni, Pb and Zn were within ± 13% of the certified values for all three steps, with the exception of Cd at Step 3. This result was only 0.07 mg/kg lower than the certified value, however, the very small quantities present makes such a small concentration difference appear large. The % RSD of each of these six elements from the three replicate samples was always less than 5%, signifying satisfactory precision.

The extracts of BCR®-701 were analysed also for their As and Sn content. The concentrations determined (mg/kg), together with their SD (± mg/kg) and % RSD (value in parenthesis) are listed in Table 6.8.

Table 6.8 Concentration (mg/kg), standard deviation (SD, ± mg/kg) and relative SD (%) of arsenic and tin obtained from the BCR®-701[44] extracts, at each step of the modified BCR procedure

PTE	Step 1	Step 2	Step 3	Step 4
As	1.87 ± 0.09 (4.81%)	18.5 ± 0.6 (3.24%)	1.56 ± 0.20 (12.8%)	45.0 ± 0.8 (1.78%)
Sn	< (63.6)	< (138)	< (8.50)	0.459 ± 0.101 (22.0%)

Results represent mean ± 1 SD, n=3

Values in parenthesis denote levels were lower than the procedural limit of detection

Arsenic was extracted mainly in Step 2 and Step 4. The low SD and % RSD indicate satisfactory accuracy and precision between replicates. Very low quantities of As were extracted in Step 1 and 3. The SD and % RSD were low and acceptable for the Step 1 extract, but relatively high for the Step 3 extract. The predominant extraction of As from the reducible fraction of the three-step modified BCR procedure is in line with what has been reported previously for As in sediments (see Section 6.1.3) [15, 31-32].

The first three extraction reagents were unable to extract detectable levels of Sn, in line with what has been reported in literature[34-35]. Step 4 (*aqua regia*) did manage to extract a small amount, although the SD and % RSD obtained were high.

6.4.3 Sediments

The concentration (mg/kg) and respective SD (± mg/kg) results obtained in each of the four steps of the modified BCR approach are represented as cumulative bars in Figure 6.2 to Figure 6.11. Each PTE's PT content, as reported in Chapter 5, is superimposed in the form of horizontal lines. This was done for ease of comparison. Figure 6.2 to Figure 6.11 data values are listed in Table A.5 to Table A.14 in the Appendix.

