THE UNIVERSITY *of* EDINBURGH

The mobility and speciation of chromium in the urban-industrial environment

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Declaration

I declare that this thesis has been composed solely by myself and that it has not been submitted, in whole or in part, in any previous application for a degree. Except where states otherwise by reference or acknowledgment, the work presented is entirely my own.

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Firstly, I would also like to thank the NERC E^3 DTP and the BGS for funding this project.

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Abstract

Chromium (Cr) is an important metal which was has been used since the industrial revolution for various applications. It can be toxic dependant on the species present and the production of Cr chemicals has left localised Cr pollution where waste from Cr chemical works was dumped. The fate of Cr, which has leached out of these waste sites, with soils, sediments and waters is dependent on its speciation and the process that leads to the changes in Cr species in the environment is currently poorly understood. The city of Glasgow in the West of Scotland was recognised as an industrial centre from the industrial revolution in the 1800s through to the late 1960s. It hosted large amounts of heavy industry gaining it a reputation as industrial powerhouse. Some of the first industries to appear along the banks of the River Clyde were weaving and dying industries. For the dying process Cr chemicals were required to fix colour pigments to the cloth so in the 1820s J&J White's Shawfield Chromium Works started to meet this demand. White developed and patented a novel way to extract Cr from chromite ore which lead to it becoming one of the largest producers of Cr chemicals in the world during its heyday. This new process involved roasting the ore with a diluent, an alkali carbonate, improving the penetration of air into the melt and leading to the more efficient conversion of insoluble trivalent Cr (Cr(III)) to soluble hexavalent Cr (Cr(VI)). This soluble Cr(VI) was leached out and converted to the desired product. This high lime process led to the production of a waste product, called chromite ore processing residue (COPR), which is highly alkaline and contained approximately 4% (w/w) of Cr of which ~30% is in the form of the significantly more toxic Cr(VI). The waste material was used as backfill at certain locations in the south of the city, including Polmadie, where it was used in football terracing and to fill in old pits. It is estimated that there was 2.5 million tonnes of this toxic waste material produced before the factory shut in 1968. Research in the late 1990s and early 2000s characterised COPR in the waste disposal sites and ways to remediate it but there was limited focus on the fate of Cr once it gets into the wider environment. This project seeks to determine the biogeochemical and environmental factors that influence the preservation of Cr(VI) and its transport once it leaves the waste disposal sites, along with its bioaccessibility in Cr polluted soils.

The study site was the Polmadie Burn, a small stream which runs alongside Richmond Park and which drains areas of COPR waste before meeting the River Clyde. Previous work has demonstrated that it has transported a large quantity of Cr from these former industrial sites into the River Clyde and concentrations therein are close to or sometimes slightly in excess of UK Environmental Quality Standards for surface waters. Initial characterisation in this study determined Cr(VI) concentrations of <4180 μg L^{-1} in the Polmadie Burn waters, <1200 mg kg^{-1} in the underlying sediments, and <2190 mg kg^{-1} in the banking soils. Total Cr concentrations in the soil and sediment were <6310 and <14900 mg kg^{-1}, respectively. Sequential extraction results showed that 63 ± 10 and 52 ± 5 % of Cr is associated with organic matter in the soils and sediments, respectively, with most of the rest associated with iron hydroxides.

The drying of soil and sediments can alter their physical and chemical properties leading to release of metals bound to them. To investigate the drying of Polmadie soils and sediments due to prolonged dry spells, drying experiments were constructed to investigate the release of Cr when soil and sediments were rewetted after different drying periods. These results showed that, in general, low concentrations of Cr were released with a maximum of 0.11 and 0.008% of the Cr released from soils and sediments, respectively. They also reveal that drying of sediments resulted in the release of Cr(VI) due to the oxidation of Cr(III) by freshly precipitated manganese oxides which form in the sediment. This process was not observed in the soils. Sorption of Cr(VI) to the soil, however, was a much more favourable process as over 96% of Cr(VI) was sorbed to the soil after a 48 h shaking period. This was not a reversible process as Cr(VI) sorbed to the banking soil was not released when the Cr loaded soil was shaken in 0.01 M calcium chloride solution showing that the Polmadie soils are a sink for Cr(VI) providing a natural resource for immobilising Cr(VI) in ground water.

The inhalation bioaccessibility of Cr in Polmadie banking soils was quantified to estimate the risk to human health. It was found that 59.3 ± 40 and 16.3 ± 3 mg kg^{-1} of bioaccessible Cr and Cr(VI), respectively, was present in the <10 μm fraction of the banking soil. This was equivalent to 15.1 ± 10 and 19.0 ± 8.3% of the total Cr and the total Cr(VI) in the <10 μm fraction being bioaccessible via inhalation. The risk to people living around the area was concluded to be minimal as the potential for creating inhalable dust from the soil was low but further work is required looking into the airborne concentrations of Cr in the area to fully quantify the airborne Cr concentrations.

This research has examined the fate of Cr in the environment once it leaches out of COPR waste. It has shown that low concentrations of Cr is leached from the Polmadie sediments and soils with the organic rich soil is able to irreversibly sorb Cr(VI) from solution. Upon drying both the soils and sediments release a small proportion of the Cr in them when rewetting. This shows that the Polmadie Burn sediment and banking soil is a sink for Cr by immobilising it and also lowers its toxicity by reducing soluble Cr(VI) to Cr(III).

Although this research has used the Polmadie Burn as a case study it gives a better understanding of the fate and species of Cr in organic rich soils. It will also help predict the mobility and speciation of Cr present in such soils giving a better understanding of the risk of Cr in these soils to human health.

Lay Summary

The city of Glasgow, Scotland was an industrial centre since the industrial revolution in the 1800s until the late 1960s. During this time it hosted large amounts of heavy industry and one such industry was the manufacturing of chromium chemicals, originally for the textile industry. A new way of extracting chromium from its ore was developed by J&J White which helped turn their chromium chemical factory, which operated between from the 1820s until 1968, the largest in the world during its heyday. In its ore, chromium is found in an immobile which has negligible toxic effects but the extraction process transformed chromium in the ore to a form which is very mobile with a high toxicity. Contact with this toxic form of chromium can cause skin irritation and lung cancer. The waste material produced from the extraction process lead to ~2.5 million tonnes of waste, which contains high concentrations of toxic chromium, being spread around Glasgow. Near the site of the former chromium factory, the Polmadie Burn, a tributary of the River Clyde, has chromium concentrations which are approximately 1000 times higher than the maximum concentrations permitted by the Scottish Environment Protection Agency. Likewise, the Polmadie banking soils and stream sediments contain large amounts of chromium. Due to the large amount of chromium in the area and the potential impact it may have on human health, it is important to determine how much there is, especially the amount in toxic forms, and identify any processes which can convert chromium between toxic and non-toxic species. This project found that the banking soils and sediment tended to convert toxic chromium to less toxic forms and also immobilised it. There was however still significant amounts of toxic chromium found in the soils and sediments. Chromium leached from the soils and sediments was very low and was released generally in the less-toxic form. Laboratory experiments simulating the amount of toxic chromium released by dust into the lungs suggested that there might be an unacceptable risk of developing cancer if exposed to the dust daily. However, due to the secluded nature of the soils and their high moisture content of the soil resulting in low dust formation, the results from this experiment should be used cautiously with further study in this area required. Overall, the soils and sediment demonstrated the ability act as a sink for chromium and they released very small amounts during leaching.

