University of Strathclyde
Department of Pure and Applied Chemistry

The Effect of Sample Pre-treatment and Speciation of Potentially Toxic Elements in Freshwater Sediments Impacted by Historical Metal Mining

By

Idowu Emmanuel Obolo

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

December 2019

‘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.’

Dedication

To the Almighty God, my strength and shield, my very present help in the times of need. Also, to my late parents His Royal Highness Festus Adefioye Obolo and Princess Victoria Omoyeni Obolo.

Acknowledgements

I am grateful to Tertiary Education Trust Fund, Nigeria, and the Federal College of Education (Technical) Akoka, Lagos, for sponsoring my PhD in the United Kingdom.

Words are not enough to express my sincere appreciation to Dr Christine Davidson. Her kind supervision, academic guidance, expertise, and support have made it possible for this programme to come to a successful end. Special thanks to Dr Richard Lord (my second supervisor) for his academic guidance, expertise, and support. He was with me in the cold giving necessary support during sediment samples collection.

Thanks to Alexander Clunie for his technical support on the ICP-MS and Mara Knapp for her assistance and for allowing me to work in the Environmental Analytical chemistry laboratory, Civil and Environmental Engineering Department. Thanks to Benjamin Nunn for helping with the QGIS maps.

I want to say a big thank you to every member of the analytical research group and technical staff in the Forensic and Analytical chemistry teaching laboratory for their numerous supports.

I deeply appreciate my wife (Princess Ayombo Omowumi Idowu-Obolo) for sacrificing all that she could for the successful completion of this programme. I also appreciate my children (Princess Ayomide Esther Obolo and Prince Olaoluwa Emmanuel Obolo) for cooperating with their mother and behaving themselves when I was absent from home.

Table of Contents

Part 1 – Analytical section

Part 2 – Environmental section

Abstract

This work involved evaluation of the impact of historical mining operations on potentially toxic elements (PTE) distribution in freshwater sediments from the catchment, of the River Derwent, UK. In parallel, the influence of sample pre-treatment on the operational speciation (fractionation) of PTE in sediment with different matrix characteristics was investigated.

Freeze, air, and oven drying separately caused less than 9 % changes in PTE fractionation relative to sediment extracted as received, while freeze storage for 12 months was worse (37.5 % changes). Iron was the analyte most prone to changes in fractionation. Sediments rich in iron (hydr)oxides appeared least stable. Harmonisation of sample pre-treatment procedures is recommended to increase results comparability.

The study confirmed that the River Derwent remains the main source of PTE contamination in the Derwent Reservoir and that the sediments are significantly enriched in Cd, Pb and Zn. Arsenic, Cd and Pb concentrations in sediments decreased along the length of the reservoir, possibly due to settlement of discrete sand-sized particles, whereas Mn concentration increased probably due to the accumulation of clay-and silt-size particles downstream. Hierarchical cluster analysis revealed three grouping: As, Cd, Cu and Pb (cluster one); Fe, Ni and Zn (cluster two); and Mn (cluster three). The potential mobility and bioavailability of As, Fe, Ni and Zn increased in sediment near the dam compared with the reservoir upstream probably due to weathering.

The PTE pollution index was in the heavily- and severely- polluted range and the mean risk assessment code of PTE in the Derwent Reservoir sediments was Cd, Mn (> 50 %: very high risk) > Zn (31- 50 %: high risk) > Ni (11- 30 %: medium risk) > As, Cu, Fe and Pb (1- 10 %: low risk). The study shows that historical mining sites are persistent source of PTE in water resources.

1. Introduction

Potentially toxic elements (PTE) are ubiquitous. Due to their persistence, PTE accumulate at varied concentrations in different compartments of the environment, such as soil, dust, and sediment[1-3]. Figure 1.1 shows the biogeochemical cycling of PTE in the different compartments of the environment[4, 5].

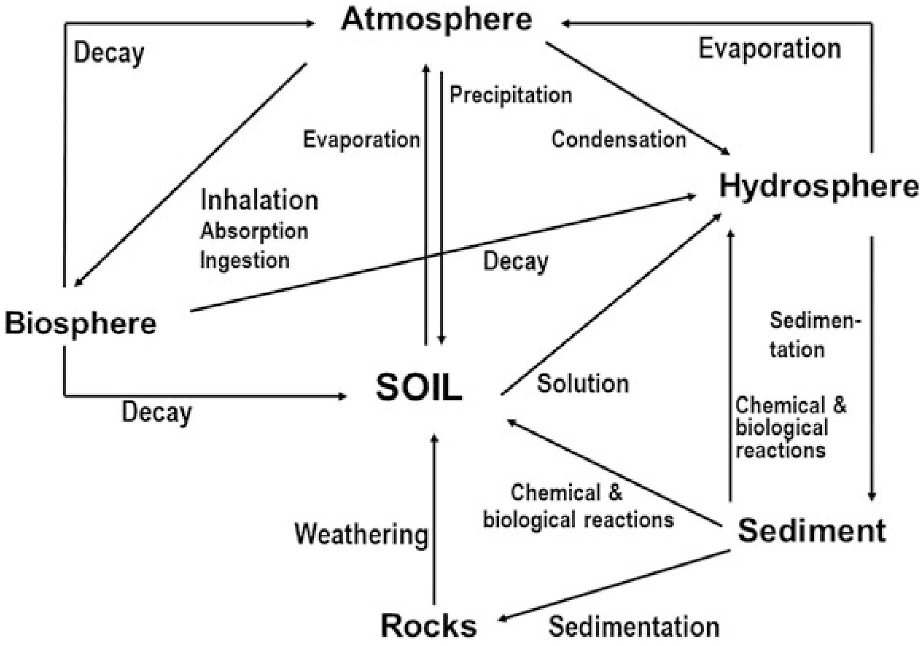


Figure 1.1 Biogeochemical cycling of potentially toxic elements in the environment[4, 5]

Sediment is formed from inorganic and organic materials suspended in, transported by, and deposited from water. Prior to sedimentation suspended particulate matters are dissolved PTE scavengers[6, 7]. The particulate matters that settled as sediment retains the sorbed PTE. Sediment has been recognized as the major sink for, and medium for dynamic adsorption and desorption of, PTE in water system[6, 8-12]. The dynamic adsorption and desorption of PTE in the sediment depends on the prevailing environmental conditions such as acidification (e.g. from acid rain, acid mine drainage and industrial effluents), reduction (e.g. post depositional burial of sediment) and oxidation (e.g. as may occur following dredging)[6, 13, 14 15]. Therefore, sediment is an important component of the biogeochemical cycle, especially, the hydrosphere.

The mobility, bioavailability and ultimately the toxicity of PTE to organisms depend on their form and the way they are bound to environmental solid samples[8, 15-18]. The

International Union of Pure and Applied Chemistry (IUPAC)[19] defined chemical species as specific forms of an element (isotopic composition, oxidation state and/or complex or molecular structure) and speciation as the distribution of an element amongst defined chemical species in a system. Ure[20] broadly divided speciation into classical (chemical compounds or oxidation state of elements), functional (the role) and operational (species are defined by the reagent(s) use to extract them) speciation[20]. The IUPAC definition of chemical species is broadly equivalent to Ure's classical speciation. Direct determination of the specific forms of sediment-bound PTE is difficult due to their association with great varieties of solid phases, their amorphous nature and the trace amount of the elements involved. Consequently, sequential extraction procedure is an indirect analytical method that has been overwhelmingly used for PTE speciation in sediments. Sequential extraction is operationally defined (depends on the reagents and method of extraction)[15, 21, 22]. In addition, studies[21, 23-27] have shown that the usual practice of drying sediments to make it stable and suitable for standard laboratory procedures (e.g. grinding, coning-and-quartering etc.) changes the natural speciation of PTE in sediments. In most cases, the time interval between sediment samples collection and extraction is an unavoidable delay. Consequently, there is need to preserve sediments prior to analysis. Therefore, the analytical section of this work is focused on providing useful guidance to help identify the appropriate sample preservation regimes for obtaining useful geochemical information on sediment-bound PTE and the associated ecological risk.

Freshwater systems include rivers, lakes, and reservoirs. Reservoirs are intermediate water system between the river and lake. Reservoirs are constructed, or modified water systems built to have reliable and controllable water resources. These are different types of reservoirs, including impoundment, cascade, and embankment. The different types of reservoirs are shown in Figure 1.2. Reservoirs formed by building dams across a river course with subsequent water inundation upstream are called impoundments. Cascades are reservoirs formed by serial dams along a river course, while embankments are off-river reservoirs. The different types of reservoir have both water inflow (input) and outflow (output). Reservoirs are utilized for different purposes including, flood control, municipal and industrial water supply, fish farming, irrigation, power generation, recreation and sometimes for waste disposal[6, 28-31]. Rivers feeding reservoirs may be impacted by PTE due to unregulated industrial and/or historical mining activities in the catchment areas[32-35]. Consequently, the impacts of PTE in the rivers are transferred to the reservoirs. In addition, surface runoff and atmospheric depositions from both near and remote sources contribute to the impact of PTE in reservoirs[6]. For ecological and public health reasons the assessment of the status of PTE in reservoirs is important to policy makers and reservoirs managers. The Derwent Reservoir and catchment (detailed description in chapter six) North East England is the case study used for the environmental studies in this work. The Derwent Reservoir was chosen, because it is an example of a reservoir impacted by old mining operations in the catchment[36-38]. Therefore, the findings from this work will be useful for policy making and the management of similar reservoirs and catchments elsewhere.

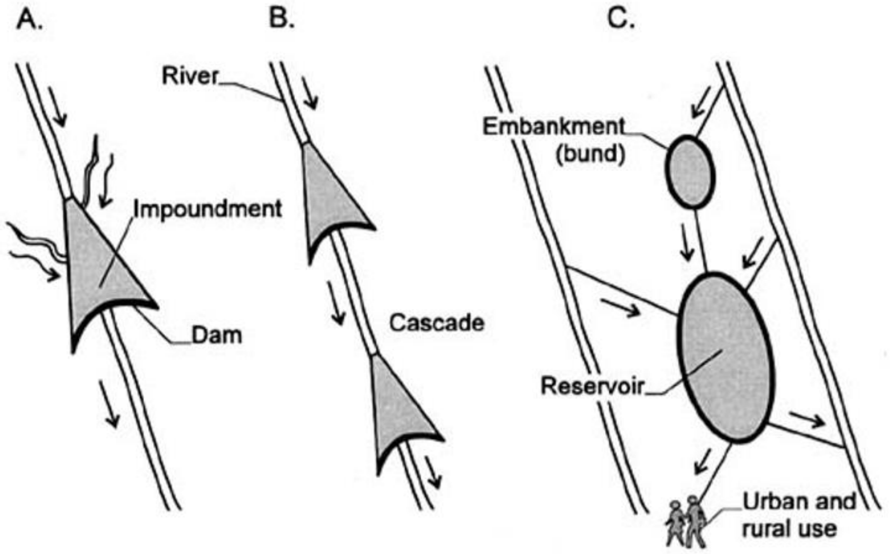


Figure 1.2. The different types of reservoirs: (A) Impoundment (B) Cascade (C) Embankment[6]

1.1. Potentially toxic elements occurrence and health implications

Potentially toxic elements have the potential to bio-accumulate (increase in concentration in the first contact organism of the food chain) and bio-magnify (increase in concentration along the food chains)[12, 39]. This puts aquatic communities and humans at the top of the food chain at risk[34, 40]. Some PTE are essential elements[41]. An element is considered essential if an organism's life cycle cannot be completed without it, and it cannot be entirely substituted by another element[42, 43]. However, deficiency or excess of essential elements can be hazardous to organisms[41, 43].

Due to considerable variations in the geology and anthropogenic activities in the catchments of inland waters, it is difficult to establish a universally acceptable background concentration for PTE in sediments. However, world average of the background concentrations for some PTE in river sediments has been estimated. For most of these PTE the average background concentration in river sediments is similar to the amount determined in shale[6, 14] and they are included in the following account of each PTE.

Arsenic

Arsenopyrite (FeAsS) is the main mineral of As. Others include arsenolite (As_4O_6), Orpiment (As_2S_3) and realgar (AsS)[2, 44, 45]. Arsenic also occurs as impurity in Cu, Pb and Zn ores[2, 44-46]. The world average background concentration of dissolved As in rivers and sediments are 1.0 µg L^{-1} and 13 mg kg^{-1} respectively[6, 47]. The arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) are the common forms of As in natural water. Arsenic (III) is the predominate form of As in anaerobic environments, while arsenic (V) is the predominate form in aerobic environments. The organic forms of As that are known as water pollutants are arsenobetaine, arsenocholine and arsenosugars[48]. Arsenic toxicity depends largely on the chemical speciation. Arsenic (III) species are generally more toxic than arsenic (V) species[2, 48]. Arsenic pollution is a global problem, with over 60 million people at risk of exposure[49]. There has been reported incidence of As pollution in Argentina, Bangladesh, Canada, Chile, China, Hungary, India, Japan, Mexico, New Zealand, Poland, Taiwan, and in the USA[50]. Chronic toxicity of As causes cancer of all human organs, abnormal pigmentation, neurological disorder, loss of appetite, hyperkeratosis, nausea, and body weakness. Acute toxicity of As causes low blood pressure, vomiting, abdominal pain, bloody diarrhoea, oesophageal and cardiomyopathy[51].

Cadmium

Cadmium is divalent (Cd^{2+}) and chemically similar to Zn[5, 44, 52]. It occurs as impurity substituting for Zinc (II) in minerals[44, 46, 52]. Zinc ores are sources of Cd pollution[2, 53]. In freshwater systems Cd is mainly found in the sediment[2, 52]. The world average background concentration of dissolved Cd in rivers and sediments are 0.001 µg L^{-1} and 0.3 mg kg^{-1} respectively[6, 47]. Cadmium has no known biological function but is generally toxic at trace concentration. Acute exposure to Cd damages the kidney and bone while chronic exposure may result in renal failure. Studies have also shown that Cd may be carcinogenic and may also increase mortality rate[2, 45, 54, 55]. The most devastating Cd poisoning recorded was the *itai itai* disease in Japan. This was attributed to eating Cd contaminated rice. The rice was grown on a farm irrigated with a river with historical mining of Cd, Pb and Zn in the catchment area[2].

Copper

Chalcopyrite ($CuFeS_2$) is the most abundant and economically viable Cu mineral. Other Cu minerals include malachite ($Cu_2(OH)_2(CO_3)_2$):carbonate), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS) and as native metallic Cu[44, 46]. Copper is also commonly found as impurity in other sulfide minerals[46]. Copper (II) forms very stable complexes with humified organic matter in the environment[46]. Consequently, dissolved Cu in water systems is strongly adsorbed to the particulate matter with preference for organic particulate matter. Due to copper’s strong adsorption to organic matter only a small fraction is found in the dissolved form as copper (II). However, below pH 5.5 Cu solubility is enhanced[2, 56]. Concentration of Cu above 5 mg L^{-1} gives water an unpleasant and bitter taste[56]. The world average background concentration of dissolved Cu in rivers and sediments are 1.4 µg L^{-1} and 45 mg kg^{-1} respectively[6, 47]. Copper is an essential trace element in both plants and animals. The human’s system has an internal mechanism that regulates Cu concentration within the body system. Due to this Cu toxicity is largely abated in human. However elevated doses of Cu could damage the kidney and the liver, cause anaemia, intestinal and stomach upset[56].

Iron

Iron is naturally abundant constituting approximately 5 % of the earth's crust, occurring mainly as iron (II) and iron (III) oxides[45, 57]. The key minerals of Fe ores are hematite (Fe_2O_3), magnetite (Fe_3O_4), goethite ($FeO(OH)$) and siderite ($FeCO_3$)[46]. The typical background concentration of Fe in soil is 7000 – 42000 mg kg^{-1} [44] and the world average concentration of dissolved Fe in unpolluted rivers is 50 µg L^{-1} [6]. Iron is an essential element that plays vital roles in many human physiological processes. Age, gender, and physiological conditions determine the minimum daily requirement of Fe which is usually 10 to 50 mg day^{-1}. The chronic toxicity of Fe is rare; when it occurs it is usually due to genetic defects. The average lethal dose of Fe is 200-250 mg kg^{-1} body weight, though death caused by ingestion of 40 mg kg^{-1} body weight has been reported[57].

Manganese

Manganese is one of the most naturally abundant elements, and it usually occurs with Fe[58]. Manganese oxides exist in various forms with variable valency, while Mn(IV) is reduced to Mn(II) in the environment under anaerobic conditions. The key mineral ores of Mn are pyrolusite (MnO_2), romanechite ($(Ba,H_2O)_2(Mn^{+4},Mn^{+3})_5O_{10}$), manganite ($MnO(OH)$, hausmannite ($Mn^{2+}Mn^{3+}{}_2O_4$), rhodochrosite ($MnCO_3$), rhodonite ($MnSiO_3$) and braunite ($Mn^{2+}Mn^{3+}{}_6[O_8|SiO_4]$)[59]. The world average background concentration of dissolved Mn rivers and sediments are 10 µg L^{-1} and 850 mg kg^{-1} respectively[6, 47]. Manganese is an essential element needed for proper functioning of several human enzymes[58]. However ingestion of elevated amounts of Mn could cause neurological disorder particularly in the aged, while deficiency, though rare, could damage the skeletal system[58, 60].

Nickel

The key mineral of Ni is pentlandite ($(Ni,Fe)_9S_8$). It is also commonly found as an impurity in other sulfide minerals. Nickel as Ni^{2+} is chemisorbed onto hydrous oxides and complexed by organic matter[46, 61]. It is also readily adsorbed by carbonate, silicate, and phosphate. Nickel is an essential trace element and above thresholds it could damage the human liver, kidney and causes eczema on skin contact[61].

Lead

Galena (PbS) is the main Pb mineral, others are anglesite ($PbSO_4$) and cerussite ($PbCO_3$)[44, 46]. Lead is released into the soil, surface water and ground water in various forms. Lead (II) and as hydroxyl complexes are the most stable forms. Lead (II) is also chemisorbed onto hydrous oxides[2, 46]. Tetramethyllead and tetraethyllead are examples of organometallic Pb in the environment. Organometallic lead is lipophilic and can easily penetrate cell membrane, resulting in bioaccumulation in the food chain[5]. The world average background concentration of dissolved Pb in river and sediment are 0.04 µg L^{-1} and 20 mg kg^{-1} respectively[6, 47]. Lead has no known biological function. It is toxic, causing adverse health effect in human such as brain, nervous system, red blood cell and kidney damage. Children below six years are more susceptible[5, 46, 62].

Zinc

Sphalerite (ZnS) and wurzites (Zn,Fe)s) are the principal ores of Zn[44, 53]. Zinc (II) is held by ion exchange, form complexes with organic matter and chemisorb onto hydr(oxides) in the environment[44, 46]. The world average background concentration of dissolved Zn in rivers and sediment are 0.2 µg L^{-1} and 95 mg kg^{-1} respectively[6, 47]. Zinc concentration in water higher than 3 mg L^{-1} cause milky iridescence, unpleasant astringent taste and when boiled gives a 'grease' film[53]. Zinc is an essential trace element in human. Acute toxicity is usually caused by accidental or deliberate ingestion of excess Zn salts for therapeutic purposes[53].

1.2. Environmental quality standards for PTE in sediment

Quantitative evaluation of the potential ecological risk associated with the amount of PTE in sediment is important for river managment[63]. However, the uncertainty on the maximum permissible levels of PTE in river sediment has made it difficult to agree on environmental quality standard (EQS) for sediment in Europe. Unlike sediment, there exist EQS for water in Europe and at the national levels under the Water Framework Directive (WFD)[64] in order to protect aquatic organism from exposure to contaminants in the water column.

The WFD[65] recognises sediment as a major sink and an important medium for dynamic adsorption and desorption of contaminants in the aquatic system. Therefore, the WFD encourages each member state to establish EQS for river sediment at national level. A number of countries including Australia and New Zealand[66, 67], Canada[68], and Netherlands[63, 69] have established sediment quality guidelines (SQGs). The SQGs give a quantitative measure of the hazardous effect of sediment-bound contaminants to aquatic organism. There is no standard for river sediment in the United Kingdom due to the high spatial variability of monitoring data and limited data on the toxicity of contaminants in river sediment[63], although draft SQGS similar to Canadian SQGs exist for England and Wales[63].

The Canadian SQGs[68] provide two values for each contaminant: a Threshold Effect Level (TEL) and a Probable Effect Level (PEL). Threshold effect levels represent the concentrations below which hazardous biological effects rarely occur. Probable effect level and above represent the range at which hazardous biological effects frequently occur. Threshold effect levels and above (but < PEL) represent the range at which hazardous biological effects occur occasionally. The Australian and New Zealand SQGs[66] provide two values for each contaminant similar to the Canadian SQGs: Interim SQGs-Low (ISQG-L) and -High (ISQG-H). The ISQG-L represents the concentrations below which hazardous biological effect rarely occur. Contaminants concentrations at ISQG-H level and above represents the range at which hazardous biological effect frequently occur. Contaminants concentrations at ISQG-L level and above (but < ISQG-H) represent the range at which hazardous biological effects occur occasionally.

The Dutch soil/sediment quality guidelines provided two values: the Target and Intervention values[63, 69]. Sites with contaminants concentrations below the Dutch Target values are considered clean with no ecological risk to aquatic organisms. Sites with PTE concentrations above the Dutch intervention values are considered an ecological risk to aquatic organisms and clean-up may be necessary. The SQGs mentioned above are listed in Table 1.1.

Table 1.1 Selected sediment quality guidelines (SQGs: mg kg^{-1})

SQGs	Potentially toxic elements					
	As	Cd	Cu	Ni	Pb	Zn
Threshold Effect Level[63, 68] (draft SQGS for England and Wales / Canadian SQGs)	5.9	0.6	36.7	18	35.0	123
Probable Effect Level[63, 68] (draft SQGS for England and Wales / Canadian SQGs)	17.0	3.5	197	35.9	91.3	315
Australian ISQG-L[67]	20	1.5	65	21	50	200
Australian ISQG-H[67]	70	10	270	52	220	410
Netherlands Target value[69]	29	0.8	100	35	85	140
Netherlands Intervention value[69]	55	12	380	210	530	720

ISQG-L: Interim sediment quality guidelines-Low. ISQG-H: Interim sediment quality guideline-High.

1.3. Freshwater sediments and processes

Freshwater sediments consist of the solid materials, porewater and overlain water. Sediments solid components can be classified as detrital, authigenic and biogenic according to their origins[6, 46, 70]:

i. Detrital sediments are products of weathering and transport of rock particles or soil, comprising of quartz, feldspars, and clay minerals. Quartz and feldspars, and clay are the persistent primary and secondary minerals in soils, respectively[46].
ii. Authigenic sediments are derived from *in situ* chemical reactions occurring within the sediment and associated water body. The authigenic components include the biochemically precipitated carbonate minerals, formation of mineral oxyhydroxides (especially of Fe and Mn), coprecipitated elements, phosphate, and pyrite (FeS_2)[6, 46, 70].
iii. Biogenic sediments are derived from the remains and waste products of living organisms. These includes the organic remains of living organisms that are persistent in the environment and some materials (e.g. calcite ($CaCO_3$) and silica ($SiO_2.nH_2O$)) used by living organisms for structural purposes, for example, in shells and skeletons[6, 46].

1.3.1. Rivers and lakes sediments

The mineralogical composition of river sediment depends on the geology of the catchment. River sediment tends to be coarser in the fast-moving parts of the river upstream compared with downstream[46]. The inflow of a river into a lake usually results in a decrease in water velocity. Consequently, coarse sediments usually settle at the river entry areas, while finer particles are transported further into the lake[6, 46, 70]. Water and wave currents within the lake caused further sorting of sediment based on particle size. Energy derived from water and wave current within the lake also move sediments from the shallow to deeper zone where sedimentation is final. The differential deposition of sediments in the deeper parts of the lake where sedimentation is final is termed 'sediment focusing'[70, 71]. The chemical nature of lake sediments depends mainly on the catchment area. Lake sediments are chemically similar to the mineral soil in the catchment, but in upland areas dominated by peat soil, they are usually more organic. Existing materials derived from the outside (river inputs, erosion and dust) of the lake are termed allochthonous, and those formed within the water body (organic debris from the decay of macrophytes and phytoplankton, and the precipitation of minerals) are termed autochthonous[6, 46, 70]. Strictly speaking sediment components derived from outside the lake are also termed allogenic[70].

1.3.2 Diagenetic processes in sediment

Diagenetic processes are the physical, chemical, and biological interactions that affect sediment properties after deposition[46]:

Physical processes

Compaction at depth is the main diagenetic physical processes that occurs in sediment. The amount of water in surface sediments can be as high as 90 % by weight[46]. At greater depth, the weight of the sediment exerts pressure, resulting in a decrease in pore water and more compacted solid. Sorting of surface sediments following resuspension by water current are also included[46, 70].

Chemical processes

Redox changings in Fe and Mn are the major chemical processes in sediments, especially in those under oxidation and reduction cycle[46, 72]. Iron exists as insoluble Fe (III), and manganese as insoluble Mn (IV) in the oxidised layer of the sediment. Below the oxidised layer the electrode potential (Eh) decreases with depth. Below the oxidised layer Mn (IV) is reduced to Mn (II), further down the sediment at lower Eh, Fe (III) is reduced to Fe (II). The redox changes in Fe occurred at lower Eh compared with Mn. Once Fe (II) and Mn (II) are in solution, they tend to diffuse upward into the oxidised layers of the porewater where they are in low concentrations and are re-oxidised. This creates a sediment profile distribution with the maximum concentration of Mn in near surface solid phase, while the maximum concentration of Mn in the porewater is slightly below. Iron shows a similar pattern but at lower depth and Eh. These patterns are shown in Figure 1.3. Although the oxides of Mn and Fe are in small amounts in sediment, they are especially important because they provide highly reactive surfaces for the adsorption of other ions[46, 72].

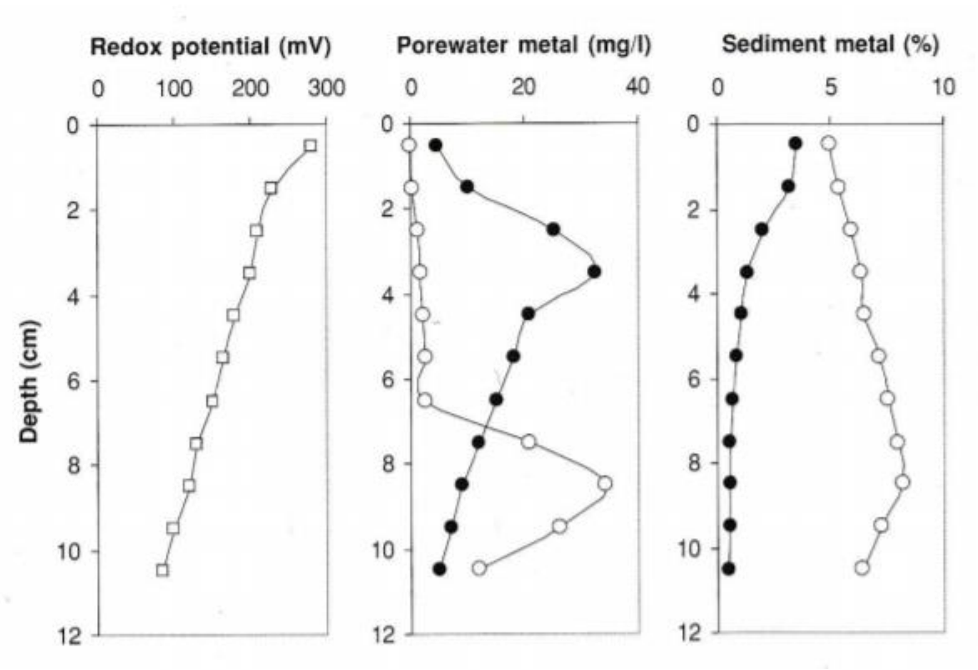


Figure 1.3 Fe and Mn distribution in a sediment profile (○ represent Fe; ● represent Mn)[46]

In highly reduced sediment methane and sulfide are produced, especially, the formation of iron sulfide (FeS). Iron sulfide is the black sediment usually found below the orange oxidised layer of recently exposed lake sediments. Exposure of such reduced sediments to aerobic conditions leads to the oxidation of Fe and S resulting in the acidification found in some river deltas[46].

Biological processes

Benthic organisms and other species feeding on them, through their activities (burrowing, feeding, excretion, respiration, and locomotion activities) cause significant physical and chemical changes (alter sediment fabric, texture, porosity, mix sediment particles, redox conditions etc.) in sediment properties[46, 72]. These biological processes are termed bioturbation[72]. Bioturbation also includes bacterial degradation of organic matter. Organisms living within the sediment can cause mixing of surface materials to depth. The extent of bioturbation depends on the population density of the species involved. Where the population density of the species is high, they may be a complete mixing of the surface sediments. Consequently, bioturbation must be taken into consideration when sediments are used as indicators of historical records of environmental changes[46]. Overall, the major processes that affect the transportation and fate of contaminants in freshwater sediments are shown in Figure 1.4.

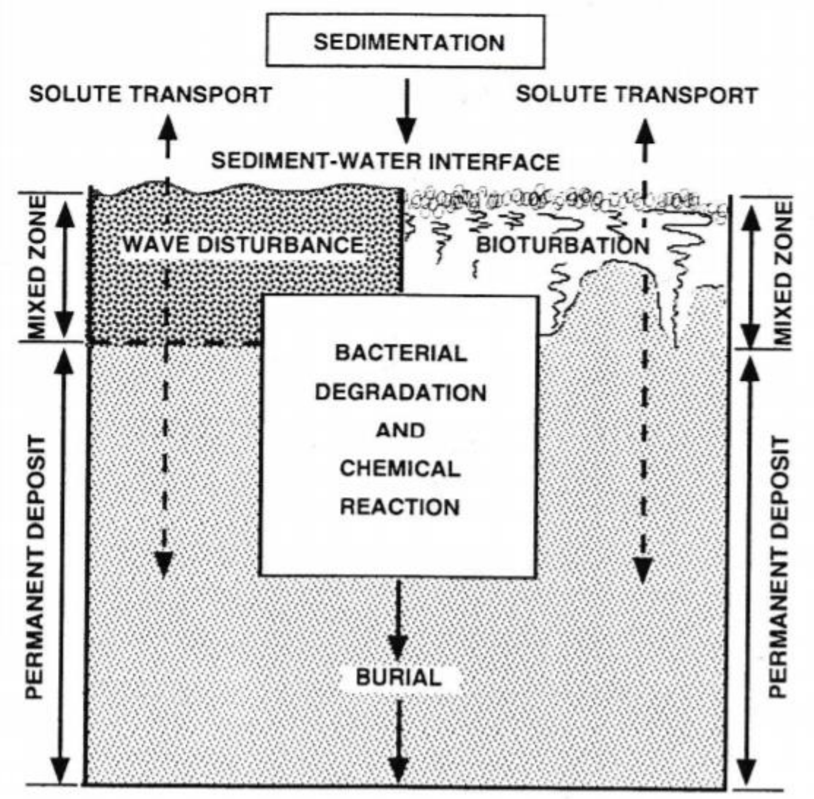


Figure 1.4 Major processes affecting the transport and fate of potentially toxic elements in freshwater sediments[72].

1.4. Soil chemistry relevant to sediment

Freshwater sediments and soil are chemically similar because they are derived mainly from the product of rock weathering and the inputs from secondary minerals[46 6, 7, 46, 73]. Sediments and soil solid phases are both in contact with water[46, 74]. The inorganic solid is made up of primary and weathered minerals including clays, carbonates (mainly calcite ($CaCO_3$), and dolomite ($MgCO_3$)), phosphates, sulfates and oxyhydroxides. The organic matter component originates from animal, plant and microbial residues[44, 46, 72, 73]. The sold phases interact with one another and with extraneous ions in the system. Clay minerals, mineral (hydr)oxides, and organic matter are the major sink for PTE in both soil and sediment[44, 46, 72]. Calcium carbonate is also an adsorbent of PTE in calcareous sediment[72]. Also both sediment and soil particle sizes can be classified as sand (> 0.05 – < 2.0 mm), silt (> 0.002 –

< 0.05 mm) and clay (< 0.002 mm)[6, 11]. It should be noted, that the clay minerals are chemically distinct from, and should not be confused with, clay particle size; although the clay mineral particles fall mainly within the clay particle size range[6, 73, 75].

1.4.1. Clay minerals

Clay minerals are an assemblage of silica tetrahedral and aluminium octahedral sheets[73]. The silica tetrahedral and aluminium octahedral sheets bond together to form the basic unit of the clay minerals referred to as unit layers. They are mainly two types of layers, the 1:1 clays and the 2:1 clays. The 1:1 clays consist of one tetrahedral sheet and one octahedral sheet bonded together by the sharing of oxygen atoms at the interface (Figure 1.5). A common example of 1:1 clays is kaolinite [$Al_2Si_2O_5(OH)_4$]. 1:1 clays layers are stacked through hydrogen bond[73, 76].

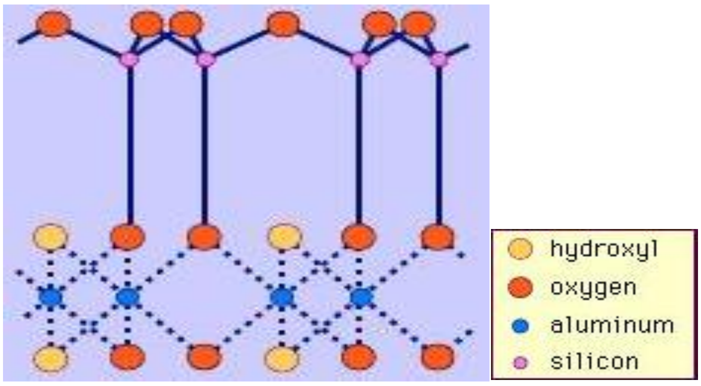


Figure 1.5 Structural representations of 1:1 clays[77].

The 2:1 clays consist of one octahedral sheet sandwiched between two tetrahedral sheets (Figure 1.6). Oxygen atoms of stacking 2:1 clays face each other; as a result hydrogen bonding is not possible. 2:1 clays layers are not strongly held together compare to 1:1 clays layers held together by hydrogen bond. A common example of 2:1 clays is montmorillonite [$Al_2(OH)Si_4O_{10}$]. 2:1 clays are sometimes referred to as expanding clay because water and ions such as Na^+ and Ca^{2+} can enter the inter-layer space, thereby causing the clay to expand[73, 78, 79].

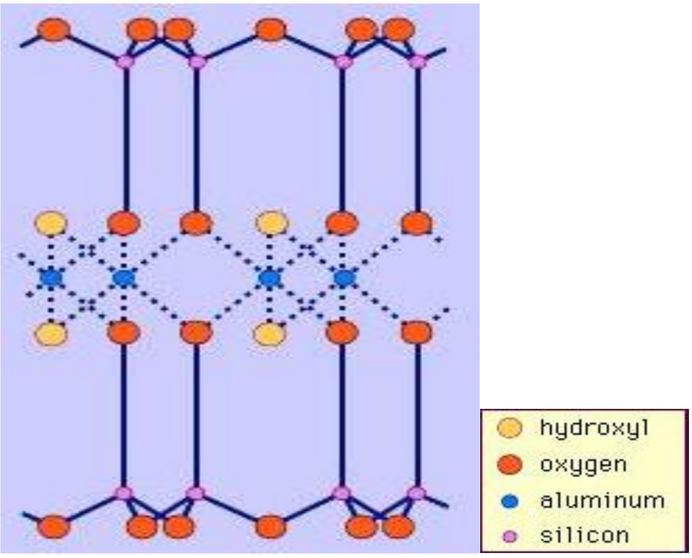


Figure 1.6 Structural representations of 2:1 clays[77].

Clay minerals are generally subject to isomorphous substitution (the substitution of a cation with another cation of similar ionic radius without altering the structure of the clay minerals lattice). In the silica tetrahedral sheet, Al^{3+} usually substitutes for Si^{4+}. Likewise, any of Fe^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Zn^{2+} or Cu^{2+} can substitute for Al^{3+} in the aluminium octahedral sheet. The substituent cations generally have lower positive charges. As a result the lattice acquires an overall net negative charge. This negative charge is associated with the four oxygen of the silica tetrahedral and the six hydroxyls of the aluminium octahedral. The negative charge resulting from isomorphous substitution is a permanent or constant charge. The permanent charges are structurally induced and are not pH dependant. Permanent charges are balanced by the absorption of cations (e.g. PTE) in the clay particle surface. Illite $[K_{0-2}Al_4(Si_{6-8}Al_{0-2})O_{20}(OH)_4]$ is an example of 2:1 clay that has varied amount of absorbed potassium (K) in the inter-layer space. The absorbed cations can be exchanged with other cations in soil or sediment solution[73, 79].

1.4.2. Mineral (hydr)oxides

Aluminium (Al), iron, and manganese are the common mineral (hydr)oxides found in soil and sediment[46, 73]. They are secondary minerals formed from Al, Fe and Mn released in weathered primary minerals. Mineral (hydr)oxides are ubiquitous, and usually found in small amounts in highly weathered soils[73]. Mineral (hydr)oxides occur as discrete crystals, mixed gels and coatings on other minerals. Gibbsite

[$Al(OH)_3$], goethite ($FeOOH$), and birnessite (MnO_2) are the common mineral (hydr)oxides found in the environment[46, 73]. Aluminium (hydr)oxides are more persistent in the environment compared with Fe and Mn (hydr)oxides. This is because, unlike Fe and Mn, Al does not undergo redox changes, it exist only as Al(III). Moderate anaerobic conditions cause the conversion of Mn(IV) to Mn (II), resulting in the small concretion of Mn oxides that is usually found in the environment. Anaerobic conditions such as in bottom sediments can lead to the reduction of Fe (III) to Fe (II). Under aerobic conditions, the Fe (II) is reoxidised to lepidocrocite (γ-FeOOH) which eventually form goethite if the oxidising condition persist[46].

Mineral (hydr)oxides are amphoteric. They can be negatively or positively charged depending on their characteristic point of zero charge and pH. This implied that oxygen in the surface of mineral (hydr)oxides can exist in three possible state. For instance FeOOH[44, 46, 73]:

$$OX - Fe - OH_2^+ \xleftrightarrow{\pm H^+} OX - Fe - OH^0 \xleftrightarrow{\pm H^+} OX - Fe - O^-$$

Due to mineral (hydr)oxides large surface area (as a result of their particle size range which is usually ≤ 0.002 mm (the clay size fraction) and reactivity (as a result of surface and structural edges functional groups), they play significant roles in the sorption of PTE in sediment[46, 72]. The hydroxyl (-OH) functional groups in the surface and structural edges can donate their protons to the surrounding solution in exchange for PTE depending on the pH[44, 46, 72, 73, 79].

1.4.3. Organic matter

Organic matter (OM) content of soil or sediment can also be referred to as humus and consists of non-humic and humic substances[46]. Example of non-humic substances include polysaccharides, protein, fats, waxes, and low molecular weight acids. Non-humic substances are readily biodegradable. Humic substances consist of biogenic (produced by living organisms) and heterogeneous organic substances, and they are more resistant to degradation. Based on the solubility of humic substances in acid and bases they are subdivided into fulvic acid, humic acid and humin. The fulvic acid is soluble at all pH values, the humic acid is insoluble at acidic pH, and the humin is insoluble at all pH[44, 46, 73, 79]. Carboxyl and phenolic groups are the predominant functional groups in humic substances. Organic matter has a pH-dependant variable negative charge. These negative charges come primarily from the deprotonation of the acidic functional group. The point of zero charge of OM is approximately pH 3[73]. As the pH value increases the amount of negative charge increases. Coupled with their high specific surface area (800 – 900 m^2 g^{-1}) and their variable charges, OM can act as sorbent and ligands for PTE. The R-COOH and –OH are the main complexing site for PTE in humic substances[46, 73, 79].

1.4.4. Cation exchange capacity

Clay minerals, amorphous minerals, and organic matter are the main constituents of soil responsible for cation exchange capacity (CEC)[73]. Characterisation of soil through CEC determination can also be extended to sediment because of the similarity in their chemistry. Therefore, the CEC can be defined as the capacity of soil or sediment to exchange absorbed cations with other cations[73, 79]. Organic matter has the highest CEC (150 - 300 cmol kg^{-1}). This is due to OM's large surface area and the predominance of variable charges[73]. The CEC of clay minerals can be compromised by impurities tightly held to the isomorphous substituted cations through hydrogen bond. Also due to the predominance of permanent charge in clay minerals, the variability of CEC as a result of pH change is less compare to OM[73]. Generally, the CEC of soil or sediment increases as pH increases due to the development of more negative charges on the organic and clay minerals[73, 79].

1.4.5. Sorption mechanisms of PTE in sediment

Potentially toxic element sorption mechanisms in soil and sediment are similar[46, 72]. The term sorption is often adopted since the exact retention mechanism of PTE in soil or sediment is usually unknown. Sorption generally involves solid uptake of PTE from the neighbouring aqueous phase. Sorption involves three mechanisms, which are adsorption, surface precipitation and absorption (fixation)[73, 80, 81]. The main factors that determine PTE sorption and distribution between the solid and aqueous phase include the physicochemical properties of soil or sediment, PTE speciation and concentration, solid : solution mass ratio, contact time and pH[72, 73, 82, 83].

The pH is the most important factor that influences PTE sorption because it determines the solid phase surface charge. High pH deprotonates the hydroxyl-groups (OH- group) on the solid phase surfaces and edges. This increases the negative charges available for PTE sorption on the solid phase surfaces. Generally, higher pH aids cation sorption. In contrast lower pH reduces the negative charges on the solid phase surfaces through protonation. As a result PTE sorption in soil and sediment decreases at low pH[72, 73, 81].

Adsorption

Adsorption occurs mainly through intermolecular interactions between the aqueous PTE and the functional groups on the soil or sediment surfaces[72, 73, 79]. This results in 2- dimensional accumulation of PTE at the solid phase/water interface. These intermolecular interactions include: inner and outer sphere complexation reactions between the PTE and functional groups on the solid phase surfaces and edges; hydrophobic expulsion of PTE complexes that contain highly non-polar organic moieties; surfactant induced adsorption of PTE that occurs as polyelectrolyte complexes on the solid phase surfaces[79, 81].

Adsorption mechanisms are often classified as specific and non-specific adsorption[81]. Specific adsorption involves inner-sphere surface complexation reactions between PTE and the OH-group on the solid phase surfaces and edges. The OH-group may come from the silanol groups and organic functional groups or other inorganic functional groups. Specific adsorption is more selective, and the binding of the chemosorbed complexes is less reversible compared to non-specific adsorption. Non-specific adsorption involves less selective, weak and reversible outer sphere electrostatic interaction. It includes interstitial water PTE exchange for the cations on the soil or sediment surfaces[46, 81, 84]. Cation exchange is an example of non-specific adsorption[81, 84].

Surface precipitation

Surface precipitation occurs through the growth of new solid phase in a 3-dimensional manner on the solid phase surfaces [73]. The PTE may precipitate as oxides, hydroxides, carbonates, sulfides and phosphates on soil or sediment surfaces[46, 72, 73, 79]. Surface precipitation, like adsorption, depends mainly on the pH and relative amount of ions present[73, 79]. As the amount of PTE adsorbed on the solid phase surfaces increases, adsorption can progress to surface precipitation. Surface precipitation occurs through homogeneous precipitate and/or co-precipitates. Homogeneous precipitate can occur when the solid phase solution is saturated with PTE, while the solid phase surface acts as a nucleation site. Surface precipitation is termed co-precipitates when the precipitates are derived from chemical species in solid phase solution and dissolution of the minerals. For co-precipitates to form, the ionic radius of sorbing PTE and chemical species from the dissolution of solid phase minerals must be similar. There is often a continuum between adsorption and surface precipitation[73].

Absorption

Absorption mechanism involves the diffusion and settling of PTE in a 3-dimensional manner into the solid phase. Potentially toxic elements after being adsorbed may diffuse into the lattice structure of the clay minerals and metal oxides. The PTE become fixed interstitially into the lattice structure of the solid phase. Liberation of the PTE from the interstitial space may require total dissolution of the solid phase[73, 81].

1.5. Extraction of PTE from environmental solid samples

Examples of environmental solid samples include soil, sediment and dust[85]. The extraction method depends on the information required and the instrumental method of analysis adopted for the determination of PTE in the environmental solid samples. Different reagents release PTE from different components of environmental solid samples[44]. Figure 1.7 summarises different approaches adopted for the determination of PTE in environmental solid samples.

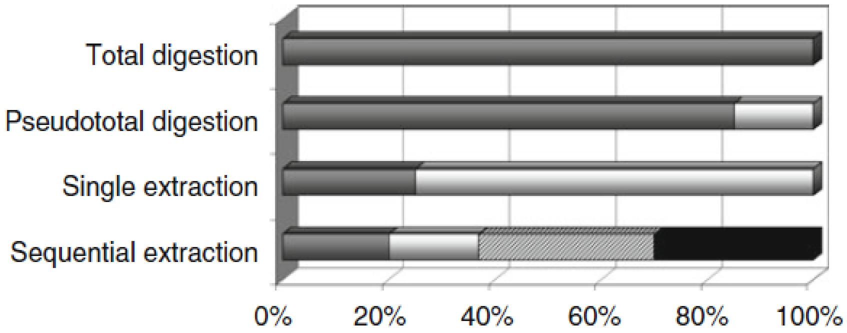


Figure 1.7 Summary of the different approaches adopted for the determination of PTE in environmental solid samples[44].

1.5.1. Total digestion

Hydrofluoric acid (HF) is the choice reagent for total digestion because it can dissolve the refractory silicate component of the soil/sediment[44, 85]. Hydrofluoric acid dissolves the entire components of soil/sediment, and the total PTE bound to the matrix are released and can be measured. Potentially toxic elements bound to the silicate matrix have minimal risk, because under normal environmental conditions they are unlikely to be released. Total digestion of the environmental solid samples can be done in a microwave assisted digestion system described in section 2.2.

1.5.2. Pseudototal digestion

The pseudototal (PT) PTE content of an environmental solid sample accounts for the hypothetically soluble and potentially mobile concentrations in the environment[44, 85]. In PT digestion all major components of the environmental solid samples are dissolved except the primary silicates. The PTE bound to the dissolved components are released and can be measured. A mixture of hydrochloric and nitric acids in the ratio 3:1 (*aqua regia*) is the reagent usually used in the PT digestion of environmental solid samples[44, 85]. Pseudototal digestion of environmental solid samples can be done in a microwave assisted digestion system described in section 2.2.

1.5.3. Single extraction

The potential mobility, bioavailability and ultimately the toxicity of PTE to organisms depend on the form and the way they are bound to environmental solid samples[15, 16]. Single extraction is a one-step procedure involving the use of a reagent (e.g. salt solution of calcium chloride, sodium nitrate and ammonium nitrate) to liberate PTE from a target fraction of the environmental solid sample[21, 44].

1.5.4. Sequential extraction

Sequential extraction partitions PTE into various fractions by applying a series of reagents of increasing vigour in a stepwise manner on the same environmental solid sample. Sequential extraction gives more information on the potential mobility, bioavailability and ultimately the toxicity of PTE to organisms in the environment than single extraction. Sequential extractions are operationally defined, although they are often intended to target specific mineral phase. Therefore, it is more accurate to refer to sequential extraction as a method of fractionation of PTE[15, 21].

One of the earliest classical sequential extraction procedures was developed by Tessier *et al*[86]. This involves a five step fractionation: exchangeable, carbonates, Fe and Mn oxides, organic matter and residual fractions. The Tessier *et al*[86] sequential extraction procedure was developed to evaluate the potential impacts of sediment-bound PTE on water body. Rapid increase in the applications of different sequential extraction procedures by different workers[15, 87-90] made meaningful results comparison difficult. Due to the need for standardization, the Community Bureau of Reference of the Commission of the European Communities (BCR) (later the Standards Measurement and Testing Programme) commissioned a project which led to a harmonised 3-steps sequential extraction procedure, and later development of a sediment certified reference material (CRM 601) for validation of the procedure in 1997[91]. The harmonised 3- steps BCR sequential extraction procedure was as stated in Table 1.2[92, 93].

Due to the problem of irreproducible results particularly in step 2, and after a thorough re-evaluation, the original BCR sequential extraction procedure was modified as stated in Table 1.3[94, 95]. The modified BCR also led to the development of a lake sediment certified reference material (CRM701)[96, 97]. In the modified BCR sequential extraction procedure the concentration of hydroxylammonium in step 2 was increased to 0.5 M and the pH was adjusted to 1.5 by adding a fixed amount (25 ml) of 2 M nitric acid. The centrifugation speed was increased from 1500 g to 3000 g for 20 minutes. In addition, it was recommended that the residue from step 3 should be digested with *aqua regia*, making it step 4. As a means of quality control, the sum of step 1-4 of the modified BCR sequential extraction scheme should be equal to the PTE concentration determined in the whole environmental solid sample using *aqua regia* digestion[15, 94 96].

Table 1.2 Original BCR sequential extraction protocol[92]

Step	Reagent	Fraction label	Nominal target phase(s)
1	0.11 mol L^{-1} CH_3COOH	Exchangeable, water-and-acid soluble	Soluble species, carbonates, and cation exchange sites
2	0.1 mol L^{-1} $NH_2OH.HCl$ at pH 2	Reducible	Fe and Mn (hydr)oxides
3	H_2O_2 (85 °C), followed by 1,0 mol L^{-1} CH_3COONH_4	Oxidisable	Organic matter and sulfides

Table 1.3 Modified BCR sequential extraction protocol[95]

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

Despite the usefulness of sequential extraction in the prediction of PTE mobility, bioavailability and associated risk in environmental studies the following pitfalls have been identified by several workers[15, 21, 98, 99]:

i. Incomplete extraction.
ii. Redistribution of analytes among phases during extraction process.
iii. Non- selectivity of reagents for target phases as they may be influenced by other experimental variables.
iv. Precipitation of new mineral phases (formation of artefacts) during extraction.
v. Analytical challenges that may arise from measuring the low levels of PTE in the fractions.

In addition to the pitfalls of sequential extraction procedures, workers using Tessier[100, 101], the original version of BCR[102, 103] and using a 6 step [104] sequential extraction scheme (described in details in chapter four) have shown that sample pre-treatment procedures changes the natural speciation of PTE in freshwater sediments. Rapin *et al.*[100], Bordas *et al.*[101] and Hjorth[105] (described in details in chapter four) have suggested that the response of PTE speciation to different sample preservation techniques may be attributed to the nature of the sediments. This hypothesis seems to be supported by the different responses of the same PTE in sediments with different matrix characteristics investigated by various workers[21, 23-27, 100, 101, 105] applying similar sample pre-treatment procedures. However, the following research gaps were noted:

i. Studies comparing changings in PTE speciation in pre-treated sediments with different natures, under the same experimental condition, using appropriate statistical techniques for data analysis are rare.
ii. Also, there is no comprehensive study, nor agreement on sample preservation techniques to stabilise PTE speciation in freshwater sediment, using the modified BCR sequential procedure[95] despite the overwhelming application of this scheme[8, 15].

Therefore, there is a need for studies that will help provide useful guidance on sample preservation techniques suitable for obtaining consistent geochemical information on PTE in freshwater sediments with different matrices, with the implications for ecological risk assessment, using the modified BCR sequential extraction procedure[95].

1.6. Freshwater sediments and reservoirs in legacy mining areas

Due to decrease in global price and environmental concerns there has been decline in mining and smelting in different parts of the world. For instance, there was a decline in mining in the United Kingdom in the early 20th century due to global decreases in metal price[63, 106]. Another example was the decrease in artisanal gold mining in El Triunfo mining district in Mexico from 1748 until the end of 20th century[107, 108]. Despite the decline in mining and smelting, the legacy of PTE impacts remain in water bodies with historical mining related activities in their catchments[63, 109-111]. Consequently, it is important to characterise the status, assess the potential mobility and bioavailability, and the ecological risk of PTE in rivers and reservoirs sediments impacted by historical mining operations in their catchments.

1.6.1. Studies on the impacts of historical mining and smelting on reservoirs sediments

Hiller *et al.*[33] studied the status of PTE in sediments of the Ruzin and Velke Kozmalovce Reservoirs in Slovakia. There was extensive mining of Cu, Fe and mercury (Hg) in the last five centuries in their catchments. Several urban wastes were also discharged into the reservoir's tributaries. Correlation analysis was carried out on the PT PTE concentrations in the sediment samples to determine possible similar sources. There were strong positive correlations between concentrations of the following PTE: Co/Cu (0.83); Co/Pb (0.92); Co/Sb (0.94); Co/Zn (0.91); Cu/Pb (0.82); Cu/Sb (0.91); Cu/Zn (0.94); Pb/Sb (0.94); Pb/Zn (0.81); Sb/Zn (0.91) and As/Cd (0.84); As/Zn (0.82); Cd/Zn (0.88); Co/Pb (0.92); Cu/Pb (0.81) in sediments of the Ruzin and Velke Kozmalovce Reservoirs, respectively. These strong positive correlations between the PTE were interpreted as an indication that they originated from similar sources. A speciation study was performed using a modified BCR sequential extraction procedure to extract PTE in the sediments obtained from both the Ruzin and Velke Kozmalovce Reservoirs. The fractions were designated, water-soluble, acid-soluble, reducible, oxidisable and residual. All the reagents used for extraction were the same as BCR sequential extraction scheme[95] except in the residual fraction where a mixture of HF/HNO_3/$HClO_4$ was used instead of *aqua regia* and distilled water for the water soluble fraction. The fractionation patterns in both reservoirs were similar. The mean percentage distributions of PTE in the sediment samples were Co > Sb > Cd > Pb > As > Cu > Zn > Hg in water-soluble fraction, Cd > Co > Zn > Cu > Ni > Pb > As > Sb > Hg in acid- soluble fraction, Pb > Zn > Cd > Cu > Ni > Co > Sb > As > Hg in reducible fraction, Hg > Cu > Zn > Cd > Ni > Pb > Co > As > Sb in oxidisable fraction and As > Sb > Ni > Co > Cu > Zn > Pb > Hg > Cd in residual fraction. Cadmium (44.9 – 52.6 %) and Zn (27.8 – 48.7 %) were found in considerable amount in the water and acid-soluble fractions. This was attributed to the binding of Cd to carbonates. The greatest amount of Pb (75.3 – 77.4%) was found in the reducible fraction, reflecting the strong association between Pb and FeOOH[44, 73]. Copper (26.5 – 36.4 %) and Hg (66.5 – 99.0 %) were the predominant PTE in the oxidisable fraction. This was interpreted as reflecting the ability of Cu and Hg to easily form stable complexes with OM. Previous studies[31, 32, 110, 112, 113] have also shown that Cu and Hg form stable complexes with OM. Arsenic, Co, Ni and Sb were found mainly in the residual fraction, indicating that As, Co, Ni and Sb were bound to the refractory mineral phase[33].

The Alqueva Reservoir in Portugal was impacted by PTE due to historical mining and smelting in the catchment dating back to 3000 BC[32, 114, 115]. Palma *et al.*[32] assessed the status of PTE in the Alqueva Reservoir sediments. Five sediment samples were collected at each occasion, in the wet and dry periods from the Alqueva Reservoir[32]. The BCR sequential extraction procedure[94, 95] was applied on the sediment samples and the results showed that Cd (wet period: 51 – 88%; dry period: 42 – 76%) and Pb (wet period: 53 – 87; dry period: 55 - 88%) were found in the highest percentage in the exchangeable and reducible fractions, respectively. Consequently, Cd was the most labile PTE. Copper (5 – 65 %) was the only PTE present in high percentage in the oxidisable fraction in both periods. Arsenic (wet period: 59 – 91 %; dry period: 82 – 92 %), Cu (wet period: 58 – 85 %; dry period: 26 – 61 %) and Zn (wet period: 58 – 93 %; dry period: 74 – 85%) were distributed mainly in the residual fraction. The rank order of potential mobility based on the percentage of PTE found in the exchangeable fraction was Cd > Pb > Cu > Zn > As[32]. The predominance of Cd, Pb, Cu and As in the exchangeable, reducible, oxidisable and residual fractions, respectively, were similar to the results of Hiller *et al.*[33]

Garcia-Ordiales *et al.*[110] investigated the status of PTE in the sediments of the Castilseras Reservoir in Spain. The Castilseras is in the Almaden Hg mining district in Spain. There was extensive mining of Hg and, to a lesser extent Ag, Pb and Zn in the catchment of the Castilseras Reservoir for more than 2000 years. The results of the application of the BCR sequential extraction procedure[95] on the Castilseras Reservoir sediments were as follows: Mn (52 %) and Zn (36 %), As (48 %), Fe (50 %) and Mn (35 %), Cu (53 %), Pb (47 %) and Zn (36 %) and, Ni (> 65 %) were found in the exchangeable, reducible, oxidisable and residual fractions, respectively. The occurrence of Ni in high proportion in the residual fraction was attributed to natural sources. The sum of each of the PTE (As, Cu, Fe, Mn, Pb and Zn) found in the labile fractions (exchangeable, reducible and oxidisable) was in the range 45 % to 88 % and, this was interpreted as indicating that these PTE were potentially bioavailable and may enter the food chain[110].

Lake Roosevelt is a reservoir located in Washington, USA. High levels of PTE in the sediments of Lake Roosevelt have been attributed primarily to the impacts of an upstream Pb-Zn smelter in Trail, British Columbia, Canada[116]. The smelters still discharged large quantities of PTE contaminated slag into the Columbia River upstream of Lake Roosevelt until the end of 1995[116]. The inflow of the Spokane River to the Lake Roosevelt was another source of PTE in the reservoir. The Spokane River was impacted by PTE due to mining activities in the drainage area[116]. Besser *et al.*[116] investigated the status of PTE in Lake Roosevelt sediments in 2004. Eight sediment samples were collected in the vicinity of Lake Roosevelt. Six of the sediment samples were collected in the Lake Roosevelt starting downstream very close to the dam. The seventh and eighth sediment samples were collected in the free-flowing reach of the Columbia River upstream and a tributary (Sanpoil River) and downstream of Lake Roosevelt, respectively. The Sanpoil River was used as a reference site because it was in an area unaffected by PTE input from the smelter. The Sanpoil River flowed into Lake Roosevelt between the first and second sampling sites downstream of the reservoir. The sediment samples collected from the free-flowing reach of the

Columbia River upstream of the reservoir had the highest PT concentration of As, Cu, Pb and Zn. Generally, the PT concentrations of PTE decreased downstream of Lake Roosevelt, except for the highest PT Cd concentration that was determined in the sediment downstream of the reservoir. Two of the sediment samples collected from the Lake Roosevelt had the lowest PT PTE concentrations, similar to that of the Sanpoil River. Consequently, the lowest PT PTE concentrations in the two sediment samples were attributed to natural source. The operationally defined fractions of PTE in the Lake Roosevelt sediments were determined using a four step sequential extraction procedure[116, 117]. Potentially toxic elements in upstream sediment samples were in greater amount in both the oxidisable and residual fractions, while in the downstream sediment samples the analytes were in greater amount in both the exchangeable and reducible fractions. The shift of PTE from less labile fractions in the upstream sediments, to more labile fractions in the downstream sediments was attributed to weathering of slag particles in the sediments as they move downstream. The distribution of PTE in the operationally defined fractions of the sediment samples of the two sites with the lowest PT concentrations and the reference site were similar. Consequently, PTE in the sediments collected from the two sites with the lowest PT concentrations and in the reference site was attributed to the regional background levels. The similarities in PT concentrations and operational speciation of PTE in the sediment samples collected in sites before and after the confluence of the Spokane River to the Lake Roosevelt were interpreted as indicating that the river had limited impacts on the status of the analyte in the reservoir.

Harding *et al.*[36] determined the concentrations of PTE in water, sediments and some aquatic plants (*Nitella Flexilis* and *Glyceria Fluitans*) in the Derwent Reservoir. Silver (Ag), Ca, Cd, cobalt (Co), Cu, Fe, magnesium (Mg), Mn, Ni, Na, Pb and Zn content of unfiltered and filtered water, sediments and plant samples were determined. Aluminium and potassium contents were also determined in the unfiltered and filtered water, and plant samples. The highest concentration of Cd, Pb and Zn in the aquatic plants studied was 21 µg g^{-1}, 875 µg g^{-1} and 750 µg g^{-1} respectively. The mean concentration of Cd (0.003 mg L^{-1}), Pb (0.065 mg L^{-1}) and Zn (0.216 mg L^{-1}) in the water column decreased by 98.3 %, 89.2 % and 70.3 % respectively downstream of the reservoir. This decrease in the concentrations of Cd, Pb and Zn compared to the water column was attributed mainly to the deposition of these PTE in the Derwent Reservoir sediments[36]. The sediment samples were digested in boiling nitric acid. The highest concentration of Cd, Pb and Zn were 18 µg g^{-1}, 1500 µg g^{-1} and 1200 µg g^{-1}, respectively. The highest concentration of Pb (1500 µg g^{-1}) was determined in sediment samples collected along the original course of the River Derwent. The mean concentrations of Cd, Pb and Zn in sediment samples were 13 µg g^{-1}, 827 µg g^{-1} and 1040 µg g^{-1}, respectively. Both Pb and Zn showed a significant negative correlation with distance downstream in the Derwent Reservoir sediments. Calcium and Ag showed a significant positive correlation with Pb in the sediment samples. The Ca and Ag determined in the sediment samples were attributed to the mining of fluorspar and galena, respectively in the catchment. The concentrations of Co, Cu, Ni and Zn showed significant correlations with Fe in the sediments. This was attributed to the binding of Co, Cu, Ni and Zn to FeOOH or co-precipitation with Fe, which were interpreted as the major possible pathways by which these PTE bind to the sediments. Harding *et al.*[36] thus showed that sediment was the major sink for PTE in the Derwent Reservoir. This is consistent with the recognition of sediment as the major sink for PTE in water systems elsewhere[6, 8-11, 30, 118]. However, the following research gaps were noted:

i. The high proportion of PTE found in the labile fraction of the reservoir sediments with legacy mining areas investigated by Hiller *et al.*[33], Palma *et al.*[32] and Garcia-Ordiales *et al*.[110] are of environmental concern. This suggest that these PTE (particularly Cd which was in high proportion in the exchangeable fraction) can easily be remobilised and enter the food chain. However, the hot nitric acid digestion conducted by Harding *et al.*[36] cannot provide useful information on the potentially mobile and bioavailability of PTE in the Derwent Reservoir sediments, thereby creating a relevant research gap for speciation analysis.

ii. The concentrations of PTE varies with sediment particle size[6, 72]. In addition, there is differential deposition of sediments based on particle size in lakes[70, 71]. However, similar to Harding *et al.*[36] work in the Derwent Reservoir, other studies in reservoirs impacted by old mining operations including Manwan in China[119], Marismillas in Spain[120], Alqueva in Portugal[28], Ruzin in Slovakia[33], Lake Roosevelt in the USA[116] and Castilseras in Spain[110] did not investigate the impacts of sediment transport on PTE status in the water bodies. This suggests that data on the impacts of sediments transport on the geochemical behaviour of PTE in reservoirs impacted by old mining operations is rare. Therefore, the assessment of the impacts of sediments transport on the geochemical behaviour of PTE in reservoirs impacted by old mining operations in the catchments is a relevant point of research.

Figure 1.8 is an illustration of potentially toxic elements cycle in a reservoir system.

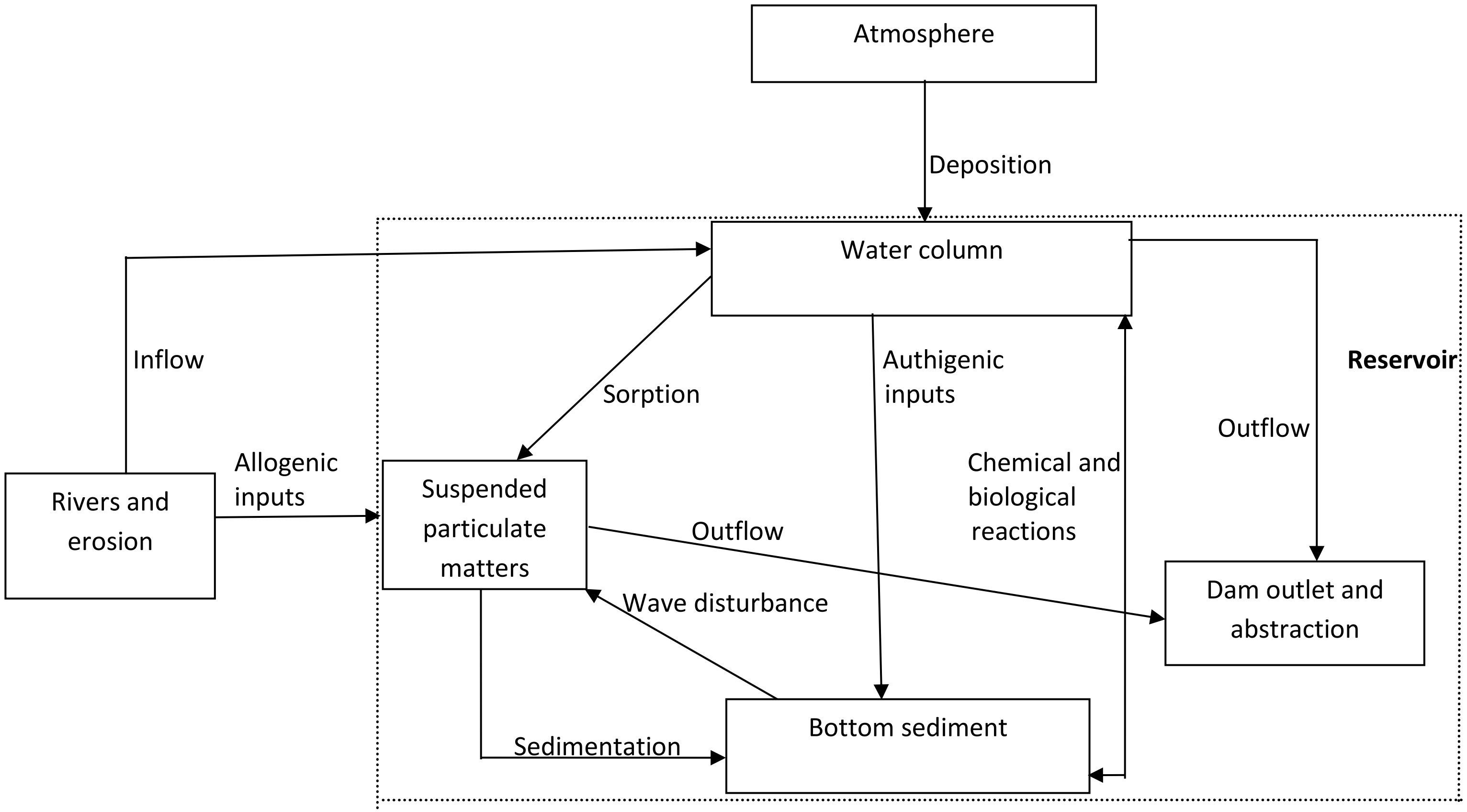


Figure 1. 8 Potentially toxic element cycle in a reservoir system.

1.7. Aims and objectives

The overall aim of this work is to provide useful guidance on the appropriate sample preservation procedures for the stabilisation of PTE in freshwater sediments with different natures, and to improve the knowledge on the analyte's geochemical behaviour in reservoir sediments impacted by historical mining operations in their catchments, using the Derwent Reservoir as a case study. The specific aims and objectives are as follows:

i. To assess the effect of sample pre-treatment procedures on the operational speciation of PTE in freshwater sediments with different matrix characteristics, using the BCR sequential extraction procedure[95]. This will help provide guidance on sample pre-treatment procedure suitable for obtaining useful geochemical information on PTE in freshwater sediments and the implications for ecological risk assessment.

ii. To assess the effects of extended freeze storage (at -18 °C for one year) on the operational speciation of PTE in freshwater sediments with different matrix characteristics, using the BCR sequential extraction procedure[95]. This will provide useful information on how long the natural speciation of PTE may be preserved in freshwater sediments, and the implications for ecological risk assessment.

iii. To conduct a preliminary investigation on the status of PTE in the Derwent catchment sediment, using *aqua regia* pseudototal digestion, sequential extraction, and sediment quality index. This will be used to assess the need of progressing with the study on PTE status in the Derwent Reservoir sediments. This will also be the first study on the potential mobility, bioavailability, and the ecological risk assessment of PTE in the River Derwent sediments.

iv. To assess the source, transportation and geochemical behaviour of PTE in the Derwent Reservoir sediments using sequential extraction, sediment transport and chemometrics. This will improve knowledge of the geochemical behaviour of PTE in reservoirs impacted by old mining operations.

v. To assess the impacts of old mining operations on the concentrations, potential mobility, bioavailability, and ecological risk assessment of PTE in the Derwent Reservoir sediment, using sequential extraction and sediment quality indices. This will be the first study on the potential mobility, bioavailability, and the ecological risk assessment of PTE in the Derwent Reservoir sediments.

2. Theory of instrumentation

2.1. Introduction

This chapter describes the fundamental theories of microwave assisted digestion systems and inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS was the main instrumental technique used to measure PTE in this work.

2.2. Microwave assisted digestion

Acid digestion aided by external heat can be used to liberate PTE bound to environmental solid sample into aqueous medium suitable for introduction into ICP-MS. A microwave assisted digestion system was used as the external heat source for acid digestion of sediments in this work.

2.2.1. Theory of microwave heating[121-131]

Microwaves are non-ionising radiation positioned between the infrared and radio frequencies regions of the electromagnetic spectrum with a frequency range of 300 MHz to 300 GHz corresponding to a wavelength of 1 cm to 1 m and an energy of 1.24 µeV to 1.24 meV. Microwaves are a combination of magnetic and electrical fields which oscillate perpendicularly to each other (Figure 2.1). The electric field is responsible for microwave induced heating and only dielectric materials are affected based on two phenomena: ionic conduction and dipole rotation. Under the influence of the changing electrical field both phenomena occur simultaneously. Most commercially available microwave ovens operate at 2.4 GHz to avoid interference with radio frequency.

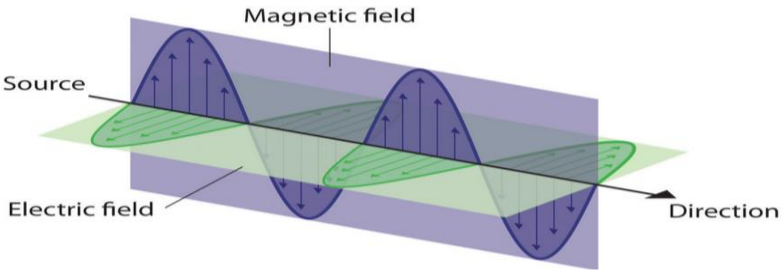


Figure 2.1 Schematic diagram of an electromagnetic wave[132].

In ionic conduction, the influence of the changing electrical field imposes electrophoretic migration on the irradiated materials. The migrating ions collide with neighbouring molecules or atoms thereby resulting in friction which eventually heats up the materials. Dipole rotation refers to the realignment of molecular ions to the changing electric field to remain at the same phase. Due to the rapid speed (4.9×10^4 times per second) at which the electrical component of the wave changes the realignment fails, causing a phase lag which results in successive molecular vibration, friction and eventually heat dissipation in the materials.

The extent to which different solvents absorb microwaves and subsequently pass on the heat generated to neighbouring molecules depend on the dissipation factor (tan δ). The dissipation factor is defined by equation 2.1.

$$\tan \delta = \varepsilon''/\varepsilon' \qquad \textbf{Equation 2.1}$$

where ε" is the dielectric loss (a measure of the efficiency of converting microwave energy into heat) and ε' is the dielectric constant (a measure of ability to absorb microwave energy). The dissipation factor is directly proportional to the microwave energy absorbed and hence the heat generated.

2.2.2. Basic components of a microwave oven

Among other vacuum tubes, the magnetron has the widest application as a source of electromagnetic radiation in microwave ovens; others include travelling wave tubes (TWTs) and klystrons. Other basic components of microwave ovens are the wave guide (used to propagate microwaves from the source), the applicator (the turn table where the sample is placed for irradiation) and the circulator to ensure the microwave is in the forward direction. The magnetron (Figure 2.2) like any other vacuum tube has an anode with high potential compare to the cathode. The anode has many cavities and the cathode is positioned at the centre attached to an external magnet that produces a strong magnetic field perpendicular to the strong electric field produced due to the high potential difference between the anode and the cathode. When a high voltage is applied, the cathode heats up giving out electrons that are accelerated towards the anode by the electric field. The magnetic field force imposes a swirling motion on the electrons as they accelerate towards the anode. A swirling cloud of electrons is created. As the electrons move around a resonant cavity oscillation is induced, thus producing an electromagnetic field with a characteristic frequency depending on the cavity's size. The electromagnetic field is harnessed from the cavity as microwave radiation *via* the output antenna or wave guide. Because magnetron tubes employ resonant structures to produce the electromagnetic field, they can only produce an output with a fixed frequency, while variable frequency electromagnetic fields are produced by TWTs.

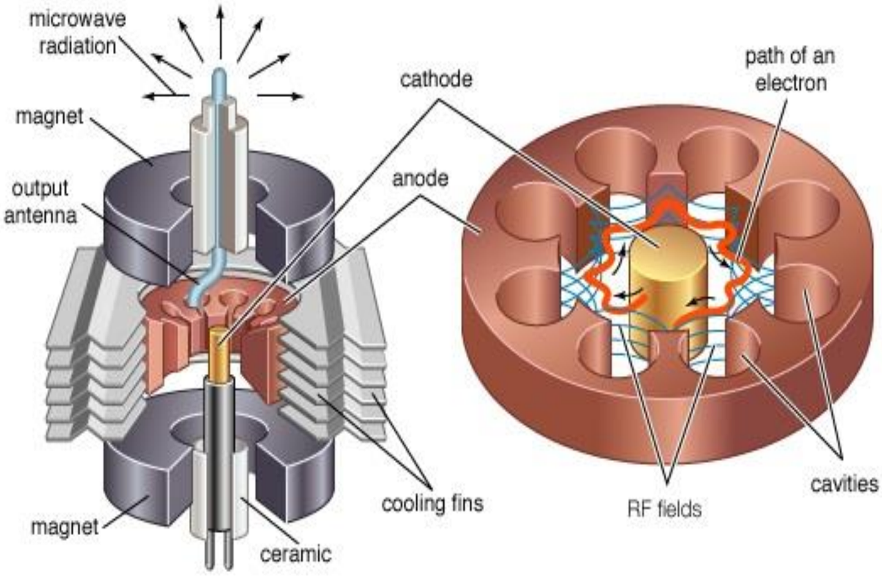


Figure 2.2 Schematic diagram of a magnetron [129].