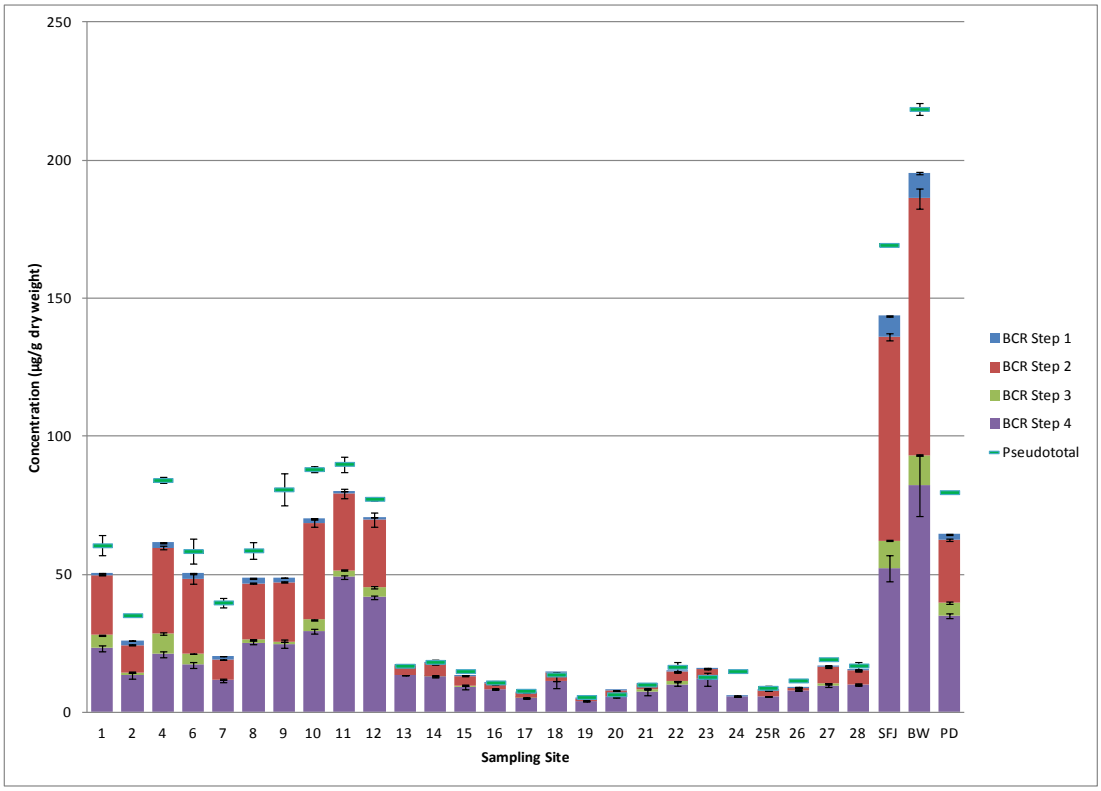

Figure 6.2 Arsenic modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

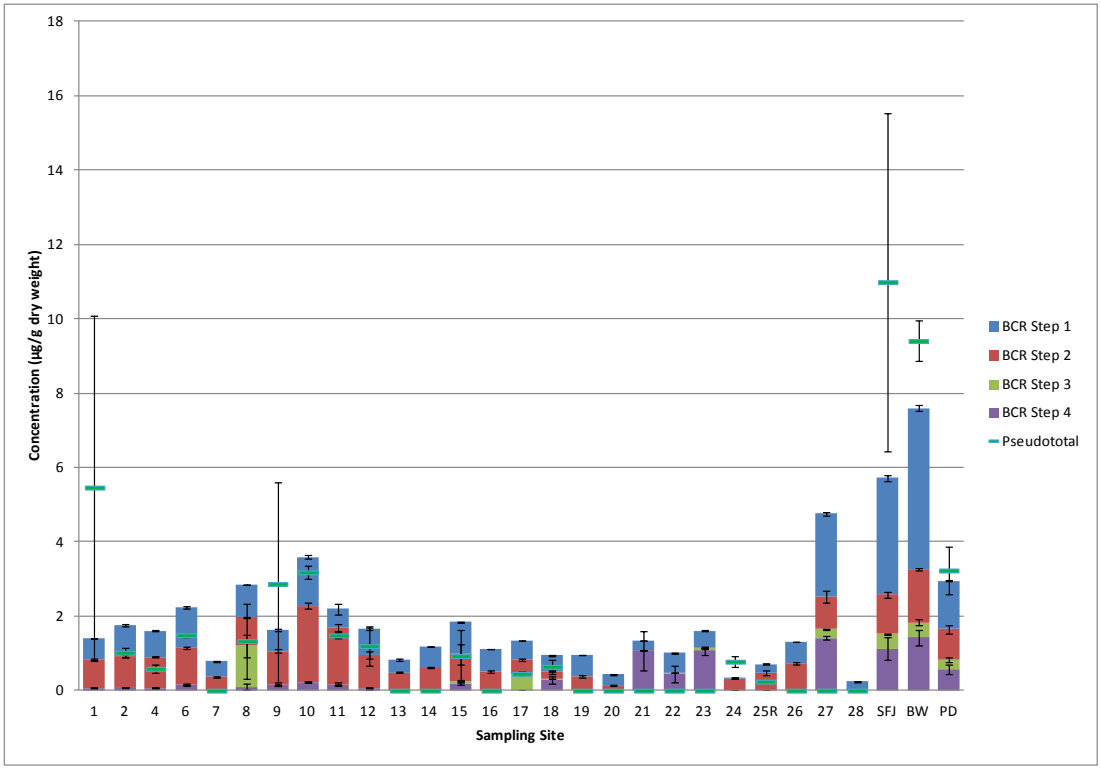

Figure 6.3 Cadmium modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

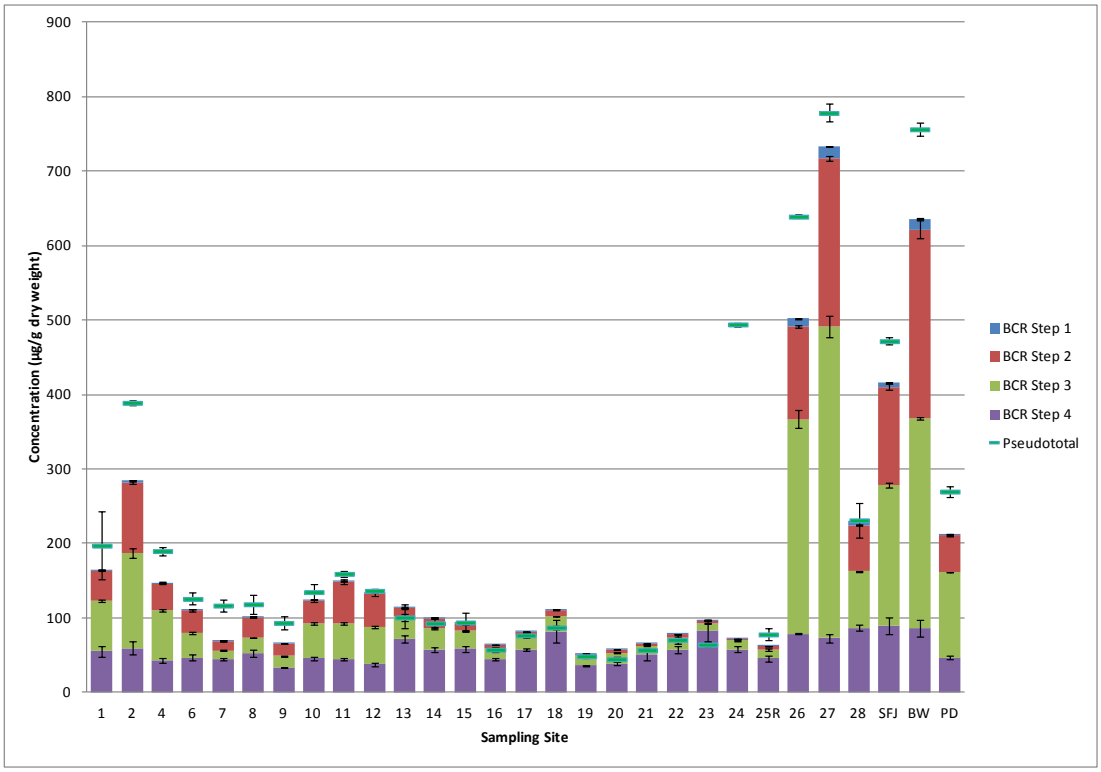

Figure 6.4 Chromium modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

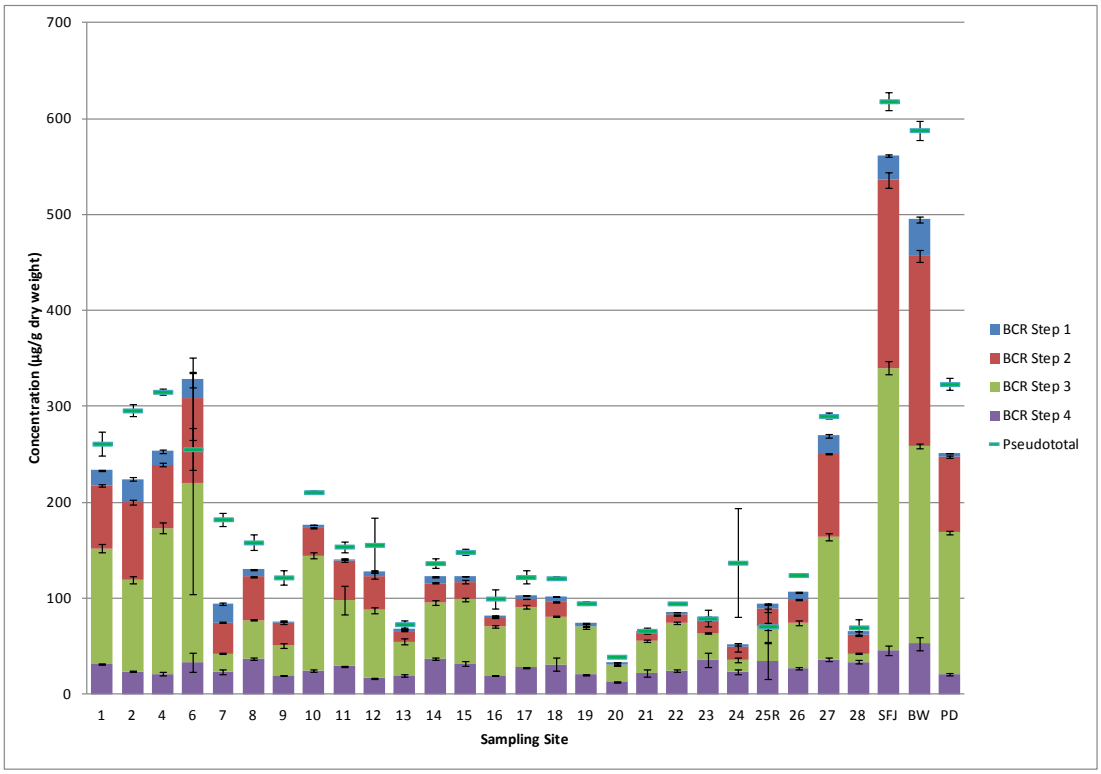

Figure 6.5 Copper modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

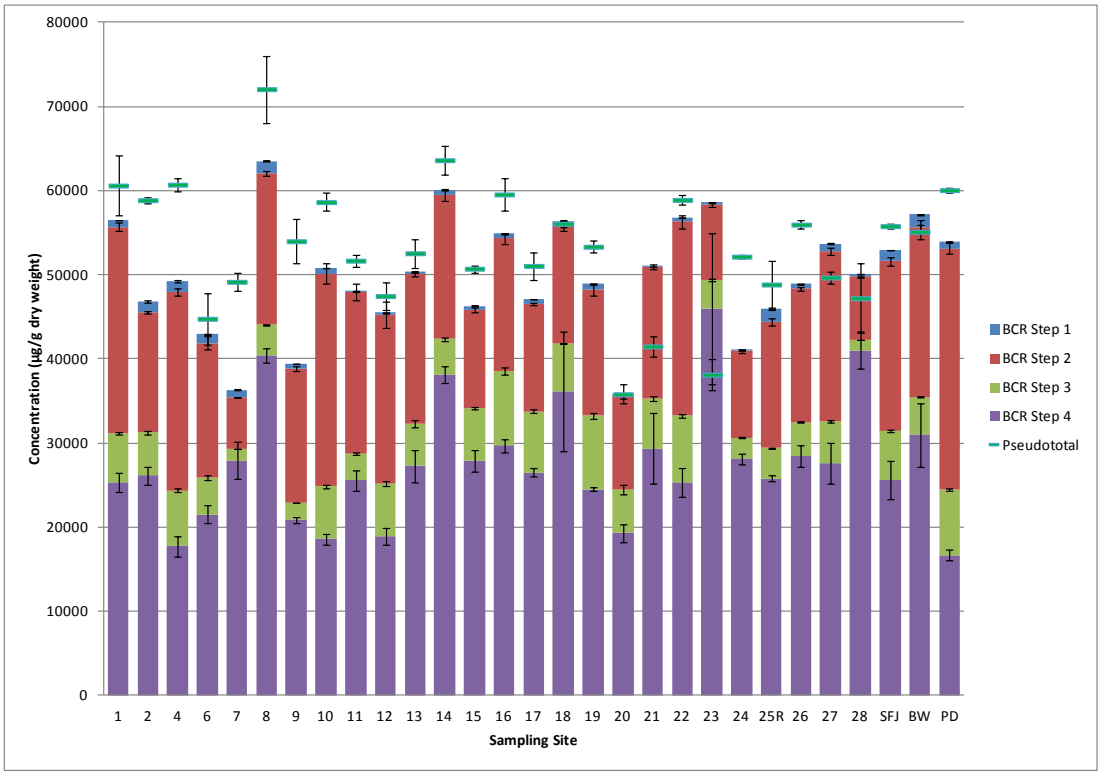

Figure 6.6 Iron modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

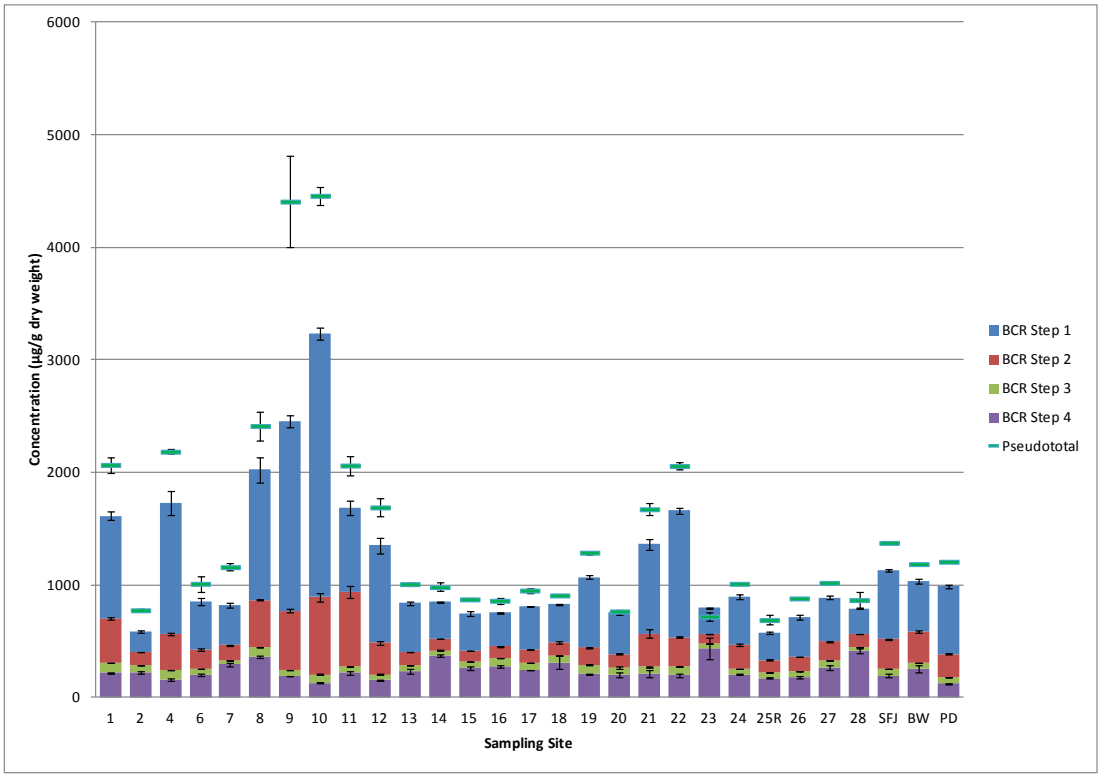

Figure 6.7 Manganese modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

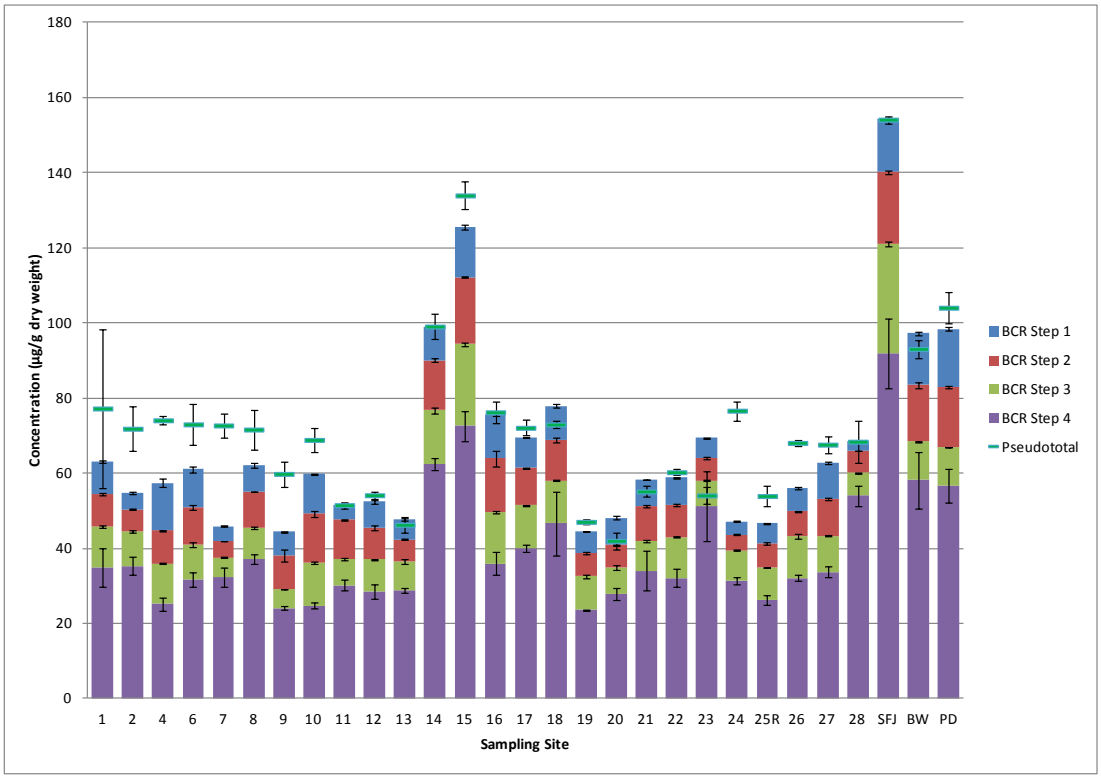

Figure 6.8 Nickel modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

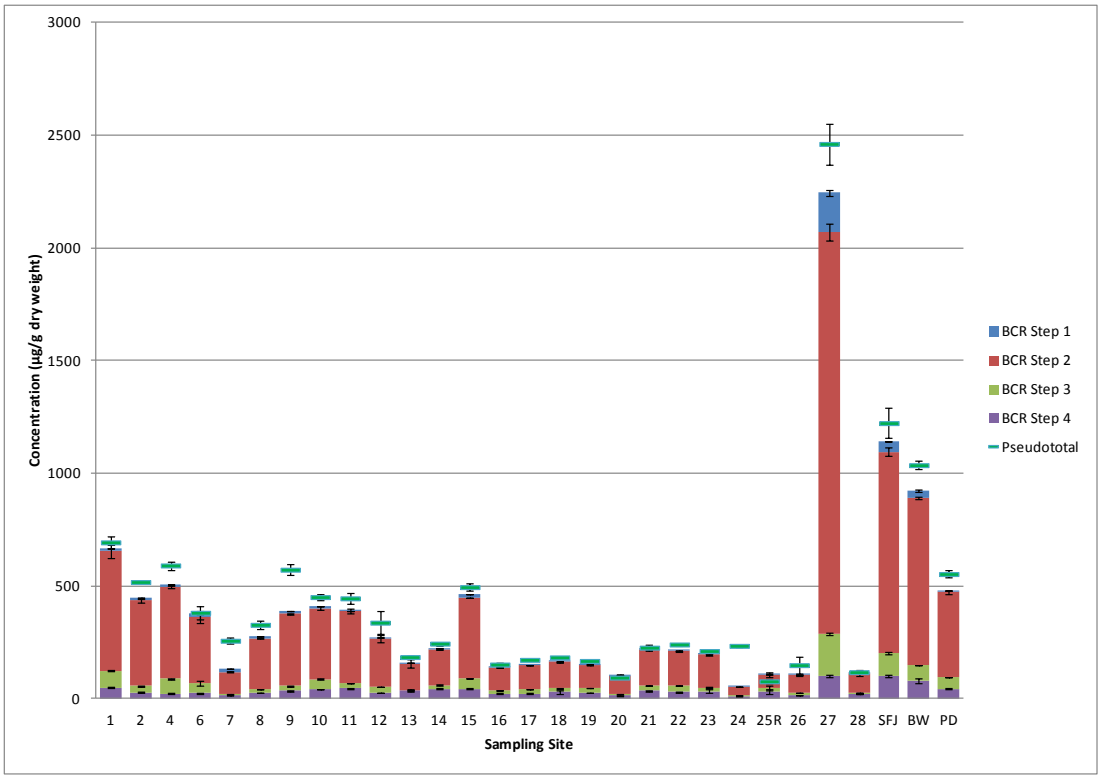

Figure 6.9 Lead modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

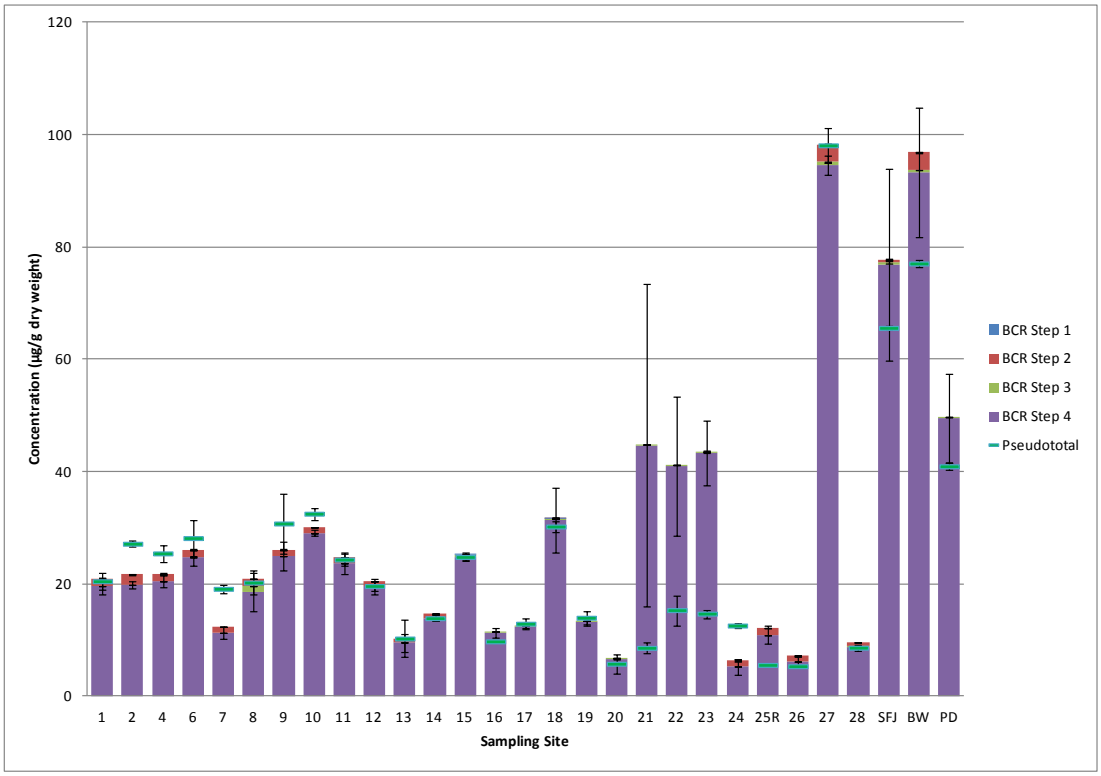

Figure 6.10 Tin modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

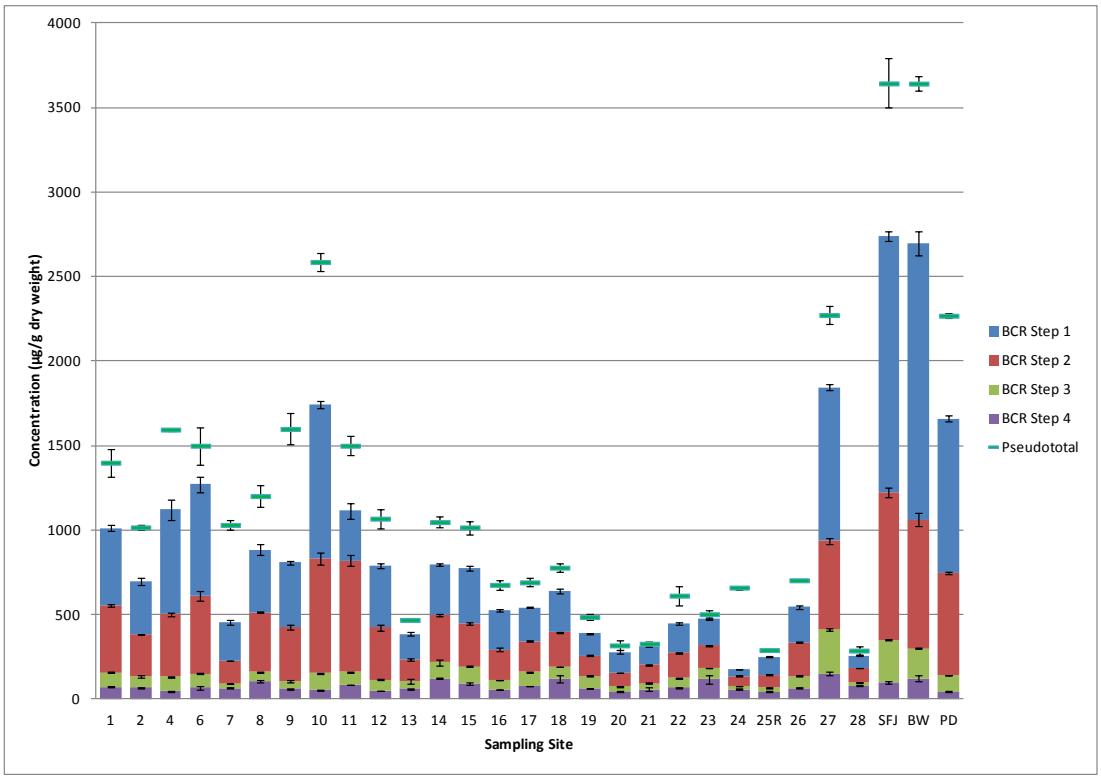

Figure 6.11 Zinc modified BCR (4-Step) and pseudototal concentrations in sediment from the Forth and Clyde Canal and Glasgow Branch (Error bars represent mean ± 1 standard deviation, n=3)

6.4.3.1 Recovery of the BCR Procedure Compared to the Pseudototal Content

In theory, the total amount of PTE isolated in the four steps of the BCR method should add up to the PT content. However, due to the greater intricacy of the BCR method, involving numerous steps, and particularly the fourth step which involves transferring the residue from a centrifuge tube to a microwave vessel, there is a greater possibility of sample loss. This was observed in the current study where mean recoveries of all PTEs, except Cd and Sn, were lower with the BCR procedure than PT values. The mean recoveries obtained were As (87.2%), Cd (147%), Cr (93.9%), Cu (86.0%), Fe (95.0%), Mn (83.4%), Ni (92.7%), Pb (88.1%), Sn (132%), and Zn (74.7%). The high recoveries of Cd and Sn are a consequence of the very low abundance, with levels close to the instrumental LOD, which contributed to high measurement uncertainty.

6.4.3.2 Fractionation Pattern of Potentially Toxic Elements in Sediment Samples

Arsenic

Arsenic in rural samples was mainly found in the residual fraction, indicating its geogenic presence. However, urban sediments had relatively higher quantities of As extracted in Step 2. This probably reflects the anthropogenic input of arsenates and arsenites which bind with the iron and manganese (hydr)oxides. The distribution pattern of As obtained from the canal sediments in this study was in conformity with that reported by previous workers (see Section 6.1.3) [15, 31-32].

Cadmium

Very low levels of Cd were determined in the various fractions for most sites. Some had considerable SD amongst replicates, due to the closeness to the instrumental LOD. However, the highest results – obtained in samples 27, SFJ, BW and PD – appear to give a consistent distribution pattern. The high content of Cd in the exchangeable fraction may reflect an association with Zn. Unfortunately there are no benchmarks (data from Glasgow soils and rural samples) to compare with.

Chromium

The distribution of Cr in urban sediments differed from that in rural samples,

which showed a similar fractionation pattern to that of the Glasgow URBSOIL soils[19]. In urban sediments, the greatest amount of Cr was found in Step 3, closely followed by Step 2, whereas in rural sediments, Step 4 was dominant. General urban soil runoff is therefore not the primary source of Cr in the canal. The use and presence of Cr is generally specific to certain types of industries, causing its presence to be and remain localised. The presence of this element may reflect discrete input(s) of contaminated material associated with historical industrial activities, such as steelmaking and tanning.

Copper

The fractionation pattern of Cu in urban sediments somewhat resembled the pattern of the Glasgow URBSOIL soils[19]. The largest amount of Cu was extracted in Step 3, closely followed by Step 2. This differed from the pattern obtained in the rural samples, where Cu was extracted mainly in Step 3, with very little extracted in Step 2. The distribution of Cu in rural sediments is presumed to mirror that in rural soils which are considered relatively uncontaminated. Therefore, the presence of Cu in the reducible fraction of urban soils is likely to originate from historical industrial contamination. The widespread urban contamination in soil is being reflected in the urban sediments.

Iron

Iron is soils and sediments – urban and rural – was mainly present in Step 2 and 4, with greater quantities in the residual phase. The similarity in quantity and fractionation pattern between urban and rural sediment samples is due to large quantities of Fe being of geochemical origin, *i.e.* present in soil minerals. Soil runoff is clearly the main source of the high quantities of Fe present in the canal sediments throughout. The natural high quantities of Fe present in soil presumably masks anthropogenic contribution.

Manganese

The fractionation pattern of Mn in both rural and urban sediments differed from that given in Glasgow URBSOIL soils[19]. Manganese was extracted mainly in

Step 2 from the soils. Manganese in topsoil would be predominantly in an oxidised form – $Mn^{IV}O_2$ – due to aeration. However, the redox conditions in bottom sediment entail that oxidised Mn is found only in the surface oxic layer, whereas reduced forms of Mn – Mn^{III}, and eventually Mn^{II} – would be found upon increasing depth as the sediment becomes anoxic. These are more mobile forms of Mn and the reason for the observed relatively high quantities extracted in Step 1. Very little Mn was extracted in Step 3, and some in Step 4, in both soils and sediments.

Relatively higher quantities of Mn were extracted in Step 2 of some sediment samples, notably samples 1 and 4 (compared to sample 2), the urban samples 8 to 12, and the three Glasgow Branch samples. This signified the relative presence of more Mn in the oxidised form. It could be explained in terms of particle size distribution, where samples with a higher proportion of the larger size fractions would contribute to a larger oxic layer *in situ*. For example, samples 1 and 4 had a slightly greater proportion of particle sizes in the sand fraction than sample 2. This was also the case for samples 9, 10 and 12. However, samples 8 and 11 had a relatively low % sand fraction and therefore the presence of oxidised Mn was due to other factors. These could include a high level of churning experienced at these particular sites, as well as a high sedimentation rate from new soil runoff. Also, the three Glasgow Branch samples had relatively high % sand fractions.

Nickel

The distribution of Ni between Step 1, 2, and 3 extracts was approximately equal and the greatest quantity was extracted from the residual fraction. This was similar in both sediments – urban and rural – and Glasgow URBSOIL soils[19]. Like Cr, the use of Ni was limited to specific industries. The presence of historical industries that made use of Ni is reflected in the determination of overall higher quantities of Ni, such as near site 14/15, but the majority of the element is still extracted in Step 4 at these locations. The similarity in fractionation pattern between urban and rural sediment samples signifies that soil runoff is the primary contributor of Ni in the canal sediments.

Lead

Lead was found mainly in the reducible fraction. Extractable content of Pb in Step 1, 3 and 4 were low in both sediment – urban and rural – and Glasgow URBSOIL soils[19] samples. Lead is a common pollutant and its presence denotes widespread anthropogenic contamination. The higher levels of Pb determined in urban sediments, compared to rural sediments, reflect urbanisation.

Tin

Tin was determined nearly in its entirety in Step 4. The results obtained showed high SD between replicates. The distribution pattern of Sn resembled that reported by previous workers (see Section 6.1.3)[34-35]. Some samples also resulted in a considerably higher BCR total (which effectively was from Step 4) than the PT content (see Chapter 5). This reaffirms doubts about the applicability of this sequential extraction method to Sn.

Zinc

The fractionation pattern of Glasgow URBSOIL soils[19] and urban sediments was similar, where the highest amount of Zn was extracted in Step 1, but closely followed by the amount in Step 2. Quantities extracted in Step 3 and 4 were minimal. This implies that soil runoff is a major contributor of Zn into the canal and that Zn contamination is widespread. Zinc, like Cu, is also a general urban pollutant. Similarly to Cu, higher quantities of Zn in the reducible fraction were extracted in urban sediments as compared to rural sediments.

6.4.3.3 Risk Assessment Code

With PTEs bound to different sediment fractions, the most labile are those whose binding strength is weakest and that may be easily leached from the sediment matrix and become mobile, greatly increasing their potential bioavailability, and hence the risk towards biota.

An assessment of the potential mobility of the respective PTEs can be obtained using the risk assessment code (RAC), which is the percentage of the PTE determined in the exchangeable fraction from the 4-step BCR process[45]. With respect to a particular PTE, when the RAC is less than 1%, the sediment is said to offer no

risk to the aquatic environment. Values between 1 and 10% reflect low risk; 11 - 30% reflect medium risk; 31 - 50% reflect high risk, while percentage greater than 50% signifies that the sediment poses a very high risk that PTEs become mobile and may enter the food chain[45].

The RAC values obtained from the 29 sediment samples of the Forth and Clyde Canal and Glasgow Branch are listed in Table 6.9.

Table 6.9 Risk Assessment Code values for the 29 sediment samples from the Forth and Clyde Canal and Glasgow Branch

Sampling Site	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sn	Zn
1	1.65	41.4	0.668	6.64	1.47	56.5	13.8	1.92	0.00	45.5
2	5.88	47.5	1.14	10.8	2.65	30.8	7.99	3.01	0.00	45.1
4	3.21	43.4	1.25	5.61	2.69	67.4	22.1	2.26	0.00	55.3
6	4.08	47.9	1.55	6.12	2.40	50.2	16.6	3.51	0.00	51.7
7	6.79	53.2	2.71	20.7	2.30	43.6	8.48	11.9	0.00	49.9
8	4.22	30.8	1.76	6.04	2.38	57.2	11.3	3.48	0.00	41.9
9	3.13	34.4	0.678	2.25	1.63	68.5	14.4	2.63	0.00	47.4
10	2.59	36.5	0.464	1.85	1.28	72.4	17.8	1.43	0.00	52.2
11	1.05	22.5	0.170	0.643	0.094	44.1	7.90	0.694	0.00	26.5
12	1.22	41.7	1.04	3.87	0.477	64.0	13.3	2.20	0.00	46.2
13	0.478	41.6	0.377	3.04	0.761	51.6	11.3	1.53	0.00	39.2
14	0.624	47.9	0.535	5.28	0.883	38.7	8.97	1.81	0.00	37.7
15	2.89	46.9	0.663	4.72	1.04	44.5	10.6	3.52	0.137	42.1
16	1.63	54.7	0.387	2.93	1.02	39.8	15.4	1.86	0.00	44.2
17	4.08	39.2	0.374	3.37	1.16	47.5	11.8	1.75	0.00	36.7
18	2.17	45.3	0.485	5.07	1.10	40.7	11.6	2.13	0.268	38.0
19	1.06	60.8	0.297	4.31	1.29	58.6	12.9	1.34	0.00	33.8
20	2.34	69.8	0.379	4.94	0.903	48.8	15.1	2.30	0.00	44.4
21	0.437	20.0	0.159	1.55	0.178	58.3	12.1	1.79	0.00	34.8
22	1.05	51.9	0.263	3.14	0.910	67.8	12.3	1.02	0.00	38.5
23	1.93	29.4	0.369	4.64	0.590	29.1	7.74	4.25	0.00	33.6
24	0.954	7.56	0.405	5.99	0.317	47.8	7.57	1.19	0.00	22.0
25	0.900	33.4	0.533	5.07	3.26	42.1	11.2	1.75	0.00	42.3
26	2.07	44.2	2.06	7.55	1.13	49.2	11.0	1.24	0.00	38.2
27	2.26	46.9	2.22	6.98	1.65	44.1	15.2	7.83	0.00	49.3
28	2.23	100	2.51	6.53	0.774	28.8	3.94	3.57	0.00	28.6
SFJ	5.28	54.9	1.46	4.56	2.56	54.3	9.29	3.97	0.00	55.3
BW	4.67	57.0	2.21	7.67	2.59	43.6	14.1	3.50	0.00	60.6
PD	3.27	44.2	1.09	1.52	1.42	60.9	15.7	1.68	0.00	55.0

The results show that most labile PTEs are Cd, Mn and Zn, with numerous sites having a RAC value greater than 50%. Although the labile nature of Cd is of concern because of the high toxicity of this element, the environmental hazard is low due to the fact that very low levels of Cd are present. The toxicities of Mn and Zn are much lower than that of Cd. The sediments offer no risk for Sn, and low risk for As, Cr and Fe since RAC values are less than 10%. The same could be said for Cu and Pb, with exception of samples 2 and 7 for Cu and sample 7 for Pb, where values were higher than 10%. Overall, Ni offers low to medium risk since RAC values spanned over two categories.

However, the RAC values only take into account the acid exchangeable fraction. The levels extracted from the reducible fraction could also potentially be mobilised with relative ease. In such a case, Pb becomes of greatest concern due to the high quantities present in the combined acid exchangeable and reducible fractions. These reached a maximum of 1960 mg/kg in sample 27. The low levels of As present reduced the environmental concern overall, although the amount of As from the combined acid exchangeable and reducible fractions in the Glasgow Branch reached a maximum of 102 mg/kg at site BW.

6.5 Conclusion

The modified BCR sequential extraction protocol[5] was applied to fractionate the PT content of the PTEs determined in the sediment samples in order to assess the lability of these PTEs.

Arsenic and Sn are not usually determined with this procedure due to their unsuitability caused by their chemical behaviour. Nevertheless, sequential extraction of these PTEs was attempted. The highest quantities of As were extracted in Step 2 and 4, whereas the highest amount of Sn was extracted in Step 4. These findings were similar to previous work reported in literature[15, 34].

The low PT levels of Cd meant that it was very difficult to obtain a fractionation pattern without having high SD values. The highest levels were obtained in the Glasgow Branch samples, where most Cd was extracted in Step 1.

The fractionation pattern of Cu, Fe, Ni, Pb and Zn obtained from the sediment samples matched the extraction distribution obtained from Glasgow soils

during the URBSOIL project[19]. The similarity implied that general urban soil runoff is the primary source of these PTEs in the canal.

The fractionation pattern of Mn was similar throughout the sediment samples but differed from that of the Glasgow soils obtained from the URBSOIL project[19]. The similarity in pattern, together with the relatively high quantities determined and the fact that Mn is not a common anthropogenic pollutant, imply that soil runoff is the main source of Mn in the canal sediments. However, the reducing conditions in the top sediment beneath the surface oxic layer is reducing the $Mn^{IV}O_2$ coming from the soil into the more mobile Mn^{II} form.

In contrast, the fractionation pattern of Cr differed between urban and rural sediments. Only the rural sediments resulted in a fractionation pattern of Cr that was similar to that of the Glasgow soils. There was a considerable amount of Cr extracted in Step 3, followed by Step 2, in urban soils, as opposed to the rural soils where Cr was mainly extracted in Step 4. The implication is that urban soil runoff is not a primary source of Cr in the urban section of the canal, but rather there exist some localised point sources.

The potential mobility order determined through the RAC calculation was given as: Cd / Mn / Zn > As / Fe / Pb > Cr / Cu > Ni > Sn. The environmental concern raised by the fact that Cd is labile is limited due to the low levels present. The PTEs present in the reducible fraction may also become mobile with relative ease. By taking into account also the amount that was found in the reducible fraction of the PTEs, Pb becomes of a general concern throughout the canal. Some concern could also be raised for As, particularly in the Glasgow Branch samples.

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7 Pseudototal Content of Mercury in Sediments of the Forth and Clyde Canal

7.1 Introduction

This chapter presents the PT Hg concentrations in the original 29 canal sediments for which concentrations of other PTE are reported in Chapter 5. Since these were not originally sampled with the intention of determining Hg – hence no special precautions were taken in their handling – nine new sediments were sampled and later also analysed.

7.1.1 The Mercury Cycle

Mercury is emitted into the atmosphere through natural and anthropogenic processes. Present day influx from human activities greatly outweighs the natural geological emissions[1-2], and this situation was worse in the past when industrial stack emissions were unfiltered and unregulated[1-2]. It has been estimated that industrialisation has brought about an increase in ambient Hg levels of about a factor of three over pre-industrialisation levels[1-2].

Mercury in the environment is circulated between different spheres - biotic and abiotic – through a series of pathways. These make up the Hg biogeochemical cycle. This cycle is represented in Figure 7.1[1].

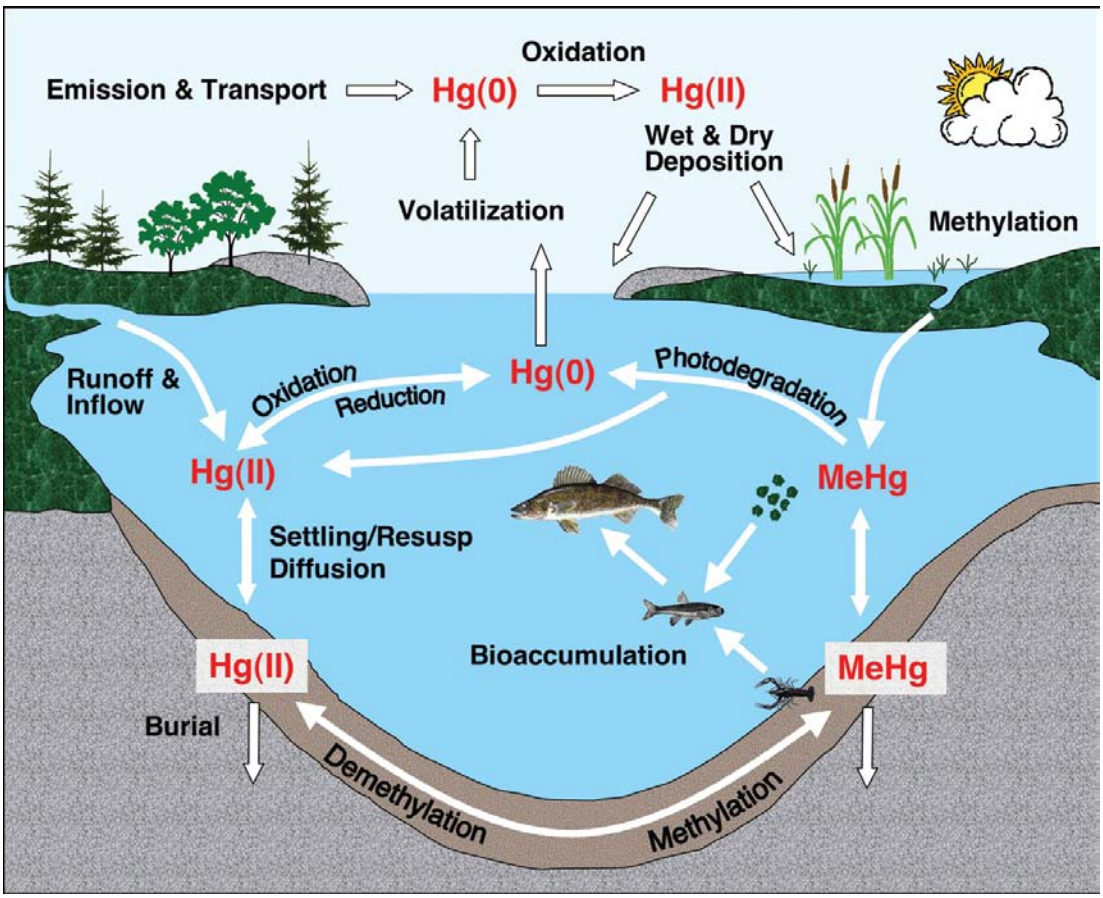

Figure 7.1 Biogeochemical cycle of mercury[1]

Natural emissions of Hg occur primarily from volcanic and associated geological activity. Areas naturally enriched in mercury can also contribute through land emissions. Oceans can also release Hg to the atmosphere through volatilization[1]. Natural Hg is emitted in elemental form[1].

Anthropogenic sources of Hg include combustion of fossil fuels (especially coal), mining, cement production, non-ferrous metal production, pig iron and steel production, chlor-alkali plants, gold production, waste disposal including incineration, and direct mercury production for use as raw material[1-2]. Anthropogenic emissions can release Hg in elemental form, divalent form, and/or adsorbed onto particulate matter (PM)[1].

Elemental Hg has an estimated atmospheric lifetime of 0.5 – 1.5 years and therefore can travel great distances[1-3]. This is attributed to the element's high ionisation energy, which gives it its relative inertness. Atmospheric Hg is estimated to be between 97 to 99% in the elemental form[3]. Its main removal process is thought

to be through photo-oxidation[1-2] to Hg^{II} by ozone and hydroxyl radicals[4]. The significant importance of atmospheric reduction of Hg^{II} back to Hg^0 is uncertain[1]. The atmospheric lifetime of Hg^{II} and Hg adsorbed onto PM ranges from a few days to a few weeks[1-2]. Oxidized forms of mercury in the atmosphere are believed to include mercury (II) chloride and mercury (II) oxide[3]. Unlike elemental Hg, inorganic Hg compounds are typically soluble and therefore deposit quickly through wet deposition[3]. Mercury adsorbed onto particulate matter may be soluble and deposit through wet deposition; however, it will deposit also through dry deposition. Therefore, direct anthropogenic emissions of Hg^{II} and Hg adsorbed onto PM are likely to limit the contamination to a regional scale[1-2].

Due to the high vapour pressure of elemental Hg, any Hg^0 on the ground will eventually vaporize. Some of the Hg^{II} and Hg adsorbed onto PM deposited on soil will be reduced. The proportion, estimated to be between 5% and 60%, depends on the soil surface and moisture content[1]. Some inorganic Hg is reduced to Hg^0 and revolatilized in a process termed prompt recycling[1-2], while a proportion may be methylated, forming Me-Hg, which is the most toxic form of mercury commonly found in the environment[1-2]. The remaining Hg^{II} will be incorporated into the soil where atmospheric emissions will occur at a slower rate. Inorganic Hg and Hg adsorbed onto PM may also be deposited onto vegetation, and this too will eventually end up in the soil via throughfall and litterfall. In soil, Hg^{II} is associated with organic matter, where it binds strongly to reduced sulfur groups[1-2].

Contaminated soil may be flushed into a watercourse, bringing Hg^{II} and Me-Hg into the aquatic environment (since both species are soluble). Some Hg^{II} will form a redox equilibrium with Hg^0, where most of the latter will vaporize into the atmosphere, while some Hg^{II} will adsorb onto particles and settle out. Some Me-Hg may undergo photodegradation and form Hg^0 and/or Hg^{II}, or be absorbed by plankton and thus enter the food chain, or adsorb onto particles and deposit as bottom sediment.

Mercury may be methylated or demethylated through bacterial action in sediments. Mercury in sediments of shallow water bodies may be resuspended, potentially re-entering the cycle. The ultimate sink of mercury is burial into deep ocean sediments, a process which occurs very slowly[1-2].

7.1.2 Environmental Quality Standards for Mercury

Due to the potential toxicity of Hg, the allowed limit values in sediments given by international organisations are similar to those for Cd and much lower than values for other PTEs. The guideline action levels for other PTEs in sediments have been presented in Chapter 5 (refer to Table 5.2 for the Dutch ALs, Table 5.5 for CEFAS's pre- and post-2004 ALs, Table 5.14 for the OSPAR Contracting Parties except Sweden, and Table 5.15 for the Canadian ALs). The two-tier guideline action values given for Hg by CEFAS (pre- and post-2004), OSPAR Contracting Parties (except Sweden) and Canada are listed in Table 7.1. The Dutch four-tier classification values for Hg are listed in Table 7.2.