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1 Introduction

1.1 Overview

Chromium (Cr), a first row transition metal, was initially isolated from the mineral crocoite ($PbCrO_4$) in 1797 by Louis-Nicholas Vauquelin (Emsley, 2012). Its name originates from the Greek word chroma, meaning colour, as many Cr-containing minerals are intensely coloured, e.g. chromium chloride hydrate is dark green and sodium chromate is bright yellow. These colour properties were first exploited in the 18th century, when "red lead" minerals were used as pigments in paints in the western world. In the early 19th century, Cr's complexing properties were recognised and it was introduced in the textile industry as a mordant, i.e. to fix dyes onto the fabric. By the mid-to-late 19th century Cr was also being used for chrome plating, leather tanning and was starting to be used in steel manufacturing (Darrie, 2001). In the early 20th century the invention of the electric arc furnace facilitated Cr being used to harden and improve the resistance of steel to oxidation. Currently, about 85% of Cr produced is used in the metallurgical industry, mainly in steel production. Modern steel contains between 11-30% Cr by weight, with its average content being 18% (USGS, 2010).

Chromium is the 10th most abundant element on Earth and is found in greater concentrations in mafic and ultramafic igneous rocks, such as peridotite, than in more felsic igneous rocks, such as granite, or in sedimentary rocks (Fendorf, 1995). The ore chromite, $(Fe,Mg)Cr_2O_4$, is the main component of the igneous cumulate rock, chromite, which occurs as orthocumulate lenses within peridotite. South Africa, along with India, Kazakhstan and Turkey, host the majority of the world's chromite reserves (48 million tonnes), and as such are currently the main ore producers (Parirenyatwa *et al.*, 2016). In recent years, the annual production of Cr ore has been rising, from 9.6 million tons in 1994 to 29 million tons in 2014 (U.S. Geological Survey, 2015,1996, Brown, 2018).

Chromium can exist in several oxidation states (-II to +VI) but only two are commonly found in the environment: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) (Emsley, 2012). These have distinctly different chemical and biological properties. Chromium(III), as found in chromite ore, is generally the more stable oxidation state under most environmental conditions, meaning its compounds typically have low solubility and are stable at low-to-neutral pH (Dhal *et al.*, 2013). Furthermore, Cr(III) is an essential trace element which plays an important part in glucose metabolism in mammals. In contrast, Cr(VI) species are generally much more soluble, are stable at high pH, and are highly toxic to mammals. In addition to pH, the ratio of Cr(III) to Cr(VI) depends upon dissolved oxygen concentration (Kotaś and Stasicka, 2000). Under strongly oxidising conditions anionic Cr(VI) species, e.g. $HCrO_4^-$ and CrO_4^{2-}, are stable over the entire pH range, whilst under reducing conditions the cationic and zero-charge Cr(III) species, e.g. Cr^{3+} and $Cr(OH)_3^0$, respectively, are favoured, with the latter being readily removed from solution around neutral pH conditions. These redox processes are important in controlling the mobility of Cr in the environment, therefore the reduction process is often exploited in strategies to minimise the impact of the highly toxic Cr(VI) species to the environment and human health (Rai *et al.*, 1989).

By contrast to reduction, oxidation, i.e. conversion of insoluble Cr(III) to soluble Cr(VI), was at the basis of the energy-intensive industrial processes used to extract Cr from its ore. An alkali carbonate, e.g. Na_2CO_3, was added before the ore was roasted in a high temperature (e.g. 1150°C) furnace. Oxygen from air was used to oxidise Cr(III) to Cr(VI), but the conversion efficiency was initially low because the highly viscous molten ore/carbonate mixture did not allow air to penetrate. Consequently, quicklime (CaO) or dolomite ($CaMgCO_3$) was added as a diluent to allow the air to penetrate the mixture thus ensuring more efficient Cr oxidation (Darrie, 2001). Sodium chromate, the primary product used for the production of chromium chemicals, was then leached out of the roasted calcine using water. This "high lime" alkali roasting process to oxidise chromite ore to dichromate was used by J&J White at their chemical works in Glasgow, Scotland, to produce Cr chemicals from 1830-1968. The Fe- and Mg-rich waste material, known as chromite ore processing residue (COPR), contains entrained Cr(VI) as well as unreacted chromite ore. Its disposal in landfill sites has led to elevated concentrations of both Cr(III) and Cr(VI) in waters, soils and sediments in southeast Glasgow and north Lanarkshire, Scotland. The same process was also used in Bolton, England; New Jersey, USA; Poland; China and India (Ding *et al.*, 2016). Although this process is now banned in many developed countries due to the hazardous waste generated, it is still being used in many developing countries such as China (Wang *et al.*, 2007).

Over the period 1999-2010, several groups of researchers, mainly in the UK and the US, published research focused on: (i) determining the composition of COPR and characterising its leaching behaviour (Geelhoed *et al.*, 2002, Farmer *et al.*, 2002), (ii) developing and implementing strategies to remediate COPR-contaminated sites

(Farmer *et al.*, 1999, Graham *et al.*, 2006); and (iii) evaluating the risk to human health associated with exposure to COPR-derived Cr (Broadway *et al.*, 2010, Farmer and Jarvis, 2009)

In the late 2000s through to mid-2010s in Glasgow, some of the most heavily COPR-contaminated sites were: (i) capped to minimise infiltration/leaching by rainwater and/or resuspension of fine dusts or; (ii) chemically remediated by converting Cr(VI) to Cr(III) and achieving exiting groundwater Cr(VI) concentrations of less than the relevant environmental quality standards. The widespread historical use of COPR as a fill material, however, means that there are numerous other sites which are still releasing Cr(VI) to ground- and surface waters. For example, the Polmadie Burn in southeast Glasgow has sediment Cr concentrations of up to ~3500 mg kg^{-1} (Whalley *et al.*, 1999), and surface water Cr concentrations of up to ~2200 µg L^{-1} (Palumbo-Roe *et al.*, 2017). These are at least an order of magnitude higher than the respective environmental quality standards in the UK and elsewhere. Therefore, there is increasing concern about a proposal to divert water away from the Polmadie Burn as part of a new water treatment plant in the locality. The impacts of such changes on Cr behaviour in the Polmadie sediment-water-banking soil system are currently unknown. Highly reducing conditions currently prevail in the sediments, consequently one area of uncertainty is the impact of drying out and subsequent oxidative processes on the sediment-bound Cr, and the extent to which Cr(VI) might be released to the Burn waters, which then flow into the River Clyde. A second question relates to the drying out of sediments, but also of the newly exposed banking soils and the risk that their atmospheric suspension might pose to human health.