2.2.3. Close and open vessel system

Microwave assisted digestion systems are generally classified into closed vessel (Figure 2.3) and open vessel systems (Figure 2.4). Either system is available as a multi-mode or a single-mode (or focused) system. In multi-mode systems samples are evenly irradiated, while in single mode or focused systems irradiation is restricted to a target zone, and consequently the sample is subjected to a relatively stronger electric field. The multi-mode system is mostly employed in closed vessel systems and the single-mode or focused system in open vessel systems. The main distinction between the closed vessel and open vessel systems is that the former is operated under controlled pressure and temperature, while the latter is operated under atmospheric pressure. Thus, the chances of cross contamination and loss of sample is lower in closed vessel system compared to open vessel system.

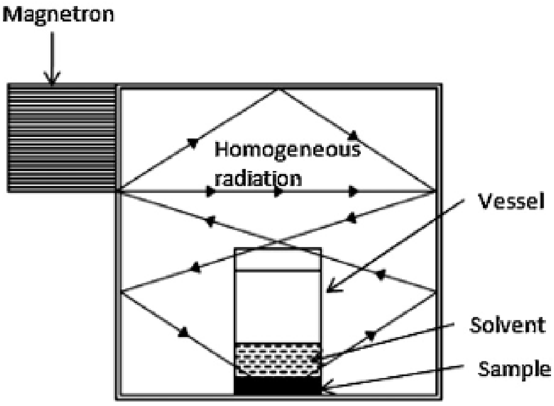


Figure 2.3 Schematic diagram of closed-vessel microwave assisted digestion system[123].

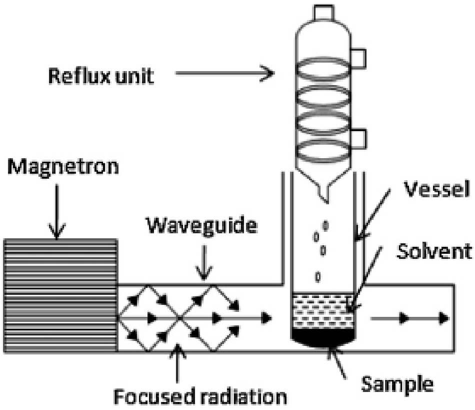


Figure 2.4 Schematic diagram of open-vessel microwave assisted digestion system[123].

2.2.4. Heating mechanism

Heating using microwave and conventional systems occurs through two different mechanisms. In conventional systems, time is taken to thermally heat the digestion vessel from the outside before heat can be transferred into the solution inside. This is due to the inbuilt thermal gradient caused by convention currents (Figure 2.5). Consequently, it takes a longer time to reach the target temperature and there is a non-uniform distribution of heat in the solution.

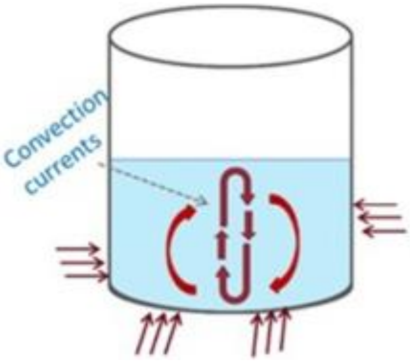


Figure 2.5 A schematic diagram of conventional heating mechanism [133].

In contrast, in microwave systems the digestion vessel (e.g. a polytetraflouroethylene vessel) is transparent to the microwave radiation, so the solution is heated directly with minimal thermal gradient. Superheating occurs (Figure 2.6) which enhances efficiency and accelerates mass transfer of the analytes from the sample matrix into the solution. It takes a relatively shorter time than conventional heating for the solvent to get to the boiling point because there is no thermal heat lost due to vessel heating. Heat distribution is uniform, enhanced by the even irradiation within the system.

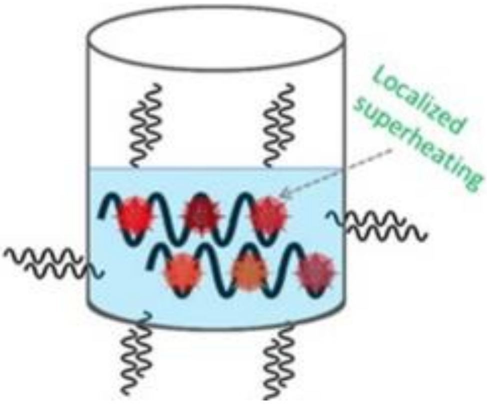


Figure 2.6 Schematic diagram of microwave heating mechanism[133].

2.3. Inductively coupled plasma mass spectrometry[44, 85, 134-138]

Inductively coupled plasma-mass spectrometry (ICP-MS) is a versatile multi-element analysis technique that offers a better detection limit (< ng g^{-1}) compared to many atomic spectroscopy techniques[44]. In addition, ICP-MS offers short analysis time, and is generally used to analyse liquid samples. However, it can also accept gaseous and solid samples. This explains the wide acceptance of ICP-MS in environmental, medical, archaeological and industrial applications. The major components of a typical ICP-MS instrument include sample introduction system, inductively coupled plasma (ICP), interface (sample and skimmer cones), ion lenses, collision and reaction cell, mass spectrometer, and detector. A schematic diagram of a typical ICP-MS instrument is shown in Figure 2.7. The use of ICP-MS for elemental analysis starts by first converting the sample to forms suitable for introduction into the plasma. The analytes are ionised in the plasma, then extracted and transported to the mass spectrometer. Ions are separated in the mass spectrometer according to mass to charge ratio. The output of resolved ions from the mass spectrometer is counted and can be converted to absolute concentration.

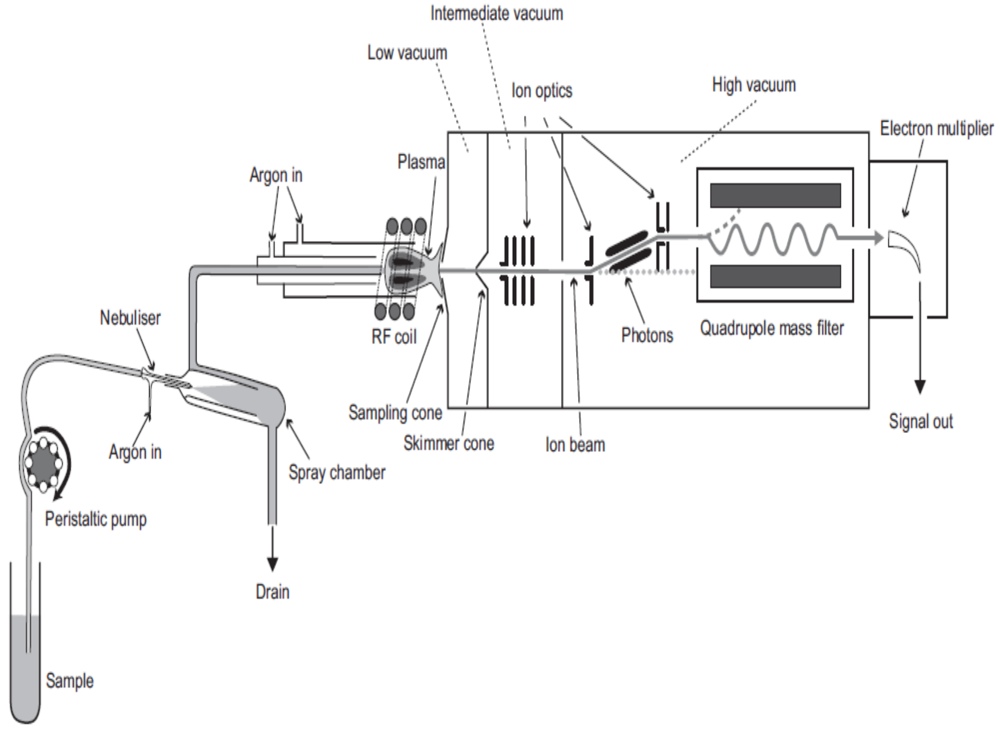


Figure 2.7 Schematic diagram of a typical ICP-MS instrument[139].

2.3.1. Sample introduction

Laser ablation, nebulisation (the combination of a nebuliser and spray chamber), electrothermal vaporisation, chromatography, hydride generation and cold vapour techniques are some of the approaches that have been developed for the introduction of solid, liquid and gaseous samples into the ICP-MS. However, samples are mostly introduced into the ICP-MS in liquid form. The combination of a nebuliser and spray chamber is common for the introduction of liquid samples into the ICP-MS.

Attention will be given to the use of a nebuliser and spray chamber, because it was the sample introduction approach employed in this work. Generally, a peristaltic pump is used to draw liquid sample through a narrow bore tube into the nebulizer to ensure a constant flow rate. The nebuliser can then be operated at an optimum flow rate of approximately 1 ml min^{-1}.

Nebulisers

The nebuliser is used to convert liquid sample into an aerosol. The aerosol is screened for droplet size using the spray chamber before it is introduced into the plasma. Nebulisers commonly used for the conversion of liquid samples into aerosol include the pneumatic concentric nebulisers (Figure 2.8a), cross flow nebuliser (Figure 2.8b), and Babington or V-groove nebuliser (Figure 2.8c).

A high speed argon carrier gas is introduced at the side arm of the pneumatic concentric nebuliser. The carrier gas exits at the pneumatic concentric nebuliser nozzle causing a lowered pressure region. As a result of the lowered pressure region, sample solution flows through the inner capillary tube of the pneumatic concentric nebuliser exiting at the nozzle. The interaction between the sample solution and carrier gas at the exit point produces a coarse aerosol. In the cross-flow nebuliser, the argon carrier gas and the sample needles are positioned perpendicular to each other. The sample solution and argon carrier gas meet at the exit points of both needles. The high speed of the argon carrier gas breaks the sample solution into coarse aerosol. Pneumatic concentric and cross flow nebulisers are both susceptible to clogging. The Babington or V-groove nebuliser is a modification of cross the flow nebuliser designed for samples with high solid content (including slurry) or viscosity. In the Babington nebuliser, sample film flows freely through a v-grooved channel over the carrier gas orifice, rather than the narrow capillary tube in pneumatic concentric and cross flow nebulisers. The escaping carrier gas of the Babington nebuliser breaks the sample film into a coarse aerosol. The Babington nebuliser is less susceptible to clogging but has poor sensitivity and is less stable compared to pneumatic concentric and cross flow nebulisers.

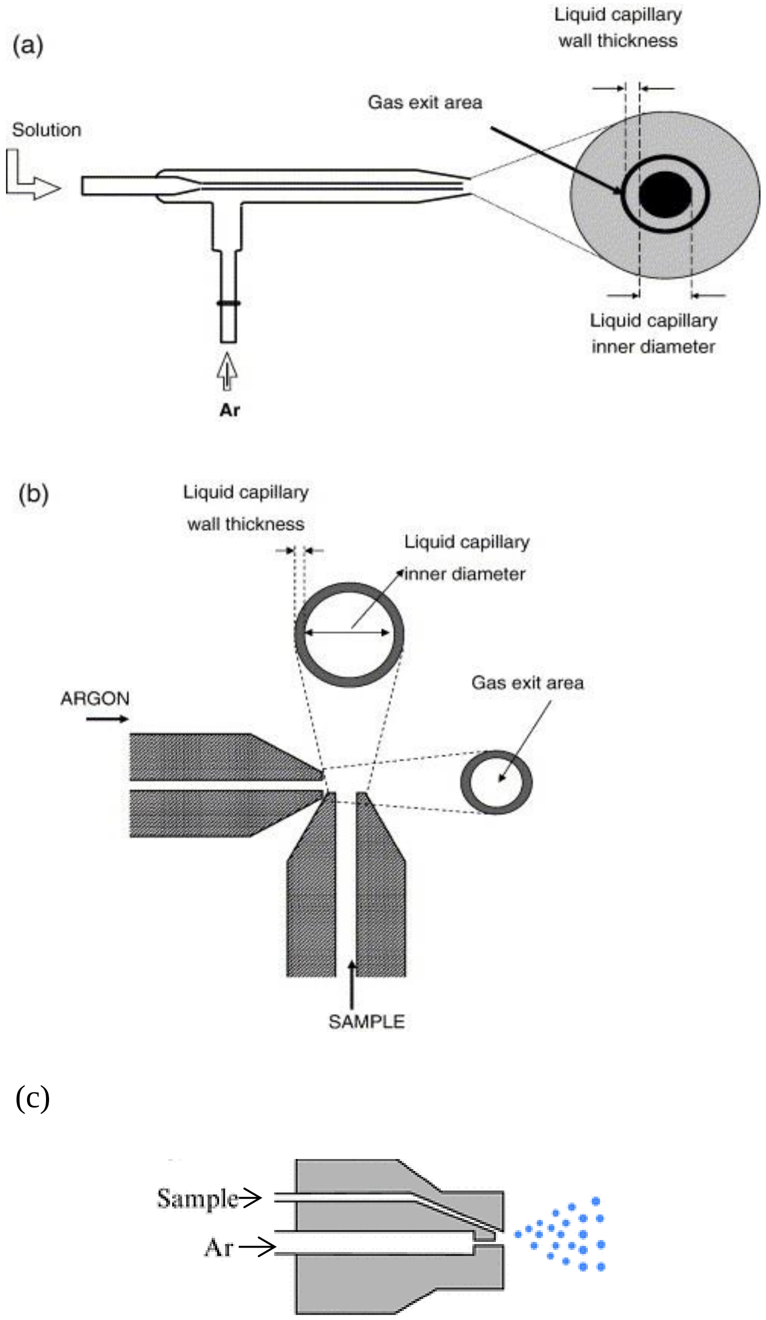


Figure 2.8 Schematic diagram of nebulisers (a) pneumatic concentric nebuliser[140] (b) cross flow nebuliser[140] (c) Babington (V-groove) nebuliser[141].

Spray Chambers

The spray chamber screens the aerosol generated in the nebuliser into an appropriate size (approximately 10 µm) suitable for efficient plasma processes (desolvation, vaporisation and ionisation)[134, 139]. There are several designs of spray chambers, including double pass (Scott-type), cyclonic and single pass spray chamber. The double pass spray chamber (Figure 2.9) is the design commonly employed in ICP-MS.

The double pass spray chamber consist of two concentric tubes with a nebuliser inlet and exit for draining excess aerosol to waste, and for introducing fine aerosol into plasma. The aerosol travels in a reverse direction to the nebuliser inlet at 180° into the plasma. The design allows the interaction of the aerosol with the inner wall of the double pass spray chamber to generate a fine aerosol, with excess draining to waste. The design of the double pass spray chamber also helps to stabilise the signal by reducing the turbulence of the nebuliser-generated aerosol.

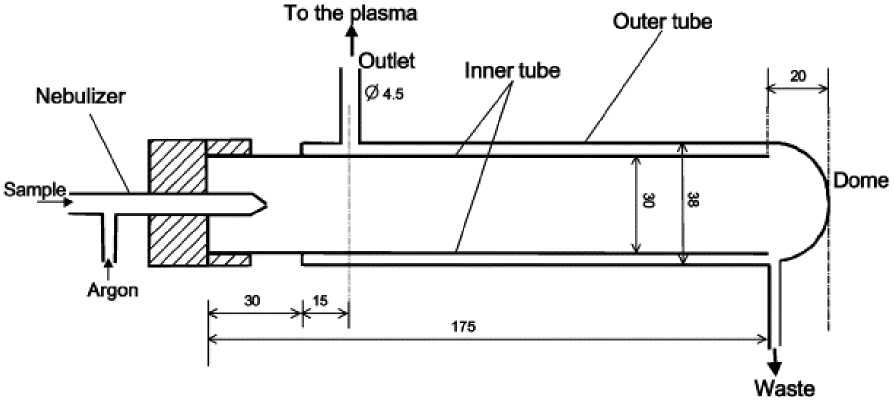


Figure 2.9 Schematic diagram of a double-pass spray chamber - dimensions are given in mm[142].

2.3.2. Inductively coupled plasma

The plasma is a confined cloud of ionised gas. The ICP torch (Figure 2.10) has three concentric glass tubes with three streams of gas. One gas stream is linked to each concentric glass tube. Most commercially available ICP instruments make use of argon gas for plasma generation because of its relative inertness[139]. The inner tube consists of a capillary tube through which sample aerosol is introduced. Both the external and intermediate tubes have tangential gas entry points. A water-cooled radiofrequency (RF) copper coil is located around the external tube. The plasma is generated within the confines of the three concentric glass tubes of the ICP torch at a power of 0.5 – 1.5 kW and a frequency of 27 or 24 MHz. The plasma temperature is usually 7000 – 10000 K.

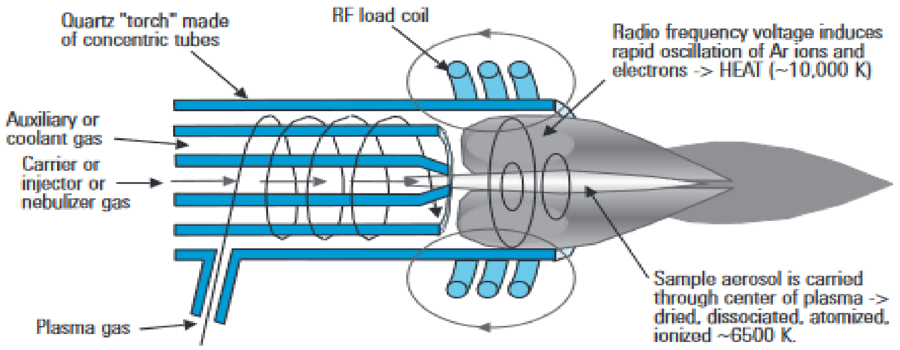


Figure 2.10 Schematic diagram of an inductively coupled plasma torch[137].

The sample carrier gas is switched off when the plasma is to be initiated. Power input to the RF copper coil generates an intense oscillatory magnetic field. A spark from a Tesla coil attached to the outside of the ICP torch is applied to generate seed electrons. The seed electrons are accelerated by the magnetic field and then collide with the argon carrier gas resulting in ionisation of the argon atoms. The plasma produced is self-sustaining with a characteristic bullet shape caused by air pull back in the ICP torch direction by the escaping high velocity (10-15 L min^{-1}) external argon gas stream. This also prevents the outer walls of the plasma torch and RF copper coil from melting by pushing the hot plasma away from them. Argon atoms, argon ions, and electrons co-exist in the plasma.

The sample carrier gas is switched on when the sample aerosol is to be introduced into the plasma. A hole is created at the centre of the plasma by the impact of sample carrier gas, thereby giving the plasma a characteristic “doughnut” or toroidal shape. Inside the plasma, the sample aerosol is dried to a solid, and then heated to a gas. Thereafter the elements to be determined absorb more energy, release electron(s) and become positively charged. The positively charged ions are then extracted into the interface region. The mechanism for the conversion of the sample aerosol into a positively charged ion in the plasma is outlined below:

Aerosol**(Desolvation)** Solid**(Vaporisation)** Gas**(Atomisation)** Atom**(ionisation)** Ion[138]

$$M(H_2O)^{+}X^{-}_{(aq)} \longrightarrow (MX)n_{(s)} \longrightarrow MX_{(g)} \longrightarrow M_{(g)} \longrightarrow M^{+}$$

2.3.3. Ion extraction and focussing

Interface

The interface is an assemblage of inverted water-cooled sample and skimmer cones (Figure 2.11) positioned between the atmospheric ICP torch and the high-vacuum mass spectrometer (MS) to allow for their coupling. This arrangement allows successful transfer of the ions produced in the plasma to the MS while the high degree of sensitivity remains intact. The sample and skimmer cones are made of nickel with orifice diameters of approximately 1.0 and 0.75 mm, respectively. Nickel is a typical material for making sample and skimmer cones because of its high thermal conductivity, relative resistance to corrosion, and robustness. The sample cone is positioned next to the atmospheric plasma (at 760 Torr atmospheric pressure) followed by the skimmer cone.

The pressure after the sample and skimmer cones is maintained at approximately 2.5 and 10^{-4} Torr, respectively. Due to the pressure differential the plasma jet and ions pass through the sample cone orifice. The skimmer cone is positioned so that it allows the passage of the central portion of the expanding jet of plasma ions through the orifice into the ion lens.

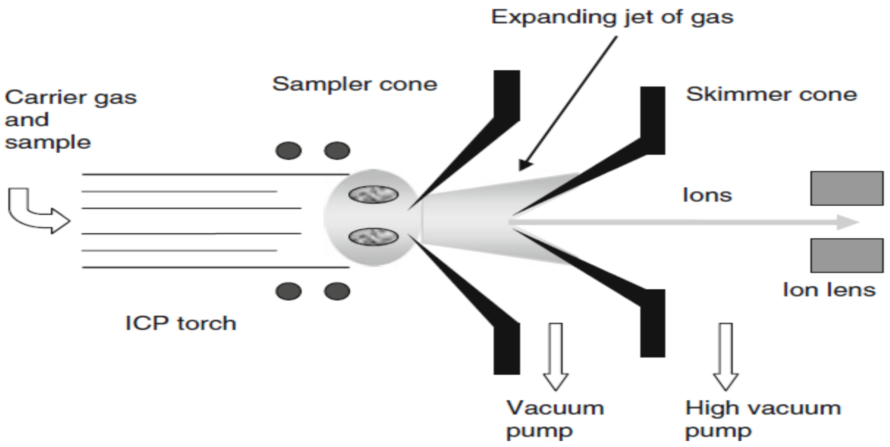


Figure 2.11 Schematic diagram of an ICP-MS interface[44].

Ion lens

The critical role of the ion lens is to focus the positively charge ions into the mass spectrometer. The ion lens is placed between the skimmer cone and mass spectrometer. The large drop of the atmospheric pressure at the chamber to approximately 10^{-14} Torr results in the diffusion of electrons off the ion lens axis (as illustrated in Figure 2.12). The ion lens is an electrostatic device with specific voltage. The ion lens prevents the divergence of the positively charged ions extracted from the interface by repulsion due to similar charge and focuses them into the mass spectrometer. The mass spectrometer is also positioned off ion beam axis to prevent plasma photons and neutral materials passing through alongside the positively charged ions into the mass spectrometer. Plasma photons and neutral materials can cause signal instability if allowed to reach the detector.

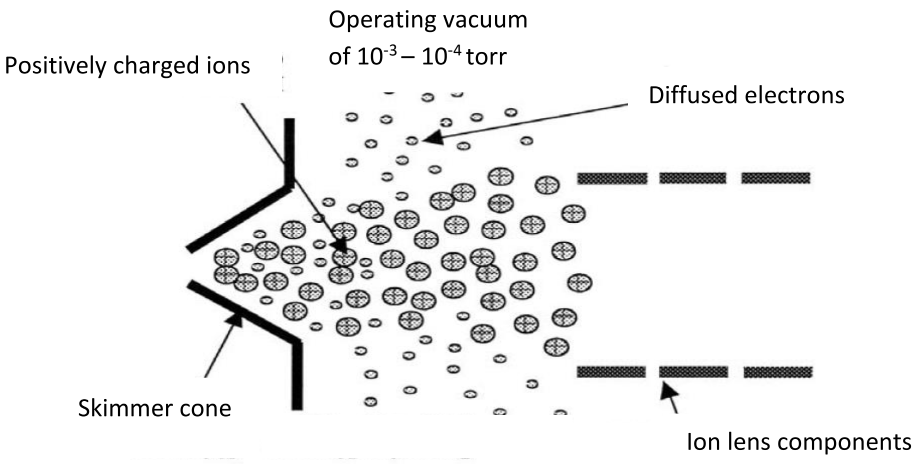


Figure 2.12 Schematic diagram of large pressure drop in ion lens chamber resulting in diffusion of electron off ion lens axis[138].

2.3.4. Mass spectrometer

The mass spectrometer separates the ions based on their mass to charge ratio (m/z). The most commonly used mass spectrometer for routine ICP-MS analysis is the quadropole analyser. A quadropole (Figure 2.13) consist of four straight metal rods positioned parallel to and equidistance from the central axis[134]. Direct current (DC) and RF are applied to opposite pair of the rods. The RF voltages have opposite sign with the same amplitude. As result, any ion entering the quadropole is subjected to an oscillatory path. When a typical DC and RF are selected, only ion of a particular m/z will be able to travel through the length of the rods to emerge at the end. Ions with larger oscillatory paths collide with the rods and are lost due to neutralization. The DC and RF setting on the rods can be changed rapidly. This is the reason the ICP-MS can perform multi-element analysis even though only one m/z can pass through the quadropole at a given time. Other mass analysers available in the market are high-resolution sector field, ion-trap, and time-of-flight mass spectrometers. The quadropole analyser has a disadvantage of being limited to unit mass resolution. However, this is adequate for most applications.

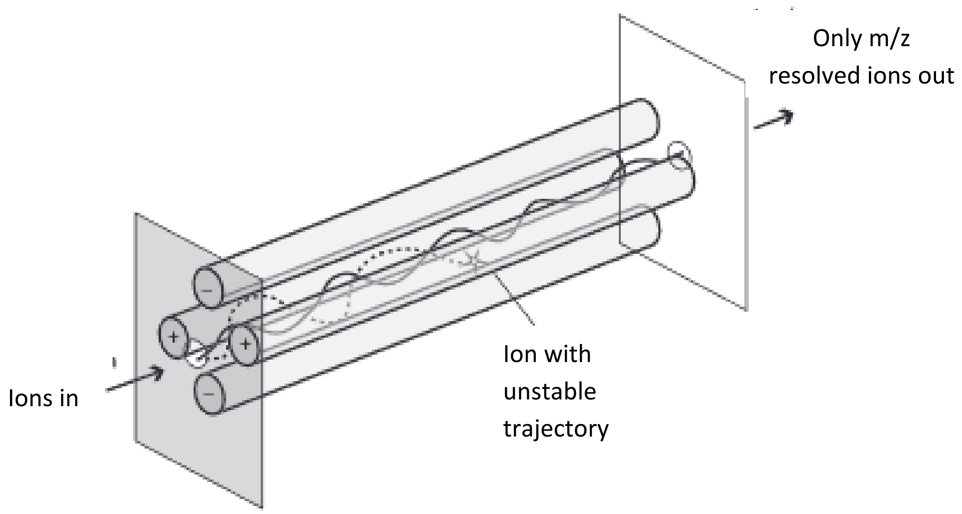


Figure 2.13 Schematic diagram of a quadropole mass analyser[139].

2.3.5. Detector

The electron multiplier tube (EMT) (Figure 2.14) is the detector commonly used in ICP-MS. The EMT is a cone-like tube with the inside coated with lead oxide (PbO) semiconducting materials. The EMT entrance is wide and has a high negative potential (e.g. -3 kV) compared to the remaining part of the tube. The emerging positive ions from the ICP-MS strike the EMT due to the attraction caused by the high negative potential at the entrance. The impact of the strike causes the release of one or more secondary electrons. Electrons released by the first impact strike the surface coating thereby releasing more electrons. This process of electron multiplication continues until a measurable amount of electrons is released. All the released electrons are attracted to the collector inside the tube. This discrete pulse of electrons generated is further amplified outside of the EMT and recorded as the number of ions counted per second. The number of ions counts for analyte of interest can be converted to absolute concentration by comparing it with the ions counts of the same analyte in a calibration reference.

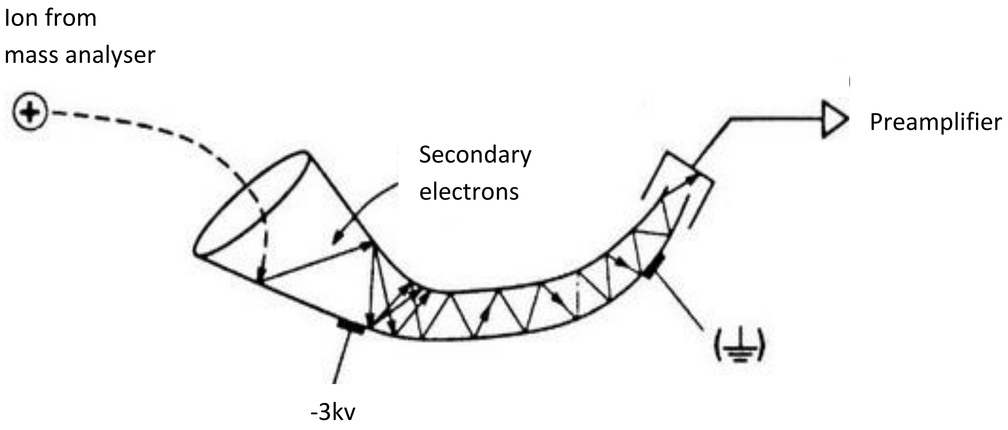


Figure 2.14 Schematic diagram of an electron multiplier tube[134].

2.3.6. Interferences

Interferences in ICP-MS are broadly classified into non-spectral (physical) and spectral interferences based on their sources. Spectral interferences are subdivided into isobaric and molecular interferences.

Physical interferences

Physical interference is associated with problems arising from the sample matrix. The wrong choice of sample-introduction device can lead to nebuliser blockage. Dissolved solids in samples can also build-up on the sample cone. As a result, the orifice size is reduced thereby making effective ion transmission through the interface difficult. Physical interferences can result in loss of sensitivity for analytes. Physical interferences can be minimised using a high-solid nebuliser, matrix-matched standards, and on-line coupling of a chromatographic separation technique to ICP-MS.

Isobaric interferences

Isobaric interferences occur when the atomic mass of different elements overlap. Isobaric interferences can be characterised and avoided by selecting alternative isotopes. For example, spectral overlap occurs between ^{58}Ni (67.9 % abundance) and ^{58}Fe (0.31 % abundance). In this case isobaric interference can be avoided by determining ^{60}Ni (26.2 % abundance) or ^{56}Fe (91.7 % abundance).

However, there are situation where isobaric interferences are not readily removed. For example, calcium with atomic mass 40 has a mass coincidence with the argon ion (atomic mass 40; 99.6 % abundance). The alternative calcium isotope (atomic mass 44) abundance (2.08 %) has low sensitivity. In this case, collision and reaction cells can be used to minimise isobaric interference by shifting m/z of the interfering analyte ion.

Molecular interferences

Molecular interferences are caused by the formation of polyatomic and doubly charged polyatomic species. Polyatomic species are formed as a result of the interaction of the analyte with the aqueous solution, plasma gas, or reagents use to prepare the sample. For example, $^{40}Ar^{14}N^{1}H^{+}$ interferes with ^{55}Mn, $^{40}Ar^{16}O^{+}$ interferes with ^{56}Fe and $^{40}Ar^{35}Cl^{+}$ interferes with ^{75}As. The formation of doubly charged species result in m/z being halved, and as a result there is a spectral overlap with singly charged elements that have equivalent m/z (e.g. ^{138}Ba interferes with ^{69}Ga). The collision and reaction cells can be used to minimise molecular interferences (details in section 2.3.6.1).

2.3.6.1 Minimising spectral interferences

Spectral interferences can be minimised by using cold plasma or collision and reaction cells. To achieve cold plasma conditions, the ICP-MS is operated at low power (0.6 kW) and high gas flow rate (1.1 L min^{-1}). It is reported that the use of cold plasma reduces the formation of Ar^{+}, ArH, ArO^{+} and Ar_2^{+} species[134, 143].

The collision and reaction cells enclose an ion guide which can be pressurised with gas[137]. The collision and reaction cells are placed between the skimmer cone and the mass spectrometer. The interactions of the gas with interfering species minimise spectral interferences. The collision and reaction cells minimise spectral interferences by operating in the collision or reaction mode. In the collision mode, the gas employed (usually helium) collides with polyatomic interferent, resulting in loss of energy of interfering species. The analyte is then separated from the low energy interfering species based on energy difference. In the reaction mode, the gas employed reacts with the molecular interference to form a new species thereby shifting the interfering analyte ion m/z. Some of the reactions employed in collision and reaction cells include:

i. Charge exchange: allows the removal of the argon plasma gas ion interference and the uncharged plasma gas formed is not then detected.

$$Ar^+ + NH_3 \longrightarrow NH_3^+ + Ar$$

ii. Proton transfer: involves the neutralisation of polyatomic interference through proton transfer thereby forming uncharged argon plasma gas which is not then detected.

$$ArH^+ + H_2 \longrightarrow H_3^+ + Ar$$

iii. Hydrogen atom transfer: the m/z of argon plasma gas ion is can be increased by one through hydrogen-atom transfer.

$$Ar^+ + H_2 \longrightarrow ArH^+ + H$$

iv. Adduct formation: allows the m/z with for example ammonia (NH_3) to increase by 17.

$$Ni^+ + NH_3 \longrightarrow Ni{+}NH_3$$

3. General experimental procedures

3.1. Introduction

This chapter outlines the general experimental procedures and data handling employed in this work. Glassware, microwave digestion tubes and sample containers were soaked in 10 % HNO_3 (general purpose grade supplied by Sigma Aldrich, UK) overnight and thoroughly rinsed with distilled water, then in double distilled deionised water, before use. All the reagents used were of analytical grade. Sample solutions were stored in polyethylene bottles and refrigerated at 4 °C prior to analysis. Data analyses were performed with IBM SPSS 24 and Minitab 18.

3.2. pH measurement[144]

3.2.1. Apparatus

i. Centrifuge tube (50 ml, Fisherbrand-Fisher Scientific, Loughborough, UK)
ii. End-over-end mechanical shaker (GFL$^{(R)}$ 3040, Gasellschaft fur Labortechnik GmbH, Burgwedel, Germany).
iii. pH meter (Metller Toledo, Schwerzenbach, Switzerland)

3.2.2. Analytical method

Approximately 5 g of air dried sediment sample was weighed into a 50 mL centrifuge tube, and 25 mL of double distilled deionised water was added. The centrifuge tube containing the mixture was stoppered and shaken on an end-over-end mechanical shaker for 1 hour. The mixture was allowed to stand for 2 hours, and the pH was measured using a calibrated pH meter.

3.3. Determination of cation exchange capacity[145]

3.3.1. Apparatus

i. Centrifuge tube (50 mL, Fisherbrand-Fisher Scientific, Loughborough,UK).
ii. End-over-end mechanical shaker (GFL$^{(R)}$ 3040, Gasellschaft fur Labortechnik GmbH, Burgwedel, Germany).
iii. ACL 4237 centrifuge (CAMLAB Limited, Cambridge, UK).
iv. Thermo Scientific iCE 3000 SERIES AA Spectrometer, UK.

3.3.2. Analytical method

Approximately 2.5 g of air dried sediment (particle size < 2 mm) was transferred to a 50 mL centrifuge tube. The combined mass of the tightly stoppered tube and sediment was recorded, and 30 ml of 0.1 mol L^{-1} barium chloride solution (Alfa Aesar, Lancaster) was added. The tube was shaken for 1 hour, and then centrifuged at 3000 g for 10 minutes. The supernatant was discarded. The addition of 30 mL of 0.1 mol L^{-1} barium chloride solution, shaking, centrifuging and discarding of the supernatant was repeated twice more. This was followed by the addition of 30 mL of 0.0025 mol L^{-1} of barium chloride solution to the sediment cake and then shaken overnight. The tube was centrifuged at 3000 g for 10 minutes. The supernatant was decanted, leaving 2.5 ml of the solution (the concentration of barium in the equilibrium solution was about 0.01 mol l^{-1}). The tube and its contents were weighed, and 30 ml of 0.020 mol L^{-1} of magnesium sulfate (Sigma-Aldrich, UK) solution was added to the sediment cake and was shaken overnight. The tube was again centrifuged at 3000 g for 10 minutes. The supernatant was decanted and filtered through 125 mm Fisher Brand FB 59023 filter paper into a conical flask. A blank was prepared by following the above procedure without the addition of the sediment. Excess magnesium in the final filtrate was determined by atomic absorption spectrometry at 285.2 nm using a Thermo Scientific iCE 3000 SERIES AA Spectrometer. Using a micro pipette, 0.200 mL of the final filtrate was transferred into a 100 ml volumetric flask, and 10 mL of acidified 10 mg L^{-1} lanthanum (III) nitrate hexahydrate (Sigma Aldrich, UK) solution was added and made up to mark with double distilled deionised water. The corrected concentration of magnesium in the solution retained by centrifugation after being treated with 0.0025 mol L^{-1} barium chloride solution was calculated using equation 3.1. The cation exchange capacity (CEC/ cmol+ kg^{-1}) of the sediment samples was calculated using equation 3.2

$$c_2 = \frac{c_1(30 + m_2 - m_1)}{30}$$

Equation 3.1

where c_2 is the corrected magnesium concentration (mmol L^{-1}) in the sediment, c_1 is the magnesium concentration (mmol L^{-1}) in the sediment, m_1 is the mass (g) of the centrifuge tube with the air dried sediment and m_2 is the mass (g) of the centrifuge tube with wet sediment.

$$CEC = \frac{(c_{b1} - c_2)3000}{m}$$

Equation 3.2

where c_{b1} is the magnesium (mmol L^{-1}) concentration in the blank and m is the mass (g) of the air dried sediment.

3.4. Determination of particle size distribution[146-148]

3.4.1 Apparatus

i. The Malvern Mastersizer 2000 (MALVERN INSTRUMENTS Worcestershire, UK).

3.4.2 Analytical method

The sediment particle size distribution (PSD) was determined using the British Standard procedure for the measurement of particle size using the Laser diffraction method. The instrumental conditions of the Malvern Mastersizer 2000 (2000M) with the wet unit (Hydro 2000SM) were set according to the British Standard procedures for the measurement of particle sizes using the Laser diffraction method: Ultrapure water (dispersant) refractive index 1.33; Quartz refractive index 1.55; absorption index 0.1; and particle size range 0.020 to 2000 µm.

The 2000M optical alignment was checked and adjusted when necessary before the start of any measurement. A blank measurement was conducted under the same experimental conditions with the sample measurement. The blank measurement was conducted to ensure the background signals were close to the baseline, immediately just before the sample measurement. A minimum of 2 minutes sampling time was observed to eradicate or minimise the effect of air bubbles.

The sediment samples were air dried and passed through a 2 mm British Standard sieve prior to particle size analysis. Approximately, 0.5 g of the air dried representative sediment sample was quantitatively transferred to the dispersion unit of the 2000M previously filled with 70 ml of ultra-pure water, and then made up to 150 ml by adding additional 80 ml of ultra-pure water. The samples were stirred at 3000 rpm in the dispersion unit and pump rate. Then the sample was passed to the laser light. The light scattering pattern (average of six measurements) produced by the sediment particles in the measurement zone were given as PSD in percent volume by the 2000M instrument software. The PSD data obtained from the 2000M were grouped into % clay (< 0.002 mm), % silt (> 0.002 - < 0.05 mm) and % sand (> 0.05 - < 2.0 mm) particle sizes according to the relative volumetric PSD.

3.5. Determination of carbonate content[149]

3.5.1. Analytical method

The carbonate content (CO_3^{2-}) of the sediment was determined using back titration. Air dried sediment (< 2 mm particle size) was ground roughly in a pestle and mortar. Approximately 10 g of the ground sediment was transferred to a conical flask, and 20 mL of 2 M HCl was added using a pipette. The sediment was allowed to react until the effervescence stopped. The conical flask was placed on the hot plate, and the contents were allowed to boil gently for 10 minutes. It was allowed to cool, then filtered into 100 mL volumetric flask, and made up to the mark with double distilled deionised water. In less than 24 hours, 10 mL of the solution was pipetted into a conical flask, and 50 mL of double deionised distilled water and 4 drops of phenolphthalein indicator was added; then 0.1 M NaOH was titrated against the solution. The titration was stopped as soon as the solution in the flask developed a permanent pink colour, and the volume of NaOH used was recorded. The % CO_3^{2-} in the air dried sediment samples were calculated using equation 3.3.

$$\% \, CO_3^{2-} = \frac{Z}{M} \times 100$$

Equation 3.3

where Z is the mass (g) of carbonate that reacted, and M is the mass (g) of the air dried sediment.

3.6. Determination of iron (hydr)oxides (FeOOH) content[150]

3.6.1. Apparatus

i. Centrifuge tube (50 mL, Fisherbrand-Fisher Scientific, Loughborough, UK).

ii. ACL 4237 centrifuge (CAMLAB Limited, Cambridge, UK).
iii. Water bath rotary shaker.
iv. Plastic syringe with 0.2 µm cellulose acetate Filter.
v. Thermo Scientific iCE 3000 SERIES AA Spectrometer UK.

3.6.2. Analytical method

The extraction solution was prepared by weighing 28.60 g of anhydrous sodium acetate (82.03 g mol^{-1}; Alfa Aesar UK) and 60.40 g of trisodium citrate dehydrate (294.1 g mol^{-1}; Alfa Aesar UK) into water, and 50.30 g of sodium dithionite (174.11 g mol^{-1}; Fisher Scientific, UK). The pH of the extraction solution was adjusted to 4.8 by adding 25 mL to 40 mL of concentrated acetic acid and made up with double distilled deionised water to 1000 mL. Approximately 10 g of air dried sediment was weighed into a bottle, and 200 mL of the extraction solution was added and the bottle was tightly closed. The bottle and content were shaken for 3.5 hours at 60 °C in a water bath rotary shaker. The suspension was allowed to cool for 30 minutes, and then 50 mL of the extractant was centrifuged for 30 minutes at 3000 g. The supernatant was taken off using a syringe and filtered through a 0.2 µm cellulose acetate filter. The first 3 mL collected was discarded. The remaining filtrate was transferred into 50 mL centrifuge tube and acidified with HNO_3 to pH 2 to 4. A blank was prepared by following the above procedure without the addition of the sediment. Iron was determined in the acidified filtrate by atomic absorption spectrometry at 248.3 nm using a Thermo Scientific iCE 3000 SERIES AA Spectrometer. The standard addition method was used to compensate for interferences. The concentration of Fe in mmol kg^{-1} and percentage content in the dry mass of the sediment was calculated using equations 3.4 and 3.5 respectively.

$$C_{\mathrm{Fe}} = (\rho_{\mathrm{Fe}} - \rho_{\mathrm{Fe,b}}) \times \frac{V}{m} \times \frac{(100+w)}{100} \times \frac{1}{55.85}$$

Equation 3.4

where C_{Fe} is the concentration (mmol kg^{-1}) of extracted iron in the sample on a dry-matter basis, ρ_{Fe} is the density (mg L^{-1}) of iron in the filtrates, $\rho_{\mathrm{Fe,b}}$ is the density (mg/L) of Fe in the blank, v is the volume of the extractant (mL) used, m is the mass (g) of the test portion and,w is the percentage water content on a mass basis.

$\% \text{ FeOOH in the dry mass of the sediment} = C_{Fe} \times 56 \times 10^{-4}$ **Equation 3.5**

3.7. Determination of moisture and organic matter content[151]

3.7.1. Apparatus

i. Analytical weighing balance (AE 200, Mettler, Leicester, UK)
ii. Oven (Memmert GMbH and Co. KG, Camlab Ltd., Cambridge, UK)
iii. Muffle furnace (Box Furnace, Elite Thermal Systems Ltd., Market Harborough, UK)

3.7.2. Analytical method

The moisture content of the sediment samples was determined in order to express the PTE concentration on a dry weight basis. Approximately 1 g of sediment sample (< 2 mm) was weighed into a dry and pre-weighed crucible and was dried in the oven at 110 °C for 24 hours. This was then transferred to a desiccator and allowed to cool for about 2 hours. The percentage moisture content of the sample was estimated using equation 3.6.

$$\% \, moisture \, content = \frac{(initial \, weight - oven \, dried \, weight) \times 100}{initial \, weight}$$

Equation 3.6

The percentage organic matter (% OM) of the sediment was estimated through loss on ignition (LOI). Crucibles containing residue from the moisture content determination were placed in a muffle furnace. The muffle furnace was programmed to ramp at 10 °C per minute, hold at 550 °C for 8 hours, and to cool to room temperature. Then the crucible with its contents was transferred to a desiccator and allowed to cool for about 2 hours. The % OM was estimated using equation 3.7.

$$\% \, OM = \frac{(oven \, dried \, weight - weight \, after \, combustion) \times 100}{oven \, dried \, weight}$$

Equation 3.7

3.8. Pseudototal digestion[44]

3.8.1. Apparatus

i. Microwave digestion tube (CEM microwave technology Ltd., Buckingham, UK).
ii. MARSXpress^{TM} microwave assisted digestion system (CEM microwave technology Ltd., Buckingham, UK).

3.8.2. Reagents

Aqua regia prepared from mixing HCl and HNO_3 (both obtained from Sigma-Aldrich, Gillingham UK) in ratio 3:1 (v/v) respectively.

3.8.3. Digestion procedure

Approximately 1 g of each sample (n = 3) was weighed into a digestion tube and 20 mL of freshly prepared *aqua regia* was added. A procedural blank (n = 3) with 20 mL *aqua regia* but no sample in the digestion tube was prepared at the same time. The digestion tube was loosely sealed with the cap and allowed to stand overnight in the fume cupboard. This was done to allow any vigorous reaction and build-up of pressure to subside. The digestion tube containing the sample mixed with *aqua regia*, and the blank, were transferred into the MARSXpress^{TM} microwave assisted digestion system. Digestion was carried out in accordance with the conditions stated in Table 3.1. At the end of the digestion, the digestion tube and its content was given sufficient time to cool, and then filtered through 125 mm Fisher Brand FB 59023 filter paper into a 100 mL standard volumetric flask. The sample residue was thoroughly washed with double distilled deionised water. The filtrate and blank were made up to the mark with double distilled deionised water to give a 20 % *aqua regia* solution. Then 1 mL of each solution was taken and made up to the mark with double distilled deionised water in a 10 mL standard volumetric flask to obtain a 2 % *aqua regia* solution considered suitable for introduction into the ICP-MS instrument.

Table 3.1 MarXpress^{TM} microwave digestion conditions for PTE extraction using *aqua regia*

Digestion tubes	17 – 25
Temperature	160 °C
Ramp time	20 minutes
Holding time	20 minutes
Power	800 watts

3.9. BCR sequential extraction procedure[94]

3.9.1. Apparatus

i. Centrifuge tube (50 mL, Fisherbrand-Fisher Scientific, Loughborough, UK).

ii. End-over-end mechanical shaker (GFL$^{(R)}$ 3040, Gasellschaft fur Labortechnik GmbH, Burgwedel, Germany).

iii. ACL 4237 centrifuge (CAMLAB Limited, Cambridge, UK).

3.9.2. Reagents

All reagents used were of analytical grade.

Solution A (acetic acid, 0.11 mol L^{-1})

A 0.43 mol L^{-1} solution of acetic acid was prepared by adding 25 ± 0.2 mL of glacial acetic acid (Sigma-Aldrich, Gillingham, UK) to approximately 0.5 L of double distilled deionised water in a 1 L standard volumetric flask and was made up to the mark with the double distilled deionised water. Exactly 250 mL of the solution was taken and diluted to 1 L in a standard volumetric flask with double distilled deionised water to obtain 0.11 mol L^{-1} acetic acid solution.

Solution B (hydroxylamine hydrochloride, 0.5 mol L^{-1})

Approximately 34.75 g of hydroxylamine hydrochloride (Fisher Scientific, Loughborough, UK) was dissolved in 400 mL of double distilled deionised water. The solution was transferred into 1 L standard volumetric flask and 25 mL of a freshly prepared 2 mol L^{-1} HNO_3 was added to the solution with a calibrated pipette. The solution was made up to the mark with double distilled deionised water to obtain 0.5 mol L^{-1} hydroxylamine hydrochloride solution. The solution was prepared on the same day that the extraction was carried out.

Solution C (hydrogen peroxide, 8.8 mol L^{-1})

The hydrogen peroxide (acid-stabilised to pH 2-3) was used as supplied by Sigma-Aldrich, Gillingham, UK.

Solution D (ammonium acetate, 1.0 mol L^{-1})

Approximately 77.08 g of ammonium acetate (Fisher Scientific, Loughborough, UK) was dissolved in 900 mL of double distilled deionised water and the pH of the ammonium acetate solution was adjusted to 2.0 ± 0.1 with concentrated HNO_3 (Sigma-Aldrich, Gillingham UK) and made up to 1 L with double distilled deionised water.

Aqua regia

The *aqua regia* was prepared as described in section 3.7.2.

Procedural blank

Procedural blanks for each batch of extraction were prepared with the same amount of reagent(s) as the samples but without the sediment present. They were carried through the complete extraction procedure at the same time as the samples.

3.9.3. Extraction procedure

The detailed extraction procedure is as stated below.

Step 1 (Exchangeable fraction)

Approximately 1 g of the sediment sample was weighed into a 50 mL centrifuge tube and 40 mL of 0.11 mol L^{-1} acetic acid was added. The centrifuge tube was stoppered, and the mixture was extracted by shaking for 16 h at room temperature on an end-over-end mechanical shaker. The mixture was mounted on the shaker as soon as the extractant solution was added and the shaken immediately. The extract was separated from the solid residue by centrifuging at 3000 g for 20 min. The supernatant was decanted into a polyethylene sample container and stored in a refrigerator at about 4 °C prior to analysis. The residue was washed with 20 mL of double distilled deionised water by shaking for 15 min on the end-over-end mechanical shaker and centrifuging at 3000 g for 20 min. The supernatant was decanted and discarded. Care was taken to ensure no solid residue was discarded.

Step 2 (Reducible fraction)

Exactly 40 mL of 0.5 mol L^{-1} hydroxylamine hydrochloride solution was added to the residue from step 1 inside the same centrifuge tube. The centrifuge tube was stoppered, and the mixture was extracted by shaking for 16 h at room temperature on the end-over-end mechanical shaker. The extract was separated from the solid residue by centrifuging at 3000 g for 20 min. The supernatant was decanted into a polyethylene sample container and stored in a refrigerator at about 4 °C prior to analysis. The residue was washed as described in step 1.

Step 3 (Oxidisable fraction)

Exactly 10 mL of 8.8 mol L^{-1} hydrogen peroxide was carefully added to the residue from step 2 inside the same centrifuge tube in small aliquots to avoid losses due to possible violent reaction. The centrifuge tube was loosely covered and digested at room temperature for 1 h with occasional manual shaking. The digestion continued for another 1 h at 85 ± 2 °C in a water bath. The cap of the centrifuge tube was removed, and the volume was reduced to less than 3 mL by further heating. Another aliquot of 10 mL of 8.8 mol L^{-1} hydrogen peroxide were carefully added, and digestion continued for another 1 h at 85 ± 2 °C in a water bath with the centrifuge tube loosely covered. The centrifuge tube cap was removed, and the volume of the liquid was reduced to about 1 mL. Exactly 50 mL of 1.0 mol L^{-1} ammonium acetate was added to the cool moisture residue and the centrifuge tube was stoppered and the mixture was extracted by shaking for 16 h at room temperature on the end-over-end mechanical shaker. The extract was separated from the solid residue by centrifuging at 3000 g for 20 min. The supernatant was decanted into a polyethylene sample container and stored in a refrigerator at about 4 °C prior to analysis. The residue was washed as described in step 1.

Step 4 (Residual fraction)

The residue from step 3 was transferred into the microwave digestion tube with 20 mL *aqua regia* and digested as described in section 3.8.

3.10. Reference materials

A secondary reference material (GLA-URM)[152, 153] was used to assess the analytical performance of the procedure for the determination of PT PTE concentrations in sediments in this study. The GLA-URM is an urban soil collected from Glasgow city during the EU URBSOIL project (which was also a PhD project), under contract EVK4-CT-2001-00053 (referred to as URBSOIL Reference Material (URM) in the EU URBSOIL project). The PT concentrations of PTE in GLA-URM were indicative values and they are listed in Table 3.2[152, 153].

A project aimed at comparing the original and the modified BCR sequential protocols using the sediment reference material (CRM601) was carried out by a group of European experts under EC contract NR. SMT4-CT96-2087 [96]. This project was an interlaboratory study, and the extractable trace elements content of CRM 601 (listed in Table 3.3) using the modified BCR sequential extraction procedure were determined [96]. The *aqua regia* extractable trace elements content of CRM601 (listed in Table 3.2) were also determined[94, 95]. The PT concentrations of PTE in the CRM 601 were indicative values [96]. The CRM 701 is recommended as reference material for the modified BCR sequential extraction scheme[96, 97], it was not available in our laboratory, but CRM 601 was, and was considered fit-for-purpose. The CRM 601 was used to assess the analytical performance of both the BCR sequential extraction scheme and *aqua regia* digestion in this work.

Table 3.2 Pseudototal concentration (mg kg^{-1}), standard deviation (SD, ± mg kg^{-1}) and % relative standard deviation (% RSD) of potentially toxic elements in the dry weight of GLA-URM and CRM601.

PTE	GLA-URM			CRM601		
	mg kg^{-1}	± mg kg^{-1}	% RSD	mg kg^{-1}	± mg kg^{-1}	% RSD
As	17.7	4.0	22.6	-	-	-
Cd	0.646	0.184	28.5	11.5	1.9	16.5
Cu	111	5.0	4.5	230	15	6.5
Fe	30600	1200	3.92	-	-	-
Mn	442	18	4.07	-	-	-
Ni	48.8	7.0	14.3	78.8	6.7	8.5
Pb	389	25	6.43	288	52	18.1
Zn	177	11	6.21	833	17	2.0

Table 3.3 The certified values of PTE (mg kg^{-1}) fractionation and standard deviation (± mg kg^{-1}) in dry weight CRM 601 using the BCR sequential extraction procedure.

PTE	Exchangeable fraction	Reducible fraction	Oxidisable fraction	Residual fraction	Sum
Cd	4.45 ± 0.67	3.95 ± 0.53	1.91 ± 1.40	1.30 ± 2.2	11.6
Cu	10.5 ± 0.8	72.8 ± 4.9	78.6 ± 8.9	60.4 ± 4.9	222
Ni	7.82 ± 0.84	10.6 ± 1.3	6.04 ± 1.30	50.5 ± 4.3	75.0
Pb	2.28 ± 1.2	205 ± 11	19.7 ± 5.8	38.0 ± 8.7	265
Zn	261 ± 13	266 ± 17	106 ± 11	161 ± 14	794

3.11. Analyses of digests and extracts

Digests and extracts were analysed for PTE content using ICP-MS (Model 7700x, Agilent Technology, UK) and the operating conditions are shown in Table 3.4.

Table 3.4 Operating conditions of ICP-MS

ICP-MS conditions	CC mode
Power (W)	1550
Quadrupole bias (V)	-15
Octopole bias (V)	-18
Nebulizer gas flow (L min^{-1})	0.85
Plasma gas flow (L min^{-1})	15
Auxiliary gas flow (L min^{-1})	0.9
Collision cell gas (L min^{-1})	He (4.5)
Internal standard	^{209}Bi, ^{115}In, ^{72}Ge and ^{45}Sc
Sample uptake rate (ml min^{-1})	1.0

3.11.1. Calibration of the Instrument

Multi-element (As, Cd, Cr, Cu, Mn, Ni, Pb, U and Zn: 10 mg L^{-1} in 2 % HNO_3) and Fe (1002 ± 4 µg mL^{-1} in 4 % HNO_3) standards (supplied by QmX Laboratories, Thaxted, UK) were used to prepare the working standard solutions by accurately measuring the appropriate amounts with micropipettes (Thermo Scientific, Vantaa, Finland). A Fe single element standard was used because of its high level in the samples. Standards were prepared in 2 % *aqua regia* and in the extractants used in the BCR sequential extraction procedure. The concentrations of the multi-element and Fe standard solutions used as calibrants are listed in Table 3.5.

Table 3.5 Concentration of multi-element (As, Cd, Cr, Cu, Mn, Ni, Pb, U and Zn) and Fe standard solutions used to prepare calibrants.

	Multi-element (As, Cd, Cr, Cu, Mn, Ni, Pb, U and Zn)		Fe	
Standard	Volume added (µL)	Concentration (µg L^{-1})	Volume added (µL)	Concentration (µg L^{-1})
1	0	0	0	0
2	10	10	4	400
3	100	100	40	4000
4	500	500	200	20000
5	1000	1000	400	40000

3.12. Data handling[85, 154, 155]

3.12.1. Limit of detection

The limit of detection (LOD) is the minimum amount of analyte that has a signal that can be distinguished from the signal arising from a reagent blank within a statistical confidence limit. Measurement of analyte concentration below the LOD is not reliable. The instrumental LOD was estimated using equation 3.8.

$$LOD = \frac{(3s)}{gradient\ of\ the\ calibration\ slope}$$

Equation 3.8

where s, is the standard deviation of the 10 replicate measurements of a blank (or of the lowest concentration of the calibration standard) calculated using equation 3.9.

$$S = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})}{n-1}}$$

Equation 3.9

where x_i is the individual value, n is the number of replicate measurements and, $\bar{x}$ is the mean as defined by equation 3.10.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Equation 3.10

The procedural limit of detection (LOD_{pro}) is the lowest analyte concentration that can be measured allowing for the method of sample preparation. This was calculated from the instrumental LOD using equation 3.11.

$$LOD_{pro} = \frac{LOD \times volume\ of\ extractant \times dilution\ factor}{mass\ of\ sample}$$

Equation 3.11

3.12.2. Precision

Precision is a measure of repeatability of an analysis. It is usually estimated as the relative standard deviation (RSD) of replicate measurements. It indicates the random error associated with the measurements. The RSD was calculated using equation 3.12.

$$RSD = \frac{s}{\bar{x}} \times 100$$

Equation 3.12

Where s is the standard deviation and $\bar{x}$ is the mean of replicate measurements.

3.12.3. Analyte concentration

The ICP-MS measured the concentration of the analyte in µg L^{-1} of the solution. These values were converted to mg kg^{-1} of the sample dry weight using equation 3.13.

$$Concentration\ (mg\ kg^{-1}) = \frac{analyte\ concentration\ (\mu g\ L^{-1}) \times volume\ (ml) \times dilution\ factor}{mass\ of\ sample\ (dry\ weight)\ in\ g}$$

Equation 3.13

3.13. Statistics[155-161]

3.13.1. The Mann-Whitney test

The Mann-Whitney test is used to test the null hypothesis that the distribution functions of two populations are equal against the alternative hypothesis that the distribution functions are not equal. The Mann-Whitney test do not depend on the normality assumption and it is the non-parametric substitute for t-test (a parametric test). The Mann-Whitney test assumptions are:

1. The two samples are randomly selected from their respective populations
2. The two groups are independent of each other
3. The measurement scale is at least ordinal

In the Mann-Whitney test all the values of sample A are listed and the number of values in sample B that is greater than each value of sample B is counted. The sum of the counts is the test statistics.

The null hypothesis is rejected if test statistics is less than or equal to the critical value at the given significant level. The p-value approach can also be used. The Mann-Whitney test (at 0.05 significance level) was used to determine if there were difference between the operational speciation of PTE in the sediment as received compare with the sample stored at -18 °C for one year. Minitab 18 was used to perform the Mann-Whitney test. The null hypothesis is rejected if $p\text{-value} < 0.05$.

3.13.2. The Kruskal-Wallis test

The Kruskal-Wallis tests the null hypothesis that the distribution functions of three or more independent populations are identical against the alternative hypothesis that some of the populations generate observations greater than the others. The Kruskal-Wallis test is designed to be sensitive to the difference among means of the different populations. Therefore, the alternative hypothesis can also be stated as: all the means of the different populations are not identical. The Kruskal-Wallis test do not depend on the normality assumption and it is the non-parametric alternative of the one-way analysis of variance. The Kruskal-Wallis test assumptions are:

1. All samples are random samples from their respective populations

2. The three or more samples are independence of each other
3. The measurement scale is at least ordinal

The probability theory of the Kruskal-Wallis test is also based on rank. Rank 1 is assigned to the smallest and, in ascending order and so on, the highest rank is assigned to the largest observation. Average rank is assigned to each of the tie like the other non-parametric test. The ith random sample size n_i is denoted by X_{i1}, X_{i2}, . . . , X_{in_i} The data can be arranged in columns as follows:

Sample 1	Sample 2 . . .	Sample k
$X_{1,1}$	$X_{2,1}$	$X_{k,1}$
$X_{1,2}$	$X_{2,2}$	$X_{k,2}$
. . .	. . .	. . .
X_{1,n_1}	X_{2,n_2}	X_{k,n_k}

The test statistic (T) is calculated using equation 3.14 or 3.15

$$T = \frac{1}{S^2}\left(\sum_{i=1}^{k}\frac{R_i^2}{n_i} - \frac{N(N+1)^2}{4}\right)$$

Equation 3.14

The R_i (the sum of the ranks assigned to the ith sample) is calculated for each sample and N is the total number of observations.

$$S^2 = \frac{1}{N-1}\left(\sum_{\substack{all\\ranks}} R(X_{ij})^2 - N\frac{(N+1)^2}{4}\right)$$

Equation 3.15

In the absence of ties S^2 simplifies to $N(N + 1)/12$ and T becomes equation 3.16

$$T = \frac{12}{N(N+1)} \sum_{i=1}^{k} \frac{R_i^2}{n_i} - 3(N+1)$$

Equation 3.16

The exact distribution for k = 3 and $n_i \leq 5$ is given in the table of quantiles of the Kruskal-Wallis test statistics for small sample size. When the exact table is not available, approximate quantiles can be obtained from the chi-squared distribution table. The null hypothesis is rejected if T is greater than the value obtained from the chi-Squared distribution table at 1 – α with the degree of freedom of k – 1. The p-value approach can also be used. The Kruskal-Wallis test at 0.05 significance level was used to determine if there were difference between the operational speciation of PTE in the sediment as received compare with the freeze dried, air dried and oven dried (at 60 °C and 110 °C). The Kruskal-Wallis test was performed with IBM SPSS 24. The null hypothesis is rejected if p-value < 0.05.

3.13.2.1 Multiple comparisons

When the null hypothesis is rejected, the Dunn test for multiple comparisons using rank sums was performed with IBM SPSS 24 to determine which of the pairs was responsible for the significant result in the Kruskal-Wallis test. The Dunn test is performed by combining the k samples and then ranked starting from the smallest to the largest, while average rank is assigned to the ties. The value of contrasts (y_m) is calculated using equation 3.17, T_i is the ranks sum of the ith sample, n_i is the sample size and p is the contrast among the means.

$$y_m = \frac{\sum_i T_i}{\sum_i n_i} - \frac{\sum_{i'} T_{i'}}{\sum_{i'} n_{i'}}$$

Equation 3.17

where m=1, … , p and the summation of *i* and *i'* are distinct subgroups of k. Each contrasted is divided by its standard deviation (σ_m).

If there are no ties:

$$\sigma_m^2 = \left(\frac{N(N+1)}{12}\right)\left(\left(\sum_i n_i\right)^{-1} + \left(\sum_{i\prime} n_{i\prime}\right)^{-1}\right)$$

Equation 3.18

where $N = \sum_{i=1}^{k} n_i$.

If there are ties, equation 3.18 must be adjusted. If there are r group of ties with sth group of tied scores which has t_s numbers then equation 3.18 becomes equation 3.19.

$$\sigma_m^2 = \left(\frac{N(N+1)}{12} - \frac{\sum_{s=1}^{r}(t_s^3 - t_s)}{12(N-1)}\right)\left(\frac{1}{\sum_i n_i} + \frac{1}{\sum_{i\prime} n_{i\prime}}\right)$$

Equation 3.19

Thus the p values are: $y_1/\sigma_1, \ldots, y_p/\sigma_p$ and each of y_m/σ_m is compared with $z_{1-\alpha/2p}$ (the 1- $\alpha/2p$ point of the standard normal distribution) at the selected α-level:

If $y_m/\alpha_m < -z_{1-\alpha/2p}$: shows that the *i*th mean is less than the *i'*th mean.

If $-z_{1-\alpha/2p} < y_m/\alpha_m < z_{1-\alpha/2p}$: shows that the two means may be similar.

if $y_m/\alpha_m > -z_{1-\alpha/2p}$: shows that the *i*th mean is greater than *i'*th mean.

3.13.3. The Spearman's rank correlation coefficient

The Spearman's rank correlation coefficient is a measure of linear relationship between the ranks of two variables. The Spearman's rank correlation coefficient does not depend on the normality assumption. Either or both set of data could be qualitative or quantitative provided the observation can be ranked. In case of ties the average of the ranks is assigned to each of the value. Spearman's rank correlation coefficient is simply Pearson's correlation computed on ranks. The Spearman's rank correlation coefficient can be calculated using equation 3.20.

$$r_s = 1 - \frac{6\sum_i d_i^2}{n(n^2-1)}$$

Equation 3.20

where r_s is the Spearman correlation coefficient, d is the difference between the two ranks and n is the number of pairs. The r_s takes a range of values from -1 to +1. A value of 0 indicates there is no linear relationship between the ranks of the two variables. A value of +1 and -1 indicates positive and negative correlation respectively. The stronger the correlation between the two variables the close is r_s to unity. The Spearman's rank correlation analysis was performed (with Minitab 18) on the PT concentrations of PTE and their physicochemical properties in the Derwent Reservoir sediments at 0.05 significance level in order to assess possible similar sources and geochemical behaviours. The null hypothesis is rejected if $p\text{-value} < 0.05$.

3.13.4. Cluster analysis

Cluster analysis (CA) is a multivariate technique whose main aim is to search for objects which are close together in variable space and divide them into groups or clusters with similar variables. Cluster analysis is divided into two, which are hierarchical and non-hierarchical methods. Hierarchical cluster analysis is an unsupervised pattern recognition technique that group objects together using agglomerative or divisive methods. Agglomerative method starts by taking single object then joining the two must similar objects, which also are the closest in the variable space, to form a cluster. This is repeated considering which objects are next in closeness, until all objects form one cluster from which the optimum numbers of clusters are chosen. Conversely, in the divisive method, in the beginning all objects are grouped in the same cluster from which optimum numbers of clusters are chosen. In non-hierarchical cluster analysis, objects are not linked, but are assigned to a cluster with the nearest centroid.

Hierarchical cluster analysis using the agglomerative approach is more frequently used than any other method. The process of hierarchical cluster analysis starts by using the distance between objects as a measure of similarity and dissimilarity.

Hierarchical cluster analysis is usually illustrated with a tree like structure known as a dendrogram. The vertical axis of a dendrogram represents the distance between clusters. The distance between two points (objects) is usually determined as the Euclidian distance in the n-dimensional space with (x_1, $x_2 \ldots x_n$) and (y_1,$y_2 \ldots y_n$) coordinates using equation 3.21. The smaller the Euclidian distance the greater the similarity between the objects. A large jump in distance is usually taken as the demarcation between optimum numbers of clusters. Hierarchical cluster analysis has been used in similar studies to distinguish the sources of PTE in sediment[11, 162-164]. In order to verify and support the results of the Spearman's rank correlation coefficient, hierarchical cluster analysis was performed on the PT concentration of PTE in the Derwent Reservoir sediments.

$$d = \sqrt{(x_1 - y_1)^2 + (x_2 - y_2)^2 + \cdots + (x_n - y_n)^2}$$

Equation 3.21

3.14. Sediment quality index

3.14.1. Geo-accumulation index

Geo-accumulation index (*I-geo*) is a single element pollution index proposed by Muller[165]. Geo-accumulation index compares PTE concentration with a reference or background value using equation 3.22. The number 1.5 is a correction factor which accounts for any variation in the background concentration of PTE.

$$I\text{-}geo = log\left(\frac{C_i}{1.5 \times B_i}\right)$$

Equation 3.22

where *I-geo* is the geo-accumulation index, C_i is the concentration of PTE in the sediment, and B_i is the background concentration of the PTE of interest. The weighted mean of the geochemical baseline values of PTE in sediment of the study area, obtained from the British Geological Survey (BGS)[166, 167] was used as the reference background concentration in this work. Muller distinguished 7 categories of sediment quality using the *I-geo*:

i. < 0; uncontaminated.
i. $0 < Igeo \leq 1$; slightly contaminated.
ii. $1 < Igeo \leq 2$; moderately contaminated.
iii. $2 < Igeo \leq 3$; moderately severely contaminated.
iv. $3 < Igeo \leq 4$; severely contaminated.
v. $4 < Igeo \leq 5$; severly extremely contaminated.
vi. $Igeo > 5$; extremely contaminated.

Geo-accumulation index has been used widely in the literature to assess sediment quality[66, 162, 168-170].

3.14.2. Enrichment factor

The enrichment factor (EF) is also a single element pollution index calculated as a ratio of PTE of interest against a normalising reference or background concentration using equation 3.23. Naturally abundant and conservative elements are chosen as normalising agents with the assumption that, they experience little or no anthropogenic input. Normalising agents account for the lithogenic and sedimentary input. Aluminium,[66, 171] and Fe[9, 172, 173] are examples of naturally abundant and conservative elements that have been used in previous studies as a normalising agent. Geochemical baseline concentration of Fe in the BGS[166, 167] was chosen as the normalising element in this work, because it is expected to have negligible anthropogenic input compared to its natural abundance. Iron also has similar geochemistry with the PTE studied in this work.

$$EF = \frac{\left({}^{x_a}/_{x_b}\right)_{sample}}{\left({}^{y_a}/_{y_b}\right)_{backgroud}}$$

Equation 3.23

where x_a is the concentration of PTE in the sediment, x_b is the concentration of the normalisation PTE in the sediment, y_a is the geochemical background concentration of PTE of interest and y_b is the geochemical concentration of the normalisation PTE. There are 5 categories of sediment qualities use to describe EF[66]:

i. EF < 2; depletion to minimum enrichment.
ii. 2 ≤ EF < 5; moderate enrichment.

iii. $5 \leq EF < 20$; significant enrichment.
iv. $20 \leq EF < 40$; very high enrichment.
v. $EF > 40$; extremely high enrichment.

Generally, EF > 1.5 is accepted as an indication of anthropogenic source[11, 174, 175].

3.14.3. Pollution index

Pollution index (PI) was proposed by Nemerow[176] due to the limitations of the single element pollution indices. Pollution index accounts for the contribution of various PTE present in sediment by using the average and maximum contamination factor to calculate the weight average. The PI is calculated using equation 3.24.

$$PI = \sqrt{\frac{\left(Cf_{average}\right)^2 + \left(Cf_{maximum}\right)^2}{2}}$$

Equation 3.24

where PI is the pollution index, C*f* is the contamination factor of individual PTE, Cf_{average} is the average of contamination factors and Cf_{maximum} is the PTE with maximum contamination factor in a given sampling site. Contamination factor is calculated using equation 3.25[177-179]. Nemerow distinguished 5 categories of sediment quality using PI:

i. $PI < 0.7$; unpolluted.
ii. $0.7 < PI < 1$; slightly polluted.
iii. $1 < PI < 2$; moderately polluted.
iv. $2 < PI < 3$; severely polluted.
v. $PI > 3$, heavily polluted.

$$Cf = \frac{C_i}{C_b}$$

Equation 3.25

where C_i is the PTE concentration and C_b is the background concentration or a reference value of the same PTE. Geochemical background concentration of PTE of interest was used as a reference value in this work. There are number of studies[66, 177, 178, 180] which have used PI to assess sediment quality.

3.14.4. Risk assessment code

The risk assessment code (RAC) is used to assess risk and mobility of the most labile fraction of PTE in sediment. It was proposed by Perin *et al*[181] and has been applied in similar studies[168, 170, 182, 183] to assess risk and mobility of PTE in sediments. It is calculated as the concentration of each PTE in the exchangeable fraction of the BCR sequential extraction (step 1) divided by the sum of the fractions (including the residual) using equation 3.26.

$$RAC = \frac{exchangeable\ (PTE)}{\begin{array}{c} exchangeable\ (PTE) + reducible\ (PTE) + \\ oxidisable\ (PTE) + residual\ (PTE) \end{array}} \times 100$$

Equation 3.26

The risk associated with the PTE content in the sediment is classified according to the following range:

i. No risk to the water body (RAC < 1 %).
ii. Low risk to the water body (RAC: 1 – 10 %).
iii. Medium risk to the water body (RAC: 11 – 30 %).
iv. High risk to the water body (RAC: 31 – 50 %).
v. Very high risk to the water body (RAC > 50 %).

Part 1: Analytical section

4. The effect of freeze, air and oven drying on the operational speciation of potentially toxic elements in freshwater sediments

4.1. Introduction

When applying the sequential extraction procedure, a dichotomy exists between maintaining a sample's intrinsic speciation, and pre-treating the sample to make it stable and more suitable for standard laboratory procedures. Studies[100-103, 105] have shown that no method of sample pre-treatment preserved the intrinsic speciation of PTE in sediments intact. To obtain the most accurate information on the operational speciation of PTE, some studies[102-104] have recommended that sediments should be analysed immediately as received. However, the unavoidable delay between sample collection and analysis has made it difficult for most workers to follow this recommendation. Examples of workers that used different sample pre-treatment procedures to preserve their sediments between 2017 and 2019 are listed in Table 4.1. The continuous use of different sample pre-treatment procedures by different studies, and the general silence on why a particular approach was adopted, suggested that workers may have arbitrarily or based on assumptions chosen a convenient technique to preserve their sediments.