Table 7.1 Sediment mercury Guideline Action Levels 1 and 2 given by various organisations

Organisation	Action Level 1 (mg/kg)	Action Level 2 (mg/kg)
CEFAS (pre-2004)[5 a]	0.3	3.0
CEFAS (post-2004)[5 a]	0.25	1.5
OSPAR Contracting Parties[b], except Sweden[5]	0.25 – 0.6	0.8 – 5
Canada[6]	0.130	0.700

[a] Centre for Environment, Fisheries and Aquaculture Science (CEFAS), which is an executive agency of the UK's Department for Environment, Food and Rural Affairs (DEFRA)

[b] Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention, 1992) Contracting Parties: Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom

Table 7.2 Sediment pollution classification system used in The Netherlands[7 a, b]

PTE	Class 1 (mg/kg) (unpolluted)	Class 2 (mg/kg) (slightly polluted)	Class 3 (mg/kg) (moderately polluted)	Class 4 (mg/kg) (very polluted)
Hg	< 0.5	0.5 – 1.6	1.6 – 10	> 10

[a] The class limits are defined for a standard sediment having 10% organic matter and 25% clay contents

[b] Sediments with concentrations in Class 3 or higher are considered of unacceptable quality and are required to undergo remediation through dredging and safe disposal

Also, the WFD's Daughter Directive, 2008/105/EC[8], suggests that the EU's Member States may opt to apply an EQS for Hg of 20 μg/kg for sediment instead of

the surface water EQS values laid down. This is the only PTE which this Directive specifically lists.

The final draft text of the Minamata Convention on Mercury, spearheaded by the United Nations Environment Programme, has been agreed on the 19th of January 2013. It is due to be signed during the conference that is to be held in Minamata, Japan, on the 10th and 11th of October 2013. This shall be a legally binding instrument for the signatory governments, with the objective being to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds by reducing atmospheric emissions from point source[9].

7.1.3 Mercury in Canal Systems

Some, albeit not all, of the studies reported in Section 5.1.1 have also measured the Hg content. The Delft Canal study[7] reported a PT Hg concentration range of 0.36 – 6.40 mg/kg in sediments originating from urban sections and a concentration range of 0.14 – 2.50 mg/kg in sediments originating from rural sections. This trend is in line with that observed for Cd, Cr and Ni, which were also of mainly anthropogenic origin in the Delft study and thus expected to be at higher levels in urban areas. Comparison of these concentration ranges with the Hg levels listed in the Dutch sediment pollution classification system reveals that both sets span between Class 1 and Class 3.

The Caland Canal study[10] in The Netherlands reported a PT Hg concentration range of < 0.2 – 0.8 mg/kg. The Begej Canal study[11] in Romania reported a PT Hg concentration range of 0.2 – 1 mg/kg, while the Indiana Harbour Canal study[12] in the USA reported a PT Hg concentration of 0.52 mg/kg. The Grand Canal study[13] in Hangzhou – Beijing, China, reported a PT Hg concentration of 0.6 mg/kg. All other studies listed in Table 5.3 and Table 5.4 did not measure Hg.

The presence of elevated levels of Hg in a canal is symptomatic of a specific anthropogenic source. The Caland Canal study[10] reported low levels for other PTEs. However, the high concentration of Cd reported in the Begej Canal[11] and the high concentration of Cr reported in the Indiana Harbor[12] and Grand Canal[13] studies

indicated the presence of anthropogenic contributions. However, no specific Hg sources were indentified in the vicinity of these canals.

The British Waterways survey of PTEs in canal sediments, carried out in 1992[14], had measured Hg in the various Scottish Canals. The PT Hg concentration determined in the Forth and Clyde Canal ranged between 0.1 and 2.7 mg/kg, and from 3 to 16.5 mg/kg in the Glasgow Branch. The determined Hg levels in the Glasgow Branch were higher than at any point sampled along the Forth and Clyde Canal. These high results were not unexpected due to the area's heavy industrial past.

The PT Hg concentration of the sediments collected from the Caledonian Canal ranged between 0 and 0.8 mg/kg, with just one sample that had a concentration of 5.7 mg/kg. The Crinan Canal survey yielded a PT Hg concentration of 0.1 to 1.3 mg/kg – here too there was one sample that had a higher concentration of 2.4 mg/kg. There is no current industrial activity in the vicinity of these canals. The Hg levels reported in the respective canal's ranges are low and may be considered background due to the lack of specific industrial point sources. The two samples (one in each canal) with the relatively higher Hg concentration may have been due to localised sources.

7.1.4 Mercury in Sediments of the Forth and Clyde Canal

The historic heavy industrialisation of the Glasgow area would have contaminated the surrounding topsoil through aerial deposition. The contaminated soil ultimately may end up in the canal following surface soil runoff. Influx of Hg through this route is a function of the amount of soil runoff and Hg levels in the soils. This depends on industrialisation and urbanisation near the canal banks.

In addition to general urban/industrial contamination from the vicinity, there is one potentially very important source of historical Hg contamination in the Forth and Clyde Canal. This is the former Nobel Westquarter Factory in Reddingmuirhead, close to the Union Canal, which used vast quantities of mercury fulminate to prepare detonators. The reconnection of the Forth and Clyde Canal with the Union Canal in 2001 has reopened the route for movement of sediment contaminated with Hg associated with this site downstream from the Union Canal through the Falkirk Wheel Junction.

7.1.4.1 Mercury Contamination from the former Nobel Westquarter Factory

Edward Charles Howard (1774 – 1816) is credited with the discovery of mercury fulminate in 1799[15], by dissolving elemental mercury in slightly diluted (ρ 1.4 g/cm^3) nitric acid and mixing with ethanol. Alfred Nobel (1833 – 1896) developed the metal blasting cap detonator using mercury fulminate to blast dynamite[15] – a product which he invented – and had it patented in 1867 (U.S. patent number 78,317)[16]. Dynamite is a mixture of nitroglycerin with an absorbent substance, forming a malleable paste. The main advantage is that, while nitroglycerin is an explosive liquid and quite difficult to handle safely, dynamite is quite stable, so much so that it requires a detonator to explode[16].

A detonator is composed of a small amount of a primary explosive, which is a compound that requires only a small amount of energy to react explosively. The energy released by its explosion is enough to overcome the high activation energy of a secondary explosive, which would be present in much higher quantities in the explosive device.

The Nobel Westquarter Factory manufactured munitions using mercury fulminate as the primary explosive in the metal blasting cap detonator and dynamite as the secondary explosive for nearly 100 years during its operation (1876 – 1968), and played a major role as part of the war effort in both World Wars.

During the factory's operation, mercury would have been transferred into the canal in solution, since the canal served as the sewer, as well as in particulate form, typically from spillages[17].

In the run up to the reopening of the Union Canal, 75,000 tons of sediment was dredged between March 2000 and May 2001 along a 9 km section. This ranged from Greenbank Road, which is from where the new segment was constructed to meet the Falkirk Wheel Junction, to the point where the A801 Bridge crosses the canal. The dredging was necessary to ensure a navigable depth as well as to avoid the spreading of potentially contaminated sediment westwards to the newly built segment and the Falkirk Wheel Junction. The Nobel Westquarter Factory stood exactly midway along this stretch of canal. This is depicted in Figure 7.2[17].

Figure 7.2[17] also shows 5 sampling points, labelled A to E, from where British Waterways collected sediment for Hg analysis before dredging commenced along the 9 km segment. The Hg results obtained were: A = 123 mg/kg, B = 619 mg/kg, C = 2360 mg/kg, D = 12,100 mg/kg and E = 24 mg/kg. The Hg levels at all of these sites are considerably higher than the established EQS levels listed in Table 7.1 and Table 7.2.

Site D, which was opposite the factory's location, was found to be extensively contaminated with Hg, with levels far higher than the other sites monitored. This decreased markedly eastwards, but gradually westwards, in line with the direction of the water flow. Water flowed westwards only until the 1930s, prior to the filling in of the connection with the Forth and Clyde Canal. The severance caused stagnation in water flow, possibly contributing to the very high Hg concentration observed at site D, following years of accumulation. This also meant that the observed spread of contamination would have been historical.

This section was found to be heavily contaminated with Hg in the 1992 British Waterways survey too[14]. Twenty five sites along the canal were sampled, although the exact locations are not available. The Hg levels determined at 21 sites ranged between 0.4 and 13.2 mg/kg. One site was determined to have 80 mg/kg of Hg, while the remaining three sites ranged between 1305 and 1571 mg/kg of Hg.

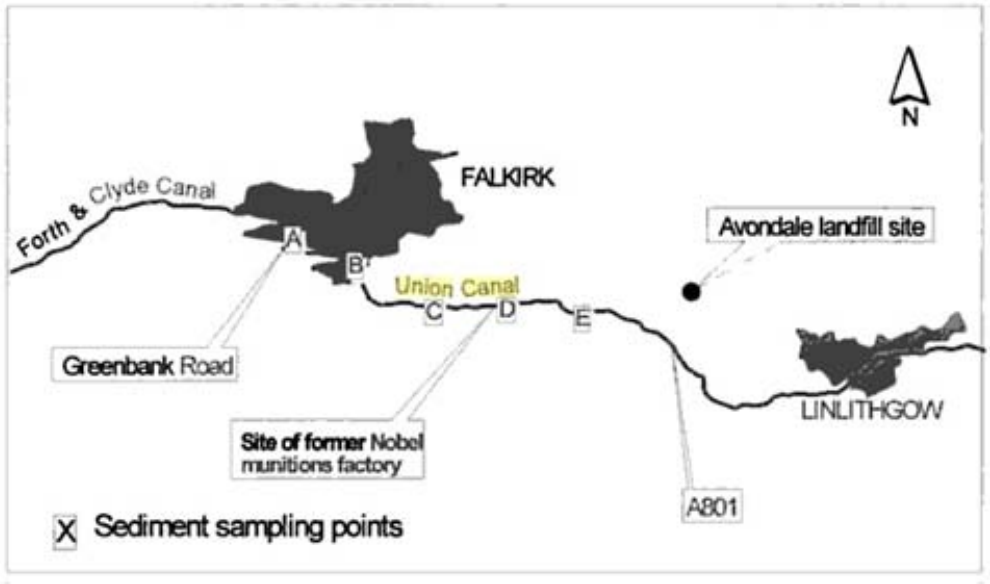

Figure 7.2 Map showing the Union Canal segment affected by mercury contamination originating from the Nobel Westquarter Factory[17]

This 2000/2001 study[17] also reported the organo-Hg content at the 5 sites – although it did not specify which compounds were determined – as a percentage of the PT Hg determined. These were: A = 0.021%, B = 0.053%, C = 0.005%, D = 0.016% and E = 0.146%. Such low levels indicated that there was no direct input of organo-Hg compounds. It was more likely that this was a product of methylation of inorganic Hg through microbial action. This process, facilitated by some strains of sulfate- and iron- reducing bacteria, converts only a small proportion of Hg^{II} into Me-Hg in sediments[1]. This will be discussed further in Chapter 8, which focuses on mercury speciation analysis. The presence of high levels of organo-Hg compounds are typically only found in areas in the vicinity of factories that are associated with manufacture, formulation, supply and use of such compounds. In contrast, all the forms of Hg involved in the Nobel Westquarter Factory's industrial process were inorganic.

Analysis of water at these 5 sites indicated that Hg was in an insoluble form in the sediment since aqueous levels were just 0.2 μg/l at site A, B, C and E, and 1.7 μg/l at site D.

The levels of Hg in the dredged sediment were considered too hazardous for any conventional disposal route[18]. An engineered monocell landfill was purposely constructed in Avondale and was designed to be suitable to take mercury contaminated waste. It was lined by an impermeable membrane that would not allow any leachate to percolate down into the underlying strata[17]. However, this landfill was not adapted to take mud paste. This necessitated the dredging contractors to mix the sediment with lime on site in appropriate hoppers and allow it to solidify over a few days. The dry cake was then transported by road and packed neatly in the landfill by compaction to take up the minimum space possible[17]. The Avondale landfill was the first and so far only hazardous waste landfill in Scotland. The proximity of the landfill to the canal, as depicted in Figure 7.2 too, was useful in that it minimised the total haulage distance covered by lorries[18]. This site has since been closed as it has served its purpose[19].

A £5.3m remediation project, carried out by I&H Brown Ltd. on the 0.25 km^2 former Nobel Westquarter Factory's site was completed in October 2006[20-21]. This project lasted 67 weeks and was undertaken to allow for the

preparation works for the building of a housing estate. This involved the removal of 300,000 m^3 of terrain, of which 75,000 m^3 was deemed contaminated[20]. The latter was subjected to onsite treatment for solidification and stabilization. This process enabled the majority of the contaminated material to be re-classed as 'stabilised non reactive hazardous waste', that was therefore suitable for disposal at a local landfill, considerably reducing disposal costs and possible secondary environmental impacts[20].

The segment of canal opposite the site was dredged and ongoing testing during the land remediation process ensured that runoff waters had permissible PTE levels for discharge into the canal. However, dredging at the adjacent sections of the Union Canal was not performed as it was out of the scope of the project[19].

The possibility of recontamination of canal sediments through surface runoff from soil where the former detonator and munitions factory stood was noted at the time of the dredging operation leading to the Union Canal's reopening[17]. This hypothesis is supported by data obtained by Cavoura as part of her Ph.D. research[22]. Ten sediment samples were collected between 17/1/12 and 23/3/12. Sampling site 1 was close to where sample E was collected, site 4 close to where sample D was collected, and site 9 close to where sample A was collected in the 2001 study[17]. Sample 10 was collected midway along the new stretch of canal built to connect the Union Canal with the Falkirk Wheel. Results obtained are listed in Table 7.3[22].

Table 7.3 Concentration (mg/kg) of mercury determined in sediments from a section of the Union Canal by Cavoura, 2012[22]

Sampling Site	Concentration of Hg (mg/kg)
10	22 ± 0.6
9	67 ± 5.6
8	122 ± 18
7	410 ± 47
6	565 ± 48
5	422 ± 107
4	199 ± 23
3	300 ± 30
2	161 ± 16
1	30 ± 3

A similar Hg distribution pattern to that observed in the 2001 survey[17] was observed along the whole stretch of canal sampled, with the exception of the low Hg concentration determined at site 4.

The distribution pattern confirms the Nobel Westquarter Factory as the likely source of Hg in the system, with a marked decrease in Hg concentration upstream (eastwards) as compared to a gradual decrease in concentration downstream (westwards). The lower concentration at site 4 was probably a result of the remediation project, but still implies a substantial contamination, relative to EQS values, and confirms the Union Canal as a potential on-going source of Hg to the Forth and Clyde Canal, which is the focus of the current work.

7.2 Aim

The aim of this work was to measure and assess factors influencing Hg distribution along the Forth and Clyde Canal and Glasgow Branch. The determination of the PT Hg levels in the original 29 canal sediments served as a preliminary quantitative analysis to obtain a general overview of the distribution of Hg. Nine sites were then selected and new sediment samples were collected, stored and handled appropriately for quantitative Hg analysis. All samples were analysed by CVAFS.

7.3 Experimental

7.3.1 Equipment

i. 4-digit weighing balance [AE200, Mettler, Leicester, UK]
ii. 4-digit weighing balance [AB204-S/FACT, Mettler Toledo, Leicester, UK]
iii. Microwave [MARSXpress™ High-Throughput Microwave Reaction System, CEM Microwave Technology Ltd., Buckingham, UK]
iv. Centrifuge [ALC 4218 CENTRIFUGE, ALC International Srl, Milano, Italy]
v. Continuous flow cold vapour generation atomic fluorescence spectrometer (CVAFS) [10.025 Millennium Merlin, P S Analytical, Kent, UK], complete with auto-sampler [CETAC ASX-510 auto-sampler, CETAC Technologies, Manchester, UK]

7.3.2 Reagents

i. Nitric Acid

(65% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

ii. Mercury Standard for ICP

(1001 mg/l in 12% (w/w) HNO_3, ρ 1.07 g/ml, Sigma-Aldrich® Company Ltd., Dorset, UK)

iii. Tin (II) chloride dihydrate

(98%, Alfa Aesar, Heysham, UK)

iv. Hydrochloric Acid

(30% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

7.3.3 Analytical Method

Preliminary quantitative analysis was carried out on the initial 29 sediment samples. Since these samples were over a year old, had been placed in plastic containers at the time of sampling, and oven dried at 30 ºC, substantial loss of Hg could have occurred. It was hoped, however, that they would show the correct concentration ratios as they have all been through the same conditions, and so serve for comparison of Hg concentration between sites. The gastropod samples from sites 3 and 5 were omitted since this work aimed at studying the mobility and distribution of Hg in sediment.

Nine locations were chosen for re-sampling. Fresh samples were collected and handled appropriately by collecting and storing in glass bottles and allowing to air dry over a number of days.

The preliminary tests were carried out on the atomic fluorescence spectrometer at the Department of Civil and Environmental Engineering at the University of Strathclyde, while the analysis of the new samples was performed on an instrument of the same model held in the Department of Chemistry at the University of Aberdeen.

7.3.3.1 Sample Digestion for Preliminary Analysis

The digestion of the sediment samples used for the preliminary analysis followed the procedure described in Section 5.2.3.1. The only difference was that

after filtration, a 10% *aqua regia* solution was prepared by dilution and taken for analysis by AFS. Further dilutions were carried out where necessary, when a sample's concentration was outside the calibration range. Dilutions were carried out using 10% *aqua regia* to avoid raising the pH too much. This procedure was in line with BS ISO 16772:2004[23].

7.3.3.2 Sample Digestion for Quantification Analysis on the new Sediment Samples

The digestion of the nine new sediment samples was carried out following an adapted version of the method suggested by the AFS instrument manufacturer: P S Analytical – Application Note 13: Mercury Determinations in Soil, Sediment & Sludge Samples[24].

This method uses an open-vessel approach, with lower temperatures and at ambient pressure, and nitric acid for digestion rather than *aqua regia*. The method was validated by determination of the Hg content of a CRM.

Nitric Acid Digestion

Using the cone and quarter technique, about 1 g of air dried sediment was accurately weighed and placed in a clean glass vial followed by 5 ml HNO_3. This was left overnight in a fume hood to allow for any vigorous reaction to subside. The cap was loosely placed on the vial to avoid airborne deposits while allowing for CO_2 to escape. This procedure was also followed with a CRM; ERM®-CC580 – Estuarine Sediment[25], using only *ca.* 0.02 g rather than *ca.* 1 g.

Microwave-Assisted Digestion

After the overnight period elapsed, the vial with its loosely held cap was placed in the microwave's open vessel carousel. The carousel could hold up to 52 vessels per run. Unlike the closed vessel carousel, locations on the open vessel carousel did not have assigned numbers for identification. The recommended temperature range of operation was such that ink would resist the heat and not evaporate, and therefore, individual vials were marked with a permanent marker. The carousel was then placed in the MARSXpress™ microwave. The infrared sensors at the base of the microwave are aligned to work only with a closed vessel carousel.

With an open vessel configuration, a temperature probe needed to be fitted in a dummy sample and plugged into the connection port situated inside the chamber itself. Samples were positioned symmetrically in the carousel to ensure homogeneous application of microwave power on all samples.

The appropriate temperature program was input and stored in the microwave for future use. The settings used are outline in Table 7.4[26].

Table 7.4 Microwave digestion program settings[26]

Microwave Parameter	Condition
Power	800 W
% Power	100
Temperature ramp time	3 minutes
Temperature control	65 ^{o}C
Hold time	20 minutes
Temperature ramp time	3 minutes
Temperature control	70 ^{o}C
Hold time	20 minutes

Upon completion of the run, the microwave automatically proceeded to a cooling down period. The carousel was then removed and placed on a bench top and each vessel was removed and placed in a fume cupboard for a few hours to allow to cool to room temperature. The cap of each vial was later securely fastened and the vials were centrifuged at 3000 g for 10 minutes.

Two grams (accurately weighed) of the supernatant digestate were collected and transferred to a new pre-weighed glass vial. To this, 20 ml of deionised water were added, thus preparing a 10% nitric acid solution. The total weight was accurately measured. These were taken for analysis by AFS. Further dilutions were carried out where necessary, when the sample's concentration was outside the calibration range. Dilutions were carried out using 5% HNO_3 to avoid raising the pH too much.

7.3.3.3 Determination of Mercury using Atomic Fluorescence Spectroscopy

Preparation of Standards

A set of Hg standard solutions with concentrations of 0.02, 0.2, 0.5, and 1 mg/kg were prepared from a 10 mg/kg working standard solution (WSS). The WSS was prepared from a 1001 mg/l Hg standard stock. All solutions were prepared in 5% HNO_3. A blank solution of 5% HNO_3 was also prepared to use as the 0 mg/kg 'standard'.

Instrument Operation

A reductant solution, made up of 2% $Sn^{II}Cl_2$ in 10% HCl, and a reagent blank solution, made up of 5% HNO_3, were prepared. The pressure of the argon used as carrier gas was set at 40 psi. The Hg lamp was switched on 2 – 3 hours before analysis was intended to start. This allowed it sufficient time to stabilize.

The AFS instrument was equipped with three aspirating tubes; one for the reductant, one for the reagent blank, and the other for the test sample. When proceeding for analysis, the instrument's peristaltic pumps were switched on through the Millennium software on a PC connected to the AFS. The instrument was made to aspirate de-ionized water from the three tubes for 10 minutes so as to serve as initial flushing of the system. This was followed by a further flushing procedure of 10 minutes, after having placed the reductant tube in the reductant solution, and the reagent blank tube and test sample tube in the reagent blank solution. Once this time elapsed, the test sample tube was affixed to the auto-sampler probe and the instrument was ready for measurement of test samples.

A measurement cycle of a test vial was divided into four stages:

- Delay time: Aspiration from vial commenced in order to prime the tubes with test sample. Any excess test sample was diverted to waste. Meanwhile, the reagent blank was mixed with the reductant in the gas/liquid separator, and gas flowed through to the detector to set the baseline. This step was set to take 15 s.
- Rise time: A switching valve was automatically activated. The reagent blank was now diverted to waste while the test sample was channelled through to

the gas/liquid separator. The gas produced after reaction with the reductant flowed through to the detector. This step was set to take 25 s. During this time, the signal rose until a steady signal was detected.

- Analysis time: This was set at 30 s, during which time the signal was steady and measurement took place.
- Memory time: The switching valve was automatically activated once more, returning to its original setting. The test sample was directed to waste while the reagent blank was allowed through. This was set at 60 s, and allowed ample time until levels fell back to baseline.

Measurement

Measurement using AFS followed a set sequence using an auto-sampler. Three replicate readings were taken for every measurement, whether for a standard, sample or blank.

In the auto-sampler rack, position 1 was reserved for the cleaning blank, while the standards' blank was placed in position 2, followed by the rest of the standards in ascending concentration order. The samples' blank was placed next, followed by the samples. The analysis sequence was as follows:

- Cleaning blank – which served as an initial washing solution
- Standards' blank – which served as the 0 mg/kg 'standard'
- Standard solutions in ascending order: 0.02, 0.2, 0.5, 1 mg/kg
- Check standard; 0.2 mg/kg
- Samples' blank
- Sample solutions

The auto-sampler probe, from rest position, went into the destined test vial and returned back once the measurement cycle was complete. Due to the detection sensitivity offered by the instrument, a cleaning blank step was inserted in the sequence after every test vial. This allowed for thorough washing of the tubing to avoid memory effects.

A check standard was run after the cleaning blank which ensued after the last calibration standard. The check standard was re-run after every nine sample vials and at the end of the sequence. The role of the check standard was to monitor for any

instrumental drift. Wherever the drift was observed to be ± 10% of the concentration of the check standard, the sequence was halted and a fresh calibration was run. The sequence was continued from the first sample vial that followed the last acceptable check standard run.

Samples that fell outside the calibration range were diluted and inserted at the end of the sequence.

7.4 Results and Discussion

7.4.1 Limit of Detection

The LOD given by the AFS instrument at The University of Strathclyde is not presented since it was only a preliminary study. The LOD given by the AFS instrument at The University of Aberdeen was 0.00691 mg/kg. This was measured in the same way as described in Section 5.3.1. This instrumental LOD was used to calculate the procedural LOD. The actual Hg concentration that could be detected in sediment samples using this method was 0.0484 μg/kg.

7.4.2 Quality Control

The performance of the method was assessed using a CRM; ERM®-CC580 – Estuarine Sediment[25]. This was not analysed during the preliminary tests but only during the analysis of the new samples. Analysis was carried out in duplicate and the concentrations of Hg obtained are listed in Table 7.5, together with the reference value and percentage recovery.

Table 7.5 Concentration of mercury (mg/kg) determined in two certified reference material (CRM) replicates and calculated % recoveries with respect to the CRM ERM®-CC580 certified value for Hg content

	CRM Certified Value			Found Value Replicate 1			Found Value Replicate 2	
PTE	mg/kg	± mg/kg		mg/kg	% Recovery		mg/kg	% Recovery
Hg	132	3		132	100		139	105

The result of replicate 1 was in line with the certified value, while the result of replicate 2 was only slightly higher, signifying that the extraction procedure and subsequent analytical determination could be deemed satisfactory.

7.4.3 Mercury Content by Atomic Fluorescence Spectroscopy

Sample digestion and analysis was carried out on a single sample portion for the preliminary tests and in duplicate for the nine new samples. The concentrations (mg/kg) of the PT Hg content determined are listed in Table 7.6. The similarity in the duplicate sample values obtained serves as an indication of the acceptable precision of the technique.