1.2 Legacy of chromium chemical production

1.2.1 Introduction

Although steelworks, chromium electroplating, and leather tanning industries all produce(d) Cr wastes, the focus of this PhD was on Cr wastes generated by chemical manufacturing. Therefore, this section gives a brief overview of the history of Cr chemical production, and then a site-specific account of the legacy of Cr contamination emanating from the J&J White's Chromium Chemical Works in Glasgow.

Commercial production of Cr chemicals can be traced back to the early 1800s in the US and the UK (Udy, 1957). The source material was chromite which has the formula (Mg, Fe) (Al, Cr, Fe)$_2$O$_4$. It is frequently described as having a spinel structure (AB$_2$O$_4$) where Mg(II) can substitute to varying extents for Fe(II), whilst Fe(III) and Cr(III) substitute for Al(III). The structure of pure (non-substituted) Fe$_2$Cr$_2$O$_4$, where Fe(II) occupies tetrahedral sites and Cr(III) occupies octahedral sites, is shown in Figure 1-1 below.

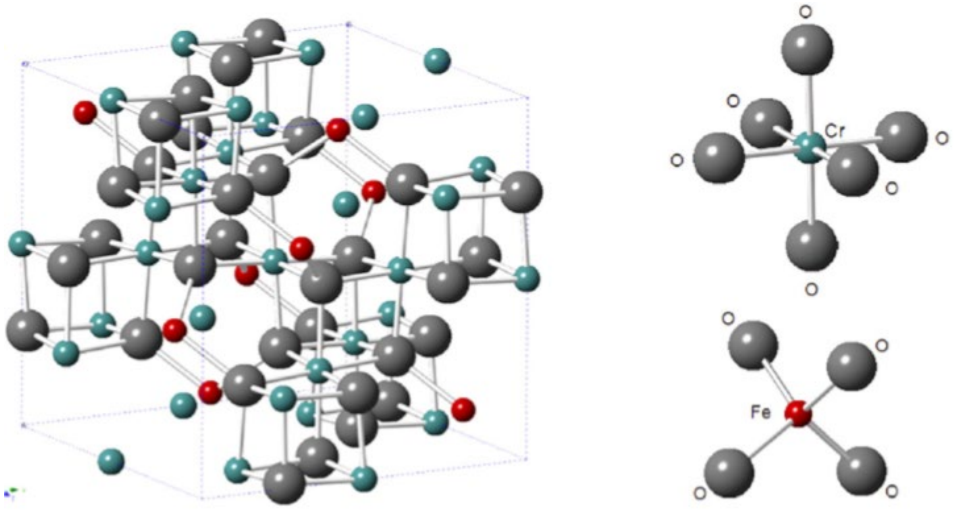

Figure 1-1: Spinel structure of FeCr$_2$O$_4$ (O = grey, Fe = red, Cr = green) (Parirenyatwa et al., 2017)

Chromite minerals may not be pure spinels and instead may occur as a mixture of spinel and corundum oxides (Al$_2$O$_3$, Fe$_2$O$_3$) (Darrie, 2001). In addition, there are also many other impurities present and a typical composition for a "chemical-grade" ore from South Africa, expressed in terms of the metal oxides, is shown in Table 1-1 below.

Table 1-1: Comparative composition of $FeCr_2O_4$ and South African chromite ore (expressed in terms of the metal oxides) (Parirenyatwa et al., 2017)

Metal Oxide	Theoretical % composition for pure $FeCr_2O_4$	% Composition
Al_2O_3		7.15
Cr_2O_3	68	48.8
Fe_2O_3		31.3
FeO	32	
MgO		7.03
CaO		0.54
MnO		0.29
SiO_2		3.45*
TiO_2		0.70
V_2O_5		0.31

*usually a SiO_2 content of <1% is favoured for chemical-grade ores to limit the formation of alkali and alkaline earth silicates.

In summary, chromite ores are Fe, Al, Mg and Si-rich with a Cr_2O_3 content varying from 15-65% w/w (Udy, 1957, Darrie, 2001). This presented challenges for Cr chemical manufacturing because the Cr was difficult to extract into pure forms (mainly dichromates) from these materials.

The extraction process evolved over time but early reports record “opening up the ore with soda and lime” in a roasting kiln (Darrie, 2001). For reasons that will be discussed in Section 1.2.2.2, lime addition became an integral part of the processes (known as “high-lime” methods) adopted in the US and the UK during the 1800s, until they were phased out in the 1960s because of the hazardous nature of the resulting waste products. Lime addition, however, continues to be used in developing countries such as China, Kazakhstan, India and Pakistan, although steps are now being taken in these countries to move to lime-free Cr chemical production (Wang *et al.*, 2007). A common feature of all processes throughout the production history, however, has been high temperature (900-1200°C) alkaline roasting with the preferred alkali metal source being Na_2CO_3.

As a consequence of the presence of large amounts of impurities and the high throughputs of ore, millions of tonnes of hazardous wastes, known as chromite ore processing residue (COPR), have been produced. Historically, approximately 1 tonne of COPR was generated per tonne of Na_2CrO_4 produced, and the COPR typically contained 8-12% Cr_2O_3 (w/w) (Darrie, 2001). Most COPR was used as back-fill due to its sandy, granular structure, e.g. for clay pits, other surface mining pits, or placed in poorly constrained landfill sites; and these locations are now often referred to as the "contaminant legacy" of Cr chemicals production. Even in the early 2000s, it was estimated that up to 600 kT y^{-1} COPR was still being generated collectively by "high-lime" Cr chemical works around the world (Darrie, 2001), and so similar concerns remain about the disposal of such highly alkaline, Cr-containing materials.

In Hudson County, USA, there were over 200 areas which contain COPR where it was used as a fill material because of its favourable physical properties (Wazna *et al.* 2007). Approximately 800,000 m^3 of COPR waste was dumped into an area of the Hudson Bay Estuary between 1905 and 1954 (Magar *et al.*, 2008).

In China approximately 6 million tonnes of COPR has been produced with disposal often occurring near densely populated areas (Min *et al.*, 2017). In India, due to the demand of Cr chemicals for leather tanning, large amounts of Cr chemicals are produced, often using the high lime extraction process (Matern *et al.*, 2016). A waste disposal site near a former Cr chemical works, which was in operation between ~1980 and 2005, contained an estimated 30,000 tonnes of waste. Other sites are still producing Cr chemical in India, with the waste material often being used in the construction of roads and other earth works due to the desirable physical properties of COPR.