Table 4.1 List of studies and the different sample pre-treatment procedures used to preserve sediments

Studies / years	Sample pre-treatment Procedures
Li Gao *et al.*[30] (2019)	Freeze dried
Suravi *et al.*[184] (2019)	Air dried
Franck *et al.*[23] (2017)	Oven dried at 40 °C
Numa et al.[185] ((2019)	Oven dried at 50 °C
Maheshwar *et al.*[186] (2018)	Oven dried at 60 °C
Muhammad *et al.*[172] (2018)	Oven dried at 85 °C
Dunja *et al.*[187] (2019)	Oven dried at 105 °C
Naglaa *et al.*[188] (2019)	Frozen at -20 °C for unspecified period
Rafael *et al.*[189] (2019)	Unspecified

4.2. Studies on the effects of sample pre-treatment procedures on the operational speciation of PTE in sediments

Rapin *et al.*[100] investigated the effects of sample pre-treatments (freeze and oven drying at 105 °C) and storage (wet storage at 4 °C and freeze at -30 °C for 20 days) on the operational speciation of PTE in sediments using the Tessier sequential extraction procedure[86]. The sediments used for this study were collected from the Maskinonge River Quebec and Clearwater Ontario (oxic sediment). The sediment samples were highly impacted by PTE. The Maskinonge River sediment was thoroughly mixed and left under 30 cm of lake water in a plastic tube undisturbed for 3 months in the laboratory. A core sample (anoxic sediment) of the Maskinonge River sediment kept undisturbed for 3 months was collected with a plexiglass tube. To assess the effect of different sample drying techniques and storage, the oxic and anoxic sediments were divided into 5 portions. Sequential extraction of the first portion (this was taken as the control) commenced less than 24 hours after collection. Separate portions of the remaining sediments were subjected to storage and the different pre-treatment procedures stated above. The handling of both oxic and anoxic subsamples during sequential extraction was done under a nitrogen atmosphere. The partitioning of Cd, cobalt (Co), Cu, Fe, Mn, Ni, Pb and Zn changed significantly at 99 % confidence level in many instances in the stored and pre-treated samples compared to the sediments as received. The significant changes observed were attributed to the application of the different sample pre-treatment procedures. Both freeze and oven drying significantly decreased the amount of Fe found in the exchangeable and carbonate fractions of the samples compared to the sediments as received. The significant decrease in the amount of Fe found in the exchangeable and carbonate fractions of the anoxic sediment seemed to be quantitatively counterbalanced by the increase in the Fe and Mn oxides fraction. Somewhat similar Fe partitioning was observed also in the oven dried oxic sediment, and for Mn in both freeze and oven dried anoxic sediment. Both freeze and oven drying were said to aid the formation of new mineral solid phases such as crystallisation of Fe-Mn oxides, oxidation of Fe, Mn and sulfides[100]. Wet storage at 4 °C for 20 days had no significant effect on the partitioning of the studied PTE in oxic sediment. For anoxic sediment, wet storage at 4 °C for 20 days significantly decreased the amount of Fe and Mn in the exchangeable and carbonates fractions, while the amount found in the reducible fraction increased. Freeze storage at -30 °C for 20 days of both the oxic and anoxic sediments had limited effects on the operational speciation of PTE. In the oxic sediment the noticeable significant effects were the increase in the amount of Zn found in the carbonate fraction and the small increase in the amount of Cd and Mn found in the organic matter fraction. In the anoxic sediment, freezing significantly increased the amount of Cu found in the carbonate fraction. Generally, the numerous significant decreases and increases of Cd, Co, Cu, Ni, Pb and Zn in the different operationally defined fractions of the sediments were attributed to their likely association with the changes in the chemistry of Fe and Mn, and possibly S.

Bordas *et al.*[101] studied the effects of freeze, air and oven (at 105 °C) drying on the operational speciation of Cd, Cu, Pb and Zn in sediment using the Tessier sequential extraction procedure[86]. The sediment used for this study was collected from the Le Palais stream (a tributary of the Vienne River) France. The sediment was divided into four portions. The first portion extraction started less than 24 hours after sampling and was used as the control. Each of the remaining three portions of the sediment were pre-treated as stated above. Freeze, air and oven drying significantly decreased the amount of Cd extracted in the exchangeable fraction. Cadmium and Cu released in the Fe-Mn oxides fraction of all the pre-treated sediments increased significantly. Also, Cd and Pb extracted in the organic matter and sulfides fraction of freeze and air dried sediment increased, respectively. Oven drying significantly increased the amount of Cd extracted in the residual fraction, while there was a significant decrease in the amount of Pb released in the same fraction. Oven drying also decreased the amount of Zn found in the carbonate fraction. The changes in the operational speciation of the studied PTE in the pre-treated sediments were attributed mainly to the crystallization of Fe and Mn oxides and oxidation of S. Bordas *et al.*[101] compared the effects of freeze and air drying on the operational speciation of Cd, Cu, Pb and Zn with the Rapin *et al.*[100] results, and the differences in operational speciation of these PTE in the pre-treated samples were attributed to the nature of the sediments. The results of previous studies on the effects of sample pre-treatment procedures on the operational speciation of some of the PTE studied in this work, using the Tessier sequential extraction scheme[86] are listed in Table 4.2.

Table 4.2 Results of studies on the effects of sample pre-treatment procedures on the operational speciation of PTE in freshwater sediment using the Tessier sequential extraction procedure[86].

PTE		FD	AD	105 °C
Cd	Exchangeable	↓[101]	↓[101]	↓[101]
	Carbonates	↔[101]	↔[101]	↔[101]
	Fe and Mn oxides	↑[101]	↑[101]	↑[101]
	Organic matter	↑[101]	↔[101]	↔[101]
	Residual	↔[101]	↔[101]	↑[101]
Cu	Exchangeable	↔[101]	↓[101]	↔[101]
	Carbonates	↔[101]	↔[101]	↓[101]
	Fe and Mn oxides	↑[101]	↑[101]	↑[101]
	Organic matter	↔[101]	↔[101]	↔[101]
	Residual	↔[101]	↔[101]	↔[101]
Fe	Exchangeable	↓[100]		↓[100]
	carbonates	↓[100]		↓[100]
	Fe and Mn oxides	↑[100]		↑[100]
	Organic matter	↔[100]		↔[100]
	Residual	↔[100]		↔[100]
Mn	Exchangeable	↑[100]		↑[100]
	Carbonates	↓[100]		↓[100]
	Fe and Mn oxides	↑[100]		↑[100]
	Organic matter	↔[100]		↔[100]
	Residual	↔[100]		↔[100]
Pb	Exchangeable	↔[101]	↔[101]	↔[101]
	Carbonates	↔[101]	↔[101]	↓[101]
	Fe and Mn oxides	↔[101]	↔[101]	↔[101]
	Organic matter	↔[101]	↑[101]	↔[101]
	Residual	↔[101]	↔[101]	↓[101]
Zn	Exchangeable	↔[101]	↔[101]	↔[101]
	Carbonates	↔[101]	↔[101]	↓[101]
	Fe and Mn oxides	↔[101]	↔[101]	↔[101]
	Organic matter	↔[101]	↔[101]	↔[101]
	Residual	↔[101]	↔[101]	↔[101]

↑: noticeable increase; ↓: noticeable decrease; and ↔: limited effect. Superscripts 100 and 101: references; FD: freeze dried; AD: air dried; and oven dried at 105 °C.

Kersten *et al.*[104] investigated the effects of freeze and oven drying at 60 °C on the operational speciation of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in freshwater sediments obtained from the Port of Hamburg harbour, Germany, using a 6 step (exchangeable, carbonates, easily reducible, moderately reducible, sulfidic/organic and residual fractions) sequential extraction procedure. Sequential extraction of a portion of the sediment as received commenced on arrival at the laboratory and this was used as a control. The handling of the control sample and extraction was done under oxygen free conditions. The sample pre-treatment procedures had varied effects on the operational speciation of PTE in the sediment but were similar in that the amount of all the analytes extracted in the sulfidic/organic fraction decreased. There was a significant increase in the amount of Cd, Ni, Pb and Zn extracted in the exchangeable and carbonates fractions of both pre-treated sediments and this was attributed to the ageing effect caused by drying the sediments. Both freeze and oven drying decreased the amount of Fe and Mn extracted in the carbonates fraction and this was attributed to the likely increase in the rate of Fe/Mn oxides crystallization in the pre-treated sediments. Generally, both pre-treatment procedures had no significant effects on the amount of the PTE extracted in the residual fraction.

Davidson *et al.*[102] studied the effects of air drying, oven drying (at 105 °C) and freezing (at -18 °C for four weeks) on the operational speciation of Cd and Pb in sediment collected from Garrion Burn, a tributary of the River Clyde, Lanarkshire, United Kingdom, using the original BCR sequential extraction procedure[92]. The residue of the oxidisable fraction of the original BCR sequential extraction scheme was digested with *aqua regia* making it the fourth step (the residual fraction). Extraction of a portion of the sediment as received (this was taken as the control) commenced on arrival to the laboratory. Air drying noticeably decrease the concentration of Cd extracted in the four steps and this was attributed to a shift into forms inaccessible to pseudototal (PT) *aqua regia* digestion. Oven drying seems to have limited effect on the partitioning of Cd, while freezing markedly increased the amount of Cd found in the oxidisable fraction. Generally, the application of the different sample pre-treatment procedures had limited effects on the operational speciation of Pb compared to Cd. The largest change was the increase in the amount of Pb found in the residual fraction of the oven dried sample compared to the sediment as received. Generally, freezing at -18 °C for four weeks had limited effect on the partitioning of Cd and Pb, except the noticeable increase in the amount of Cd extracted from the oxidisable fraction.

Shuzhen *et al.*[103] study was similar to Davidson *et al.*[102] except that freezing was not included in their study and oven drying of the sediment samples were done at 85 °C for 24 hours. Shuzhen *et al.*[103], in addition to Cd and Pb, included chromium (Cr), Cu, Ni and Zn in their study. The sediments used for this study were collected from seven different locations in Guanting Reservoir China. The original BCR sequential extraction procedure[92] was applied on the pre-treated sediments. The exchangeable fraction was the most affected by the application of the different sample pre-treatment procedures. Generally, the amount of PTE found in the exchangeable fraction decreased as the drying temperature increased. The effect of the application of the different sample pre-treatment procedures on the extraction of PTE in the reducible fraction was less compared to the exchangeable fraction. There was a noticeable decrease in the amount of Zn found in the reducible fraction, while Cd and Cu extracted in the same fraction of the pre-treated sediments increased. The increase in PTE extracted in the reducible fraction was attributed to the oxidation of Fe, Mn and S in agreement with Rapin *et al.*[100]. Application of the different sample pre-treatment procedures had less effect on the amount of Cr, Pb and Ni extracted in the reducible and oxidisable fractions. Both freeze and air drying markedly decreased the amount of Zn found in the oxidisable fraction of the sediments, while their effects were minimal on oxidisable Cu.

Hjorth[105] studied the effect of freeze drying on operational speciation of aluminium (Al), calcium (Ca), magnesium (Mg), Fe, Mn, phosphorus (P), silicon (Si), S (representing PTE-scavenging mineral phases of the sediment), Cu, Pb and Zn in sediments collected from Lake Dammsjon, Mellan Ovre, Mellan Marviken and Visnaren in Sweden. Dammsjon and Mellan Ovre sediments were extracted using the original BCR sequential extraction procedure[92], while Mellan Marviken and Visnaren sediments were extracted using the modified BCR sequential extraction procedure[95]. Sediment handling and extractions were done under a nitrogen atmosphere. Freeze drying transferred Cu, Pb and Zn from the oxidisable to reducible and exchangeable fractions. The changes in the operational speciation of Cu, Pb and Zn were limited in the sediment rich in organic matter (OM), and this was attributed to the PTE being largely bound to OM rather than S. However, Al and Si shifted from the oxidisable to the reducible fraction in the freeze dried sediments rich in OM. Generally, freeze drying transferred Fe from the exchangeable and oxidisable to the reducible fraction. The shift in P from exchangeable to reducible fraction tended to mimic the partitioning of Fe in the freeze dried sediment. The largest proportion of S was found in the exchangeable fraction, which was attributed to the partial oxidation of the oxidisable phase of the freeze dried sediments. The S found in the exchangeable fraction of the freeze dried sediments was suggested to have probably existed as sulfate or S. Freeze drying had a minimal effect on the operational speciation of Ca and Mn in the sediments. The results of previous studies on the effects of sample pre-treatment procedures on the operational speciation of some of the PTE studied in this work, using the original BCR sequential extraction scheme[92] are listed in Table 4.3

Table 4.3 Results of studies on the effects of sample pre-treatment procedures on the operational speciation of PTE in freshwater sediment using the original BCR sequential extraction procedure[92].

PTE		FD	AD	85 °C	105 °C
Cd	Exchangeable	↔[102] ↓[103]	↔[102] ↑[103]	↔[103]	↔[102]
	Reducible	↔[102] ↑[103]	↔[102] ↑[103]	↑[103]	↔[102]
	Oxidisable	↑[102] ↔[103]	↔[102] ↔[103]	↔[103]	↔[102]
	Residual	↔[102]	↓[102]		↔[102]
Cu	Exchangeable	↔[103] ↑[105]	↔[103]	↔[103]	
	Reducible	↑[103] ↔[105]	↑[103]	↑[103]	
	Oxidisable	↔[103] ↔[105]	↔[103]	↑[103]	
	Residual	↔[105]			
Fe	Exchangeable	↓[105]			
	Reducible	↑[105]			
	Oxidisable	↔[105]			
	Residual	↔[105]			
Mn	Exchangeable	↔[105]			
	Reducible	↔[105]			
	Oxidisable	↔[105]			
	Residual	↔[105]			
Ni	Exchangeable	↔[103]	↔[103]	↔[103]	
	Reducible	↔[103]	↔[103]	↔[103]	
	Oxidisable	↔[103]	↔[103]	↔[103]	
	Residual				
Pb	Exchangeable	↔[102] ↔[103] ↑[105]	↔[102] ↔[103]	↔[103]	↔[102]
	Reducible	↔[102] ↔[103] ↔[105]	↔[102] ↔[103]	↔[103]	↔[102]
	Oxidisable	↔[102] ↔[103] ↔[105]	↔[102] ↔[103]	↔[103]	↔[102]
	Residual	↔[102] ↔[105]	↔[102]		↑[102]
Zn	Exchangeable	↔[103] ↑[105]	↓[103]	↔[103]	
	Reducible	↔[103] ↔[105]	↓[103]	↔[103]	
	Oxidisable	↓[103] ↔[105]	↓[103]	↔[103]	
	Residual	↔[105]			

↑: noticeable increase; ↓: noticeable decrease; and ↔: limited effect. Superscripts 102, 103 and 105: references; FD: freeze dried; AD: air dried; and oven dried at 85 °C and 105 °C.

4.3. Aims and objectives

i. To obtain freshwater sediments with different proportions of the target nominal mineral phases of the BCR sequential extraction procedure[95]. This was done to assess the effects of sample pre-treatments on the operational speciation of PTE in sediments with different matrix compositions, using the BCR sequential extraction procedure[95].
ii. To determine the sediment pH, CEC and solid phases (carbonate, iron (hydr)oxides and organic matter) content. This was done to characterise the sediment samples.
iii. To assess the effect of freeze, air and oven drying on the apparent ecological status of PTE in the sediments as determined using the risk assessment code (RAC). This will provide guidance on the caution that is needed when utilising the results obtained from the assessment of ecological status of PTE in pre-treated sediments.

4.4. Experimental

4.4.1. Sampling and sample pre-treatment procedures

Sediment samples were collected from the River Derwent and the River Wear, UK. The River Derwent and the River Wear sediments were impacted by PTE due to historical mining and smelting in the catchment. A gold panner's suction pump was used to collect two sediment samples from the catchment of the River Derwent (at Derwent Reservoir spill-way, labelled DØ and Carrick's Haugh, labelled D1) and one from the River Wear (at Stanhope, labelled SH). The River Wear sediment at Stanhope was targeted for high % CO_3^{2-} content because there was historical limestone quarrying in the catchment downstream of similar impacts from Pb-Zn mining. The gold panner's suction pump lifted the uncemented sediment particle < 20 mm diameters. The sediments were field sieved to < 2 mm using a stainless steel British Standard sieve and kept under 15 cm of their own river's water in a high-density polyethylene bucket. On return to the laboratory, the samples were allowed to settle then excess water was decanted and the sediment was stored in the cold room at 4 °C. In less than 48 hours the sediments were divided into 6 portions and labelled, as received (AR), and according to the pre-treatment procedures to be applied: freeze dried (FD), after been frozen for 6 weeks at -18 °C; air dried (AD) for 3 weeks; oven dried (at 60 °C and 110 °C) for 24 hours; and frozen at -18 °C for one year (a study on the effects of storage on the operational speciation of PTE in these latter sediments is in chapter 5). The pseudototal digestion and sequential extraction of AR commenced immediately and this was used as the control.

4.4.2. pH measurement

The sediment pH was determined as described in sections 3.2.

4.4.3. Determination of cation exchange capacity

The cation exchange capacity (CEC) of the sediments was determined as described in section 3.3.

4.4.4. Determination of carbonate content

The carbonate (% CO_3^{2-}) content of the sediments was determined as described in section 3.5.

4.4.5. Determination of iron (hydr)oxides

The iron (hydr)oxides (% FeOOH) content of the sediments were determined as described in section 3.5.

4.4.6. Determination of moisture and organic matter content

The moisture and organic matter (% OM) content of the sediments were determined as described in section 3.7.

4.4.7. Pseudototal digestion

The sediments were digested using microwave assisted *aqua regia* digestion as described in section 3.8. The digests were analysed for the pseudototal concentration of PTE in the sediment using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

4.4.8. BCR sequential extraction

The different fractions of PTE in the sediments as received and pre-treated were extracted using the BCR sequential extraction procedure as described in section 3.9. The extracts were analysed for PTE concentrations using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

4.5. Results and discussion

4.5.1. Characterisation of sediment

The pH, CEC, % CO_3^{2-}, % FeOOH and % OM of the sediment samples are listed in Table 4.4. The FeOOH was determined, because Fe(II) is the freshwater sediment component (associated with the reducible phase) most susceptible to re-oxidation[46]. Sediment SH has the highest % CO_3^{2-} content and pH (8.08). Sediment SH has the lowest CEC, % FeOOH and % OM content. Sediment D1 was highest in % OM content followed by DØ, while DØ has the highest % FeOOH content followed by D1. Sediment D1 was also richer in CO_3^{2-} than DØ. Sediment D1 with pH 6.47 has the lowest but approximately the same pH as DØ (pH 6.48); this can be attributed to the influence of its high organic matter content mitigated by the neutralising effects of the carbonate content, which was higher than that of DØ. Clay minerals contribute considerably to CEC [73, 79]. Sediment DØ has the highest CEC followed by D1; this may be attributed to clay minerals in addition to the contribution of other mineral phases. The sum of % CO_3^{2-}, % FeOOH and % OM are 6.21 %, 11.6 % and 14.3 % in DØ, D1 and SH respectively. This indicated that DØ may have the highest proportion of clay minerals followed by D1 and SH.

Table 4.4 Sediment characteristics

Physicochemical properties	Sediment samples		
	SH	DØ	D1
pH	8.08	6.48	6.47
CEC (cmol+/kg)	1.52	5.04	2.27
% CO_3^{2-}	11.1	0.53	1.01
% FeOOH	0.042	0.15	0.056
% OM	3.16	5.53	10.5
Σ % (CO_3^{2-} + FeOOH + OM)	14.3	6.21	11.6

4.5.2. Pseudototal concentration determination and sequential extraction of PTE in sediments

4.5.2.1. Limits of detection

Instrumental limits of detection (LOD_{inst}) and procedural limits of detection (LOD_{pro}) for PT PTE determination and the BCR sequential extraction procedure steps using the ICP-MS are listed in Table 4.5. The LOD was always lower than the concentrations of the PTE determined.

Table 4.5 Instrumental limits of detection (LOD) and procedural limits of detection (LOD_{pro}) for the pseudototal PTE determination and the BCR sequential extraction steps using ICP-MS

PTE	Exchangeable fraction		Reducible fraction		Oxidisable fraction		Residual fraction/ pseudototal	
	LOD (µg L^{-1})	LODpro (mg kg^{-1})	LOD (µg L^{-1})	LODpro (mg kg^{-1})	LOD (µg L^{-1})	LODpro (mg kg^{-1})	LOD (µg L^{-1})	LODpro (mg kg^{-1})
As	0.0144	0.0155	0.0741	0.0592	0.00609	0.00381	0.00860	0.00430
Cd	0.00825	0.00660	0.00655	0.00524	0.00381	0.00238	0.0851	0.0425
Cu	0.137	0.109	0.0465	0.0372	0.0301	0.0188	0.0173	0.00866
Fe	2.40	1.92	2.21	1.77	1.70	1.06	0.348	0.174
Mn	0.0127	0.0102	0.0201	0.0161	0.00299	0.00187	0.0272	0.0136
Ni	0.00330	0.00264	0.0145	0.0116	0.0130	0.00814	0.0183	0.00195
Pb	0.000966	0.000773	0.00159	0.00127	0.00250	0.00156	0.000407	0.000204
Zn	0.133	0.106	0.0790	0.0632	0.114	0.0709	0.140	0.0701

4.5.2.2. Quality control for pseudototal analysis

The CRM 601 was used to assess the analytical performance of the PT PTE determination in the sediment. The amounts of PT PTE in CRM 601 were indicative values. All analyses were carried out in triplicate. A blank solution was also analysed at regular intervals during the ICP-MS analysis for quality check. The PT PTE concentrations, standard deviations, % relative standard deviations (% RSD) and % recoveries are listed in Table 4.6. The % RSD for the PT PTE determination was less than 10 %, indicating good results precision. The % recoveries of 91 % to 106 % for all the PTE measured were satisfactory.

Table 4.6 Pseudototal concentration (mg kg^{-1}, n = 3), standard deviation (SD, ± mg kg^{-1}), % relative standard deviation (% RSD) and % recovery of PTE in dry weight of CRM 601.

PTE	Obtained values			Indicative values		% Recovery
	mg kg^{-1}	± mg kg^{-1}	% RSD	mg kg^{-1}	± mg kg^{-1}	
Cd	10.5	0.5	4.38	11.5	1.9	91
Cu	235	8	3.43	230	15	102
Ni	78.8	2.3	2.92	78.8	6.7	100
Pb	273	13	4.76	288	52	95
Zn	879	46	5.23	833	17	106

4.5.2.3. Quality control for sequential extraction

Table 4.7 compares the obtained and certified values[95] of PTE concentration (mg kg^{-1}) in the certified reference material (CRM 601) using the BCR sequential extraction procedure (analysed in triplicate). The % recoveries of the BCR sequential extraction steps were 38 % to 128 %, and for the sum of the steps were 90 % to 103 %. The low % recovery of Cd in the residual fraction may be attributed to low level of the analyte and large standard deviation. A blank solution was also analysed at regular intervals during the ICP-MS analysis for quality checks.

Table 4.7 Comparison of the obtained and certified values of PTE fractions (mg kg^{-1}, n = 3), standard deviation (SD; ± mg kg^{-1}) in dry weight CRM 601 using the BCR sequential extraction scheme.

	PTE	Exchangeable fraction	Reducible fraction	Oxidisable fraction	Residual fraction	Sum
Obtained	Cd	4.66 ± 0.19	3.64 ± 0.06	1.56 ± 0.06	0.491± 0.062	10.2
Certified		4.45 ± 0.67	3.95 ± 0.53	1.91 ± 1.40	1.30 ± 2.2	11.6
% recovery		105	92	82	38	90
Obtained	Cu	10.8 ± 0.02	74.2 ± 1.8	71.8 ± 2.6	67.8 ± 5.0	225
Certified		10.5 ± 0.8	72.8 ± 4.9	78.6 ± 8.9	60.4 ± 4.9	222
% recovery		103	102	91	112	101
Obtained	Ni	8.47 ± 0.60	10.9 ± 0.25	7.72 ± 0.20	50.1 ± 2.5	77.2
Certified		7.82 ± 0.84	10.6 ± 1.3	6.04 ± 1.30	50.5 ± 4.3	75.0
% recovery		108	103	128	99	103
Obtained	Pb	1.61 ± 0.07	208 ± 5.3	18.8 ± 1.9	42.9 ± 2.2	271
Certified		2.28 ± 1.2	205 ± 11	19.7 ± 5.8	38.0 ± 8.7	265
% recovery		71	102	95	113	102
Obtained	Zn	288 ± 8.8	265 ± 3.4	122 ± 2.7	184 ± 16	799
Certified		261 ± 13	266 ± 17	106 ± 11	161 ± 14	794
% recovery		110	100	115	114	101

4.5.2.4. Pseudototal concentration and fractionation of PTE in the sediment as received and pre-treated

The PT As (5.34 – 66.9 mg kg^{-1}), Cd (2.38 – 34.2 mg kg^{-1}), Cu (12.2 – 47.9 mg kg^{-1}), Fe (18300 – 126000 mg kg^{-1}), Mn (744 – 5200 mg kg^{-1}), Ni (16.3 – 41.8 mg kg^{-1}), Pb (269 – 3960 mg kg^{-1}) and Zn (1220 – 9160 mg kg^{-1}) concentrations determined in this study were similar to those found in freshwater sediments with historical mining and smelting in the catchment area [28, 33, 34, 119, 169, 190-192]. The effect of freeze, air and oven (at 60 °C and 110 °C) drying on the operational speciation of As, Cd, Cu, Fe, Mn, Ni, Pb and Zn in the sediments are presented in mg kg^{-1} and % concentration in Figures 4.1 to 4.8. The numerical data are listed in Table A.1 to A.3 in the appendix.

The PT PTE concentrations (mg kg^{-1}) are represented by the horizontal lines drawn across the bar charts in Figures 4.1 to 4.8.

The Kruskal-Wallis test followed by Dunn test (multiple comparisons) was used to identify any significant difference in the amount of PTE liberated by PT *aqua regia* digestion in the pre-treated samples compared with the sediment as received. The effect of the sample pre-treatment procedures on the operational speciation of PTE are presented by element, and for each PTE, there is a Kruskal-Wallis and a multiple comparisons test. If the null hypothesis is retained after a Kruskal-Wallis test, no multiple comparisons were conducted. The bold-red values in the Kruskal-Wallis tables indicate significant changes caused by the application of different pre-treatment procedures on the PT concentration and operational speciation of PTE in the samples compared with the sediment as received. The bold-red results in the multiple comparison tables are the significant results indicating the sample pre-treatment procedure(s) responsible for the significant changes in the Kruskal-Wallis test compared with the sediment as received. There were instances where the Kruskal-Wallis test was significant, but the multiple comparisons indicated no significant results. This happen because the overall effect of the nominal variables on the ordinal variables cannot be pinpoint to a specific pair at 0.05 significance level[160]. The null hypothesis was retained at p-value > 0.05.

4.5.2.4.1. Pseudototal concentration of PTE in the sediment as received and pre-treated.

The results of the statistical test comparing the PT concentration of PTE in the sediment as received and pre-treated are listed in Table 4.8a and Table 4.8b. Generally, the application of the different pre-treatment procedures did not significantly affect the amount of PTE liberated by PT *aqua regia* digestion compared with the sediment as received. However, there were few significant changes. Freeze drying significantly decreased the amount of Cd and Pb liberated by PT *aqua regia* digestion in SH and DØ, respectively. Davidson *et al.*[102] reported a decrease in the amount of Cd accessible to PT *aqua regia* digestion in air dried sediment. Huang *et al.*[26] also indicated that sample pre-treatment procedures may aid the occlusion of PTE in the clay minerals of soil. Sediment and soil have similar chemistry. Therefore, the significant decrease in the amount of PTE liberated by PT *aqua regia* digestion in the affected pre-treated sediment samples may be attributed to the occlusion of the analytes in the clay minerals. The multiple comparisons test did not show any difference at 0.05 significant levels in the amount of Cd and Pb liberated by PT *aqua regia* digestion in the pre-treated D1, while the significant result in DØ was due to the difference in PT Cd concentration in the freeze and air dried sample.

Table 4.8a Kruskal–Wallis test at 0.05 significance level for PT PTE concentration (mg kg^{-1}; n = 3) in the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Sediment samples	Kruskal – Wallis test p-value							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
SH	0.493	**0.050**	0.723	0.057	0.202	0.149	0.675	0.249
DØ	0.209	**0.014**	0.101	0.085	0.073	0.053	**0.042**	0.077
D1	0.291	**0.038**	0.271	0.070	0.415	0.375	0.705	**0.043**

Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick’s Haugh (D1). The red bold number represents significant result.

Table 4.8b Multiple comparison test at 0.05 significance level for PT PTE concentration in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C)

PTE	multiple comparisons test p-value													
	SH					DØ					D1			
	FD	AD	60 °C	110 °C		FD	AD	60 °C	110 °C		FD	AD	60 °C	110 °C
As	–	–	–	–		–	–	–	–		–	–	–	–
Cd	**0.026**	1.00	1.00	1.00		1.00	0.176	1.00	1.00		1.00	1.00	1.00	1.00
Cu	–	–	–	–		–	–	–	–		–	–	–	–
Fe	–	–	–	–		–	–	–	–		–	–	–	–
Mn	–	–	–	–		–	–	–	–		–	–	–	–
Ni	–	–	–	–		–	–	–	–		–	–	–	–
Pb	–	–	–	–		**0.019**	1.00	1.00	1.00		–	–	–	–
Zn	–	–	–	–		–	–	–	–		1.00	1.00	1.00	1.00

Sediments: Stanhope (SH); Derwent Reservoir spillway (DØ) and Carrick’s Haugh (D1). The red bold number represents significant result. The dash means no post hoc test was conducted.

4.5.2.4.2. Fractionation pattern of PTE in the sediment as received and pre-treated

The operational speciation of As in the sediments as received and pre-treated are shown in Figure 4.1 and listed in Tables A.1 – A.3 in the appendix.

Arsenic

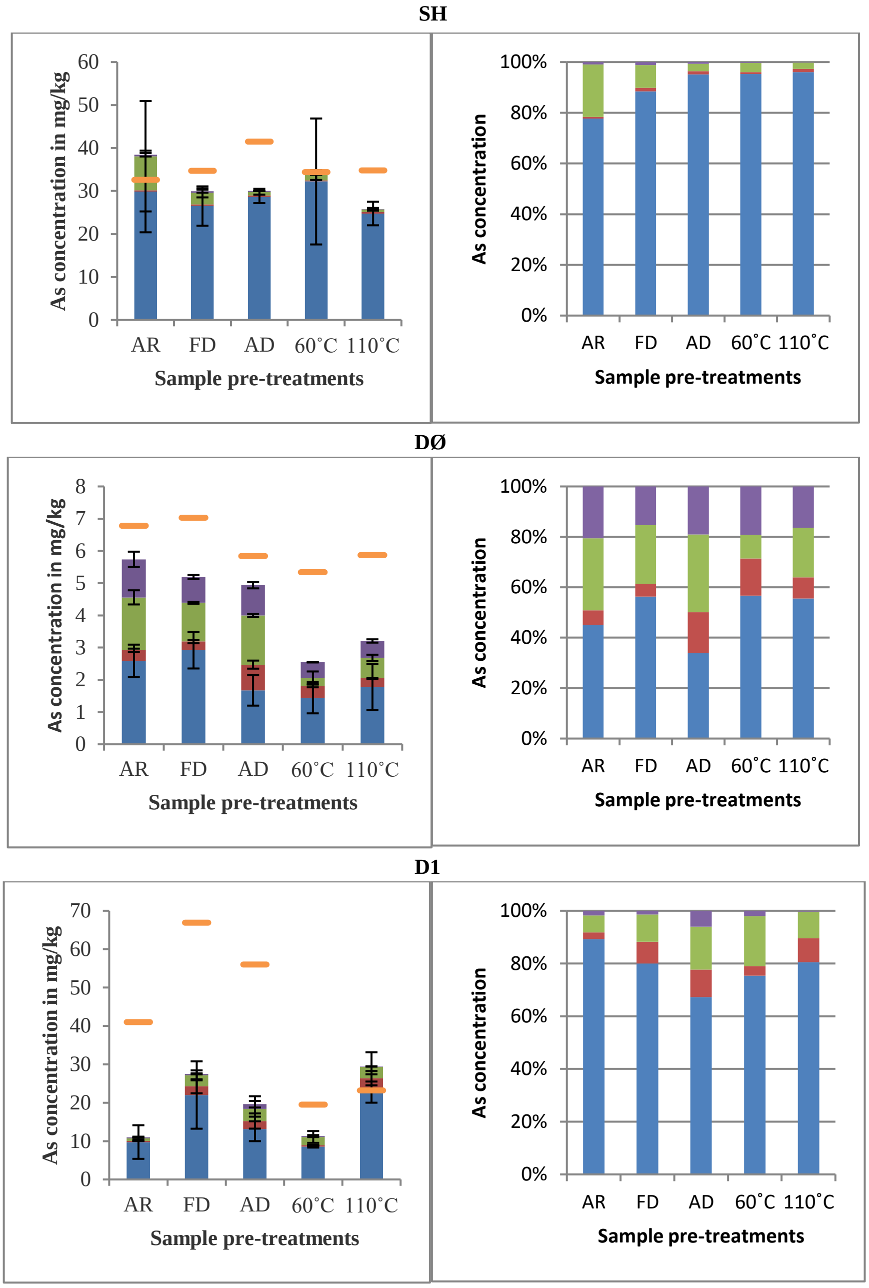


Figure 4.1 Operational speciation of As (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal 🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Arsenic was partitioned in the sediments as received in the following order: oxidisable (0.62 %) < exchangeable (0.91 %) < reducible (21 %) < residual (78 %) in SH; oxidisable (5.8 %) < exchangeable (21 %) < reducible (29 %) < residual (45 %) in DØ; and exchangeable (1.8 %) < oxidisable (2.6 %) < reducible (6.4 %) < residual (89 %) in D1. Generally, the largest amount of As was found in the residual followed by the reducible fraction in the sediments as received, reflecting the known affinity of As for FeOOH[33, 44, 193].

The results of the statistical test comparing the amount of As extracted from the different fractions of freeze, air and oven dried (at both 60 °C and 110 °C) samples to similar fractions in the sediment as received are listed in Table 4.9a and Table 4.9b. Generally, application of the different pre-treatment procedures did not significantly affect the amount of As extracted in step 1 (the exchangeable fraction), step 2 (the reducible fraction), step 3 (the oxidisable fraction) and step 4 (the residual fraction) of SH and D1. The significant results in the Kruskal-Wallis test in step 3 and 4 of D1 cannot be pinpointed to a specific pair at 0.05 significance level with the multiple comparisons test. The % recoveries (41 % to 127 %) of the sequential extraction of As with respect to PT concentration in all pre-treated D1 may be attributed to the poor homogeneity of the analyte in the sample. For SH, the % recoveries (72 % to 118 %) of the sequential extraction of As with respect to PT concentration in all pre-treated samples support the hypothesis that sample pre-treatments had limited effect on the operational speciation of the analyte in the sediment.

For DØ, oven drying at 60 °C significantly decreased the amount of As extracted in step 1 and 2. The decrease in the amount of As extracted in step 1 may be attributed to the binding of As to newly formed iron oxides as a result of oxidation in DØ oven dried at 60 °C. Guanxing *et al.*[194] also attributed decrease in the amount of As extracted in the most labile fraction of freeze, air and oven dried soil to the formation of iron oxides using a modified Wenzel's sequential extraction procedure[195]. It is also known that FeOOH bind to OM in soil under oxic conditions[73, 196, 197]. Therefore, the occlusion of FeOOH-bound As in the oxidisable phase of DØ oven dried at 60 °C may be responsible for the decrease in the amount of the analyte found in step 2. The difference in the amount of As found in freeze and air dried DØ was responsible for the significant result in step 3. The % recoveries (48 % to 85 %) of the sequential extraction of As with respect to PT concentration in all pre-treated DØ may be attributed to the poor homogeneity of the analyte in the sample.

Table 4.9a Kruskal–Wallis test at 0.05 significance level for As concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	0.074	**0.013**	0.073
Reducible	0.323	**0.012**	0.530
Oxidisable	0.157	**0.022**	**0.025**
Residual	0.844	0.068	**0.039**

The red bold number represents significant result.

Table 4.9b Multiple comparisons test at 0.05 significance level for As concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C).

	multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	–	–	–	–
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	–	–	–	–
DØ				
Exchangeable	1.00	1.00	**0.019**	0.137
Reducible	1.00	1.00	**0.026**	0.285
Oxidisable	1.00	1.00	1.00	1.00
Residual	–	–	–	–
D1	–	–	–	–
Exchangeable	–	–	–	–
Reducible	–	–	–	–
Oxidisable	0.137	0.285	1.00	0.062
Residual	0.358	1.00	1.00	0.176

The red bold number represents significant result. The dash means no post hoc test was conducted.

The operational speciation of Cd in the sediments as received and pre-treated are shown in Figure 4.2 and listed in Tables A.1 – A.3 in the appendix.

Cadmium

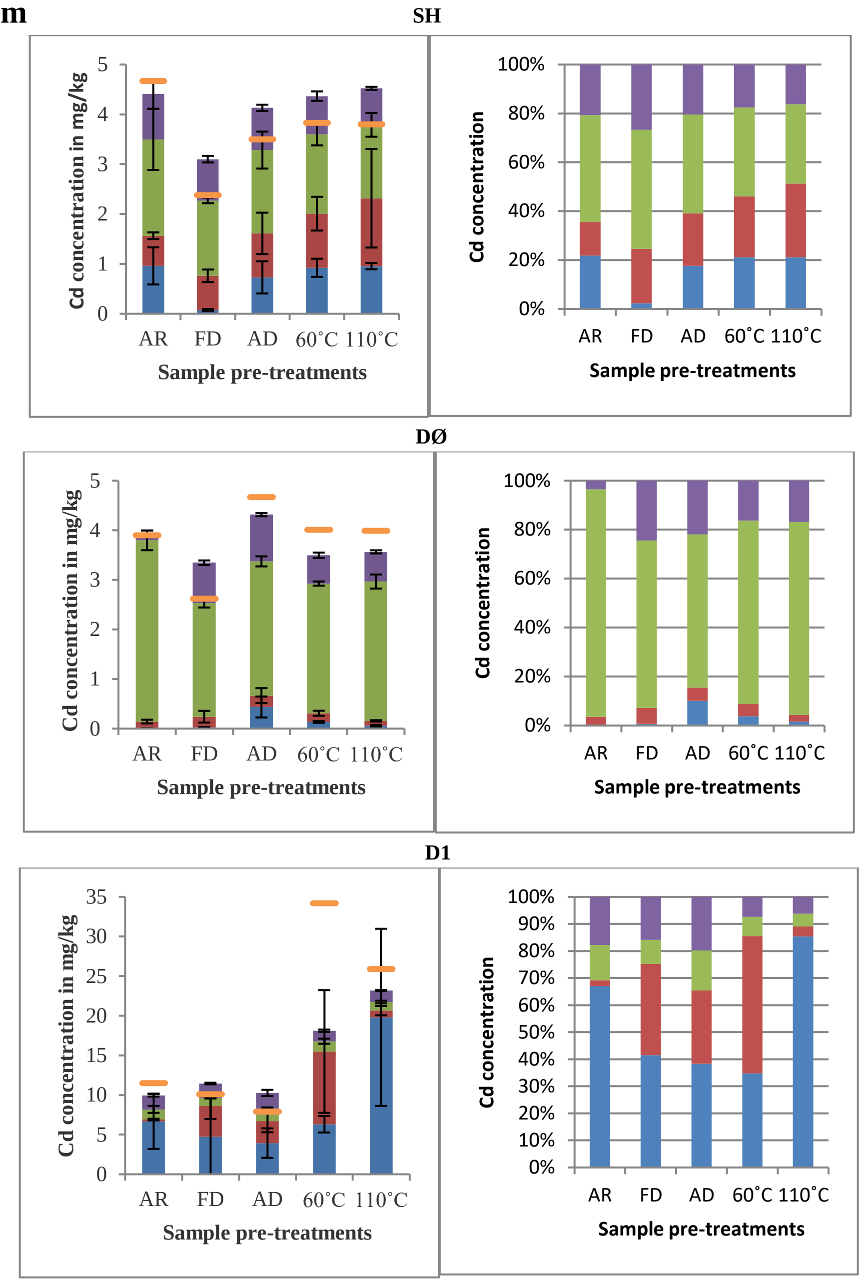


Figure 4.2 Operational speciation of Cd (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal 🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Cadmium was partitioned in the sediment as received in the following order: oxidisable (14 %) < exchangeable (21 %) < residual (22 %) < reducible (44 %) in SH;

residual (0.12 %) < exchangeable (3.4 %) < oxidisable (3.5 %) < reducible (93 %) in DØ; and oxidisable (2.1 %) < reducible (13 %) < exchangeable (18 %) < residual (67 %) in D1. Similar to previous studies[101-103], the fractionation of Cd in the different sediments as received were not the same, although the highest concentrations of the analyte were extracted from step 4 of SH and DØ.

The results of the statistical test comparing the amount of Cd extracted from the different fractions of freeze, air and oven (at both 60 °C and 110 °C) dried samples to similar fractions in the sediment as received are listed in Table 4.10a and Table 4.10b. Application of the different sample pre-treatment procedures did not significantly affect the amount of Cd extracted in the various fractions of SH and D1, and step 3 of DØ. The significant result in the Kruskal-Wallis test in step 1 and 3 of D1 cannot be pinpointed to any pair at 0.05 significance level with the multiple comparisons test. However, significant effects were noted for some samples in other fractions.

For DØ, air and oven drying at 60 °C significantly increased the amount of Cd extracted in step 1 and 4, respectively, while there was a decrease in the amount of the analyte found in step 2 of the freeze dried sample. The significant increase in the amount of Cd extracted in step 1 of the air dried DØ may be attributed to the analyte co-precipitation with calcium carbonate[73] aided by drying. Kersten *et al.*[104] also reported an increase the amount of Cd extracted in a carbonates fraction using a 6 step sequential extraction procedure, and attributed it to the shift of PTE to more labile fraction caused by the ageing effects of drying on the sediments.

Generally, the % recoveries of the sequential extraction with respect to the PT concentration in SH (94 % to 130 %), DØ (87 % to 128 %) and D1 (53 % to 130 %) indicated that the application of the different sample pre-treatment procedures had limited effect on the operational speciation of Cd in the sediments. The wide range of the % recoveries of Cd may be attributed to the low levels of the analyte in the sediments.

Table 4.10a Kruskal–Wallis test at 0.05 significance level for Cd concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	0.468	**0.012**	**0.029**
Reducible	0.693	**0.016**	0.223
Oxidisable	0.463	0.109	**0.041**
Residual	0.115	**0.009**	0.089

The red bold number represents significant result.

Table 4.10b Multiple comparisons test at 0.05 significance level for Cd concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C).

	multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	–	–	–	–
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	–	–	–	–
DØ				
Exchangeable	0.137	**0.010**	1.00	1.00
Reducible	**0.010**	0.225	1.00	1.00
Oxidisable	–	–	–	–
Residual	1.00	0.137	**0.010**	1.00
D1				
Exchangeable	1.00	1.00	0.446	1.00
Reducible	–	–	–	–
Oxidisable	0.106	0.358	0.106	1.00
Residual	–	–	–	–

The red bold number represents significant result. The dash means no post hoc test was conducted.

The operational speciation of Cu in the sediment as received and pre-treated are shown in Figure 4.3 and listed in Tables A.1 – A.3 in the appendix.

Copper

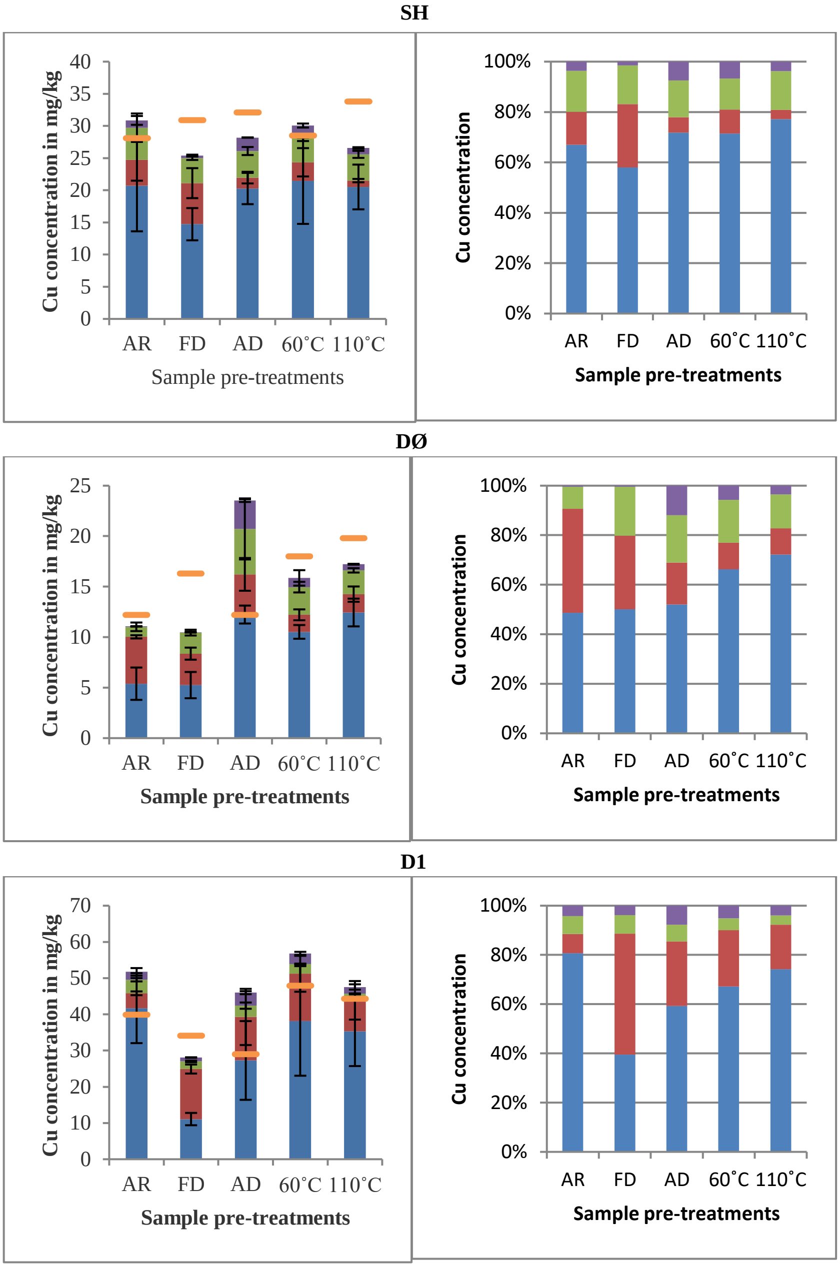


Figure 4.3 Operational speciation of Cu (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: StanHope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ▬ Exchangeable ▬ Reducible ▬ Oxidisable ▬ Residual

Copper was partitioned in the sediment as received in the following order: exchangeable (3.6 %) < oxidisable (13 %) < reducible (16 %) < residual (67 %) in

SH; exchangeable (0.4 %) < reducible (9.0 %) < oxidisable (42 %) < residual (49 %) in DØ; and exchangeable (4.2 %) < reducible (7.3 %) < oxidisable (7.9 %) < residual (81 %) in D1. Generally, the largest amount of Cu was found in step 4 followed by step 3 in the sediments as received, reflecting the known strong affinity of Cu for OM[44, 198] (except in SH where more Cu was extracted in step 2 compared to step 3).

The results of the statistical test comparing the amount of Cu extracted from the different fractions of freeze, air and oven (at both 60 °C and 110 °C) dried samples to similar fractions in the sediment as received are listed in Table 4.11a and Table 4.11b. Application of the different pre-treatment procedures did not significantly affect the amount of Cu extracted in the various fractions of SH, step 3 and 4 of DØ and step 1, 3 and 4 of D1. The significance change in the Kruskal-Wallis test in step 1 were between the freeze and air sample in both SH and D1, while the significant results cannot be pinpointed to a specific pair in step 3 and 4 of DØ at 0.05 significance level with the multiple comparisons test. However, significant effects were noted for some samples in other fractions.

For DØ, there was a significance increase in the amount of Cu extracted in step 1 of air dried sample, while the amount of the analyte found in step 2 decreases. Similar to DØ, there was also a significant decrease in the amount of Cu extracted in step 2 of D1 oven dried at 110 °C. The decrease in the amount of Cu found in step 2 of both DO and D1 were accompanied by slight increase in step 3 and 4 of both sediments, indicating that the analyte were also converted to more refractory forms. This is consistent with the suggestions of Thomson *et al.*[199] and Bordas *et al.*[101] that Cu may be converted to more refractory forms in oven dried sediments. The % recoveries of the sequential extraction of Cu with respect to PT concentration were SH (79 % to 110 %), DØ (64 % to 193 %) and D1 (82 % to 159 %). The wide range of the % recoveries of Cu in DØ and D1 may be attributed to the poor homogeneity of the analyte in the sediments.

Table 4.11a Kruskal–Wallis test at 0.05 significance level for Cu concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	**0.020**	**0.016**	**0.039**
Reducible	0.730	**0.019**	**0.028**
Oxidisable	0.063	**0.023**	0.252
Residual	0.149	**0.016**	0.082

The red bold number represents significant result.

Table 4.11b Multiple comparisons test at 0.05 significance level for Cu concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C)

	Multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	1.00	0.828	1.00	1.00
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	–	–	–	–
DØ				
Exchangeable	1.00	**0.035**	1.00	0.679
Reducible	1.00	**0.019**	0.137	1.00
Oxidisable	1.00	1.00	0.081	0.106
Residual	1.00	0.176	1.00	0.137
D1				
Exchangeable	1.00	0.446	1.00	1.00
Reducible	0.285	1.00	1.00	**0.026**
Oxidisable	–	–	–	–
Residual	–	–	–	–

The red bold number represents significant result. The dash means no post hoc test was conducted.

The operational speciation of Fe in the sediment as received and pre-treated are shown in Figure 4.4 and listed in Table A.1 – A.3 in the appendix.

Iron

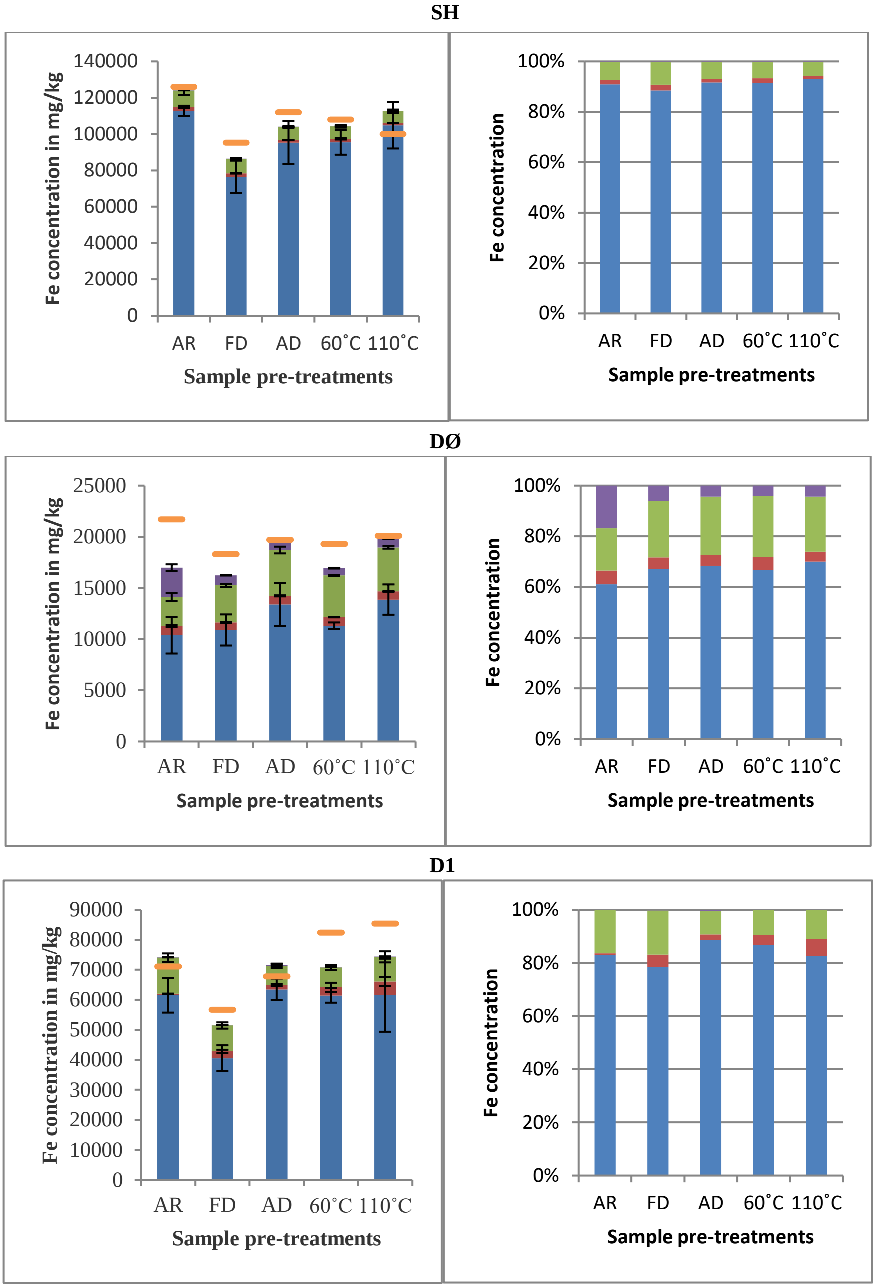


Figure 4.4 Operational speciation of Fe (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ■ Exchangeable ■ Reducible ■ Oxidisable ■ Residual

Iron was partitioned in the sediment as received in the following order: exchangeable (0.11 %) < oxidisable (1.7 %) < reducible (7.3 %) < residual (91 %) in SH; oxidisable (5.4 %) < reducible (17 %) ≈ exchangeable (17 %) < residual (61 %) in DØ; and exchangeable (0.14 %) < oxidisable (0.72 %) < reducible (16 %) < residual (83 %) in D1. Generally, more than 60 % of Fe was extracted from the residual followed by the amount found in the reducible fraction (except in DØ where an approximately equal amount of Fe was extracted in the exchangeable and reducible fractions) in the sediments as received. This indicated that Fe in the sediments was mainly from geogenic source, reflecting its natural abundance[45, 57]. Similar studies[105, 200] also extracted Fe mainly in the residual fraction of sediments as received.

The results of the statistical test comparing the amount of Fe extracted from the different fractions of freeze, air and oven dried (at both 60 °C and 110 °C) samples to similar fractions in the sediment as received are listed in Table 4.12a and Table 4.12b. Application of the different pre-treatment procedures did not significantly affect the amount of Fe extracted in step 2 and 3 of SH, step 4 of DØ and step 1 and 4 of D1. The significant results in the Kruskal-Wallis test for step 2 and 3 cannot be traced to a specific pair in the pre-treated SH with multiple comparisons test at 0.05 significance level. However, significant effects were noted for some samples in other fractions.

For SH, there were significant decrease in the amount of Fe extracted in step 1 and 4 of the freeze dried sample. The % recoveries of the sequential extraction of Fe with respect to PT concentration in all pre-treated SH were 91 % to 113 %. Generally, this indicated that the application of the different pre-treatment procedures had limited effect on the fractionation of Fe in SH, except in the freeze dried sample. For DØ, oven drying at 60 °C significantly decreased the amount of Fe extracted in step 1. There was a significant decrease in the amount of Fe extracted in step 3 of the freeze dried DØ, while the amount of the analyte found in step 2 of air dried DØ increased. The decrease in the amount of Fe found in step 1 of freeze dried SH and DØ oven dried at 60 °C, as well as the increase in amount of the analyte found in step 2 of air dried DØ may be attributed to the formation of iron oxides and oxidation of the oxidisable mineral phase[201]. Rapin *et al.*[100] and Bordas *et al.*[101] also attributed the increase in Fe extracted in the reducible fraction of freeze, air and oven dried freshwater sediment to the formation of iron oxides and oxidation of sulfides. The % recoveries of the sequential extraction of Fe with respect to PT concentration in all pre-treated DØ were 88 % to 99 %, indicating that the significant results were due to the application of the different sample pre-treatment procedures.

For D1, air drying significantly decreased the amount of Fe extracted from step 2, while the amount of the analyte extracted in step 3 of the sediment oven dried at 110 °C D1 increased significantly. The increase in the amount of Fe found in step 3 of D1 oven dried at 110 °C may be attributed to the occlusion of FeOOH associated with OM in the oxidisable phase because there was also a noticeable decrease in the amount of the analyte in step 2. There is evidence in literature that some FeOOH binds to soil OM[196, 197, 202], which may also happen in sediment. The % recoveries of the sequential extraction of Fe with respect to PT concentration in all pre-treated D1 were 86 % to 105 %, indicating that the significant results were due to the application of the different sample pre-treatment procedures.

Table 4.12a Kruskal–Wallis test at 0.05 significance level for Fe concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	**0.036**	**0.012**	0.693
Reducible	**0.045**	**0.012**	**0.036**
Oxidisable	**0.028**	**0.024**	**0.015**
Residual	**0.048**	0.145	0.32

The red bold number represents significant result.

Table 4.12b Multiple comparison test at 0.05 significance level for Fe concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C).

	Multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	**0.047**	1.00	1.00	0.679
Reducible	1.00	1.00	0.358	0.446
Oxidisable	1.00	1.00	1.00	0.176
Residual	**0.035**	1.00	1.00	1.00
DØ				
Exchangeable	1.00	0.285	**0.010**	0.552
Reducible	1.00	**0.025**	1.00	0.062
Oxidisable	**0.047**	1.00	1.00	0.446
Residual	–	–	–	–
D1				
Exchangeable	–	–	–	–
Reducible	1.00	**0.047**	0.106	1.00
Oxidisable	0.358	1.00	0.358	**0.014**
Residual	–	–	–	–

The red bold number represents significant result. The dash means no post hoc test was conducted.

The operational speciation of Mn in the sediment as received and pre-treated are shown in Figure 4.5 and listed in Tables A.1 – A.3 in the appendix.

Manganese

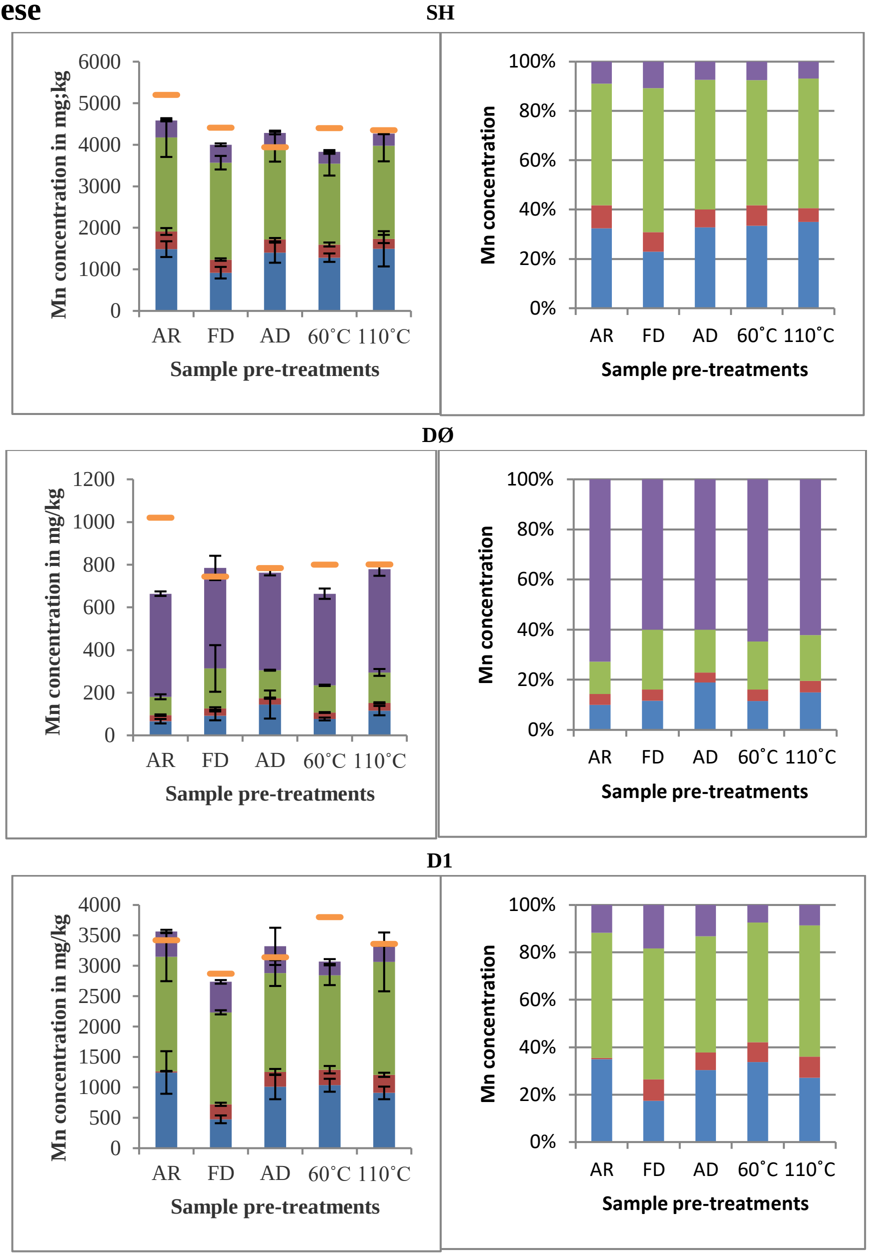


Figure 4.5 Operational speciation of Mn (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ▬ Exchangeable ▬ Reducible ▬ Oxidisable ▬ Residual

Manganese was partitioned in the sediment as received in the following order: exchangeable (8.9 %) < oxidisable (9.3 %) < residual (32 %) < reducible (49 %) in

SH; oxidisable (4.3 %) < residual (10 %) < reducible (13 %) < exchangeable (73 %) in DØ; and oxidisable (0.59 %) < exchangeable (12 %) < residual (35 %) < reducible (53 %) in D1. The largest amount of Mn was found in step 2 followed by step 4 in SH and D1 as received. For DØ as received, the largest amount of Mn was found in step 1 followed by step 2. The partitioning of Mn in the sediments as received was consistent with the main forms of the analyte in soil. Manganese occurs mainly in the water soluble and exchangeable forms (as found in DØ as received) and, as insoluble Mn oxides (as found in SH and D1 as received) in soil[44]. Baeyens *et al.*[200] and Kersten *et al.*[104] also found the largest proportion of Mn in the exchangeable fraction of freshwater sediments as received.

The results of the statistical test comparing the amount of Mn extracted from the different fractions of freeze, air and oven dried (at both 60 °C and 110 °C) samples to similar fractions in the sediment as received are listed in Table 4.13a and Table 4.13b. Generally, the application of different pre-treatment procedures did not significantly affect the operational speciation of Mn in all the sediment samples, except the significant decrease in the amount of the analyte extracted in step 4 of D1. The % recoveries of the sequential extraction of Mn with respect to PT concentration in the pre-treated samples were SH (87 % to 109 %), DØ (65 % to 106 %) and D1 (81 % to 104 %). This further showed that the application of the different sample pre-treatment procedures had limited effect on the operational speciation of Mn in the sediment samples. Rapin *et al.*[100] also reported that the application of different pre-treatment procedures had limited effect on the operational speciation of Mn in freshwater sediments using the Tessier sequential extraction procedure[86].

Table 4.13a Kruskal–Wallis test at 0.05 significance level for Mn concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	**0.026**	0.161	0.051
Reducible	0.520	0.095	0.488
Oxidisable	0.371	0.161	0.065
Residual	0.107	0.131	**0.050**

The red bold number represents significant result.

Table 4.13b Multiple comparisons test at 0.05 significance level for Mn concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C).

	Multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	1.00	1.00	0.285	0.552
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	–	–	–	–
DØ				
Exchangeable	–	–	–	–
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	–	–	–	–
D1				
Exchangeable	–	–	–	–
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	**0.035**	1.00	1.00	1.00

The red bold number represents significant result. The dash means no post hoc test was conducted.

The operational speciation of Ni in the sediment as received and pre-treated are shown in Figure 4.6 and listed in Tables A.1 – A.3 in the appendix.

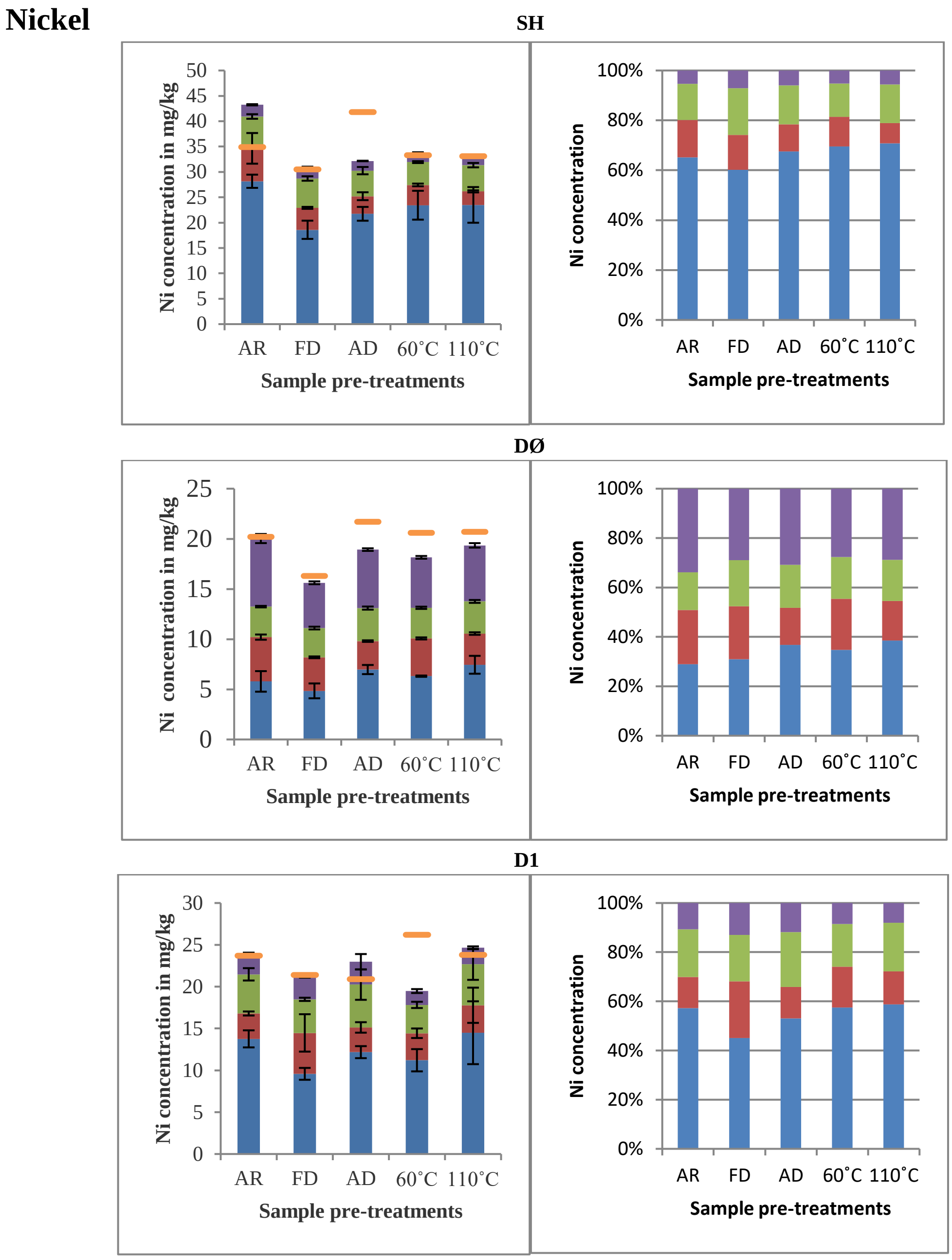


Figure 4.6 Operational speciation of Ni (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

Nickel was partitioned in the sediment as received in the following order: exchangeable (5.3 %) < reducible (15 %) ≈ oxidisable (15 %) < residual (65 %) in SH; reducible (15 %) < oxidisable (22 %) < residual (29 %) < exchangeable (34 %) in DØ; and exchangeable (11 %) < oxidisable (13 %) < reducible (20 %) < residual (57 %) in D1. The largest amount of Ni was extracted in step 4, while the smallest amount was found in step 1 of SH and D1 as received. The largest amount of Ni was found in step 1 of DØ. Shuzhen *et al.*[103] using the original BCR sequential extraction procedure found the largest amount of Ni in the exchangeable fraction of the sediment as received, although the amount of the analyte in the residual fraction was not reported.

The results of the statistical test comparing the amount of Ni extracted from the different fractions of freeze, air and oven dried (at both 60 °C and 110 °C) samples to similar fractions in the sediment as received are listed in Table 4.14a and Table 4.14b. Application of the different pre-treatment procedures had no significant effect on the amount of Ni extracted from the various fractions of D1, step 3 and 4 of SH and step 2 and 4 of DØ. The significant results in the Kruskal-Wallis test for step 1 in D1 is between the freeze and oven dried samples at 60 °C, while the result in step 4 of DØ and D1 cannot be pinpointed to any pair at 0.05 significance level with the multiple comparisons test. However, significant effects were noted for some samples in other fractions.

For SH, oven drying at 60 °C significantly decreased the amount of Ni extracted in step 1 and 2. For DØ, freeze and air drying significantly decreased the amount of Ni extracted in step 1 and 3, respectively. The formation of iron oxides and oxidation of the oxidisable mineral phase as suggested by previous studies[23, 100, 101], were probably the plausible explanation for the shift of Ni from step 1 of SH oven dried at 60 °C and freeze dried DØ. In the case of air dried DØ, Ni seemed to have shifted from step 3 to step 2 and 4 with the slight increase of the analyte in these fractions. Shuzhen *et al.*[103] reported a similar noticeable decrease in the amount of Ni extracted in step 1 (with limited effect in step 2 and 3) of a freeze, air and oven dried sediment. The % recoveries of the sequential extraction of Ni with respect to PT concentration in all pre-treated were SH (77 % to 124 %), DØ (87 % to 99 %) and D1 (74 % to 110 %).

The % recoveries tend to support the attribution of the significant results in SH and DØ to the application of the different sample pre-treatment procedures.

Table 4.14a Kruskal–Wallis test at 0.05 significance level for Ni concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	**0.024**	**0.011**	**0.031**
Reducible	**0.033**	0.098	0.204
Oxidisable	0.071	**0.009**	0.397
Residual	0.051	**0.022**	**0.038**

The red bold number represents significant result.

Table 4.14b Multiple comparisons test at 0.05 significance level for Ni concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C).

	Multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	1.00	0.446	**0.047**	0.225
Reducible	1.00	0.358	**0.035**	0.552
Oxidisable	–	–	–	–
Residual	–	–	–	–
DØ				
Exchangeable	**0.010**	1.00	0.137	1.00
Reducible	–	–	–	–
Oxidisable	1.00	**0.010**	1.00	0.137
Residual	1.00	0.679	1.00	1.00
D1				
Exchangeable	1.00	1.00	0.285	1.00
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	0.062	1.00	0.679	1.00

The red bold number represents significant result. The dash means no post hoc test was conducted.

The operational speciation of Pb in the sediment as received and pre-treated are shown in Figure 4.7 and listed in Tables A.1 – A.3 in the appendix.

Lead

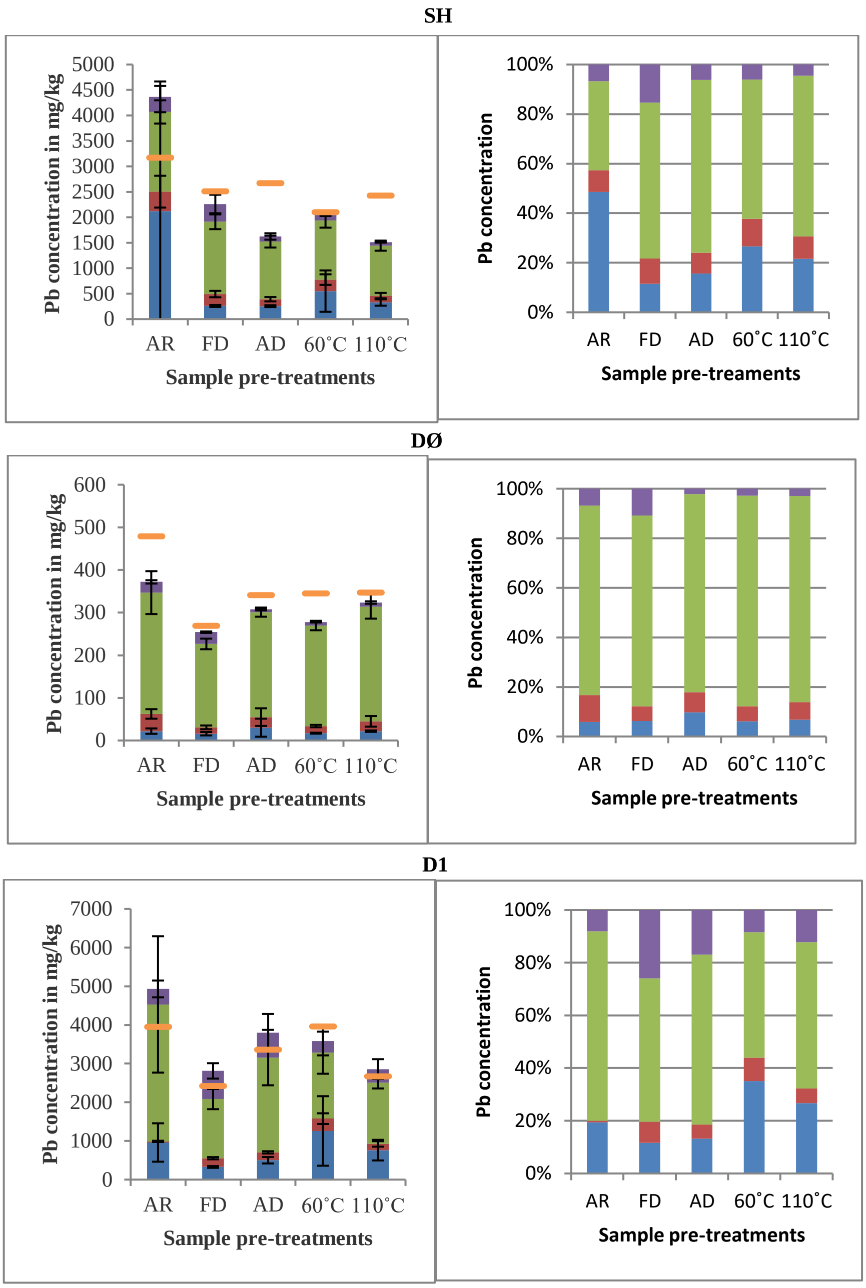


Figure 4.7 Operational speciation of Pb (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ■ Exchangeable ■ Reducible ■ Oxidisable ■ Residual

Lead was partitioned in the sediment as received in the following order: residual (10 %) < exchangeable (12 %) < oxidisable (15 %) < reducible (63 %) in SH; residual

(5.9 %) < exchangeable (6.8) < oxidisable (11) < reducible (77 %) in DØ; and oxidisable (0.56 %) < exchangeable (8.1 %) < residual (20 %) < reducible (72 %) in D1. Lead was found mainly in step 2 of all the sediments as received. This agreed with previous studies[23, 44], which indicated that mineral (hydr)oxides are good sink for Pb. Davidson *et al.*[102] and Bordas *et al.*[101] also found the largest proportion of Pb in the reducible fraction of the sediments as received.