Table 7.6 Concentration (mg/kg) of mercury determined in the sediment samples analysed

	Preliminary Analysis	**Analysis of the New Samples**	
Sampling Site	**Hg (mg/kg)**	**Replicate 1 Hg (mg/kg)**	**Replicate 2 Hg (mg/kg)**
1	0.782	-	-
2	1.26	-	-
4	0.909	-	-
6	0.618	-	-
7	0.303	-	-
8	0.592	-	-
9	0.495	-	-
10	0.710	-	-
11	0.999	-	-
12	0.742	-	-
13	0.461	-	-
14	0.370	-	-
15	0.546	0.589	0.592
16	0.228	-	-
17	0.225	-	-
18	0.282	-	-
19	7.98	1.94	2.09
20	0.869	-	-
21	0.391	-	-
22	0.363	-	-
23	0.218	-	-
24	7.54	5.75	5.78
25	10.2	9.19	9.09
26	9.89	3.38	3.38
27	2.60	4.13	4.22
28	0.657	-	-
SFJ	3.23	4.36	4.42
BW	10.6	6.01	5.91
PD	1.36	2.23	2.26

With reference to the preliminary tests, only sediments samples 16, 17 and 23 had Hg levels below CEFAS (post-2004) AL 1. Samples 19, 24, 25, 26, 27, SFJ, BW

and PD were above AL 2, while the remaining samples had levels between AL 1 and AL 2. None of the new samples had levels below AL 1. Sample 15 had a concentration between AL 1 and AL 2 whereas all other samples had levels which were above AL 2. Although Hg concentrations varied between the two sets of samples, the levels in the respective samples remained in the same AL class.

The preliminary tests have revealed a widespread presence of Hg, together with particular 'hot spots' of contamination. Higher Hg levels are evident at Bowling Basin, samples 19 and 24 – 27, and the Glasgow Branch, when compared to the sediment PT Hg concentration ranges reported for the Caledonian Canal and the Crinan Canal in the 1992 British Waterways survey[14], as well as the other studies[10-13]. This implies the presence of direct anthropogenic influence.

The samples collected from the three sites in Bowling Basin (samples 1, 2 and 4) point to the presence of a local source of Hg since the concentrations obtained appear slightly higher than adjacent and most other sites. This could be related to the activity associated with the area being a harbour, notably the increased residence time of vessels. Historically, Hg was used as the biocide additive in antifouling paint. Any remnants of its presence attributed to that source are possible, but this is dependent on dredging activity that has been carried out.

The historical presence of heavy industrialisation in Glasgow is evidenced particularly by the amount of Hg determined along the Glasgow Branch, which was at the centre of the industrial zone. Contamination with Hg in the surroundings would have occurred through aerial dispersion from stack emissions[1]. The Hg concentrations of the inner city samples 10, 11 and 12 are slightly higher than Hg levels in samples from more distant sites.

The urban samples 6 to 9 and the rural samples 13 to 15 appear to have similar Hg levels. The Hg concentration at site 7 was around half that obtained at site 6 and 8. Sample 7 was collected from just upstream of the Dalmuir Drop Lock (36a), which was only installed prior to the canal's reopening in 2001. The surrounding area has seen a great increase in real estate works, which involved, amongst other works, soil and terrain shifting[27]. The original soil was removed to make way for construction and replaced with different, less contaminated soil for landscaping.

Mercury levels decrease from sample 16 eastwards, which continues until sample 18. The considerable increase in Hg concentration at sample 19 indicates the presence of a local source. The Hg concentration in sample 20 was higher than most rural samples. This may have been affected by sample 19, which was upstream, or by localised sources. After sample 20, Hg levels decreased substantially and gradually until sample 23.

Site 24 is just upstream of the Golden Jubilee Lock at the Falkirk Wheel Junction while site 25 is just downstream at a similar distance. The increase of Hg levels at samples 24 and 25 indicates that the junction of the Forth and Clyde Canal with the Union Canal at the Falkirk Wheel is serving as a source of Hg. Levels at sample 26 are also quite high, and gradually decrease until sample 28. The presence of local sources contributing to the determined Hg levels cannot be ruled out.

Sample location 15 was chosen as a background reference for the batch of new samples since it was situated somewhat midway along a stretch of rural land, and it is understood that historically it has been always so, with little direct anthropogenic influence in the vicinity[28-29]. Input of Hg into the canal in such a location was expected to be mainly from diffuse sources *e.g.* soil runoff or atmospheric deposition.

Sample 19 was also from the rural segment of the canal; however, the preliminary analysis result was substantially higher than the Hg concentration determined in the analogous new sample. Historically there was a coal pit and associated works in the vicinity of the south bank of the canal. Recent [Google Earth, 2009] aerial photography of that area revealed a clear patch of land amongst the surrounding vegetation, signifying substantial contamination of the land to the present day. Also, on the north bank there is the Craigmarloch feeder lade, which may collect contaminated soil from along a considerably large catchment area and transport it all the way down into the canal. The considerable change in Hg levels observed over time indicates that this site is quite dynamic.

Samples 24 and 25 may be scrutinized together because of their proximity. Both sets of results imply that this junction is a source of Hg into the system. Mercury levels were lower in the new samples, but the distribution ratio between

sample 24 and 25 was similar. Water entering the Forth and Clyde Canal through the Golden Jubilee Lock distributes incoming suspended sediment in a radial fashion, contaminating sediment at site 24 even though this is situated upstream. The slow water flow of about 0.1 m/s offers only slight counteraction. This may be the reason why the concentration in sample 24 appeared slightly lower than sample 25 in both instances.

There is no lock in the stretch of canal between site 25 and site 26, allowing sediment movement. Both results at site 26 indicate the presence of Hg contamination, however, the variation observed was wide. Some contamination originating from upstream sources is possible, but localised input is also likely. Temporal localised input may have contributed to the high result determined in the preliminary tests.

Sample 27 is situated further downstream and right after a flight of 11 locks from site 26 (locks 6 – 16). Movement of sediment along a lock is believed to be minimal due to their structure, and especially after such a series of locks as in this case, so the contribution of Hg from site 26 is likely to be minimal. Site 27 is surrounded by a sub-urban industrial area; this area has historically served the same purpose where there were various iron works and foundries. Mercury is present in iron works and therefore the land in the area, which contributes to soil runoff, may be contaminated.

The results at the three sites along the Glasgow Branch show that there is a consistent, considerable level of Hg contamination present. The input of Hg into the Glasgow Branch is believed to be from diffuse sources such as soil runoff due to the general urban soil contamination from historical industrial stack emissions. The Hg concentration in sample BW determined in the preliminary analysis was nearly double the concentration determined in the analogous new sample. The decrease in Hg concentration observed may be due to dredging operations at this section of the canal.

7.4.3.1 Comparison with the 1992 British Waterways Survey Data[14]

Forth and Clyde Canal

With reference to Table 7.6, the Hg concentrations determined in the new sediment samples ranged between 0.589 and 9.19 mg/kg. This has increased considerably from the 1992 reported levels, which ranged between 0.1 and 2.7 mg/kg[14]. A crucial difference between 1992 and the present is that the Forth and Clyde Canal was reopened for navigation at the turn of the century. This was coupled with another major feat – the reconnection with the Union Canal. This latter fact appears to be acting as a new and stable point source of Hg into sediments of the Forth and Clyde Canal. The highest Hg concentration in the new sediment samples, as well as in the preliminary analysis, was determined at site 25, which is just downstream of the junction with the Falkirk Wheel basin.

Another new potential point source of Hg into the canal is the Craigmarloch feeder lade that replenishes water into the canal, near sampling site 19. This feeder lade was now relevant and essential, whereas in 1992 it was not since the canal was derelict and disused. Although the Hg concentrations determined in the new samples at site 19 were within the range reported in the 1992 survey, the preliminary analysis result on the sediment from the same site was substantially higher, denoting the potential variability of the source.

Glasgow Branch

The Hg concentration range determined from the new sediment samples in the Glasgow Branch ranged between 2.23 and 6.01 mg/kg, whereas the levels reported in the 1992 survey ranged between 3 and 16.5 mg/kg[14].

Therefore, conversely to the situation with the Forth and Clyde Canal, the reopening of the canal to navigation appears to have brought about a decrease in contamination levels in sediment. This decrease is believed to be due to the dredging operations and extensive landscaping of the surroundings carried out prior to the canal's reopening. Nevertheless, it is apparent that Hg input into the canal is still occurring.

7.5 Conclusion

From the preliminary tests it was evident that there exists a widespread presence of Hg, including in rural areas. An urban/rural divide in Hg concentration was evident, similar to that observed with other anthropogenic PTEs reported in Chapter 5. However, levels of Hg were augmented at certain 'hot-spots', notably at site 19, near and downstream of the Falkirk Junction, and in the Glasgow Branch. These results were corroborated with the concentrations determined in the nine new sediment samples – all samples had levels above the CEFAS Guideline AL 1.

The sample from site 19 had Hg levels that were considerably higher than those from other rural samples nearby. The Craigmarloch feeder lade could be acting as a point source of Hg at this site. The result obtained in the preliminary tests was considerably higher than that from in the new sample, indicating that contamination at this site is present and variable.

The junction with the Union Canal at the Falkirk Wheel near site 24/25 appears to be a point source of Hg too. It is likely that the source of this Hg is contaminated soil from near the former Nobel Westquarter munitions factory in Reddingmuirhead. Sediment contaminated with Hg originating from soil runoff at this site is presumably being transported downstream. However, the levels determined in samples 26 and 27 indicate that they may be localised input of Hg from the Bonnybridge sub-urban (industrial) area.

The high levels obtained in the three Glasgow Branch sediment samples indicate the presence of a widespread and diffuse source such as soil runoff. This is likely a legacy of the heavy industrial past of this area.

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8 Methylmercury Content in Sediments of the Forth and Clyde Canal

8.1 Introduction

Methylmercury was measured in the nine new sediment samples collected for the measurement of PT Hg content (see Chapter 7). This was done because the presence of Me-Hg in sediment is of greater environmental concern due to the higher toxicity exhibited compared to elemental or In-Hg.

8.1.1 Toxicity of Methylmercury

Methylmercury is the most common organic form of Hg found in the environment. It is soluble, mobile, and has the ability to quickly enter the aquatic food chain[1]. The organic moiety of the molecule offers considerable solubility in the fat of biological tissue compared to Hg^0 or In-Hg[1]. Apart from the exhibited toxicity, the greatest concern raised by the presence of Me-Hg in the environment is its ability to bioconcentrate in living organisms and then further biomagnify up the food chain.

Concentrations in carnivorous fish at the top of food chains are biomagnified on the order of 10,000 – 100,000 times the concentrations found in ambient waters[2-3]. Such biomagnification in piscivorous fish compared with fish at lower levels of the food chain has been demonstrated[4-5]. Human exposure to Me-Hg occurs primarily through the consumption of contaminated seafood.

The toxicity of Me-Hg is higher than that of Hg^0 or In-Hg. Lethal doses for acute human oral exposure to In-Hg have been estimated to be 29 – 50 mg Hg/kg[6]. In rats, the oral LD_{50} for In-Hg ranged from 25.9 to 77.7 mg Hg/kg as mercuric chloride[7]. The deaths have been attributed to renal failure, cardiovascular collapse, and severe gastrointestinal damage[6, 8].

Lethal doses for acute human oral exposure to food contaminated with Me-Hg have been estimated to be 10 – 60 mg Hg/kg[9-10]. Neurotoxicity, especially to the brain and central nervous system, may occur at doses as low as 3 μg/kg in humans[11]. The LD_{50} for oral exposure of rats to Me-Hg compounds has been estimated at 16 mg Hg/kg (single dose)[12], 3.1 mg Hg/kg/day for 26 weeks[13], and

0.69 mg Hg/kg/day for up to 2 years[14]. The Me-Hg fatally affected the central nervous system[9, 15]. Pneumonia, nonischemic cardiomyopathy and renal failure have been reported as prominent secondary causes of death[8, 15].

The presence of Me-Hg in the environment may be due to direct anthropogenic influx or through a bacteria-mediated process of methylation of In- Hg.

8.1.1.1 Direct Input of Methylmercury

The most widely known incident involving human exposure to Me-Hg and that first shed light on the toxic effects of Me-Hg was the incident in Minamata city, Kumamoto prefecture, Japan. This branded the Me-Hg poisoning effects as the Minamata disease. The cause of the disease was first acknowledged in 1956. It was caused by the release of Me-Hg in the industrial wastewater effluent from the Chisso Corporation's chemical factory. The plant used mercury sulfate as a catalyst for the production of acetaldehyde. A side reaction led to the production of small quantities of Me-Hg. This process lasted from 1932 to 1968, when the production method was discontinued. The Me-Hg released bioaccumulated in shellfish and fish in Minamata Bay. This seafood served as a major food source for the local population[11]. Levels of Hg in seafood were found to range between 5.61 and 35.7 mg/kg. The Hg content in hair of local inhabitants that ate such seafood reached a maximum of 705 mg/kg, showing considerable further bioaccumulation[16].

However, the central government did not act, leading to a second outbreak of the Minamata disease in Kanose village, Niigata Prefecture, in 1965. Similarly to the Minamata incident, vast quantities of Me-Hg were discharged through industrial wastewater effluent from the Showa Electrical Company's chemical plant, which used the same process for acetaldehyde production. The Me-Hg released into the Agano River bioaccumulated up the food chain, contaminating fish which was a main food source for the local population[11].

Another major incident occurred in Iraq, where consumption of bread prepared with flour made from wheat and barley treated with Me-Hg as a fungicide

caused a similar poisoning outbreak. Methylmercury concentration in the wheat flour ranged from 4.8 to 14.6 mg/kg, with a mean level of 9.1 mg/kg[9].

8.1.1.2 Bacteria-Mediated Methylation of Inorganic Mercury

The Hg cycle has been described in Chapter 7, Section 7.1.1. A small portion of Hg^{II} is converted to Me-Hg. Methylation of Hg is facilitated by some strains of sulfate- and iron- reducing bacteria[17-18]. Sediments are important environments where methylation occurs[19-20].

These bacteria thrive at the geochemical interface between oxic and anoxic conditions[21]. A number of environmental factors, such as Hg^{II} concentrations, sulfide concentrations, total organic carbon, redox potential, the sediment structure, composition[22-27], and the presence of amorphous Fe^{III} (hydr)oxides and sulfate[28], are known to affect the rate of Me-Hg formation by influencing the supply of bioavailable Hg^{II} and/or the microbial activity. Methylmercury production has also been measured in the water column in lakes[29-30].

A study on the distribution of PT Hg and Me-Hg content in sediments from two sites within the Venice Lagoon in Italy[31] has shown that at the first site, which was located near a depositional area, levels of PT Hg averaged 622 ± 214 μg/kg while levels of Me-Hg averaged 1.25 ± 0.63 μg/kg, and at the other site, situated in an open area, levels of PT Hg averaged 387 ± 93 μg/kg while levels of Me-Hg averaged 0.53 ± 0.30 μg/kg. This shows that the Me-Hg content was *ca.* 0.2% of the PT Hg content at site 1 and *ca.* 0.1% of the PT Hg content at site 2.

In another study on sediments of the Venice Lagoon[32], sediment samples were collected near river mouths. At one site, levels of PT Hg averaged 1520 μg/kg, while levels of Me-Hg averaged 1.14 μg/kg. At the other site, levels of PT Hg averaged 4490 μg/kg, while levels of Me-Hg averaged 1.70 μg/kg. The river emptying near this latter site historically received effluent from a chlor-alkali plant.

In the Sacramento River Basin in California[33], which was a historically recipient of Hg from Hg mining and Au mining (where Hg was used in the recovery of Au), the highest reported level of Hg in sediments was 450 μg/kg, whereas the

highest reported level for Me-Hg was 2.84 μg/kg, although not at the same sampling site. This meant that the percentage of Me-Hg would not surpass 0.63% of PT Hg.

The low percentage of Me-Hg (≤ ~0.5%) from PT Hg in sediments originating from bacteria-mediated methylation of Hg is comparable with other studies[34].

8.1.2 Environmental Quality Standards for Methylmercury

So far, no EQS for Me-Hg in sediment has been introduced in European legislation. Directive 2008/105/EC suggests that Member States should adopt an EQS of 20 μg/kg for Hg and its compounds in sediment and/or biota[35].

Since toxicity effects arise from the biomagnification of Me-Hg rather than direct absorption from water exposure, a biota-based approach to EQSs is preferred. An EQS for biota also accounts for Hg bioavailability issues.

Commission Regulation (EC) No 466/2001 notes the toxicity posed by Me-Hg and sets a maximum level of 0.5 or 1.0 mg Hg/kg wet weight in fishery products, depending on the species[36]. The European Commission recommends that pregnant women, breast feeding women and children should limit their consumption of large predatory fish[37].

The National Research Council of the United States of America established an intake limit of 0.7 μg/kg body weight (bw) per week.

The Joint FAO/WHO Expert Committee On Food Additives (JECFA) set a provisional tolerable weekly intake (PTWI) of 1.6 μg/kg bw during their 61st meeting in 2003[38]. During the 67th meeting in 2006, the Committee noted that life-stages other than the embryo and fetus may be less sensitive to Me-Hg. Therefore, the Committee considered that intakes of up to about twice the existing PTWI would not pose any neurotoxic risk in adults, although it recommended that women of childbearing age should still not exceed the PTWI[38].

8.2 Aim

The aim of this section of work was to determine the proportion of the PT Hg content – determined in the nine new samples in Chapter 7 – that is Me-Hg, and hence by difference, also the amount of In-Hg present.

8.3 Experimental

8.3.1 Equipment

i. Weighing balance [AB204-S/FACT, Mettler Toledo, Leicester, UK]

ii. Mechanical shaker [built in-house]

iii. Centrifuge [ALC 4218 CENTRIFUGE, ALC International Srl, Milano, Italy]

iv. pH meter [HI8521, Hanna Instruments, Leighton Buzzard, UK]

v. Gas Chromatography [Hewlett Packard HP6850 GC, Agilent Technologies UK Ltd., Wokingham, UK], coupled with Inductively Coupled Plasma – Mass Spectrometer [7500 Series ICP-MS, Agilent Technologies UK Ltd., Wokingham, UK] (GC-ICP-MS)

8.3.2 Reagents

i. Hydrochloric Acid
(30% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

ii. Sodium acetate
(Anhydrous, Amresco – VWR International, Lutterworth, UK)

iii. Glacial acetic acid (AA)
(AnalaR NORMAPUR® BDH Prolabo – VWR International, Lutterworth, UK)

iv. Methanol
(AnalaR NORMAPUR® BDH Prolabo – VWR International, Lutterworth, UK)

v. Tetramethyl ammonium hydroxide (TMAH)
(25% (w/w) aqueous solution, Alfa Aesar, Heysham, UK)

vi. Sodium tetrapropylborate ($NaBPr_4$)
(Chemos GmbH, Regenstauf, Germany)

vii. Isooctane
(≥ 99.0% ACS Reagent, Sigma-Aldrich® Company Ltd., Dorset, UK)

viii. Enriched Methyl-^{201}Hg standard
(25 mg/l, Prepared and certified at Aberdeen University)

ix. Mercury (II) chloride
(≥ 99.5% ACS Reagent, Sigma-Aldrich® Company Ltd., Dorset, UK)

x. Methylmercury (II) chloride powder Sigma-aldrich UK
(Pestanal® analytical standard, Sigma-Aldrich® Company Ltd., Dorset, UK)

8.3.3 Analytical Method

This procedure was applied to the nine new samples collected for the determination of PT Hg content in Chapter 7. Preliminary quantitative analysis was carried out to obtain an indication of the Me-Hg content of each sample. This was necessary to calculate the amount of standard solution necessary to add to each sample, for the isotopic dilution mass spectrometry (IDMS) technique, which was used for more accurate quantification.

All samples were analysed using GC-ICP-MS. The blank was treated similarly to the sample solutions, but without addition of any sediment. The whole procedure was carried out in the Department of Chemistry at the University of Aberdeen.

Sample Digestion

This procedure followed the acid leaching method described by Bermejo-Barrera *et al.*[39], modified for use on sediment rather than hair. Using the cone and quarter technique, about 0.5 g of air dried sediment was accurately weighed and placed in a clean glass vial followed by 3 ml of 4% (w/w) HCl. This was shaken mechanically for 2 minutes and then centrifuged for 20 minutes at 3000 rpm. The supernatant was transferred into a new glass vial using a Pasteur pipette, while a further 2 ml of 4% (w/w) HCl were added to the residue. This was once again shaken mechanically for 2 minutes and centrifuged for 20 minutes at 3000 rpm. The supernatant was transferred to the 3 ml collected previously using a Pasteur pipette, forming a 5 ml combined extract.

Derivatization

During the centrifugation waiting time, an acetate buffer solution (sodium acetate / acetic acid) was prepared. The pH of the solution was adjusted to 3.9 ± 0.1 using TMAH and AA as necessary. Also, a 1% (w/v) $NaBPr_4$ aqueous solution was prepared and stored in a dark freezer at -20 ºC until use.

One ml from the 5 ml combined extract was transferred into a new glass vial. To this, 5 ml of pH-adjusted acetate buffer, 1 ml of 1% (w/v) $NaBPr_4$ and 1 ml of isooctane were added in the aforementioned order. The mixture was manually shaken vigorously for 5 minutes and then centrifuged for 10 minutes at 3000 rpm. The top organic layer was extracted into a GC vial using a Pasteur pipette and stored at -20 ºC until taken for analysis.

Preparation of Standards

Two separate 10 mg/kg aqueous solutions were prepared from a 934 ± 3 mg/kg (w/w aq.) $HgCl_2$ stock solution and a 9543 +/-2 mg/kg (w/w in methanol) Me-Hg chloride stock solution respectively. One ml from each 10 mg/kg solution was transferred into a separate new glass vial for derivatization following a similar procedure to that described for samples.

An aliquot of 100 µl from each separate derivatized solution was transferred to a new glass vial, together with 800 µl isooctane, to form 1 ml of a 1 mg/kg mixed WSS. A set of mixed standard solutions with concentrations of 0.1, 0.01, and 0.001 mg/kg were prepared from the 1 mg/kg mixed WSS. A blank solution of isooctane was also prepared to use as the 0 µg/l 'standard'.

Instrument Operation

The analyses were carried out on a Hewlett Packard HP6850 gas chromatograph coupled with an Agilent Technologies 7500 Series inductively coupled plasma mass spectrometer. The GC was fitted with a Rtx®-1 capillary column from Thames Restek UK Ltd. (Crossbond® 100% PDMS (polydimethyl siloxane) Silcosteel®, 30 m long, 0.59 mm internal diameter, 1 µm film diameter).

The following temperature programme was applied: the initial oven temperature was set to 50 ºC and held for the first minute, then raised to 250 ºC at a heating rate of 50 ºC/min, and held at the final temperature for 7 minutes before the oven cooled down to 50 ºC prior to the initiation of another run.

The injection volume was 1 µl and the instrument was set to splitless mode. Injection was done manually. The injector port was kept at a temperature of 240 ºC. Helium was used as a carrier gas and the column flow rate was set at 10 ml/min.

A capillary column with a carrier gas mixture – Ar, Xe and O_2, and set at 350 ml/min – was joined with the outlet of the GC column where the latter was connected to the inner tube of a transfer line. This was connected to the inner cylinder of the ICP torch at the other end. The transfer line used was 1 m long, built in-house and made of two concentric layers of Silcosteel® capillary columns. The inner tube had an internal diameter of 0.22 mm and an outer diameter of 0.53 mm. It was connected to a heating wire and a temperature probe, and set at a temperature of 220 ºC. The outer tube had an internal diameter of 1 mm and an outer diameter of 1.59 mm. It was encapsulated in a thermally insulated sheath to maintain the temperature.

The ICP was fitted with a microcentric nebulizer pump and a perfluoroalkoxy (PFA) nebulizer. A 25 µg/l Tl solution in 1% HNO_3 was continuously aspirated and mixed with the sample flow coming from the transfer line. The nebulizer flow rate and the auxiliary Ar flow rate were set at 1 l/min, while the plasma Ar flow rate was set at 16 l/min. The spray chamber was of the cyclonic type and at room temperature. The ICP was fitted with Ni cones.

The concentrations of the most abundant isotopes of Hg were determined in each standard, sample replicate and blank, with the ICP-MS. These were ^{199}Hg, ^{200}Hg, ^{201}Hg, and ^{202}Hg. Thallium, as ^{203}Tl and ^{205}Tl, was used as an internal standard. The instrument operating conditions are listed in Table 8.1.

Table 8.1 Agilent 7500 inductively coupled plasma mass spectrometry (ICP-MS) operating conditions

ICP-MS Parameters	Condition
RF Power	1380 W
Carrier Gas (Argon)	1 l/min
Dilution Mode (HMI [a])	OFF
Makeup Gas (Argon)	0.35 l/min
MicroMist Nebulizer Pump	0.3 rps [b] (≡ 1000 ml/min)
Collision Mode	OFF

[a] HMI = High Matrix Interface; [b] rps = revolution per second, where rps = ml/min x 0.0003

Measurement

Measurement using the GC-ICP-MS followed the sequence: blank, followed by the standard solutions in ascending order, then the sample solutions. The syringe was washed with isooctane initially before collecting the blank, and washed again with isooctane in between every injection. The run time between injection and elution was about 7 minutes, whereas the total time between each injection was about 10 minutes; the difference was due to the time allowed for the oven to cool back to the initial temperature.

The MS detector was set to perform a full-scan ranging from 100 to 300 AMU. The retention times of the potentially observed species in the chromatogram are as follows:

- Elemental Hg: 30 – 60 s
- Tl internal standard: 90 – 120 s
- Methyl-Hg: 130 – 175 s
- Ethyl-Hg: 180 – 200 s
- Inorganic Hg: 200 – 220 s

The respective species identified were confirmed by matching with library spectra. The respective peak areas were computed by the instrument's software on the attached computer, and subsequently recorded.

8.4 Results and Discussion

8.4.1 Preliminary Quantitative Analysis

Limit of Detection

In GC analysis, the LOD of an analyte is defined as that concentration which yields a measured peak (signal, S) that is significantly different from the background response (noise, N) given by the blank. The LOD of an analyte is determined when S/N = 3.

The instrumental LODs given by the GC-ICP-MS at The University of Aberdeen for the respective isotopic species of Me-Hg measured are given in Table 8.2.

Table 8.2 Instrumental limits of detection (µg/l) obtained for the isotopes of methylmercury (Me-Hg) determined using gas chromatography inductively coupled plasma mass spectrometry

Me-Hg Isotope	Limit of Detection (µg/l)
Me-^{199}Hg	0.203
Me-^{200}Hg	0.214
Me-^{201}Hg	0.199
Me-^{202}Hg	0.231

The instrumental LODs were used to calculate the procedural LOD value. The actual Me-Hg concentration that could be detected in sediment samples was 1.06 ng/g.