1.2.2 Legacy of J&J White's Chromium Chemical Works in Glasgow, Scotland

1.2.2.1 History of the Chemical Works

Glasgow, in the former industrial belt of Scotland, has been left with a legacy of Cr contamination. This occurs in the south of the city due to the operation of J&J White's Chemical Works which, in the 19th and early 20th centuries, was a world leader in the manufacture of Cr chemicals. The Shawfield Chemical works started as a soap and soda manufacturing factory in the early 1800s but this business failed. In 1830 the White family started manufacturing potassium dichromate on the site which was originally used by local printers and dyers, who used it as a mordant for fixing many dyes to cloth and also to manufacture a chrome yellow pigment. In 1833 the factory stopped manufacturing other chemicals and focused solely on the manufacture of potassium dichromate which it continued to produce from Turkish and Russian chromite ore. The factory grew in size until it covered approximately a 20 acre (8.1 ha) area along the River Clyde and employed, at its maximum, more than 500 workers. The demand for chromium chemicals increased as they were used for more and more industrial processes, such as bleaching of oils and fats, and leather tanning. The output from the Shawfield chemical works, at its peak, was greater than all other factories of its kind in Great Britain (MacLehose, 1886). This commercial success was largely due to the development of a new method for extracting chromate from chromite ore as described in Section 1.2.2.2 below. The factory closed in 1968 due to the rising costs of transportation and the decline in demand for chromium chemicals.

1.2.2.2 Extraction Process

To extract Cr, ground up ore was mixed with an alkali carbonate, such as Na_2CO_3, which was roasted in a furnace at 1150°C. To allow the penetration of air into the melt to oxidise Cr(III) to Cr(VI) a diluent, quicklime (CaO) or dolomite ($CaMg(CO_3)_2$), was added. This “high-lime” process was favoured not only because it increased the efficiency of oxidation to Cr(VI), but it also neutralised silicates and immobilised vanadium (V), another potentially toxic element which is present at near-percent level in chromite ores (Darrie, 2001). Equation 1.1 below summarises the chemical reaction relating to this process:

$$4\,\mathrm{FeCr_2O_4} + 8\,\mathrm{Na_2CO_3} + 7\,\mathrm{O_2} \xrightarrow[\mathrm{CaO/CaMg(CO_3)_2}]{1150^\circ\mathrm{C}} 8\,\mathrm{Na_2CrO_4} + 2\,\mathrm{Fe_2O_3} + 8\,\mathrm{CO_2}$$

Equation 1.1

Due to its high solubility, Na_2CrO_4 can be leached with water and treated with H_2SO_4, and then KCl, which produces the desired product of $K_2Cr_2O_7$. This was then sold to be used in various industrial and manufacturing processes (Darrie, 2001).

1.2.2.3 Chromite Ore Processing Residue (COPR)

The by-product from the roasting and leaching process, known as COPR, had no commercial value so was sent for use as landfill. It had a sand-like texture, and its chemical composition was found to be similar to cement and alkaline municipal waste incinerator bottom ash (Geelhoed *et al.*, 2002). Chromite ore processing residue was stored at a landfill site near the chemical works (Figure 1-2) but was also distributed around South Glasgow where it was used as backfill for pits and terracing for football grounds (Figure 1-3) (Farmer *et al.*, 2002). In these areas, the made ground containing COPR has total Cr concentrations of < 3.6 % w/w and Cr(VI) concentrations of < 8,500 mg kg^{-1}. In all cases the pH of these soils and waters leaching from the COPR is between pH 7.1 – 12.8, with the groundwater having pH > 11 (Farmer *et al.*, 2002).This leads to high concentrations of Cr that leaches out of the made ground into the surrounding environment. A study on the urban soil geochemistry of Glasgow found that 22% of the top soils examined exceed the 2002 UK Contaminated Land Exposure Assessment Generic Assessment Criteria for residential land use Soil Guideline Value of 130 mg kg^{-1} (Fordyce, 2012). This highlights the persistence of Cr in Glasgow soils and the potential impact of Cr pollution on South Glasgow.

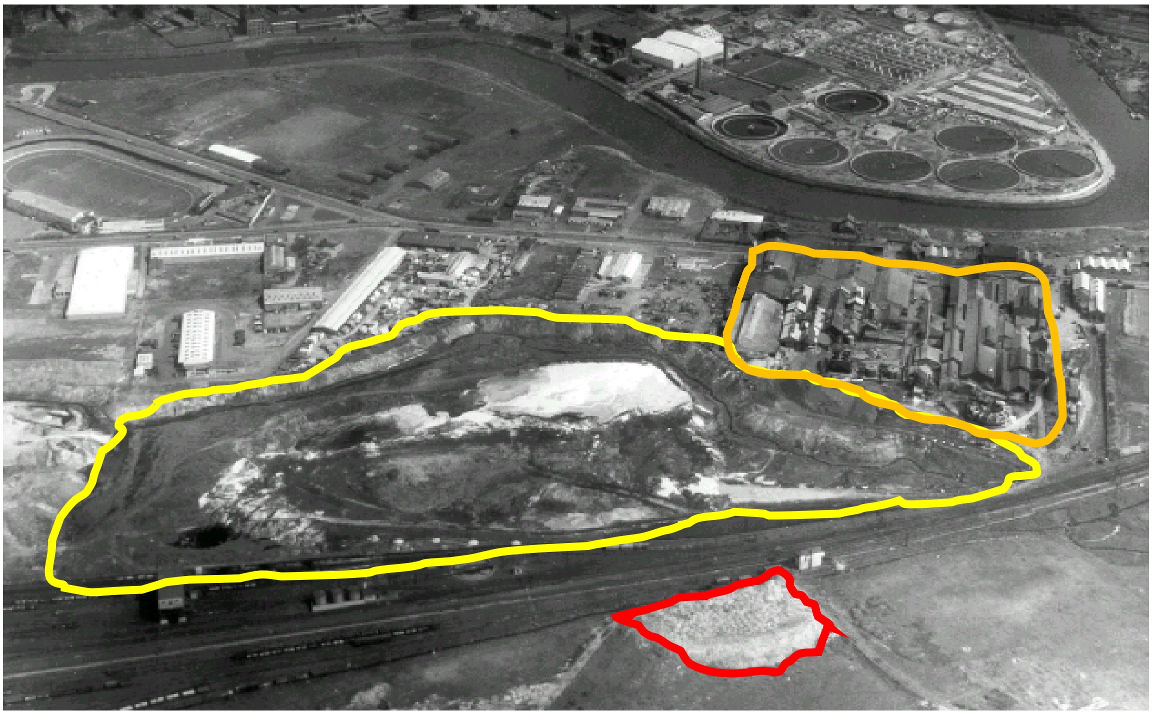

Figure 1-2: Aerial photograph of southeast Glasgow in the 1950s showing the location of the J&J White Chemical Works (orange outline), the COPR disposal area (yellow outline) and seepage of COPR waste under the railway line (red outline) (photograph provided by Mr James Farquar, then-retired employee).