The results of the statistical test comparing the amount of Pb extracted from the different fractions of freeze, air and oven dried (at both 60 °C and 110 °C) samples to similar fractions in the sediment as received are listed in Table 4.15a and Table 4.15b. Generally, the application of the different sample pre-treatment procedures did not significantly affect the amount of Pb extracted in the various fractions of the sediments, except the decrease in the amount of the analyte found in step 2 of SH oven dried at 110 °C and freeze dried DØ. The significant result in Kruskal-Wallis test in step 1 of DØ cannot be pinpointed to any pair in the multiple comparisons test at 0.05 significance level.

For SH, the % recoveries of the sequential extraction of Pb with respect to PT concentration were as received (138 %), freeze (90 %), air (61 %) and oven dried at both 60 °C (98 %) and 110 °C (62 %). The high and low % recoveries of Pb in SH as received and air dried, respectively, may be attributed to the poor homogeneity of the analyte in the sample. The % recoveries of the sequential extraction of Pb with respect to the PT concentrations for DØ (78 % to 95 %) and D1 (91 % to 125 %) tend to support the suggestions that application of the various sample pre-treatment procedures had limited effects on the extraction of the analyte in the sediments. Shuzhen *et al.*[103] also reported that sample pre-treatments had limited effect on the operational speciation of Pb in air and oven dried sediment using the original BCR sequential extraction procedure[92].

Table 4.15a Kruskal–Wallis test at 0.05 significance level for Pb concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	0.058	**0.030**	0.264
Reducible	**0.029**	**0.022**	0.122
Oxidisable	0.380	0.207	0.063
Residual	0.312	0.246	0.059

The red bold number represents significant result.

Table 4.15b Multiple comparisons test at 0.05 significance level for Pb concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C).

	Multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	–	–	–	–
Reducible	1.00	0.358	0.679	**0.047**
Oxidisable	–	–	–	–
Residual	–	–	–	–
DØ				
Exchangeable	1.00	0.225	0.552	1.00
Reducible	**0.047**	1.00	0.679	1.00
Oxidisable	–	–	–	–
Residual	–	–	–	–
D1				
Exchangeable	–	–	–	–
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	–	–	–	–

The red bold number represents significant result. The dash means no post hoc test was conducted.

The operational speciation of Zn in the sediment as received and pre-treated are shown in Figure 4.8 and listed in Tables A.1 – A.3 in the appendix.

Zinc

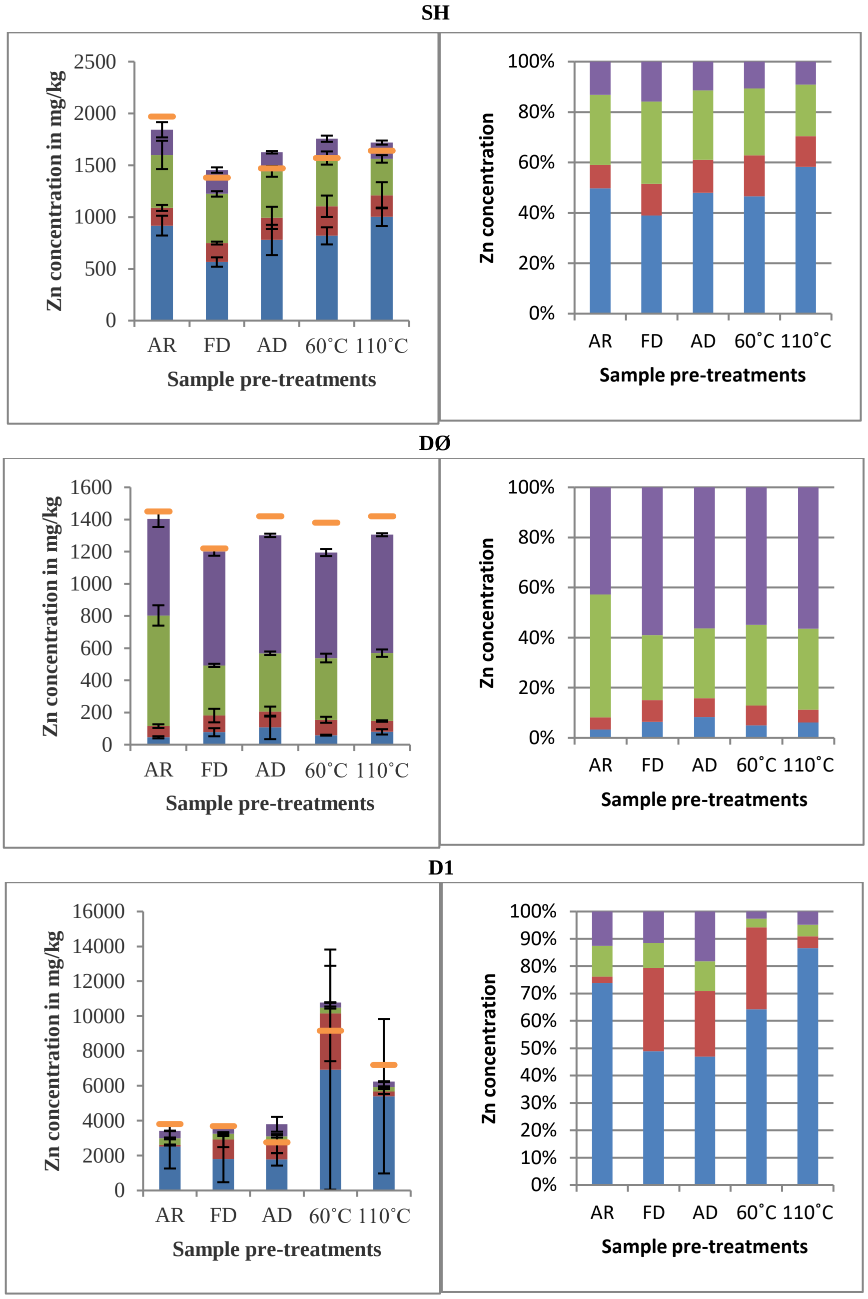


Figure 4.8 Operational speciation of Zn (mg kg^{-1} and %) in sediment as received (AR) and pre-treated (Freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C). The error bar represents the mean ± standard deviation and n = 3. Sediments: StanHope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal 🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Zinc was partitioned in the sediment as received in the following order: oxidisable (9.3 %) < exchangeable (13 %) < reducible (28 %) < residual (50 %) in SH; residual

(3.3 %) < oxidisable (5.0 %) < exchangeable (43 %) < reducible (49 %) in DØ; and oxidisable (2.4 %) < reducible (11 %) < exchangeable (13 %) < residual (74 %) in D1. The largest amounts of Zn were extracted in step 4 of SH and D1 and, step 2 of DØ as received. Generally, the partitioning pattern of Zn in all the sediments as received were somewhat similar with that of Cd, reflecting the similarity in their chemistry[44, 73].

The results of the statistical test comparing the amount of Zn extracted from the different fractions of freeze, air and oven dried (at both 60 °C and 110 °C) samples to similar fractions in the sediment as received are listed in Table 4.16a and Table 4.16b. Generally, the application of the different pre-treatment procedures did not significantly affect the amount of Zn extracted in the sediments, except the decrease in the amount of the analyte found in step 2 of freeze dried DØ. The significant results in the Kruskal-Wallis test in step 4 of SH is between the freeze and the sample oven dried at 110°C, while the results cannot be pinpointed to a specific pair in step 1 of DØ and D1, and step 3 of D1 at 0.05 significance level with the multiple comparisons test. The % recoveries of the sequential extraction of Zn with respect to PT concentration in all pre-treated were SH (93 % to 112 %), DØ (86 % to 98 %) and D1 (87 % to 137 %). The % recoveries supported the suggestions that the application of the different pre-treatment procedures had limited effect on the operational speciation of Zn in the sediments.

Table 4.16a Kruskal–Wallis test at 0.05 significance level for Zn concentration (mg kg^{-1}; n = 3) in step 1 - 4 of the BCR sequential extraction scheme for the sediments (SH, DØ and D1): as received; freeze dried; and air dried; oven dried at 60 °C and 110 °C.

Step	Kruskal-Wallis test p-value		
	SH	DØ	D1
Exchangeable	0.098	**0.026**	**0.030**
Reducible	0.132	**0.013**	0.065
Oxidisable	0.493	0.106	**0.047**
Residual	**0.039**	0.090	0.552

The red bold number represents significant result.

Table 4.16b Multiple comparisons test at 0.05 significance level for Zn concentration in step 1 - 4 of the BCR sequential extraction scheme in the sediments as received compare with the pre-treated samples (freeze dried (FD); air dried (AD); oven dried at 60 °C and 110 °C).

	Multiple comparisons test p-value			
SH	FD	AD	60 °C	110 °C
Exchangeable	–	–	–	–
Reducible	–	–	–	–
Oxidisable	–	–	–	–
Residual	0.225	1.00	1.00	1.00
DØ				
Exchangeable	0.679	0.176	1.00	0.081
Reducible	**0.010**	0.225	0.828	1.00
Oxidisable	–	–	–	–
Residual	–	–	–	–
D1				
Exchangeable	1.00	1.00	0.358	1.00
Reducible	–	–	–	–
Oxidisable	0.137	0.446	0.137	1.00
Residual	–	–	–	–

The red bold number represents significant result. The dash means no post hoc test was conducted.

4.5.2.5. The overall effects of different sample pre-treatment procedures on the operational speciation of PTE in the freshwater sediments.

Table 4.18 is the summary of the effects of sample pre-treatment procedures on the operational speciation of PTE in the sediment samples. Figure 4.9 is a graph of the number of significant changes in operational speciation of PTE in the pre-treated samples compared with the sediments as received (as indicated by the Kruskal-Wallis test followed by multiple comparisons test) against the applied sample pre-treatment procedures.

Table 4.18 Summary of the effects of sample pre-treatments on the operational speciation of PTE in sediments.

PTE	Sediment samples / sample pre-treatment procedures											
	SH				DØ				D1			
	FD	AD	60 °C	110 °C	FD	AD	60 °C	110 °C	FD	AD	60 °C	110 °C
As 🟪	⇔	⇔	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔
🟥	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟦	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
Cd 🟪	⇔	⇔	⇔	⇔	⇔	⇧	⇔	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟥	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟦	⇔	⇔	⇔	⇔	⇔	⇔	⇧	⇔	⇔	⇔	⇔	⇔
Cu 🟪	⇔	⇔	⇔	⇔	⇔	⇧	⇔	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔	⇩
🟥	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟦	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
Fe 🟪	⇩	⇔	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇔	⇔	⇔	⇧	⇔	⇔	⇔	⇩	⇔	⇔
🟥	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔	⇔	⇧
🟦	⇩	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
Mn 🟪	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟥	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟦	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔
Ni 🟪	⇔	⇔	⇩	⇔	⇩	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟥	⇔	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔	⇔
🟦	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
Pb 🟪	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇔	⇩	⇩	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟥	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟦	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
Zn 🟪	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟩	⇔	⇔	⇔	⇔	⇩	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟥	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔
🟦	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔	⇔

Sediments: StanHope (SH); Derwent Reservoir spill-way (DØ); and Carrick's Haugh (D1). Sample pre-treatment procedures: Freeze dried (FD); Air dried (AD); Oven dried at 60 °C and 110 °C.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual ⇧ Increase in amount ⇩ Decrease in amount ⇔ No significant effect .

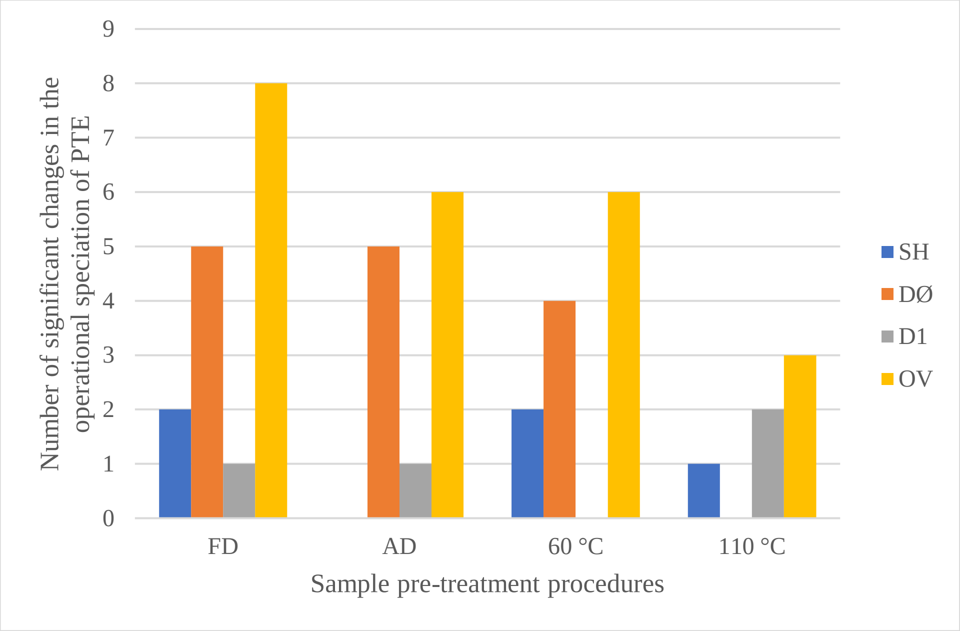


Figure 4.9 Number of significant changes in operational speciation of PTE in the pre-treated sediments. Sediments: StanHope (SH); Derwent Reservoir spill-way (DØ); and Carrick's Haugh (D1). Sample pre-treatment procedures: Freeze dried (FD); Air dried (AD); Oven dried(at 60 °C and 110 °C). Overall effects of the sample pre-treatment procedures (OV).

Air drying and oven drying at 60 °C and 110 °C had the least effect (no significant effect) on the operational speciation of PTE in SH, D1 and DØ respectively. Freeze and air drying seperately caused one significant change in operational speciation of PTE in D1. Oven drying at 110 °C also produced one significant change in the operational speciation of PTE in SH. Similar to the effect of freeze and air drying in SH, oven drying at 110 °C also produced two significant results in D1, while oven drying at 60 °C caused four significant changes in the operational speciation of PTE in DØ. Freeze and air drying seperately caused four significant change in operational speciation of PTE in DØ. Iron was the PTE most prone to sample pre-treatment procedures with seven significant changes in operational speciation of the analyte in the pre-treated sediments followed by Ni (four significant results). As and Pb (two significant results for each PTE), Cd and Cu (three significant results for each PTE), and Mn and Zn (one significant result for each PTE).

Sediment DØ had the highest % FeOOH was the most susceptible to redistribution of PTE (14 significant results) during the application of the different sample pre-treatment procedures. This was somewhat consistent with previous studies[100, 101, 104] which have indicated that changes in operational speciation of PTE in sediments during the application of different pre-treatment procedures may be attributed to the chemistry of FeOOH. Sediment SH with the highest % CO_3^{2-} had 5 significant redistributions of PTE in the pre-treated samples compared with the sediment as received. Sediment D1 had the highest % OM and was least perturbed (with four significant results) by sample pre-treatment compared with the other samples. Similarly, Hjorth[105] also reported limited changes in operational speciation of PTE in freeze dried sediment rich in OM. Overal, air and oven drying at 60 °C had a simlar effect of six significant changes, while freeze drying had the greatest impacts with eight significant changes in the operation speciation of PTE in the pre-treated sample compared to the sediment as received. Oven drying at 110 °C had the least impact with three significant changes in the operational speciation of PTE in the pretreated samples compared with the sediment as received.

4.5.2.6. The effects of different sample pre-treatment procedures on ecological risk assessment

The effect of freeze, air and oven (at both 60 °C and 110 °C) drying on the results that would be obtained for ecological risk assessment using the risk assessment code (RAC)[181] of PTE in the sediments are listed in Table 4.19. The RAC of the PTE in the pre-treated samples were compared with that of the sediments as received. The green shade represents overestimated risk, while the red shade represents underestimated risk. Freeze, air, oven drying at both 60 °C and 110 °C had eight (six overestimated and two underestimated risk), four (three overestimated and one underestimated risk), seven (two overestimated and five underestimated risk) and eight (three overestimated and five underestimated risk) false risk values, respectively. The effects of sample pre-treatments on risk did not show a definite trend, indicating that it was characteristic of the individual sediment matrix, except freeze drying that consistently gave a considerable overestimated risk for Pb in all the sediments. However, underestimation of risk is potentially more dangerous because we are missing possible ecological risk.

Table 4.19 The effect of sample pre-treatment procedures on ecological risk of PTE in sediments using the risk assessment code.

SH/PTE	Reference	Sample pre-treatments / Risk Assessment Code			
	As received	Freeze dried	Air dried	Oven dried at 60 °C	Oven dried at 110 °C
As	0.906	**1.23**	0.68	0.305	0.229
Cd	20.7	26.7	20.5	17.5	16.2
Cu	3.69	1.51	7.45	6.65	3.73
Fe	0.106	0.0764	0.105	0.126	0.0818
Mn	8.95	**11.0**	7.31	7.46	6.77
Ni	5.36	7.12	5.95	5.25	5.54
Pb	6.77	**15.4**	6.23	6.02	4.54
Zn	13.2	15.9	11.5	10.6	9.13
D0/PTE					
As	20.6	15.4	19.0	19.2	29.4
Cd	3.43	**24.5**	**21.9**	**16.3**	**16.8**
Cu	0.395	0.409	**19.1**	**5.78**	**3.52**
Fe	14.4	**6.11**	**4.38**	**4.12**	**4.29**
Mn	73.0	60.0	60.0	65.0	62.0
Ni	34.0	**30.0**	31.0	**28.0**	**29.0**
Pb	6.76	**11.0**	2.10	2.80	2.95
Zn	43.0	59.0	56.0	55.0	56.0
D1/PTE					
As	1.81	1.40	2.97	1.99	0.367
Cd	17.9	15.8	19.7	**7.35**	**6.21**
Cu	6.10	3.84	7.76	5.19	3.96
Fe	0.140	0.221	0.324	0.114	0.143
Mn	11.7	18.3	13.3	**7.33**	**8.63**
Ni	11.0	13.0	11.8	**8.51**	**8.02**
Pb	8.13	**25.9**	**17.0**	8.50	**12.2**
Zn	12.6	11.6	18.2	2.67	4.82

Green shade: overestimated risk. Red shade: underestimated risk.

4.6. Conclusion

Generally, the application of the different pre-treatment procedures did not significantly affect the amount of PTE liberated by PT *aqua regia* digestion compared with in the sediment as received, except the significant decrease in Cd and

Pb concentrations in the freeze dried SH and DØ, respectively. The significant decrease in the amount of PTE liberated by PT *aqua regia* digestion in the freeze dried SH and DØ were attributed to the occlusion of the analytes in the clay minerals.

None of the sample pre-treatment procedures (freeze, air and oven drying at both 60 °C and 110 °C) investigated preserved the intrinsic speciation of the PTE in the sediments intact, using the BCR sequential extraction procedure[95]. In addition, the effects of the application of different sample pre-treatment procedures on the operational speciation of PTE (even the same PTE) in the different sediments were not the same, reflecting the influence of their different natures. Freeze drying caused eight significant changes followed by air and oven drying at 60 °C. Both air and oven drying at 60 °C seperately caused six significant changes each in the operation speciation of PTE in the pretreated samples compared with in the sediment as received. Overall, oven drying at 110 °C had the least significant effects (three significant changes) on the operational speciation of PTE in the pretreated sample compared with in the sediment as received. Sediment DØ with the highest proportion of FeOOH was the most susceptible to redistribution of PTE during pre-treatment. Also, Fe was the PTE most prone to sample pre-treatment with seven significant changes in operational speciation in the pre-treated sediment followed by Ni (four significant results), Cd and Cu (three significant results for each PTE), As and Pb (two significant results for each PTE) and, Mn and Zn (one significant results for each PTE).

The effects of different pre-treatment procedures on the apparent ecological status of PTE in the sediments were assessed using the RAC. Air drying had four false risk values, followed by oven drying at 60 °C (with seven false risk values), and freeze and oven drying at 110 °C seperately caused eight false risk values. The false risk values are made up of underestimated and overestimated risk. The underestimated risk are potentially more dengereous because safety is assumed while there is possible ecological risk.

To obtain the most accurate information on the operational speciation of PTE, and the risk they may pose, the recommendation by previous workers[102-104] that freshwater sediments should be analysed immediately as received is also recommended by the current study. Where this is not feasible, air and oven drying (at both 60 °C and 110 °C) is preferred to freeze drying. However, in order to increase comparability of results between laboratories using the BCR sequential extraction scheme[95], sample pre-treatment procedure should be harmonised. It is also important to be mindful of the sample pre-treatment procedure that was used to stabilise the sediment when giving advice on the risk associated with the PTE in the sample.

5. The effects of freeze storage for one year on the operational speciation of potentially toxic elements in freshwater sediments

5.1. Introduction

Whilst chapter four discussed the effects of sample pre-treatment and short-term storage over periods of days or weeks, it is often necessary to store sediment samples for longer period or re-visit historical samples for further analysis. Davidson *et al.*[102] and Rapin *et al.*[100]stored freshwater sediment at -18 °C for 28 days and at -30 °C for 20 days, respectively prior to sequential extraction. Generally, both studies reported that freeze storage had limited effect on the operational speciation of PTE in freshwater sediments, except the noticeable increase in the amount of Cd extracted from the oxidisable fraction in the Davidson *et al*.[102] work (discussed in section 4.2). Therefore, where storage of sediment samples is required, freezing may be a suitable approach.

5.2. Aims and objectives

i. To assess the effects of freeze storage at -18 °C for one year on the operational speciation of PTE in freshwater sediments with different matrix composition using the BCR sequential extraction procedure[95]. This will provide useful information on how long the natural speciation of PTE may be preserved in freshwater sediment.
ii. To assess the effects of freeze storage at -18 °C for one year on the apparent ecological status of PTE in freshwater sediments as determined using the RAC. This will provide guidance on the caution that is needed when utilising the results obtained from the assessment of ecological status of PTE in frozen sediment.

5.3. Experimental

5.3.1. Sampling and sample preparation

Sampling and storage at -18 °C for one year (20th June 2017 to 20th June 2018) was done as described in section 4.4.1. The frozen sediments were unfrozen inside their container by placing them on the laboratory bench overnight (10 hours). This was followed immediately by pseudototal digestion and sequential extraction of the wet sediments.

5.3.2. Determination of moisture content

The moisture of the sediments was determined as described in section 3.7.

5.3.3. Pseudototal digestion

The sediments were digested using microwave assisted *aqua regia* digestion as described in section 3.8. The digests were analysed for the pseudototal concentration of PTE in the sediment using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

5.3.4. BCR sequential extraction

The different fractions of PTE in the sediments as received and frozen were extracted using the BCR sequential extraction procedure as described in section 3.9. The extracts were analysed for PTE fractions in the sediment using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

5.4. Results and discussion

5.4.1. Pseudototal concentration determination and sequential extraction of PTE in sediments

5.4.1.1. Limits of detection

The instrumental limits of detection (LOD) and procedural limits of detection (LOD_P) for PT PTE determination and the BCR sequential extraction steps are listed in Table 5.1. The LOD was always lower than the concentrations of the PTE determined.

Table 5.1 Instrumental limits of detection (LOD) and procedural limits of detection (LOD_{pro}) for the pseudototal PTE determination and the BCR sequential extraction steps using ICP-MS

PTE	Exchangeable fraction		Reducible fraction		Oxidisable fraction		Residual fraction/ pseudototal	
	LOD (µg L^{-1})	LODpro (mg kg^{-1})	LOD (µg L^{-1})	LODpro (mg kg^{-1})	LOD (µg L^{-1})	LODpro (mg kg^{-1})	LOD (µg L^{-1})	LODpro (mg kg^{-1})
As	0.000503	0.000201	0.0188	0.0150	0.00865	0.00433	0.183	0.183
Cd	0.0129	0.0103	0.0437	0.0350	0.00751	0.00376	0.00567	0.00567
Cu	0.443	0.177	0.585	0.468	1.16	0.0580	0.0162	0.0162
Fe	1.34	1.07	2.89	2.31	6.06	0.303	0.471	0.471
Mn	0.0838	0.0670	0.271	0.217	0.355	0.0178	0.0107	0..0107
Ni	0.00812	0.00650	0.0399	0.0319	0.217	0.0109	0.00441	0.00441
Pb	0.0374	0.0300	0.343	0.274	0.488	0.0244	0.0246	0.0246
Zn	0.202	0.162	0.198	0.154	0.281	0.0109	0.192	0.192

5.4.1.2 Quality control for pseudototal analysis

The CRM 601 was used to assess the analytical performance of the PT PTE determination in the sediments. The amounts of PT PTE in CRM 601 were indicative values. All analyses were carried out in triplicate. A blank solution was also analysed at regular intervals during the ICP-MS analysis for quality check. The PT PTE concentrations, standard deviation, % relative standard deviation (%RSD) and % recovery are listed in Table 5.2. The % RSD for the PT PTE determination was less than 10 %, indicating good results precision. The % recoveries of 90 % to 105 % for all the PTE measured were satisfactory.

Table 5.2 Pseudototal concentration (mg kg^{-1}, n = 3), standard deviation (SD; ± mg kg^{-1}), % relative standard deviation (% RSD) and % recovery of PTE in dry weight of CRM 601.

	Obtained values			Indicative values		
PTE	mg kg^{-1}	± mg kg^{-1}	% RSD	mg kg^{-1}	± mg kg^{-1}	% Recovery
Cd	10.3	0.2	1.94	11.5	1.9	90
Cu	228	4	1.75	230	15	99
Ni	80.7	2.2	2.73	78.8	6.7	102
Pb	278	6	2.20	288	52	97
Zn	871	31	3.54	833	17	105

5.4.1.3. Quality control for sequential extraction

Table 5.3 compares the certified[95] and obtained values of PTE concentration (mg kg^{-1}) in the different fractions of the certified reference material (CRM 601) using the BCR sequential extraction procedure (analysed in triplicate). The % recoveries of the BCR sequential extraction steps were 38 % to 114 %, and for the sum of the steps were 84 % to 110 %. The low % recovery of Cd in the residual fraction may be attributed to low level of the analyte and large standard deviation. A blank solution was also analysed at regular intervals during the ICP-MS analysis for quality checks.

Table 5.3 Comparison of the obtained and certified values of PTE fractions (mg kg^{-1}, n = 3), standard deviation (SD; ± mg kg^{-1}) in dry weight CRM 601 using the BCR sequential extraction scheme.

		Exchangeable fraction	Reducible fraction	Oxidisable fraction	Residual fraction	Sum
Obtained	Cd	4.15 ± 0.05	3.70 ± 0.01	1.40 ± 0.05	0.499 ± 0.024	9.75
Certified		4.45 ± 0.67	3.95 ± 0.53	1.91 ± 1.40	1.30 ± 2.2	11.6
% recovery		93	94	73	38	84
Obtained	Cu	10.8 ± 0.02	63.6 ± 0.1	71.7 ± 1.4	59.4 ± 1.78	206
Certified		10.5 ± 0.8	72.8 ± 4.9	78.6 ± 8.9	60.4 ± 4.9	222
% recovery		103	87	91	98	93
Obtained	Ni	7.51 ± 0.44	10.6 ± 0.3	6.51 ± 0.23	49.9 ± 1.73	74.5
Certified		7.82 ± 0.84	10.6 ± 1.3	6.04 ±	50.5 ± 4.3	75.0
% recovery		96	100	108	99	99
Obtained	Pb	1.61 ± 0.07	211 ± 1	14.6 ± 0.9	42.7 ± 2.0	270
Certified		2.28 ± 1.2	205 ± 11	19.7 ± 5.8	38.0 ± 8.7	265
% recovery		71	103	74	112	102
Obtained	Zn	284 ± 3	302 ± 2	105 ± 2	178 ± 7	86
Certified		261 ± 13	266 ± 17	106 ± 11	161 ± 14	794
% recovery		108	114	99	111	110

5.4.1.4. Pseudototal concentration and fractionation of PTE in the sediment as received and frozen

The effects of freeze storage at -18 °C for one year on the operational speciation of As, Cd, Cu, Fe, Mn, Ni, Pb and Zn in the sediments are represented in mg kg^{-1} and % concentration in Figures 5.1 to 5.8. The numerical data are listed in Tables A.1 – A.3 in the appendix. The PT PTE concentrations (mg kg^{-1}) are represented by the horizontal lines drawn across the bar charts in Figures 5.1 to 5.8. The Mann-Whitney test was used to determine whether there was a significant difference at 0.05 significance level between the PT concentration (Table 5.4) and operational speciation of PTE in the frozen samples stored at -18 °C for one year compared with in the sediment as received. The effects of freeze storage at -18 °C on the operational speciation of PTE are presented by element, and for each PTE there is a Mann-Whitney test table. The bold-red values in the Mann-Whitney test tables indicate the significant changes caused by freeze storage on the PT concentration and operational speciation of PTE in the samples compared with in the sediments as received. However, it should be noted that the high moisture content of the wet sediment may prevent obtaining a truly homogenised sample. This is a possible limitation given the relatively small mass of sample used for each test in this study.

5.4.1.4.1. Pseudototal concentration of PTE in the sediment as received and frozen

The results of the statistical test comparing the PT concentration of PTE in the frozen samples (at -18 °C for one year) and in the sediments as received are listed in Table 5.4. Freeze storage did not significantly affect the amount of PTE liberated by PT *aqua regia* digestion compared with in the sediment as received in SH and D1, except the significant decrease in the amount of Fe liberated in frozen SH. This may be attributed to the occlusion of Fe in the clay minerals of the frozen SH. Previous studies have indicated that sample pre-treatments may aid the occlusion of PTE in the clay minerals of soil[26, 203], and the same process may occur in sediment because of the similarities in their chemistry[46]. Conversely, there were significant increases in the amount of As, Cd, Cu, Ni and Zn liberated by PT *aqua regia* digestion in the frozen DØ compared with in the sediment as received, while the concentration of Mn decreased. The significant increase in the amount of these PTE in the frozen DØ may be attributed to the transfer of the analytes to forms more accessible to PT *aqua regia* digestion.

Table 5.4 Mann-Whitney test at 0.050 significance level for PT concentration (n = 3) of PTE in sediments (SH, DØ and D1) as received compared with in the samples stored at -18 °C for one year.

Sediments	Mann-Whitney test p-value							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
SH	0.191	0.500	0.669	**0.040**	0.191	0.095	0.191	0.669
DØ	**0.040**	**0.040**	**0.040**	0.191	**0.040**	**0.040**	0.191	**0.040**
D1	0.331	0.331	0.191	0.669	0.331	0.331	0.331	0.331

The bold red number represents significant result.

5.4.1.4.2. Fractionation pattern of PTE in the sediment as received and frozen

The operational speciation of As in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.1 and listed in Tables A.1 – A.3 in the appendix.

Arsenic

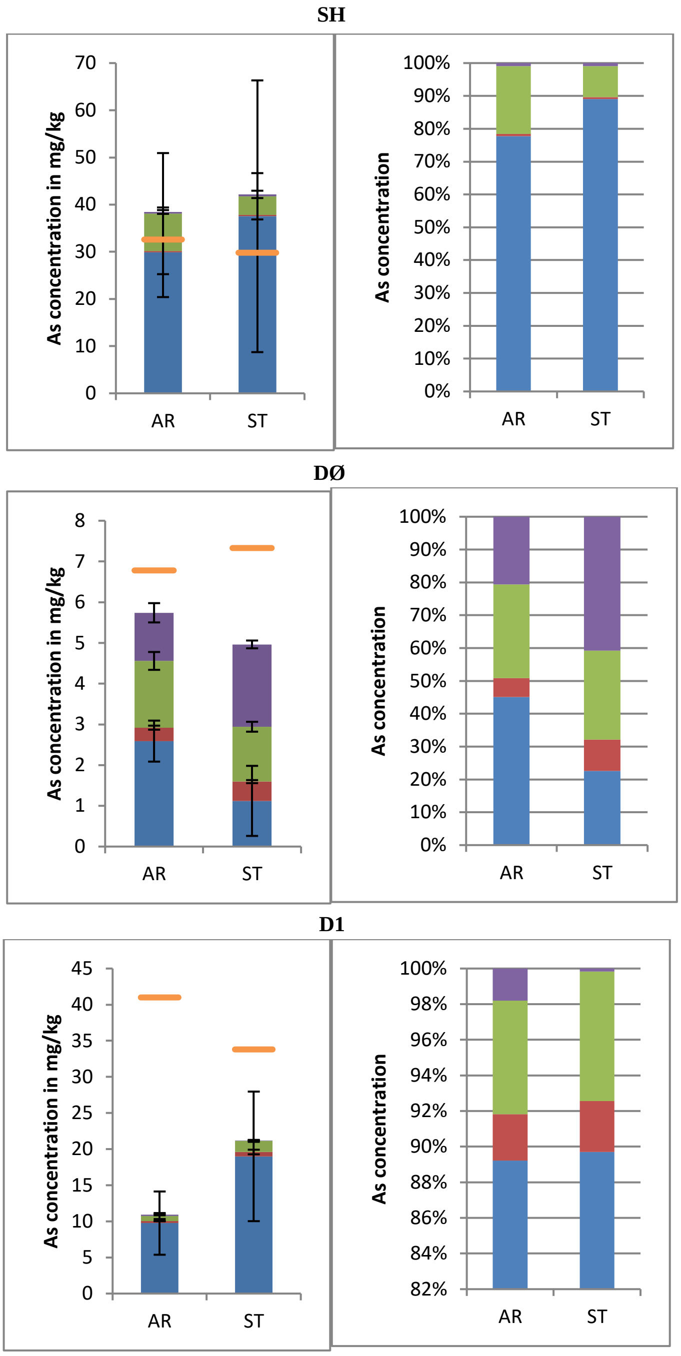


Figure 5.1 Operational speciation of As (mg kg^{-1} and %) in sediment as received and sample stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ▬ Exchangeable ▬ Reducible ▬ Oxidisable ▬ Residual

The results of the statistical test comparing the amount of As extracted from the different operationally defined fractions of the frozen samples (at -18 °C for one year) with in the sediment as received are listed in Table 5.5. Freeze storage did not significantly affect the amount of As extracted in step 1, 2, 3 and 4 of SH, step 4 of DØ and, step 3 and 4 of D1. However, significant effects were noted for some samples in other fractions. There was significant increase in the amount of As extracted from step 1 and 3 while step 2 decreased in the frozen DØ. This may be attributed to ageing effect which tends to increase the mobility[104] of As in the frozen DØ. There were significant decrease and increase in the amount of As extracted in step 1 and 2 of frozen D1, respectively. The shift of As from step 1 to 2 in the frozen D1 may be attributed to the formation of FeOOH. Formation of FeOOH may be possible in frozen sediments due to the presence of air bubbles in ice, which also make them a porous solid[204-206]. The % recoveries of the sequential extraction with respect to PT concentration of As in the frozen SH, DØ and D1 were 140 %, 68 % and 63 %, respectively, reflecting probably the poor homogeneity of the analyte in the sediment samples. The high moisture content in the sediments may have prevented obtaining properly homogenised samples.

Table 5.5 Mann-Whitney test at 0.05 significance level for As concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	0.331	**0.040**	**0.040**
Reducible	0.331	**0.040**	**0.040**
Oxidisable	0.500	**0.040**	0.095
Residual	0.500	0.095	0.095

The red bold number represents significant result.

The operational speciation of Cd in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.2 and listed in Tables A.1 – A.3 in the appendix.

Cadmium

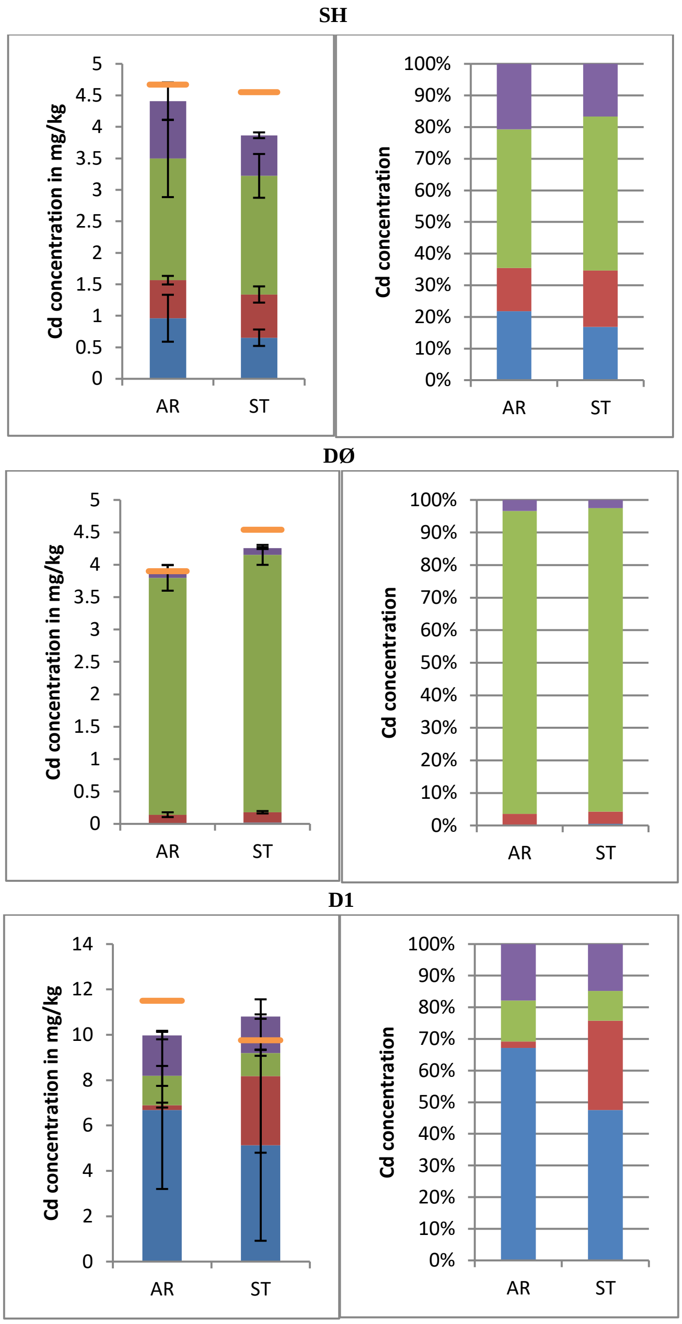


Figure 5.2 Operational speciation of Cd (mg kg^{-1} and %) in sediment as received (AR) and sample stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal 🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The results of the statistical test comparing the amount of Cd extracted from the different fractions of the frozen samples (at -18 °C for one year) with similar fractions in the sediment as received are listed in Table 5.6. Generally, freeze storage did not significantly affect the operational speciation of Cd in all the samples compared with in the sediments as received, except the increase in the amount of the analyte in step 3 and 4 of D1 and DØ respectively. The % recoveries of the sequential extraction with respect to PT concentration of Cd in the frozen SH, DØ and D1 were 85 %, 94 % and 111 %, respectively. Generally, the % recoveries tend to support the hypothesis that freeze storage at -18 °C for one year had limited effect on the operational speciation of Cd in the sediment samples.

Table 5.6 Mann-Whitney test at 0.05 significance level for Cd concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	0.095	0.331	0.095
Reducible	0.500	0.095	0.699
Oxidisable	0.331	0.331	**0.040**
Residual	0.191	**0.040**	0.331

The red bold number represents significant result.

The operational speciation of Cu in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.3 and listed in Tables A.1 – A.3 in the appendix.

Copper

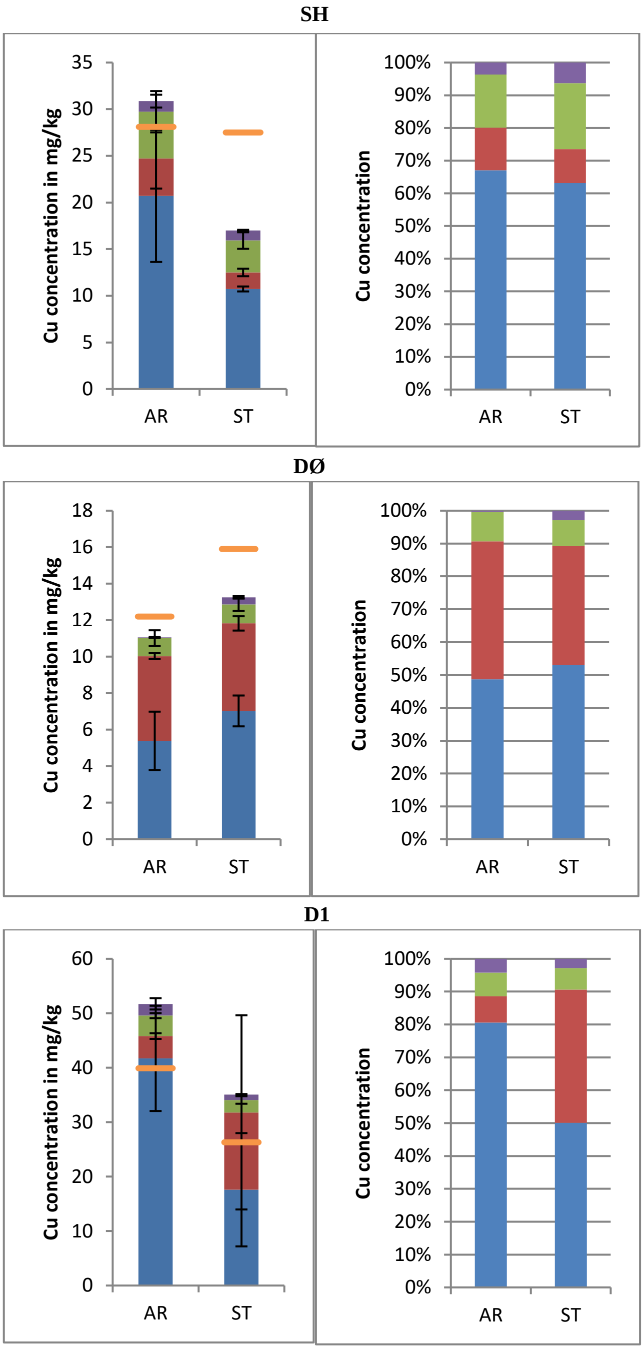


Figure 5.3 Operational speciation of Cu (mg kg^{-1} and %) in sediment as received (AR) and sample stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ■ Exchangeable ■ Reducible ■ Oxidisable ■ Residual

The results of the statistical test comparing the amount of Cu extracted from the different fractions of the frozen samples (at -18 °C for one year) with similar fractions in the sediment as received are listed in Table 5.7. Generally, there was no significant redistribution of Cu within the operationally defined fractions of the frozen sediment, except the increase in step 1 of DØ and the decrease in step 2 and 4 of D1 and SH respectively. For D1, there was an apparent increase in the oxidisable Cu in the frozen sample, but the result was not significantly different compared with in the sediment as received. The % recoveries of the sequential extraction with respect to PT concentration of Cu in the frozen SH, DØ and D1 were 62 %, 84 % and 133 %, respectively, indicating probably the poor homogeneity of the analyte and samples due to the high moisture content.

Table 5.7 Mann-Whitney test at 0.05 significance level for Cu concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	0.331	**0.040**	0.191
Reducible	0.191	0.669	**0.040**
Oxidisable	0.331	0.500	0.500
Residual	**0.040**	0.095	0.191

The red bold number represents significant result.

The operational speciation of Fe in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.4 and listed in Tables A.1 – A.3 in the appendix.

Iron

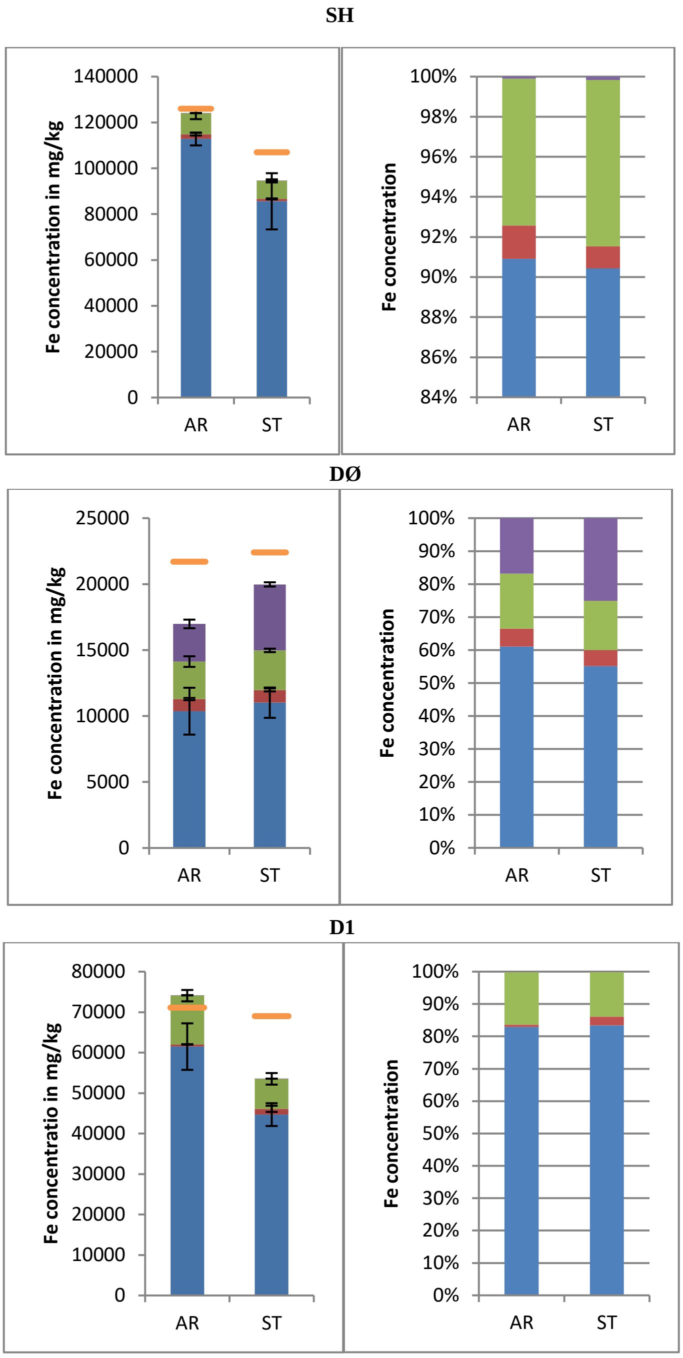


Figure 5.4 Operational speciation of Fe (mg kg^{-1} and %) in sediment as received (AR) and sample stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ■ Exchangeable ■ Reducible ■ Oxidisable ■ Residual

The results of the statistical test comparing the amount of Fe extracted from the different fractions of the frozen samples (at -18 °C for one year) with similar fractions in the sediment as received are listed in Table 5.8. Freeze storage did not significantly affect the amount of Fe extracted in step 2 of SH, step 2, 3 and 4 of DØ. However, significant effects were noted in some samples in other fractions. Freeze storage significantly decreased the amount of Fe extracted from step 1, 3 and 4 of SH. The % recovery (88 %) of the sequential extraction with respect to PT concentration tend to support the hypothesis that freeze storage was responsible for the change in Fe speciation in SH. There was a significant decrease in the amount of Fe extracted in step 1, 2 and 4 of D1, which may be attributed to the formation of FeOOH and subsequent shift of OM-bound FeOOH[196, 197, 202] to the oxidisable phase (step 3) in frozen sample. There was a significant increase in the amount of Fe extracted from step 1 of DØ. The % recoveries of the sequential extraction with respect to PT concentration of Fe in the frozen DØ and D1 were 89 % and 78 %, respectively. The % recoveries indicated there was limited effect on the operational speciation of Fe in frozen DØ, while it supports the attribution of the significant results in D1 to freeze storage.

Table 5.8 Mann-Whitney test at 0.05 significance level for Fe concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	**0.040**	**0.040**	**0.040**
Reducible	0.669	0.669	**0.040**
Oxidisable	**0.040**	0.191	**0.040**
Residual	**0.040**	0.669	**0.040**

The red bold number represents significant result.

The operational speciation of Mn in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.5 and listed in Tables A.1 – A.3 in the appendix.

Manganese

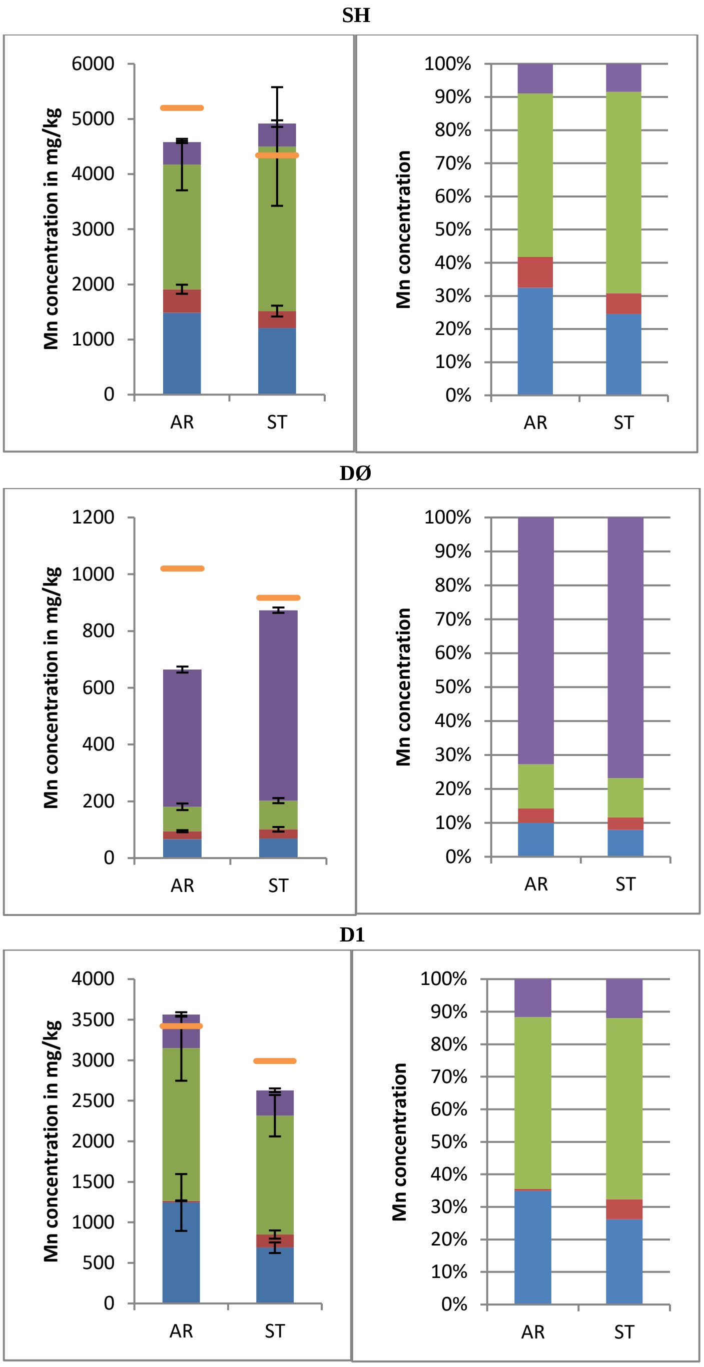


Figure 5.5 Operational speciation of Mn (mg kg^{-1} and %) in sediment as received (AR) and sample stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ■ Exchangeable ■ Reducible ■ Oxidisable ■ Residual

The results of the statistical test comparing the amount of Mn extracted from the different fractions of the frozen samples (at -18 °C for one year) with similar fractions in the sediment as received are listed in Table 5.9. Statistical tests indicated no significant differences in the amounts of Mn extracted from the various fractions of frozen SH and DØ (except step 1 of DØ where an increase occurred). The % recoveries of the sequential extraction with respect to PT concentration of Mn in the frozen SH and DØ were 113 % and 95 %, respectively, supporting the hypothesis that freeze storage had limited effects on the operational speciation of Mn in SH and DØ. For D1, there was a significant decrease in the amount of Mn found in step 1 and 4, while the amount of the analyte released in step 3 increased in the frozen sample. The redistribution of Mn is somewhat similar to the change in fractionation of Fe in the frozen D1, reflecting probably the association between the analytes. This suggested that freeze storage also aided the shift of Mn associated with the OM-bound FeOOH[196, 197, 202] to the oxidisable phase. The % recovery of the sequential extraction with respect to PT concentration of Mn in the frozen D1 was 88 %, supporting the attribution of the significant results to freeze storage.

Table 5.9 Mann-Whitney test at 0.05 significance level for Mn concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	0.500	**0.040**	**0.040**
Reducible	0.191	0.095	0.191
Oxidisable	0.095	0.331	**0.040**
Residual	0.095	0.500	**0.040**

The red bold number represents significant result.

The operational speciation of Ni in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.6 and listed in Tables A.1 – A.3 in the appendix.

Nickel

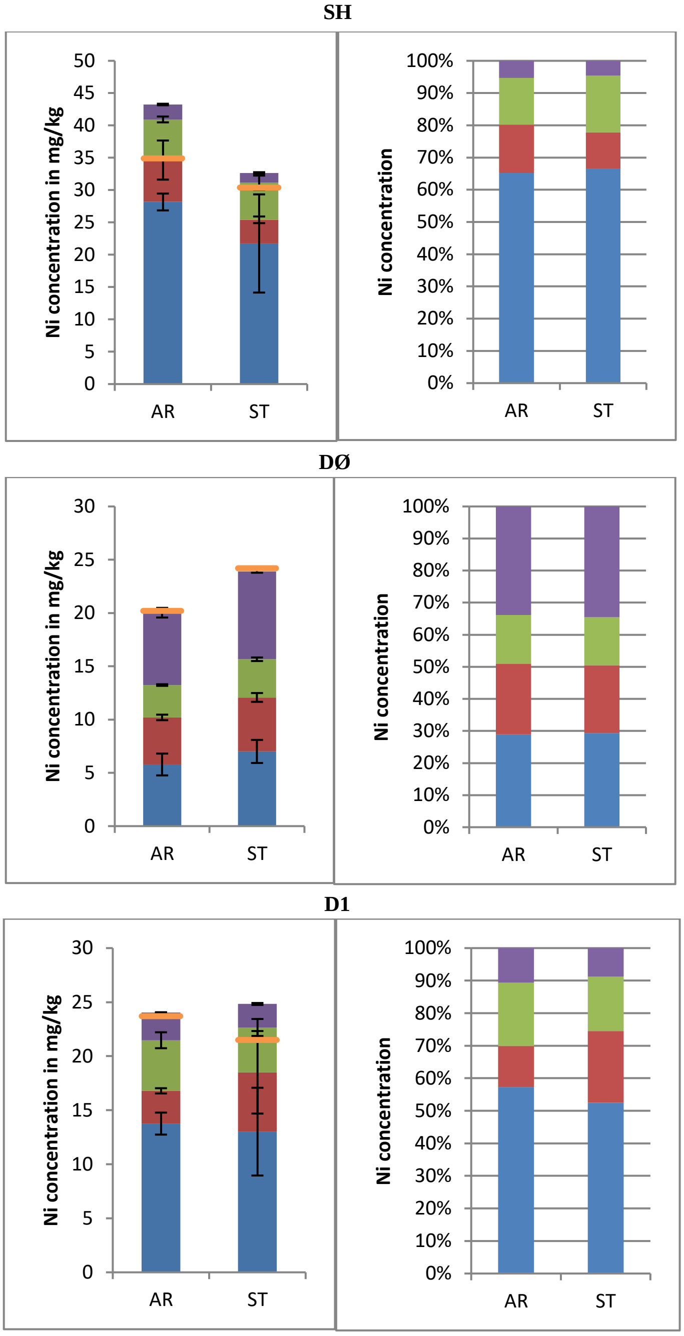


Figure 5.6 Operational speciation of Ni (mg kg^{-1} and %) in sediment as received (AR) and sample stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal 🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The results of the statistical test comparing the amount of Ni extracted from the different fractions of the frozen samples (at -18 °C for one year) with similar fractions in the sediment as received are listed in Table 5.10. Freeze storage did not significantly affect the amount of Ni extracted in step 2, 3 and 4 of SH and D1 and, step 4 of DØ. However, significant effects were noted for some samples in other fractions. There was a significant decrease in the amount of Ni extracted from step 1 of frozen SH and D1. The % recoveries of the sequential extraction with respect to PT concentration of Ni in the frozen SH and D1 were 108 % and 115 % respectively. This indicated that freeze storage had a limited effect on the operational speciation of Ni in SH and D1. There was a significant increase in the amount of Ni extracted in step 1, 2 and 3 of DØ. Taken together with the significant increase in PT concentration of Ni in the frozen DØ, and the % recovery (98 %) of the sequential extraction with respect to PT concentration, indicated that freeze storage transferred the analyte to forms more accessible to PT *aqua regia* digestion. The significant increase in the amount of Ni extracted in all the operationally defined fractions of frozen DØ (including significant increase in PT concentration) is consistent with the suggestions that depending on the applied sample preservation and digestion technique PTE occluded in the clay minerals of soil (probably also sediment) may or may not be accessible to PT *aqua regia* digestion[26, 203].

Table 5.10 Mann-Whitney test at 0.05 significance level for Ni concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	**0.040**	**0.040**	**0.040**
Reducible	0.331	**0.040**	0.699
Oxidisable	0.331	**0.040**	0.331
Residual	0.331	0.191	0.331

The red bold number represents significant result.

The operational speciation of Pb in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.7 and listed in Tables A.1 – A.3 in the appendix.

Lead

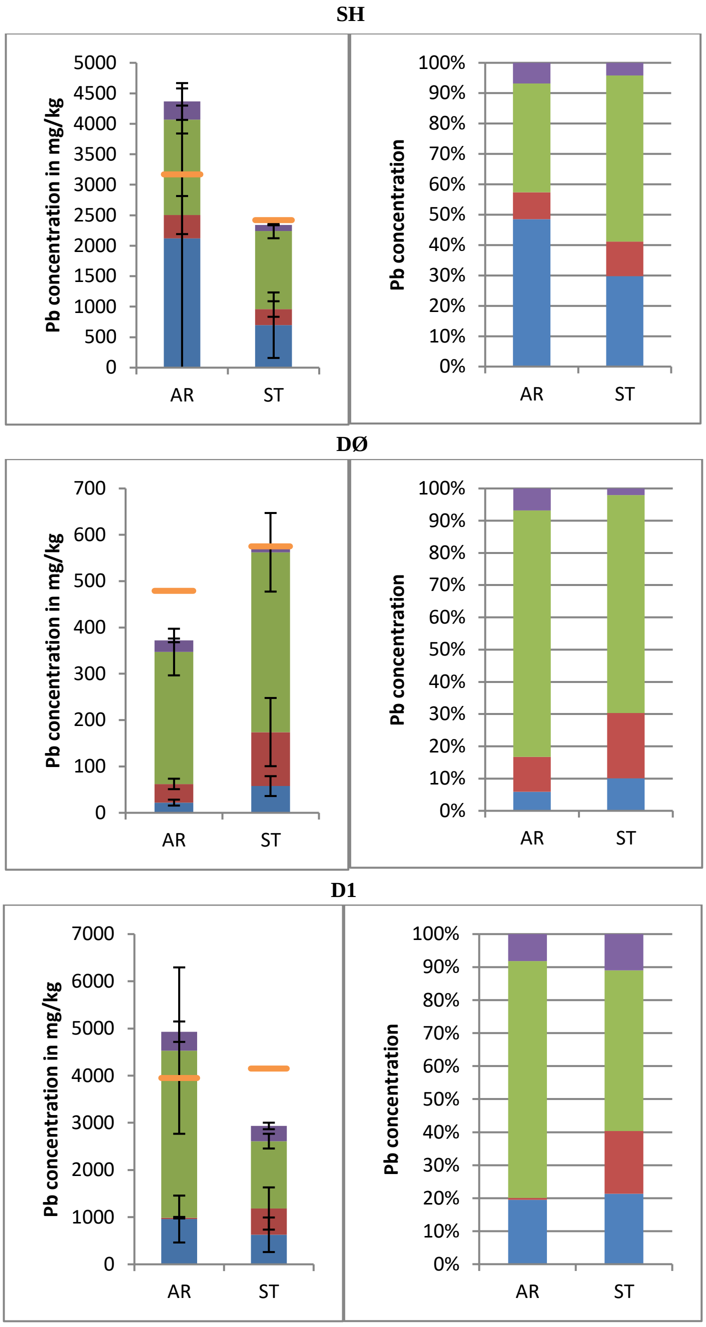


Figure 5.7 Operational speciation of Pb (mg kg^{-1} and %) in sediment as received (AR) and samples stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal ▬ Exchangeable ▬ Reducible ▬ Oxidisable ▬ Residual

The results of the statistical test comparing the amount of Pb extracted from the different fractions of the frozen samples (at -18 °C for one year) with similar fractions in the sediment as received are listed in Table 5.11. Freeze storage did not significant affect the amount of Pb extracted from step 1,3 and 4 of SH, step 2 of DØ and step 1 and 4 of D1. However, significant effects were noted for some samples in other fractions. The only significant effect in the frozen SH was the decrease in the amount of Pb found in step 2. The % recovery (97 %) of the sequential extraction with respect to PT concentration supports the suggestion that freeze storage had limited effect on the operational speciation of Pb in SH. There was a significant decrease in the amount of Pb extracted in step 1, while the amount of the analyte found in step 3 and 4 increased in the frozen DØ. Taken together with the % recovery (100 %) of the sequential extraction with respect to PT concentration indicated that freeze storage was responsible for the change in the operational speciation of Pb in DØ. For D1, there was a significant decrease in the amount of Pb extracted from step 2, while the amount of the analyte found in step 3 increased in the frozen D1. The % recovery of the sequential extraction with respect to PT concentration of Pb in the frozen D1 was 71 %. The significance decrease in the amount of Pb in step 1 of the frozen DØ may be attributed to the association of the analyte with a newly formed FeOOH, while the significant increase in the amount of the analyte in step 3 of both frozen DØ and D1 may be due to the occlusion of FeOOH-bound Pb in the oxidisable mineral phase. Studies[197, 202] have indicated that it is possible for the PTE associated with the OM-bound FeOOH to be occluded in the oxidisable mineral phase.

Table 5.11 Mann-Whitney test at 0.05 significance level for Pb concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	0.095	**0.040**	0.699
Reducible	**0.040**	0.095	**0.040**
Oxidisable	0.699	**0.040**	**0.040**
Residual	0.500	**0.040**	0.331

The red bold number represents significant result.

The operational speciation of Zn in the sediments as received and frozen (at -18 °C for one year) are shown in Figure 5.8 and listed in Tables A.1 – A.3 in the appendix.

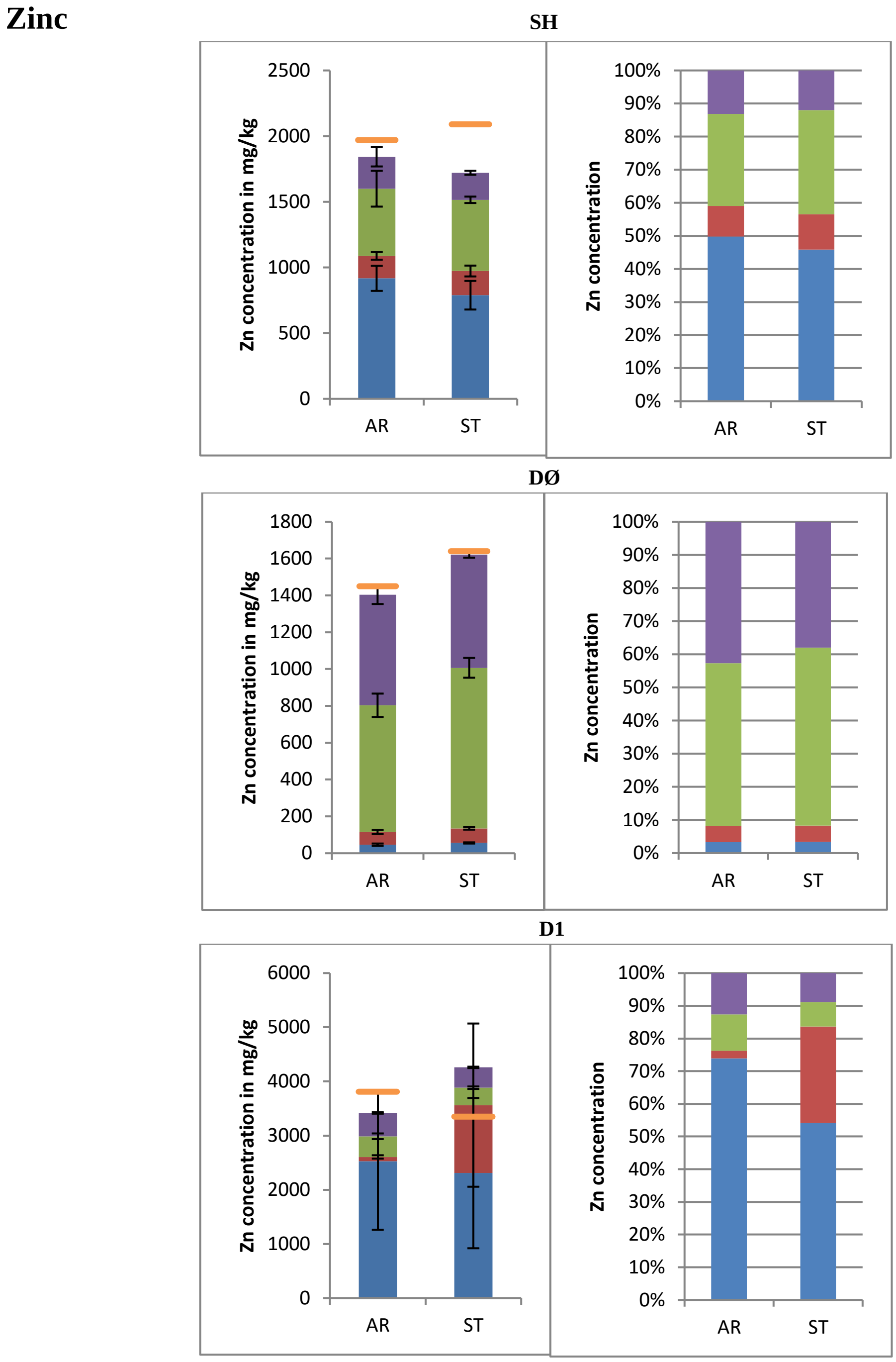


Figure 5.8 Operational speciation of Zn (mg kg^{-1} and %) in sediment as received (AR) and sample stored at -18 °C for one year (ST). The error bar represents the mean ± standard deviation and n = 3. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ) and Carrick's Haugh (D1).

— Pseudototal 🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The results of the statistical test comparing the amount of Zn extracted from the different fractions of the frozen samples (at -18 °C for one year) with similar fractions in the sediment as received are listed in Table 5.12. Freeze storage did not significantly affect the amount of Zn extracted in the various fractions of SH, step 1, 3 and 4 of DØ and, step 2 and 4 of D1. However, significant effects were noted for some samples in other fractions. The % recovery of the sequential extraction with respect to PT concentration of Zn in the frozen SH was 82 %, supporting the suggestion that freeze storage at -18 °C for one year had limited effect on the operational speciation of Zn in SH. There was a significant increase in the amount of Zn extracted from step 2 of the frozen DØ. Taken together with the significant increase in PT concentration of Zn in the frozen DØ, and the % recovery (99 %) of the sequential extraction with respect to PT concentration, suggested that freeze storage transferred the analyte to forms more accessible to PT *aqua regia* digestion. For D1, there was a significant decrease in the amount of Zn found in step 1, while the amount of the analyte extracted in step 3 increased in the frozen sample. With the % recovery (127 %) of the sequential extraction with respect to PT concentration of Zn in the frozen D1, poor homogeneity of the analyte and sample may be responsible for the significant results.

Table 5.12 Mann-Whitney test at 0.05 significance level for Zn concentration (n = 3) in step 1-4 of the BCR sequential extraction scheme for sediments (SH, DØ and D1) as received compared with in the sample stored at -18 °C for one year.

Step	Mann-Whitney test p-value		
	SH	DØ	D1
Exchangeable	0.331	0.331	**0.040**
Reducible	0.331	**0.040**	0.191
Oxidisable	0.500	0.191	**0.040**
Residual	0.191	0.095	0.699

The red bold number represents significant result.

5.4.1.5. The overall effects of freeze storage at -18 °C for one year on the operational speciation of PTE in the freshwater sediments

Table 5.13 is the summary of the effects of freeze storage at -18 °C for one year on the operational speciation of PTE in the sediment samples.The number of significant change in the operational speciation of PTE in samples frozen at -18 °C for one year compared with in the sediment as received are represented in Figure 5.9.

Table 5.13 Summary of the effect of freeze storage at -18 °C for one year on the operational speciation of PTE in the freshwater sediments.

Sediment	Changes in operational speciation of PTE in the frozen sediment							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
SH	🟪 ⇔	🟪 ⇔	🟪 ⇔	🟪 ⇩	🟪 ⇔	🟪 ⇩	🟪 ⇔	🟪 ⇔
	🟩 ⇔	🟩 ⇔	🟩 ⇔	🟩 ⇔	🟩 ⇔	🟩 ⇔	🟩 ⇩	🟩 ⇔
	🟥 ⇔	🟥 ⇔	🟥 ⇔	🟥 ⇩	🟥 ⇔	🟥 ⇔	🟥 ⇔	🟥 ⇔
	🟦 ⇔	🟦 ⇔	🟦 ⇩	🟦 ⇩	🟦 ⇔	🟦 ⇔	🟦 ⇔	🟦 ⇔
DØ	🟪 ⇧	🟪 ⇔	🟪 ⇧	🟪 ⇧	🟪 ⇧	🟪 ⇧	🟪 ⇩	🟪 ⇔
	🟩 ⇩	🟩 ⇔	🟩 ⇔	🟩 ⇔	🟩 ⇔	🟩 ⇧	🟩 ⇔	🟩 ⇧
	🟥 ⇧	🟥 ⇔	🟥 ⇔	🟥 ⇔	🟥 ⇔	🟥 ⇧	🟥 ⇧	🟥 ⇔
	🟦 ⇔	🟦 ⇧	🟦 ⇔	🟦 ⇔	🟦 ⇔	🟦 ⇔	🟦 ⇧	🟦 ⇔
D1	🟪 ⇩	🟪 ⇔	🟪 ⇔	🟪 ⇩	🟪 ⇩	🟪 ⇩	🟪 ⇔	🟪 ⇩
	🟩 ⇧	🟩 ⇔	🟩 ⇩	🟩 ⇩	🟩 ⇔	🟩 ⇔	🟩 ⇩	🟩 ⇔
	🟥 ⇔	🟥 ⇧	🟥 ⇔	🟥 ⇧	🟥 ⇧	🟥 ⇔	🟥 ⇧	🟥 ⇧
	🟦 ⇔	🟦 ⇔	🟦 ⇔	🟦 ⇩	🟦 ⇩	🟦 ⇔	🟦 ⇔	🟦 ⇔

Sediments: StanHope (SH); Derwent Reservoir spill-way (DØ); and Carrick's Haugh (D1).
🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual
⇧ Increase in amount ⇩ Decrease in amount ⇔ No significant effect .

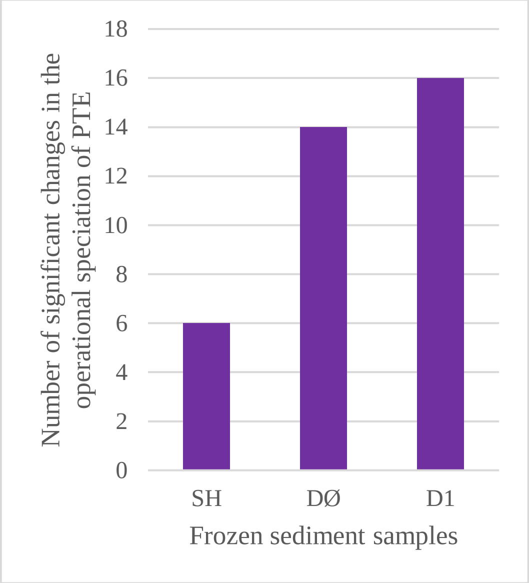


Figure 5.9 Number of significant changes in the operational speciation of PTE in the sediment samples frozen at -18°C for one year. Sediments: Stanhope (SH); Derwent Reservoir spill-way (DØ); and Carrick's Haugh (D1).

There were 6, 14 and 16 significant changes in the operational speciation of PTE in SH, DØ and D1 frozen at -18 °C for one year respectively compared with in the sediment as received. Overall, there were 36 (37.5 %) significant changes in the operational speciation of PTE in the frozen samples compared with the sediment as received. The operational speciation of Fe was the most prone to change in the frozen sediments with eight significant results, followed by Pb (six significant results), As and Ni (five significant results for each analyte), Mn (four significant results), Cu and Zn (three significant results for each analyte) and Cd (two significant results). There was also a considerable change in the operational speciation of PTE in the frozen DØ. This is somewhat consistent with the results of the effect of sample pre-treatment procedures on the operational speciation of PTE in sediment studied in chapter four. Sediment DØ had the highest proportion of FeOOH and was the most prone to the redistribution of PTE in the pre-treated samples.