Quality Control

The performance of the preliminary quantitative analysis was assessed using a CRM; ERM®-CC580 – Estuarine Sediment[40]. Analysis was carried out on a single sample portion, using only 0.2 g rather than 0.5 g, as was used for the sediment samples. The concentration of Me-Hg obtained is listed in Table 8.3, together with the reference value and percentage recovery.

Table 8.3 Concentration (mg/kg) of methylmercury (Me-Hg) determined and calculated % recovery with respect to ERM®-CC580 certified value for Me-Hg content

	ERM®-CC580			Found Value	
Parameter	**mg/kg**	**± mg/kg**		**mg/kg**	**% Recovery**
Me-Hg	75	4		85.5	114

The result obtained was higher than the certified concentration range. This further stressed the need and importance of the IDMS technique for a more accurate quantification of the Me-Hg content.

Preliminary Determination of the Methylmercury Content in the Sediment Samples

Sample extraction and analysis was carried out on a single sample portion. The Me-Hg concentrations determined are listed in Table 8.4.

Table 8.4 Concentration (μg/kg) of methylmercury (Me-Hg) determined in the nine new sediment samples during the preliminary quantification analysis [a]

Sampling Site	Me-Hg (μg/kg)
15	1.54
19	3.13
24	10.3
25	8.59
26	9.39
27	3.29
SFJ	1.43
BW	4.03
PD	3.20

These indicative values were used to calculate the amount of enriched Me-^{201}Hg necessary to be spiked to each sample prior to extraction, as part of the IDMS technique.

8.4.2 Accurate Quantification Analysis

Isotope Dilution Mass Spectrometry using Me-^{201}Hg

The IDMS internal standard technique was applied to the CRM as well as the nine sediment samples. An example calculation for the determination of the amount of enriched Me-^{201}Hg necessary to be spiked is given using the CRM.

The CRM has a certified content value of 75 ± 4 μg/kg. Since 0.2 g was used, the actual content of Me-Hg in the test sample was 15 ng. The natural abundance of ^{201}Hg is 13.18%, while that of ^{202}Hg is 29.86%. Therefore, from those 15 ng, 1.98 ng was Me-^{201}Hg, while 4.48 ng was Me-^{202}Hg. In order to get a Me-^{201}Hg:Me-^{202}Hg ratio of 1:1, 2.50 ng of Me-^{201}Hg had to be spiked into the sediment.

A 20 μg/kg enriched Me-^{201}Hg WSS was prepared from the certified standard prepared at The University of Aberdeen. Therefore, 125 μg of WSS were required to spike 2.50 ng of Me-^{201}Hg.

This same WSS was used to spike the nine sediment samples with the appropriate amount, which was calculated from the Me-Hg concentrations listed in Table 8.4. These quantities of WSS are listed in Table 8.5.

Table 8.5 Quantity (µg) of 20 µg/kg enriched Me-^{201}Hg working standard solution (WSS) necessary to spike the respective samples for isotope dilution mass spectrometry

Sampling Site	Quantity of 20 µg/kg Me-^{201}Hg WSS to be spiked (µg)
15	7
19	13
24	43
25	36
26	39
27	14
SFJ	8
BW	17
PD	13

The 10 Me-^{201}Hg enriched samples (nine sediment samples and the CRM) were then stored in a cool place (-20 ºC) until taken for analysis.

Determination of the Methylmercury Content in the Certified Reference Material and Sediment Samples enriched with Me-^{201}Hg

Sample extraction and analysis was carried out in duplicate. The Me-Hg concentrations obtained, together with the calculated mean values, are listed in Table 8.6.

Table 8.6 Concentration (µg/kg) of methylmercury (Me-Hg) determined in the Me-^{201}Hg isotopically enriched sediment samples analysed

Sample	Me-Hg (µg/kg)		
	Replicate 1	Replicate 2	Mean
CRM	74.6	72.8	73.7
15	3.20	3.68	3.44
19	4.76	4.60	4.68
24	15.1	13.1	14.1
25	9.24	10.2	9.69
26	11.3	8.14	9.70
27	5.98	6.18	6.08
SFJ	8.63	12.3	10.5
BW	12.8	12.1	12.5
PD	8.99	8.68	8.83

The mean % recovery of the CRM was now 98.3% of the certified value, and well within the certified range, indicating a considerable improvement over the preliminary test result, as well as the fact that this method offers acceptable accuracy. The use of IDMS as an internal standard method meant that the Me-Hg results of the sediment samples listed in Table 8.6 are more accurate that those listed in Table 8.3 and Table 8.4. The similarity in the duplicate sample values obtained serves as an indication of the acceptable precision of the technique.

The Me-Hg concentrations of all sediment samples determined with the Me-^{201}Hg enrichment were higher than when determined in the preliminary analysis. The greatest difference was observed with sample SFJ (~7 times higher), followed by sample BW (~3 times higher), sample PD (~2.8 times higher) and sample 15 (~2.2 times higher).

The In-Hg content of each sample was determined through a simple calculation whereby the mean Me-Hg content (see Table 8.6) was subtracted from the PT content of Hg (see Table 7.6 Analysis of the new samples). The calculated In-Hg content in the sediment samples is listed in Table 8.7.

Table 8.7 Calculated inorganic mercury (In-Hg) concentrations (µg/kg) present in the nine new sediment samples analysed

Sampling Site	In-Hg (µg/kg)
15	588
19	2010
24	5750
25	9140
26	3370
27	4170
SFJ	4380
BW	5950
PD	2240

The PT Hg content can therefore be subdivided into the % of Me-Hg and In-Hg. These are listed in Table 8.8.

Table 8.8 Percentage of methylmercury (Me-Hg) and inorganic mercury (In-Hg) present in the nine new sediment samples analysed

Sampling Site	% Me-Hg	% In-Hg
15	0.58	99.42
19	0.23	99.77
24	0.25	99.75
25	0.11	99.89
26	0.29	99.71
27	0.15	99.85
SFJ	0.24	99.76
BW	0.21	99.79
PD	0.39	99.61

The results clearly show that the Hg present in the sediment samples is overwhelmingly in the inorganic form. In comparing the PT Hg and Me-Hg levels obtained in this study with those in literature[31-34], the levels of Me-Hg in top layer sediments never surpasses a few µg/kg, irrespective of the amount of PT Hg present.

This may be due to low levels of the methylating bacteria present in the sampling stratum – at the sediment-water interface, which is mainly oxic – since these bacteria thrive near anoxic conditions.

8.5 Conclusion

The overall low levels of Me-Hg obtained in all sediment samples analysed indicate that soil runoff is not a source near these areas. No historical records of the presence of industries which produced or made use of Me-Hg along the entire canal could be found. The levels of Me-Hg were < 0.59% of the PT Hg present and determined in Chapter 7. The Me-Hg present is likely an *in situ* product of natural bacteria-mediated methylation of the In-Hg present.

The importance of the IDMS method has been highlighted by the fact that a more accurate result of the Me-Hg content of the CRM analysed was obtained.

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9 Organotin Content in Sediments of the Forth and Clyde Canal

9.1 Introduction

The organotin compounds MBT, DBT and TBT were measured alongside Me-Hg in the same nine new sediment samples. This was done because, similar to Hg, the presence of these organotin compounds in sediment is of greater environmental concern due to their higher toxicity exhibited, compared to elemental or inorganic Sn.

9.1.1 Toxicity of Organotin Compounds

The biocidal ability of trisubstituted organotin compounds were discovered in the late 1950s at the Institute of Organic Chemistry TNO, Utrecht, The Netherlands, and their first application was as a timber preservative some years later[1].

The effectiveness of organotins as biocides contributed to the rapid widespread incorporation of these compounds into various products, causing organotins to enter the environment and ecosystems through various routes[1]. Organotins were subsequently used in fungicides, miticides, nematocides, ovicides, rodent repellents and antifouling paints. Tributyltin, triphenyltin and tricyclohexyltin exhibit the greatest toxicity towards organisms, making them the most commonly used organotin compounds for biocidal purposes[1].

Inorganic tin is generally considered as being sparingly toxic[1-2], but the toxicity of organotins varies greatly, depending on the number of substituted organic groups, as well as their type, on the tin centre[1].

The general trend observed is that any trisubstituted organotin, R_3SnX, exhibits the greatest toxicity towards living organisms. Disubstituted organotins, R_2SnX_2, exhibit less toxicity while monosubstituted organotins, $RSnX_3$, exhibit even less toxicity. The anionic X group is independent of the biocidal activity of the organotin cation except when it itself is toxic; in such cases, the deleterious effect of the biocide compound is further enhanced[1]. It however tends to affect the properties like volatility and solubility of the parent organotin[2]. Tetrasubstituted organotins

exhibit a delayed toxic effect on organisms, possibly following degradation to a trisubstituted compound[1].

Toxicity depends not only on the level of substitution but also varies widely depending on the nature of the R groups, whether aliphatic or aryl, and the chain length of the attached groups[1]. Some examples of common side groups on trisubstituted organotins are listed in Table 9.1[1].

Table 9.1 Side groups on trisubstituted organotins and their target organisms[1]

Side Chain Groups	Spectrum of Target Organisms
$-CH_3$	Insects
$-C_2H_5$	Mammals
$-C_4H_9$	Fish, Algae, Mussels, Molluscs, Fungi
$-C_6H_5$	Fungi, Molluscs, Fish
Cyclo-C_6H_{11}	Mites, Fish

Toxicity is typically expressed in terms of the median lethal dose (LD_{50}), which is the amount of a compound required to kill half a test population. The LD_{50} values for rats of some organotins used as biocides are listed in Table 9.2[2].

Table 9.2 A list of median lethal dose (LD_{50}) values (mg/kg) of various organotin compounds on rats[2]

Organotin Compound	LD_{50} (mg/kg)
Me_3SnCl	9-20
Me_2SnCl_2	74-237
Et_3SnCl	10
Et_2SnCl_2	66-94
Bu_3SnCl	122-349
Bu_2SnCl_2	112-219
$BuSnCl_3$	2200-2300
Bu_4Sn	>4000
Oct_4Sn	50000

Maximum mammalian toxicity is reached by a trisubstituted organotin with ethyl functional groups. The most toxic organotin compound to mammals reported is

Et_3SnOAc with a LD_{50} of 4 mg/kg for rats. It is presumed that the acetoxy anion group, *X*, plays a part in the biocidic effect of the compound.

The maximum toxicity for most marine organisms, in particularly invertebrates, is reached by trisubstituted organotins with butyl functional groups. The LD_{50} and the array of target organisms decreases drastically after an n-alkyl chain length of C_5, such that octyltin derivatives are essentially non-toxic[1].

9.1.2 Industrial Applications of Organotin Compounds

Tin's various organometallic derivatives exhibit a wide array of different physical, chemical and biological properties, placing Sn amongst the widest commercially used elements[1]. This meant that elemental tin is considered as one of the world's major pollutants, and is found in various compounds, locations and levels of contamination.

The main industrial use of organotin compounds is as the principle active-ingredient in commercially available biocide products. Due to the diverse properties exhibited by the various compounds, different organotins have been used to fit different purposes.

Organotin compounds of the type R_3SnX with short-chain n-alkyl groups, cyclohexane or phenyl rings as the substituted derivatives are the most widely used due to their high biocidic effectiveness. In instances where milder biocides are required, organotins bearing slightly longer n-alkyl chains or of the type R_2SnX_2 and $RSnX_3$ are typically used[1]. Table 9.3[1] lists the organotin compounds used in some of the most common commercially available biocides.

Organotins of the type R_4Sn have little commercial value due to their low reactivity and hence effectiveness. Their main use is as precursors in the production of the less-alkylated and more ecotoxic derivatives[1-2].

Table 9.3 Application as a biocide and respective optimal organotin compound used[1]

Industrial Application	Organotin Class and Compound
Antifouling paint (Wide range Biocide)	R_3SnX ; R = Bu, Ph
Agrochemicals (Fungicide, Insecticide, Miticide, Antifeedant)	R_3SnX ; R = Bu, Ph, Cy
Wood preservation (Insecticide, Fungicide)	R_3SnX ; R = Bu
Materials protection [stone, leather, paper] (Fungicide, Algicide, Bactericide)	R_3SnX ; R = Bu
Impregnation of textile (Insecticide, Antifeedant)	R_3SnX ; R = Ph
Poultry farming (Dewormer)	R_2SnX_2 ; R = Bu

The other important industrial uses of organotin compounds are in the plastics and glass industries. Trisubstituted organotins are seldom used due to fear of potential intoxication from leaching after their application, but rather the disubstituted and monosubstituted types, as shown in Table 9.4[1]. These are the major applications of organotin compounds nowadays; organotins for biocidal purposes are estimated to make up only about 20% of total organotin production[3].

Table 9.4 Application other than as a biocide and respective ideal organotin compound used[1]

Industrial Application	Organotin Class and Compound
PVC stabilizers (Stabiliser against thermal and photo degradation)	R_2SnX_2 ; R = Me, Bu, Oct $RSnX_3$; R = Me, Bu, Oct
Glass treatment (Precursor for tin (IV) oxide films on glass)	R_2SnX_2 ; R = Me $RSnX_3$; R = Me, Bu

Organotins are added during production of polyvinyl chloride (PVC) as a stabilizer for protection against photo and thermal degradation[1]. Polyvinyl chloride is one of the most widely used types of plastic, typically used as electrical cable insulation, toys, hoses, tubing for wastewater, drainage water as well as potable water, packaging material and food and beverage containers. The PVC decomposes upon heating to 180 ºC – 200 ºC or on prolonged exposure to light due to the loss of HCl from the polymer, causing discoloration and embrittlement[4], as depicted in Figure 9.1[4].

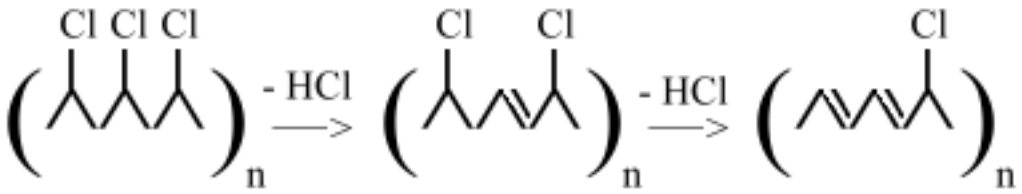

Figure 9.1 Dehydrochlorination of polyvinyl chloride[4]

The methyl, butyl or octyltin monoalkylated and dialkylated derivative compounds are the preferred organotin stabilizers, usually having the anionic group isooctyl mercaptoacetate[5]. The organotin additives inhibit atmospheric oxidation of the polymer by acting as antioxidants; the isooctyl mercaptoacetate replaces the chloride on the polymer, thus preventing the dehydrochlorination reaction. Between 5 to 20 g of the organotins are added to every kg of PVC during production[1].

In the glass industry, disubstituted or monosubstituted organotins are added to the molten glass during production, where they undergo pyrolytic oxidation due to the high temperatures forming a surface layer of tin (VI) oxide. The SnO_2, like other metallic oxides, acts as a semiconductor. Sometimes it may be doped with fluoride, which replaces O^{2-}, therefore acting as an electron donor to reduce the resistivity of SnO_2 to serve better its purpose as an electron and thermal conductor[6]. Its wider use is in the production of photovoltaic panels[6].

9.1.2.1 Organotin-based Antifouling Paints

Fouling is an unwanted growth of biota, typically barnacles and algae, on a surface immersed in water. Vessel hulls not protected by antifouling systems may gather 150 kg/m^2 of fouling in less than six months of being at sea[7].

The increased surface area and weight caused by fouling can lead to an increase of fuel consumption of up to 40 to 50%, due to the increase in resistance to movement[7]. Tributyltin has proved to be an extremely efficient and widely used marine biocide in antifouling paints[1-2,7-8]. It reduces hull roughness (which includes roughness due to fouling, but also structural roughness on a clean hull, smoothed by the use of self-polishing copolymer (SPC)-TBT paint[8]), hence preventing drag (thus allowing faster sailing and saving on various shipping-related expenses), improving

manoeuvrability and speed per unit of fuel, and lowering environmental pollution by carbon dioxide and sulfur dioxide emissions[9]. Some relevant calculations were given by Abbott *et al.*[8].

An antifouling paint consists of a film-forming material consisting of a biocidal ingredient and a pigment[1]. Small amounts of the biocide molecules leach into the water from such paint when applied to a vessel's hull. Upon release, the biocide repels the settling of fouling organisms on the vessel's bottom.

When TBT was introduced into antifouling paints, it was considered less harmful than biocides used in antifouling systems at the time, such as dichlorodiphenyltrichloroethane, arsenic and mercury compounds. Tributyltin is a broad spectrum algaecide, fungicide, insecticide and miticide, and proved to be toxic and effective in killing the organisms that would attach to the ship's hull.

TBT was first introduced in the 1960s in the form of free association paints, typical of that time, and re-introduced in the 1970s in its SPC formulation. The use of SPC-TBT antifouling paints was widespread and by the mid-1980s, they were used on over 80% of the commercial fleet, and were also widely popular and applied onto small vessels like pleasure craft[7].

Free Association Antifouling Paint

The biocide molecules are physically mixed and dispersed in the resinous paint matrix, from which they leach into the sea water, killing any marine organisms that attach to the hull[1]. The release rate for the biocide in the free association paint into the water is uncontrolled and tends to be high initially after application, and decreases with time, with the effect wearing off in 18 to 24 months[7].

The reason for the observed release rate is that initially, biocide molecules situated close to the sea water interface can easily diffuse out, whilst the biocide molecules situated deeper inside the paint coating layer have a longer distance to travel through the resinous matrix. Apart from this, the microchannels in the paint surface can become clogged up, for example by aragonite[1], hindering the release of biocide molecules into the water. The leaching of TBT from free association paints is depicted in Figure 9.2[7].

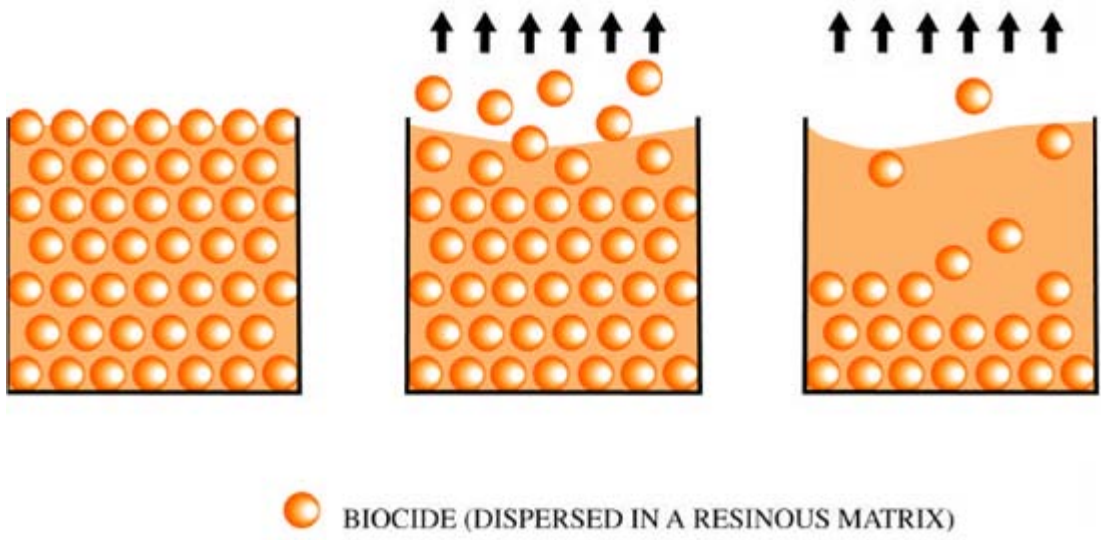

Figure 9.2 Release of biocide in free association antifouling paint[7]

Self-Polishing Copolymer Paint

In the SPC paints, the organotin biocide molecules are chemically bonded to the polymer base. The leaching rate of these paints is controlled because the biocide is released when sea water reacts with the surface layer of the paint. Sea water hydrolyses the TBT copolymer bond and the TBT biocide and copolymer resin are slowly released at a controlled rate. Once the surface layer is worn off, the reaction to release the biocide is repeated with the newly exposed underlying layer[7].

The result is that the leaching rate is the same throughout the life of the paint, providing a uniform antifouling performance for the duration of the paint's lifetime[1]. Since the biocidic components are only released at the paint's surface, the release rate is relatively lower than that of free association paints, making it possible for vessels bearing the SPC-TBT paint to spend 3 to 5 years without the need for repainting[1, 7-8]. The leaching of TBT from SPC paints is depicted in Figure 9.3[7].

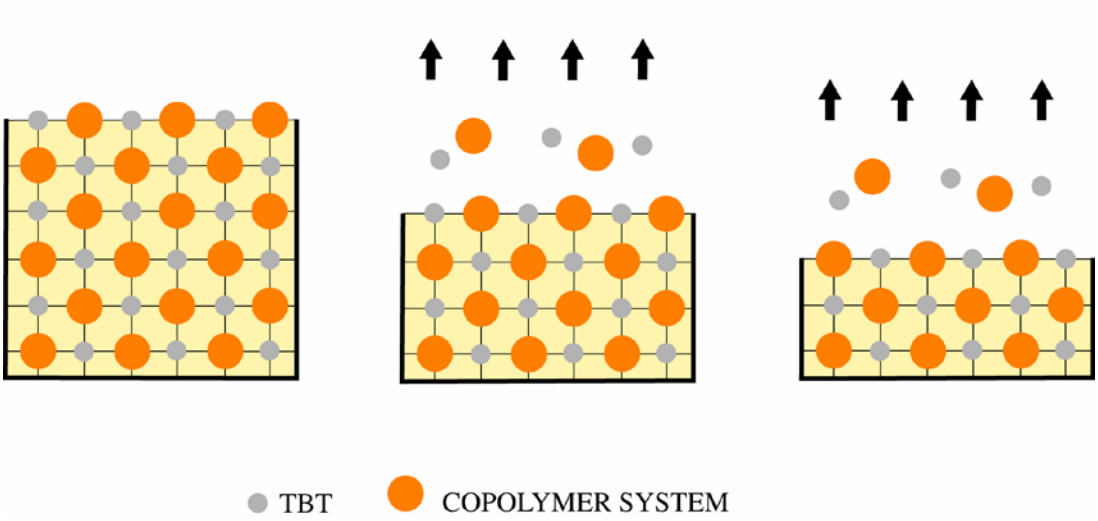

Figure 9.3 Release of biocide in self-polishing copolymer paint[7]

A typical polymer base that was used for the formation of the copolymer with TBT was the methacrylate polymer. The repeating unit of the copolymer structure is shown in Figure 9.4[3], where a –O-CH_3 moiety was replaced by a –O-TBT moiety. Water hydrolyses the bond between the tin core of TBT and the polymer, forming a hydroxide on both ends.

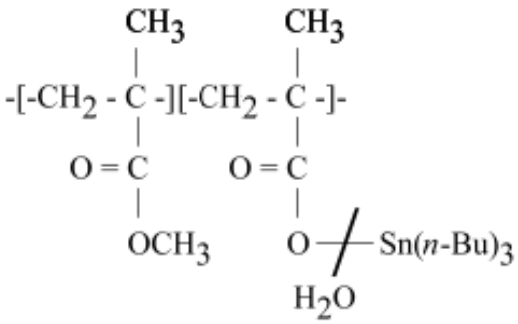

Figure 9.4 Methacrylate tributyltin copolymer[3]

Ecotoxicity of Tributyltin

Apart from being toxic to humans, the main problem exhibited by TBT was its persistence in the marine environment[7]. It exhibits chronic and acute poisoning towards a wide array of aquatic organisms even at low concentrations of 1-2 ng/l[1]. Lethal concentrations are in the range of 0.04 - 16 µg/l for short-term exposures on marine invertebrates[1].

Hulls freshly painted with self-polishing copolymer paints used to leach TBT at a rate of 6 mg (of Sn) per cm^2 per day. This reduced over the span of some weeks to the ideal leaching rate of 1.6 µg (of Sn) per cm^2 per day[10].

Thus during the peak years of TBT use, the amount introduced into Earth's water must have been extraordinary! Indeed, it has been claimed to be the most widely deliberately introduced pollutant into the environment[10]. The TBT levels in sediment in enclosed areas such as ports and harbours, which are called at by numerous small and large vessels, and in narrow waterways frequented by numerous leisure crafts, and especially in areas near shipbuilding facilities and dockyards where hulls were painted and repainted, are expected to be very high. Such areas do not have a high rate of water turnover and offer a high sediment surface area. Accumulation of high levels can occur over the years because TBT's residence time in the water column is relatively short and it tends to adsorb to the sediment[11]. In contrast, levels in sediment in open seas are expected to be low due to dispersion of TBT by the ocean currents.

The ecotoxic effects of TBT have been widely documented. It was the collapse of the oyster industry in Arcachon, France, in the late 1970's due to shell deformations and reproductive failure[10, 12] which provided the first evidence of the ecological impact of TBT after serving its purpose as an antifouling agent.

Other documented effects of TBT in the environment are reviewed by Diez *et al.*[10]; these are: impotence of neogastropods and gastropods; reduction of dogwhelks population; retardation of growth in mussels; and immunological dysfunction in fish. The most widely studied effect is imposex in certain species of gastropods, whereby females develop the male organs and thus would be unable to reproduce, causing a rapid decline in population numbers.

Laboratory tests performed on rats gave no evidence of teratogenic or carcinogenic effects but showed that DBT and TBT cause immunosuppression[10]. Little has been reported on the toxicity of TBT and other organotins on humans. Symptoms reported for dialkyltin and trialkyltin poisoning are vomiting, headache, visual defects and electroencephalographic abnormalities, as well as irritation of the skin and respiration tract[10].

Laboratory tests showed that MBT, DBT and TBT affected adversely natural killer lymphocytes in human blood, which are a primary immune defensive system against tumour and virally infected cells. Thymocytes, which are also part of the human immune system, have shown a decrease in viability of about 50% after 24 hour *in vitro* exposure to 500 µg/l of DBT[10, 13]. It has been suggested that the toxic effects of organotin compounds in the blood may be amplified if in conjunction with exposure to other pollutants, such as polychlorinated biphenyls (PCBs)[10].