Figure 1-3: Photograph ca 2000 showing COPR used for terracing at Rutherglen Glencairn Junior Football Ground, south east Glasgow, Scotland (provided by Dr Margaret Graham, University of Edinburgh).

An estimated 2.5 M tonnes of COPR was produced and distributed around south east Glasgow and north Lanarkshire over the period 1830-1968. In addition to unreacted chromite, COPR contains a large variety of minerals which were formed during the roasting process, and weathering products formed as the material weathers under ambient conditions. Analysis of Glasgow COPR samples collected at contaminated sites in the early 2000s showed that it contained 4% (w/w) Cr, of which 30% was Cr(VI). The major element composition of Glasgow COPR is shown in Table 1-2.

Table 1-2: Elemental content of COPR waste in Glasgow (Geelhoed et al., 2002)

Element	COPR Content (% w/w)
Ca	18.1
Mg	12.6
Al	12.0
Fe	8.31
Si	4.61
Cr	4.00
S	0.438
Na	0.200

The minerals present in COPR can be split into three categories: i) unreacted ore, ii) phases formed during high temperature roasting process, and iii) weathering products formed in the waste disposal site. Quantitative X-ray powder diffraction (XRPD) analysis of COPR samples showed that the Cr(III) phases were unreacted chromite and the high temperature alteration product, brownmillerite (Table 1-3) (Hillier *et al.*, 2003). The Cr(VI) containing minerals in COPR were weathering products formed in the disposal site, primarily hydrocalumite ($Ca_4Al_2(OH)1_2CrO_4.6H_2O$), hydrogarnet ($Ca_3Al_2((Cr/Si/H_4)O_4)_3$) and to a lesser extent, ettringite ($Ca_6Al_2(OH)_{12}(CrO_4)_3.26\ H_2O$.

Chromium(VI) in hydrocalumite is found in the mineral interlayer resulting in it being exchangeable and prone to leaching, especially at high pH. In hydrogarnet, Cr(VI) is incorporated into the 3D structure of the mineral and is therefore much more stable to leaching (Figure 1-4). This is reflected in the high concentration of Cr(VI) still being released from COPR into receiving waters, over 40 years after waste emplacement (Palumbo-Roe *et al.*, 2017, Farmer *et al.*, 2002, Graham *et al.*, 2006). This high pH in surface water flowing through COPR leads to the dissolution of Cr(VI). The leaching of Cr from COPR has been investigated by Geelhoed *et al.* (2002, 2003). Their work has suggested that Cr(VI) may be leached for a long time from COPR, which has a high acid neutralisation capacity (13 mol H^+ kg^{-1} dry COPR). At high pH (pH 10.5 to 11.7) it is suggested that mineral solubility was the controlling factor for determining Cr(VI) release. Decreasing the pH below 8 lead to a reduction in aqueous Cr(VI) concentrations, most likely due to the release of Fe and Al into solution followed by the precipitation of Fe/Al hydroxides which sorb Cr(VI). Therefore, in order to remediate these sites there must be a physical or chemical barrier in place to stop the leaching of Cr(VI) from COPR and to reduce the mobility of this toxic species. Remediation methods are described below.

Table 1-3: Quantitative XRPD analysis of COPR samples from contaminated sites in Glasgow (Hillier et al., 2003)

Mineral	% w/w	Formula	Cr oxidation state
Unreacted Ore			
Chromite	6	$(Fe,Mg)Cr_2O_4$	III
High Temperature Alteration Products			
Brownmillerite	14	$Ca_2(Al,Fe,Cr)_2O_5$	III
Periclase	7	MgO	-
Larnite	1	Ca_2SiO_4	-
Weathering Products			
Brucite	7	$Mg(OH)_2$	-
Calcite	5	$CaCO_3$	-
Aragonite	1	$CaCO_3$	-
Potential Cr(VI) Phases			
Ettringite	1	$Ca_6Al_2(SO_4)_2(OH)_{12}.26H_2O$	III, VI
Hydrocalumite	5	$Ca_4(Al,Fe)_2(OH)_{12}(OH)_2.6H_2O$	III, VI
Hydrogarnet	23	$Ca_3(Al,Fe)_2(H_4O_4)_3$	VI
Amorphous Phases			
Glass	30	?	?