5.4.1.6. The overall effects of freeze storage at -18 °C for one year on ecological risk assessment

The effects of freeze storage at -18 °C for one year on the results that would be obtained for ecological risk assessment using risk assessment code (RAC)[181] of PTE in the sediment samples are listed in Table 5.14. The RAC of the PTE in the frozen samples were compared with in the sediments as received. The green shade represents overestimated risk, while the red shade represents underestimated risk. Overall, freeze storage at -18 °C for one year resulted in five false RAC values; four underestimated and one overestimated risk of the PTE present in the frozen sediment samples.

Table 5.14 The effect of freeze storage at -18 °C for one year on ecological risk of PTE in sediments using the risk assessment code.

Sediment samples	Potentially toxic elements / Risk Assessment code							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
SH as received	0.906	20.7	3.69	0.106	8.95	5.36	6.77	13.2
SH frozen	0.383	14.2	3.89	0.0543	9.56	4.93	4.07	**9.86**
DØ as received	20.6	3.43	0.395	14.4	73.0	34.0	6.76	43.0
DØ frozen	27.6	**0.0231**	**2.41**	22.3	73.2	34.0	2.07	37.6
D1 as received	1.81	17.9	6.10	0.140	11.7	11.0	8.13	12.6
D1 frozen	**0.110**	16.4	3.84	0.0614	11.0	**10.0**	7.76	11.2

Green shade: overestimated risk. Red shade: underestimated risk.

5.5. Conclusion

Generally, freeze storage did not significantly affect the amount of PTE liberated by PT *aqua regia* digestion compared with in the sediment as received in SH and DØ, except the decrease in PT Fe in SH. There was also a significant decrease in the amount of Mn liberated by PT *aqua regia* digestion in the frozen DØ compared with in the sediments as received. The decrease in PT concentration of Fe and Mn in SH and DØ, respectively, were attributed to the occlusion of the analytes in the frozen samples. Conversely, there were significant increase in the amount of As, Cd, Cu, Ni and Zn liberated by PT *aqua regia* digestion in frozen DØ compared with in the sediment as received. This was attributed to the transfer of As, Cd, Cu, Ni and Zn to forms more accessible to PT *aqua regia* digestion in the frozen DØ.

Freeze storage at -18 °C for one year had severe effects on the operational speciation of PTE in sediments compared to Davidson *et al.*[102] (stored freshwater sediments at -18 °C for 28 days) and Rapin *et al.*[100] (stored freshwater sediments at -30 °C for 20 days) studies. Both Davidson *et al.*[102] and Rapin *et al.*[100] reported that freeze storage had limited effect on the operational speciation of PTE in the sediments studied. There were 36 (37.5 %) significant changes in the operational speciation of PTE in the frozen samples investigated compared with in the sediment as received. Consequently, freeze storage at -18 °C for one year did not preserve the natural speciation of PTE intact in the sediments investigated. The RAC of the PTE in the frozen samples were compared with in the sediments as received. Freeze storage at -18 °C for one year resulted in five false RAC values compared with in the sediments as received.

Part 2 – Environmental section

6. Study site and literature review

6.1. Introduction

This account is on the Derwent Reservoir and catchment. The Derwent catchment is situated in the North Pennine Area of Outstanding Natural Beauty and part of the Northern Orefield, England. The account is largely from previous studies[36, 37, 207], 50 Derwent facts[208], a monograph of the Northern Mine Research Society[38], the geology of the Northern Pennine Orefield[209], the British Geological Survey[166, 167] and personal observation. The account covers the geography, geology and old mining operations and previous studies on PTE pollution in the Derwent catchment[36, 37, 207].

6.2. Geography of Derwent catchment

The Northern Pennine Orefield is approximately 1500 square miles and this include parts of the Counties Cumbria (previously also Cumberland and Westmorland), Northumberland, Durham and Yorkshire[209]. The Derwent catchment includes parts of the Counties Northumberland and Durham, and it covers the area draining directly into the Derwent Reservoir. The catchment average rainfall is 953 mm. The catchment land comprises of arable land, grassland, moorland, forestry, and a few urban developments with low population density. The catchment land-use is mainly sheep farming[36, 37, 208].

6.2.1. Derwent Reservoir

The Derwent Reservoir is owned by Northumbrian Water Limited England[208]. The Derwent Reservoir is on the River Derwent along the border of County Durham and Northumberland west of Consett. Three farms and two cottages were demolished, and about 3.2 km of roads were submerged to make way for the reservoir. The Derwent Reservoir is 5.6 km long, has a surface area of 4 km^2, maximum capacity of 50 000 000 m^3 and slopes to a maximum depth of 30 m near the dam[36, 208]. Its construction was completed in 1966 and it is one of the largest reservoirs in England. The Derwent Reservoir is used mainly for public water supply (abstracted for treatment at Mosswood water treatment works by Northumbrian Water Limited), recreation purposes (hosting a sailing club) and trout fishing[36, 208]. The River Derwent account for over 80 % of water fed into the Derwent Reservoir[36, 37]. The River Derwent enters the Derwent Reservoir at a shallow area set aside as a nature reserve (public access to the nature reserve is prohibited (Figure 6.1)) close to Carrick's Haugh. The nature reserve was established to create attractive habitats for birds. In addition to the River Derwent, there are also small and shallow tributaries, (including Cow Burn, Acton Burn, Wood House Burn, Cronkley Burn and Pow Hill) feeding into the Derwent Reservoir (Figure 6.1).

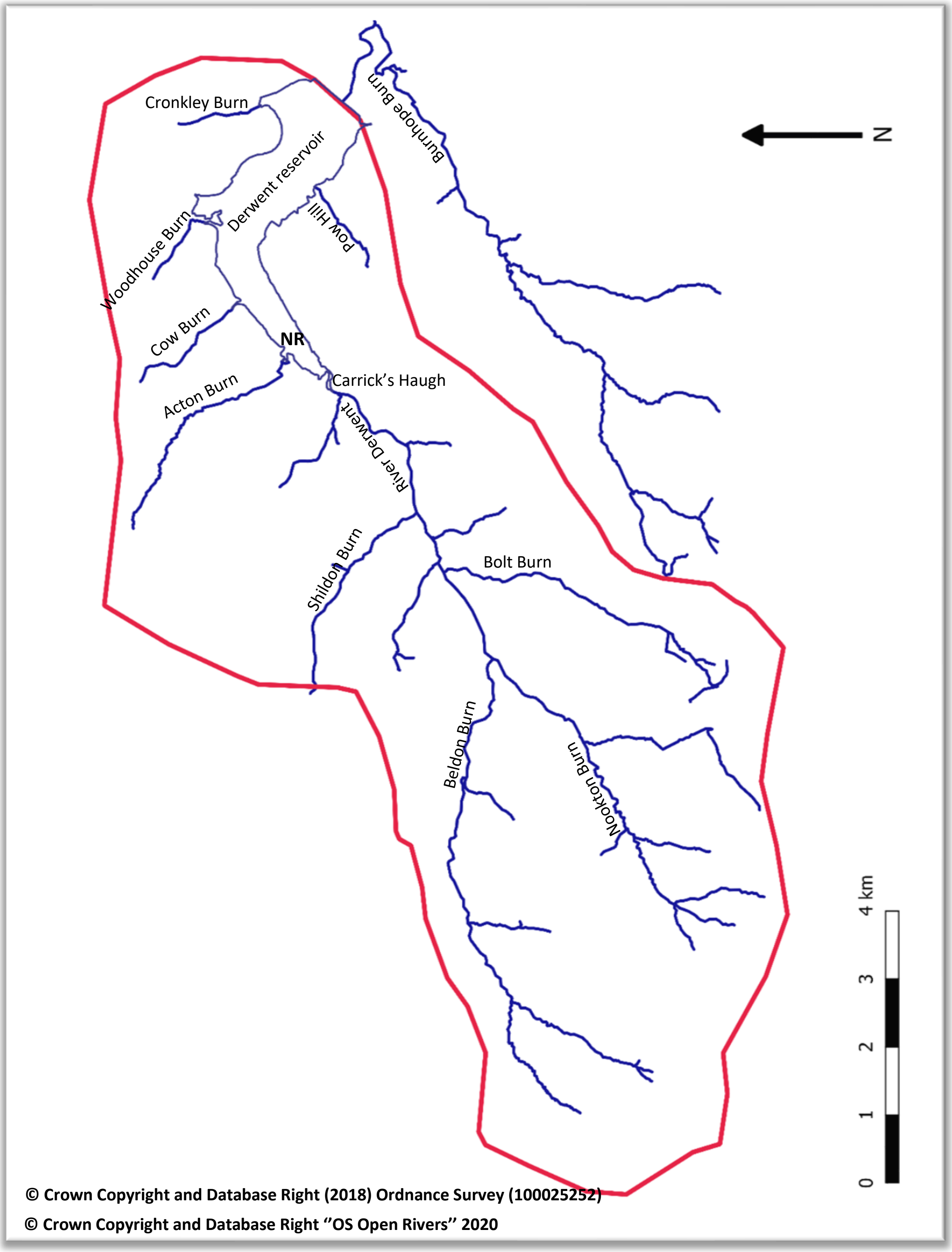


Figure 6.1 Map of the Derwent Reservoir and catchment. The red line shows the draining area of the catchment. NR: nature reserve.

6.2.2. River Derwent

The headwaters of the River Derwent are in the North-East region of the Northern Pennine Orefield[209]. The River Derwent is formed approximately 5km upstream from the Derwent Reservoir by the confluence of Beldon Burn and Nookton Burn. The River Derwent flows easterly towards the Derwent reservoir. The river and reservoir water are brown in colour as a result of the wide area of peat in the draining area of Beldon Burn, Nookton Burn and Bolt’s Burn. Bolt’s Burn and Shildon Burn are the two major tributaries feeding the River Derwent downstream of the confluence of Beldon Burn and Nooktoon Burn. The confluence of Bolt’s Burn and Shildon Burn with the River Derwent are approximately 3.5 km and 2.5 km upstream from the reservoir, respectively. Bolt’s Burn is the largest tributary feeding the River Derwent. There was evidence of extensive old mine workings in the draining areas of Bolt’s Burn. Sheldon Burn is also bordered by the evidence of old mines workings. The River Derwent is a major tributary of the River Tyne downstream from the Derwent Reservoir and is centred between the villages of Blanchland in Northumberland and Hunstanworth in Durham.

6.3. Geology of Derwent catchment

For descriptive purposes the Northern Pennine Orefield was subdivided into nine areas[209]. Figure 6.2 is a sketch map (from the geology of the Northern Pennine Orefield, Tyne to Stainmore) of the nine areas of the Northern Pennine and their main formations. The nine areas are Escarpment, Alston Moor, West Allendale, East Allendale, Weardale, Derwent Valley, Teesdale, Haydon Bridge area and Durham Coalfield[209]. The Derwent valley is situated in the Derwent catchment.

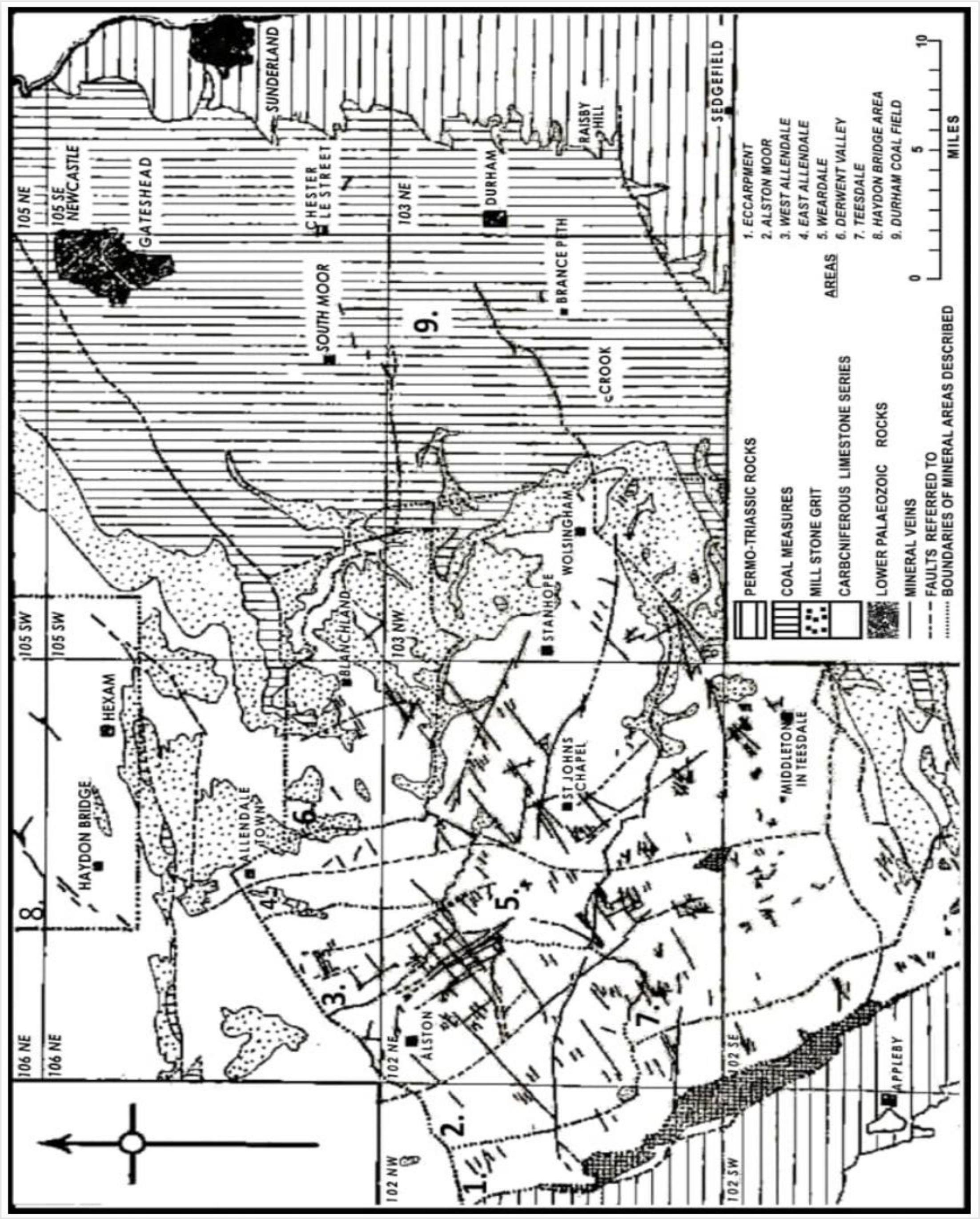


Figure 6.2 sketch map of the nine areas of the Northern Pennine and their main formations (adapted from the geology of the Northern Pennine Orefield, Tyne to Stainmore)[209].

The surface rock formations in the Derwent Catchment belong to the Carboniferous Limestone Series, consisting mainly of sandstone beds. The sandstone beds occur between the Crag and Upper Felltop Limestone. The formations were laid down in delta channels during the Rogerley and Coalcleugh marine transgressions. All strata in the catchment are overlain by the Millstone Grit series and underlain by the Great Limestone

Most mineralisation occurred in and around the Great Limestone. However, mineral deposition is not confined to strata at this level. Mineralising fluid often forces their ways upward through the hard beds which resulted in deposition at higher stratigraphic levels. The Hunstanworth and Shildon veins which are the most important groups in the Derwent catchment were formed in this way. The formation of ore shoots at high stratigraphic levels has been attributed to the thick sandstone beds in the Derwent catchment[209].

Most of the veins in the Derwent catchment are dominated by fluorspar. Samples taken in 1941 from Red Vein west of Whiteheaps Shaft had 91.2 % fluorspar, 7.8 % silica, 1 % calcium carbonate and 2 – 3 % sulfides[38]. This agrees with the Derwent Mining Company records that galena content was rarely above 6 %[38]. A more recent discovery showed that silver occurred as discrete mineral phase[38] contrary to previous report that it occurred as solid solution in galena[209]. Metalliferous ores such as: chalcopyrite (Cu); sphalerite (Zn), and iron minerals (pyrite, siderite and limonite) are also present in the Derwent catchment[38, 166, 167]. Sphalerite is common mostly in Shildon Burn mines but not in commercial quantity[38].

6.4. Historical mining operations in the Derwent catchment

There were extensive metal mining operations that lasted for more than five centuries in the Derwent catchment[38, 209]. The knowledge of early mine operations in the Derwent catchment is limited to the available records that Shildon Mine existed prior to 1475 [38]. In 1475 Edward IV leased Shildon Mine together with three others outside the region to his bothers. Charles I in December 1624 also leased all the silver within 10 miles of Muggleswick to the Duke of Buckingham for 21 years. Unfortunately, the duke died on the 23rd August 1628. Most likely a small amount of work was done under the duke’s lease.

Lead was the major ore mined in the Derwent catchment until late 19th century, when use was found for fluorspar[38, 209]. The names of mine and smelter companies that operated in the Derwent catchment and Pb production from 1848 to 1882 are listed in

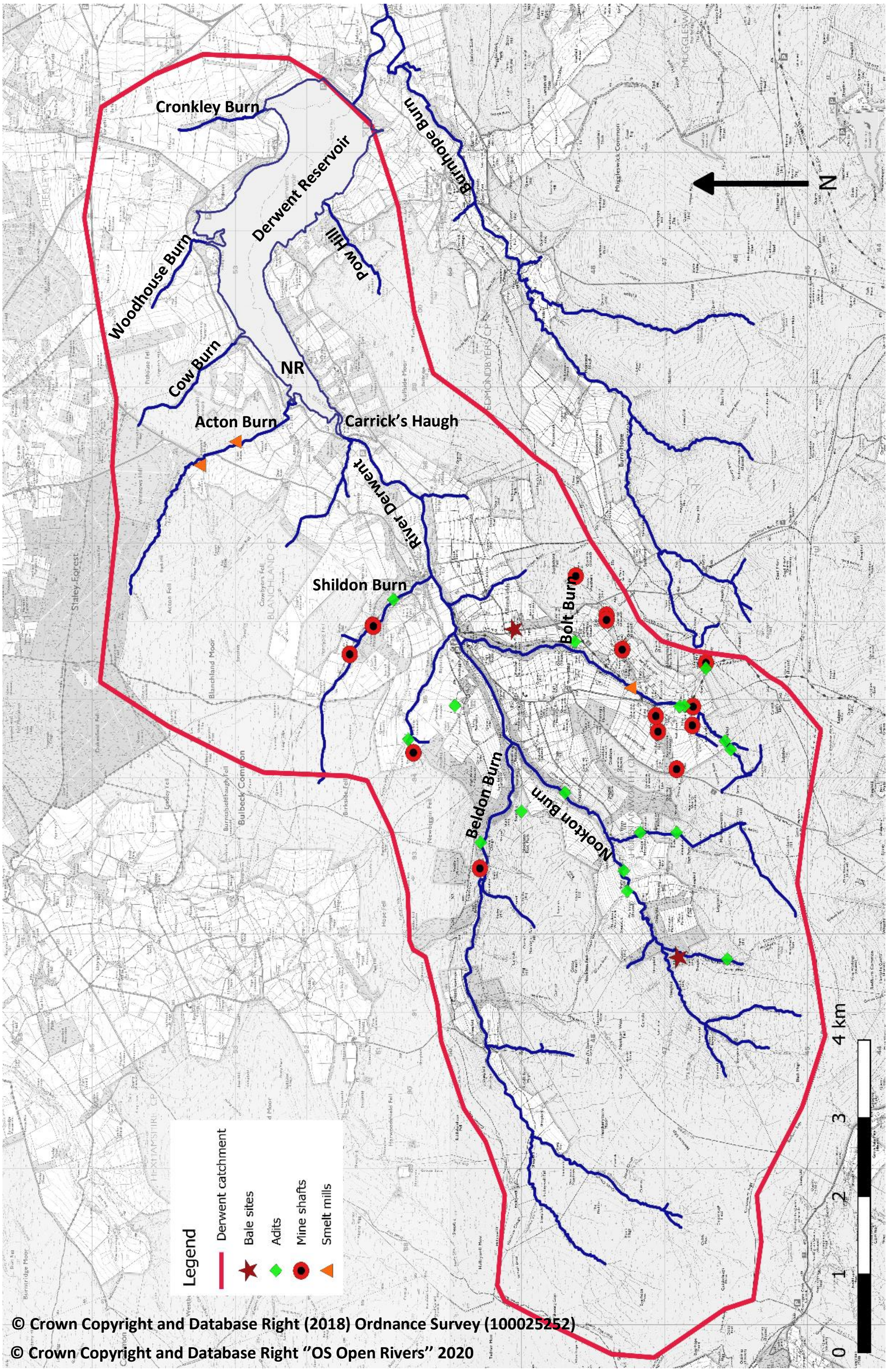
Tables 6.1 and 6.2 respectively[38]. Figure 6.3 shows where old mining operations took place in the Derwent catchment[210]. The British Steel Company also worked the Whiteheaps mine for fluorspar. The total recorded production of fluorspar in the Derwent catchment in 1948 was 15,269 long tons[209]. The closure of Whiteheaps fluorspar mine in 1987 ended the long tradition of mining operations in the Derwent catchment[38].

Table 6.1 List of former mine and smelter companies in the Derwent catchment[38].

Serial No	Companies	Date	Metal mined
1	The London lead company	1708 - 1800	lead
2	Skottowe, Cookson and Company	1745 - 1764	Silver and lead
3	The Erringtons and Partners	1747 - 1789	lead
4	Easterby, hall and company	1800-1812	lead
5	Arkindale and the derwent mines company	1812-1817	lead
6	Messrs Hall, Puller and Company	1817-1835	lead
7	The Derwent mines company	1835-1868	lead
8	Derwent lead mining and smelting company ltd	1876 - 1882	lead
9	Beldon and North Derwent Mining Company	1856-1868	lead
10	New beldon Lead Mining Company Limited	1868-1873	lead

Table 6.2 Lead production by the Derwent mines from 1848 to 1882[38].

Year	Ore tons	Lead tons
1848	1480	1046
1849	1389	1001
1850	1770	1280
1851	1600	1200
1852	1133	875
1853	1330	1000
1854	1000	800
1855	1720	1240
1856	1940	1350
1857	1493	1120
1858	1463	1106
1859	1496	1100
1860	1400	1010
1861	1485	1052
1862	1415	1011
1863	1656	1181
1864	1584	1201
1865	1681	1229
1866	1417	1889
1867	1586	1197
1868	1415	1054
1869	1152	848
1870	890	649
1871	917	656
1872	762	565
1873	490	352
1874	312	231
1875	401	282
1876	328	278
1877	410	275
1878	418	293
1879	386	289
1880	470	282
1881	325	195
1882	55	35



© Crown Copyright and Database Right (2018) Ordnance Survey (100025252)

© Crown Copyright and Database Right "OS Open Rivers" 2020

Figure 6.3 Map showing sites where mining related activities took place in the Derwent Reservoir catchment. NR:nature reserved[210].

At the time of this account, most of the remains of the mining industry have been cleared to restore the land except the vast mine waste site at Whiteheaps around the middle reaches of the draining area of Bolt's Burn. The Whiteheaps mine waste site is 52500 m^2 and is highly prone to erosion (Figure 6.4).

Figure 6.4 Whiteheaps mine waste site in the draining area of Bolt's Burn.

6.5. Previous studies on PTE pollution in the Derwent Reservoir and catchment

Studies conducted by Harding *et al.*[36] (detailed description of the study is in section 1.6.1) and Burrows *et al.*[37] in 1978 and 1983 respectively revealed that the River Derwent and the Derwent reservoir were impacted by PTE due to active and old mining operations in the catchment. The Whiteheaps fluorspar mine[38] was the still operating when Harding *et al.*[36] and Burrows *et al.*[37] conducted their studies. Harding *et al.*[36] referring to an unpublished work concluded that the active fluorspar mine was a significant source of PTE in the River Derwent compared to the old mine workings. The source of Cd and Zn was associated with the dissolved water used to drain the mine workings while particulate Pb was attributed to discharge from the fluorspar processing plant.

Burrows *et al.*[37] determined the concentration of Cd, Pb and Zn in filtered water, sediment and some benthic macroinvertebrates in the River Derwent. Their study stretched just above the confluence of Bolt's Burn with the River Derwent to the Derwent Reservoir. Samples (sediments, water and macroinvertebrates) were collected at Bolt's Burn near the confluence with the River Derwent, at the River Derwent before the confluence of Bolt's Burn and after the confluence downstream, near the reservoir and at the Derwent Reservoir after the river entry. Similar to Harding *et al.*[36], dry weight of the solid samples was digested in boiling nitric acid. The concentration of Cd (0.8 µg g^{-1} – 3.8 µg g^{-1}), Pb (96 µg g^{-1} – 120 µg g^{-1}) and Zn (82 µg g^{-1} – 122 µg g^{-1}) in the sediment before the entry of Bolt's Burn and after the confluence Cd (3.1 µg g^{-1} – 11.4 µg g^{-1}), Pb (1600 µg g^{-1} – 3120 µg g^{-1}) and Zn (550 µg g^{-1} – 2760 µg g^{-1}) showed that Bolt's Burn obviously increases the concentration of PTE in the River Dewent. Higher concentrations of PTE were also determined downstream of the confluence compared with the water before the entry of Bolt's Burn to the River Derwent: upstream (Cd (0.0003 mg L^{-1} – 0.0004 mg L^{-1}), Pb (0.003 mg L^{-1} – 0.011 mg L^{-1}) and Zn (0.016 mg L^{-1} – 0.029 mg L^{-1})) and downstream (Cd (0.0005 mg L^{-1} – 0.0008 mg L^{-1}), Pb (0.010 mg L^{-1} – 0.019 mg L^{-1}) and Zn (0.156 mg L^{-1} – 0.390 mg L^{-1})) of the confluence. Obviously, Bolt's Burn entry to the River Derwent lead to a significant increase in Cd, Pb and Zn concentrations in both water and sediments compared with the analytes' levels upstream of the confluence. A similar order of higher PTE concentrations (Zn > Pb > Cd) were found in the water, sediment and macroinvertebrate downstream compared with upstream of the confluence of Bolt's Burn to the River Derwent[37]. Harding *et al.*[36] also found a similar order of these PTE concentrations (Zn > Pb > Cd) in the water and sediment of the Derwent Reservoir.

7. River sediments

7.1. Introduction

This chapter is on the preliminary assessment of the status of PTE in Derwent Reservoir catchment sediments. This work was conducted to assess the need of progressing with the study on the status of PTE in the Derwent Reservoir based on the analytes' fate in the catchment sediments. Previous studies[36, 37] on the status of PTE in the River Derwent (the main source of water in the Derwent Reservoir) sediment was described in section 6.5. It is also important to note that the speciation study conducted in this work provided the first assessment on the potential mobility and bioavailability of PTE in the River Derwent sediments. The PT concentrations of PTE in rivers sediments impacted by old mining operations in their catchment areas are listed in Table 7.1. The PT concentrations of Cd, Pb and Zn in the River Derwent sediments listed in Table 7.1, exceeded the PEL[63, 68], ISQG-H[67] and Netherlands Intervention values[69] (SQGs value are listed in Table 1.1). This indicated that PTE in the River Derwent sediments were potentially an ecological risk to aquatic organisms.

Table 7.1 Concentration (mg kg^{-1}) of potentially toxic elements in river sediments with historical mining and smelting in the catchment area

Rivers	Potentially toxic elements							Ores mined / smelted in the catchment
	As	Cd	Cu	Mn	Ni	Pb	Zn	
River Twymyn, Wales, UK[106]		1.5 - 44	44 - 2560			593 - 6410	159 - 6960	Pb and Zn
River Wear, UK[211]			10 - 340			20 - 15000	40 - 1500	Baryte, fluorite, Pb and Zn
Mala Panew River, Poland[212]		0.18 - 559	3.97 - 483			36 - 3310	126 - 11200	Pb and Zn
River Somes, Romania[213]		0.8 - 110	12 - 8400			28 - 6800	64 - 19600	Ag, Au, Cu, Pb and Zn
River Tinto, Spain[214]		1 - 23	1800 - 26500			3200 - 16500	600 - 67300	Au, Ag,Cu, Pb and Zn
Lahn River, Germany[215]			18 - 152			19 - 232	63 - 741	Cu, Fe and Pb
Gardon of Ales River, France[192]	13.3 - 51.8	0.20 - 3.11				26.0 - 168	82.2 - 338	Ag, Pb, Sb, Zn
Zijiang River, China[169]	6.90 - 74.3	0.61 - 7.10	18.4 - 59.0	571 - 2107	21.5 - 52.3	12.7 - 104	42.4 - 252	Antimony (Sb)
Przemsza River, Poland[111]		13 - 154				670 - 9450	765 - 28200	Au,Pb and Zn
River Derwent, UK[37]		0.6 - 13.8				96 - 3120	82 - 2760	Pb and fluorite

7.2. Study area

Details of the study area are in chapter six

7.2.1. Aims and objectives

i. To determine the maximum hypothetical potentially mobile PTE in the Derwent catchment sediments using the PT *aqua regia* digestion. The PT concentrations of PTE will be used to assess the impacts of old mining operations on the analytes' levels in the Derwent catchment sediments.
ii. To assess the speciation of PTE in the Derwent Reservoir catchment sediments using the BCR sequential extraction scheme[95]. This will provide useful information on the operational speciation of PTE in the Derwent catchment sediments, and the first assessment on the potential mobility and bioavailability of the analytes in the River Derwent sediments.
iii. To assess the quality of the Derwent Reservoir catchment sediments using SQGs and sediment quality indices. This will provide useful estimates of the impacts of old mining operations on PTE contamination and toxicity to aquatic organisms in the Derwent catchment sediments.

7.3. Experimental

7.3.1. Sampling and sample preparation

The sediment sample collection was part of a previous study conducted by Lord in May 2014[210]. A gold panner's suction pump was used to collect the sediment samples. The sampling points are shown in Figure 7.1. The sampling points cover the inputs and outputs of the Derwent Reservoir, and the River Derwent tributaries. The River Derwent is the main source of water in the Derwent Reservoir. Also, most of the old mining operations were conducted in the draining areas of the tributaries feeding the River Derwent (Figure 7.1). Therefore, for a comprehensive assessment of the impacts of old mining operations on PTE status in the River Derwent, and consequently, the Derwent Reservoir, sediment samples were collected from the river and its tributaries: Carrick's Haugh (D1); Shildon Burn (D2); above Shildon Burn before the confluence with the River Derwent (D3); Bolt's Burn (D5); above Bolt's Burn before the confluence with the River Derwent (D4); upstream of the River

Derwent at Beldon Burn (D7); and Nookton Burn (D6). In order to assess the impacts of the other tributaries feeding the Derwent Reservoir, sediment samples were also collected at the entering points of Cow Burn (DRN4), Acton Burn (DRN3), Wood House Burn (DRN2), Cronkley Burn (DRN1) and Pow Hill (PH) into the Derwent Reservoir. Sediment samples were also collected at the outputs to assess the impact of the contaminants in Derwent Reservoir on the status of PTE downstream from the dam. Sediment samples were collected downstream from the dam at Derwent Reservoir spill-way (DØ), Derwent Bridge (DB), Eddy's Bridge (ED) Burnhope Burn (BB) and Wallish Walls (WW)). The sediment samples were field sieved to < 2 mm and then < 150 µm using stainless steel British Standard sieves. The filtrate was allowed to settle then excess water was decanted and the residual filtrate washed into a high-density polyethylene bottle. On return to the laboratory the sediment was dried overnight at 60 °C and then ground in an agate ball mill.

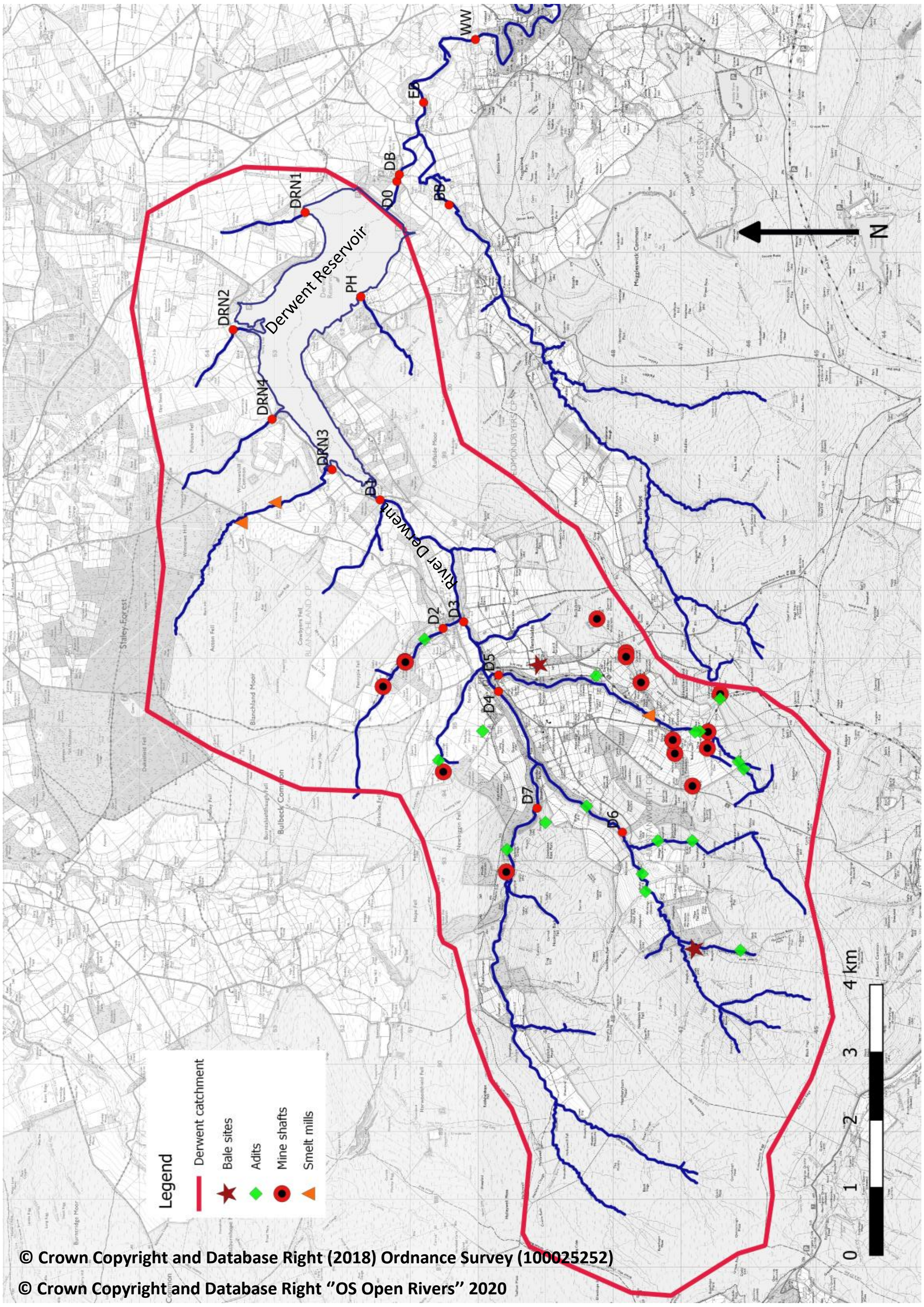


Figure 7.1 Map showing the sampling points in the Derwent Reservoir catchment. The red circles show where sediment samples were collected. Carrick's Haugh (D1), Shildon Burn (D2), above Shildon Burn (D3), above Bolt's Burn (D4), Bolt's Burn (D5), Nookton Burn (D6), Beldon Burn (D7), Cronkley Burn (DRN1), Woodhouse Burn (DRN2), Acton Burn (DRN3), Cow Burn (DRN4), Pow Hill (PH), Burnhope Burn (BB), Derwent Reservoir spill-way (DØ), Derwent Bridge (DB), Eddy's Bridge (ED) and Wallish Walls (WW).

7.3.2. pH measurement and % organic matter

The sediment pH and % organic matter (% OM) were determined as described in sections 3.2 and 3.7 respectively.

7.3.3. Pseudototal digestion

The sediments were digested using microwave assisted *aqua regia* digestion described in section 3.8. The digests were analysed for the pseudototal concentrations of PTE in the sediments using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

7.3.4. BCR sequential extraction

The different operationally defined fractions of PTE in three sediments of the River Derwent (D4, D5 and D1), a stream feeding directly into the Derwent Reservoir (DRN3) and downstream from the Derwent Reservoir (DØ) were extracted using the BCR sequential extraction procedure as described in section 3.9. The extracts were analysed for PTE concentrations using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

7.4. Results and discussion

7.4.1. Characterisation of sediment

The pH values and % organic matter content (% OM) of the sediment samples collected from the inputs to, and downstream of, the Derwent Reservoir are listed in Table 7.2. The % OM of the input's sediments ranged from 3.64% to 13.6% and was low compared to 5.93 % to 17.0 % downstream from the reservoir. The River Derwent samples (D1 – D7) had the lowest % OM, the other streams feeding the Derwent Reservoir (DRN1 – DRN4) had higher % OM, but the highest values were at DØ and DB. The richer a sediment is in % OM the more acidic it should be. Generally, the inputs had the highest pH values, while the outputs sediments had the lowest pH values as expected. Generally, the sediments pH was approximately neutral, indicating that the sections of the streams studied were not recently exposed to any acid input as suggested by previous studies[173, 216].

Table 7.2 The pH values and % organic matter content of the sediment samples collected from upstream and downstream from the Derwent Reservoir

Sampling site	pH	% organic Matter
D7	7.08	3.64
D6	7.05	5.58
D4	6.64	4.19
D5	7.40	3.74
D3	7.10	4.74
D2	7.04	5.19
D1	7.15	4.97
DRN4	6.71	8.62
DRN3	7.03	8.41
DRN2	7.24	12.4
DRN1	7.25	9.23
PH	5.58	13.6
DØ	6.22	17.0
DB	6.10	16.2
BB	7.54	6.43
ED	7.75	5.93
WW	7.47	6.88

7.4.2. Pseudototal concentration determination and sequential extraction of PTE in sediments

7.4.2.1. Limits of detection

Instrumental limits of detection (LOD_{inst}) and procedural limits of detection (LOD_{pro}) for PT PTE concentration determined and the BCR sequential extraction procedure steps using the ICP-MS are listed in Table 7.3. The different LOD_{inst} and LOD_{pro} reflected the relative sensitivity of the instrument to the different PTE measured. The LOD was always lower than the concentrations of the PTE determined.

Table 7.3 Instrumental limits of detection (µg L^{-1}) and procedural limits of detection (mg kg^{-1}) for pseudototal PTE determination and the BCR sequential extraction step using the ICP-MS.

PTE	Exchangeable fraction		Reducible fraction		Oxidisable fraction		Residual fraction/pseudototal	
	LOD$_{inst}$ (µg L^{-1})	LOD$_{pro}$ (mg kg^{-1})	LOD$_{inst}$ (µg L^{-1})	LOD$_{pro}$ (mg kg^{-1})	LOD$_{inst}$ (µg L^{-1})	LOD$_{pro}$ (mg kg^{-1})	7LOD$_{inst}$ (µg L^{-1})	LOD$_{pro}$ (mg kg^{-1})
As	0.0167	0.000668	0.422	0.0169	0.678	0.0337	0.0183	0.0183
Cd	0.0143	0.000572	0.00347	0.000139	0.00903	0.000452	0.00252	0.00252
Cu	0.123	0.00492	0.0320	0.00128	0.0840	0.00420	0.623	0.623
Fe	1.07	0.0428	1.35	0.0540	13.1	0.655	0.245	0.245
Mn	0.0190	0.000760	0.0358	0.00143	0.133	6.65	0.0246	0.0246
Ni	0.0158	0.000632	0.0372	0.00149	0.0251	0.00126	0.00621	0.00621
Pb	0.0130	0.000520	0.0690	0.00276	0.0577	0.00289	0.0124	0.0124
Zn	1.42	0.0568	0.415	00166	0.313	0.0157	0.0690	0.0690

7.4.2.2. Quality control for pseudototal analysis

A secondary reference material, Glasgow soil (GLA-URM)[152, 153] was analysed along with the sediment samples in order to assess the analytical performance during the PT PTE concentration determination in this work. All analyses were performed in triplicate. A blank solution was also analysed at regular intervals during the ICP-MS analysis for quality check. The PT PTE concentrations measured, standard deviations, % relative standard deviation (% RSD) and % recoveries are listed in Table 7.4. The obtained PT PTE concentrations were within the standard deviation of the indicative values. The % RSD were < 11 %, except for As (13.8 %), Fe (13.6 %), Mn (11.6 %) and Ni (13.4 %). The % recovery of 82 % to 106 % for all the PTE measured was satisfactory.

Table 7.4. Pseudototal concentration (mg kg^{-1}, n = 3), standard deviation (SD, ± mg kg^{-1}), % relative standard deviation (% RSD) and % recovery of the potentially toxic elements in the dry weight of GLA-URM.

PTE	GLA-URM [152, 153]						% Recovery
	Indicative values			obtained values			
	mg kg^{-1}	± mg kg^{-1}	% RSD	mg kg^{-1}	± mg kg^{-1}	% RSD	
As	17.7	4.0	22.6	18.8	2.6	13.8	106
Cd	0.646	0.184	28.5	0.528	0.04	7.58	82
Cu	111	5.0	4.5	104	11	10.6	94
Fe	30600	1200	3.92	26400	3580	13.6	86
Mn	442	18	4.07	423	49	11.6	96
Ni	48.8	7.0	14.3	49.9	6.7	13.4	102
Pb	389	25	6.43	383	40	10.4	99
Zn	177	11	6.21	165	17	10.3	93

7.4.2.3. Pseudototal PTE concentrations in Derwent Reservoir catchment sediments

The PT concentration of PTE in sediments of the inputs to, and outputs of, the Derwent Reservoir are represented in Figure 7.2 to 7.9 (detailed data are listed in Table B.1 in the appendix) with the draft England and Wales SQGs[63] superimposed as horizontal lines. The green and red horizontal lines drawn across the figures represent TEL and PEL values, respectively. Sediment quality guideline values for Fe and Mn are rare. General discussion on the PT concentrations of PTE in the sediment samples is at the end of this section.

Arsenic

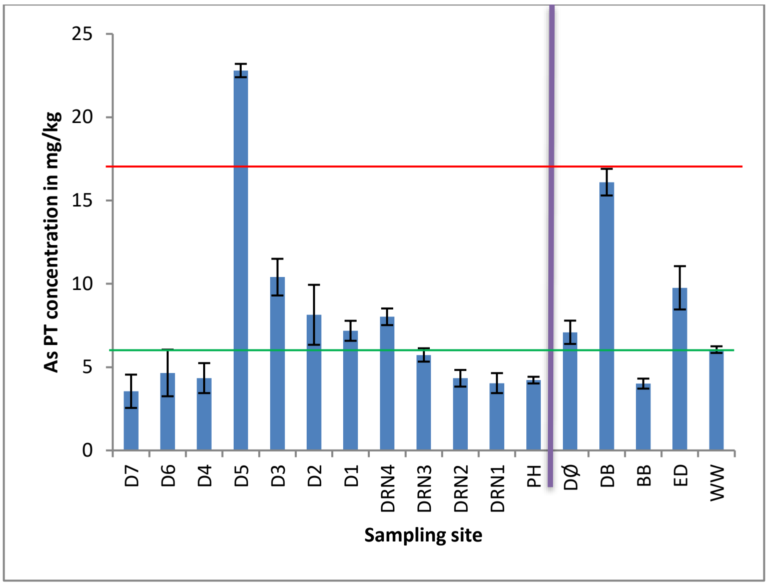


Figure 7.2 Arsenic pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal line (green: TEL; red: PEL). The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

The PT concentrations of As (3.55 – 22.8 mg kg^{-1}) determined in the Derwent catchment sediments (Figure 7.2 and Table B.1 in the appendix) were comparable with the amount of the analyte found in the sediments of the Gardon of Ales River, France[192] and Zijiang River, China[169]. Both rivers were impacted by old mining operations in their draining areas[169, 192]. The PT concentration of As determined in D7, D6, D4, DRN3, DRN2, DRN1, PH and BB were below the TEL value, implying rare ecological risk to aquatic organisms[63, 68]. The PT concentrations of As in D3, D2, D1, DRN4, DB, DØ, ED and WW were between the TEL and < PEL values, implying occasional ecological risk to aquatic organisms[63, 68]. The PT concentration of As in D5 was higher than the PEL value, indicating the likelihood of frequent ecological risk to aquatic organisms[63, 68].

Cadmium

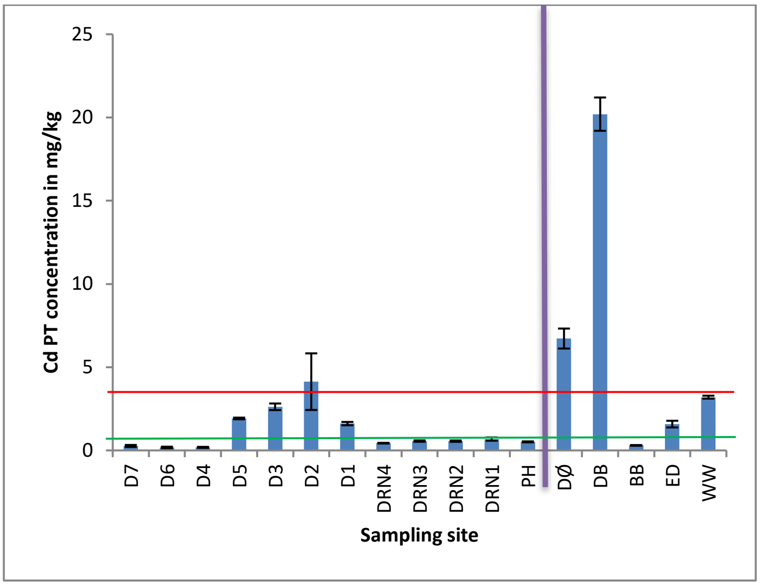


Figure 7.3 Cadmium pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal lines (green: TEL; red: PEL). The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

Generally, the PT concentrations of Cd (0.174 – 20.0 mg kg^{-1}) determined in the Derwent catchment sediments (Figure 7.3 and Table B.1 in the appendix) were comparable with the analyte levels in other rivers sediments with old mining operations in their draining areas. Examples of such rivers listed in Table 7.1 are the River Tees, UK[217], River Tinto, Spain[214], Gardon of Ales River, France[192] and Zijiang River, China[169]. Also, the PT concentrations of Cd (0.174 – 4.13 mg kg^{-1}) determined in the River Derwent sediment were comparable with 0.6 – 13.8 mg kg^{-1} reported by Burrows *et al.*[37] in 1983 in the same river sediment. The PT concentration of Cd determined in D7, D6, D4, DRN4, DRN3, DRN2, PH and BB were below the TEL value[63, 68]. The PT concentrations of Cd in D5, D3, D1, DRN1, ED and WW were between the TEL and < PEL values[63, 68]. The PT concentrations of Cd in D2, DB and DØ were above the PEL value[63, 68].

Copper

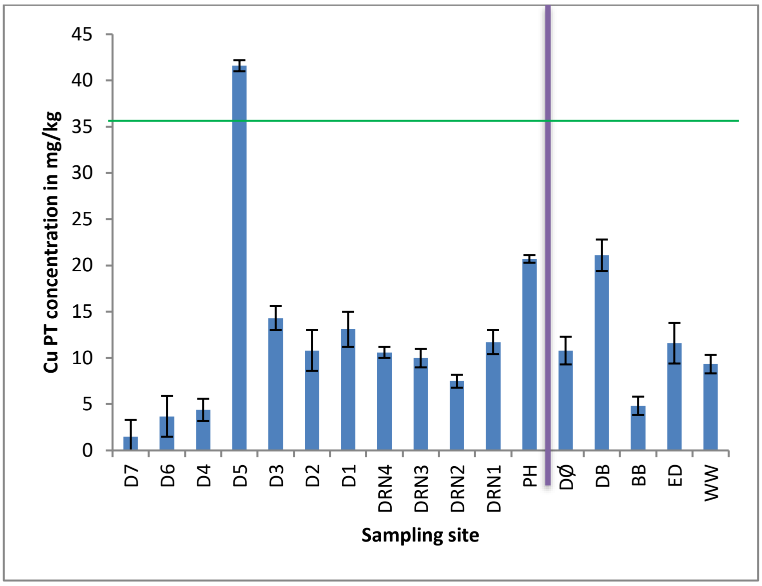


Figure 7.4 Copper pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as green horizontal line (TEL). The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

The PT concentrations of Cu (1.49 – 41.6 mg kg^{-1}) determined in this work (Figure 7.4 and Table B.1 in the appendix) were low compared with similar studies listed in Table 7.1; this may be attributed to the low levels of the analyte in the ores. The PT concentrations of Cu in most of the sediment samples were below the TEL value, except in D5 where it was between the TEL and < PEL values[63, 68].

Iron

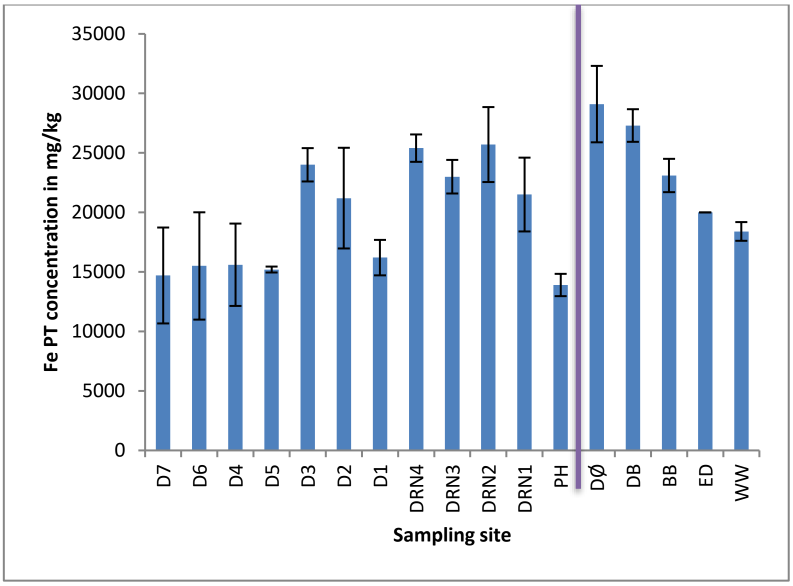


Figure 7.5 Iron pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments. The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

The PT concentrations of Fe (13900 – 29100 mg kg^{-1}) determined in the Derwent catchment sediments (Figure 7.5 and Table B.1 in the appendix) were by far higher than for any other PTE, and this was as a result of its natural abundance[44]. Generally, there are no SQGs for Fe because of its natural abundance and rare toxicity[57]. There are no SQGs for Fe in England and Wales[63], Australia[67], Canada[68] or the Netherlands[63].

Manganese

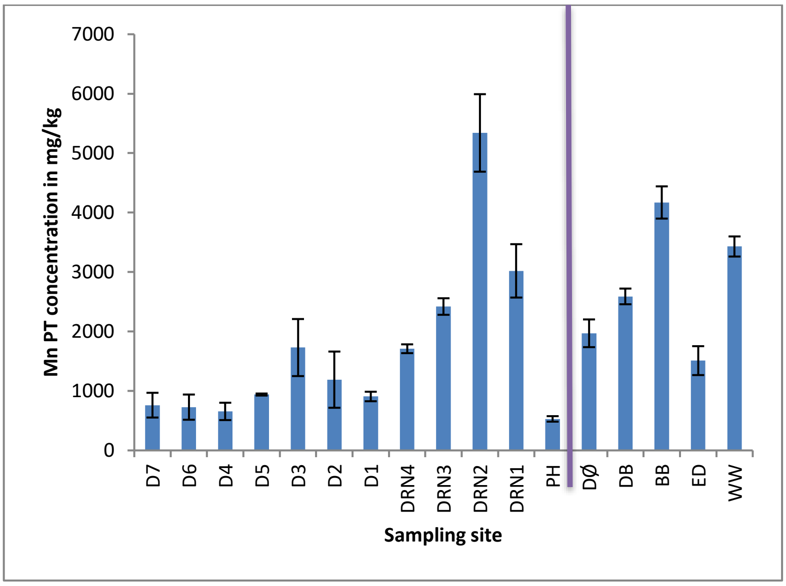


Figure 7.6 Manganese pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments. The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

The PT concentrations of Mn (530 – 4170 mg kg^{-1}) in the Derwent catchment sediments (Figure 7.6 and Table B.1 in the appendix) were the next highest after Fe, and were comparable with the amount of the analyte determined in the Zijiang River sediment in China[169] (Table 7.1). Manganese SQGs are also rare because of its natural abundance. For instance, there are no SQGs for Mn in England and Wales[63], Australia[67], Canada[68] or the Netherlands[63].

Nickel

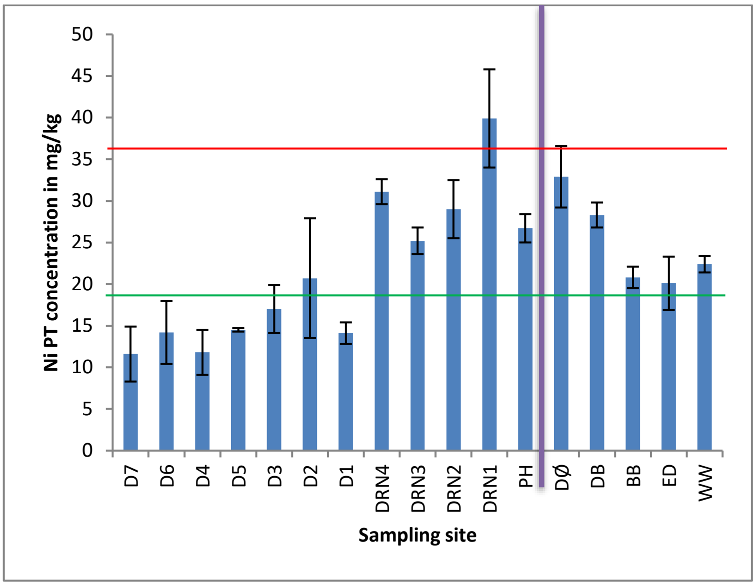


Figure 7.7 Nickel pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal line (green: TEL; red: PEL). The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

Generally, the PT concentrations of Ni (11.6 – 39.9 mg kg^{-1}) determined in the Derwent catchment sediments (Figure 7.7 and Table B. 1 in the appendix) were comparable with the amount of the analyte in a similar study conducted by Zhang *et al*[169]. The PT concentration of Ni in DRN1 was above the PEL value[63, 68]. Nickel PT concentrations in D7, D6, D4, D5, D3 and D1 were below the TEL value[63, 68]. The PT concentrations of Ni in D2, DRN4, DRN3, DRN2, PH, DB, DØ, BB, ED and WW were between the TEL and < PEL values[63, 68].

Lead

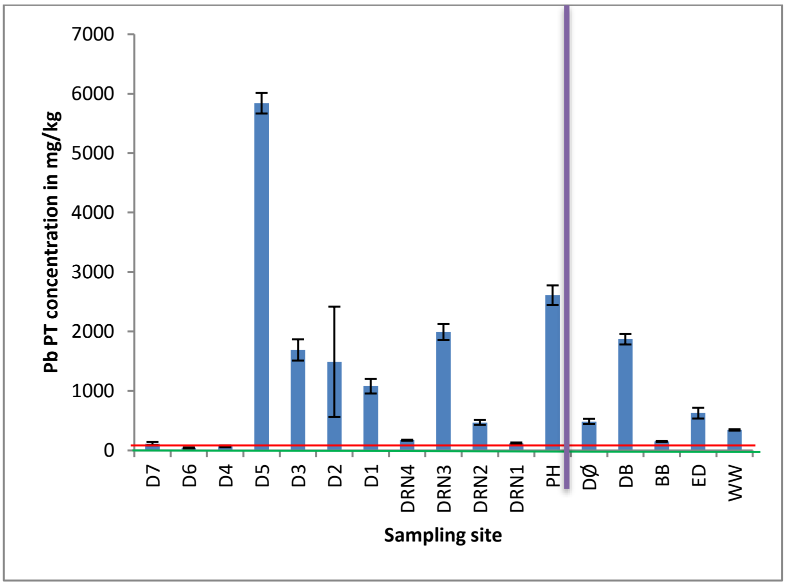


Figure 7.8 Lead pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal line (green: TEL; red: PEL). The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

The PT concentration of Pb (41.9 – 5840 mg kg^{-1}) determined in the Derwent catchment sediments (Figure 7.8 and Table B.1 in the appendix) were comparable with the amount of the analyte (96 – 3120 mg $kg^{-1)}$ reported by Burrows *et al.*[37] in 1983 in the River Derwent sediment. The PT concentration of Pb determined in the sediment samples were also comparable with the amount of the analyte in other river sediments (the River Twymyn, Wales, UK[106], the River Somes, Romania[213], the River Tinto, Spain[214] and Lahn River, Germany[215]) with old mining operations in their draining areas. Generally, the PT concentrations of Pb in the sediment samples were far above the PEL value, except D6 and D4 where concentrations were between the TEL and < PEL values[63, 68].

Zinc

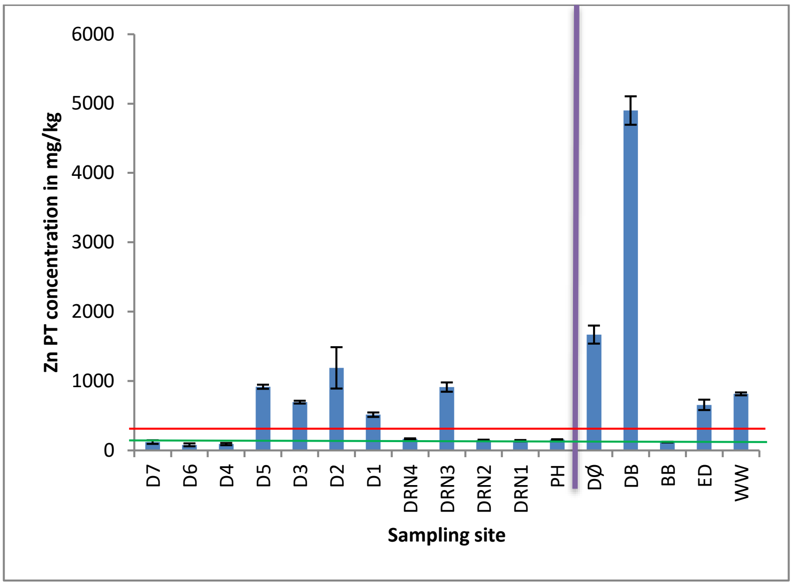


Figure 7.9 Zinc pseudototal concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal line (green: TEL; red: PEL). The purple vertical line demarcates the inputs from outputs of the Derwent Reservoir.

The PT concentrations of Zn (80.7 – 1190 mg kg^{-1}) determined in the River Derwent sediment (Figure 7.9 and Table B.1 in the appendix) were comparable with 82 – 2760 mg kg^{-1} reported by Burrows *et al.*[37] in 1983 in the same river sediment. The PT concentrations of Zn determined the Derwent catchment sediments were comparable with the amount of the analyte in rivers (e.g. the River Twymyn, Wales, UK[106], Mala Panew River, Poland[212], Lahn River, Germany[215] and Zijiang River, China[169]) sediments in legacy mining areas. The PT concentrations of Zn determined in D5, D3, D2, D1, DRN3, DB, DØ, ED and WW were above the PEL value[63, 68]. The PT concentrations of Zn in DRN4, DRN2, DRN1 and PH were between the TEL and < PEL values, and in D7, D6, D4 and BB were below the TEL value[63, 68].

General discussion on pseudototal concentrations

Considerable amount of soil contaminated by old mining operations usually end up as sediment in adjacent rivers[46, 218]. Therefore, the baseline concentration of PTE in soil may be used to assess the impacts of old mining operations in river sediments. The PT concentrations of PTE in the Derwent Catchment sediments were compared with the baseline values in the UK rural soil, except Fe which was compared with the background concentration in global soil. Iron was compared with the background concentration in global soil because baseline value for UK rural soil is rare. The PT concentrations of As (3.55 – 22.8 mg kg^{-1}), Cu (1.49 – 41.6 mg kg^{-1}), Mn (530 – 4170 mg kg^{-1}) and Ni (11.6 – 39.9 mg kg^{-1}) determined in the Derwent catchment sediments were comparable with the baseline concentrations 0.5 – 143 mg kg^{-1}, 2.27 – 96.7 mg kg^{-1} , 10.0 – 12200 mg kg^{-1} and 1.16 – 216 mg kg^{-1} in the UK rural soil[47], respectively, while the PT Fe (13900 – 29100 mg kg^{-1}) was comparable with background concentration (7000 – 42000 mg kg^{-1}) in global soil[44]. This suggested that old mining operations had limited impacts on the status of As, Cu, Fe, Mn and Ni in the Derwent catchment. The PT concentrations of Cd, Pb and Zn in D5 (Cd:1.92 mg kg^{-1}, Pb: 5840 mg kg^{-1} and Zn: 918 mg kg^{-1}), D3 (Cd: 2.62 mg kg^{-1}, Pb: 1690 mg kg^{-1} and Zn: 696 mg kg^{-1}), D2 (Cd: 4.13 mg kg^{-1}, Pb: 1490 mg kg^{-1} and Zn: 1190 mg kg $^{-1}$), DB (Cd: 20.2 mg kg^{-1}, Pb: 1870 mg kg^{-1} and Zn: 4900 mg kg^{-1}), DRN3 (Pb: 1990 mg kg^{-1} and Zn: 913 mg kg^{-1}), PH (Pb: 2610 mg kg^{-1}), DØ (Cd: 10.8 mg kg^{-1} and Zn:1670 mg kg^{-1}), ED (Zn: 657 mg kg^{-1}) and WW (Cd: 3.20 mg kg^{-1} and Zn: 815 mg kg^{-1}) were higher than the baselines values in UK rural soil. The baseline concentrations of Cd, Pb and Zn in UK rural soil are 0.10 – 1.80 mg kg^{-1}, 2.60 – 713 mg kg^{-1} and 2.63 – 442 mg kg^{-1} [47], respectively. This indicated that historical mining and smelting had significant impacts on the status of Cd, Pb and Zn in the Derwent catchment.

The PT concentrations of As, Cd, Cu, Pb and Zn in DB were considerably higher than in DØ, indicating that there were inputs of these PTE in DB different from within the Derwent Reservoir. Sediment DØ was the closest to the dam downstream from the reservoir. The remarkably high PT concentration of Cd and Zn in DB compared with in any other sediment samples was of notable interest, because of their chemical similarities and natural association in Zn ores[44, 52]. Arsenic and Cu also occur as impurities in Pb and Zn ores[44, 53]. Consequently, the comparatively high PT concentrations of As, Cd, Cu, Pb and Zn in DB may be attributed to historical spillage of transported metal ores from the bridge to the river, or the PTE accumulation/mineralisation in this area. However, As, Cu and Pb PT concentrations in D5 were higher than in DB. The PT concentration of Pb in D5, DRN3 and PH were also higher than in DB, this may be attributed to old mining operations in their draining areas. This was consistent with the relics of old mining operations (shafts, adits, bale sites and smelt mills) found on the draining areas of D5 and DRN3 as shown in Figure 7.1.

The PT concentrations of As, Cd, Cu, Pb and Zn determined in D5 were remarkably high compared with the amount determined in D4, D6 and D7 above the confluence of Bolt's Burn to the River Derwent. Obviously, the high PT concentrations of As, Cd, Cu, Pb and Zn in D5 increased the concentrations of these PTE in the sediment downstream of the confluence of Bolt's Burn to the River Derwent compared to upstream. This indicated that Bolt's Burn was the main source of As, Cd, Cu, Pb and Zn entering the Derwent Reservoir through the River Derwent. These findings were consistent with the report of Burrows *et al*[37] in 1983 (this study was described in detail in section 6.5), which also identified Bolt's Burn as main source of Cd, Pb and Zn in the River Derwent downstream of the confluence. This suggested that Bolt's Burn remains a significant source of Cd, Pb and Zn in the River Derwent.

7.4.2.4. Quality control for sequential extraction

Quality control of the BCR sequential extraction procedure for the fractionation of the PTE in the sediment samples was carried out by determining the % recovery with respect to the PT PTE concentration. Officially the residual fraction is not part of the BCR sequential extraction, but it was recommended as a means for quality control[95]. Palma *et al.*[32] also used the internal check of the results of the BCR sequential extraction scheme as a means of quality control, using % recovery of the sum of the four steps with respect to the PT PTE concentration in sediments. The PT PTE concentrations, % relative standard deviations and % recoveries are listed in Table B. 2 to Table B. 9 in the appendix. The mean % recovery of each PTE was As (73 %), Cd (131 %), Cu (161 %), Fe (106 %), Mn (140 %), Ni (128 %), Pb (124 %) and Zn (119 %). A blank solution was also analysed at regular interval during the ICP-MS analysis for quality check.

7.4.2.5. Fractionation of PTE in the Derwent Reservoir catchment sediments

Concentrations of As, Cd, Cu, Fe, Mn, Ni, Pb and Zn in the operationally defined fractions of five of the sediment samples were determined using the BCR sequential extraction procedure. Three of the samples were from the River Derwent, which is the main source of water in the Derwent Reservoir. Acton Burn sediment sample was also selected, because it was an additional minor source of water inflow to the Derwent Reservoir with evidence of old mining operations in the draining area (Figure 7.1). The Derwent Reservoir spill-way sediment was also selected, because it was the most appropriate of the samples for the assessment of the Derwent Reservoir impacts on the PTE status downstream from the dam. The five sediment samples were as follows:

D5 – Bolt's Burn, which has been shown to be a major source of PTE input to the River Derwent
D4 – upstream of Bolt Burn
D1 – Carrick's Haugh, just upstream of the point where the River Derwent enters the Derwent Reservoir
DRN 3 – Acton Burn, which is also a potential contributor of PTE to the Derwent Reservoir
DØ – Derwent Reservoir spill-way, just downstream from the reservoir

The concentration of PTE in mg kg^{-1} and % obtained in each step of the BCR sequential extraction scheme are represented in Figure 7.10 to 7.17, and the data are listed in Table B.2 to Table B.9 in the appendix. Following the recommendation of ANZECC[67], the sum of the three most labile fractions of the BCR sequential extraction scheme were compared with the SQGs, to assess the ecological risk of the PTE to aquatic organisms. General discussion on the sequential extraction of PTE in the sediment samples is at the end of this section.

Arsenic

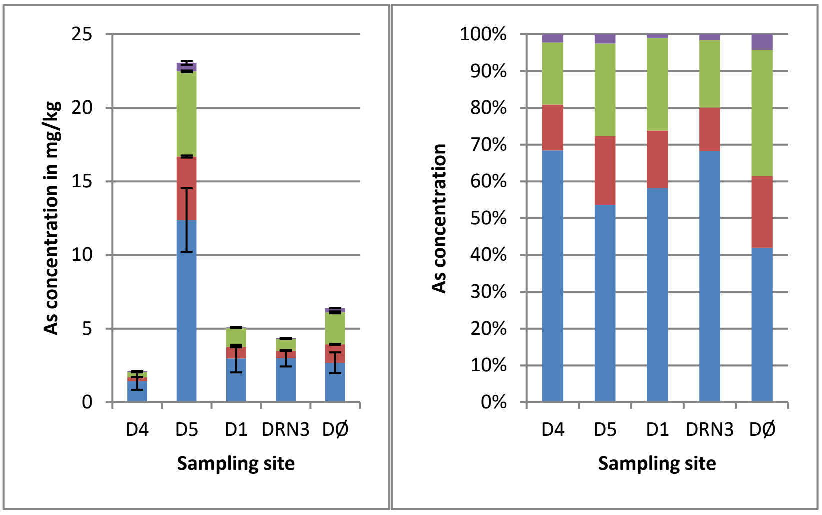


Figure 7.10 The distribution of As (mg kg^{-1} and % concentration) in the operationally defined fractions of Derwent Reservoir catchment sediments. The error bar represents the mean ± standard deviation and n = 3.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Arsenic (Figure 7.10 and Table B.2 in the appendix) was found mainly in the residual (42 – 63 %), followed by the reducible (17 – 34 %), oxidisable (17 – 27 %) and exchangeable (0.9 – 4 %) fractions. The high proportion of As in the residual fraction indicated that the analyte was strongly bound to the mineral lattice, while the considerable amount in the reducible fraction was a reflection of its strong affinity for Fe/Mn(hydr)oxides[44, 73]. The operational speciation of As in this work was comparable with the analyte partitioning in the Gardon of Ales River sediments[192]. The Gardon of Ales River, France, was impacted by old mining operations in the draining area[192]. The concentration of As in the labile fractions (exchangeable, reducible and oxidisable fractions) of D4 (0.66 mg kg^{-1}), D1 (2.13 mg kg^{-1}), DRN3 (1.39 mg kg^{-1}) and DØ (3.70 mg kg^{-1}) were below the TEL value (5.9 mg kg^{-1}), indicating rare ecological risk to aquatic organisms[63, 68]. The concentration of As found in the labile fractions of D5 (20.7 mg kg^{-1}) was higher than the PEL value (17.0 mg kg^{-1}), indicating likelihood of frequent ecological risk to aquatic organisms[63, 68].

Cadmium

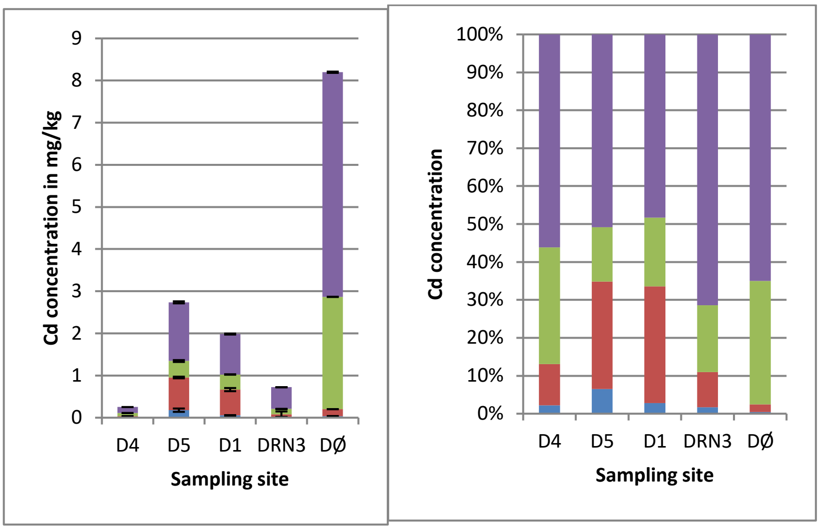


Figure 7.11 The distribution of Cd (mg kg^{-1} and % concentration) in the operationally defined fractions of sediments collected from the Derwent Reservoir catchment using the BCR sequential extraction procedure (error bar represent the mean ± standard deviation and n = 3).

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Cadmium (Figure 7.11 and Table B.3 in the appendix) was found mainly in the exchangeable fraction (48 – 71 %), and this is of considerable concern because of the high toxicity of the analyte. There was also a considerable amount of Cd in the reducible (14 – 33 %) and oxidisable (2 – 31 %) fractions, while the residual Cd was 0.43 – 6.4 %. The distribution of Cd in the operationally defined fractions of the sediments was comparable with similar studies in rivers (the River Twymyn, Wales, UK[106], the Mala Panew River, Poland[212] and the Gardon of Ales River, France[192]) with historical mining and smelting in the catchment areas. The concentration of Cd in the labile fractions of D4 (0.25 mg kg^{-1}) was below TEL value (0.6 mg kg^{-1})[63, 68], while D5 (2.56 mg kg^{-1}), D1 (1.93 mg kg^{-1}) and DRN3 (0.72 mg kg^{-1}) were between the TEL and PEL (3.50 mg kg^{-1}) values, indicating occasional ecological risk to aquatic organisms[63, 68]. The concentration of Cd in the labile fractions of DØ (8.16 mg kg^{-1}) was higher than the PEL value (3.5 mg kg^{-1})[63, 68].

Copper

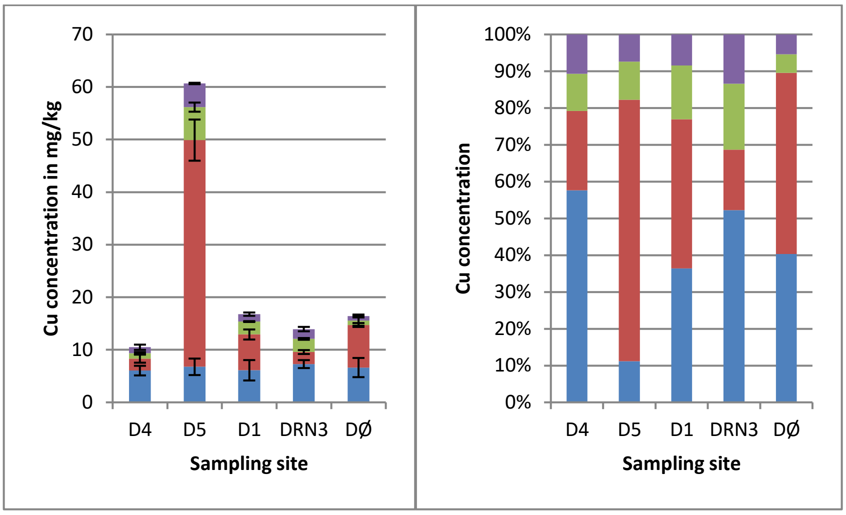


Figure 7.12 The distribution of Cu (mg kg^{-1} and % concentration) in the operationally defined fractions of Derwent Reservoir catchment sediments. The error bar represents the mean ± standard deviation and n = 3.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Copper (Figure 7.12 and Table B.4 in the appendix) was found mainly in the oxidisable fraction (16 – 71 %) followed by the residual fraction (11 - 58 %), reflecting its strong affinity for organic matter[32, 44, 73, 219, 220]. The exchangeable and reducible Cu were (6 – 14 %) and (5 – 18 %), respectively. Similar studies in rivers sediments (the River Twymyn, Wales, UK[106], the Mala Panew River, Poland[212] and the Gardon of Ales River, France[192]) in legacy mining areas also reported considerable amount of Cu in the oxidisable fraction. The concentration of Cu in the labile fractions of D4 (4.45 mg kg^{-1}), D1 (10.7 mg kg^{-1}), DRN3 (6.66 mg kg^{-1}) and DØ (9.81 mg kg^{-1}) were below the TEL value (35.7 mg kg^{-1})[63, 68], except D5 (54.0 mg kg^{-1}). The concentration of Cu in the labile fraction of D5 was between the TEL (35.7 mg kg^{-1}) and PEL (197 mg kg^{-1}) values[63, 68].