Based on the studies carried out on mammals, particularly rats, a tolerable daily intake (TDI) of the TBT cation for humans has been calculated by Penninks[14], which is 0.25 µg/kg bw per day. This value incorporates a safety factor of 100 due to uncertainties in extrapolating values obtained from laboratory tests on rats to humans. For DBT, the TDI value quoted is approximately 0.25 µg/kg bw per day too, although more thorough testing needs to be carried out to confirm a definite value[15]. The USEPA (1997) adopted a value of 0.3 µg/kg bw per day as an oral reference dose for TBT oxide, while the WHO adopted the value of 0.25 µg/kg bw per day of TBT as a reference for exposure which is not likely to cause any adverse effects to humans.

Humans risk exposure to organotins via three primary routes: mainly, ingestion of contaminated foodstuffs like seafood coming from areas that were subjected to TBT in antifouling paints; from exposure to household items containing organotin compounds which leach, in particular through contact with skin; or from drinking liquids stored in organotin-treated PVC containers. Although the latter two routes are expected to be quite unlikely, or if present would be in very low doses, the same cannot be said for the ingestion route. In areas subjected to heavy TBT contamination, ingestion of seafood may well contributed to an intake which is above the suggested TDI value. In the majority of countries, no data on organotin levels in seafood products are available[15]. Unfortunately, normal cooking procedures does not convert the organotins compounds to the sparingly toxic inorganic tin[16].

Organotins contamination in settled urban dust has been claimed by Decelis and Vella[17], implying that when organotin contaminated sediments are dredged and dumped in landfills, the dust that becomes airborne after drying may be carrying organotins. This becomes more worrying if the airborne particulate matter is

< 2.5 μm in diameter ($PM_{2.5}$), since such microparticles are able to penetrate through the respiratory system into the lungs and bloodstream.

Studies on concentrations of organotins in human tissue have been sparse. Takahashi *et al.*[18] found concentrations of MBT, DBT, TBT in the livers of Japanese people in the concentration ranges 14 – 22 μg/kg wet weight, 45 – 78 μg/kg wet weight, and < 2 μg/kg wet weight respectively; while a study on Poles[13] reported that total butyltin content was between 2.4 – 11 μg/kg wet weight. It may be the case that persons found with relatively high levels of organotins in their bodies have a high seafood based diet and perhaps live close to busy ports and dockyards.

9.1.3 Fate of Organotin Compounds in Water

Organotin compounds may undergo a variety of biogeochemical reactions, producing a range of new organotin species or inorganic tin compounds. Figure 9.5[19] illustrates the various pathways that are possible once an organotin molecule enters the aquatic environment. The main reactions organotins can undergo in the water are:

(a) Bioaccumulation, which can lead to imposex in some gastropod species;

(b) Deposition or release from biota on death or consumption by another organism;

(c) Biotic (by bacteria) and abiotic (catalytical and photocatalytical) degradation;

(d) Photolytic degradation and resultant free radical production.

Less common chemical transformation reactions that may occur are:

(e) Biomethylation by bacteria;

(f) Demethylation by bacteria;

(g) Disproportionation reactions.

The presence of other chemicals coming from other sources of pollution, particularly sulfur and mercury, may lead to:

(h) Sulfide-mediated disproportionation reactions;

(i) SnS formation;

(j) Formation of methyl iodide by reaction of dimethyl b-propiothetin (DMPT) with aqueous iodide and subsequent;

(k) CH_3I methylation of SnX_2;

(l) CH_3I methylation of SnS;

(m) Transmethylation reactions between organotins and mercury.

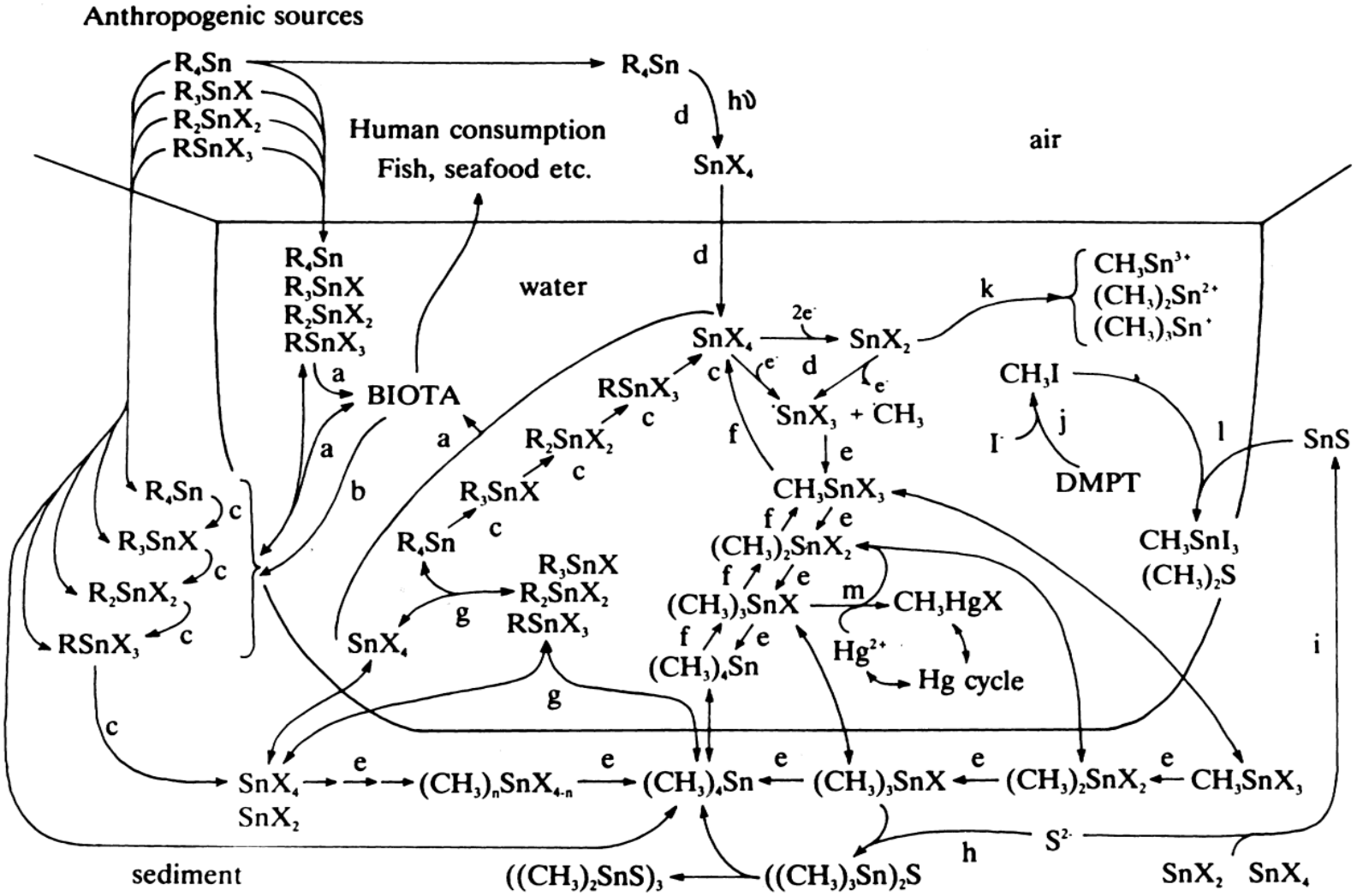

Figure 9.5 Various biogeochemical reaction pathways possible for organotin molecules in the aquatic environment[19]

Thus, TBT can be broken down in water into less toxic DBT and MBT[1, 7] and possibly inorganic tin (IV)[20]. The rate of degradation may vary considerably, from a few days to a few weeks, depending on the conditions present[7]. Due to the hydrophobicity of the TBT molecules, unless they are degraded, they tend to adsorb to the sediment and accumulate.

Decomposition of TBT is slower when in sediment as compared to when in water, especially if oxygen is completely excluded – TBT may remain present for several years[7]. Embayment areas, especially ports and estuaries, which receive considerable amounts of silt from upstream, all have a considerable amount of sediment which further serves as a sink for TBT, leaving the area possibly contaminated for several years[7].

Although DBT and MBT are less toxic than TBT, they still are of environmental concern[1]. Both compounds exhibit a greater solubility in water than TBT, potentially giving rise to extensive water contamination[1]. Both MBT and DBT may be present as a result of direct input by leaching from PVC materials[1], but such a contribution is negligible in practical terms on many occasions. Unlike TBT, MBT and DBT are not prime ingredients in antifouling paint.

Occurrence of these two compounds in the environment is generally due to TBT degradation. The butyltin degradation index (BDI) is a useful mathematical tool used to predict whether TBT contamination is recent by calculating the ratio between the two main degradation products (DBT and MBT) over the parent compound (TBT)[10]. This is given in Equation 9.1[10].

Equation 9.1 Butyltin Degradation Index (BDI)

$$BDI = \frac{[MBT] + [DBT]}{[TBT]}$$

Following the determination of the concentration of MBT, DBT and TBT at any particular site, a BDI of less than 1 would indicate a possible recent TBT input, whereas a BDI greater than 1 would signify that TBT input had stopped some considerable time ago[10]. Unfortunately, this is only indicative because the rate of degradation of TBT depends critically on the environmental conditions present.

9.1.4 Legal Restrictions on Tributyltin Compounds

Organotin compounds were initially classified as dangerous substances about 35 years ago within the European Economic Area, when Council Directive 76/464/EEC[21] was issued. Many countries, including the UK, outlawed the use of TBT-based self-polishing antifouling paints for small vessels such as yachts and pleasure boats under 25 metres in length in the 1980s due to the increase in scientific evidence for the ecotoxicology of TBT[7]. The harmful environmental effects of organotin compounds were first brought to the attention of the Marine Environment Protection Committee (MEPC) of the International Maritime Organization (IMO), the United Nations Agency concerned with the safety of shipping and the prevention of marine pollution, in 1988. In 1990, the MEPC adopted Resolution 46[22] which recommended all World Governments to outlaw TBT-based paints on vessels smaller than 25 m in length and eliminate the use of such paints bearing a leaching rate of more than 4 μg TBT per cm^2 per day.

EU Commission Directive 1999/51/EC[23] banned the placing of organotin-based biocide paints on the European internal market, as well as inhibiting further application of such products on the hulls of vessels less than 25 m in length, on any vessel that navigates on inland waterways and lakes, and on cages, floats, nets and any other appliances or equipment used for fish or shellfish farming, and on any totally or partly submerged appliances or equipment. Subsequently, EU Commission Directive 2002/62/EC[24] extended the ban to all vessels irrespective of their length and intended use, be it marine, coastal, estuarine, inland waterways or lakes. Organotin compounds are also prohibited from being used as substances or as constituents of preparations for use in treatment of industrial waters.

In 2001, the IMO convened the International Convention on the Control of Harmful Antifouling Systems on Ships[7] and adopted a resolution, legally binding amongst its members, calling for a global prohibition on the application of organotin compounds which act as biocides in antifouling systems on ships by 1 January 2003. All ships were not to apply or re-apply organotin compounds which act as biocides in antifouling systems. Use of TBT was completely banned as of 1 January 2008, where upon vessels were prohibited from applying such compounds on their hulls, external parts and surfaces, or else must bear a coating that forms a barrier to such

compounds leaching from the underlying non-compliant antifouling systems. This applies to all vessels (including fixed and floating platforms, floating storage units, and floating production storage and offtake units)[7].

Even though the use and presence of organotin compounds as biocides in paints has nowadays been banned nearly globally, there may still exist numerous vessels that have not adhered to the law, particularly in developing countries, and which will thus still be contributing to environmental damage. The assessment of the extent of such ecotoxicological damage caused, especially by their widespread use in past years, is an ongoing process. Modern antifouling paints are now based on copper compounds and pesticides.

CEFAS issues AL Guidelines for TBT. Original and recently revised (2004) guideline EQS values are listed in Table 9.5[25]. No change was made to AL 1, but AL 2 was lowered. There exists no ALs for DBT or MBT.

Table 9.5 Existing and Revised (2004) Action Level Guideline values established by CEFAS[25]

Parameter	Action Level 1 (pre-2004) mg/kg	Action Level 2 (pre-2004) mg/kg	Action Level 1 (post-2004) mg/kg	Action Level 2 (post-2004) mg/kg
TBT	0.100	1.00	0.100	0.500

All values refer to dry weight

The Surface Water (Dangerous Substances) (Classification) (Scotland) Regulations 1998[26], S/I 1998/250 (S.9), sets down EQS values for the concentration of TBT in inland waters at 0.02 µg/l, which is a widely agreed benchmark[8], and for coastal waters and relevant territorial waters at 0.002 µg/l. These values are similar to those in the UK Surface Waters (Dangerous Substances) Regulations 1997[27], S/I 1997/2560, for England and Wales. The WFD Daughter Directive 2008/105/EC[28] set a new lower EQS value of 0.0015 µg/l for TBT compounds (as the TBT cation) in inland surface waters and other surface waters.

It is evident that EQS values for TBT in waters are far lower than those in sediment. This reflects the fact that, whereas TBT is sequestered in sediment, it exerts its toxic effects when dissolved as it is more mobile and bioavailable.

9.1.5 Organotin Compounds in the Environment

Reported TBT levels are usually highest near areas where anthropogenic activities related to pleasure boating or shipping were located, such as marinas, ports, harbours, ship-building yards and ship-repairing yards. For example, levels of TBT in sediments from the shipyard canals of Gdansk, Poland, ranged from 2.6 to 40 mg/kg[29].

In a study on estuarine superficial sediments from Gipuzkoa, Spain, the determined MBT ranged from 102 to 340 mg/kg, DBT ranged from 17.8 to 84.1 mg/kg, while TBT ranged from 5.93 to 649 mg/kg. The authors report their highest TBT value for a sediment sample collected where a shipyard was located[30]. There appears to have been considerable degradation of TBT into DBT and particularly to MBT in most other locations.

Tributyltin levels reported in other studies include finding a maximum of 45 mg/kg in an enclosed bay in South Korea[31] and a maximum of 178 mg/kg in the Grand Harbour of Malta[32]. Levels of TBT found in the sediments from German Baltic Sea marinas ranged from 0.57 to 17.0 mg/kg[33].

In a study by Bangkedphol *et al.*[34], sediment and water samples were collected in 2007 from two sites within the Forth and Clyde Canal – Port Dundas and Bowling Basin – and analysed for TBT and DBT. Results reported for Bowling Basin showed that TBT in sediment (162 µg/kg) was much higher than in water (0.85 µg/l); DBT was not detected in sediment but was found at 1 µg/l in water. At Port Dundas, TBT in sediment was 149 µg/kg, while in water was found at 0.2 µg/l; DBT in sediment was 108 µg/kg and in water was 0.19 µg/l. This study confirms that organotin compounds are mainly found adsorbed to sediments rather than in solution, as frequently reported in literature[11].

9.2 Aim

The aim of this work was to determine the TBT content, as well as the degradation products DBT and MBT, in sediments from nine selected sites along the Forth and Clyde Canal and Glasgow Branch. This served to assess the persistence of these compounds in the system.

9.3 Experimental

9.3.1 Equipment

i. Weighing balance [AB204-S/FACT, Mettler Toledo, Leicester, UK]

ii. Mechanical shaker [built in-house]

iii. Centrifuge [ALC 4218 CENTRIFUGE, ALC International Srl, Milano, Italy]

iv. pH meter [HI8521, Hanna Instruments, Leighton Buzzard, UK]

v. Gas Chromatography [Hewlett Packard HP6850 GC, Agilent Technologies UK Ltd., Wokingham, UK], coupled with Inductively Coupled Plasma – Mass Spectrometer [7500 Series ICP-MS, Agilent Technologies UK Ltd., Wokingham, UK] (GC-ICP-MS)

9.3.2 Reagents

i. Hydrochloric Acid
(30% for trace analysis, Sigma-Aldrich® Company Ltd., Dorset, UK)

ii. Sodium acetate
(Anhydrous, Amresco – VWR International, Lutterworth, UK)

iii. Glacial acetic acid
(AnalaR NORMAPUR® BDH Prolabo – VWR International, Lutterworth, UK)

iv. Tetramethyl ammonium hydroxide
(25% (w/w) aqueous solution, Alfa Aesar, Heysham, UK)

v. Sodium tetrapropyl borate
(Chemos GmbH, Regenstauf, Germany)

vi. Isooctane
(≥ 99.0% ACS Reagent, Sigma-Aldrich® Company Ltd., Dorset, UK)

vii. Monobutyltin Chloride
(97%, Acros Organics – Fisher Scientific, UK Ltd., Loughborough, UK)

viii. Dibutyltin Chloride
(97%, Acros Organics – Fisher Scientific, UK Ltd., Loughborough, UK)

ix. Tributyltin Chloride
(95%, Acros Organics – Fisher Scientific UK Ltd., Loughborough, UK)

9.3.3 Analytical Method

The sample digestion and derivatization, as described in Section 8.2.3.3, served also to extract organotins in the same test sample that was then taken for analysis of Me-Hg.

The analysis of organotins was carried out in tandem with the analysis of Me-Hg on the GC-ICP-MS instrument. Organotins were only determined on the test samples which had been spiked with enriched Me-^{201}Hg standard. The same isooctane blank used for Me-Hg analysis was used.

Preparation of Standards

A combined stock solution of 1000 mg/l of MBT, DBT and TBT was prepared from the respective commercially available material. A 100 mg/l WSS was prepared by dilution, from where standard solutions of concentrations 2, 4, 6, 8 and 10 mg/l were later prepared. All solutions were made up using chromatography grade isooctane.

Instrument Operation

The same instrument, GC column, and GC and ICP-MS settings as described in Section 8.2.3.3 were used since analysis of organotins was performed in tandem with that of Me-Hg.

The concentrations of the most abundant isotopes of Sn were determined in each standard, sample replicate and blank, with the ICP-MS. These were ^{118}Sn and ^{120}Sn. Thallium, as ^{203}Tl and ^{205}Tl, was similarly used as the internal standard.

Measurement

The m/z scan range that the MS was set to perform covered the range necessary for organotin detection. The MBT, DBT and TBT elute in the aforementioned order and each peak was identified from their specific retention times, which were 4.30 – 4.60 min, 5.70 – 6.00 min and 6.95 - 7.25 min respectively. These were matched with library spectra. The respective peak areas were computed by the software on a PC connected with the instrument and subsequently recorded.

9.4 Results and Discussion

9.4.1 Limit of Detection

The instrumental LODs given by the GC-ICP-MS at The University of Aberdeen for the respective isotopes of the organo-Sn species determined were measured in the same way as described in Section 8.4.1. These are given in Table 9.6.

Table 9.6 Instrumental limits of detection (μg/l) obtained for the isotopes of organotin compounds determined using gas chromatography inductively coupled plasma mass spectrometry

Organotin Isotope	Limit of Detection (μg/l)
MBT-^{118}Sn	0.106
MBT-^{120}Sn	0.114
DBT-^{118}Sn	0.107
DBT-^{120}Sn	0.109
TBT-^{118}Sn	0.114
TBT-^{120}Sn	0.118

The instrumental LODs were used to calculate the procedural LOD values. The actual concentrations that could be detected in sediment samples for the respective organotin compounds were MBT (0.550 μg/kg), DBT (0.541 μg/kg) and TBT (0.580 μg/kg).

9.4.2 Quality Control

In the absence of the availability of a CRM with certified values of MBT, DBT and TBT in sediment samples, two sediment samples (15 and SFJ) were spiked with 50 μl from the 100 mg/l mixed WSS. This concentration was selected so as to be much higher than the levels expected to be present in the samples. These spiked samples were then subjected to the same procedure as test samples. The recoveries of Sn species from the spiked samples are given in Table 9.7.

Table 9.7 Recovery of monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) from the spiked samples

Sample	MBT (mg/kg)		DBT (mg/kg)		TBT (mg/kg)	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
15	10.1	10.2	10.2	10.0	10.1	10.1
SFJ	10.1	10.0	10.1	10.2	10.4	10.3

The results obtained were within 5% of the spiked amount. Taking into account possible contribution from the respective organotin compounds already present in the samples, this serves as a good indication that the derivatization and extraction methods were sufficiently suitable.

9.4.3 Determination of the Organotin Content using Gas Chromatography Inductively Coupled Plasma Mass Spectrometry

Analysis for the organotin compounds was carried out in duplicate. The concentrations of MBT, DBT and TBT obtained are listed in Table 9.8.

Table 9.8 Concentration of monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) determined in the sediment samples analysed

Sampling Site	MBT (µg/kg)		DBT (µg/kg)		TBT (µg/kg)	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
15	35.2	41.8	46.1	52.2	40.2	56.1
19	46.5	53.4	56.1	59.4	68.3	60.3
24	51.7	48.3	68.3	75.3	84.6	72.4
25	49.2	47.1	43.5	54.1	103	95.8
26	34.6	44.9	54.5	60.7	78.7	86.3
27	28.8	36.6	45.6	57.9	84.8	76.2
SFJ	26.7	30.5	46.7	52.5	168	154
BW	31.3	39.4	50.1	47.2	196	182
PD	67.8	75.8	116	110	147	138

The very low results obtained are comparable with the data published by Bangkedphol *et al.*[34] on the canal sediments. The Port Dundas results appeared quite

similar between studies. This may have been due to the fact that no remediation work has been carried out on the area, which remains derelict to this day. Unfortunately, no samples from Bowling Basin were analysed for organotin compounds in the current work.

Total content of organotin compounds in the Forth and Clyde Canal samples appears to be slightly lower than that from the Glasgow Branch. The current determined TBT levels in samples 15, 19, 24, 26 and 27 are below the current CEFAS AL 1 EQS value of 100 μg/kg. The result obtained from sample 25 appears to be borderline with this value. The three samples from the Glasgow Branch appear to surpass this value, but do not come close to CEFAS's AL 2 EQS value of 500 μg/kg. There exist no EQS values for DBT and MBT.

The BDI values for the nine sediment samples analysed are calculated and given in Table 9.9.

Table 9.9 Butyl degradation index for the nine sediment samples analysed

Sampling Site	Butyltin Degradation Index
15	1.81
19	1.67
24	1.55
25	0.97
26	1.17
27	1.04
SFJ	0.48
BW	0.44
PD	0.75

The BDI values for the sediment samples from the Forth and Clyde Canal are slightly higher than those from the Glasgow Branch. Samples SFJ and BW had the lowest BDI values, reflecting the fact that proportionally more TBT was found in these samples than MBT and DBT combined together. The BDI value of PD found was similar to that reported by Bangkedphol *et al.*[34] for the same site, which was 0.72.

The relatively higher content of TBT, coupled with the lowest BDI values for samples collected from site SFJ and BW may suggest a recent TBT input in the currently navigable part of the Glasgow Branch. Nevertheless, preservation of historical TBT cannot be ruled out since the overall quantities were small. An analogous situation was reported by Bangkedphol *et al.*[34], where only TBT was determined in the Bowling Harbour sediment.

9.5 Conclusion

Historical records did not reveal the presence of industrial or smaller scale activities near the banks of the canal that produced or made use of these organotin compounds. The low levels of MBT, DBT and TBT determined in the sediments further supports the hypothesis that the surrounding soil is not contaminated and that their presence is not linked to soil runoff. The presence of these compounds in sediments is commonly attributed to the direct consequence of the application of TBT-based antifouling paints onto vessels' hulls.

The low levels found are likely a result of a coincidence of factors: the canal was closed for navigation at the time when TBT-based paint was placed on the market, and therefore historical input is thought to have been limited; the extensive dredging that took place prior to the canal's reopening is likely to have removed most of the historical organotin compounds that were present; the absence of a stable source such as soil runoff serves at maintaining at present levels low; and that current use is limited if none at all.

The BDI index values obtained, particularly in samples SFJ and BW, may imply that there could have been recent input of TBT. This could also be implied from the study by Bangkedphol *et al.*[34] at Bowling Basin. However, the presence of historical TBT having been preserved should not be underestimated, as well as the fact that the overall low levels of TBT, DBT and MBT may infer uncertainty to the results.

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10 Conclusion and Further Work

10.1 Conclusion

This study aimed to obtain a broad picture of the overall status of the Forth and Clyde Canal system just over a decade after it was re-opened for navigation. The canal sediments potentially act as a sink and store of inorganic and organometallic PTE contaminants. Under the right conditions, PTEs may become labile and therefore the sediments could also act as a source. The extensive catchment areas of the canal meant that it is liable to receive considerable quantities of material influx via runoff from the banks, and therefore, the state of the canal reflects the state of the surrounding environment. The canal's course flows through urban, sub-urban and rural areas. Some urban areas near Glasgow have been impacted heavily with historical industrial activities. The canal also receives input from the vessels that navigate in the canal, although this contribution is likely to be comparatively much less than soil runoff.

The Forth and Clyde Canal and the Glasgow Branch leading to the Port Dundas Basin from the Stockingfield Junction in Maryhill were subdivided into approximately 2 km intervals to designate sampling locations. Initial sampling was carried out in 2010 when a total of 28 samples were collected in the Forth and Clyde Canal and another three from the Glasgow Branch. Sampling sites 3 and 5 in the Forth and Clyde canal consisted of numerous gastropods only; no sediment was collected.

The 31 samples were initially analysed for their PT content of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn. The results obtained from the sediment samples served as an initial determination of maximum concentrations of potentially mobile PTEs present. The fractionation pattern of these 10 PTEs were determined through application of the modified BCR sequential extraction protocol to the sediment samples.

An overview of the distribution of Hg was obtained following analysis of the PT Hg concentration in the same 29 sediment samples. This served as a preliminary

quantitative analysis only since substantial loss of Hg could have occurred, because the samples were not initially destined for Hg analysis. Nine sites were then selected for re-sampling and new sediment samples were collected in 2012. These were stored and handled appropriately for quantitative Hg analysis.

These same nine new sediment samples were used for the determination of Me-Hg, MBT, DBT and TBT.