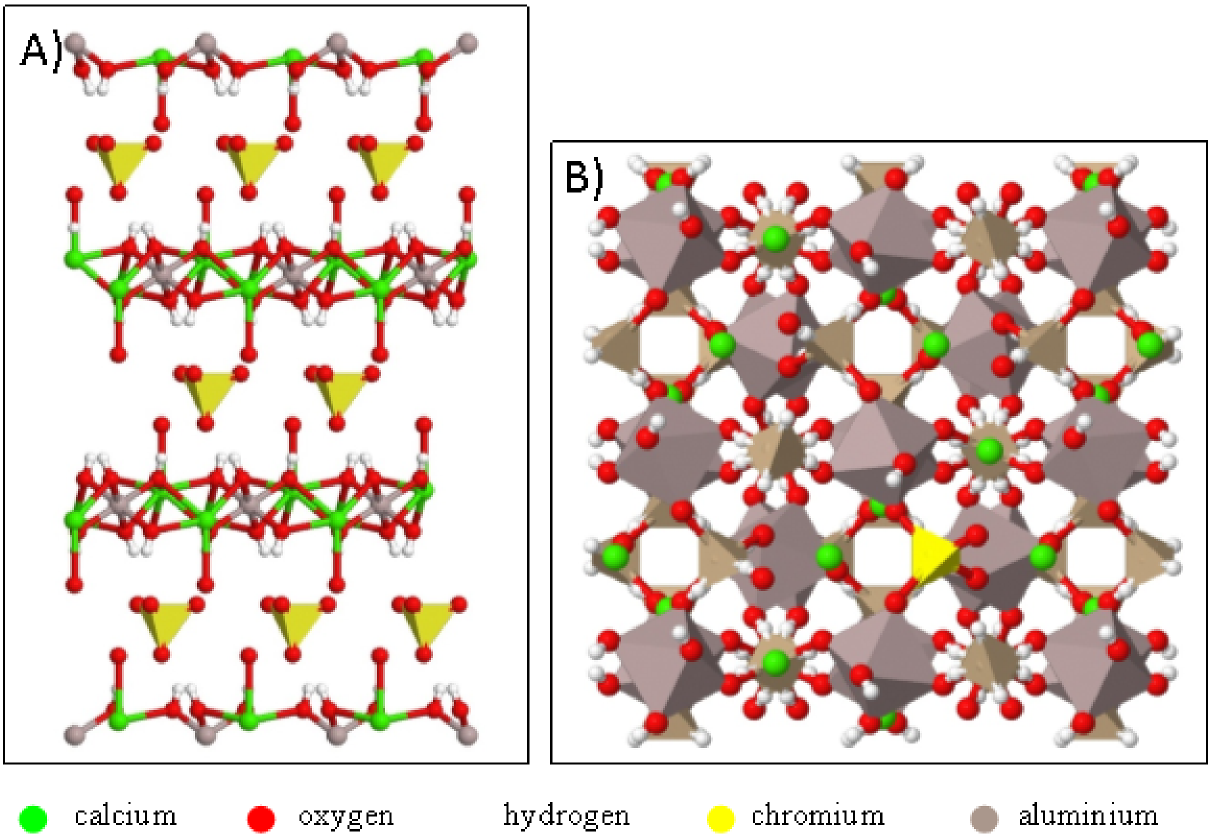

Figure 1-4: Structure of A) hydrocalumite showing exchangeable Cr(VI) in the interlayers and B) hydrogarnet showing Cr(VI) as part of the 3D mineral structure

1.3 Remediation of COPR-contaminated sites

The remediation of contaminated land is required if there is an unacceptable risk posed to humans. The method used to remediate a site often has to be tailored to the site and depends on the scale of the pollution along with the pollutant and site's chemical and physical properties (Rao *et al.*, 2017). Approaches often used to remediate land contaminated with inorganic contaminates, such as Cr, are to remove and replace the material, create a physical barrier to remove the pathway of exposure – such as capping the land, or chemical treatment methods which convert the metal into an immobile or less toxic species by processes such as stabilisation or oxidation/reduction (Rao *et al.*, 2017, Ying, 2018).

Due to the large mass of soil which contains elevated Cr concentrations, the removal of material and replacement with fresh soil is prohibitively expensive, and although capping of Cr contaminated land will reduce the exposure of dust and solid phase material, the leaching of Cr(VI) from the waste into groundwater may still occur. Therefore, chemical reduction strategies where there is irreversible reduction of Cr(VI) to Cr(III) are thought to be the best remediation strategies (He *et al.*, 2018). There have been many remediation strategies developed using Fe species, organic matter (OM) or sulfides to reduce Cr(VI) in soils (Wang *et al.*, 2019, Graham *et al.*, 2006, Guan *et al.*, 2019), but in the extreme alkaline pH of COPR, remediation strategies which were developed for acidic to neutral pH ranges may not be applicable (Graham *et al.*, 2006). One such method developed for the remediation of Cr(VI) in alkaline waste was the use of calcium polysulfide (CaS_x), which has been shown to effectively remediate Cr in alkaline ground water and COPR waste, and has been successfully demonstrated to reduce Cr(VI) concentrations (Wazne *et al.*, 2007).

Calcium polysulfide was used in 2013 to successfully remediate a 1-hectare site for the Clyde Gateway Project in Glasgow near the former J&J White Chromium works (Graham *et al.*, 2006, Bewley and Sojka, 2013). This, along with the capping of COPR by building the new M74 motorway extension on top of one of the disposal sites, effectively encasing it in concrete, have been two notable COPR remediation works in Glasgow. However, there is still unknown land which contains high concentration of Cr(VI) which is hard to access, for example buried several metres below the surface. Leaching of Cr(VI) from these sites will continue to pollute groundwater and the fate of this Cr is unknown when it interacts with sediments and banking soils.

1.4 Fate of chromium in contaminated waterways

Waterways are dynamic systems where the contrasting environment of the oxic water, anoxic sediments, and banking soils have different influences on the fate of Cr. In areas where COPR has been dumped, the fate of Cr is important in assessing risk of oxidation and rerelease of Cr. In the Hudson Bay, New Jersey USA, sediment near the COPR disposal site has total Cr and Cr(VI) concentrations of up to 9190 and 30.7 mg kg^{-1}, respectively, whilst Cr(VI) concentrations of the water were below the limit of detection (LoD). The oxidation of Cr(III) in the sediments was measured and determined to be minimal with no Cr(VI) detected after the suspension of sediment in oxic water (Magar *et al.*, 2008, Martello *et al.*, 2007). This suggests that Cr is immobilised in these sediments. A study by Wadhawan *et al.* (2013) of Baltimore Harbour USA, showed that the anoxic sediments were able to reduce and immobilise Cr(VI), however the resuspension of the sediment did result in the re-oxidation of Cr(III). The contrasting results highlight the impact that site specific conditions have on the fate of Cr in different areas.

In Glasgow, the Polmadie Burn drains an area which contains COPR and runs within 20 m of the former Cr chemical works. This stream, a tributary to the River Clyde, is mainly culverted but its final 500 m section, along the perimeter of Richmond Park is exposed. The stream is surrounded by steep, highly vegetated banks and the water level is weakly influenced by the tidal stream of the River Clyde. The burn water, sediment, and banking soil contain elevated Cr concentrations with up to 6.28 mg L^{-1} measured in surface waters and < 8,740 mg kg^{-1} of Cr in the sediments (Palumbo-Roe *et al.*, 2017, Farmer *et al.*, 2002). A study by Palumbo-Roe *et al.* (2017) investigated the persistence of Cr(VI) in the hyporheic zone and compositional changes on Cr in the hyporheic zone along with its potential for the attenuation of Cr. They found that Cr(VI) in the hyporheic zone Cr was able to reduce, and immobilise Cr(VI), but the poor exchange and long half-life of solutes in the hyporheic resulted in the low attenuation of Cr(VI) from the burn water (Palumbo-Roe *et al.*, 2017). This provided insight into one of the many potential processes that affects the fate of Cr in urban waterways, but there are still many other processes which need to be considered if the fate of Cr in this system is to be understood, for example:

i) The release of Cr from sediments during resuspension
ii) The banking soil and sediment Cr association (i.e. is it bound to Fe hydroxides, OM or COPR minerals? etc.)
iii) The species of Cr released from soils and sediments, and the impact of environmental changes
    a. such as the long-term dry spells on the leachability of Cr when the material is rewetted or
    b. how flooding events impact the release and attenuation of Cr

It is important to investigate the potential risk that the area has on the exposure of Cr to the local population due to the site’s history. The COPR cause high concentrations of Cr in nearby waters, soils, and sediments whilst new housing is under construction in the area. Evaluation of the processes outlined, along with investigating the mobility and speciation of Cr in the area, are key in beginning to understand the exposure risk of Cr in the area and human health.