Iron

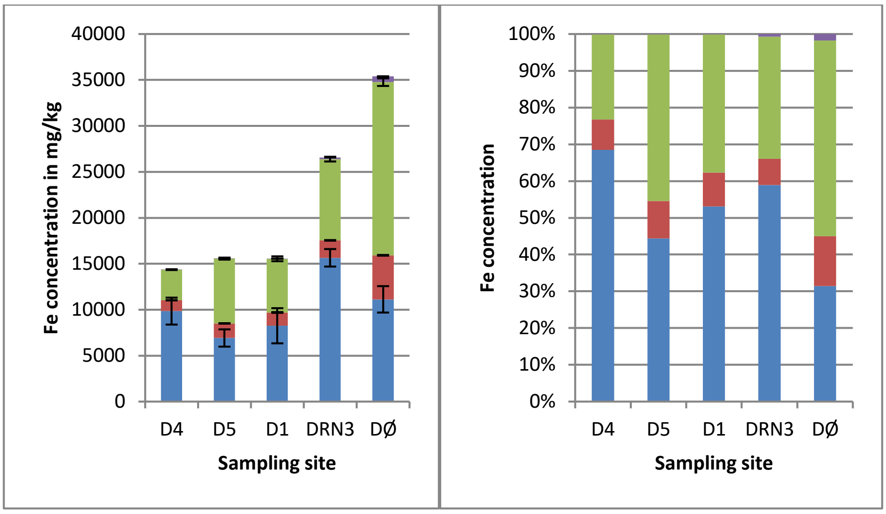


Figure 7.13 The distribution of Fe (mg kg^{-1} and % concentration) in the operationally defined fractions of Derwent Reservoir catchment sediments. The error bar represents the mean ± standard deviation and n = 3.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Iron (Figure 7.13 and Table B.5 in the appendix) was mainly found in the reducible (23 – 53 %) and residual (31 – 69 %) fractions of all the sediment samples. The % distributions of Fe in the exchangeable and oxidisable fractions were approximately 0.13 – 2 % and 7 – 16 % respectively. Iron was also found mainly in the residual fraction of the Sonora River sediments. The Sonora River is in Mexico, and the water body was impacted by historical mining and smelting in the catchment. The considerable amount of Fe in the residual fraction indicated that the analyte was mainly associated with the mineral lattice. Overall, Fe occurred mainly in the reducible and residual fractions, this taken together with the PT concentration in all the samples, indicated that the speciation of the analyte was predominantly associated with its natural forms.

Manganese

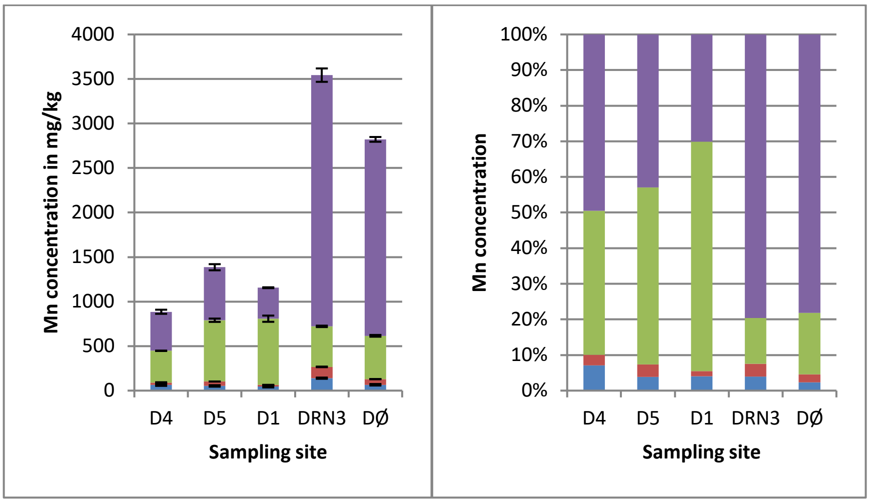


Figure 7.14 The distribution of Mn (mg kg^{-1} and % concentration) in the operationally defined fractions of Derwent Reservoir catchment sediments. The error bar represents the mean ± standard deviation and n = 3).

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Manganese (Figure 7.14 and Table B.6 in the appendix) was found mainly in the exchangeable (30 – 80 %) followed by reducible (13 – 64 %) fractions. The partitioning of Mn in the Derwent catchment sediments was consistent with the main forms of the analyte in soil. Manganese occurs mainly in the water soluble and exchangeable forms and, as insoluble Mn oxides in soil[44]. The oxidisable and residual Mn were approximately 2 – 4 % and 2 – 7 % respectively.

Nickel

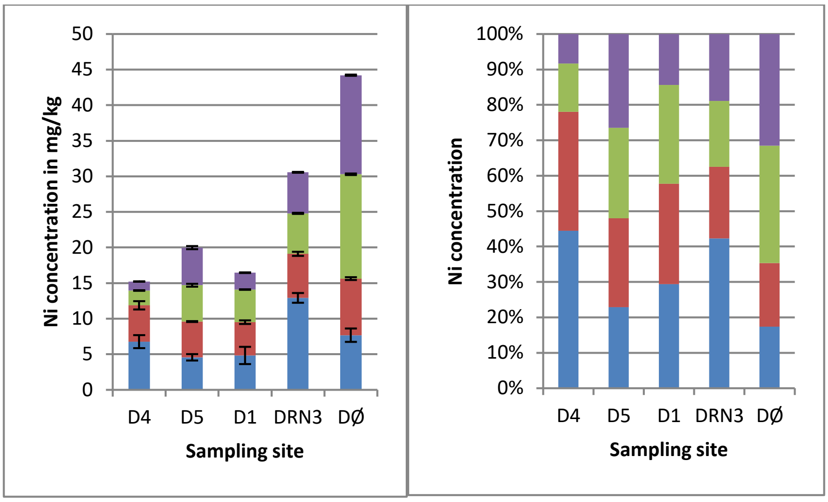


Figure 7.15 The distribution of Ni (mg kg^{-1} and % concentration) in the operationally defined fractions of Derwent Reservoir catchment sediments. The error bar represents the mean ± standard deviation and n = 3.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The distribution of Ni in the operationally defined fractions of the sediment samples (Figure 7.15 and Table B.7 in the appendix) were exchangeable (8 – 32 %), reducible (14 – 33 %), oxidisable (18 – 34 %) and residual (17 – 45 %) fractions. The partitioning of Ni in the sediment samples somewhat followed similar trend with the operational speciation of Fe, probably reflecting the association between these PTE[44]. The concentration of Ni in the labile fractions of the D4 (8.44 mg kg^{-1}), D5 (15.4 mg kg^{-1}), D1(11.6 mg kg^{-1}) and DRN3 (17.7 mg kg^{-1}) were below the TEL value (18 mg kg^{-1}), while at output DØ (36.5 mg kg^{-1}) was above PEL value (35.9 mg kg^{-1})[63, 68].

Lead

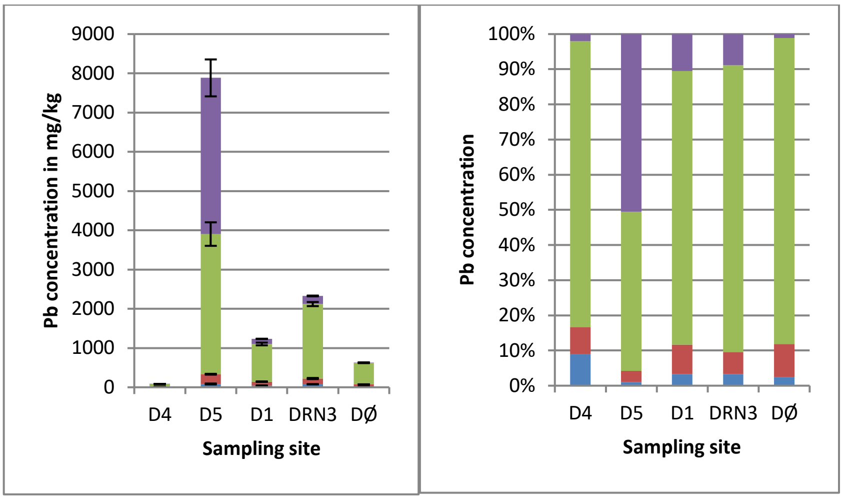


Figure 7.16 The distribution of Pb (mg kg^{-1} and % concentration) in the operationally defined fractions of Derwent Reservoir catchment sediments. The error bar represents the mean ± standard deviation and n = 3.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The distribution of Pb in the operationally defined fractions of the Derwent catchment sediments (Figure 7.16 and Table B.8 in the appendix) were exchangeable Pb (1 – 51 %), reducible (45 – 87 %), oxidisable (3 – 9 %) and reducible (1 – 9 %). The high proportion of Pb in the reducible fraction can be attributed to the strong affinity of the analyte for Fe/Mn (hydr)oxides[44, 73]. Previous studies in rivers sediments (the River Twymyn, Wales, UK[106], the Mala Panew River, Poland[212] and the Gardon of Ales River, France[192]) impacted by old mining operations also reported comparable proportions of Pb in the reducible fraction. The amount of Pb found in the labile fractions of D5 (7800 mg kg^{-1}), D1 (1190 mg kg^{-1}), DRN3 (2250 mg kg^{-1}) and DØ (613 mg kg^{-1}) were far above the PEL value (91.3 mg kg^{-1})[63, 68]. The concentration of Pb in the labile fractions of D4 was between the TEL (35.0 mg kg^{-1}) and PEL values.

Zinc

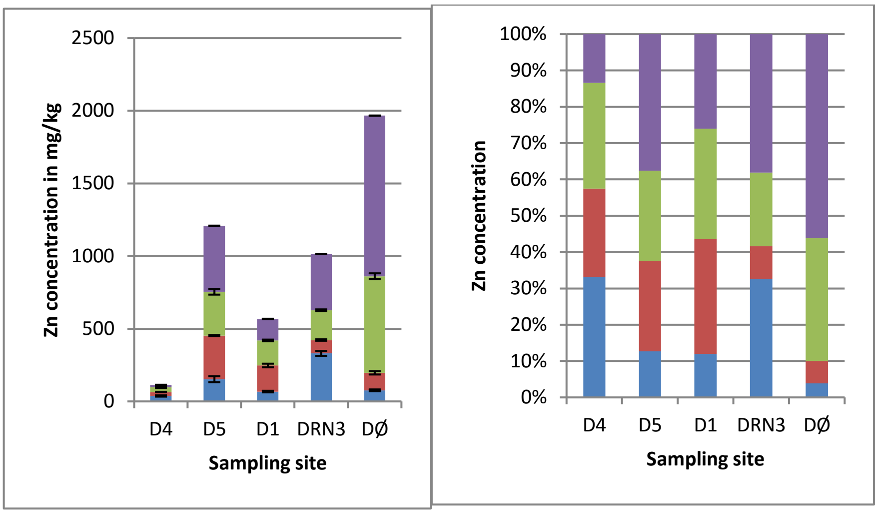


Figure 7.17 The distribution of Zn (mg kg^{-1} and % concentration) in the operationally defined fractions of Derwent Reservoir catchment sediments. The error bar represents the mean ± standard deviation and n = 3).

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The operational speciation of Zn in the Derwent catchment sediment (Figure 7.17 and Table B.9 in the appendix) was exchangeable (13 – 56 %), reducible (20 – 34 %), oxidisable (6 – 32 %) and residual (4 – 33 %) fractions. Previous studies in rivers (the River Twymyn, Wales, UK[106], the Mala Panew River, Poland[212] and the Gardon of Ales River, France[192]) with the legacy of mining also reported similar considerable distribution of Zn in all the operationally defined fractions of the sediments. The concentration of Zn found in the labile fractions of D5 (1060 mg kg^{-1}), D1 (500 mg kg^{-1}), DRN3 (685 mg kg^{-1}) and DØ (1890 mg kg^{-1}) were higher than the PEL value (315 mg kg^{-1})[63, 68]. The concentration of Zn in the labile fractions of D4 (75.6 mg kg^{-1}) was below the TEL value (123 mg kg^{-1})[63, 68].

General discussion on sequential extraction

The labile fractions (exchangeable, reducible and oxidizable fractions) accounted for 94 – 99 % of Cd, 42 – 89 % of Cu, 93 – 98 % of Mn, 56 – 83 % of Ni, 91 – 99 % of Pb and 67 – 96 % of Zn in the Derwent catchment sediments (D5, D4, D1, DRN3 and DØ) studied. The exchangeable PTE are the most mobile and bioavailable[16, 18, 221]. However, Calmano *et al* [222] showed that changing redox conditions in the environment may mobilise Cd, Cu, Pb and Zn from the reducible and oxidisable fractions of contaminated sediments to even more labile fractions. This suggested that the considerable proportions of Cd, Cu, Mn, Ni, Pb and Zn in the labile fractions of the Derwent catchment sediments were potentially mobile and bioavailable under different redox conditions in the environment. The high percentage of Cd (48 – 71 %) and Mn (30 – 80 %) in the exchangeable fraction of the Derwent catchment sediments and Pb (51 %) in exchangeable D5 are of environment concerns. This also indicated that Cd, Mn and Pb in the sediments can easily have negative impacts on the quality of water. Comparatively, As and Fe were in small proportion in the exchangeable and high percentage in the residual fraction; As (exchangeable (0.9 – 4 %) and residual (42 – 63 %)) and Fe (exchangeable (0.089 – 1.78 %) and residual (31 – 69 %)). This indicated that As and Fe were the least mobile and bioavailable PTE in the Derwent catchment sediments.

The distribution of As, Cd, Cu and Zn in the operationally defined fractions of D5 and D1 for each PTE in the sediment was somewhat similar but different from in D4, except the oxidisable Cu of D5 which was considerably higher. Dissolved PTE initially occurred in the exchangeable fraction. Therefore, the high proportion of Pb (51 %) in the exchangeable fraction, in addition to the comparatively high PT concentration in D5, indicated that there was an active input of the analyte from into Bolt’s Burn. Overall, the fractionation pattern taken together with the high PT concentrations supported the hypothesis that D5 was a significant source of As, Cd, Cu, Pb and Zn entering the Derwent Reservoir through the River Derwent.

The operational speciation of As, Fe and Pb in the inputs D1 and DRN3 for each PTE was somewhat similar but different from the output DØ downstream of the Derwent Reservoir. Also, the operational speciation of Cd, Cu, Ni and Zn for each PTE in inputs D1 and DRN3 were different for each PTE in the sediments. The distribution of Cd, Cu, Ni and Zn in the operationally defined fractions of output DØ for each of these PTE in the sediment was also different from in inputs D1 and DRN3. This indicated that some changes in the speciation of As, Cd, Cu, Fe, Ni and Zn occurred in the Derwent Reservoir. The distribution of Mn in the operationally defined fractions of D5 and D1 were similar, likewise DRN3 and DØ were similar, but the two pairs of sediments were dissimilar particularly in terms of the size of the exchangeable fraction. Taken together with the high concentration at input DRN3, this suggested that the River Derwent may not be the main source of Mn in the Derwent Reservoir despite being the major source of water.

7.4.3. Sediment quality index

The SQGS are a good place to start the assessment of sediment quality. However, for a better understanding of PTE status and their synergistic impacts, other approaches such as geo-accumulation index (*I-geo*)[165, 169], enrichment factor (EF)[66, 169] pollution index (PI)[66, 176] and risk assessment code (RAC) are also important. The *I-geo,* EF, PI and RAC were previously defined in section 3.14. The *I-geo*, EF and PI were calculated using the PT concentrations, while the RAC was calculated using the operationally defined fractions of PTE in the sediments. The weighted mean of the geochemical baseline values of PTE[166, 167] (data in Table B.10 in the appendix) present in the Derwent Reservoir catchment sediments were used as the reference background concentrations in the evaluation of the *I-geo*, EF and PI. The mean *I-geo*, mean EF and PI of the PTE present in the Derwent Reservoir catchment sediments are represented in Figure 7.18, 7.19 and 7.20, respectively.

Geo-accumulation index

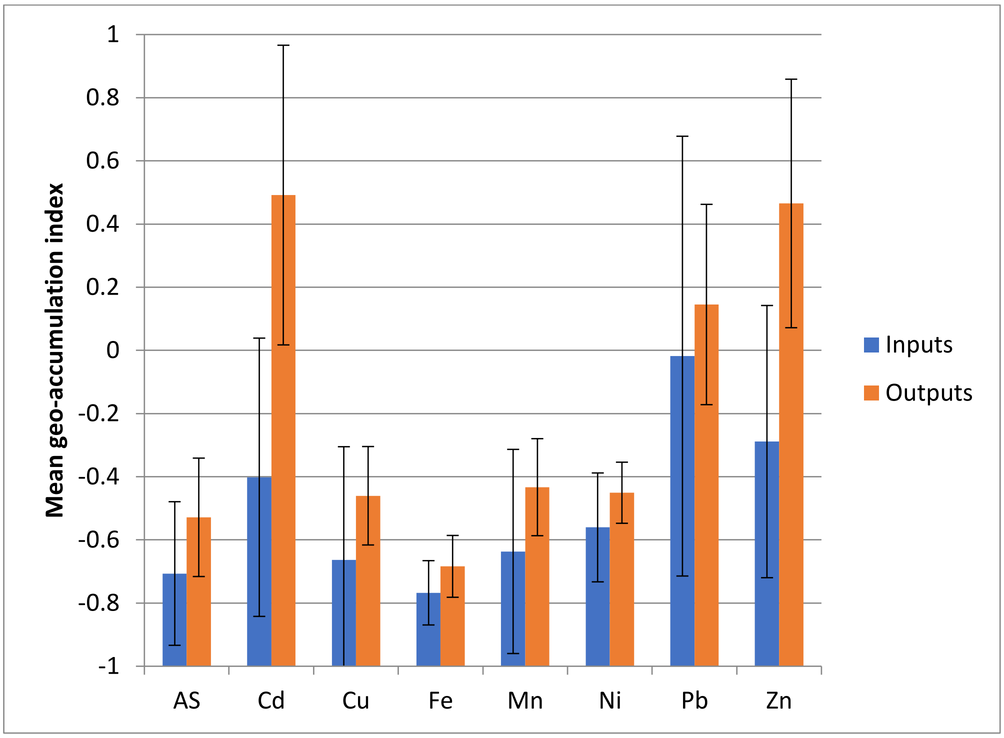


Figure 7.18 Mean geo-accumulation index of the PTE determined in the Derwent Reservoir catchment sediments. Error bar represents standard deviation. Inputs to the Derwent Reservoir: D7, D6, D4, D5, D3, D2, D1, DRN4, DRN3, DRN2, DRN1 and PH. Outputs of the Derwent Reservoir: DØ, DB, BB, ED and WW.

The trends (Figure 7.18 and Table B.11 in the appendix) of the mean *I-geo* values of all the PTE in the inputs and outputs sediments of the Derwent Reservoir were similar. The mean *I-geo* values for all the PTE were higher in the outputs of the Derwent Reservoir compared to the inputs. The mean *I-geo* values for all the PTE studied were less than 0 in the inputs, indicating that the PTE present in the inputs' sediments were mainly associated with the geology of the area. Similarly, the mean *I-geo* values for As, Cu, Fe, Mn and Ni was less than 0 downstream from the Derwent Reservoir, while those of Cd, Pb and Zn which were greater than 0 but less than 1. This indicated that the outputs sediments were slightly contaminated by Cd, Pb and Zn. Generally, based on the *I-geo*[165, 169] the sediment-bound PTE may be attributed to the geology of the study area. In a similar study, Hector *et al*[173] reported *I-geo* values below 0 in approximately 95 % of the sediment-bound PTE in the Sonora River Mexico, and attributed it to the geology of the study area.

Enrichment factor

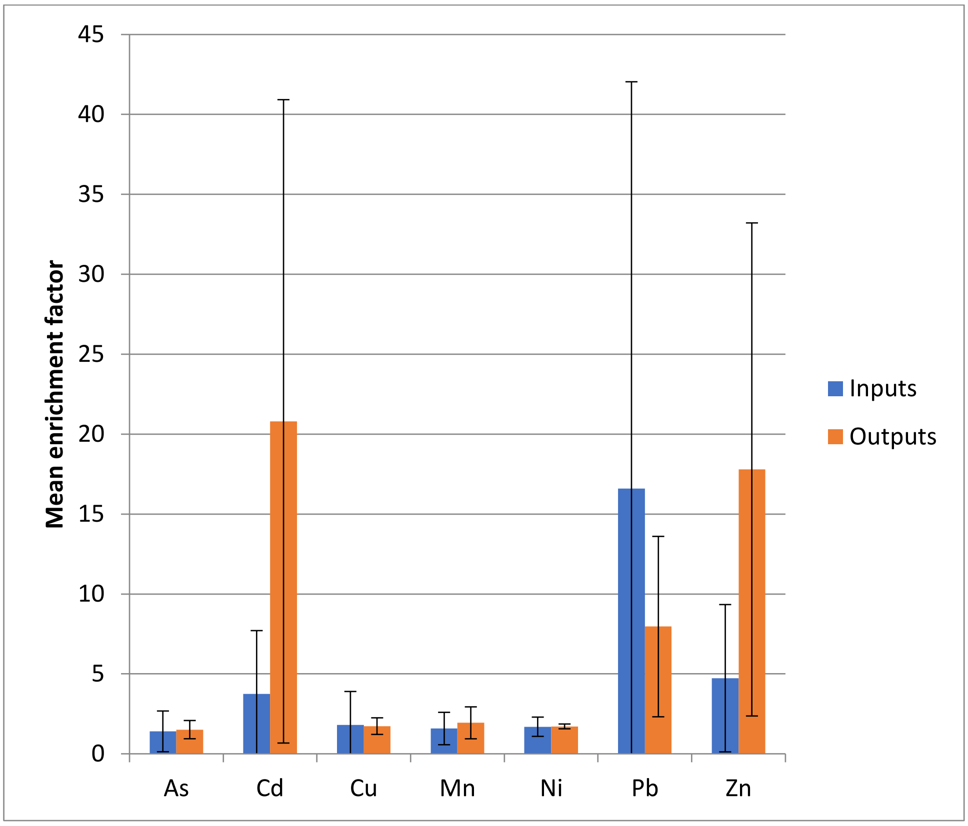


Figure 7.19 Mean enrichment factor of the PTE determined in the Derwent Reservoir catchment sediments. Error bar represent standard deviation. Inputs: D7, D6, D4, D5, D3, D2, D1, DRN4, DRN3, DRN2, DRN1 and PH. Outputs: DØ, DB, BB, ED and WW.

The mean EF value (Figure 7.19 and Table B.12 in the appendix) for As, Cu, Mn and Ni in the inputs (1.40, 1.80, 1.58 and 1.69 respectively) and outputs (1.51, 1.73, 1.94 and 1.71 respectively) of the Derwent Reservoir were less than 2, implying minimum enrichment. Cadmium and Zn had mean EF value of 3.74 and 4.70 in the inputs and Pb (7.96) in the outputs, implying moderate and significant enrichment, respectively. Lead had mean EF value of 16.6 in the inputs, implying significant enrichment. The mean EF values for Cd and Zn in the outputs were 20.8 and 17.8 respectively, implying significant enrichment. Enrichment factor > 1.5 is generally accepted as an indication of anthropogenic input[11, 174, 175]. Generally, the mean EF values obtained in this study were greater than 1.5, except for As, confirming that the sediments were impacted with PTE due to historical mining and smelting in the Derwent Reservoir catchment area.

Pollution index

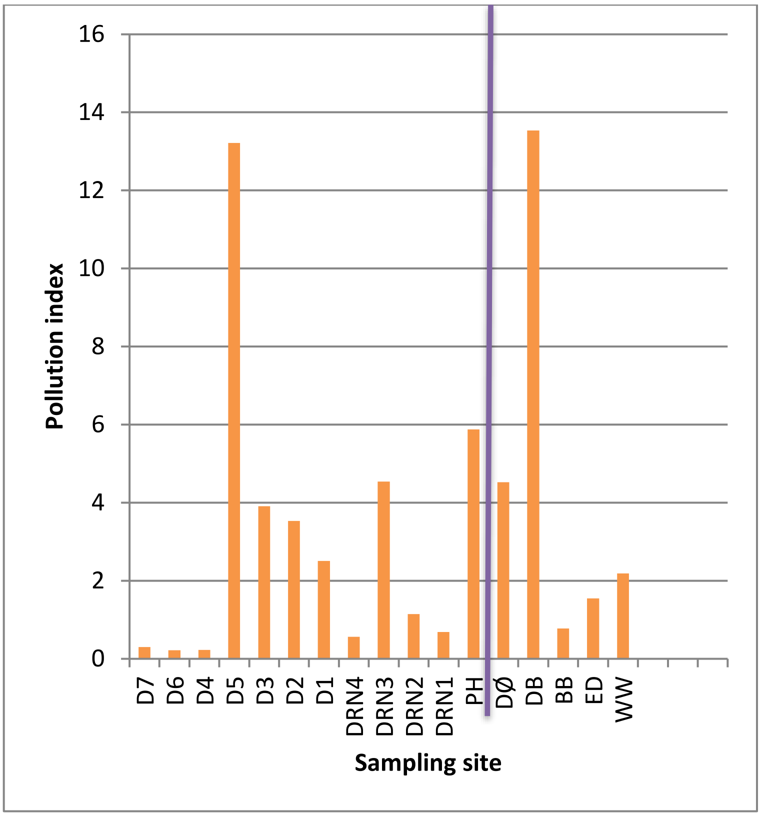


Figure 7.20 Pollution index of PTE in the Derwent Reservoir catchment sediments. The purple vertical line demarcates the inputs from downstream from the Derwent Reservoir.

Figure 7.20 and Table B.13 in the appendix revealed that the PI values for D7 (0.3), D6 (0.2), D4 (0.2), DRN4 (0.6) and DRN1 (0.68) were lower than 0.7, implying that the site were unpolluted. The BB was slightly polluted with PI value of 0.8. The DRN2 and ED were moderately polluted with the PI values of 1.1 and 1.5 respectively. The PI value for D1 (2.5) and WW (2.2) were higher than 2 but less than 3, implying that the sites were severely polluted. The PI value for D5 (13), D3 (3.9), D2 (3.5), DRN3 (4.5), PH (5.9), DB (14) and DØ (4.5) were higher than 3, implying that the sites were heavily polluted. The PI values indicating severe and heavy pollution in D5, D3, D2, D1, DB, DØ and WW seems to be consistent with As (Figure 7.2), Cd (Figure 7.3), Pb (Figure 7.8) and Zn (Figure 7.9) with PT concentration range from above TEL to above PEL values, which implied occasional and frequent ecological risk to aquatic organisms.

Risk assessment code

The risk assessment codes (RAC) of the sediment-bound PTE determined in this study are listed in Table 7.5. Generally, the RAC for Fe was less than 1 %, indicating no risk, except in DØ where it was in low risk range (1 – 10 %). Arsenic RAC was in the low risk range (1 – 10 %) in the sediments, except in D1 where it was less than 1 %, indicating no risk. Cadmium and Mn were both in the high risk (31 – 50 %) or very high risk range (> 50 %), except in D1 where Mn was in the medium risk range (11 – 30 %). Generally, Cu was in the low risk range (1 – 10 %), except in D4 and DRN3 where it was in the medium risk range (11 – 30 %). Nickel RAC was either high risk (31 – 50 %) or medium risk range (11 – 30 %), except in D4 where it was in the low risk range (1 – 10 %). Lead RAC in D5 was in the very high risk range (> 50 %), while it was in the medium risk range (11 – 30 %) in D1 and low risk range (1 – 10 %) in D4, DRN3 and DØ. The RAC for Zn in D4 and D1, D5 and DRN3 and DØ were in the medium (11 – 30 %), high (31 – 50 %) and very high risk (> 50 %) range respectively.

The mean RAC rank order was Fe (< 1 %: no risk) < As, Cu (1- 10 %: low risk) < Ni, Pb (11- 30 %: medium) < Zn (31- 50 %: high risk) < Cd, Mn (> 50 %: very high risk). The RAC accounted only for the exchangeable, but the reducible fraction could also be potentially mobile under reducing redox conditions[219, 222, 223]. Therefore, the considerable amount of Ni, Pb and Zn found in the reducible fraction of all the sediment samples, as well as As and Cd found in the reducible fraction of D5 and DØ respectively raised further environmental concerns under reducing redox conditions.

Table 7.5 Risk assessment code of potentially toxic elements in the Derwent Reservoir catchment sediments

Sediments	Risk assessment code (%)							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
D4	🟦 2.30	🟥 56.0	🟪 10.7	🟩 0.13	🟨 49.5	🟦 8.29	🟦 2.03	🟪 13.3
D5	🟦 2.53	🟥 50.7	🟦 7.41	🟩 0.13	🟨 42.9	🟪 26.4	🟥 50.5	🟨 37.6
D1	🟩 0.92	🟨 48.5	🟦 8.39	🟩 0.09	🟨 30.1	🟪 14.4	🟪 10.5	🟪 26.1
DRN3	🟦 1.65	🟥 72.2	🟪 13.5	🟩 0.71	🟥 79.6	🟪 18.9	🟦 8.90	🟨 38.1
D0	🟦 4.36	🟥 65.0	🟦 5.46	🟦 1.78	🟥 78.2	🟨 31.5	🟦 1.10	🟥 56.2
Mean RAC	🟦 2.35	🟥 58.5	🟦 9.10	🟩 0.57	🟥 56.1	🟪 19.9	🟪 14.6	🟨 34.3

🟩 No risk to water body 🟦 Low risk to water body 🟪 Medium risk to water body

🟨 High risk to water body 🟥 Very high risk to water body

7.5. Conclusion

Generally, the PT concentrations of PTE determined in the Derwent Reservoir catchment sediments were comparable with previous studies (listed in Table 7.1) around the world with historical mining and smelting in the catchment areas. Bolt's Burn was identified as the main source of As, Cd, Cu, Pb and Zn entering the Derwent Reservoir through the River Derwent. These findings were consistent with the report of Burrows *et al*[37] in 1983, which also identified Bolt's Burn as main source of Cd, Pb and Zn in the River Derwent downstream of the confluence. This suggested that Bolt's Burn was a significant source of Cd, Pb and Zn in the River Derwent for a long time (>25 years), and consequently also to the Derwent Reservoir. There were comparatively high PT concentrations of As, Cd, Cu, Pb and Zn in DB, and this was attributed to historical spillage of transported metal ores to the river from the bridge or accumulation/mineralisation of the analytes. Generally, the PT concentrations of PTE in the Derwent Reservoir catchment sediments were comparable with the baseline values in UK rural soil (Fe was compared with the background concentration in global soil), except Cd, Pb and Zn which were higher. This indicated that old mining operations had significant impacts on the status of Cd, Pb and Zn in the Derwent catchment.

The ecological risk associated with the PT PTE concentrations determined was quantitatively evaluated using the draft SQGs for England and Wales[63, 68]. Approximately 5.9 %, 18 %, 5.9 %, 88 % and 53 % of the PT As, Cd, Ni, Pb and Zn concentrations determined were above the PEL values, respectively, while 47 %, 35

%, 5.9 %, 59 %, 12 % and 24 % of the PT As, Cd, Cu, Ni, Pb and Zn were between the TEL and PEL values, respectively. The remaining 47 %, 47 %, 94 %, 35 % and 24 % of the PT As, Cd, Cu, Ni, Pb and Zn concentrations were below the TEL values, respectively. In decreasing order, PT PTE indicating likelihood of frequent ecological risk to aquatic organisms in the study area were: Pb > Zn > Cd > Ni ≈ As.

The BCR sequential extraction was conducted on D4, D5, D1, DRN3 and DØ. Generally, the distribution of PTE in operationally defined fractions of D1 and DRN3 were not like in DØ, which indicated that changes in PTE speciation occurred in the Derwent Reservoir. The labile fractions of PTE present in sediments give more accurate information on the potentially mobile and bioavailable fractions[18, 222] compared to the PT concentration. Therefore, the labile fractions were also used to assess the ecological risk associated with the PTE present in the sediments. The percentage distribution of the ecological risk associated with the concentrations of PTE in the labile fractions of the sediments were as follows: approximately 80 % of Pb and Zn, 20 % of As, Cd and Ni in the labile fractions were above the PEL values; approximately 60 % of Cd and 20 % of Cu were between TEL and PEL values; and approximately 80 % of As, Cu, and Ni and, 20 % of Cd and Zn were below the TEL values.

For better understanding of PTE status and their synergistic impacts, the *I-geo*[165, 169], EF[66, 169] PI[66, 176] and RAC were also used to assess sediment quality. Generally, the mean *I-geo* value of PTE in the Derwent Reservoir catchment sediments were less than 0, except for Cd, Pb and Zn which were greater than 0 but less than 1, reflecting the geology of the area and slightly contaminated sediment respectively. Generally, the average EF values obtained in this study were greater than 1.5, except for As in the inputs which was lower. This indicated that the sediments were impacted by PTE due to old mining operations in the Derwent catchment. Results obtained from PI assessment revealed that approximately 29 %, 6 %, 12 %, 12 % and 41 % of the sites sampled were unpolluted, slightly polluted, moderately polluted, severely polluted, and heavily polluted, respectively. The PI values indicated severe and heavy pollution in D5, D3, D2, D1, DB, DØ and WW, and this tends to agree with the SQGs assessment of PT concentrations of As, Cd, Pb and Zn in the sediments. The PT concentrations of As, Cd, Pb and Zn in D5, D3, D2, D1, DB, DØ and WW were from above TEL to above PEL values, implying occasional and frequent ecological risk to aquatic organisms. Based on the RAC the risk associated with the PTE in the sediments were estimated as Cd, Mn (very high risk) > Zn (high risk) > Ni, Pb (medium risk) > Cu, As (low risk) > Fe (no risk).

The PT concentrations of PTE in the input and output sediments clearly indicated that the impacts of historical mining and smelting remained in the Derwent Reservoir. In addition, the difference in the operational speciation of PTE in the input and output sediments indicated that some geochemically interesting changes in speciation occurred in the Derwent Reservoir. Therefore, a study assessing the speciation of PTE in the Derwent Reservoir sediment itself is important because this water body is used mainly for public water supply and recreation purposes, including sport fishing for edible species. An assessment of PTE status in reservoir sediments with historical mining and smelting in the catchment, using the Derwent Reservoir as a case study is reported in chapter eight.

8. Reservoir sediments

8.1 Introduction

This chapter is on the assessment of the status of PTE in the Derwent Reservoir sediments. Detailed description of the previous study conducted by Harding *et al*[36] in 1978 on the concentrations of PTE in water, sediments and some aquatic plants in the Derwent Reservoir is in section 1.6.1. However, the hot nitric acid digestion performed by Harding *et al*[36] provided information only on the maximum hypothetical potentially mobile PTE in the Derwent Reservoir sediments. Therefore, speciation analysis of PTE in the Derwent Reservoir sediments was a relevant research gap. Chapter seven shows clear differences between PTE speciation in the inputs and outputs sediments of the Derwent Reservoir, while chapter four indicates that these results were not an artefact of drying. This confirmed that some geochemically interesting changes in PTE speciation occurred in the Derwent Reservoir that requires further investigation. In addition, study on the potential mobility, bioavailability, and the implications for ecological risk assessment of PTE in the Derwent Reservoir sediments is important, because the reservoir is used mainly for public water supply and recreational purposes. Previous studies on the speciation of PTE in reservoirs sediments with old mining operations in the catchment areas have been described in section 1.6.1. The PT of the PTE in reservoir sediments with historical mining and smelting in the catchment areas are listed in Table 8.1. The PT concentrations of Cd, Pb and Zn determined by Harding *et al*[36] in the Derwent Reservoir sediments are listed in Table 8.1. The PT concentrations of Cd, Pb and Zn in the Derwent Reservoir sediments listed in Table 8.1, exceeded the PEL[63, 68], ISQG-H[67] and Netherlands Intervention values[69] (SQGs values are listed in Table 1.1). This indicated that PTE in the Derwent Reservoir sediments were also a potential ecological risk to aquatic organism.

Table 8.1 Pseudototal **c**oncentrations (mg kg^{-1}) of potentially toxic elements in reservoirs sediments with historical mining and smelting in the catchment area

Resevoirs	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn	Ores mined / smelted in the catchment
Castilseras Reservoir, Spain[110].	8.32 – 14.3	-	7.45 – 21.5	30500 – 51700	433 – 666	27.7 – 60.3	21.0 – 50.8	65.6 – 117	Ag, Hg, Pb and Zn
Marismillas Reservoir, Spain[120].	977 – 12100	0.280 – 43.4	63.2 – 7450	53000 – 350000	52.2 – 723	2.30 – 220	61.3 – 11900	190 – 8760	Ag, Hg, Pb and Zn
Lake Roosevelt Reservoir, Washington, USA[116]	2.80 – 22.0	0.2 – 7.7	10 – 2800	-	-	-	9 – 1110	54 – 26000	Pb and Zn
Ruzin Reservoir, Slovakia[33].	42.7 – 73.2	1.0 – 1.7	152 – 875	-	-	46.1 – 101	47.0 – 114	252 – 872	Cu, Fe and Hg
Velke Kozmalovce Reservoir, Slovakia[33].	29.6 – 47.9	2.1 – 3.0	64.2 – 96.6	-	-	12.1 – 17.2	55.1 – 77.3	355 – 561	Cu, Fe and Hg
Manwan Reservoir, China[119].	10.3 – 72.6	0.24 – 2.58	15.9 – 56.3	19100 – 37900	247 – 769	-	17.0 – 92.2	45.3 – 260	
Alqueva Reservoir, Portugal[28].	9.80 – 41.0	0.600 – 1.80	15.3 – 46.6	21000 – 85000	500 – 4600	18.9 – 53.6	23.4 – 52.5	53.5 – 128	Ag, Cu, Fe and Pb
Derwent Reservoir, UK[36]	-	3 – 18	-	-	-	-	250 – 1500	200 – 1200	Pb and Fluorspar

8.2. Study area

Details of the study area are in chapter six

8.2.1. Aims and objectives

i. To determine the maximum hypothetical potentially mobile PTE in the Derwent Reservoir sediments using pseudototal (PT) *aqua regia* digestion. The PT concentrations of PTE will be used to assess the impacts of historical mining and smelting on the analytes' levels in the Derwent Reservoir sediments.
ii. To assess the levels of potentially mobile PTE in the Derwent Reservoir sediments using the BCR sequential extraction procedure[95]. The operational speciation of PTE in the Derwent Reservoir sediment will provide a useful guide on source identification. It will also provide the first assessment of the levels of the potentially mobile and bioavailable PTE in the Derwent Reservoir sediments.
iii. To assess the quality of the Derwent Reservoir sediments using SQGs and sediment quality indices. This will provide useful estimate of the impacts of historical and smelting on PTE contamination and toxicity to aquatic organisms in the Derwent Reservoir sediments.
iv. To assess the source, transportation and geochemical behaviours of PTE in the Derwent Reservoir sediments using the Spearman's correlation coefficient and hierarchical cluster analysis

8.3. Experimental

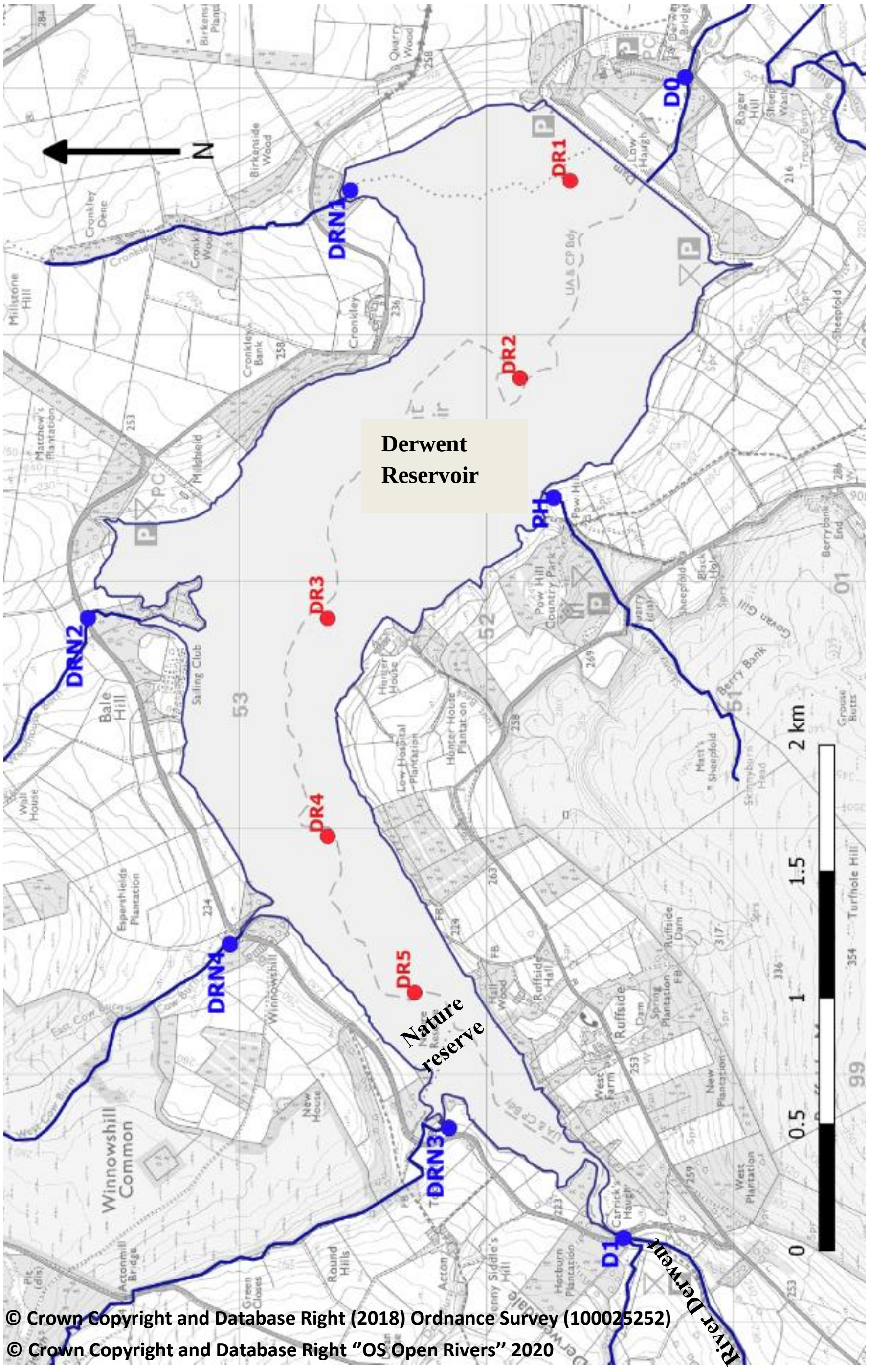
8.3.1. Sampling and sample preparation

Five sediment samples were collected in October 2018 approximately along the centre line of the Derwent Reservoir from a boat using a 0.5 L stainless steel Van Veen grab (Figure 8.1 and 8.2), targeting the original course of the River Derwent[36]. A handheld Global Positioning System was used to record the sampling sites, starting from the dam area at approximately 1 km intervals. The sampling sites were:

i. DR1 (NZ 02625 51662)
ii. DR2 (NZ 01825 51865)
iii. DR3 (NZ 00851 52644)
iv. DR4 (NY 99967 52739)

v. DR5 (NY 99334 52292)

The last sample (DR5) was collected close to the nature reserve area in the Derwent Reservoir. A more westerly sample could not be collected because it was prohibited to enter the nature reserve. Sediments DR1, DR2, DR3, DR4 and DR5 were collected after the entry points of Cronkley Burn (DRN1), PowHill (PH), Woodhouse Burn (DRN2), Cow Burn (DRN4) and Acton Burn (DRN3) into the Derwent Reservoir, respectively. These sampling sites were selected to assess the impacts of the small and shallow tributaries on the status of PTE in the Derwent Reservoir sediments, in addition to the main contributions from the River Derwent. Acton Burn was an additional source of water in the Derwent Reservoir. In addition, there were old mining operations in the catchment of the River Derwent and Acton Burn (Figure 7.1). The depths of the sampling sites were taken using the rope attached to the Van Veen grab. The depths of the sampling sites were as illustrated in Figure 8.3: DR5 (≈ 2 m); DR4 (≈ 15 m); DR3 (≈ 25 m); DR2 (≈ 30 m); and DR1 (≈ 25 m).



© Crown Copyright and Database Right (2018) Ordnance Survey (100025252)
© Crown Copyright and Database Right "OS Open Rivers" 2020

Figure 8.1 The Derwent Reservior and catchment sampling sites. The red circles show where sediment samples were collected in the Derwent Reservoir. The blue circles show the inputs (Carricks Haugh (D1), Acton Burn (DRN3), Cow Burn (DRN4), Woodhouse Burn (DRN2), Cronkley Burn (DRN1) and Pow Hill (PH)) and downstream (Derwent Reservoir spill-way (DØ)) from the Derwent Reservoir.

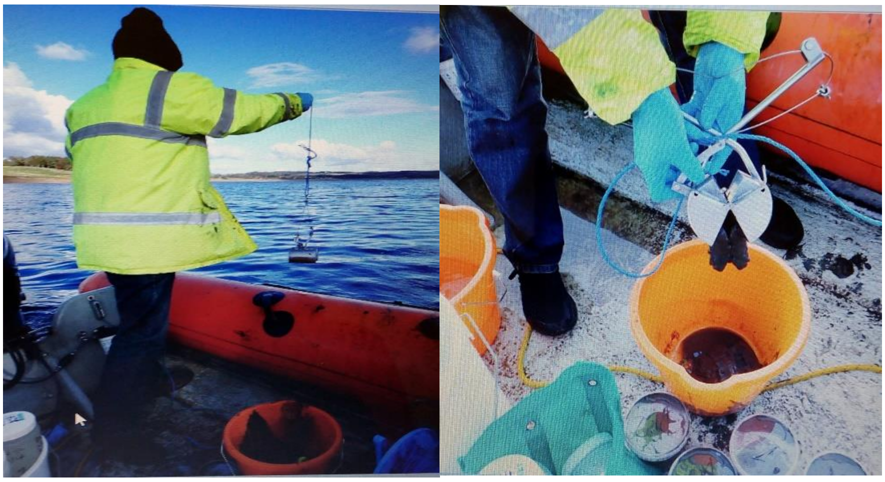


Figure 8.2 Collection of Derwent Reservoir sediment samples from a boat using Van Veen grab.

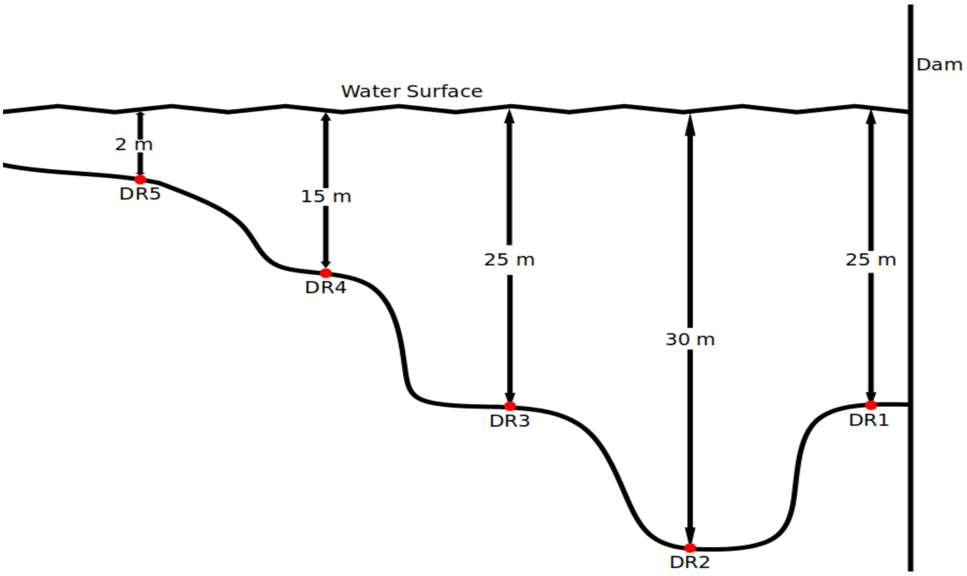


Figure 8.3 Schematic diagram of Derwent Reservoir sampling sites depth. The red circles represent the depth where sediment samples were collected.

The sediment samples were transferred into polyethylene containers and sealed with airtight lids. The sediment samples were fine and free from vegetation. The sediments were returned to the laboratory on the same day they were collected, and air drying of the samples for 3 weeks commenced immediately. All the air dried sediment samples passed through a British Standard sieve < 2 mm. The particle size distribution (PSD) of the air dried sediment samples was determined as described in section 3.4. All analyses (physicochemical properties, PT PTE concentration and sequential extraction) were performed on the air dried sediment samples.

8.3.2. pH measurement and % organic matter

The sediments pH and % organic matter (% OM) were determined as described in sections 3.2 and 3.7, respectively.

8.3.3. Pseudototal digestion

The sediments were digested using microwave assisted *aqua regia* digestion as described in section 3.8. The digests were analysed for the PT concentration of PTE in the sediments using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

8.3.4. BCR sequential extraction

The different operationally defined fractions of PTE in the Derwent Reservoir sediments (DR1, DR2, DR3 DR4 and DR5) were extracted using the BCR sequential extraction procedure as described in section 3.9. The extracts were analysed for PTE concentrations using ICP-MS (Model 7700x, Agilent Technology, UK) as described in section 3.11.

8.4. Results and discussion

8.4.1. Characterisation of sediment

The pH, % OM, and PSD of all the Derwent Reservoir sediment samples are listed in table 8.2. The Derwent Reservoir sediment samples had comparable % OM and pH values, suggesting that they were from similar source(s). The particle sizes (PS) of all the Derwent Reservoir sediment samples were in the range 0.316 µm – < 631 µm. The work in chapter seven of this current work and Harding *et al.*[36] study were carried out using sediment samples with PS < 150 µm and < 210 µm, respectively. Approximately 76 % and 86 % of all the Derwent Reservoir sediment samples was % PS < 150 µm and < 210 µm, respectively. The difference in PS of the Derwent Reservoir sediment in this work (86 % < 210 µm) and in Harding *et al*[36] (99 % < 210 µm) may be attributed to the different methods of analyses. Harding *et al.*[36] determined the PS of the Derwent Reservoir sediments using the sieving method. In this study, the % clay and silt tend to increase downstream, while the % sand decreased, indicating that clay and silt accumulated downstream in the Derwent Reservoir.

Table 8.2 The pH, organic matter content (% OM) and particle size (PS) of the Derwent Reservoir sediment.

Sampling site	pH	% OM	Minimum PS (µm)	Maximum PS (µm)	% PS < 150 µm	%PS < 210 µm	% clay < 0.002 mm	% silt > 0.002 – < 0.05 mm	% sand > 0.05 – < 2.0 mm
DR5	5.21	13.3	0.417	< 631	78.0	89	2.19	39.9	57.9
DR4	5.31	13.4	0.363	< 631	70.0	81	4.18	41.4	54.5
DR3	5.30	12.2	0.417	< 631	69.0	80	4.56	42.3	53.2
DR2	5.31	13.6	0.363	< 631	75.0	86	5.54	44.0	50.5
DR1	6.16	12.8	0.316	< 631	86.0	95	6.93	51.6	41.5
Mean	5.46	13.1	0.375	< 631	75.6	86.2	4.68	43.8	51.2

8.4.2. Pseudototal concentration determination and sequential extraction of PTE in sediment

8.4.2.1. Limits of detection

Instrumental limits of detection (LOD_{inst}) and procedural limits of detection (LOD_{pro}) for PT PTE determination and the BCR sequential extraction procedure steps using the ICP-MS are listed in Table 8.3. The LOD was always lower than the concentrations of the PTE determined.

Table 8.3 Instrumental limits of detection (μg L^{-1}) and procedural limits of detection (mg kg^{-1}) for pseudototal PTE determination and the BCR sequential extraction step using the ICP-MS.

PTE	Exchangeable fraction		Reducible fraction		Oxidisable fraction		Residual fraction/ pseudototal	
	LOD_{inst} (μg L^{-1})	LOD_{pro} (mg kg^{-1})	LOD_{inst} (μg L^{-1})	LOD_{pro} (mg kg^{-1})	LOD_{inst} (μg L^{-1})	LOD_{pro} (mg kg^{-1})	LOD_{inst} (μg L^{-1})	LOD_{pro} (mg kg^{-1})
As	0.000503	0.000201	0.169	0.0338	0.00413	0.00207	0.201	0.215
Cd	0.00952	0.00381	0.00340	0.000680	0.00139	0.000695	0.00129	0.00160
Cu	0.443	0.177	0.0322	0.00644	0.153	0.0765	0.0415	0.0519
Fe	3.23	1.29	1.72	0.344	2.10	1.05	3.99	4.99
Mn	0.277	0.111	0.0677	0.0135	0.0400	0.0200	0.00428	0.00535
Ni	0.0226	0.00904	0.0142	0.00710	0.0175	0.00875	0.00708	0.00885
Pb	0.211	0.0844	0.0558	0.0112	0.0118	0.00590	0.00929	0.0116
Zn	0.775	0.310	0.148	0.0296	0.0631	0.0316	0.146	0.183

8.4.2.2. Quality control for pseudototal analysis

The CRM 601 was used to assess the analytical performance of the PT PTE concentrations determination in the sediment samples. The PT concentrations of PTE in CRM 601 were indicative values. All analyses were carried out in triplicate. The PT PTE concentrations, standard deviation, % relative standard deviation (%RSD) and % recovery is listed in Table 8.4. The obtained values were within the standard deviation of the indicative values and the % RSD for the PT PTE concentrations determination were less than 10 %, indicating good results precision. The % recovery of 88 % to 103 % for all the PTE measured was satisfactory. A blank solution was also analysed at regular intervals during the ICP-MS analysis for quality check.

Table 8.4 Pseudototal concentration (mg kg^{-1}, n = 3), standard deviation (SD; ± mg kg^{-1}), % relative standard deviation (% RSD) and % recovery of PTE in dry weight of CRM 601.

PTE	Obtained values			Indicative values		% Recovery
	mg kg^{-1}	± mg kg^{-1}	% RSD	mg kg^{-1}	± mg kg^{-1}	
Cd	10.1	0.8	7.97	11.5	1.9	88
Cu	226	20	8.84	230	15	98
Ni	81.2	6.7	8.20	78.8	6.7	103
Pb	273	19	7.06	288	52	95
Zn	858	67	7.75	833	17	103

8.4.2.3. Pseudototal PTE concentrations in Derwent Reservoir sediments

The PT concentrations of PTE in the Derwent Reservoir sediment samples are represented in Figure 8.4 to 8.11. (detailed data are listed in Table B.14 in the appendix). The PT concentrations of PTE in the Derwent Reservoir sediments were compared with the inputs (DRN1, DRN2, DRN3, DRN4, D1 and PH) and output (DØ) results presented in chapter seven of this thesis. This was done to assess the possible impacts of the inputs on the status of PTE in the Derwent Reservoir sediments and downstream from the dam. The green and the red horizontal lines superimposed on Figure 8.4 to 8.11 represent the draft England and Wales SQGs[63]. The green and red horizontal lines represent the TEL and PEL values, respectively. General discussion on the PT concentration of PTE in the sediment samples is at the end of this section.

Arsenic

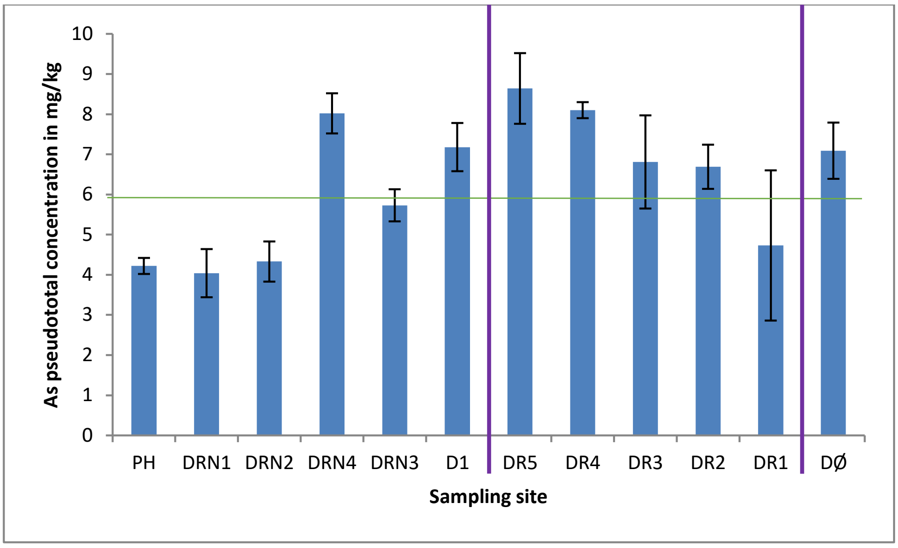


Figure 8.4 Arsenic PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as green horizontal line (TEL). The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentrations of As (4.73 – 8.64 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 8.4 and Table B.14 in the appendix) were comparable with the amount of the analyte found in the Lake Roosevelt[116] and Castilseras[110] Reservoirs sediments. The Castilseras in Spain[110] and Lake Roosevelt in the USA[116] are examples of reservoirs in legacy mining areas. The PT concentration of As in DR5, DR4, DR3 and DR2 were between the TEL and < PEL values, indicating occasionally ecological risk to aquatic organisms[63, 68]. The PT concentration of As in DR1 was below the TEL value, indicating rare ecological risk to aquatic organisms[63, 68].

Cadmium

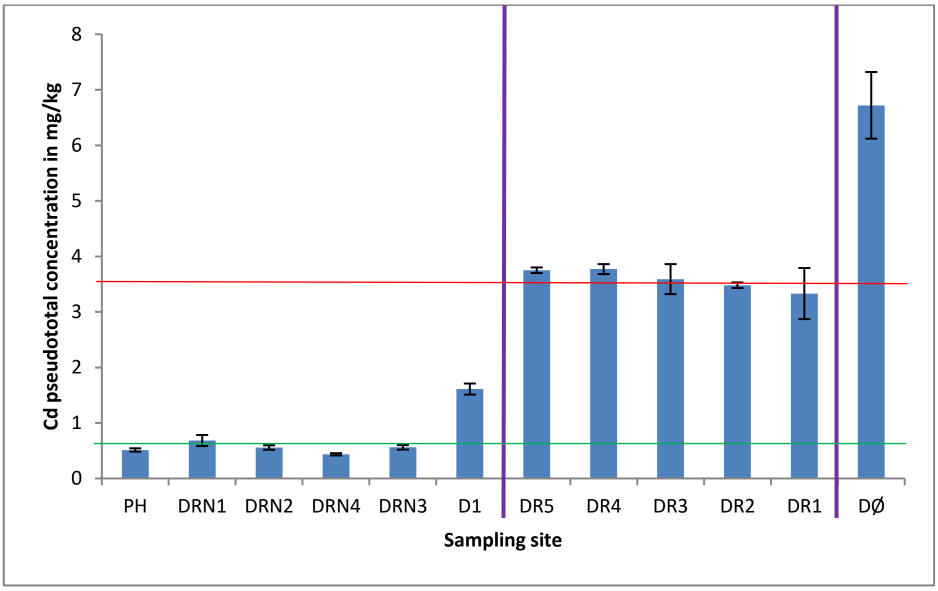


Figure 8.5 Cadmium PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal lines (green: TEL; red: PEL). The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentrations of Cd (3.33 – 3.77 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 8.5 and Table B.14 in the appendix) were comparable with the amount of the analyte found in the Lake Roosevelt[116] and Velke Kozmalovce Reservoir[33] sediments. The Velke Kozmalovce Reservoir in Slovakia was also impacted by old mining operations in the catchment[33]. The PT concentration of Cd in DR5, DR4 and DR3 were above the PEL value, indicating a likelihood of frequent ecological risk to aquatic organisms[63, 68]. The PT concentration of Cd in DR2 and DR1 was between the TEL and < PEL values, indicating occasional ecological risk to aquatic organisms[63, 68].

Copper

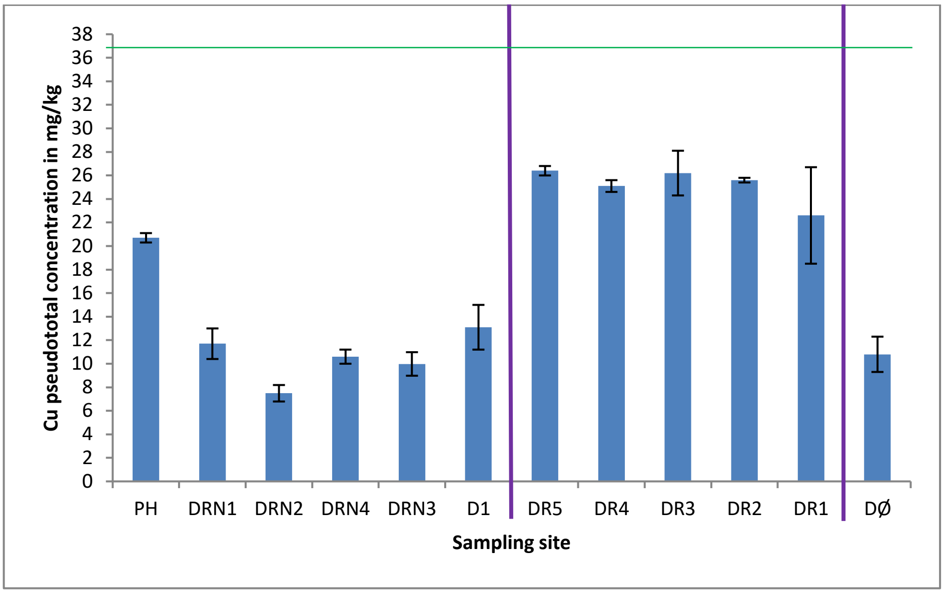


Figure 8.6 Copper PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as green horizontal line (TEL). The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentrations of Cu (22.6 – 26.4 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 8.6 and Table B.14 in the appendix) were comparable with the amount of the analyte found in the Alqueva[28] and Manwan[119] Reservoirs sediments. The Alqueva Reservoir in Portugal[28] and Manwan Reservoir in China[119] were also impacted by historical mining activities in the catchment areas. The PT concentration of Cu in DR1, DR2, DR3, DR4 and DR5 were below the TEL value[63, 68].

Iron

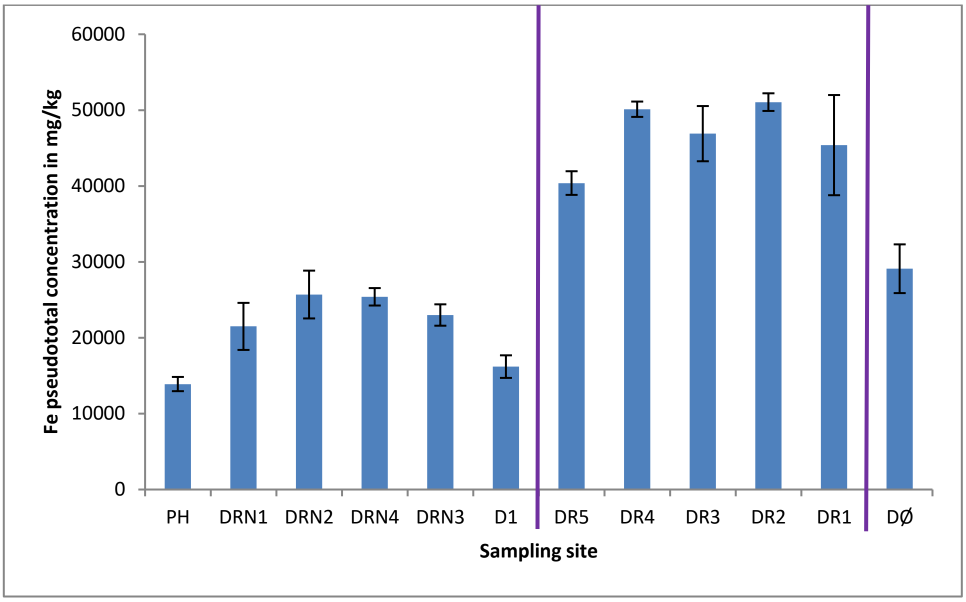


Figure 8.7 Iron PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments. The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentrations of Fe (40400 – 51100 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 8.7 and Table B.14 in the appendix) were comparable with the amount of the analyte found in the Marismillas[120], Manwan[119] and Alqueva[28] Reservoirs sediments. The Marismillas Reservoir in Spain was also impacted by old mining operations in the catchment[120]. Sediment quality guideline values for Fe are rare due to its natural abundance[44] and rare toxicity[57].

Manganese

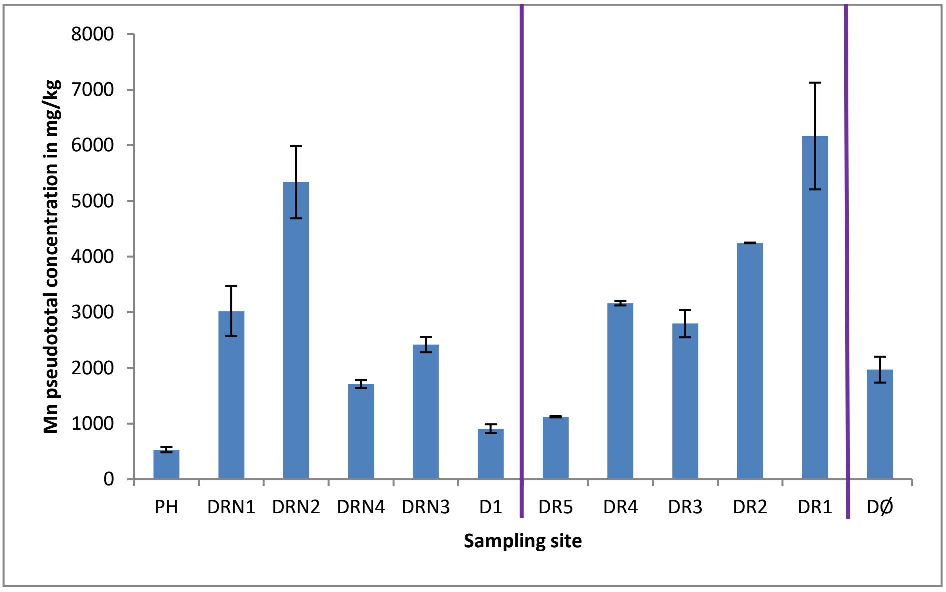


Figure 8.8 Manganese PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments. The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentrations of Mn (1120 – 6170 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 8.8 and Table B.14 in the appendix) were comparable with the amount of the analyte found in the Alqueva Reservoir sediments[28]. Like Fe, SQGs for Mn is also rare. Manganese is also naturally abundant in nature[44]

Nickel

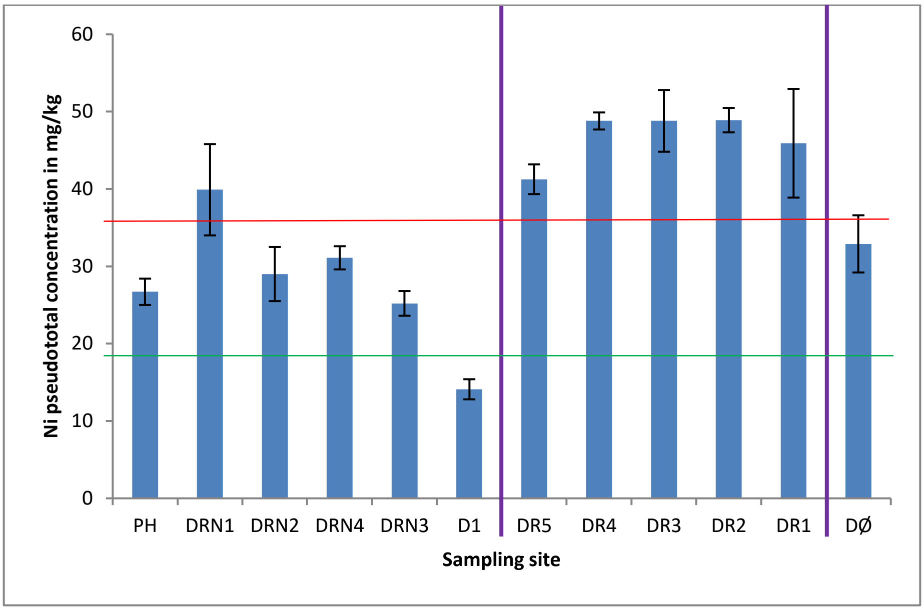


Figure 8.9 Nickel PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal lines (green: TEL; red: PEL). The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentrations of Ni (41.3 – 49.0 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 9.9 and Table B.14 in the appendix) were comparable with the amount of the analyte found in the Castilseras[110] and the Alqueva[28] Reservoirs sediments. The PT concentration of Ni in DR1, DR2, DR3, DR4 and DR5 were above the PEL value[63, 68].

Lead

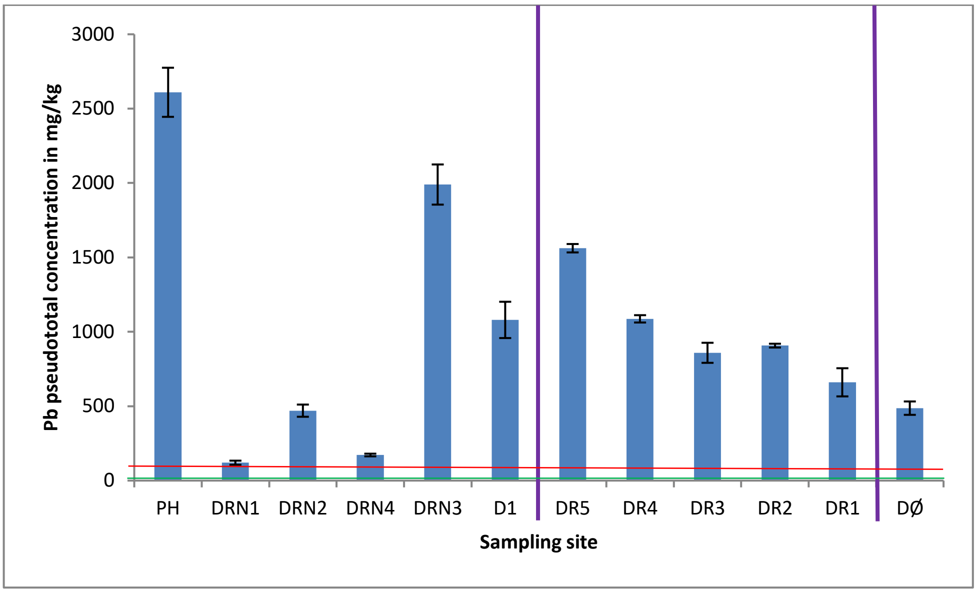


Figure 8.10 Lead PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal lines (green: TEL; red: PEL). The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentrations of Pb (661 – 1560 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 8.10 and Table B.14 in the appendix) were comparable with the amount of the analyte found in Lake Roosevelt[116] and Marismillas[120] Reservoirs sediments. The PT concentration of Pb in DR5, DR4, DR3, DR2 and DR1 were above the PEL value[63, 68].

Zinc

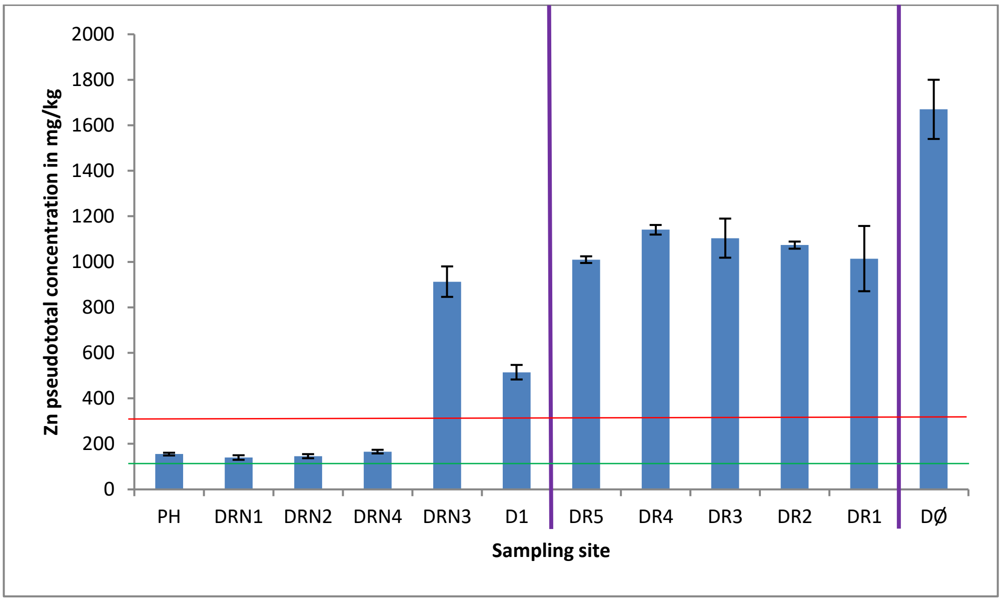


Figure 8.11 Zinc PT PTE concentration (mg kg^{-1}; error bar represent mean ± standard deviation; n=3) in the Derwent Reservoir and catchment sediments with the draft England and Wales Sediment Quality Guidelines superimposed as horizontal lines (green: TEL; red: PEL). The two purple vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

The PT concentration of Zn (1010 – 1140 mg kg^{-1}) determined in the Derwent Reservoir sediments (Figure 8.11 and Table B.14 in the appendix) were comparable the amount of the analytes found in Lake Roosevelt[116] and Marismillas[120] Reservoirs sediments. The PT concentration of Zn in DR5, DR4, DR3, DR2 and DR1 were above the PEL value[63, 68].