An urban/rural divide in the PTE content of sediments was clearly evident, except for Fe. Levels of PT Fe content were about 50 g/kg. Iron is widely abundant in soils. The evenly distributed high levels of Fe indicated that soil runoff was a main source of sediment in the canal. This high level of geogenic Fe present appeared to be masking any potential anthropogenic contribution.

Sediments collected from the urban areas of the canal had higher quantities of all the other measured PTEs than those from rural areas. This almost certainly reflected the contaminated status of the surrounding urban soils along the banks of the canal; a legacy of anthropogenic contribution from the heavy industrial past of Glasgow.

A widespread presence of As and Pb was observed along the canal, particularly along the urban segment. This is typical for these PTEs since they are commonly dispersed via air deposition. Arsenic was a common product of flue gas emitted from furnace stacks, whereas Pb was emitted by petrol vehicular exhaust until recently (2000). Some exceptionally high results of Pb were obtained at specific sites. This reflected input from point sources that could be traced back using historical records.

The levels of Cd determined were very low, barely detectable at times, indicating that this PTE was not involved in any former industrial process in the vicinity of the canal. Some Cr and Ni are naturally present in soils, but the respective levels were augmented at specific sites close to former industrial plants that made use of them, such as at site BW for Cr, where there was a tanning industry, and at site 15 where there was a nickel works.

Copper and Zn are naturally abundant in soils, but are also widely used metals in industry, leading to a widespread anthropogenic contamination. Their

levels in sediments collected from urban areas were higher than in rural areas. Manganese is also naturally abundant in soil. Industrial use of Mn is more limited compared to metals such as Cu, Fe and Zn, although its presence was evident in higher quantities in urban sediments.

This study showed that locks act as effective physical barriers in hindering sediment movement along the canal. This is seen by having large differences in PTEs originating from one location and another situated on the other side of a lock, but not when found in an interlock segment.

The gastropods collected are freshwater species. The gastropods from site 3, within Bowling Harbour, are likely subject of considerable bioaccumulation. The striking difference in PTE levels obtained between the two gastropod samples is worth mentioning since these were only about 150 m apart, albeit separated by a lock. The gastropods were collected live, and their presence in such high numbers indicated that sediment dynamics in both locations were rather low-key, allowing their population to grow and, particularly those at site 3, the ability to adapt to withstand the levels of PTEs determined.

Sequential extraction following the modified BCR protocol was then applied to the 29 sediment samples to obtain information on metal binding forms and hence on the potential mobility, bioavailability and toxicity that the PTEs present may infer to biota. The mobility order given by the sequential extraction work carried out on the sediments collected was: Cd / Mn / Zn > Ni > Cu / Pb > As / Cr / Fe > Sn.

The low levels of Cd limit the environmental hazard. However, a small proportion of Ni, as well as some Pb, As and Cr may be potentially labile. These PTEs may be harmful if biota is exposed to considerable amounts. The other labile PTEs are unlikely to cause any toxic effects at the levels present.

Interestingly, sequential extraction revealed considerable amount of Mn in the exchangeable phase, symptomatic of the reduction of $Mn^{IV}O_2$, which originates from surface soil runoff, due to the presence of anoxic conditions in the top sediment. This demonstrated how shallow the surface oxic layer is and the relative ease of exposure of the anoxic layer by churning from currents, contributing to the release of reduced, mobile, PTEs into the water body.

Whereas the remediation work carried out as part of the reopening of the canal served to remove considerable quantities of PTEs from the canal, the reconnection with the Union Canal at the Falkirk Wheel has had an opposite effect with regards to Hg since the junction appears to be acting as a new point source for Hg. The Hg in sediments of the Forth and Clyde Canal downstream of the Falkirk Wheel Junction is likely to be originating from land that historically housed a munitions and detonator factory in Reddingmuirhead near Polmont. This Hg is likely being transferred into the Union Canal via soil runoff and transported downstream into the Forth and Clyde Canal.

Input from soil runoff does not appear to be a source of Me-Hg and organotin compounds in the Forth and Clyde Canal. No historical records of their industrial production or use in the vicinity of the canal could be found. This was reflected in the very low levels determined in sediments. The presence of Me-Hg can be attributed to *in situ* natural bacteria-mediated methylation of In-Hg. The levels of Me-Hg were < 0.59% of the total Hg present. This is similar to typical levels reported in literature for such natural production.

Presence of organotin compounds in canals is typically a result of application of TBT-based antifouling paint on vessels' hulls. In time, TBT degrades to DBT and later MBT. The reason for the low levels present in these sediments is believed to be two-fold: the canal was closed for navigation in 1963, around the time when TBT-based paint was placed on the market; and, the canal sediments were extensively dredged prior to the canal's reopening in 2000, and still are dredged periodically to ensure a navigable depth. Therefore, historically it is likely that the input of TBT was small, and without current sources of organotin compounds, the levels may continue to decrease following further dredging operations.

Overall, the current determined PTE levels (except Hg) are lower than those determined by British Waterways in a survey they carried out in 1992. The canal was derelict at that time, and has since been dredged prior to its reopening. It is likely that there was some accumulation *in situ* at that time; however, the general current status

appears to indicate that there still is considerable input of PTEs as a result of polluted urban soils. Present determined levels are generally higher than EQS values.

Further remediation and rehabilitation work needs to be focused at source, *i.e.* on the terrain surrounding the banks of the canal. This would restrict the amount of PTEs that enter the canal.

10.2 Further Work

The sampling locations selected were determined by dividing the canal into 2 km segments in order to collect a representative number of samples over the entire stretch. No consideration of the contamination status of the soil on the banks surrounding the canal was taken at the time of sampling.

A more in-depth study of the canal sediments is warranted, focusing on 'areas of interest', *i.e.* locations indicated in the current research to be associated with different types of historical industrial activities in the vicinity of the canal or found to have high analyte concentrations. This could be augmented by sampling the soil on the banks of the canal and compare PTE levels with those obtained in the sediments. Similarity in results would confirm that soil runoff is the major contributor of sediment at that particular location.

Only the heavier constituent particles of soil sediment out in the water column upon runoff into the canal. The lighter particle size fractions remain suspended. The assessment of the canal's status could be widened to include also analysis of dissolved PTE content as well as PTE levels adsorbed onto suspended matter. The PTE levels are expected to be highly variable since they are dependent on influx, which is a highly dynamic process. To account for this factor, numerous sampling sessions should be organised over a number of weeks/months.

The bioavailability of PTEs could be studied further by including analysis on biota. This could be done by using indigenous species such as gastropods, which in this study have shown to be potential receptors for bioaccumulation, or by using biomonitors such as mussels on strings or fish in cages.

Another aspect to look into is to assess the dynamics of sediment movement. Some areas of the canal are in a trough and thus will receive considerably more input from soil runoff than areas which are level. Other areas are elevated and cannot

receive soil runoff. Therefore, sediment at these sites must have been transported downstream. The sediment transport across a lock, and particularly, along interlock segments, also could be further assessed.

Some Mn was found in an exchangeable form throughout the canal, albeit in relatively higher quantities in the urban sediments. Further insight is needed to determine what compound Mn is present, in an attempt to determine its source.

A Appendix

This appendix holds the various tables of raw data which have been pictorially represented within the text of this thesis in the appropriate sections.

A.1 From Chapter 5

A.1.1 From Section 5.3.3

The concentration (mg/kg) and SD (± mg/kg) of the 10 PTEs determined in the gastropod samples, which are represented in Figure 5.1, are listed and sub-divided into Table A.1 and Table A.2. The aforementioned tables also contain the respective calculated % RSD.

Table A.1 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of As, Cd, Cr, Cu and Fe in gastropods from site 3 and 5 in the Forth and Clyde Canal

	As			Cd			Cr			Cu			Fe		
Sample	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**
3	66.6	3.3	4.95	8.36	1.18	14.1	197	14	7.11	1810	551	30.4	91900	4890	5.32
5	28.0	2.0	7.14	< LOD	-	-	76.8	4.6	5.99	140	5	3.57	15500	1390	8.97

Results represent mean ± 1 SD, n=3.

Table A.2 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Mn, Ni, Pb, Sn and Zn in gastropods from site 3 and 5 in the Forth and Clyde Canal

	Mn			Ni			Pb			Sn			Zn		
Sample	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**
3	1740	85	4.89	97.4	18.0	18.5	3750	934	24.9	478	19	3.97	1750	129	7.37
5	1380	71	5.14	35.8	3.1	8.66	93.8	12.8	13.6	2.66	1.17	44.0	407	45	11.1

Results represent mean ± 1 SD, n=3.

A.1.2 From Section 5.3.4

The concentration (mg/kg) and SD (± mg/kg) of the 10 PTEs determined in the sediment samples, which are represented in Figures 5.2 to 5.11, are listed and sub-divided into Table A.3 and Table A.4. The aforementioned tables also contain the respective calculated % RSD.

Table A.3 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of As, Cd, Cr, Cu and Fe in Forth and Clyde Canal and Glasgow Branch sediments

	As			Cd			Cr			Cu			Fe		
Sample	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**
1	60.5	3.6	5.95	5.46	4.62	84.6	197	46	23.4	261	12	4.60	60600	3550	5.86
2	35.2	0.3	0.85	1.02	0.13	12.7	389	4	1.03	296	6	2.03	58900	402	0.68
4	84.1	1.1	1.31	0.588	0.125	21.3	190	5	2.63	315	3	0.95	60700	797	1.31
6	58.4	4.5	7.71	1.49	0.05	3.36	126	8	6.35	256	22	8.59	44800	3120	6.96
7	39.8	1.7	4.27	< LOD	-	-	117	8	6.84	183	7	3.83	49200	1100	2.24
8	58.7	3.1	5.28	1.33	1.01	75.9	118	13	11.0	158	8	5.06	72100	3990	5.53
9	80.8	6.0	7.43	2.87	2.74	95.5	93.5	8.5	9.09	122	8	6.56	54000	2600	4.81
10	88.1	1.0	1.14	3.18	0.17	5.35	135	10	7.41	211	2	0.95	58600	1070	1.83
11	90.0	2.8	3.11	1.49	0.07	4.70	159	4	2.52	154	6	3.90	51700	761	1.47
12	77.3	0.6	0.78	1.20	0.50	41.7	137	3	2.19	156	29	18.6	47500	1680	3.54
13	16.9	0.2	1.18	< LOD	-	-	101	5	4.95	73.3	4.0	5.46	52600	1700	3.23
14	18.2	0.7	3.85	< LOD	-	-	92.9	6.0	6.46	137	5	3.65	63600	1720	2.70
15	14.9	0.3	2.01	0.931	0.702	75.4	94.0	12.8	13.6	149	4	2.68	50700	423	0.83
16	10.8	0.5	4.63	< LOD	-	-	57.5	3.9	6.78	100	10	10.0	59500	1960	3.29
17	7.78	0.34	4.37	0.451	0.037	8.20	76.8	2.6	3.39	122	7	5.74	51100	1660	3.25
18	13.7	0.3	2.19	0.642	0.191	29.8	87.3	2.9	3.32	121	2	1.65	56100	362	0.65

19	5.54	0.34	6.14	< LOD	-	-	48.7	2.4	4.93	95	1.7	1.79	53300	744	1.40
20	6.52	0.17	2.61	< LOD	-	-	44.8	3.0	6.70	39.3	1.4	3.56	35800	1140	3.18
21	10.1	0.4	3.96	< LOD	-	-	57.0	1.7	2.98	66.3	3.3	4.98	41500	1260	3.04
22	16.5	1.9	11.5	< LOD	-	-	70.7	5.7	8.06	94.9	0.2	0.21	58900	593	1.01
23	12.8	0.7	5.47	< LOD	-	-	64.3	2.9	4.51	79.3	8.9	11.2	38100	1800	4.72
24	14.9	0.1	0.67	0.778	0.154	19.8	494	3	0.61	137	57	41.6	52200	200	0.38
25	19.5	0.3	1.54	5.37	0.51	9.50	883	11	1.25	309	5	1.62	58600	521	0.92
26	11.5	0.3	2.61	< LOD	-	-	639	2	0.31	124	1	0.81	56000	478	0.85
27	19.2	0.3	1.56	< LOD	-	-	778	12	1.54	290	3	1.03	49700	699	1.41
28	16.9	1.4	8.28	< LOD	-	-	231	23	9.96	69.9	8.3	11.9	47200	4130	8.75
SFJ	169	1	0.59	11.0	4.5	40.9	472	4	0.85	618	9	1.46	55800	222	0.40
BW	219	2	0.91	9.40	0.55	5.85	756	8	1.06	588	10	1.70	55100	859	1.56
PD	79.7	0.3	0.38	3.23	0.64	19.8	270	7	2.59	323	7	2.17	60100	327	0.54

Results represent mean $\pm$ 1 SD, n=3.

< LOD denotes that levels are below the instrumental limit of detection.

Table A.4 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Mn, Ni, Pb, Sn and Zn in Forth and Clyde Canal and Glasgow Branch sediments

	Mn			Ni			Pb			Sn			Zn		
Sample	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**	**mg/kg**	**± mg/kg**	**% RSD**
1	2070	66	3.19	77.2	21.2	27.5	694	26	3.75	20.5	1.5	7.32	1400	83	5.93
2	776	8	1.03	71.8	5.9	8.22	518	3	0.58	27.2	0.5	1.84	1020	15	1.47
4	2180	21	0.96	74.1	1.2	1.62	591	19	3.21	25.4	1.5	5.91	1600	8	0.50
6	1010	68	6.73	73.0	5.3	7.26	381	29	7.61	28.2	3.2	11.3	1500	110	7.33
7	1160	31	2.67	72.7	3.3	4.54	257	13	5.06	19.1	0.7	3.66	1030	31	3.01
8	2410	126	5.23	71.6	5.4	7.54	328	17	5.18	20.3	2.1	10.3	1200	64	5.33
9	4410	404	9.16	59.8	3.4	5.69	573	23	4.01	30.8	5.3	17.2	1600	93	5.81
10	4460	78	1.75	68.9	3.1	4.50	451	13	2.88	32.5	1.1	3.38	2590	52	2.01
11	2060	86	4.17	51.5	0.8	1.55	446	23	5.16	24.3	1.2	4.94	1500	59	3.93
12	1690	82	4.85	54.1	1.1	2.03	338	51	15.1	19.6	0.9	4.59	1070	56	5.23
13	1010	19	1.88	46.2	2.1	4.55	185	7	3.78	10.3	3.3	32.0	469	9	1.92
14	981	37	3.77	99.0	3.3	3.33	245	8	3.27	13.9	0.6	4.32	1050	30	2.86
15	873	14	1.60	134	4	2.99	495	16	3.23	24.8	0.8	3.23	1020	39	3.82
16	860	24	2.79	76.2	3.0	3.94	152	6	3.95	9.78	0.3	3.07	676	26	3.85
17	951	25	2.63	72.1	2.1	2.91	173	2	1.16	12.9	0.9	6.98	691	23	3.33
18	908	6	0.66	73.0	0.8	1.10	184	5	2.72	30.2	0.9	2.98	778	22	2.83

19	1290	18	1.40	47.0	0.7	1.49	168	5	2.98	14.0	1.2	8.57	486	16	3.29
20	766	10	1.31	42.0	2.2	5.24	93.9	1.1	1.17	5.79	1.67	28.8	318	31	9.75
21	1670	52	3.11	55.1	1.4	2.54	227	14	6.17	8.63	0.93	10.8	328	11	3.35
22	2060	34	1.65	60.3	0.8	1.33	241	4	1.66	15.4	2.7	17.5	613	56	9.14
23	720	33	4.58	54.1	2.1	3.88	212	1	0.47	14.7	0.7	4.76	503	24	4.77
24	1010	8	0.79	76.6	2.6	3.39	235	5	2.13	12.6	0.5	3.97	660	10	1.52
25	1030	8	0.78	73.4	0.6	0.82	2740	56	2.04	122	7	5.74	2610	86	3.30
26	881	8	0.91	68.1	0.8	1.17	149	38	25.5	5.36	0.23	4.29	704	7	0.99
27	1020	9	0.88	67.6	2.2	3.25	2460	91	3.70	98.1	3.1	3.16	2270	51	2.25
28	866	76	8.78	68.4	5.7	8.33	118	8	6.78	8.66	0.51	5.89	288	24	8.33
SFJ	1370	12	0.88	154	1	0.65	1220	66	5.41	65.6	0.3	0.46	3640	146	4.01
BW	1190	13	1.09	93.1	2.5	2.69	1040	17	1.63	77.1	0.7	0.91	3640	41	1.13
PD	1210	4	0.33	104	4	3.85	553	15	2.71	41.0	0.7	1.71	2270	14	0.62

Results represent mean $\pm$ 1 SD, n=3.

A.2 From Chapter 6

A.2.1 From Section 6.5.3

The concentration (mg/kg) and SD (± mg/kg) of the 10 PTEs determined in the sediment samples, which are represented in Figures 6.2 to 6.11, are listed and sub-divided into Table A.5 to Table A.14. The aforementioned group of tables also contain the respective calculated % RSD.

Table A.5 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of As from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

As	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	0.834	0.033	3.96	21.7	0.2	0.92	4.82	0.27	5.60	23.2	1.2	5.17	50.6
2	1.52	0.13	8.55	9.84	0.22	2.24	1.25	0.21	16.8	13.3	1.0	7.52	25.9
4	1.98	0.23	11.6	31.0	0.6	1.94	7.48	0.56	7.49	21.1	1.0	4.74	61.6
6	2.05	0.14	6.83	27.2	1.7	6.25	3.94	0.16	4.06	17.2	1.0	5.81	50.4
7	1.38	0.09	6.52	7.32	0.02	0.27	< LOD	-	-	11.6	0.7	6.03	20.3
8	2.05	0.19	9.27	20.2	0.2	0.99	1.24	0.01	0.81	25.2	0.8	3.17	48.7
9	1.52	0.03	1.97	21.6	0.3	1.39	0.746	0.090	12.1	24.8	1.5	6.05	48.7
10	1.82	0.02	1.10	35.1	1.4	3.99	4.02	0.39	9.70	29.4	0.9	3.06	70.0
11	0.837	0.066	7.89	27.8	1.8	6.47	2.38	0.11	4.62	49.1	0.7	1.43	80.1
12	0.865	0.037	4.28	24.4	2.5	10.2	3.71	0.37	9.97	41.7	0.7	1.68	70.7
13	0.0812	0.0057	7.02	3.44	0.17	4.94	< LOD	-	-	13.5	0.2	1.48	17.0
14	0.111	0.003	2.70	4.55	0.200	4.40	0.174	0.054	31.0	13.0	0.5	3.85	17.8
15	0.393	0.033	8.40	3.42	0.33	9.65	0.706	0.066	9.35	9.08	0.60	6.61	13.6
16	0.171	0.015	8.77	1.97	0.12	6.09	< LOD	-	-	8.38	0.22	2.63	10.5
17	0.298	0.007	2.35	1.68	0.04	2.38	0.180	0.059	32.8	5.14	0.17	3.31	7.30
18	0.314	0.022	7.01	2.75	0.05	1.82	< LOD	-	-	11.4	2.6	22.8	14.5

19	0.0542	0.0059	10.9	0.860	0.077	8.95	< LOD	-	-	4.22	0.13	3.08	5.13
20	0.189	0.010	5.29	1.97	0.04	2.03	< LOD	-	-	5.91	0.42	7.11	8.07
21	0.0448	0.0043	9.60	1.87	0.09	4.81	0.893	0.03	3.36	7.44	1.09	14.7	10.2
22	0.155	0.006	3.87	3.44	0.21	6.10	1.05	0.07	6.67	10.2	0.7	6.86	14.8
23	0.305	0.004	1.31	3.54	0.11	3.11	< LOD	-	-	12.0	2.5	20.8	15.8
24	0.0559	0.0062	11.1	< LOD	-	-	< LOD	-	-	5.8	0.1	1.72	5.86
25	0.0713	0.0021	2.95	2.16	0.03	1.39	< LOD	-	-	5.69	0.02	0.35	7.92
26	0.187	0.017	9.09	0.860	0.036	4.19	< LOD	-	-	7.97	0.2	2.51	9.02
27	0.377	0.010	2.65	6.0	0.100	1.67	0.771	0.093	12.1	9.57	0.56	5.85	16.7
28	0.343	0.002	0.58	5.04	0.07	1.39	< LOD	-	-	9.96	0.37	3.71	15.3
SFJ	7.58	0.31	4.09	73.7	1.4	1.90	9.98	0.36	3.61	52.3	4.8	9.18	144
BW	9.12	0.27	2.96	93.0	3.7	3.98	11.1	0.3	2.70	82.1	10.9	13.3	195
PD	2.10	0.04	1.90	22.6	0.4	1.77	4.79	0.4	8.35	35.0	1.0	2.86	64.5

< LOD denotes that levels are below the instrumental limit of detection.

Table A.6 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Cd from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Cd	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	0.581	0.013	2.24	0.755	0.029	3.84	< LOD	-	-	0.0685	0.023	33.6	1.40
2	0.835	0.020	2.40	0.847	0.025	2.95	< LOD	-	-	0.0776	0.016	20.6	1.76
4	0.696	0.019	2.73	0.832	0.013	1.56	< LOD	-	-	0.0740	0.0164	22.2	1.60
6	1.07	0.04	3.74	1.00	0.03	3.00	< LOD	-	-	0.159	0.025	15.7	2.23
7	0.416	0.027	6.49	0.366	0.014	3.83	< LOD	-	-	< LOD	-	-	0.782
8	0.875	0.008	0.91	0.770	0.004	0.52	1.10	0.29	26.4	0.101	0.086	85.1	2.85
9	0.56	0.04	7.14	0.906	0.058	6.40	< LOD	-	-	0.162	0.048	29.6	1.63
10	1.31	0.04	3.05	2.06	0.08	3.88	< LOD	-	-	0.225	0.015	6.67	3.60
11	0.493	0.139	28.2	1.53	0.09	5.88	< LOD	-	-	0.170	0.038	22.4	2.19
12	0.689	0.027	3.92	0.902	0.098	10.9	< LOD	-	-	0.0635	0.0270	42.5	1.65
13	0.344	0.020	5.81	0.484	0.021	4.34	< LOD	-	-	< LOD	-	-	0.828
14	0.567	0.007	1.23	0.617	0.010	1.62	< LOD	-	-	< LOD	-	-	1.18
15	0.865	0.012	1.39	0.719	0.263	36.6	0.0847	0.0092	10.9	0.175	0.031	17.7	1.84
16	0.616	0.006	0.97	0.510	0.039	7.65	< LOD	-	-	< LOD	-	-	1.13
17	0.530	0.001	0.19	0.367	0.036	9.81	0.456	0.038	8.33	< LOD	-	-	1.35
18	0.428	0.010	2.34	0.194	0.008	4.12	0.0446	0.0055	12.3	0.279	0.104	37.3	0.946

19	0.586	0.005	0.85	0.357	0.020	5.60	0.0208	0.0065	31.3	< LOD	-	-	0.964
20	0.304	0.014	4.61	0.131	0.011	8.40	< LOD	-	-	< LOD	-	-	0.435
21	0.270	0.009	3.33	< LOD	-	-	< LOD	-	-	1.08	0.52	48.1	1.35
22	0.522	0.007	1.34	< LOD	-	-	0.0452	0.0041	9.07	0.440	0.233	53.0	1.01
23	0.473	0.016	3.38	< LOD	-	-	0.0644	0.0061	9.47	1.07	0.11	10.3	1.61
24	0.0260	0.0019	7.31	0.318	0.002	0.63	< LOD	-	-	< LOD	-	-	0.344
25	0.238	0.025	10.5	0.475	0.053	11.2	< LOD	-	-	< LOD	-	-	0.713
26	0.579	0.006	1.04	0.731	0.029	3.97	< LOD	-	-	< LOD	-	-	1.31
27	2.23	0.05	2.24	0.878	0.168	19.1	0.228	0.011	4.82	1.42	0.04	2.82	4.76
28	0.243	0.008	3.29	< LOD	-	-	< LOD	-	-	< LOD	-	-	0.243
SFJ	3.14	0.09	2.87	1.05	0.07	6.67	0.389	0.027	6.94	1.13	0.29	25.7	5.71
BW	4.33	0.08	1.85	1.43	0.04	2.80	0.411	0.073	17.8	1.42	0.22	15.5	7.59
PD	1.31	0.01	0.76	0.818	0.104	12.7	0.264	0.071	26.9	0.568	0.135	23.8	2.96

< LOD denotes that levels are below the instrumental limit of detection.