1.5 Human health impacts associated with exposure to chromium

Although exposure to high levels of Cr(III) can have a detrimental effect on human health, these instances are more rare than exposure to Cr(VI). Moreover, Cr(III) is an essential element for animal and human health. The main concern relates to the toxic effects of Cr(VI). Importantly, different exposure routes can lead to a range of health problems (PHE, 2007, ATSDR, 2012). Acute Cr(VI) poisoning usually occurs from oral administration and can be fatal. Such severe exposure is unlikely to occur naturally, instead it is mainly linked to occupational exposure with recorded cases, usually due to accidental exposures or suicide attempts. Although not directly related to humans, the lethal dose 50 (LD_{50}) for rats ingesting Cr(VI) was observed to be 16 mg kg^{-1} and 29 mg kg^{-1} for female and male rats, respectively. Chronic exposure to Cr is more likely to occur through inhalation and skin contact (ATSDR, 2012). Chromium(VI) is a carcinogen and inhalation of Cr(VI) has been proven to result in lung cancer (WHO, 2000). Short term exposure through skin contact can lead to contact dermatitis, burns, and necrosis of the skin. Longer term exposure can lead to so-called “chrome holes” which are the formation of deep ulcers on the skin (PHE, 2007)

There is a difference in toxicity between the two Cr oxidation states mainly because Cr(VI) is more readily absorbed by the body than Cr(III). Furthermore, Cr(VI) has a greater ability than Cr(III) to efficiently cross the cell membrane, where it is subsequently reduced to Cr(III) which then becomes trapped in the cells. This ‘trapped’ Cr(III) can then interact with cellular macromolecules, such as DNA to cause mutation (USEPA, 1998). The Cr(VI) reduction also produces reactive intermediates, Cr(V) and Cr(IV), which cause further damage to tissue and DNA. The tissue damage and mutations are considered to be the first steps in the development of the serious health effects detailed above.

People who work with Cr and its chemicals are most at risk from chronic health effects. This was even recognised in the early 20th century when the effects of Cr on worker health started to be investigated (Bloomfield and Blum, 1928, Trumper, 1931). Lung cancer was common in workers at chrome works and others who were exposed to high concentrations of Cr dust. At the current time, those who work in chromate production, i.e. the stainless steel industry (especially welders), and chrome pigmentation, are likely to be exposed to the highest concentrations of airborne Cr(VI) (ATSDR, 2012).

The general population can also be exposed to Cr(VI) due to inhaling particulate Cr in ambient air, drinking Cr(VI) contaminated water, or ingesting food contaminated with Cr. This generally occurs from living near industries that use Cr or near Cr waste disposal sites. It is important to recognise that the concentrations of Cr(VI) found in environmental matrices such as dusts, soils/sediments, and water, do not necessarily reflect the percentage of Cr absorbed by the body (Broadway *et al.*, 2010, Jardine *et* *al.*, 2013). Contaminants incorporated on dust particles suspended in the air can be inhaled where toxic metals, such as Cr(VI), can be absorbed into the body through the lungs. The percentage of the contaminant absorbed from the dust into the lungs is determined as the inhalation bioaccessibility. Contaminants in soil/sediment or water that are ingested can also be absorbed through the gastrointestinal tract. The percentage of a contaminant absorbed through the gastrointestinal tract, i.e. the oral bioavailability, is an important factor in determining the health risks that may be associated with land contamination. A previous study on COPR-contaminated soil from Glasgow demonstrated that due to the low pH of the stomach and high organic matter content of the soil, Cr(VI) was readily reduced to the relatively nontoxic Cr(III) form making the oral bioaccessibility of Cr in the tested soils around 5% (Broadway *et al.*, 2010). This suggested a lesser risk of uptake from ingested Cr, so the main risk is perceived to be from inhaled Cr where there have been limited studies on its inhalation bioaccessibility. The study by Broadway *et al.* (2010) did some limited inhalation bioaccessibility testing and suggested that Cr(VI) was bioaccessible but more work is needed to confirm their findings.

1.6 Overarching aims and specific objectives

South Glasgow has a legacy of Cr pollution due to the disposal of COPR in landfill and using the material for terracing in sports grounds etc. These areas impacted with COPR have been extensively studied, but the fate of Cr once it gets into the wider environment has yet to be fully understood. Specifically, the fate of Cr in urban waterways needs to be investigated to understand the scope of the persistence and potential rerelease of Cr from stream banking soils and sediments. Changes in the environment, specifically the flow of urban streams, can change over time due to the diversion of water courses in the forever adapting urban areas, or due to changes in the climate leading to greater variability in rainfall. This may lead to changes in the speciation of Cr and/or its release from previously stable states, which may in turn have a negative effect on human health. The impact of soils with elevated Cr concentrations on human health is important to understand, especially as land is being reclaimed for housing and public space due to the ever-expanding population. This may expose more people to Cr and the potential health effects of Cr, a known carcinogen, in dust has not been fully quantified.

To address these issues and improve understanding of Cr behaviour in a contaminated urban environment, the central aim of this thesis was to identify and characterise the processes which control Cr retention and release in the Polmadie sediment-water-banking soil system in southeast Glasgow, through direct analysis of environmental samples and through laboratory simulations of drying and rewetting processes. A second aim was then to evaluate the inhalation bioaccessibility of the fine fractions of soils and assess the likely risk to human health. These aims were achieved through the following specific objectives:

1. Evaluate the temporal trends of the constituents of the Polmadie Burn through a freedom of information request to the Scottish Environment Protection Agency who provide a dataset of parameters spanning the years 1967 – 2017.
2. Quantify the concentrations and speciation of Cr(III) and Cr(VI) in the Polmadie Burn water, sediment, and banking soils, and identify their associations through sequential analysis of the soils and sediments.
3. Evaluate the effect that drying and rewetting has on the species and release of Cr from contaminated sediment and banking soil of the Polmadie Burn.
4. Predict the ability of the soils and sediment to act as a sink and source of Cr.
5. Define the inhalation bioaccessibility of Cr in the <10 µm fraction of banking soil and sediment of the Polmadie Burn.

2 Literature review of the environmental chemistry of chromium

2.1 Introduction

Chromium is found in its 3+ and 6+ oxidation states in the environment, both of which have contrasting chemical and physical properties, namely the solubility and binding to particles (Rai *et al.*, 1989). The solubility of Cr(III) is generally very low due to its tendency to form insoluble hydroxides complexes at pH >5 and its high affinity for organic matter (OM). On the other hand, Cr(VI) is generally soluble at pH >4 and forms weak surface complexes with soil/sediment particles. Therefore, the speciation of Cr must be understood to predict its mobility in the environment. This section reviews current knowledge regarding the oxidation and reduction reactions of Cr, along with the binding of Cr(III) and Cr(VI) to evaluate its mobility within waters, soils, and sediments.