General discussion on pseudototal concentrations

The PT concentration of As determined in the Derwent Reservoir sediment were comparable with the amount of the analyte in all the inputs and downstream from the dam at DØ, suggesting that all the inputs probably had significance influence on the status of the analyte in the Derwent Reservoir.

The PT concentration of Cd, Cu, Fe and Ni in the inputs and output sediments were lower than the amount of these PTE in the Derwent Reservoir sediment, except Cd in the output (DØ) which was higher. This suggested that PH, DRN1, DRN2 and DRN4 had limited impacts on the status of Cd, Cu, Fe and Ni in the Derwent Reservoir. Also, the trends of the PT concentration of Ni and Fe in the Derwent Reservoir sediment were somewhat similar, probably reflecting the natural association between these analytes due to their chemical similarities[44].

The PT concentration of Mn in the inputs (DRN1, DRN2, DRN3 and DRN4) and in DØ downstream of the dam was comparable with the analyte concentration in the Derwent Reservoir sediment, except D1 and PH, which were lower. This suggested that DRN1, DRN2, DRN3 and DRN4 probably had significance influence on the status of Mn in the Derwent Reservoir. However, the PT concentration of Mn increased dramatically along the length of the Derwent Reservoir sediments downstream, indicating that the main carrier of the analyte accumulated preferentially towards the dam.

The PT concentration of Pb in inputs DRN1, DRN2 and DRN4 were lower than the amount of the analyte in the adjacent sampling sites DR1, DR2, DR3 and DR4, respectively, while the analyte concentration in PH was far higher than in adjacent DR1 in the Derwent Reservoir. This suggested that inputs DRN1, DRN2 and DRN4 had limited impacts on the status of Pb in the Derwent Reservoir, while PH may be a contributing source of the analyte in DR2 and DR1, because of the comparatively high PT concentration of Pb determined in the sample. The PT concentration of Pb in the main input D1 and DRN3 were comparable with the amount of the analyte in DR5 and DR4, indicating that Acton Burn and the River Derwent were significant sources of the analyte in the Derwent Reservoir.

The PT concentrations of Zn in DR1, DR2, DR3, DR4 and DR5 were similar and more comparable with the amount of the analyte in DRN3. The PT concentration of Zn determined in the other inputs (D1, DRN4, DRN2, DRN1 and PH) were low compared with the amount of the analyte in the Derwent Reservoir sediment. This indicated that Acton Burn alongside with the main input (the River Derwent) were the significant sources of Zn in the Derwent Reservoir. Like Cd, the PT concentration of Zn in the output DØ was higher than the amount of the analyte determined in the inputs and the Derwent Reservoir sediments. This suggested that there was an accumulation or unknown source of Cd and Zn within the Derwent Reservoir or immediate discharge point. This probably was also a reflection of the association of Cd with Zn ores[44, 46, 52].

The PT concentrations of Cd (3.33 – 3.77 mg kg^{-1}), Pb (661 – 1560 mg kg^{-1}) and Zn (1010 – 1140 mg kg^{-1}) determined in the Derwent Reservoir sediments in this work were comparable with the amount of Cd (3 – 18 mg kg^{-1}), Pb (250 – 1500 mg kg^{-1}) and Zn (200 – 1200 mg kg^{-1}) in the same reservoir sediments reported by Harding *et al*.[36] in 1978. This suggested that the levels of PTE contamination in the Derwent Reservoir has not changed over the years since mining ceased. However, the PT concentrations of As (4.73 – 8.64 mg kg^{-1}), Cu (22.6 – 26.4 mg kg-^{1}), Mn (1120 – 6170 mg kg^{-1}) and Ni (49.0 – 41.3 mg kg^{-1}) in the Derwent Reservoir sediments were comparable with the baseline values (As (0.5 – 143 mg kg^{-1}), Cu (2.27 – 96.7 mg kg^{-1}), Mn (10.0 – 12200 mg kg^{-1}) and Ni (1.16 – 216 mg kg^{-1})) in the UK rural soil[47]. Also, the PT concentration of Fe in the Derwent Reservoir sediments was comparable with the analyte background level in global soil[44]. While the PT concentrations of Cd (3.33 – 3.77 mg kg^{-1}), Pb (661 – 1560 mg kg^{-1}) and Zn (1070 – 1140 mg kg^{-1}) were higher than the baseline values (Cd (0.10 – 1.80 mg kg^{-1}), Pb (2.60 – 713 mg kg^{-1}) and Zn (2.63 – 442 mg kg^{-1})) in the UK rural soil[47]. This comparison is similar to the trend of PT PTE concentrations in the Derwent catchment sediments described in chapter seven. Like in the Derwent catchment sediments (studied in chapter seven), this also suggested that historical mining and smelting in the catchment had limited impact on the status of As, Cu, Fe, Mn and Ni in the Derwent Reservoir, while Cd, Pb and Zn were significantly enriched.

8.4.2.4. Quality control for sequential extraction

Table 8.5 compares the certified and obtained values[95] of PTE concentrations (mg kg^{-1}) in the certified reference material (CRM 601) using the BCR sequential extraction procedure (analysed in triplicate). The % recoveries of the BCR sequential extraction procedure were 33 % to 127 %, and for the sum of the steps were 79 % to 99 %. The low % recoveries of Cd in the residual fraction may be attributed to low level of the analyte and the large standard deviation. A blank solution was also analysed at regular interval during the ICP-MS analysis for quality checks.

Table 8.5 Comparison of the obtained and certified values of PTE fractions (mg kg^{-1}, n = 3), standard deviation (SD; ± mg kg^{-1}) in dry weight CRM 601 using the BCR sequential extraction scheme.

		Exchangeable fraction	Reducible fraction	Oxidisable fraction	Residual fraction	Sum
Obtained	Cd	3.88 ± 0.07	3.48 ± 0.03	1.40 ± 0.05	0.430± 0.026	9.19
Certified		4.45 ± 0.67	3.95 ± 0.53	1.91 ± 1.4	1.30 ± 2.2	11.61
% recovery		87	88	73	33	79
Obtained	Cu	10.8 ± 0.02	75.4 ± 0.96	62.4 ± 2.2	51.0 ± 1.8	200
Certified		10.5 ± 0.8	72.8 ± 4.9	78.6 ± 8.9	60.4 ± 4.9	222
% recovery		103	104	79	84	90
Obtained	Ni	7.25 ± 0.40	9.88 ± 0.18	6.73 ± 0.12	47.6 ± 1.7	71.4
Certified		7.82 ± 0.84	10.6 ± 1.3	6.04 ± 1.3	50.5 ± 4.3	75
% recovery		93	93	111	94	95
Obtained	Pb	1.61 ± 0.07	194 ± 2	25.0 ± 0.7	36.6 ± 3.6	258
Certified		2.28 ± 1.2	205 ± 11	19.7 ± 5.8	38.0 ± 8.7	265
% recovery		71	95	127	96	97
Obtained	Zn	256 ± 3.77	245 ± 4	116 ± 2	164 ± 7	783
Certified		261 ± 13	266 ± 17	106 ± 11	161 ± 14	794
% recovery		98	92	109	102	99

8.4.2.5. Fractionation of PTE in Derwent Reservoir sediments

Concentration of As, Cd, Cu, Fe, Mn, Ni, Pb and Zn in the different operationally defined fractions of the Derwent Reservoir sediments were determined using the BCR sequential extraction procedure. The concentration of PTE in mg kg^{-1} and % obtained in each step of the BCR sequential extraction scheme are represented in Figure 8.12 –

8.19, and the data are listed in Table B.15 – A.22 in the appendix. The operational speciation of PTE in the Derwent Reservoir sediments was compared with the main inputs (D1 and DRN3) and output (DØ) results from chapter seven of the current work. This was done to compare the sources of PTE in the Derwent Reservoir and downstream of the dam. The fractionation of PTE in the main inputs (D1 and DRN3) and output (DØ) are included in Figure 8.12 to 8.19 for easy comparison with the results obtained from the Derwent Reservoir sediments. The sum of PTE in the labile fractions (exchangeable, reducible and oxidisable) of the sediment samples were compared with the SQGs values to assess the ecological risk of the analyte to aquatic organisms as recommended by ANZECC[67]. General discussion on the sequential extraction of PTE in the sediment samples is at the end of this section.

Arsenic

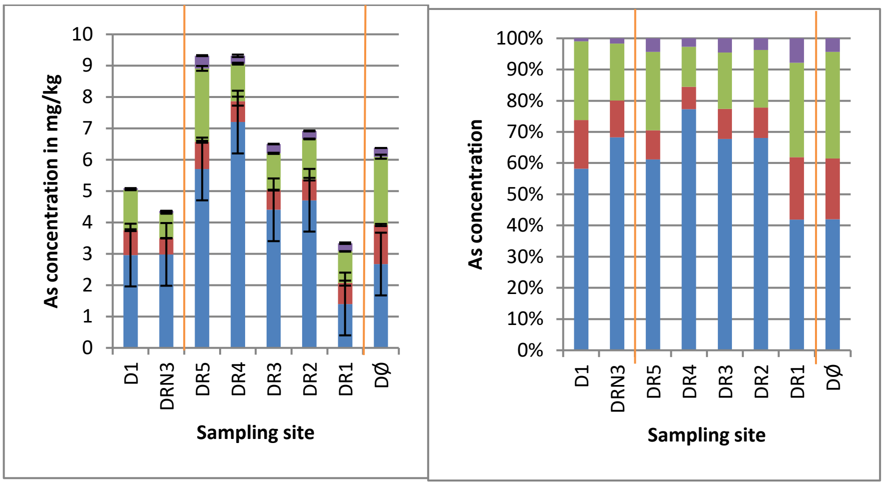


Figure 8.12 The distribution of As (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment samples. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Arsenic (Figure 8.12 and Table B.15 in the appendix) was found mainly in the residual (49 – 77 %) followed by reducible (13 – 27 %), oxidisable (7.16 – 17.7% and exchangeable (2.7 – 7.0 %) fractions of the Derwent Reservoir sediments. Hiller *et al.*[33] and Palma *et al.*[32] also found the largest proportion of As in the residual fraction with a considerable amount of the analyte in the reducible fraction of the Velke Kozmalovce[33] and Alqueva[32] Reservoirs sediments, respectively. The considerable amount of As found in the reducible fraction reflects the analyte's strong affinity for

Fe/Mn(hydr)oxides[44]. The concentration of As in the labile fractions (exchangeable, reducible and oxidisable) of DR1 (1.94 mg kg^{-1}), DR2 (2.21 mg kg^{-1}), DR3 (2.09 mg kg^{-1}), DR4 (2.12 mg kg^{-1}) and DR5 (3.61mg kg^{-1}) were below the TEL value (5.90 mg kg^{-1}), indicating rare ecological risk to aquatic organisms[63, 68].

Cadmium

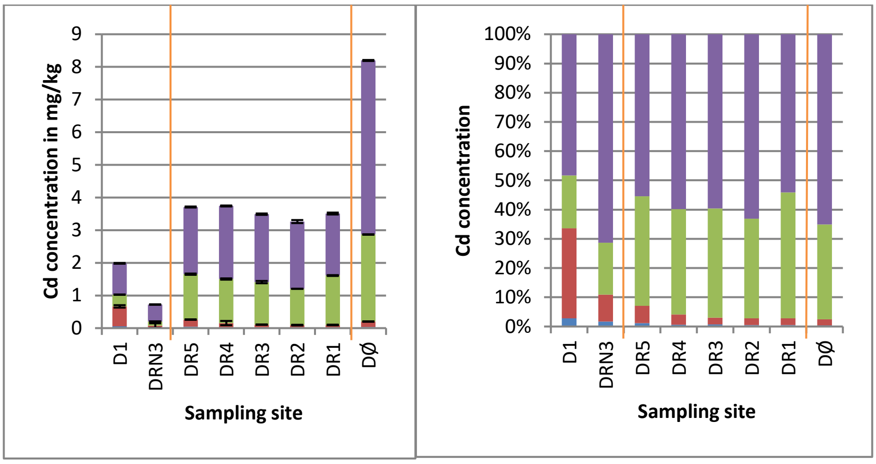


Figure 8.13 The distribution of Cd (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment samples. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Cadmium (Figure 8.13 and Table B.16 in the appendix) was found mainly in the exchangeable (54 – 63 %) followed by considerable amount of the analyte (34 – 43 %) in the reducible fraction of the Derwent Reservoir sediments. Cadmium was also found mainly in the exchangeable fraction of the Velke Kozmalovce[33] and Alqueva[32] Reservoirs sediments. The concentration of Cd in the labile fractions of DR1 (3.49 mg kg^{-1}), DR2 (3.25 mg kg^{-1}) and DR3 (3.46 mg kg^{-1}) were between the TEL (0.60 mg kg^{-1}) and < PEL (3.50 mg kg^{-1}) values, indicating occasional ecological risk to aquatic organisms[63, 68]. The concentration of Cd in the labile fractions of DR4 (3.71 mg kg^{-1}) and DR5 (3.67 mg kg^{-1}) were just above the PEL value, indicating the likelihood of frequent ecological risk to aquatic organisms[63, 68].

Copper

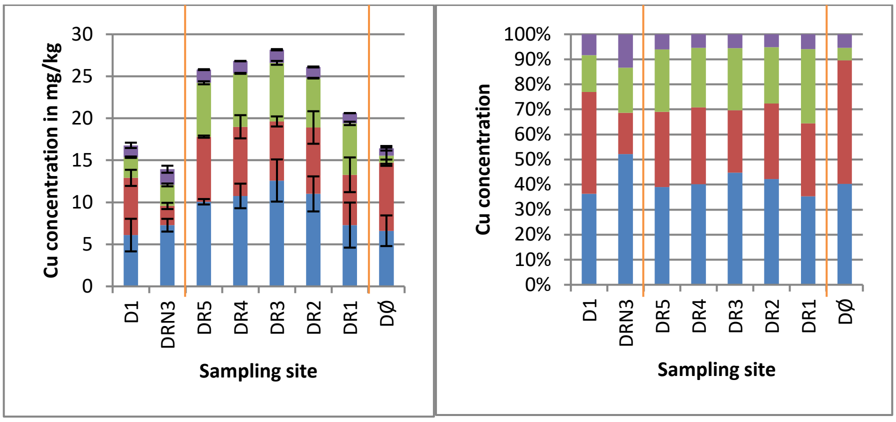


Figure 8.14 The distribution of Cu (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment samples. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The distribution of Cu in the operationally defined fractions (Figure 8.14 and Table B.17 in the appendix) of the Derwent Reservoir sediments was in the range: exchangeable (5.1 – 6.1 %); reducible (23 – 30 %); oxidisable (29 – 31 %); and residual fraction (35 – 45 %). Similar studies also found Cu in a considerable amount in the oxidisable fraction of the Castilseras[110], Velke Kozmalovce[33] and Alqueva[32] Reservoirs sediments, reflecting the known affinity of the analyte for OM[34, 35, 111]. However, the high proportion of Cu in the residual fraction indicated that a considerable amount of the analyte was associated with the mineral lattice of the Derwent Reservoir sediments. The concentration of Cu in the labile fractions of DR1 (13.3 mg kg^{-1}), DR2 (15.1 mg kg^{-1}), DR3 (15.6 mg kg^{-1}), DR4 (16.0 mg kg^{-1}) and DR5 (15.7 mg kg^{-1}) were below the TEL value (35.7 mg kg^{-1})[63, 68].

Iron

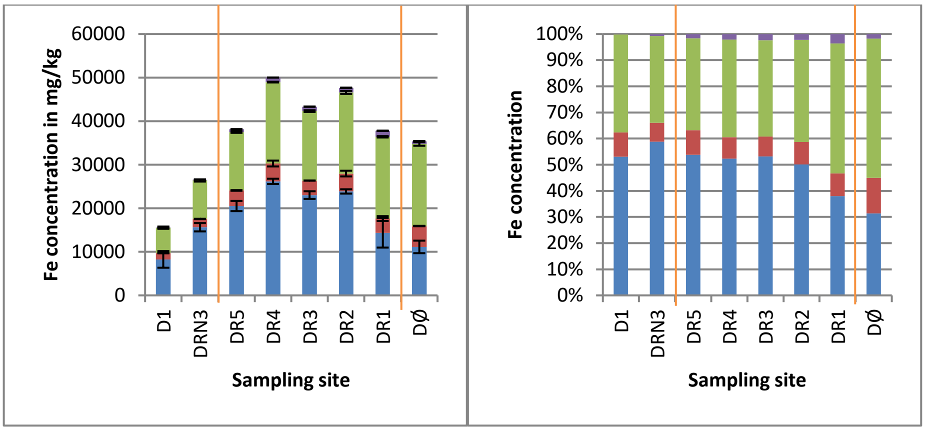


Figure 8.15 The distribution of Fe (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment samples. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Iron (Figure 8.15 and Table B.18 in the appendix) was mainly found in the reducible (35 – 50 %) and the residual (38 – 54 %) fractions of the Derwent Reservoir sediments. Garcia-Ordiales *et al.*[110]also found approximately 50 % of Fe in the reducible fraction of the Castilseras Reservoir sediments. The determination of Fe mainly in the reducible and residual fractions of the Derwent Reservoir sediments suggested that historical mining and smelting has limited impacts on the speciation of the analyte. Potentially toxic elements in the residual fraction are associated mainly with the mineral lattice[44].

Manganese

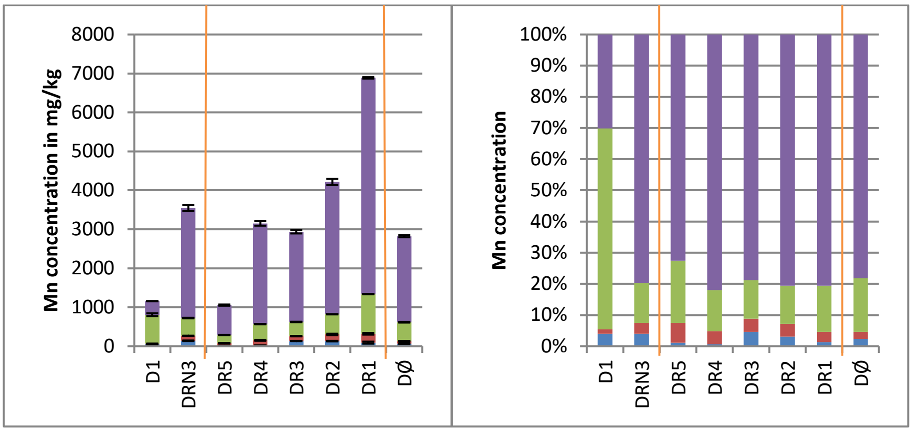


Figure 8.16 The distribution of Mn (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment samples. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Manganese (Figure 8.16 and Table B.19 in the appendix) was found mainly in the exchangeable (73 – 81 %) followed by reducible (12 – 20 %) fractions of the Derwent Reservoir sediments. Garcia-Ordiales *et al.*[110] also found a considerable amount of Mn in the exchangeable and reducible fractions of the Castilseras Reservoir sediments. Similar to Garcia-Ordiales *et al.*[110] suggestion the high proportion of Mn in the exchangeable fraction may easily enter the food chain through dissolution followed by ingestion and/or absorption by organisms in the environment[46, 72].

Nickel

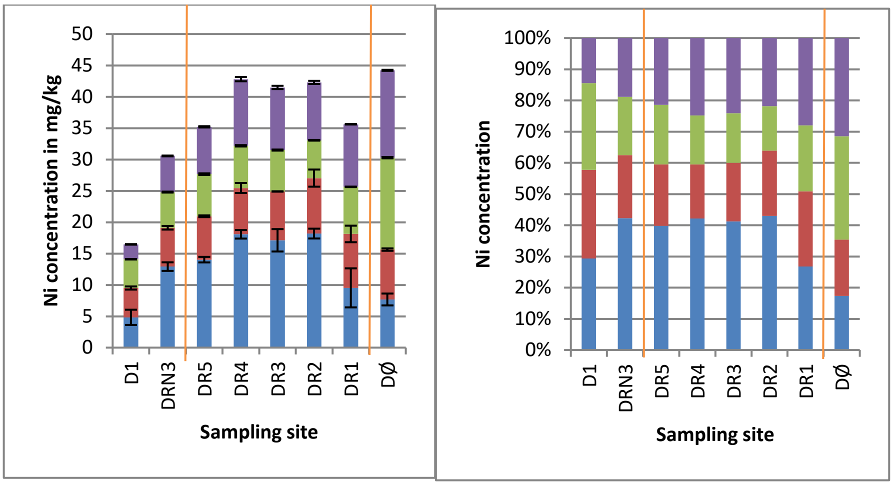


Figure 8.17 The distribution of Ni (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment sample. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

The distribution of Ni in the operationally defined fractions (Figure 8.17 and Table B.20 in the appendix) of the Derwent Reservoir sediments was in the range: exchangeable (21 – 28 %); reducible (14 – 21 %); oxidisable (17 – 24 %); and residual fraction (27 – 43 %). Similar studies in Castilseras[110], Velke Kozmalovce[33] and Alqueva Reservoirs[28] sediments also found Ni mainly in the residual fraction, and similar to these studies it is suggested that mining had limited impact on the analyte status in the water bodies. The concentration of Ni in the labile fractions of DR5 (21.2 mg kg^{-1}), DR4 (24.7 mg kg^{-1}), DR3 (24.4 mg kg^{-1}), DR2 (24.1 mg kg^{-1}) and DR1 (26.1 mg kg^{-1}) were between the TEL (18 mg kg^{-1}) and PEL (35.9 mg kg^{-1}) values[63, 68].

Lead

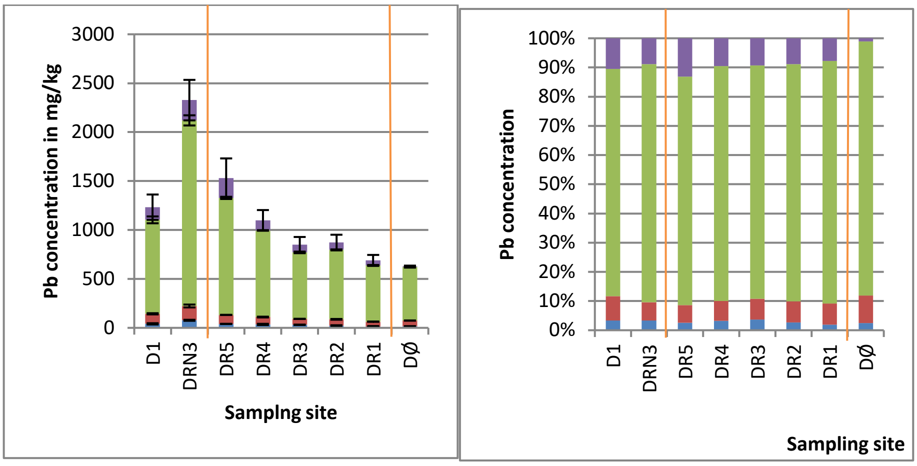


Figure 8.18 The distribution of Pb (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment samples. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Lead (Figure 8.18 and Table B.21 in the appendix) was found mainly in the reducible fraction (78 – 83 %) of the Derwent Reservoir sediments, reflecting the strong affinity of the analyte for Fe/Mn (hydr)oxides[44]. This is consistent with similar studies conducted in Velke Kozmalovce[33] and Alqueva Reservoirs[32, 33] which also found Pb in high proportions in the reducible fraction of the sediments. The concentration of Pb in the labile fraction of DR1 (677 mg kg^{-1}), DR2 (851 mg kg^{-1}), DR3 (818 mg kg^{-1}), DR4 (1064 mg kg^{-1}) and DR5 (1494 mg kg^{-1}) were well above the PEL value (91.3 mg kg^{-1})[63, 68].

Zinc

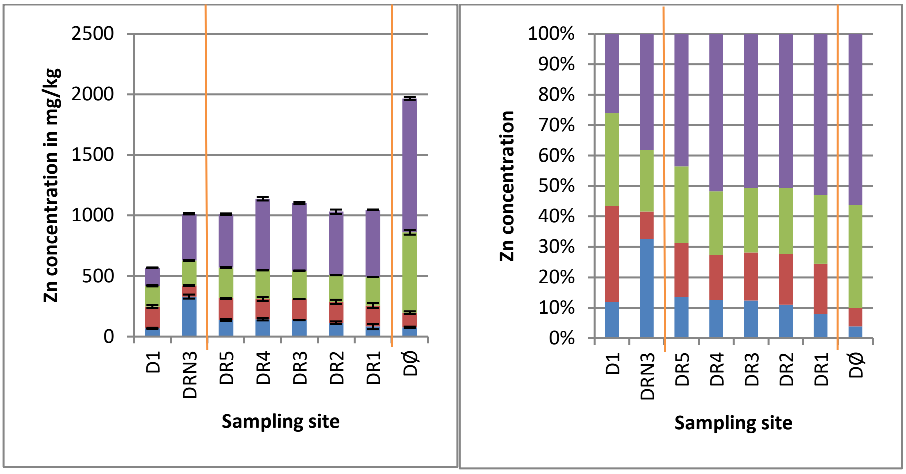


Figure 8.19 The distribution of Zn (mg kg^{-1} and % concentration) in the operationally defined fractions of the Derwent Reservoir, inputs and output sediment samples. The error bar represents the mean ± standard deviation and n = 3. The two orange vertical lines demarcate the inputs, the Derwent Reservoir and output sediment samples.

🟪 Exchangeable 🟩 Reducible 🟥 Oxidisable 🟦 Residual

Zinc (Figure 8.19 and Table B.22 in the appendix) was found mainly in the exchangeable fraction (44 – 53 %) of the Derwent Reservoir sediments. Besser *et al.*[116] and Hiller *et al.*[33] also found considerable amount of Zn in the exchangeable fraction of the Lake Roosevelt and Velke Kozmalovce Reservoirs sediments, respectively. The concentration of Zn in the labile fractions of DR1 (964 mg kg^{-1}), DR2 (917 mg kg^{-1}), DR3 (966 mg kg^{-1}), DR4 (996 mg kg^{-1}) and DR5 (873 mg kg^{-1}) were above the PEL value (315 mg kg^{-1})[63, 68].

General discussion on sequential extraction

The fractionation pattern of As, Fe, Ni and Pb in the inputs D1 and DRN3 were somewhat similar with the analytes' speciation in the Derwent Reservoir sediment DR5 as expected; the River Derwent (D1) and Acton burn (DRN3) were the main and additional source of water in the Derwent Reservoir, respectively. The operational speciation of Cd, Cu, Mn and Zn in DR5 were more comparable with the fractionation patterns of the analytes in input DRN3 than in D1. This suggested that DRN3 may be influencing the status of Mn in the Derwent Reservoir sediments. In addition, the noticeable increase in the PT concentrations of Cd, Cu and Zn in the Derwent Reservoir sediment compared with in D1 and DRN3 was probably an indication of the mineralisation of these analytes in the reservoir. Also, that Cd is always associated with Zn ores[44, 46, 52].

The fractionation patterns of As in DR5 and DR4 were slightly different from each other. The adjacent input (DRN4) may possibly have altered the speciation of As in DR4, because the PT concentration of the analyte in both samples was similar. The operational speciation of As in DR3 and DR2 were similar but different from in DR5, DR4 and DR1. The distribution of Cd, Cu, Fe, Mn, Ni, Pb and Zn in the operationally defined fractions of all the Derwent Reservoir sediment samples was somewhat similar for each analyte. This suggested that inputs DRN1, DRN2 and PH had limited impacts on the status of Cd, Cu, Fe, Mn, Ni, Pb and Zn in the Derwent Reservoir. There was a dramatic increase in the PT concentration of Mn downstream, and the similarity in their fractionation pattern in all the Derwent Reservoir sediment samples and DRN3 suggested that DRN3 may have had an influence on the status of the analyte in the reservoir. Also, the partitioning of Mn in the Derwent Reservoir sediments was consistent with the main forms of the analyte in soil. Manganese occurs mainly in the water soluble and exchangeable forms and as insoluble Mn oxides in soil[44]. This Suggested that Mn in the Derwent Reservoir sediments were predominantly from soil. However, there was a noticeable increase in the proportion of As, Fe, Ni and Zn in the labile fractions of the Derwent Reservoir sediment near the dam (DR1), and this may be attributed to weathering downstream within the reservoir.

Generally, the fractionation pattern of As, Fe, Mn, Ni and Pb in the Derwent Reservoir sediment (DR1) near the dam and downstream from the reservoir (DØ) were somewhat similar as expected, except the comparatively high amount of oxidisable Cu in DØ. This suggested that there was a considerable input of Cu in the oxidisable form downstream of the dam different from within the Derwent Reservoir, or there was a switch from reducible to oxidisable fraction. The high PT concentrations of Cd and Zn determined in DØ compared with DR1 might be attributed to the accumulation of the analytes downstream of the Derwent Reservoir, as indicated by the increasing concentrations and proportions of exchangeable and reducible fractions.

Considerable amount of As (23 – 58 %), Cd (99 – 99.5 %), Cu (55 – 65 %), Fe (46 – 62 %), Mn (95 – 99 %), Ni (57 – 73 %), Pb (96 – 98 %) and Zn (86 – 92 %) were determined in the labile fractions (exchangeable, reducible and oxidisable fractions) of the Derwent Reservoir sediment, indicating that significant proportions of different forms of these PTE were potentially mobile and bioavailable under different redox conditions[222]. However, the exchangeable fraction is the most potentially mobile and bioavailable fraction of PTE in sediments[16, 18, 221]. Therefore, the high proportion of exchangeable Cd (54 – 63 %), Mn (67 – 81 %) and Zn (44 – 53 %) determined in the Derwent Reservoir sediment were of concern, because they may easily have negative impact on the quality of water, as well enter the food chain. The exchangeable Cd is particularly of concern because of its high toxicity[2, 45, 54, 55]. Also, the noticeable increase in the proportion of As, Fe, Ni and Zn in the labile fractions of the Derwent Reservoir sediment downstream indicated that the potential mobility and bioavailability of these analytes were higher near the dam. This could be of significance if quantities of reservoir sediments were returned to the river by flushing activities.

8.4.3. Chemometrics

8.4.3.1. Correlation analysis

The Spearman’s rank correlation analysis at 0.05 significant level (results in Table 8.6) performed on the PT concentrations of PTE in the Derwent Reservoir sediments, physicochemical properties, distance and depth of the sampling sites in order to assess source, transportation and geochemical behaviours of the analytes.

Table 8.6 The Spearman's rank correlation coefficients of PT PTE concentrations in the Derwent Reservoir sediments, physicochemical properties, distance and depth of sampling sites.

	As (mg kg^{-1})	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Fe (mg kg^{-1})	Mn (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Clay (%)	Silt (%)	Sand (%)	Distance (km)
As (mg kg^{-1})												
Cd (mg kg^{-1})	**0.900***											
Cu (mg kg^{-1})	0.700	0.400										
Fe (mg kg^{-1})	-0.300	0.00	-0.300									
Mn (mg kg^{-1})	**-0.900***	-0.700	**-0.900***	0.400								
Ni (mg kg^{-1})	-0.359	-0.103	-0.205	**0.975***	0.359							
Pb (mg kg^{-1})	**0.900***	0.800	0.600	-0.100	-0.700	-0.205						
Zn (mg kg^{-1})	0.205	0.564	-0.103	0.667	-0.103	0.632	0.103					
Clay (%)	**-1.00***	**-0.900***	-0.700	0.300	**0.900***	0.359	**-0.900***	-0.205				
Silt (%)	**-1.00***	**-0.900***	-0.700	0.300	**0.900***	0.359	**-0.900***	-0.205	**1.00***			
Sand (%)	**1.00***	**0.900***	0.700	-0.300	**-0.900***	-0.359	**0.900***	0.205	**-1.00***	**-1.00***		
Distance (km)	**-1.00***	**-0.900***	-0.700	0.300	**0.900***	0.359	**-0.900***	-0.205	**1.00**	**1.00***	**-1.00***	
Depth	-0.821	-0.718	-0.359	0.667	0.667	0.763	-0.667	0.079	0.821	0.821	-0.821	0.865

The red asterisked numbers are significant correlations at the 0.05 significant level.

Arsenic, Cd and Pb showed a significant positive correlation with the sand-size particles of the Derwent Reservoir sediments. The sand-size particles may be metal ores and/or slag containing As, Cd and Pb. Therefore, the increase in the amount of As (Figure 8.12), Cd (Figure 8.13) and Pb (Figure 8.18) in the labile fractions downstream may be attributed to the weathering of metal ores and/or slag in the Derwent Reservoir. Besser *et al*.[116] in a similar study also attributed the increase in the amount of PTE in the labile fractions of sediments to the weathering of slag downstream in the Lake Roosevelt Reservoir in the USA. There was also a significant positive correlation between As and Pb. Sand-size particles usually settle out first[46]. Therefore, the significant negative correlation between the sand-size particles of the Derwent Reservoir sediments and distance probably explains the decrease in the amount of As, Cd and Pb along the length of Derwent Reservoir downstream. Similar to Harding *et al.*[36] studies in the Derwent Reservoir, there was a significant negative correlation between Pb and distance. Taken together with the decrease in the PT concentration downstream and the results of the operational speciation, the significant positive correlation between As and Cd, as well as As and Pb further indicated that the River Derwent was the main source of these PTE in the Derwent Reservoir. There was a significant negative correlation between the sand-size particle and Mn in the Derwent Reservoir sediments.

Both clay- and silt-size particles showed significant positive correlations with the amount of Mn in the Derwent Reservoir sediments. This indicated that Mn was mainly associated with fine grain particles size in the Derwent Reservoir. There was also a significant positive correlation of both the clay- and silt-grain size particles in the Derwent Reservoir sediments with distance. This indicated that both the clay- and silt-size particles accumulated in the Derwent Reservoir sediments downstream. This probably explains the significant increase in the amount of Mn in the Derwent Reservoir sediments downstream, which also suggested that clay- and silt-grain size particles were the major carrier of the analyte in the Derwent Reservoir. Li Gao *et al*[19] suggested that the decrease in water flow rate aided the accumulation of fine grain particles downstream in the Three Gorges Reservoir in China, which may also be the case in the Derwent Reservoir. Copper showed significant negative correlation with

Mn, suggesting that the association between both analytes in the Derwent Reservoir sediments were limited.

There was a positive significant correlation between Fe and Ni, while both analytes also had similar correlation with the other parameters of the Derwent Reservoir sediments investigated. The correlation of Fe and Ni with distance and depth of sampling sites were also similar. Iron and Ni are usually found together in nature[44]. Harding *et al.*[36] also reported that there was a significant positive correlation between Fe and Ni in the Derwent Reservoir sediments. Zinc had no significant relationship with any of the other PTE, distance, water depth and the different sediment particle size, suggesting there may be some differences in the analyte source and transport in the Derwent Reservoir. This may involve the mineralisation of Zn in the Derwent Reservoir.

8.4.3.2. Cluster analysis

The hierarchical cluster analysis was carried out to verify and support the results of the correlation analysis. Figure 8.20 is the dendogram of hierarchical cluster analysis of PT PTE concentrations in the Derwent Reservoir sediments. The dendogram revealed three main clusters (cluster one: As-Cd-Cu-Pb; cluster two: Fe-Ni-Zn; and cluster three: Mn) based on the PT concentrations of PTE in the Derwent Reservoir sediments.

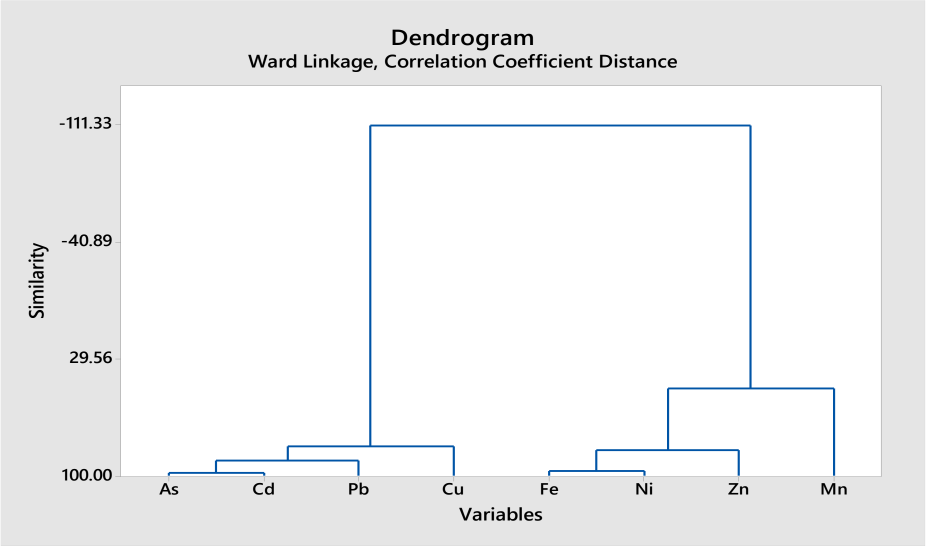


Figure 8.20 Dendogram of hierarchical cluster analysis of PT PTE concentrations in the Derwent Reservoir sediments

Cluster one support the result of correlation analysis that the River Derwent was a significant source of As, Cd and Pb in the Derwent Reservoir sediments. The inclusion of Cu cluster one also suggested that the River Derwent had a considerable impact on the status of the analyte in the Derwent Reservoir sediments. Arsenic, Cd and Cu are associated with Pb and fluorspar ores[44]. Therefore, As, Cd, Cu and Pb in cluster one indicated that historical mining of Pb and fluorspar in the catchment had a significant impact on the status of these PTE in the Derwent Reservoir. Iron and Ni are more closely related, than any of these two analytes with Zn in cluster two. The PT concentrations of Fe (40400 – 51100 mg kg^{-1}) and Ni (41.3 – 49.0 kg mg^{-1}) are also comparable with baseline values (Fe: 7000 – 4200 mg kg^{-1} and Ni: 1.16 – 216 mg kg^{-1})[44, 47]. These can be attributed to the natural abundance of Fe and its association with Ni in nature[73]. This also suggested that old mining operations had limited impacts on the status of the Fe and Ni in the Derwent Reservoir. Considering the disparity in cluster two and the PT concentrations of Zn (1010 – 1140 mg kg^{-1}), which were higher than the baseline value in the UK rural soils (2.63 – 442 mg kg^{-1})[47] suggested that historical mining and smelting mining in the catchment had a significant impact on the analyte status in the Derwent Reservoir sediment. Cluster three with only Mn confirmed the dissimilarity between the geochemical behaviour of the analyte and the other PTE. Manganese was the only PTE that had a significant positive correlation with clay- and silt-size particles and, distance, with consequent increase in concentration along the length of the Derwent Reservoir sediments downstream. This indicated that the clay- and silt-size particles were the major carrier (or sink) of Mn in the Derwent Reservoir.

8.4.4. Sediment quality index

The *I-geo*, EF and PI were calculated using the PT PTE concentrations, and the RAC was calculated using the operationally defined fractions of PTE in the sediments as previously defined in section 3.14.4 The weighted mean of the geochemical baseline values of PTE[166, 167] (data in Table B.10 in the appendix) in the Derwent Reservoir sediments were used as the reference background concentrations in the evaluation of the *I-geo*, EF and PI. The mean *I-geo*, mean EF and PI of the PTE in the Derwent Reservoir sediments are represented in Figure 8.21, 8.22 and 8.23, respectively.

Geo-accumulation index

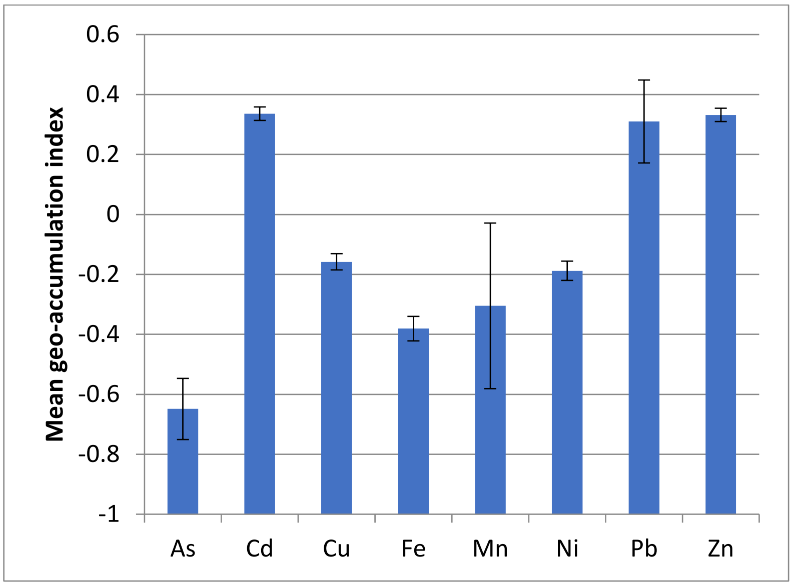


Figure 8.21 Mean geo-accumulation index of the PTE determined in the Derwent Reservoir sediments. Error bars represent standard deviation and n = 5.

Generally, the mean *I-geo* values for the PTE (As, Cu, Fe, Mn and Ni) were less than 0, except for Cd, Pb and Zn, which were greater than 0 but less than 1 in the Derwent Reservoir sediments (Figure 8.21 and Table B.23 in the appendix). This indicated that As, Cu, Fe, Mn and Ni concentrations were at the same levels with the geology of the study area, while the Derwent Reservoir sediments were slightly contaminated by Cd, Pb and Zn[165]. This is consistent with the results of the assessment of *I-geo* for PTE in the Derwent Reservoir catchment sediments in chapter seven of the current study. The *I-geo* values for Cd, Pb and Zn tend to support the results of the comparison of the PT concentrations of these PTE in the Derwent Reservoir sediments with the baseline values in the UK rural soil, which indicated that the analytes were enriched due to historical mining and smelting in the catchment.

Enrichment factor

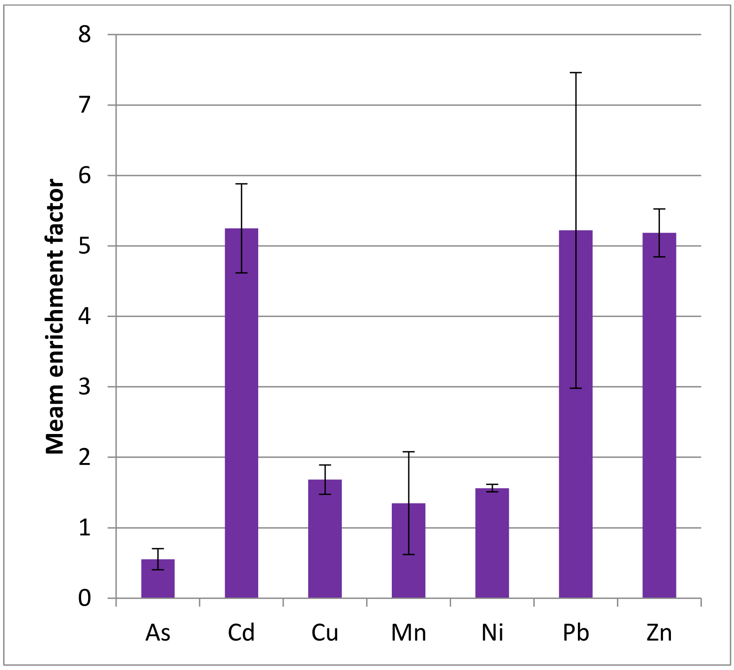


Figure 8.22 Mean enrichment factor of the PTE determined in the Derwent Reservoir sediments. Error bars represent standard deviation and n = 5.

The mean EF values (Figure 8.22 and Table B.24 in the appendix) for As, Cu, Mn and Ni were 0.554, 1.68, 1.35, 1.56 respectively, implying minimal enrichment. The mean EF values for Cd, Pb and Zn were 5.25, 5.22 and 5.19 respectively, implying significant enrichment. Enrichment factors greater than 1.5 are generally accepted as an indication of an anthropogenic input[11, 174, 175]. Generally, the mean EF values obtained for PTE in this study were > 1.5, except for As and Mn, indicating that the Derwent Reservoir sediments were impacted by historical mining and smelting in the catchment area. The significant enrichment of the Derwent Reservoir sediments with Cd, Pb and Zn confirmed that historical mining and smelting of Pb, Zn (probably) and fluorspar processing in the catchment were responsible for the elevated status of PTE in the reservoir.

Pollution index

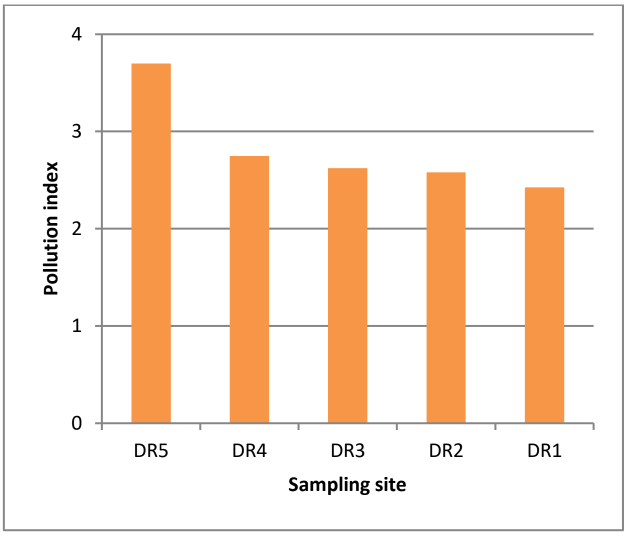


Figure 8.23 Pollution index of PTE in the Derwent Reservoir sediment.

The PI of PTE (Figure 8.23 and Table B.25 in the appendix) revealed that the Derwent Reservoir sediments were heavily (DR5: 3.70) and severely (DR4: 2.75; DR3: 2.62; DR2: 2.58 and DR1: 2.43) polluted[176]. This probably explains why no surviving macrophyte was found in the sediment samples collected from both the deep and shallow areas of the Derwent Reservoir. The PI decrease downstream somewhat replicates the general trend of PTE in the Derwent Reservoir sediment, except for the significant increase in Mn concentration downstream.

Risk assessment code

The risk assessment codes (RAC)[181] of the sediment-bound PTE determined in this study are listed in Table 8.7. The RAC for As, Cu, Fe and Pb were in low risk range (1 – 10 %), except in DR5 where Pb was in the medium risk range (11 – 30 %). This indicated that Pb was less mobile and bioavailable in DR4, DR3, DR2 and DR1 compared to in DR5 with respect to the exchangeable fraction. The RAC for Ni was in the medium risk range (11 – 30 %). Cadmium, Mn and Zn were in the very high risk range (> 50 %), except in DR5 where Zn was in high risk range (31 – 50 %). This indicated that Zn was more mobile in DR4, DR3, DR2 and DR1 compared to DR5. The mean RAC rank order was Cd, Mn (> 50 %: very high risk) > Zn (31- 50 %: high risk) > Ni (11- 30 %: medium risk) > As, Cu, Fe and Pb (1- 10 %: low risk). The RAC accounted only for the exchangeable, but the reducible fraction could also be potentially mobile under reducing redox conditions[219, 223]. Therefore, the considerable amount of Cd, Fe and Pb found in the reducible fraction of the sediment samples, raised further environmental concerns under reducing redox conditions in the Derwent Reservoir.

Table 8.7 Risk assessment code of potentially toxic elements in the Derwent Reservoir sediments

Sediments	Risk assessment code (%)							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
DR5	4.36	55.7	6.05	1.69	67.1	21.4	13.3	43.6
DR4	2.69	59.9	5.45	2.08	78.7	24.8	9.45	51.8
DR3	4.55	59.6	5.53	2.33	78.8	24.1	9.27	50.6
DR2	3.69	63.2	5.13	2.21	80.6	21.9	8.86	50.7
DR1	7.84	54.3	5.92	3.60	80.5	28.0	7.76	53.0
Mean RAC	4.63	58.4	5.62	2.38	77.1	24.0	9.73	49.9

🟩 No risk to water body
🟦 Low risk to water body
🟪 Medium risk to water body
🟨 High risk to water body
🟥 Very high risk to water body

8.5. Conclusion

Generally, the PT concentrations of PTE determined in the Derwent Reservoir sediments in this work were comparable with similar studies[28, 33, 110, 116, 119, 120] (listed in Table 8.1) in reservoirs impacted by historical mining and smelting in the catchment areas around the world. However, the amount of Cd, Pb and Zn in the Derwent Reservoir sediments were higher than the baseline values in the UK rural soil, while the PT concentrations of other PTE were comparable. This indicated that Cd, Pb and Zn concentrations in the Derwent Reservoir sediment were enriched due to historical mining and smelting in the catchment.

The PT concentrations of Cd, Pb and Zn determined in the Derwent Reservoir sediments in 1978 by Harding *et al.*[36] are comparable with the results of this work conducted in 2018, suggesting that these PTE remained approximately at the same levels in the Derwent Reservoir sediments for about 40 years.

The PT concentrations of Cd, Cu, Fe, Ni, Pb and Zn determined in the Derwent Reservoir sediment were higher compared with the amount of the analytes in the inputs, except Pb in input PH. Generally, this suggested that the inputs had limited impacts on the status of Cd, Cu, Fe, Ni, Pb and Zn in the Derwent Reservoir, except the River Derwent (the main source of water) and may be Acton Burn (the other source of water with old mining operations in the draining areas). Although, the PT concentration of Mn in the Derwent Reservoir sediments were comparable with the amount in the inputs DRN1, DRN2, DRN3 and DRN4, the analyte concentration increased towards the dam, suggesting that the main carrier of, or the analyte itself, accumulated towards the dam.

The ecological risk associated with the PT PTE concentrations determined in the Derwent Reservoir sediments was evaluated using the draft SQGs for England and Wales [63, 68]. The PT concentrations of Ni, Pb and Zn in all the Derwent Reservoir sediments investigated were above the PEL values, while Cu was below the TEL value. The PT concentration of As in DR5, DR4, DR3 and DR2 and, DR1 were between the TEL and < PEL and, below the TEL values, respectively. The PT concentration of Cd in DR5, DR4 and DR3 and, DR2 and DR1 were above the PEL and, between the TEL and < PEL values, respectively.

The fractionation patterns of As, Fe, Ni and Pb in the inputs D1 and DRN3 were somewhat similar with the analytes' speciation in the Derwent Reservoir sediment (DR5). The operational speciation of Cd, Cu, Mn and Zn in DR5 were more comparable with the fractionation pattern of the analytes in input DRN3 than in D1. This suggests that the source representing DRN3 may have had significance influence on the status of Cd, Cu, Mn and Zn in the Derwent Reservoir sediments.

Approximately, 99 – 99.5 %, 55 – 65 %, 95 – 99 %, 96 – 98 % and 86 – 92 % of Cd, Cu, Mn, Pb and Zn were found in the labile fractions (exchangeable, reducible and oxidisable fractions) of the Derwent Reservoir sediments respectively, indicating that significant proportions of these PTE were potentially mobile and bioavailable under different redox conditions. There were also high proportion of Cd (54 – 63 %), Mn (73 – 81 %) and Zn (44 – 53 %) in the exchangeable fraction of the Derwent Reservoir sediments, indicating that these analytes may easily enter the water column. Also, there were noticeable increases in the proportion of As, Fe, Ni and Zn in the labile fractions of the Derwent Reservoir sediment downstream, suggesting that the potential mobility and bioavailability of these analytes increased near the dam, and the abstraction point.

The PT concentrations of Cd and Zn in DØ were high compared with the amount in the Derwent Reservoir sediments, coupled with the dissimilarities in their fractionation patterns, suggested that there were accumulation of these analytes in sediments downstream from the dam to an even greater extent than is found within the reservoir sediments.

The concentrations of PTE in the labile fractions of the Derwent Reservoir sediments were compared with SQGs in order to more accurately assess the ecological risk of the sediment-bound PTE. The concentrations of As and Cu in the labile fractions (were below TEL value), Ni (was between the TEL and < PEL values), and Pb and Zn (were above the PEL value) in all the Derwent Reservoir sediment samples investigated. While the concentration of Cd in the labile fractions of DR1, DR2 and DR3 were between the TEL and < PEL, values in DR4 and DR5 were above PEL value.

Arsenic, Cd and Pb showed a significant positive correlation with sand-size particles. There was also a significant negative correlation between the sand-size particles and distance. This indicated that the sand-size particles were the main carrier of As, Cd and Pb in the Derwent Reservoir sediments, as well as explaining the decrease in the PT concentrations of the analytes in the Derwent Reservoir sediments downstream. There was a significant positive correlation between As and Pb, also As and Cd, suggesting that the analytes were mainly from a similar source. Taken together with the decrease in the PT concentrations of As, Cd and Pb downstream and the somewhat similar fractionation pattern of the analytes, this suggested that the River Derwent was the main source of these PTE in the Derwent Reservoir which were carried as particulate load. There was a significant positive correlation between the clay- and silt-size particles and Mn. This indicated that the clay- and silt-size particles were the main carrier (or accumulation site) of Mn in the Derwent Reservoir sediments. There was also a significant positive correlation between the clay- and silt-size particles and distance. This explains the increase in PT concentration of Mn towards the dam. There was a significant positive correlation between Fe and Ni, both analytes also showed similar insignificant correlation with other parameters. This was probably a reflection of the natural association between Fe and Ni due to the similarities in their chemistry. Copper showed significant negative correlation with Mn. This indicated that Cu and Mn had limited influence on each other’s status in the Derwent Reservoir sediments. Zinc had no significant correlation with any of the other PTE, distance, water depth and the different sediment particle size, suggesting there were some further complexities in the analyte source, transport and fate in the Derwent Reservoir compared with other PTE.

The Hierarchical cluster analysis dendogram revealed three main clusters: cluster one (As-Cd-Cu-Pb); cluster two (Fe-Ni-Zn); and cluster three (Mn). Cluster one supports the result of correlation analysis that As, Cd and Pb were from similar source. The inclusion of Cu in cluster one also suggested that the River Derwent had a considerable impact on the status of this analyte in the Derwent Reservoir sediments. Iron and Ni are more closely related, then any of these two analytes with Zn in cluster two. The PT concentrations of Fe and Ni are also comparable with the baseline values in soil, reflecting their natural abundance. This suggested that old mining operations had limited impacts on the status of the Fe and Ni in the Derwent Reservoir. Considering the disparity in cluster two and the PT concentration of Zn, which was higher than the baseline value in soil suggested that old mining operation had a significant impact on the analyte status in the Derwent Reservoir sediment. Cluster three with only Mn tend to confirm the dissimilarity between the geochemical behaviour of the analyte and the other PTE. Generally, the PT concentrations of all the PTE tend to decrease downstream, except Mn which showed a significant increase in concentration, in the Derwent Reservoir sediments towards the dam.

Sediment quality indices (*I-geo*, EF, PI and RAC) were also used to assess the quality and synergetic impacts of PTE in the Derwent Reservoir sediments. The mean *I-geo* values for the PTE (As, Cu, Fe, Mn and Ni) were less than 0, except for Cd, Pb and Zn, which were greater than 0 but less than 1. Consequently, As, Cu, Fe, Mn and Ni concentrations were attributed to the geology of the catchment, while the Derwent Reservoir sediments were slightly contaminated by Cd, Pb and Zn. Similar results were found in the assessment of *I-geo* for PTE in the Derwent Reservoir catchment sediments in chapter seven of this thesis. Generally, the mean EF values obtained for PTE in this study were greater than 1.5, except for As (0.554) and Mn (1.35). Enrichment factor greater than 1.5 is generally accepted as an indication of anthropogenic input[11, 174, 175]. The mean EF values for Cd, Pb and Zn were 5.25, 5.22 and 5.19 respectively, implying significant enrichment. The significant enrichment of the Derwent Reservoir sediments with Cd, Pb and Zn indicated that historical mining and smelting in the catchment had great impacts on the status of PTE in the reservoir. Results obtained from PI assessment revealed that the Derwent Reservoir sediments were heavily (DR5) and severely (DR4, DR3, DR2, and DR1) polluted, which probably explains why no surviving macrophyte was found in the samples.

The mean RAC rank order of PTE in the Derwent Reservoir sediments was Cd, Mn (> 50 %: very high risk) > Zn (31- 50 %: high risk) > Ni (11- 30 %: medium risk) > As, Cu, Fe and Pb (1- 10 %: low risk). The RAC accounted only for the exchangeable fraction, but the reducible fraction can also be potentially mobile under reducing redox conditions[219, 223]. Therefore, the considerable amount of Cd, Fe and Pb found in the reducible fraction of the sediment samples, raised further environmental concerns under reducing redox conditions in the Derwent Reservoir.

9. Conclusions and future work

9.1. Conclusions

Neither the sample pre-treatment procedures nor freeze storage at -18 °C for one year preserved the natural speciation of PTE in the sediments investigated intact. Freeze, air and oven drying at 60 °C caused 8 (8.3 %), 6 (6.3 %) and 6 (6.3 %) significant changes in the operation speciation of PTE in the pretreated samples, respectively, relative to the sediment as received. Overall, oven drying at 110 °C caused the least significant changes (3 (3.1 %) significant changes) in the operational speciation of PTE in the pretreated samples compared with in the sediment as received. Freeze storage at -18 °C for one year had the worst effect with 36 (37.5 %) significant changes in the operational speciation of PTE in the pretreated samples compared with in the sediment as received. Iron and the sediment with the highest proportion of FeOOH were the most prone to sample pre-treatment procedures. This seems to support the suggestions[100, 101, 104] that changes in the operational speciation of PTE in pre-treated sediment is associated mainly with the chemistry of FeOOH.

The operational speciation of the same PTE responded differently to the same sample pre-treament procedure in the three sediments with different matrices investigated. Therefore, it is clear from the results of this work that the response of PTE speciation to sample pre-treatment procedures depends on the sediment nature. In order to increase comparability of results between laboratories using the BCR sequential extraction scheme, harmonisation of sample pre-treatment procedures, and oven drying at 110 °C is recommended by this current work.

Generally, the PT concentrations of PTE determined in the Derwent Reservoir catchment sediments were comparable with the amounts in other river sediments[169, 192, 212-215, 224] with historical mining operations in the catchment areas around the world. The PT concentrations of As, Cu, Mn and Ni in the Derwent catchment sediments were comparable with the baseline values in the UK rural soil, except Cd, Pb and Zn that were higher. The PT concentration of Fe in the Derwent Reservoir was also comparable with the background concentration in global soil. Overall, this suggested that Cd, Pb and Zn concentrations in the Derwent catchment sediments were enriched due to historical mining and smelting in the catchment.

The PT concentrations of As, Cd, Cu, Pb and Zn determined in Bolt's Burn sediment were high compared with the amount determined in the samples above the confluence with the River Derwent. The high PT concentrations of As, Cd, Cu, Pb and Zn in Bolt's Burn apparently increased the concentrations of these PTE in sediments downstream of the confluence compared with upstream of the River Derwent. This is consistent with the report of Burrows *et al*[37] in 1983, which also identified Bolt's Burn as the main source of Cd, Pb and Zn in the River Derwent downstream of the confluence. This indicated that Bolt's Burn is persistently a significant source of PTE in the River Derwent and consequently the Derwent Reservoir.

The PT concentrations of PTE in the Derwent Reservoir sediments were also comparable with the amount in reservoirs sediments[28, 33, 110, 116, 119, 120] with historical mining and smelting in the catchment areas around the world. Like the catchment sediments, it was only the PT concentrations of Cd, Pb and Zn in the Derwent Reservoir sediments that were higher than the baseline values in the UK rural soil.

The PT concentrations of Cd, Cu, Fe, Ni, Pb and Zn determined in the Derwent Reservoir sediment were higher compared with the amount of the analytes in the inputs, except Pb in Pow Hill (one of the small and shallow tributaries) sediment. However, the PT concentration of Pb in adjacent sediment sample collected in the Derwent Reservoir was low compared with the amount of the analyte in Pow Hill. Generally, this suggested that the inputs had limited impacts on the status of Cd, Cu, Fe, Ni, Pb and Zn in the Derwent Reservoir, except the River Derwent (the main source of water) and probably Acton Burn (the other minor source of water with old mining operations in the draining areas). Although, the PT concentration of Mn in the Derwent Reservoir sediments was comparable with the amount of the analyte in the small and shallow tributaries sediments. However, the PT concentration of Mn increased dramatically towards the dam.

The PT concentrations of Cd, Pb and Zn determined in the Derwent Reservoir sediments in this work is comparable with the amount of the analytes determined in the same reservoir sediments in 1978 by Harding *et al*[36]. The striking similarity in the PT concentrations of Cd, Pb and Zn in this work with Harding *et al.*[36] study suggested that these analytes have remained at the same levels in the Derwent

Reservoir sediments for about 40 years. This indicated that the current inputs are not cleaner, so are not diluting the lower older deposit.

The fractionation pattern of As, Fe, Ni and Pb in D1 and DRN3 sediments were somewhat similar with the analytes' speciation in the Derwent Reservoir sediment (DR5: the first sample after the entering of the River Derwent to the Derwent Reservoir). The operational speciation of Cd, Cu, Mn and Zn in DR5 were more comparable with the fractionation pattern of the analytes in DRN3 than in D1. This suggested that Acton Burn may possibly have had a considerable influence on Cd, Cu, Mn, and Zn status in the Derwent Reservoir.

Approximately, 23 – 58 %, 99 – 99.5 %, 55 – 65 %, 46 – 62 %, 95 – 99 %, 96 – 98 % and 86 – 92 % of As, Cd, Cu, Fe, Mn, Pb and Zn were found in the labile fractions (exchangeable, reducible and oxidisable fractions) of the Derwent Reservoir sediments, respectively, indicating that these PTE were potentially mobile and bioavailable under different redox conditions. There was also a noticeable increase in the proportion of As, Cu, Fe, Mn, Ni and Zn in the labile fractions of the Derwent Reservoir sediment near the dam, indicating that the potential mobility and bioavailability of these analytes is higher near the dam compared with upstream of the Derwent Reservoir. High proportion of exchangeable Cd (54 – 63 %), Mn (67 – 81 %) and Zn (44 – 53 %) were determined in the Derwent Reservoir sediments, and this is of concern, because the exchangeable fraction is the most potentially mobile and bioavailable. Consequently, the exchangeable Cd, Mn and Zn may easily enter the water column, especially if the sediment is disturbed.

The fractionation pattern of As, Fe, Mn, Ni and Pb in the Derwent Reservoir sediment samples collected closest to the dam and closest downstream from the reservoir (Derwent Reservoir spill-way) were somewhat similar as expected. Conversely, higher amounts of oxidisable Cu was found in the Derwent Reservoir spill-way sediment compared with the Derwent Reservoir sediments. This suggested that there was a considerable input of Cu in the oxidisable form in the Derwent Reservoir spill-way sediment different from within the Derwent Reservoir, or there was a switch from the reducible to the oxidisable fraction.

There were dissimilarities in the fractionation patterns of Cd and Zn in the Derwent Reservoir spill-way sediment compared with in the sediment collected closest to the dam in the Derwent Reservoir. The dissimilarities in the fractionation patterns taken together with the high PT concentrations of Cd and Zn in the Derwent spill-way sediment compared with the amount in the sediment collected closest to the dam, suggested that there were accumulation or mineralisation/input of the analytes downstream from the dam different from within the Derwent Reservoir.

Arsenic, Cd and Pb showed a significant positive correlation with sand-size particles. This indicated that the sand-size particles were the main carrier of As, Cd and Pb in the Derwent Reservoir sediments. The significant negative correlation between the sand-size particles and distance explains the decrease in As, Cd and Pb PT concentrations towards the dam. There were significant positive correlations between the clay- and silt-size particles and Mn, and the clay- and silt-size particles with distance. This indicated that the clay- and silt-size particles were the main carrier of Mn, as well explains the increase in the analyte concentration in the sediments along the length of the Derwent Reservoir towards the dam. There was a significant positive correlation between Fe and Ni, both analytes also showed similar insignificant correlation with other parameters, reflecting their natural association. The remaining correlation analysis results were either significantly negative or not significant, generally indicating limited impacts among the variables.

The hierarchical cluster analysis dendogram revealed three main clusters: cluster one (As-Cd-Cu-Pb); cluster two (Fe-Ni-Zn); and cluster three (Mn). Cluster one supports the result of correlation analysis indicating As, Cd and Pb in the Derwent Reservoir sediments were mainly from similar sources. The inclusion of Cu in cluster one indicated that the River Derwent was also the main source of the analyte in the Derwent Reservoir. Iron and Ni are more closely related, then any of these two analytes with Zn in cluster two. The PT concentrations of Fe and Ni are also comparable with the baseline values. Consequently, Fe and Ni in cluster two were probably a reflection of the limited impacts of old mining operations on the analytes' status in the Derwent Reservoir. The disparity in cluster two, taken together with the PT concentration of Zn, which was also higher than the baseline value was probably a reflection of the impacts of historical mining and smelting in the catchment on the analyte status in the Derwent Reservoir. Cluster three with only Mn tend to confirm the dissimilarity between the geochemical behaviour of the analyte and the other PTE. Generally, the PT concentrations of all the PTE tend to decrease downstream, except Mn which showed a significant increase in concentration, in the Derwent Reservoir sediments towards the dam.

The mean *I-geo* values for As, Cu, Fe, Mn and Ni were less than 0, except for Cd, Pb and Zn, which were greater than 0 but less than 1 in the Derwent Reservoir sediments. The mean *I-geo* values suggested that the Derwent Reservoir sediment was not contaminated by As, Cu, Fe, Mn and Ni, while slight contamination by Cd, Pb and Zn occurred. A somewhat complementary results were obtained for the mean EF values of PTE in the Derwent Reservoir Sediments. The mean EF values obtained for PTE in this study were greater than 1.5, except for As (0.554) and Mn (1.35). Enrichment factor greater than 1.5 are generally accepted as an indication of anthropogenic input[11, 174, 175]. The mean EF values for Cd, Pb and Zn were 5.25, 5.22 and 5.19 respectively, implying significant enrichment. This is also consistent with the results obtained from the comparison of PTE in the Derwent sediments with the baseline values in UK rural soil.

The PTE PI assessment indicated that the Derwent Reservoir sediments were in heavily to severely polluted range. This probably explains why no surviving macrophyte was found in the sediments, even in the shallow areas. The mean RAC rank order of PTE in the Derwent Reservoir sediments was Cd, Mn (> 50 %: very high risk) > Zn (31- 50 %: high risk) > Ni (11- 30 %: medium risk) > As, Cu, Fe and Pb (1- 10 %: low risk). The RAC accounted only for the exchangeable fraction, but the reducible fraction could also be potentially mobile under reducing redox conditions[219, 223]. Consequently, the considerable amount of Cd, Fe and Pb determined in the reducible fraction of the sediment samples raised further environmental concerns under reducing redox conditions in the Derwent Reservoir.

9.2. Derwent Reservoir and catchment management

The striking similarity in the PT concentrations of Cd, Pb and Zn in the Derwent Reservoir sediments in this work compared with Harding *et al.*[36] study conducted about 40 years ago on the same reservoir sediments, suggested that there were active inputs of particulate matter with unabated PTE levels in the draining areas of the water feeding directly into the Derwent Reservoir, especially, the River Derwent and Acton Burn. In addition, the PT concentrations of Cd, Pb and Zn in the Derwent Reservoir and catchment sediments were higher than the baseline values in the UK rural soil. This is also consistent with the results of the assessment of the sediment quality, using the *I-geo* and EF. Both *I-geo* and EF indicated that the Derwent Reservoir and catchment sediments were slightly contaminated and significantly enriched by Cd, Pb and Zn due to old mining operations in the catchment.

Phytostabilisation of PTE in the Derwent catchment is a potential solution for the mitigation of further inputs of particulate matter with high PTE burden into the Derwent Reservoir through the feeder waters. Whiteheaps (Figure 6.4) is an example of mine waste site in the drainage area of Bolt's Burn that requires urgent attention. Phytostabilisation involves the using of vascular plants with canopies and wide root system[225-228]. Phytostabilisation intercept rainfalls and wind velocity, strengthens the soil (through root growth) and slows surface runoff (thereby increasing water infiltration)[225-228]. Simon *et al.*[227] found that gamma grass and switch grass improved the streambank stability in an experiment conducted in an unstable streambank in Northern Mississippi, USA. There was also higher infiltration under the grass cover during rainfall compared with bare ground. Therefore, phytostabilisation using gamma grass and switch grass have the potential to improve the stability of the Derwent catchment and the associated PTE.

Successful phytostabilisation of PTE in the drainage areas of the Derwent Reservoir catchment should be followed by regular flushing of the reservoir at similar velocity to the water natural flow rate downstream of the dam, most importantly during and after flooding. Flushing is the scouring out of accumulated fine sediment through the lower level outlet in a reservoir[229]. The expectation is that any suspended particulate matter with PTE burden will be flushed out of the Derwent Reservoir. Flushing has been successfully used to remove suspended and accumulated fine sediments in the Gmud Reservoir in Austria and the Gebidem Reservoir in Switzerland[229]. The effectiveness of this approach would need to be balanced against the impacts of flushing on the status of PTE downstream from the reservoir. In addition, sluicing of the Derwent Reservoir could be considered. Sluicing is the release of water fast enough to mobilise bottom sediments[230, 231]. This would also help to decrease the level of PTE contamination in the Derwent Reservoir but would have considerable impacts downstream.

This study also revealed that the clay- and silt-size particles were the major carrier of Mn in the Derwent Reservoir sediments and that the analyte accumulated towards the dam. In addition, the exchangeable Mn in the Derwent Reservoir sediments was 73 – 81 %, indicating the analyte was entering the water column. The exact location of the abstraction point was kept secret for security reasons, but it was somewhere around the dam. Therefore, the abstraction of fine particle sizes should be avoided to minimise the uptake of Mn into the water treatment plant.

9.3. Future work

In order to increase comparability of results between laboratories applying the BCR sequential extraction scheme, harmonisation of sample pre-treatment procedures has been recommended by this study. However, the effect of sample pre-treatment procedures on sediments with different particle size may vary and should be investigated prior to harmonisation.

Apparently, the Derwent Reservoir is contaminated with PTE. The RAC also indicated that the potential mobility of some of the PTE in the Derwent Reservoir sediments are at very high risk, suggesting that the analytes are entering the water column. Therefore, the concentration of PTE in the Derwent Reservoir water should be determined and compared with water quality standards to assess the level of contamination.

It is also likely that fish in the Derwent Reservoir are ingesting the PTE in the water system. This is important because the Derwent Reservoir is also used for trout fishing. Fishermen are currently obliged to remove, weigh and record any fish caught, so these are likely to be eaten. The amount of PTE in the Derwent Reservoir fish should be determined to assess the contamination levels and the implications for human's health.

The fate of PTE in suspended particulate matter is an indication of the current impacts of the analytes from the catchments on the receiving water bodies. This study indicated that the current inputs into the Derwent Reservoir sediments are not cleaner compared with the inputs 40 years ago. To investigate this hypothesis the concentration and speciation of PTE in the suspended particulate matter should be determined and compared with a sediment core profile. This will also provide useful information on the current impacts of the catchments on the status of PTE in the water bodies and a guide for remediation in the drainage areas.

Phytostabilisation has been recommended as a potential solution for decreasing further inputs of particulate matter contaminated with PTE into the Derwent Reservoir due to historical mining and smelting in the catchment. Successful phytostabilisation should be followed by assessing the impacts of flushing on the` status of PTE downstream from the Derwent Reservoir. The results of the investigation should be assessed with consideration of the effectiveness of flushing as an effective approach for PTE control and for monitoring the success of phytostabilisation in the drainage areas of reservoirs with historical mining and smelting in the catchments.

In addition to the Derwent Reservoir, sediments of many other water resources in the UK have been significantly impacted by PTE due to old mining operations in the catchments[63, 106, 211]. Consequent, there is need for studies to help establish a standard SQGs for rivers and reservoirs sediments (although, draft SQGs for England and Wales exist[63]) to drive appropriate catchment management and clean-up in the UK.

Generally, there is need for further investigation of PTE status in areas with historical and current metalliferous mining in the catchment of water resources, since, as shown in the current study, these can significantly impact sediment quality.

References

1. C. S. C. Wong, X. Li and I. Thornton, *Environmental Pollution*, 2006, 142, 1-16.
2. R. A. Wuana and F. E. Okieimen, *International Scholarly Reseearch Notices*, 2011, 2011, 1-17.
3. X. Lu, L. Wang, L. Y. Li, K. Lei, L. Huang and D. Kang, *Journal of Hazardous Materials*, 2010, 173, 744-749.
4. *Chemical ecotoxicology,* J. Paasivirta, Lewis Publishers, Chelsea, 1991.
5. *PHEs, Environment and Human Health,* Eds. C. Bini and J. Bech, Springer, London, 2014.
6. *Water Quality Assessment - a Guide to Use of Biota, Sediment and Water in Environmental Monitoring,* Ed. D. Chapman, University press, Cambridge, 1996.
7. *Sedimentology Process and Product,* M. R. Leeder, Chapman Hall, London, 1992.
8. *Methodologies for Soil and Sediment Fractionation Studies,* A. Sahuquillo, G. Rauret, A. M. Ure, H. Muntau and Ph. Quevauviller, Royal Society of Chemistry, Cambridge UK., 2002.
9. L. K. Pandey, J. Park, D. H. Son, W. Kim, M. S. Islam, S. Choi, H. Lee and T. Han, *Science of The Total Environment*, 2019, 651, 323-333.
10. X. Peng, S. Xiong, W. Ou, Z. Wang, J. Tan, J. Jin, C. Tang, J. Liu and Y. Fan, *Journal of Hazardous Materials*, 2017, 323, 139-146.
11. A. R. Ipeaiyeda and P. C. Onianwa, *Applied Water Science*, 2018, 8, 161.
12. C. Zhang, Yu, G. Zeng, M. Jiang, Z. Yang, F. Cui, M. Zhu, L. Shen and L. Hu, *Environment International*, 2014, 73, 270-281.
13. W. Salomons, N. M. de Rooij, H. Kerdijk and J. Bril, *Hydrobiologia*, 1987, 149, 13-30.
14. *Metal Pollution in Aquatic Environment,* U Forstner and G.T. W. Wittmann, Springer - Verlag, New York, 1981.
15. J. R. Bacon and C. M. Davidson, *Analyst*, 2008, 133, 25- 46.
16. *Chemical Speciation in the Environment*, Eds. A. M. Ure and C. M. Davidson, Blackwell, Oxford, 2nd edn. edn., 2002.