Table A.7 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Cr from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Cr	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	1.10	0.04	3.64	40.5	0.6	1.48	67.7	1.1	1.62	55.4	6.9	12.5	165
2	3.24	0.23	7.10	93.9	1.2	1.28	128	6	4.69	59.4	8.8	14.8	285
4	1.84	0.19	10.3	35.7	0.7	1.96	67.7	0.9	1.33	42.6	3.2	7.51	148
6	1.72	0.13	7.56	30.1	1.8	5.98	33.1	1.4	4.23	46.7	3.7	7.92	112
7	1.91	0.13	6.81	12.0	0.3	2.50	11.5	0.2	1.74	45.0	1.5	3.33	70.4
8	1.81	0.16	8.84	27.1	0.5	1.85	21.5	0.3	1.40	52.3	4.6	8.80	103
9	0.447	0.002	0.45	16.2	0.3	1.85	16.2	0.7	4.32	33.0	0.3	0.91	65.8
10	0.576	0.019	3.30	30.6	1.5	4.90	47.4	1.2	2.53	45.5	1.8	3.96	124
11	0.255	0.134	52.5	57.0	3.0	5.26	47.2	1.4	2.97	45.0	1.8	4.00	149
12	1.40	0.04	2.86	45.1	3.4	7.54	50.7	1.3	2.56	37.4	2.8	7.49	135
13	0.427	0.050	11.7	11.1	1.5	13.5	29.5	16.0	54.2	72.4	5.0	6.91	113
14	0.536	0.011	2.05	13.3	0.7	5.26	28.7	1.0	3.48	57.6	2.7	4.69	100
15	0.614	0.032	5.21	9.05	0.17	1.88	24.6	0.4	1.63	58.4	4.1	7.02	92.7
16	0.247	0.013	5.26	4.19	0.19	4.53	15.2	0.7	4.61	44.2	1.3	2.94	63.8
17	0.307	0.004	1.30	5.06	0.14	2.77	19.6	0.6	3.06	57.0	1.4	2.46	82.0
18	0.542	0.040	7.38	8.28	0.28	3.38	20.5	0.2	0.98	82.2	15.6	19.0	112

19	0.154	0.004	2.60	2.16	0.11	5.09	13.4	0.6	4.48	36.1	0.9	2.49	51.8
20	0.220	0.009	4.09	4.86	0.10	2.06	14.2	1.0	7.04	38.8	2.9	7.47	58.1
21	0.105	0.009	8.57	2.81	0.09	3.20	11.8	0.6	5.08	51.1	7.6	14.9	65.8
22	0.207	0.005	2.42	5.17	0.2	3.87	15.7	0.3	1.91	57.7	5.2	9.01	78.8
23	0.357	0.001	0.28	3.68	0.14	3.80	9.91	0.19	1.92	82.9	14.6	17.6	96.8
24	0.290	0.008	2.76	1.61	0.14	8.70	11.8	0.4	3.39	58.0	4.5	7.76	71.7
25	0.335	0.009	2.69	4.86	0.25	5.14	12.1	1.0	8.26	45.4	4.7	10.4	62.7
26	10.4	0.6	5.77	125	2	1.60	289	12	4.15	78.5	0.9	1.15	503
27	16.2	0.4	2.47	226	3	1.33	418	14	3.35	73.0	5.7	7.81	733
28	5.78	0.09	1.56	61.7	0.7	1.13	76.7	0.8	1.04	86.4	4.1	4.75	231
SFJ	6.09	0.08	1.31	132	4	3.03	189	4	2.12	89.4	10.5	11.7	416
BW	14.1	0.5	3.55	253	12	4.74	283	1	0.35	85.9	11.5	13.4	636
PD	2.32	0.06	2.59	49.3	0.6	1.22	115	1	0.87	46.6	2.3	4.94	213

Table A.8 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Cu from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Cu	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	15.5	0.8	5.16	65.6	1.4	2.13	120	4	3.33	32.0	0.8	2.50	233
2	24.2	2.1	8.68	80.8	2.8	3.47	95.5	3.5	3.66	23.9	0.8	3.35	224
4	14.2	1.9	13.38	66.0	1.5	2.27	152	5	3.29	21.4	1.9	8.88	254
6	20.1	8.5	42.3	88.3	43.2	48.9	186	116	62.4	33.5	9.8	29.3	328
7	19.6	1.5	7.65	32.6	1.00	3.07	19.1	1.00	5.24	23.4	1.9	8.12	94.7
8	7.87	0.63	8.01	45.0	0.9	2.00	40.5	0.7	1.73	37.0	1.2	3.24	130
9	1.72	0.07	4.07	23.9	1.1	4.60	31.3	2.6	8.31	19.4	0.2	1.03	76.3
10	3.27	0.21	6.42	29.0	1.2	4.14	120	3	2.50	24.7	1.00	4.05	177
11	0.903	0.441	48.8	41.4	2.1	5.07	69.0	14.5	21.0	29.2	0.9	3.08	141
12	4.98	0.21	4.22	35.8	3.4	9.50	71.0	3.3	4.65	16.9	0.4	2.37	129
13	2.07	0.12	5.80	11.5	0.5	4.35	35.1	3.2	9.12	19.7	1.4	7.11	68.4
14	6.47	0.17	2.63	20.2	0.7	3.47	58.6	2.4	4.10	37.3	1.5	4.02	123
15	5.81	0.31	5.34	18.3	1.4	7.65	66.5	2.00	3.01	32.5	2.2	6.77	123
16	2.41	0.13	5.39	8.85	0.66	7.46	51.2	1.4	2.73	19.8	0.4	2.02	82.3
17	3.47	0.09	2.59	8.00	0.4	5.00	63.1	2.3	3.65	28.3	0.5	1.77	103
18	5.16	0.29	5.62	15.7	0.5	3.18	49.7	0.8	1.61	31.3	6.6	21.1	102

19	3.18	0.06	1.89	< LOD	-	-	50.4	2.1	4.17	20.4	0.3	1.47	74.0
20	1.64	0.04	2.44	< LOD	-	-	18.6	2.00	10.8	13.0	0.5	3.85	33.2
21	1.02	0.05	4.90	9.26	0.26	2.81	33.8	1.2	3.55	22.0	3.6	16.4	66.1
22	2.68	0.03	1.12	8.41	0.41	4.88	49.8	1.1	2.21	24.5	1.6	6.53	85.4
23	3.77	0.13	3.45	13.7	0.3	2.19	27.3	0.7	2.56	36.3	7.5	20.7	81.1
24	3.13	1.29	41.2	13.5	4.9	36.3	12.4	2.7	21.8	23.3	2.1	9.01	52.3
25	4.78	0.44	9.21	18.2	4.1	22.5	36.3	17.6	48.5	35.2	19.7	56.0	94.5
26	8.05	0.47	5.84	23.9	0.8	3.35	47.5	2.4	5.05	27.2	1.6	5.88	107
27	18.8	1.5	7.98	86.9	0.8	0.92	127	4	3.15	36.6	2.00	5.46	269
28	4.31	0.08	1.86	19.0	0.2	1.05	8.83	0.27	3.06	33.8	1.8	5.33	65.9
SFJ	25.6	0.8	3.13	196	8	4.08	294	7	2.38	45.7	4.6	10.1	561
BW	38.0	3.1	8.16	198	6	3.03	206	2	0.97	52.8	7.1	13.4	495
PD	3.84	0.13	3.39	79.3	1.1	1.39	147	2	1.36	21.5	1.2	5.58	252

< LOD denotes that levels are below the instrumental limit of detection.

Table A.9 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Fe from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Fe	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	831	47	5.66	24500	488	1.99	5850	142	2.43	25300	1160	4.58	56500
2	1240	101	8.15	14300	140	0.98	5120	245	4.79	26100	1100	4.21	46800
4	1320	180	13.6	23500	395	1.68	6670	208	3.12	17700	1220	6.89	49200
6	1030	65	6.31	16000	785	4.91	4280	288	6.73	21500	1050	4.88	42800
7	834	68	8.15	6150	34	0.55	1370	33	2.41	28000	2160	7.71	36400
8	1510	136	9.01	17900	268	1.50	3680	70	1.90	40400	824	2.04	63500
9	641	10	1.56	15900	305	1.92	2020	55	2.72	20900	327	1.56	39500
10	649	47	7.24	25300	1210	4.78	6230	227	3.64	18600	644	3.46	50800
11	45.1	27.8	61.6	19300	1010	5.23	3150	145	4.60	25600	1250	4.88	48100
12	217	25	11.5	20100	1610	8.01	6240	256	4.10	19000	1010	5.32	45600
13	384	25	6.51	17700	196	1.11	5057	454	8.98	27200	1950	7.17	50300
14	530	8	1.51	17200	738	4.29	4200	190	4.52	38100	1060	2.78	60000
15	479	26	5.43	11700	262	2.24	6230	152	2.44	27900	1330	4.77	46300
16	560	25	4.46	15700	615	3.92	8890	408	4.59	29700	824	2.77	54900
17	547	16	2.93	12700	188	1.48	7260	229	3.15	26500	508	1.92	47000
18	622	46	7.40	13900	605	4.35	5720	44	0.77	36100	7090	19.6	56300

19	632	18	2.85	15000	666	4.44	8720	339	3.89	24500	208	0.85	48900
20	324	22	6.79	11100	259	2.33	5100	584	11.5	19300	1070	5.54	35800
21	91.0	24.3	26.7	15600	300	1.92	5940	234	3.94	29300	4190	14.3	50900
22	517	14	2.71	23000	813	3.53	8010	218	2.72	25300	1700	6.72	56800
23	346	8	2.31	8880	228	2.57	3450	133	3.86	45900	9000	19.6	58600
24	130	9	6.92	10300	248	2.41	2460	88	3.58	28200	646	2.29	41100
25	1500	27	1.80	15000	392	2.61	3590	31	0.86	25800	305	1.18	45900
26	554	28	5.05	15800	247	1.56	4010	121	3.02	28500	1310	4.60	48900
27	883	26	2.94	20300	416	2.05	4940	120	2.43	27600	2350	8.51	53700
28	388	9	2.32	7510	117	1.56	1230	47	3.82	41000	2230	5.44	50100
SFJ	1350	47	3.48	20200	479	2.37	5760	117	2.03	25600	2260	8.83	52900
BW	1480	57	3.85	20200	818	4.05	4480	16	0.36	31000	3770	12.2	57200
PD	766	15	1.96	28600	590	2.06	7840	151	1.93	16700	647	3.87	53900

Table A.10 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Mn from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Mn	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	913	34	3.72	397	13	3.27	85.2	1.0	1.17	219	8	3.65	1610
2	181	13	7.18	118	1	0.85	64.1	2.7	4.21	223	11	4.93	586
4	1160	104	8.97	321	8	2.49	85.5	1.9	2.22	157	11	7.01	1720
6	428	28	6.54	169	9	5.33	52.1	4.3	8.25	204	11	5.39	853
7	358	23	6.42	132	7	5.30	37.3	0.5	1.34	295	17	5.76	822
8	1160	109	9.40	414	4	0.97	90.1	1.3	1.44	361	7	1.94	2030
9	1680	52	3.10	528	18	3.41	50.1	1.3	2.59	194	2	1.03	2450
10	2340	52	2.22	683	42	6.15	78.2	3.8	4.86	129	5	3.88	3230
11	742	63	8.49	660	56	8.48	61.3	1.0	1.63	218	11	5.05	1680
12	865	69	7.98	281	18	6.41	52.0	2.1	4.04	154	9	5.84	1350
13	432	14	3.24	120	2	1.67	52.5	3.7	7.05	234	16	6.84	839
14	329	4	1.22	101	3	2.97	49.8	2.1	4.22	370	13	3.51	850
15	331	18	5.44	97.6	3.0	3.07	54.7	1.3	2.38	261	16	6.13	744
16	299	9	3.01	103	5	4.85	71.5	1.4	1.96	278	8	2.88	752
17	384	3	0.78	114	1	0.88	65.0	1.7	2.62	246	4	1.63	809
18	336	9	2.68	121	9	7.44	57.5	0.4	0.70	312	60	19.2	827

19	628	19	3.03	153	6	3.92	82.0	2.6	3.17	208	1	0.48	1070
20	370	25	6.76	126	7	5.56	64.0	11.3	17.7	198	20	10.1	758
21	795	48	6.04	297	39	13.1	58.6	2.8	4.78	213	30	14.1	1360
22	1130	26	2.30	261	4	1.53	74.4	2.2	2.96	200	15	7.50	1670
23	231	8	3.46	82.8	2.9	3.50	45.5	0.6	1.32	436	91	20.9	795
24	428	21	4.91	216	9	4.17	48.6	1.6	3.29	203	4	1.97	896
25	243	8	3.29	108	4	3.70	51.3	0.6	1.17	175	3	1.71	577
26	350	21	6.00	125	3	2.40	54.5	2.3	4.22	182	9	4.95	712
27	391	16	4.09	164	6	3.66	62.1	1.9	3.06	271	21	7.75	888
28	228	4	1.75	117	2	1.71	30.1	0.8	2.66	417	21	5.04	792
SFJ	614	8	1.30	264	4	1.52	58.2	1.9	3.26	195	18	9.23	1130
BW	451	18	3.99	278	10	3.60	50.3	0.3	0.60	256	32	12.5	1040
PD	601	13	2.16	207	3	1.45	53.8	0.5	0.93	125	6	4.80	987

Table A.11 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Ni from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Ni	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	8.69	0.36	4.14	8.69	0.25	2.88	10.8	0.4	3.70	34.9	5.2	14.9	63.1
2	4.37	0.32	7.32	6.03	0.11	1.82	9.00	0.31	3.44	35.4	2.4	6.78	54.8
4	12.7	1.17	9.21	8.71	0.25	2.87	10.8	0.1	0.93	25.1	1.7	6.77	57.3
6	10.1	0.8	7.92	9.92	0.57	5.75	9.32	0.73	7.83	31.7	2.0	6.31	61.0
7	3.89	0.21	5.40	4.43	0.09	2.03	5.34	0.26	4.87	32.2	2.6	8.07	45.9
8	7.02	0.64	9.12	9.50	0.12	1.26	8.47	0.29	3.42	37.1	1.4	3.77	62.1
9	6.37	0.21	3.30	8.91	1.54	17.3	4.94	0.04	0.81	24.2	0.5	2.07	44.4
10	10.6	0.2	1.89	13.1	0.8	6.11	11.4	0.4	3.51	24.7	0.8	3.24	59.8
11	4.08	0.44	10.8	10.3	0.2	1.94	7.05	0.29	4.11	30.2	1.5	4.97	51.6
12	6.95	0.51	7.34	8.45	0.54	6.39	8.39	0.21	2.50	28.6	1.9	6.64	52.4
13	5.38	0.30	5.58	5.85	0.22	3.76	7.85	0.72	9.17	28.7	0.6	2.09	47.8
14	8.88	0.11	1.24	13.4	0.5	3.73	14.3	0.7	4.90	62.4	1.7	2.72	99.0
15	13.2	0.6	4.55	17.8	0.3	1.69	21.8	0.4	1.83	72.5	4.1	5.66	125
16	11.7	0.4	3.42	14.2	2.2	15.5	13.7	0.3	2.19	36.0	3.1	8.61	75.6
17	8.23	0.02	0.24	9.97	0.25	2.51	11.3	0.3	2.65	40.1	0.9	2.24	69.6
18	9.02	0.37	4.10	10.8	0.6	5.56	11.5	0.3	2.61	46.6	8.5	18.2	77.9

19	5.72	0.13	2.27	6.29	0.29	4.61	8.92	0.36	4.04	23.6	0.1	0.42	44.5
20	7.25	0.49	6.76	5.99	0.24	4.01	7.12	0.58	8.15	27.7	1.6	5.78	48.1
21	7.05	0.02	0.28	9.16	0.32	3.49	7.94	0.32	4.03	34.1	5.1	15.0	58.3
22	7.22	0.08	1.11	8.63	0.28	3.24	10.8	0.2	1.85	32.2	2.5	7.76	58.9
23	5.37	0.21	3.91	5.98	0.26	4.35	6.82	0.23	3.37	51.2	9.2	18.0	69.4
24	3.58	0.13	3.63	4.12	0.17	4.13	8.07	0.06	0.74	31.4	1.0	3.18	47.2
25	5.2	0.1	1.92	6.51	0.27	4.15	8.76	0.12	1.37	26.1	1.3	4.98	46.6
26	6.17	0.31	5.02	6.57	0.18	2.74	11.2	0.6	5.36	32.1	0.8	2.49	56.0
27	9.54	0.25	2.62	9.82	0.29	2.95	9.64	0.17	1.76	33.7	1.4	4.15	62.7
28	2.7	0.1	3.70	5.78	0.06	1.04	6.05	0.11	1.82	54.0	2.7	5.00	68.5
SFJ	14.4	0.3	2.08	19.1	0.5	2.62	29.1	0.6	2.06	91.9	9.3	10.1	155
BW	13.7	0.6	4.38	15.0	0.7	4.67	10.3	0.1	0.97	58.1	7.6	13.1	97.1
PD	15.5	0.4	2.58	16.0	0.3	1.88	10.2	0.1	0.98	56.7	4.5	7.94	98.4

Table A.12 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Pb from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Pb	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	12.8	0.8	6.25	531	29	5.46	75.4	4.0	5.31	48.8	3.4	6.97	668
2	13.5	0.1	0.74	377	8	2.12	29.6	2.6	8.78	28.5	2.3	8.07	449
4	11.5	0.4	3.48	409	5	1.22	65.7	2.5	3.81	23.1	2.2	9.52	509
6	13.2	2.1	15.9	293	28	9.56	45.8	9.8	21.4	24.5	1.6	6.53	377
7	16.1	0.2	1.24	99.1	2.2	2.22	6.27	0.35	5.58	13.7	0.3	2.19	135
8	9.69	0.14	1.44	225	2	0.89	18.7	0.3	1.60	24.9	1.1	4.42	278
9	10.2	0.5	4.90	320	2	0.63	21.3	1.5	7.04	35.5	2.8	7.89	387
10	5.84	0.07	1.20	315	9	2.86	46.5	4.6	9.89	40.6	0.6	1.48	408
11	2.71	1.05	38.7	317	10	3.15	25.0	0.5	2.00	45.9	1.3	2.83	391
12	6.01	0.32	5.32	214	14	6.54	28.6	1.6	5.59	24.8	0.5	2.02	273
13	2.42	0.36	14.9	119	19	16.0	< LOD	-	-	36.2	5.5	15.2	158
14	4.04	0.05	1.24	159	1	0.63	15.5	1.1	7.10	44.8	3.2	7.14	223
15	16.3	0.2	1.23	358	2	0.56	46.3	1.1	2.38	43.8	2.6	5.94	464
16	2.63	0.06	2.28	104	1	0.96	12.0	0.6	5.00	23.2	0.8	3.45	142
17	2.65	0.04	1.51	108	2	1.85	17.4	0.6	3.45	23.2	0.7	3.02	151
18	3.56	0.31	8.71	118	2	1.69	16.3	1.0	6.13	29.2	6.4	21.9	167

19	2.03	0.02	0.99	105	1	0.95	20.9	0.6	2.87	24.9	0.6	2.41	153
20	2.44	0.09	3.69	81.3	1.5	1.85	9.22	1.16	12.6	13.2	0.7	5.30	106
21	3.98	0.13	3.27	161	3	1.86	23.1	0.2	0.87	34.8	4.4	12.6	223
22	2.18	0.04	1.83	153	3	1.96	27.8	0.2	0.72	31.0	2.2	7.10	214
23	8.66	0.61	7.04	145	4	2.76	16.1	2.5	15.5	34.1	6.0	17.6	204
24	0.661	0.030	4.54	40.1	0.5	1.25	3.65	0.22	6.03	11.3	0.5	4.42	55.7
25	1.91	0.37	19.4	58.0	10.0	17.2	19.4	9.3	47.9	29.7	11.2	37.7	109
26	1.33	0.04	3.01	79.1	3.2	4.05	9.02	0.23	2.55	17.7	0.6	3.39	107
27	176	14	7.95	1780	38	2.13	185	7	3.78	102	4	3.92	2240
28	4.12	0.61	14.8	86.1	8.4	9.76	4.69	0.24	5.12	20.4	1.3	6.37	115
SFJ	45.4	1.7	3.74	894	20	2.24	101	5	4.95	101	4	3.96	1140
BW	32.3	4.3	13.3	742	5	0.67	67.9	0.6	0.88	81.8	10.6	13.0	924
PD	8.07	0.04	0.50	377	8	2.12	51.6	2.2	4.26	44.5	1.8	4.04	481

< LOD denotes that levels are below the instrumental limit of detection.

Table A.13 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Sn from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Sn	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	< LOD	-	-	1.20	0.1	8.33	< LOD	-	-	19.6	1.5	7.65	20.8
2	< LOD	-	-	1.80	0.1	5.56	< LOD	-	-	19.9	0.7	3.52	21.7
4	< LOD	-	-	1.26	0.15	11.9	< LOD	-	-	20.5	1.0	4.88	21.8
6	< LOD	-	-	1.19	0.01	0.84	< LOD	-	-	24.8	1.5	6.05	26.0
7	< LOD	-	-	1.08	0.01	0.93	< LOD	-	-	11.4	1.1	9.65	12.5
8	< LOD	-	-	1.12	0.01	0.89	1.07	0.03	2.80	18.6	3.4	18.3	20.8
9	< LOD	-	-	1.12	0.09	8.04	< LOD	-	-	25.0	2.6	10.4	26.1
10	< LOD	-	-	0.970	0.05	5.15	< LOD	-	-	29.1	0.6	2.06	30.1
11	< LOD	-	-	1.04	0.04	3.85	< LOD	-	-	23.7	1.9	8.02	24.7
12	< LOD	-	-	0.882	0.048	5.44	< LOD	-	-	19.6	1.4	7.14	20.5
13	< LOD	-	-	0.780	0.026	3.33	< LOD	-	-	9.53	1.58	16.6	10.3
14	< LOD	-	-	0.815	0.042	5.15	< LOD	-	-	14.0	0.5	3.57	14.8
15	0.0347	0.024956	71.9	< LOD	-	-	0.394	0.119	30.2	24.8	0.4	1.61	25.2
16	< LOD	-	-	< LOD	-	-	0.224	0.037	16.5	11.3	0.8	7.08	11.5
17	< LOD	-	-	< LOD	-	-	0.203	0.016	7.88	12.4	0.2	1.61	12.6
18	0.08512	0.028651	33.7	0.0176	0.0100	56.8	0.275	0.006	2.18	31.4	5.7	18.2	31.8

19	< LOD	-	-	< LOD	-	-	0.190	0.030	15.8	13.2	0.7	5.30	13.4
20	< LOD	-	-	< LOD	-	-	0.178	0.020	11.2	6.68	0.02	0.30	6.858
21	< LOD	-	-	< LOD	-	-	0.185	0.030	16.2	44.7	28.7	64.2	44.9
22	< LOD	-	-	< LOD	-	-	0.231	0.037	16.0	41.0	12.5	30.5	41.2
23	< LOD	-	-	< LOD	-	-	0.239	0.112	46.9	43.3	5.8	13.4	43.5
24	< LOD	-	-	1.09	0.12	11.0	< LOD	-	-	5.31	1.41	26.6	6.40
25	< LOD	-	-	1.19	0.05	4.20	< LOD	-	-	11.0	1.7	15.5	12.2
26	< LOD	-	-	1.04	0.03	2.88	< LOD	-	-	6.15	0.85	13.8	7.19
27	< LOD	-	-	3.10	0.11	3.55	0.578	0.078	13.5	94.6	1.7	1.80	98.3
28	< LOD	-	-	0.578	0.038	6.57	0.166	0.029	17.5	8.86	0.21	2.37	9.60
SFJ	< LOD	-	-	0.404	0.092	22.8	0.500	0.186	37.2	76.8	17.1	22.3	77.7
BW	< LOD	-	-	3.22	0.11	3.42	0.387	0.018	4.65	93.2	11.5	12.3	96.8
PD	< LOD	-	-	< LOD	-	-	0.181	0.009	4.97	49.6	7.8	15.7	49.8

< LOD denotes that levels are below the instrumental limit of detection.

Table A.14 Concentration (mg/kg), standard deviation (SD, ± mg/kg), and calculated relative SD (% RSD) of Zn from the respective BCR sequential extraction steps in sediments from the Forth and Clyde Canal and Glasgow Branch

Zn	Step 1			Step 2			Step 3			Step 4			BCR Total
Sampling Site	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg	± mg/kg	% RSD	mg/kg
1	460	17	3.70	394	7	1.78	85.2	2.5	2.93	73.2	2.5	3.42	1012
2	315	22	6.98	251	2	0.80	64.6	6.2	9.60	67.6	4.5	6.66	698
4	619	58	9.37	370	9	2.43	85.3	2.6	3.05	45.7	3.0	6.56	1120
6	657	49	7.46	463	29	6.26	83.1	2.2	2.65	67.2	7.5	11.2	1270
7	227	13	5.73	135	1	0.74	26.0	1.4	5.38	66.5	4.7	7.07	455
8	370	31	8.38	353	4	1.13	54.2	2.5	4.61	107	5	4.67	884
9	383	10	2.61	319	14	4.39	44.9	7.1	15.8	60.4	1.1	1.82	807
10	909	21	2.31	678	35	5.16	98.6	2.6	2.64	54.6	2.9	5.31	1740
11	295	45	15.3	658	31	4.71	78.3	4.0	5.11	82.9	1.4	1.69	1110
12	364	16	4.40	310	17	5.48	64.8	3.2	4.94	49.6	2.5	5.04	788
13	151	10	6.62	128	6	4.69	45.8	12.0	26.2	60.6	2.4	3.96	385
14	301	5	1.66	278	6	2.16	95.2	18.9	19.9	123	4	3.25	797
15	326	15	4.60	253	6	2.37	101	2	1.98	93.5	6.6	7.06	774
16	232	7	3.02	179	10	5.59	57.9	1.3	2.25	56.5	1.4	2.48	525
17	199	1	0.50	183	4	2.19	85.0	1.6	1.88	75.6	1.4	1.85	543
18	242	14	5.79	201	5	2.49	74.3	1.2	1.62	119	21	17.6	636

19	131	3	2.29	121	4	3.31	72.1	2.6	3.61	64.7	1.0	1.55	389
20	124	8	6.45	80.7	1.8	2.23	30.7	3.1	10.1	44.3	3.6	8.13	280
21	109	3	2.75	109	4	3.67	36.3	1.6	4.41	58.9	9.1	15.4	313
22	173	4	2.31	151	4	2.65	57.0	1.2	2.11	67.3	6.0	8.92	448
23	160	5	3.13	133	5	3.76	64.7	0.6	0.93	119	26	21.8	477
24	38.5	1	2.60	59.8	3.8	6.35	19.9	1.6	8.04	57.0	3.3	5.79	175
25	106	3	2.83	75.2	4.4	5.85	24.4	4.3	17.6	44.7	1.7	3.80	250
26	209	12	5.74	201	3	1.49	71.9	2.8	3.89	64.5	4.3	6.67	546
27	910	16	1.76	521	16	3.07	262	6.8	2.60	151	10	6.62	1840
28	73.7	1.7	2.31	84.6	1.1	1.30	19.6	0.7	3.57	79.5	4.4	5.53	257
SFJ	1520	31	2.04	873	25	2.86	251	5	1.99	99.7	9.0	9.03	2744
BW	1630	73	4.48	761	38	4.99	178	4	2.25	122	16	13.1	2690
PD	912	19	2.08	607	10	1.65	95.9	1.5	1.56	44.0	1.8	4.09	1660