17. P. Lee, M. Kang, S. Yu, K. Ko, K. Ha, S. Shin and J. H. Park, *Chemosphere*, 2017, 184, 74-85.
18. C. Hu, X. Yang, J. Dong and X. Zhang, *Chemosphere*, 2018, 209, 848-856.
19. M. Templeton Douglas, F. Ariese, R. Cornelis, L. Danielsson, H. Muntau, P. Leeuwen and R. Lobinski, in *Pure and Applied Chemistry*, 2000, 72, 1453-1470.
20. A. M. Ure, *Microchimica Acta*, 1991, 104, 49-57.
21. C. R. M. Rao, A. Sahuquillo and J. F. Lopez Sanchez, *Water, Air, and Soil Pollution*, 2008, 189, 291-333.
22. Z. A. Jo and W. D. C., *International Journal of Analytical Chemistry*, 2010, 2010.
23. F. Frémion, B. Mourier, A. Courtin-Nomade, J. Lenain, A. Annouri, P. Fondanèche, T. Hak and F. Bordas, *Science of The Total Environment*, 2017, 605-606, 666-676.
24. Z. Li, L. Wu, H. Zhang, Y. Luo and P. Christie, *Journal of Soils and Sediments*, 2015, 15, 1510-1519.
25. G. G. Vasile, I. G. H. Tanase and C. Dinu, *Analytical Letters*, 2010, 43, 1199-1206.
26. G. Huang, Z. Chen, J. Sun, F. Liu, J. Wang and Y. Zhang, *Environmental Science and Pollution Research*, 2015, 22, 8367-8374.
27. B. Wang, B. Huang, Y. B. Qi, W. Y. Hu and W. X. Sun, *Chinese Chemical Letters*, 2012, 23, 1287-1290.
28. P. Palma, L. Ledo, S. Soares, I. R. Barbosa and P. Alvarenga, *Science of The Total Environment*, 2014, 470–471, 780-790.
29. A. C. Torregroza-Espinosa, E. Martínez-Mera, D. Castañeda-Valbuena, L. C. González-Márquez and F. Torres-Bejarano, *Bulletin of Environmental Contamination and Toxicology*, 2018, 101, 61-67.
30. L. Gao, B. Gao, D. Xu, W. Peng and J. Lu, *Science of The Total Environment*, 2019, 648, 197-205.
31. O. A. Lipatnikova, *Moscow University Geology Bulletin*, 2018, 73, 366-374.
32. P. Palma, L. Ledo and P. Alvarenga, *CATENA*, 2015, 128, 174-184.

33. E. Hiller, Ľ. Jurkovič and M. Šutriepka, *Bulletin of Environmental Contamination and Toxicology*, 2010, 84, 635-640.

34. V. A. Souza and J. C. Wasserman, *Journal of South American Earth Sciences*, 2015, 63, 208-216.

35. H. Zhu, H. Bing, Y. Wu, J. Zhou, H. Sun, J. Wang and X. Wang, *Science of The Total Environment*, 2019, 664, 79-88.

36. J. P. C. Harding and B. A. Whitton, *Water Research*, 1978, 12, 307-316.

37. I. G. Burrows and B. A. Whitton, *Hydrobiologia*, 1983, 106, 263-273.

38. *Allendale, Tynedale and Derwent Lead mines,* R. A. Fairbairn, The Northern Mine Research Society, Keighley, UK., 2000.

39. A. Gopinath, S. M. Nair, N. C. Kumar, K. V. Jayalakshmi and D. Pamalal, *Environmental Earth Sciences*, 2010, 59, 1245-1266.

40. M. L. Alonso Castillo, I. Sánchez Trujillo, E. Vereda Alonso, A. García de Torres and J. M. Cano Pavón, *Marine Pollution Bulletin*, 2013, 76, 427-434.

41. S. Gaiss, D. Amarasiriwardena, D. Alexander and F. Wu, *Environmental Pollution*, 2019, 252, 657-665.

42. *Principle of Biochemistry,* D. L. Nelson, A. L. Lehinger and M. Micheal, Freeman, New York, 2013.

43. L. Fu, X. Lu, K. Niu, J. Tan and J. Chen, *Science of The Total Environment*, 2019, 673, 768-776.

44. *Heavy Metal in Soils*, Ed. B. J. Alloway, Springer, London, 2013.

45. *Trace Elements from Soil to Human,* A. Kabata-Pendis. and A. B. Mukherjee, Springer, Berlin Heidelberg, 2007.

46. *Environmental Chemistry at a Glance,* I. Pulford and H.Flower, Blackwell, Oxford, 2006.

47. UK Soil and Herbage Pollution Survey, S. M. Ross, M. D. Wood, D. Copplestone, M. Warriner and P. Crook, Environment Agency, Bristol, 2007.

48. J. C. Ng, *Environmental Chemistry,* 2005, 2, 146-160.

49. V. K. Sharma and M. Sohn, *Environment International*, 2009, 35, 743-759.

50. D. Mohan and C. U. Pittman Jr, *Journal of Hazardous Materials*, 2007, 142, 1-53.

51. WHO/SDE/WSD/03.04/75/Rev/1, Arsenic in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2011.
52. WHO/SDE/WSH/03.04/80/Rev/1. Cadmium in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2011.
53. WHO/SDE/WSH/03.04/17. Zinc in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2003.
54. L. Järup and A. Åkesson, *Toxicology and Applied Pharmacology*, 2009, 238, 201-208.
55. S. Satarug, J. R. Baker, S. Urbenjapol, M. Haswell-Elkins, P. E. B. Reilly, D. J. Williams and M. R. Moore, *Toxicology Letters*, 2003, 137, 65-83.
56. WHO/SDE/WSH/03.04/88. Copper in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2004.
57. WHO/SDE/WSH/03.04/08. Iron in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2003.
58. WHO/SDE/WSH/03.04/104/Rev/1. Manganese in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2004.
59. Manganese processing, J. H. Downing, https://www.britannica.com/technology/manganese-processing., accessed 18/04/2020
60. L. J. Evans, G. A. Spiers and G. Zhao, *International Journal of Environmental Analytical Chemistry*, 1995, 59, 291-302.
61. WHO/SDE/WSH/05.08/55. Nickel in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2005.
62. WHO/SDE/WSH/03.04/09/Rev/1. Lead in Drinking-water, Background Document for Development of WHO Guidelines for Drinking-water Quality, 2011.
63. Assessment of Metal Mining - Contaminated River Sediments in England and Wales, Environment Agency, UK, November 2008.

64. Directive 2000/60/EC of the European Parliament and of the Council, Establishing a Framework for Community Action in the Field of Water Policy.

65. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy. Amending and Subsequently Repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and Amending Directive 2000/60/EC of the European Parliament and of the Council.

66. G. O. Duodu, A. Goonetilleke and G. A. Ayoko, *Environmental Pollution*, 2016, 219, 1077-1091.

67. ANZECC and ARMCANZ, Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, No. 4, Vol. 1, 2000.

68. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, Canadian Council of Minister of the Environment, Winnipeg, 2001.

69. M. G. Macklin, P. A. Brewer, K. A. Hudson-Edwards, G. Bird, T. J. Coulthard, I. A. Dennis, P. J. Lechler, J. R. Miller and J. N. Turner, *Geomorphology*, 2006, 79, 423-447.

70. *Lake Sediment and Environmental History*. Eds. E. Y. Haworth and J. W. G. Lund, Leicester University Press, Leicester, 1984.

71. G. E. Likens and M. B. Davis, *Internationale Vereinigung Fur Theoretische Und Angewandte Limnologie Verhandlungen*, 1975, 19, 982-993.

72. *Metal Contaminated Aquatic Sediments,* Ed. b. H. E. Allen, Michigan, Ann Arbor, 1995.

73. *Environmental Soil Chemistr,* D. L. Sparks, Academic Press, London, 2003.

74. Soil Pollution, I. A. Mirsal, Springer, Berlin, 2008.

75. Basic Hydrologic Science Course Runoff Processes. The COMMET Program, http://wegc203116.uni-graz.at/meted/hydro/basic/Runoff/print_version/04-soilproperties.htm, accessed: 07/01/2017.

76. *Minerals in Soil Environments*, Eds. J. B. Dixon and S. B. Weed, Soil Science Society of America, Madison, USA, 1989.

77. Encyclopaedia Britannica, https://www.britannica.com/science/clay-mineral., accessed: 19/11/2019.

78. *Environmental Chemistry,* P. O. Neill, Blackie Academic and Professional, London UK, 1998.

79. *Principle of Soil Chemistry*, K. H. Tan, Taylor and Francis Group, USA, 2011.

80. P. Sipos, T. Németh, V. K. Kis and I. Mohai, *Journal of Hazardous Materials*, 2009, 168, 1512-1520.

81. H. B. Bradl, *Journal of Colloid and Interface Science*, 2004, 277, 1-18.

82. X. Xu, R. Huang, J. Liu and Y. Shu, *Environmental Toxicology and Chemistry*, 2019, 38, 464-473.

83. J. Marković, M. Jović, I. Smičiklas, M. Šljivić-Ivanović, A. Onjia, K. Trivunac and A. Popović, *Ecotoxicology and Environmental Safety*, 2019, 174, 305-314.

84. B. E. Reed and M. R. Matsumoto, *Journal of Environmental Engineering*, 1993, 119.

85. *Environmental Trace Analysis: Techniques and Applications*, J. R. Dean, Wiley, Chichester, 2014.

86. A. Tessier, P. G. C. Campbell and M. Bisson, *Analytical Chemistry*, 1979, 51, 844 - 851.

87. B. S. Deborah H. Oughton, G. Riise, H. Lien, G. Ostby and A. Nmrren *ANALYST*, 1992, 117, 481 - 486.

88. A. C. Chang, A. L. Page, J. E. Warneke and E. Grgurevic, *Journal of Environmental Quality*, 1984, 13, 33 - 38.

89. P. O. Scokart, K. Meeus-verdinne and R. De Borger, *International Journal of Environmental Analytical Chemistry*, 1987, 29, 305.

90. M. J. Gibson and J. G. Farmer, *Environmental Pollution Series B, Chemical and Physical*, 1986, 11, 117-135.

91. P. Quevauviller, G. Rauret, J. F. López-Sánchez, R. Rubio, A. Ure and H. Muntau, *Science of The Total Environment*, 1997, 205, 223-234.

92. P. Quevauviller, G. Rauret, H. Muntau, A. M. Ure, R. Rubio, J. F. López-Sánchez, H. D. Fiedler and B. Griepink, *Fresenius' Journal of Analytical Chemistry*, 1994, 349, 808-814.

93. Ph. Quevauviller and G. Rauret and B. Griepink, *International Journal of Environmental Analytical Chemistry*, 1993, 51, 231-235.

94. G. Rauret, J. F. Lopez-Sanchez, A. Sahuquillo, E. Barahona, M. Lachica, A. M. Ure, C. M. Davidson, A. Gomez, D. Luck, J. Bacon, M. Yli-Halla, H. Muntau and Ph. Quevauviller, *Journal of Environmental Monitoring*, 2000, 2, 228-233.

95. G. Rauret, J. F. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure and P. Quevauviller, *Journal of Environmental Monitoring*, 1999, 1, 57-61.

96. R. A. Sutherland, *Analytica Chimica Acta*, 2010, 680, 10-20.

97. G. R. M. Pueyo, D. Luck, M. Yli-Halla, H. Muntau, Ph. Quevauviller and J. F. Lopez-Sanchez, *Journal of Environmental Monitoring*, 2001, 3.

98. A. Sahuquillo, J. F. López-Sánchez, R. Rubio, G. Rauret, R. P. Thomas, C. M. Davidson and A. M. Ure, *Analytica Chimica Acta*, 1999, 382, 317-327.

99. G. Rauret, *Talanta*, 1998, 46, 449-455.

100. F. Rapin, A. Tessier, P. G. C. Campbell and R. Carignan, *Environmental Science and Technology*, 1986, 20, 836-840.

101. F. Bordas and A. C. M. Bourg, *Water, Air, and Soil Pollution*, 1998, 103, 137-149.

102. C. M. Davidson, L. E. Wilson and A. M. Ure, *Fresenius' Journal of Analytical Chemistry*, 1999, 363, 134-136.

103. S. Zhang, S. Wang and X. Shan, *chemical speciation and Bioavailability*, 2001, 13, 69-74.

104. M. Kersten and U. Förstner, *Marine Chemistry*, 1987, 22, 299-312.

105. T. Hjorth, *Analytica Chimica Acta*, 2004, 526, 95-102.

106. P. Byrne, I. Reid and P. J. Wood, *Journal of Soils and Sediments*, 2010, 10, 683-697.

107. A. S. Sobrino-Figueroa, O. F. Becerra-Rueda, V. R. Magallanes-Ordóñez, A. Sánchez-González and A. J. Marmolejo-Rodríguez, *Environmental Monitoring and Assessment*, 2014, 187, 1-8.

108. M. A. Sánchez-Martínez, A. J. Marmolejo-Rodriguez, R. Millian-Gomez, A. Sanchez-Gonzalez, V. R. Magallanes-Ordonez, J. A. Romero-Guadarrama and J. M. Murillo-Jimenez., *Journal of Iberian Geology*, 2013, 39, 97-110.
109. P. Byrne and P. J. Wood and I. Reid, *Critical Reviews in Environmental Science and Technology*, 2012, 42:19, 2017-2077.
110. E. García-Ordiales, S. Covelli, J. M. Esbrí, J. Loredo and P. L. Higueras, *CATENA*, 2016, 147, 394-403.
111. M. Strzebońska, E. Jarosz-Krzemińska and E. Adamiec, *Water, Air and Soil Pollution*, 2017, 228, 141.
112. C. Caplat, H. Texier, D. Barillier and C. Lelievre, *Marine Pollution Bulletin*, 2005, 50, 504-511.
113. E. D. A. Passos, J. C. Alves, I. S. dos Santos, J. d. P. H. Alves, C. A. B. Garcia and A. C. Spinola Costa, *Microchemical Journal*, 2010, 96, 50-57.
114. J. Delgado, C. Barba-Brioso, J. M. Nieto and T. Boski, *Science of The Total Environment*, 2011, 409, 3666-3679.
115. P. Palma, P. Alvarenga, V. L. Palma, R. M. Fernandes, A. M. V. M. Soares and I. R. Barbosa, *Environmental Monitoring and Assessment*, 2010, 165, 539-552.
116. J. M. Besser, W. G. Brumbaugh, C. D. Ivey, C. G. Ingersoll and P. W. Moran, *Archives of Environmental Contamination and Toxicology*, 2008, 54, 557-570.
117. A. J. Paulson, R. J. Wagner, R. F. Sanzolone and S. E. *Open-File Report 2006 - 1350. US Geological Survey, Reston, VA.*, 2006.
118. F. Frémion, F. Bordas, B. Mourier, J. Lenain, T. Kestens and A. Courtin-Nomade, *Science of The Total Environment*, 2016, 547, 282-294.
119. C. Wang, S. Liu, Q. Zhao, L. Deng and S. Dong, *Ecotoxicology and Environmental Safety*, 2012, 82, 32-39.
120. T. Valente, J. A. Grande, M. L. de la Torre, P. Gomes, M. Santisteban, J. Borrego and M. A. Sequeira Braga, *Journal of Geochemical Exploration*, 2015, 157, 66-76.
121. S. Chandrasekaran, S. Ramanathan and T. Basak, *Food Research International*, 2013, 52, 243-261.

122. M. S. Venkatesh and G. S. V. Raghavan, *Biosystems Engineering*, 2004, 88, 1-18.

123. Y. M. Vivekananda M, Hemalatha S, *PHCOG REV*, 2007, 1.

124. J. L. Luque-García and M. D. Luque de Castro, *Talanta*, 2004, 64, 571-577.

125. J. L. Luque-García and M. D. Luque de Castro, *TrAC Trends in Analytical Chemistry*, 2003, 22, 90-98.

126. E. T. Thostenson and T. W. Chou, *Composites Part A: Applied Science and Manufacturing*, 1999, 30, 1055-1071.

127. V. Camel, *TrAC Trends in Analytical Chemistry*, 2000, 19, 229-248.

128. R. Japón-Luján, J. M. Luque-Rodríguez and M. D. Luque de Castro, *Analytical and Bioanalytical Chemistry*, 2006, 385, 753-759.

129. Encyclopaedia Britannica, https://www.britannica.com/technology/magnetron., accesses: 10/102018

130. C. Chan, R. Yusoff, G. Ngoh and F. W. Kung, *Journal of Chromatography A*, 2011, 1218, 6213-6225.

131. Conventional and Microwave Heating Mechanisms, https://www.researchgate.net/figure/237050495_fig2_Figure-1-Conventional-and-microwave-heating-mechanisms., accessed: 26/08/2016.

132. *General Chemistry: Principles, Patterns and Applications*, B. A. Averill and P. Eidredge, FlatWorld, Boston, 2011.

133. V. G. Gude, P. Patil, E. Martinez-Guerra, S. Deng and N. Nirmalakhandan, *Sustainable Chemical Processes*, 2013, 1, 5.

134. *Practical Inductively Coupled plasma Spectroscopy*, J. R. Dean, Wiley, Chichester, 2005.

135. *Encyclopedia of Analytical Chemistry*, Ed. R. A. Meyers, John Wiley and Sons, Chichester, 2000.

136. K. L. Linge and K. E. Jarvis, *Geostandards and Geoanalytical Research*, 2009, 33, 445-467.

137. *ICP-MS Inductively Coupled Mass Spectrometry. A Primer*, https://www.chem-agilent.com/pdf/ICP-MS_Primer.pdf.,accessed: 06/02/2019, 2019.

138. *Practical Guide to ICP-MS,* R. Thomas, Marcel Dekker, New York, USA, 2004.

139. K. L. Linge and K. E. Jarvis, *GEOSTANDARDS and GEOANALYTICAL RESEARCH*, 2009, 33, 445-467.

140. J. L. Todolí and J. M. Mermet, *Spectrochimica Acta Part B: Atomic Spectroscopy,* 2006, 61, 239-283.

141. Z. Wange and P. Yang, *Journal of Analytical Atomic spectrometry,* 2014, 29, 2091-2103.

142. G. Schaldach, L. Berger, I. Razilov and H. Berndt, *Spectrochimica Acta Part B: Atomic Spectroscopy,* 2002, 57, 1505-1520.

143. D. W.ollenweber, S. Strabburg and G. Wünsch, *Fresenius Journal Analytical Chemistry,* 1999, 433-437.

144. British Stardard, Soil Quality - Determination of pH, BS ISO 10390: 2005.

145. British Stardard, Soil Quality - Determination of effective cation exchange capacity and base saturation level using barium chloride solution, BS EN 11260: 2011.

146. British Standard, Particle size analysis - Laser diffraction method, BS ISO 13320: 2009.

147. M. I. limited, Worcestershire, 2007.

148. I. Callesen, H. Keck and T. J. Andersen, *Journal of Soils and Sediments*, 2018, 18, 2500-2510.

149. Sustainable Agriculture for Sub-Saharan Africa, http://www.sassa.org.uk/index.php/Analytical Methods: Carbonate_Titration. accessed: 10/02/2017.

150. British Standard, Extraction of crystalline iron oxides and hydroxides with dithionite, BS EN ISO: 2012.

151. British Stardard, Characterization of sludgees - Determination of the loss on ignition of dry mass. BS EN 12879: 2000.

152. C. M. Davidson, A. Nordon, G. J. Urquhart, F. Ajmone-Marsan, M. Biasioli, A. C. Duarte, E. Diaz-Barrientos, H. Grcman, A. Hodnik, I. Hossack, A. S. Hursthouse, K. Ljung, F. Madrid , E. Otabbong and S. Rodrigues, *International Journal of Environmental Analytical Chemistry,* 2007, 87.

153. G. J. Urquhart, PhD, University of Strathclyde, 2005.

154. *Data Analysis for Chemistry: an Introductory Guide for Students and Laboratory Scientists,* D. B. Hibbert and J. J. Gooding, Oxford University Press, New York, 2006.

155. *Statistics and Chemometrics for Analytical Chemistry,* J. N. Miller, J. C. Miller and R. D. Miller, Pearson, UK, 2018.

156. *Statistics for Evidence-Based Practice in Nursing,* M. Kim and C. Mallory, Jones and Bartlett, Burlington, 2017.

157. *Practical Nonparametric Statistics,* W. J. Conover, John Wiley and Sons, Inc., New York, 1999.

158. *Problem Solving. A statistician's guide,* C. Chatfield, Chapman and Hall, London, 1995.

159. *Design and Analysis of Experiments,* D. C. Montgomery, John Wiley, Hoboken, USA, 2005.

160. O. J. Dunn, *Technometrics*,1964, 6, 241-252.

161. IBM Support, Post hoc comparisons for the Kruskal-Wallis test https://www.ibm.com/support/pages/node/418831, accessed 03/27/2020.

162. Y. Zhao, M. Xu, Q. Liu, Z. Wang, L. Zhao and Y. Chen, *Marine Pollution Bulletin*, 2018, 137, 601-609.

163. R. Mirza, M. Moeinaddini, S. Pourebrahim and M. A. Zahed, *Marine Pollution Bulletin*, 2019, 145, 526-535.

164. Z. Ji, H. Zhang, Y. Zhang, T. Chen, Z. Long, M. Li and Y. Pei, *Chemosphere*, 2019, 124425.

165. G. Muller, *Geo.-journal*, 1969, 2, 108-118.

166. *Regional Geochemistry of the Lake Distric and Adjacent Areas,* British Geological Survey, Keyworth, Nottingham, 1992.

167. *Regional Geochemistry of North-East England,* British Geological Survey, Keyworth, Nottingham, 1996.

168. K. Prabakaran, R. Nagarajan, S. Eswaramoorthi, A. Anandkumar and F. M. Franco, *Chemosphere*, 2019, 219, 933-953.

169. Z. Zhang, Y. Lu, H. Li, Y. Tu, B. Liu and Z. Yang, *Science of The Total Environment*, 2018, 645, 235-243.

170. C. Sun, Z. Zhang, H. Cao, M. Xu and L. Xu, *Chemosphere*, 2019, 219, 538-545.

171. T. Li, G. Sun, C. Yang, K. Liang, S. Ma, L. Huang and W. Luo, *Science of The Total Environment*, 2019, 651, 344-356.

172. M. Saleem, J. Iqbal, G. Akhter and M. H. Shah, *Journal of Geochemical Exploration*, 2018, 184, 199-208.

173. H. M. Guzmán, A. Gómez-Álvarez, J. L. Valenzuela-García, M. A. Encinas-Romero, A. I. Villalba-Atondo and K. K. Encinas-Soto, *Environmental Earth Sciences*, 2019, 78, 145.

174. G. Xu, J. Liu, S. Pei, G. Hu and X. Kong, *Journal of Geochemical Exploration*, 2016, 168, 26-35.

175. Z. Hakima, M. Mohamed, M. Aziza, M. Mehdi, E. B. Meryem, Z. Bendahhou and B. Jean-Francois, *Environmental Science and Pollution Research*, 2017, 24, 7970-7981.

176. Stream, *lake, estuary and ocean pollution*, N. L. Nemerow, OSTI.GOV, USA, 1991.

177. J. P. Brady, G. A. Ayoko, W. N. Martens and A. Goonetilleke, *Environmental Monitoring and Assessment*, 2015, 187, 306.

178. G. O. Duodu, A. Goonetilleke and G. A. Ayoko, *Marine Pollution Bulletin*, 2017, 117, 523-531.

179. Y. Palacios-Torres, J. D. de la Rosa and J. Olivero-Verbel, *Environmental Pollution*, 2019, 113290.

180. Vu, Chi Thanh Lin, Chitsan Shern, Chien-Chuan Yeh, Gavin Le, Van Giang Tran, Huu Tuan, *Ecological Indicators*, 2017, 82, 32-42.

181. G. Perin, M. Lucchese, R. Cirillo, L. Dotta, M. L. Zanette and A. A. Orio, *Metal in the Environment*, 1985, 2, 454 - 456.

182. D. C. Oyeyiola AO, Olayinka KO, and Alo BI, *Environmental Monitoring Assessment*, 2014, 186, 7321 - 7333.

183. S. Consani, M. C. Ianni, L. Cutroneo, E. Dinelli, C. Carbone and M. Capello, *Marine Pollution Bulletin*, 2019, 139, 221-230.

184. S. Kalita, H. P. Sarma and A. Devi, *Environmental Pollution*, 2019, 250, 969 - 980.

185. N. N. Sosa, H. V. Kulkarni, S. Datta, E. Beilinson, C. Porfido, M. Spagnuolo, M. A. Zárate and J. Surber, *Science of The Total Environment*, 2019, 695, 133673.

186. M. R. Nasnodkar and G. N. Nayak, *Arabian Journal of Geosciences*, 2018, 11, 505.

187. D. Rađenović, Đ. Kerkez, D. T. Pilipović, M. Dubovina, N. Grba, D. Krčmar and B. Dalmacija, *Science of The Total Environment*, 2019, 684, 186-195.

188. N. F. Soliman, A. M. Younis and E. M. Elkady, *Chemosphere*, 2019, 222, 165-174.

189. R. A. Cabral-Tena, A. Córdova, F. López-Galindo, A. A. Morales-Aranda, A. Reyes-Mata, A. Soler-Aburto and G. Horta-Puga, *Environmental Monitoring and Assessment*, 2019, 191, 214.

190. Ö. Fındık and M. A. Turan, *Bulletin of Environmental Contamination and Toxicology*, 2012, 88, 193-197.

191. F. Mireles, J. L. Pinedo, J. I. Davila, J. E. Oliva, R. J. Speakman and M. D. Glascock, *Microchemical Journal*, 2011, 99, 20-25.

192. E. Resongles, C. Casiot, R. Freydier, L. Dezileau, J. Viers and F. Elbaz-Poulichet, *Science of The Total Environment*, 2014, 481, 509-521.

193. J. Kumpiene, A. Lagerkvist and C. Maurice, *Waste Management*, 2008, 28, 215-225.

194. J. Sun, R. Yu, G. Hu, G. Su and Y. Zhang, *CATENA*, 2018, 171, 440-449.

195. W. W. Wenzel, N. Kirchbaumer, T. Prohaska, G. Stingeder, E. Lombi and D. C. Adriano, *Analytica Chimica Acta*, 2001, 436, 309-323.

196. C. Mikutta and R. Kretzschmar, *Environmental Science and Technology*, 2011, 45, 9550-9557.

197. E. Neubauer, W. D. C. Schenkeveld, K. L. Plathe, C. Rentenberger, F. von der Kammer, S. M. Kraemer and T. Hofmann, *Science of The Total Environment*, 2013, 461-462, 108-116.

198. M. S. Edgar Hiller, *Journal of Hydrology and Hydromechanics*, 2008, 56, 45 - 58.

199. E. A. Thomson, S. N. Luoma, D. J. Cain and C. Johansson, *Water, Air, and Soil Pollution*, 1980, 14, 215-233.

200. W. Baeyens, F. Monteny, M. Leermakers and S. Bouillon, *Analytical and Bioanalytical Chemistry*, 2003, 376, 890-901.

201. B. L. Larner, A. S. Palmer, A. J. Seen and A. T. Townsend, *Analytica Chimica Acta*, 2008, 608, 147-157.

202. M. Shimizu, J. Zhou, C. Schröder, M. Obst, A. Kappler and T. Borch, *Environmental Science & Technology*, 2013, 47, 13375-13384.

203. M. Chen and L. Q. Ma, *Soil Science Society of America Journal*, 2001, 65, 491-499.

204. F. Chu, S. Gao, X. Zhang, X. Wu and D. Wen, *Applied Physics Letters*, 2019, 115, 073703.

205. F. Chu, X. Zhang, S. Li, H. Jin, J. Zhang, X. Wu and D. Wen, *Physical Review Fluids*, 2019, 4, 071601.

206. S. Wildeman, S. Sterl, C. Sun and D. Lohse, *Physical Review Letters*, 2017, 118, 084101.

207. C. M. Maynard and S. N. Lane, *River Research Applications*, 2012, 28, 692-702.

208. Derwent Reservoir 50 facts, https://www.chroniclelive.co.uk/news/history/50-facts-about-derwent-reservoir-13346588., accessed: 10/09/2019.

209. *Geology of the Northern Pennine Orefield, Tyne to Stainmore*, K. C. Dunham, His Majesty's Stationery Office, London, 1948.

210. Understanding the sources of metals within the catchment feeding Mosswood WTW and associated relationship with weather and underlying geology, R. Lord, Department of Civil and Environmental Engineering, University of Strathclyde, UK, 2015.

211. R. A. Lord and P. A. Morgan, *Environmental Geochemistry and Health*, 2003, 25, 95-104.

212. U. Aleksander-Kwaterczak and E. Helios-Rybicka, *Journal of Soils and Sediments*, 2008, 9, 13.

213. M. G. Macklin, P. A. Brewer, D. Balteanu, T. J. Coulthard, B. Driga, A. J. Howard and S. Zaharia, *Applied Geochemistry*, 2003, 18, 241-257.

214. E. Galán, J. L. Gómez-Ariza, I. González, J. C. Fernández-Caliani, E. Morales and I. Giráldez, *Applied Geochemistry*, 2003, 18, 409-421.

215. C. W. Martin, *CATENA*, 2019, 174, 174-183.

216. A. Gómez-Álvarez, J. L. Valenzuela, S. Aguayo-Salinas, D. Meza-Figueroa, J. Ramírez-Hernándezc and G. Ochoa-Ortega, *Chemical Speciation Bioavailability*, 2007, 19, 25 - 35.

217. K. Hudson-Edwards, M. Macklin and M. Taylor, *Science of The Total Environment*, 1997, 194-195, 437-445.

218. J. S. Rieuwerts, K. Mighanetara, C. B. Braungardt, G. K. Rollinson, D. Pirrie and F. Azizi, *Science of The Total Environment*, 2014, 472, 226-234.

219. C. K. Jain, D. S. Malik and R. Yadav, *Environmental Monitoring and Assessment*, 2007, 130, 129-139.

220. O. I. Davutluoglu, G. Seckin, C. B. Ersu, T. Yilmaz and B. Sari, *Journal of Environmental Management*, 2011, 92, 2250-2259.

221. S. J. Beane, S. D. W. Comber, J. Rieuwerts and P. Long, *Chemosphere*, 2016, 153, 294-306.

222. W. Calmano, J. Hong and U. Forstner, *Water Science and Technology*, 1993, 28, 223-235.

223. M. Jabłońska-Czapla, K. Nocoń, S. Szopa and A. Łyko, *Environmental Monitoring and Assessment*, 2016, 188, 262.

224. D. E. Walling, P. N. Owens, J. Carter, G. J. L. Leeks, S. Lewis, A. A. Meharg and J. Wright, *Applied Geochemistry*, 2003, 18, 195-220.

225. S. Singh - Singh, *International Journal of Green and Herbal Chemistry*, 2012, 133-139.

226. *Advances in Agronomy*, Ed. D. L. Sparks, Academic Press, USA, 2011.

227. A. Simon and A. J. C. Collison, *Earth Surface Processes and Landforms*, 2002, 27, 527-546.

228. J. Vangronsveld, R. Herzig, N. Weyens, J. Boulet, K. Adriaensen, A. Ruttens, T. Thewys, A. Vassilev, E. Meers, E. Nehnevajova, D. Lelie and M. Mench., *Environmental Science Pollution Research*, 2009, 16, 765 - 794.

229. The Feasibility of Flushing Sediment from Reservoirs. Oversea Development Administration of the British Government, E. Atkinson, HR Wallingford, Oxon, November 1997, Project: Reservoir Sedimentation. Project No. R5839.

230. F. Frémion, A. Courtin-Nomade, F. Bordas, J. Lenain, P. Jugé, T. Kestens and B. Mourier, *Science of The Total Environment*, 2016, 562, 201-215.

231. G. M. Kondolf, Y. Gao, G. W. Annandale, G. L. Morris, E. Jiang, J. Zhang, Y. Cao, P. Carling, K. Fu, Q. Guo, R. Hotchkiss, C. Peteuil, T. Sumi, H. Wang, Z. Wang, Z. Wel, B. Wu, C. Wu and C. T. Yang, *Earth's Future*, 2014, 2, 256-280.

Appendix A

Table A.1 Operational speciation, PT concentration (mg kg^{-1} ± SD; n = 3) and % recovery of PTE in sediment SH during sample pre-treatments and storage.

	SH						
	Step	As received	Freeze dried	Air dried	Oven dried at 60 °C	Oven dried at 110 °C	Frozen at -18 °C for one year
As	Exchangeable	0.348 ± 0.406	0.370 ± 0.349	0.205 ± 0.047	0.103 ± 0.051	0.0592 ± 0.0116	0.114 ± 0.012
	Reducible	7.95 ± 12.80	2.67 ± 1.06	0.861 ± 0.675	1.26 ± 1.15	0.652 ± 0.323	3.96 ± 4.91
	Oxidisable	0.239 ± 0.044	0.414 ± 0.102	0.383 ± 0.006	0.243 ± 0.077	0.323 ± 0.277	0.274 ± 0.220
	Residual	29.9 ± 9.5	26.5 ± 4.6	28.6 ± 1.4	32.2 ± 14.7	24.8 ± 2.7	37.5 ± 28.8
	Sum	38.4	30.0	30.1	33.8	25.8	41.8
	Pseudototal	32.6 ± 4.0	34.7 ± 6.4	41.5 ± 8.4	34.4 ± 8.5	34.8 ± 8.4	29.8 ± 4.7
	% recovery	118	87	72	98	74	140
Cd	Exchangeable	0.913 ± 0.297	0.828 ± 0.066	0.847 ± 0.063	0.766 ± 0.096	0.732 ± 0.030	0.645 ± 0.046
	Reducible	1.93 ± 0.612	1.51 ± 0.06	1.67 ± 0.37	1.59 ± 0.221	1.47 ± 0.239	1.88 ± 0.35
	Oxidisable	0.604 ± 0.068	0.689 ± 0.126	0.882 ± 0.415	1.09 ± 0.34	1.36 ± 0.99	0.686 ± 0.129
	Residual	0.961 ± 0.373	0.073 ± 0.021	0.730 ± 0.323	0.921 ± 0.182	0.956 ± 0.063	0.653 ± 0.131
	Sum	4.41	3.1	4.13	4.37	4.52	3.86
	Pseudototal	4.67 ± 0.87	2.38 ± 0.30	3.5 ± 0.8	3.83 ± 0.32	3.80 ± 0.94	4.55 ± 1.02
	% recovery	94	130	118	114	119	85
Cu	Exchangeable	1.14 ± 0.69	0.384 ± 0.147	2.10 ± 0.03	2.00 ± 0.31	0.993 ± 0.121	1.07 ± 0.08
	Reducible	5.01 ± 2.21	3.90 ± 0.30	4.13 ± 0.62	3.72 ± 0.42	4.08 ± 0.55	3.42 ± 0.89
	Oxidisable	4.02 ± 3.23	6.38 ± 2.33	1.70 ± 0.90	2.88 ± 2.20	0.992 ± 0.259	1.77 ± 0.40
	Residual	20.7 ± 7.1	14.7 ± 2.5	20.3 ± 2.4	21.5 ± 6.7	20.5 ± 3.5	10.7 ± 0.3
	Sum	30.9	25.4	28.2	30.1	26.6	17.0
	Pseudototal	28.1 ± 8.2	30.9 ± 13.0	32.1 ± 7.7	28.5 ± 6.1	33.8 ± 6.9	27.5 ± 9.3
	% recovery	110	82	88	106	79	62
Fe	Exchangeable	132 ± 24	66 ± 4	109 ± 12	132 ± 55	92.4 ± 8.0	58.1 ± 38.9
	Reducible	9090 ± 251	7940 ± 398	7070 ± 542	6810 ± 672	6450 ± 915	7850 ± 681
	Oxidisable	2070 ± 567	1940 ± 107	1460 ± 31	1920 ± 411	1310 ± 73	1050 ± 219
	Residual	113000 ± 280	76400 ± 8950	95400 ± 11900	95500 ± 6840	105000 ± 12700	85600 ± 12300
	Sum	124000	86400	104000	104000	113000	94600
	Pseudototal	126000 ± 6560	95300 ± 9320	112000 ± 17300	108000 ± 3930	100000 ± 4850	107000 ±5900
	% recovery	98	91	93	96	113	88

Table A.1 continues;

Operational speciation, PT concentration (mg kg^{-1} ± SD; n = 3) and % recovery of PTE in sediment SH following sample pre-treatments and storage.

	SH						
	Step	As received	Freeze dried	Air dried	Oven dried at 60 °C	Oven dried at 110 °C	Frozen at -18 °C for one year
Mn	Exchangeable	410 ± 19	432 ± 33	313 ± 30	285 ± 45	289 ± 12	415 ± 60
	Reducible	2260 ± 467	2330 ± 163	2250 ± 373	1940 ± 284	2250 ± 376	2990 ± 1080
	Oxidisable	426 ± 82	316 ± 29	313 ± 40	317 ± 49	237 ± 99	307 ± 98
	Residual	1480 ± 190	920 ± 139	1400 ± 242	1280 ± 101	1490 ± 424	1210 ± 130
	Sum	4580	4000	4280	3820	4270	4920
	Pseudototal	5200 ± 550	4410 ± 485	3940 ± 318	4400 ± 718	4350 ± 419	4340 ± 703
	% recovery	88	91	109	87	98	113
Ni	Exchangeable	2.31 ± 0.20	2.20 ± 0.13	1.91 ± 0.05	1.77 ± 0.17	1.84 ± 0.12	1.50 ± 0.12
	Reducible	6.28 ± 0.45	5.78 ± 0.44	5.04 ± 0.72	4.50 ± 0.18	5.16 ± 0.43	5.75 ± 1.09
	Oxidisable	6.48 ± 3.02	4.32 ± 0.19	3.47 ± 0.77	4.00 ± 0.26	2.67 ± 0.21	3.66 ± 0.52
	Residual	28.0 ± 1.3	18.6 ± 1.8	21.7 ± 1.4	23.4 ± 2.9	23.5 ± 3.5	21.8 ± 7.6
	Sum	43.1	30.9	32.1	33.7	33.2	32.7
	Pseudototal	34.9 ± 1.1	30.5 ± 2.7	41.8 ± 8.9	33.3 ± 3.4	33.1 ± 1.1	30.4 ± 3.3
	% recovery	124	101	77	101	100	108
Pb	Exchangeable	296 ± 302	348 ± 181	101 ± 63	124 ± 35	68.6 ± 9.7	98.4 ± 3.7
	Reducible	1570 ± 229	1420 ± 145	1130 ± 117	1160 ± 140	981 ±100	1280 ± 118
	Oxidisable	383 ± 312	234 ± 62	136 ± 43	227 ± 104	136 ± 52	266 ± 128
	Residual	2120 ± 2460	259 ± 19	255 ± 18	550 ± 407	326 ± 63	696 ± 537
	Sum	4370	2260	1620	2060	1510	2340
	Pseudototal	3170 ± 951	2510 ± 366	2670 ± 1020	2100 ± 592	2426 ± 166	2420 ± 759
	% recovery	138	90	61	98	62	97
Zn	Exchangeable	243 ± 74	230 ± 27	185 ± 12	186 ± 30	157 ± 20	206 ± 15
	Reducible	512 ± 136	475 ± 27	449 ± 52	466 ± 64	351 ± 37	542 ± 25
	Oxidisable	171 ± 29	183 ± 14	213 ± 107	285 ± 103	209 ± 126	184 ± 41
	Residual	915 ± 95	566 ± 45.7	779 ± 146	819 ± 83	1000 ± 89	789 ± 109
	Sum	1840	1450	1630	1760	1720	1720
	Pseudototal	1970 ± 428	1380 ± 118	1470 ± 293	1570 ± 136	1640 ± 281	2090 ± 734
	% recovery	93	106	111	112	105	82

Table A.2 Operational speciation, PT concentration (mg kg^{-1} ± SD; n = 3) and % recovery of PTE in sediment DØ during sample pre-treatments and storage.

	DØ						
		As received	Freeze dried	Air dried	Oven dried at 60 °C	Oven dried at 110 °C	Frozen for -18 °C for one year
As	Exchangeable	1.18 ± 0.23	0.799 ± 0.064	0.939 ± 0.098	0.488 ± 0.006	0.523 ± 0.051	2.02 ± 0.10
	Reducible	1.64 ± 0.22	1.20 ± 0.03	1.53 ± 0.05	0.240 ± 0.203	0.635 ± 0.098	1.35 ± 0.12
	Oxidisable	0.330 ± 0.049	0.268 ± 0.054	0.800 ± 0.125	0.373 ± 0.048	0.266 ± 0.015	0.473 ± 0.038
	Residual	2.59 ± 0.50	2.92 ± 0.57	1.67 ± 0.47	1.44 ± 0.48	1.78 ± 0.71	1.12 ± 0.86
	Sum	5.74	5.19	4.94	2.54	3.20	4.96
	Pseudototal	6.78 ± 0.28	7.03 ± 1.53	5.84 ± 0.67	5.34 ± 0.55	5.87 ± 0.83	7.33 ± 0.42
	% recovery	85	74	85	48	55	68
Cd	Exchangeable	0.135 ± 0.06	0.819 ± 0.045	0.944 ± 0.032	0.571 ± 0.053	0.599 ± 0.032	0.105 ± 0.015
	Reducible	3.66 ± 0.20	2.29 ± 0.09	2.71 ± 0.10	2.62 ± 0.04	2.81 ± 0.14	3.97 ± 0.15
	Oxidisable	0.137 ± 0.037	0.215 ± 0.118	0.231 ± 0.150	0.174 ± 0.051	0.0962 ± 0.0147	0.156 ± 0.019
	Residual	0.00488 ± 0.00219	0.0218 ± 0.0116	0. 436 ± 0.211	0.135 ± 0.019	0.0592 ± 0.0151	0.0234 ± 0.0086
	Sum	3.94	3.35	4.32	3.50	3.56	4.25
	Pseudototal	3.90 ± 0.19	2.62 ± 0.22	4.67 ± 0.32	4.01 ± 0.30	3.99 ± 0.38	4.54 ± 0.11
	% recovery	101	128	93	87	89	94
Cu	Exchangeable	0.0439 ± 0.0259	0.0429 ± 0.0412	2.81 ± 0.14	0.919 ± 0.765	0.606 ± 0.041	0.383 ± 0.066
	Reducible	0.990 ± 0.425	2.08 ± 0.29	4.50 ± 3.02	2.74 ± 0.52	2.36 ± 0.22	1.04 ± 0.35
	Oxidisable	4.64 ± 0.16	3.12 ± 0.60	3.98 ± 1.62	1.69 ± 0.53	1.82 ± 0.76	4.80 ± 0.39
	Residual	5.39 ± 1.59	5.25 ± 1.29	12.2 ± 0.9	10.5 ± 0.7	12.4 ± 1.4	7.03 ± 0.85
	Sum	11.1	10.5	23.5	15.9	17.2	13.3
	Pseudototal	12.2 ± 1.4	16.3 ± 8.8	12.2 ± 0.9	18.0 ± 1.7	19.8 ± 1.7	15.9 ± 2.3
	% recovery	91	64	193	88	87	84
Fe	Exchangeable	2850 ± 327	996 ± 31	858 ± 46	698 ± 40	854 ± 17	5000 ± 161
	Reducible	2840 ± 402	3610 ± 145	4480 ± 331	4090 ± 49	4310 ± 128	3000 ± 120
	Oxidisable	915 ± 83	741 ± 42	856 ± 52	854 ± 24	788 ± 9	967 ± 111
	Residual	10400 ± 1780	10900 ± 1520	13400 ± 210	11300 ± 333	13900 ± 1480	11000 ± 1150
	Sum	19800	16300	19600	16900	19900	20000
	Pseudototal	21700 ± 353	18300 ± 246	19700 ± 1020	19300 ± 970	20100 ± 2190	22400 ± 1010
	% recovery	91	90	99	88	99	89

Table A.2 continues;

Operational speciation, PT concentration (mg kg^{-1} ± SD; n = 3) and % recovery of PTE in sediment DØ during sample pre-treatments and storage.

	DØ						
		As received	Freeze dried	Air dried	Oven dried at 60 °C	Oven dried at 110 °C	Frozen for -18 °C for one year
Mn	Exchangeable	483 ± 11	471 ± 57	457 ± 13	430 ± 24	484 ± 31	671 ± 10
	Reducible	86.1 ± 11.7	188 ± 109	131 ± 2	127 ± 3	143 ± 16	101 ± 9
	Oxidisable	28.5 ± 3.7	34.6 ± 5.8	29.9 ± 2.9	30.3 ± 1.9	35.8 ± 3.5	32.4 ± 8.1
	Residual	66.2 ± 10.4	91.3 ± 20.9	144 ± 66	76.7 ± 6.7	116 ± 22	69.0 ± 8.2
	Sum	664	785	762	664	779	873
	Pseudototal	1020 ± 28	744 ± 69	784 ± 27	800 ± 16	801 ± 105	917 ± 61
	% recovery	65	106	97	83	97	95
Ni	Exchangeable	6.79 ± 0.45	4.51 ± 0.14	5.83 ± 0.13	5.03 ± 0.14	5.59 ± 0.22	8.25 ± 0.13
	Reducible	3.04 ± 0.08	2.91 ± 0.14	3.29 ± 0.15	3.05 ± 0.11	3.21 ± 0.14	3.59 ± 0.17
	Oxidisable	4.42 ± 0.16	3.35 ± 0.09	2.84 ± 0.08	3.76 ± 0.10	3.11 ± 0.13	5.07 ± 0.41
	Residual	5.79 ± 1.02	4.85 ± 0.74	6.97 ± 0.46	6.31 ± 0.07	7.44 ± 0.89	7.01 ± 1.08
	Sum	20.0	15.6	18.9	18.2	19.4	23.90
	Pseudototal	20.2 ± 0.9	16.3 ± 0.7	21.7 ± 0.8	20.6 ± 0.4	20.7 ± 2.4	24.3 ± 0.7
	% recovery	99	96	87	88	94	98
Pb	Exchangeable	25.2 ± 4.0	27.6 ± 1.8	6.46 ± 2.38	7.70 ± 0.09	9.52 ± 2.90	11.9 ± 2.6
	Reducible	285 ± 50	196 ± 12.4	246 ± 11	236 ± 11	269 ± 28	388 ± 85
	Oxidisable	40.3 ± 11.2	14.9 ± 4.4	24.9 ± 20.7	16.7 ± 2.8	23.0 ± 13	117 ± 74
	Residual	22.0 ± 6.4	15.9 ± 4.0	30.0 ± 21.1	17.1 ± 1.2	21.9 ± 1.7	57.6 ± 21.4
	Sum	373	254	307	278	323	575
	Pseudototal	479 ± 140	269 ± 9.80	341 ± 32	345 ± 15	347 ± 60	575 ± 206
	% recovery	78	95	90	80	93	100
Zn	Exchangeable	599 ± 50	709 ± 27	733 ± 11	656 ± 23	736 ± 9	616 ± 17
	Reducible	688 ± 64	312 ± 10	363 ± 11	384 ± 27	422 ± 23	872 ± 54
	Oxidisable	69.5 ± 11.5	103 ± 42.	98.3 ± 30.8	95.5 ± 19	67.1 ± 4.7	78.7 ± 6.5
	Residual	46.0 ± 6.7	77.5 ± 25.1	107 ± 73	59.1 ± 2.9	79.9 ± 16.7	55.8 ± 3.3
	Sum	1400	1200	1300	1200	1310	1620
	Pseudototal	1450 ± 45	1220 ± 50	1420 ± 57	1380 ± 38	1420 ± 100	1640 ± 79
	% recovery	97	98	92	86	92	99

Table A.3 Operational speciation, PT concentration (mg kg^{-1} ± SD; n = 3) and % recovery of PTE in sediment D1 during sample pre-treatments and storage.

	D1						
	Step	As received	Freeze dried	Air dried	Oven dried at 60°C	Oven dried at 110 °C	Frozen at -18 °C for one year
As	Exchangeable	0.197 ± 0.092	0.386 ± 0.137	1.18 ± 0.87	0.225 ± 0.261	0.108 ± 0.052	0.0372 ± 0.0227
	Reducible	0.697 ± 0.415	2.84 ± 1.30	3.20 ± 3.26	2.15 ± 1.54	2.94 ± 3.82	1.54 ± 0.14
	Oxidisable	0.284 ± 0.030	2.29 ± 1.83	2.05 ± 1.98	0.410 ± 0.059	2.69 ± 1.87	0.605 ± 0.319
	Residual	9.75 ± 4.38	22.0 ± 8.78	13.2 ± 3.2	8.52 ± 0.21	23.7 ± 3.7	19.0 ± 9.0
	Sum	10.9	27.5	39.7	11.3	29.4	21.2
	Pseudototal	41.0 ± 34	66.9 ± 4.2	56.0 ± 54.5	19.5 ± 2.3	23.2 ± 6.2	33.8 ± 10.4
	% recovery	52	41	71	58	127	63
Cd	Exchangeable	1.78 ± 0.16	1.82 ± 0.10	2.03 ± 0.39	1.33 ± 0.14	1.44 ± 0.06	1.60 ± 0.10
	Reducible	1.29 ± 0.44	1.02 ± 0.08	1.52 ± 0.20	1.29 ± 0.32	1.09 ± 0.16	1.02 ± 0.13
	Oxidisable	0.211 ± 0.11	3.87 ± 1.65	2.78 ± 1.41	9.18 ± 7.75	0.853 ± 0.586	3.05 ± 3.38
	Residual	6.69 ± 3.49	4.75 ± 4.87	3.93 ± 1.86	6.31 ± 1.04	19.8 ± 11.2	5.13 ± 4.21
	Sum	9.97	11.5	10.3	18.1	23.2	10.8
	Pseudototal	11.5 ± 1.3	10.1 ± 1.9	7.90 ± 1.53	34.2 ± 20.6	25.9 ± 11.7	9.76 ± 5.19
	% recovery	87	114	130	53	90	111
Cu	Exchangeable	2.17 ± 1.04	1.08 ± 0.07	3.57 ± 0.41	2.95 ± 0.43	1.90 ± 0.73	1.01 ± 0.08
	Reducible	3.75 ± 0.46	2.10 ± 0.21	3.12 ± 0.86	2.68 ± 0.13	1.78 ± 0.12	2.28 ± 0.69
	Oxidisable	4.10 ± 0.52	13.8 ± 1.3	12.0 ± 7.8	13.0 ± 5.0	8.58 ± 5.32	14.2 ± 17.8
	Residual	25.3 ± 10.2	11.1 ± 1.7	27.3 ± 10.9	38.2 ± 15.1	35.3 ± 9.6	17.6 ± 10.4
	Sum	35.3	28.1	46.0	56.8	48	35.1
	Pseudototal	39.9 ± 19.1	34.1 ± 6.9	29.0 ± 5.4	47.9 ± 10	44.3 ± 11	26.3 ± 6.9
	% recovery	89	82	159	119	108	133
Fe	Exchangeable	104 ± 36	114 ± 41	232 ± 282	80.6 ± 8.6	106 ± 24	42.4 ± 10.7
	Reducible	12100 ± 1400	8560 ± 1050	6440 ± 705	6650 ± 886	8170 ± 1850	7410 ± 1430
	Oxidisable	534 ± 65	2330 ± 509	1440 ± 282	2680 ± 1550	4610 ±1490	1430 ± 764
	Residual	61800 ± 5820	40500 ± 4320	63500 ± 3580	61500 ± 2420	61500 ± 12200	44700 ± 2820
	Sum	74500	51500	71600	70900	74400	53600
	Pseudototal	71100 ± 13200	56700 ± 3500	67800 ± 9040	82400 ± 4220	85400 ± 19100	69000 ± 10700
	% recovery	105	91	106	86	87	78

Table A.3 continues;

Operational speciation, PT concentration (mg kg^{-1} ± SD; n = 3) and % recovery of PTE in sediment D1 during sample pre-treatments and storage.

	D1						
	Step	As received	Freeze dried	Air dried	Oven dried at 60°C	Oven dried at 110 °C	Frozen at -18 °C for one year
Mn	Exchangeable	416 ± 27	501 ± 30	440 ± 31	225 ± 39	290 ± 27	314 ± 23
	Reducible	1880 ± 402	1510 ± 34	1630 ± 212	1550 ± 163	1860 ± 484	1470 ± 255
	Oxidisable	21.0 ± 4.68	247 ± 26	244 ± 50	256 ± 61	298 ± 34	162 ± 51
	Residual	1240 ± 350	475 ± 64	1010 ± 204	1040 ± 106	909 ± 104	688 ± 66
	Sum	3560	2740	3320	3070	3360	2630
	Pseudototal	3420 ± 1070	2870 ± 197	3140 ± 403	3800 ± 331	3360 ± 708	2990 ± 697
	% recovery	104	95	106	81	100	88
Ni	Exchangeable	2.57 ± 0.03	2.75 ± 0.16	2.72 ± 0.93	1.66 ± 0.23	1.98 ± 0.17	2.17 ± 0.09
	Reducible	4.68 ± 0.74	4.01 ± 0.19	5.12 ± 1.82	3.39 ± 0.37	4.89 ± 1.86	4.15 ± 0.78
	Oxidisable	3.03 ± 0.24	4.89 ± 2.23	2.95 ± 0.63	3.23 ± 0.57	3.28 ± 2.11	5.49 ± 3.82
	Residual	13.6 ± 1.0	9.58 ± 0.71	12.2 ± 0.7	11.2 ± 1.3	14.5 ± 3.8	13.0 ± 4.1
	Sum	23.9	21.2	23.0	19.5	24.7	24.8
	Pseudototal	23.7 ± 1.3	21.4 ± 1.1	20.9 ± 2.1	26.2 ± 12.4	23.8 ± 1.7	21.5 ± 3.4
	% recovery	101	99	110	74	104	115
Pb	Exchangeable	401 ± 217	728 ± 199	644 ± 483	305 ± 374	348 ± 256	322 ± 69
	Reducible	3540 ± 1760	1530 ± 261	2450 ± 717	1710 ± 544	1590 ± 153	1430 ± 156
	Oxidisable	28.6 ± 15.9	226 ± 29	204 ± 29	319 ±138	160 ± 71	557 ± 447
	Residual	959 ± 497	328 ± 23	501 ± 83	1260 ± 899	762 ± 267	626 ± 366
	Sum	4930	2810	3800	3590	2860	2940
	Pseudototal	3950 ± 2850	2420 ± 228	3360 ± 188	3960 ± 1800	2670 ± 628	4150 ± 1120
	% recovery	125	116	113	91	107	71
Zn	Exchangeable	432 ± 14	425 ± 42	689 ± 424	288 ± 21	301 ± 27	375 ± 13
	Reducible	381 ± 53	334 ± 419	413 ± 71	341 ± 61	266 ± 34	322 ± 23
	Oxidisable	80.2 ± 31.2	1120 ± 430	909 ± 542	3220 ± 2730	270 ± 141	1260 ± 1510
	Residual	2520 ± 1260	1800 ± 1330	1780 ± 356	6930 ± 6890	5410 ± 4430	2310 ± 1390
	Sum	3420	3680	3790	10800	6250	4270
	Pseudototal	3810 ± 230	3690 ± 831	2760 ± 362	9160 ± 5050	7200 ± 1870	3350 ± 1670
	% recovery	90	100	137	118	87	127

Appendix B

Table B.1 Pseudototal potentially toxic elements concentrations (mg kg^{-1} ± SD; n = 3) in Derwent Reservoir catchment sediments.

Sampling site	Potentially toxic elements							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
D7	3.55 ± 1.0	0.268±0.06	1.49 ± 1.8	14700± 4030	761 ± 208	11.6 ± 3.3	114 ± 27	120 ± 26
D6	4.65 ± 1.4	0.174±0.05	3.68 ± 2.2	15500 ± 4510	728 ± 212	14.2 ± 3.8	41.9 ± 9.9	80.7 ± 21.0
D4	4.34 ± 0.9	0.183±0.03	4.38 ± 1.21	15600 ± 3460	656 ± 146	11.8 ± 2.7	68.0 ± 15.0	91.1 ± 16.1
D5	22.8 ± 0.4	1.92 ± 0.05	41.6 ± 0.6	15200 ± 249	940 ± 17	14.5 ± 0.2	5840 ± 174	918 ± 30
D3	10.4 ± 1.1	2.62 ± 0.20	14.3 ± 1.3	24000 ± 1400	1730 ± 480	17.0 ± 2.9	1690 ± 178	696 ± 20
D2	8.14 ± 1.8	4.13 ± 1.7	10.8 ± 2.2	21200 ± 4230	1190 ± 473	20.7 ± 7.2	1490 ± 929	1190 ± 298
D1	7.18 ± 0.6	1.61 ± 0.1	13.1 ± 1.9	16200 ± 1490	907 ± 80	14.1 ± 1.3	1080 ± 122	515 ± 32
DRN4	8.02 ± 0.5	0.435 ± 0.02	10.6 ± 0.6	25400 ± 1150	1710 ± 74	31.1 ± 1.5	172 ± 9	166 ± 8
DRN3	5.73 ± 0.4	0.560 ± 0.04	9.98 ± 1.0	23000 ± 1410	2420 ± 139	25.2 ± 1.6	1990 ± 135	913 ± 67
DRN2	4.33 ± 0.5	0.557 ± 0.04	7.49 ± 0.7	25700 ± 3150	5340 ± 652	29.0 ± 3.5	470 ± 41	146 ± 9
DRN1	4.04 ± 0.6	0.683 ± 0.1	11.7 ± 1.3	21500 ± 3100	3020 ± 449	39.9 ± 5.9	120 ± 14	140 ± 10
PH	4.22 ± 0.2	0.513 ± 0.03	20.1 ± 0.4	13900 ± 936	530 ± 46	26.7 ± 1.7	2610 ± 165	155 ± 6
BB	4.01 ± 0.3	0.302 ± 0.02	4.82 ± 1.0	23100 ±1400	4170 ± 271	20.8 ± 1.3	149 ± 8.1	120 ± 5
DB	16.1 ± 0.8	20.2 ± 1.0	21.1 ± 1.7	27300 ± 1370	2590 ± 132	28.3 ± 1.5	1870 ± 88	4900 ± 205
DØ	7.09 ± 0.7	6.72 ± 0.6	10.8 ± 1.5	29100 ± 3210	1970 ± 233	32.9 ± 3.7	487 ± 45	1670 ± 130
D1-ED	9.76 ± 1.3	1.58 ± 0.2	11.6 ± 2.2	20000 ± 2.20	1510 ± 243	20.1 ± 3.2	628 ± 91	657 ± 75
WW	6.05 ± 0.2	3.20 ±0.09	9.33 ± 1.0	18400 ± 786	3430 ± 169	22.4 ± 1.0	345 ± 11	815 ± 21
TEL	5.9	0.6	35.7			18	35.0	123
PEL	17.0	3.5	197			35.9	91.3	315

Table B.2 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of As from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
As	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	0.048	1.97	0.35	2.01	0.26	1.63	1.43	41.3	2.09	4.34	20.2	48
D5	0.585	22.8	15.8	1.02	4.32	1.67	12.4	17.5	23.1	22.8	17	101
D1	0.047	17.8	1.29	0.93	0.79	3.62	2.96	31.8	5.09	7.18	7.7	71
DRN3	0.072	0.79	0.8	2.22	0.52	0.78	2.98	18.8	4.37	5.73	6.6	76
D0	0.278	0.35	2.18	2.99	1.25	2.71	2.67	26.4	6.38	7.09	10	70
MEAN % REC												73

Table B.3 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of Cd from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Cd	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	0.14	0.54	0.08	2.77	0.027	9.65	0.006	34.8	0.25	0.18	19.2	140
D5	1.38	1.75	0.39	5.72	0.775	2.55	0.178	22.2	2.74	1.92	2.5	143
D1	0.96	1.16	0.36	1.45	0.611	6.17	0.055	10.3	1.98	1.61	6.9	123
DRN3	0.52	0.34	0.13	1.38	0.066	104	0.012	49.2	0.72	0.560	7.3	129
D0	5.33	0.28	2.67	0.1	0.166	1.25	0.035	10.8	8.2	6.73	8.3	122
MEAN % REC												131

Table B.4 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of Cu from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Cu	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	1.12	44.4	1.06	18	2.27	33.9	6.04	15.1	10.5	4.38	28	240
D5	4.5	2.97	6.28	13.8	43.1	9.08	6.76	23.2	60.7	41.6	1.5	146
D1	1.41	22.5	2.46	3.32	6.81	14.1	6.1	31.8	16.8	13.1	14.6	128
DRN3	1.87	22.5	2.5	6.75	2.29	16.3	7.23	10.4	13.9	9.98	10.3	140
D0	0.89	30.8	0.83	116	8.1	4.6	6.62	27.5	16.3	10.8	13.8	152
											MEAN % REC	161

Table B.5 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of Fe from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Fe	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	18.7	27.5	3329	1.11	1178	1.45	9847	14.7	14400	15600	22.2	92
D5	21.0	58	7053	2	1586	0.1	6920	14	15600	15200	2	103
D1	13.9	6.03	5842	4.54	1444	2.79	8253	23.2	15600	16200	9.2	96
DRN3	189	4.72	8843	2.93	1898	1.66	15646	6.09	26600	23000	6.13	116
D0	630	1.26	18843	2.21	4795	0.78	11126	12.9	35400	29100	11	122
											MEAN % REC	106

Table B.6 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of Mn from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Mn	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	438	5.25	358	0.49	26.3	19.1	62.7	15.3	885	656	22.3	135
D5	595	5.78	688	2.71	49.3	1.47	52.8	15.9	1390	940	1.81	147
D1	348	1.36	744	4.72	16.9	11.2	46.2	22.9	1160	907	8.82	127
DRN3	2821	2.67	455	1.77	127	2.77	140	4.87	3540	2420	5.74	146
D0	2206	1.22	486	2.03	63	2.03	65.8	13.1	2820	1970	11.8	143
											MEAN % REC	140

Table B.7 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of Ni from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Ni	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	1.26	0.65	2.08	1.97	5.1	11.4	6.77	13.5	15.2	11.8	23.2	129
D5	5.28	4.18	5.1	3.94	5.02	1.21	4.57	9.8	20	14.5	1.3	138
D1	2.37	1.87	4.58	0.75	4.68	5.4	4.83	25.1	16.5	14.1	9.2	117
DRN3	5.77	1.04	5.69	1.36	6.19	4.68	12.9	5.3	30.6	25.2	6.5	121
D0	13.9	0.59	14.7	0.72	7.95	2.46	7.68	12.3	44.2	33.0	11.2	134
											MEAN % REC	128

Table B.8 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of Pb from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Pb	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	1.72	7.78	69	1.81	6.54	4.77	7.65	16.3	84.9	68	22.1	125
D5	3980	11.8	3570	8.39	249	4.05	83.7	14.5	7880	5840	2.98	135
D1	130	3.48	960	3.63	103	6.02	40.7	16.3	1230	1080	11.3	114
DRN3	207	4.82	1897	2.74	146	10	77.3	6.7	2330	1990	6.78	117
D0	6.92	1.27	547	1.14	59	2.46	15.5	12.7	629	487	9.24	129
											MEAN % REC	124

Table B.9 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and the % recovery (%REC) of Zn from the BCR sequential extraction scheme in Derwent Reservoir catchment sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Zn	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
D4	15.2	1.49	33.1	19.1	27.6	3.42	37.6	12.6	114	91	17.7	125
D5	455	5.05	300	6.41	300	1.18	153	13.3	1210	918	3.27	132
D1	148	2.06	173	3.2	179	6.98	67.8	8.2	568	515	6.21	110
DRN3	387	1.66	205	2.64	91.9	5.36	330	5.05	1020	913	7.34	111
D0	1105	0.97	665	2.97	120	9.63	76.6	7.62	1970	1670	7.78	118
											MEAN % REC	119

Table B.10 The geochemical baseline concentrations of PTE in the Derwent Reservoir catchment sediments

PTE	Weighted mean (mg kg^{-1})
As	20.4
Cd	1.10
Cu	24.1
Fe	74782
Mn	4096
Ni	47.9
Pb	318
Zn	330

Table B.11 Mean geo-accumulation index (*I-geo)* for PTE in the Derwent Reservoir catchment sediments

PTE	Mean *I-geo*	
	Inputs	Outputs
As	-0.706	-0.529
Cd	-0.402	0.491
Cu	-0.664	-0.460
Fe	-0.768	-0.684
Mn	-0.637	-0.433
Ni	-0.561	-0.451
Pb	-0.0182	0.145
Zn	-0.289	0.465

Table B.12 Mean enrichment factor (EF) for PTE in the Derwent Reservoir catchment sediments

PTE	Mean EF	
	Inputs	Outputs
As	1.40	1.51
Cd	3.74	20.8
Cu	1.80	1.73
Mn	1.58	1.94
Ni	1.69	1.71
Pb	16.6	7.96
Zn	4.73	17.8

Table B.13 Pollution index (PI) for PTE in the Derwent Reservoir catchment sediments

Sampling sites	PI
D7	0.300
D6	0.223
D4	0.226
D5	13.2
D3	3.91
D2	3.53
D1	2.51
DRN4	0.562
DRN3	4.55
DRN2	1.14
DRN1	0.685
PH	5.88
DØ	4.52
DB	13.5
BB	0.781
ED	1.55
WW	2.19

Table B.14 Pseudototal potentially toxic elements concentrations (mg kg^{-1} ± SD; n = 3) in the Derwent Reservoir sediments

Sampling site	Potentially toxic elements							
	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
DR5	8.64 ± 0.87	3.75 ± 0.05	26.4 ± 0.4	40400 ± 1600	1120 ± 11	41.3 ± 1.9	1560 ± 28	1010 ± 15
DR4	8.10 ± 0.19	3.77 ± 0.09	25.1 ± 0.4	50100 ± 1010	3160 ± 39	48.8 ± 1.1	1090 ± 25	1140 ± 21
DR3	6.81 ± 1.16	3.59 ± 0.27	26.2 ± 1.9	46900 ± 3640	2800 ± 248	48.8 ± 4.0	859 ± 67	1100 ± 86
DR2	6.68 ± 0.55	3.48 ± 0.05	25.6 ± 0.2	51100 ± 1160	4250 ± 7	49.0 ± 1.6	907 ± 13	1070 ± 16
DR1	4.73 ± 1.87	3.33 ± 0.46	22.6 ± 4.1	45400 ± 6600	6170 ± 959	45.9 ± 7.0	661 ± 95	1010 ± 143
Mean	6.99	3.58	25.2	46800	3500	46.8	1020	1070

Table B.15 Concentration (mg/kg), % relative standard deviation (% RSD) and % recovery (%REC) of As from the various BCR sequential extraction steps in the Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
As	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	0.406	3.7	2.34	3.3	0.867	3.5	5.70	5.5	9.32	8.64	10	108
DR4	0.250	16	1.20	2.5	0.667	21.	7.20	8.2	9.31	8.10	2.4	115
DR3	0.296	3.1	1.17	1.5	0.628	2.0	4.40	4.0	6.50	6.81	17	95
DR2	0.255	5.4	1.28	0.9	0.672	6.1	4.71	1.1	6.92	6.68	8.2	104
DR1	0.262	9.2	1.01	0.8	0.665	12	1.40	1.1	3.34	4.73	40	71
CRM601	1.59	0.9	7.54	1.0	1.60	1.8	8.40	10	19.14	22.4	4.8	86

Table B.16 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and % recovery (%REC) of Cd from the various BCR sequential extraction steps in Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Cd	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	2.06	0.7	1.39	1.4	0.218	2.3	0.0436	13	3.70	3.74	1.4	99
DR4	2.24	0.7	1.34	1.4	0.132	49	0.0229	3.7	3.74	3.77	2.3	99
DR3	2.08	1.0	1.30	2.7	0.0816	2.0	0.0252	54	3.49	3.58	7.5	97
DR2	2.06	2.3	1.11	0.3	0.0763	14	0.0165	3.4	3.26	3.48	8.2	94
DR1	1.90	1.6	1.51	0.9	0.0806	11	0.0167	66	3.50	3.33	14	105
CRM601	3.88	1.8	3.48	1.0	1.32	3.6	0.430	6.0	9.12	10.1	8.0	90

Table B.17 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and % recovery (%REC) of Cu from the various BCR sequential extraction steps in Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Cu	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	1.56	3.5	6.40	3.0	7.74	1.7	10.0	3.2	25.8	26.4	1.7	98
DR4	1.46	1.8	6.35	0.9	8.23	17.	10.8	14	26.8	25.1	1.8	107
DR3	1.56	4.7	6.97	3.3	7.02	8.5	12.6	20	28.2	26.2	7.3	108
DR2	1.34	4.1	5.87	0.7	7.90	25	11.0	19	26.1	25.6	0.6	102
DR1	1.22	1.1	6.11	3.3	5.98	35	7.29	37	20.6	22.6	18	91
CRM601	10.8	0.02	75.4	1.3	62.4	3.6	51.0	3.6	200	226	8.8	89

Table B.18 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and % recovery (%REC) of Fe from the various BCR sequential extraction steps of Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Fe	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	642	0.8	13400	1.4	3570	2.2	20500	5.7	38100	40400	3.9	94
DR4	1040	2.4	18600	0.4	4100	16	26200	2.3	50000	50100	2.0	100
DR3	1010	3.0	16000	1.3	3320	0.9	23000	3.8	43300	46900	7.8	92
DR2	1050	2.7	16000	1.3	3320	0.9	23000	3.8	43300	46900	7.8	92
DR1	1360	1.1	18800	0.9	3260	17	14400	24	37800	45400	16	83
CRM601	35.5	6.0	4260	1.7	2080	2.4	28400	4.8	34800	40900	7.4	85

Table B.19 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and % recovery (%REC) of Mn from the various BCR sequential extraction steps in Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Mn	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	765	2.0	210	1.4	66.8	2.7	103	9.2	1140	1120	1.0	102
DR4	2580	2.3	416	1.0	132	9.1	150	4.8	3280	3160	1.2	104
DR3	2310	1.8	364	1.8	124	0.6	134	2.6	2930	2800	9.0	105
DR2	3400	2.4	517	0.8	172	11	130	6.3	4220	4240	0.2	99
DR1	5540	0.3	1020	0.6	228	10	90.4	29	6880	6160	16	112
CRM601	269	1.0	190	1.9	58.8	3.1	402	6.0	920	1030	8.0	89

Table B.20 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and % recovery (%REC) of Ni from the various BCR sequential extraction steps in Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Ni	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	7.54	1.3	6.70	2.0	6.92	1.7	14.0	3.1	35.2	41.2	4.7	85
DR4	10.6	3.1	6.72	1.6	7.38	11	18.0	3.8	42.8	48.8	2.3	88
DR3	9.98	2.6	6.60	1.3	7.79	0.4	17.1	11	41.5	48.8	8.2	85
DR2	9.22	2.7	6.02	0.9	8.84	16	18.2	4.3	42.2	48.8	3.2	86
DR1	9.98	0.3	7.50	0.5	8.58	15	9.54	33	35.6	45.9	15	78
CRM601	7.25	5.6	9.88	1.8	6.73	1.7	47.6	3.4	71.4	81.2	8.2	88

Table B.21 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and % recovery (%REC) of Pb from the various BCR sequential extraction steps in Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Pb	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	202	0.4	1200	0.9	92.0	1.2	40.1	3.5	1520	1560	1.8	98
DR4	104	1.3	885	0.3	75.3	5.1	34.9	18	1100	1080	2.3	101
DR3	78.8	2.0	679	1.2	60.5	1.7	31.1	3.1	850	858	7.9	99
DR2	77.4	2.8	710	0.7	64.0	6.2	23.0	15	874	07	1.4	96
DR1	53.6	0.9	574	0.8	49.8	3	13.4	34	691	660	14	105
CRM601	1.61	4.4	194	0.9	25.0	2.8	36.6	9.7	258	273	7.1	94

Table B.22 Concentration (mg kg^{-1}), % relative standard deviation (% RSD) and % recovery (%REC) of Zn from the various BCR sequential extraction steps in Derwent reservoir sediments

	EXCHANGEABLE FRACTION		REDUCIBLE FRACTION		OXIDISABLE FRACTION		RESIDUAL FRACTION			PSEUDOTOTAL		
Zn	Mean	%RSD	Mean	%RSD	Mean	%RSD	Mean	%RSD	SUM	Mean	%RSD	%REC
DR5	440	1.6	254	1.6	178	1.7	137	4.7	1010	1010	2.0	100
DR4	590	2.5	238	1.2	168	9.4	143	6.7	1140	1140	2.0	100
DR3	558	1.7	234	0.7	174	0.7	136	1.3	1100	1100	8.0	100
DR2	523	3.3	222	0.9	172	11	114	10	1030	1070	2.0	96
DR1	554	0.6	237	0.2	173.	12	82.7	27	1050	1010	14	103
CRM601	256	1.5	244	1.6	116	2.1	164	4.2	783	858	7.6	91

Table B.23 Mean geo-accumulation index (*I-geo)* for PTE in the Derwent Reservoir sediments

PTE	Mean *I-geo*
As	-0.649
Cd	0.336
Cu	-0.158
Fe	-0.381
Mn	-0.305
Ni	-0.188
Pb	0.310
Zn	0.332

Table B.24 Mean enrichment factor (EF) for PTE in the Derwent Reservoir sediments

PTE	Mean EF
As	0.554
Cd	5.25
Cu	1.68
Mn	1.35
Ni	1.56
Pb	5.22
Zn	5.19

Table B.25 Pollution index (PI) for PTE in the Derwent Reservoir sediments

Sampling sites	PI
DR5	3.70
DR4	2.75
DR3	2.62
DR2	2.58
DR1	2.43