2.1.1 Overview of the properties of chromium oxidation states in the environment

2.1.1.1 Chromium(III)

The mobility of Cr in soils is affected by a number of factors such as: the Cr species present, pH, redox potential, the minerals present, competing ions present, and the OM content (Kim and Dixon, 2002, Kotaś and Stasicka, 2000, Rai *et al.*, 1989, Fendorf, 1995, Richard and Bourg, 1991). Chromium(III) is generally the more common oxidation state in reducing environments. It is also the dominant species in soils with a high OM content and low Mn concentrations. This is because OM is a main reductant for most redox-sensitive metals in the natural environment (Stevenson, 1982), with reduction rates that increase with decreasing pH. At pH >5 it forms insoluble hydroxides, but when the pH decreases below pH 5 Cr(III) becomes soluble (Fendorf, 1995). The insoluble nature of Cr(III) hydroxides at mildly acid to alkaline pH means that most soils and sediments contain very low concentrations of truly dissolved Cr(III), i.e. free ions and hydrolysis complexes. As well as forming hydroxide compounds, Cr(III) also forms stable complexes with OM. Where this occurs, the solubility of OM can greatly increase the release of Cr into solution through its binding to dissolved and colloidal OM (Puzon *et al.*, 2005).

2.1.1.2 Chromium(VI)

The main Cr(VI) species found in the environment are chromate (CrO_4^{2-}) and dichromate ($HCrO_4^-$), as shown in Figure 2-1. Under extremely oxidising conditions, these are stable across almost the entire pH range but under moderately oxidising conditions, the main stability zone for Cr(VI) is limited to higher pH values. Unlike Cr(III), the common Cr(VI) species found in the environment are very soluble at mildly acidic to alkaline pH and only form weak interactions with the soil (Rai *et al.*, 1989). However, as the pH drops below pH 4 Cr(VI) is strongly adsorbed from solution (Bradl, 2004). Due to the differences in the environmental behaviour of Cr(III) and Cr(VI) the redox reactions controlling the interconversion between the species must be considered.

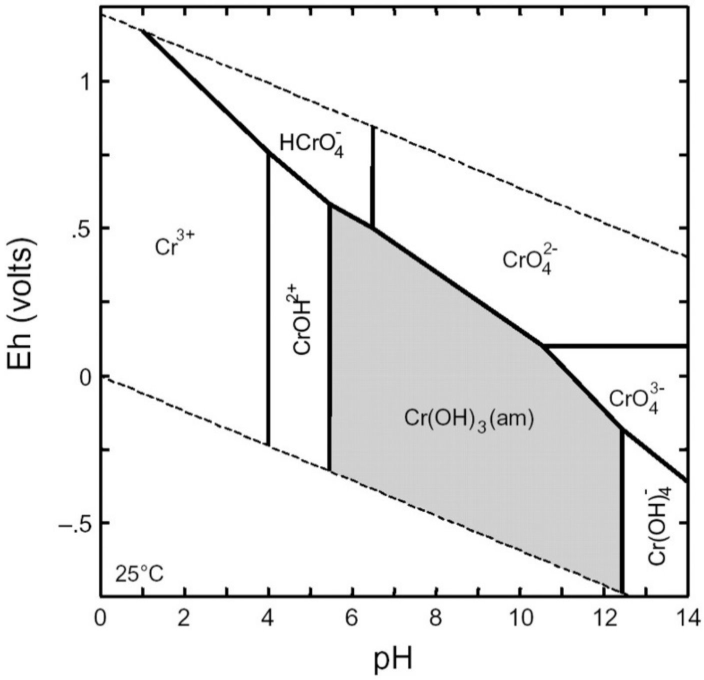

Figure 2-1: An Eh-pH diagram showing the speciation of chromium in natural aquatic systems (Reeder et al., 2006).

2.2 Redox reactions

2.2.1 Chromium(III) Oxidation

Due to the high standard reduction potential of the Cr(VI)/Cr(III) redox couple of +1.33 V, Mn(IV) oxide-mediated Cr oxidation is the only environmentally relevant pathway for the oxidation of Cr(III) (Saleh *et al.*, 1989). The Mn(IV)/Mn(II) standard reduction potential is +1.49 V and so Mn(IV) can oxidise the reduced species of any redox couple with a lower potential value (Fandeur *et al.*, 2009). The rate of Cr(III) oxidation is also dependent on the solution pH, initial Cr(III) concentration, and initial MnO_2 surface area (Fendorf and Zasoski, 1992). Different crystalline structures of Mn oxides have all been shown to oxidise Cr(III) to Cr(VI) (Kotaś and Stasicka, 2000, Fendorf, 1995, Kim and Dixon, 2002), and so the process is not limited by the requirement for formation of a specific Mn(IV)O_2 phase.

In Cr contaminated estuarine sediment systems that undergo transformation from reducing to oxidising conditions, Mn(II) in the sediment porewaters becomes oxidised to Mn(IV) which may be removed from solution to form surface coatings on sediment particles. The formation of these fresh Mn(IV) surfaces is considered to be an important trigger for Cr(III) oxidation, especially under neutral to alkaline conditions (Wadhawan *et al.*, 2013, Reijonen and Hartikainen, 2016). Only <1% Cr(III) was oxidised to Cr(VI) at pH 7 but this increased to ~19% at pH 10 (Wadhawan *et al.*, 2013). More generally, however, a small percentage of Cr(VI) has been attributed to Cr oxidation by Mn oxides, even in non-contaminated soils.

Chromium(III) oxidation to Cr(VI) is favourable over a wide range of pH values in soils (Fendorf and Zasoski, 1992, James *et al.*, 1997, Pan *et al.*, 2017). The rate at which Cr(III) oxidation occurs however, depends of the chemistry of the soil environment. At low pH (pH <5), the high solubility of Cr(III) should favour high rates of oxidation but the competing reduction reactions, described below, will result in a low net Cr(VI) production in contrast to the results of research conducted on pure MnO_2 minerals (Reijonen and Hartikainen, 2016, Wadhawan *et al.*, 2013). The surface alteration of the Mn oxides will influence the oxidation of Cr(III). Oxidation is fast within the first 30 min, after which the reaction is greatly inhibited. This is due to the formation of Cr precipitates on the MnO_2 surfaces, which block the active sites for Cr(III) oxidation resulting in a reduced Mn surface area and the decline in the oxidation rate (Fendorf and Zasoski, 1992, Świetlik, 2002).

Other Cr(III) oxidation pathways have also been studied. Oxygen has been shown to oxidise Cr(III) to Cr(VI) but, due to kinetic constraints, it is not thought to be an important pathway in the environment as reaction rates are much lower than the Mn oxide-mediated pathway. Hydrogen peroxide and hydroxide radicals have also been observed to oxidise Cr(III) in oxic surface waters, but in subsurface environments these reactions are unlikely due to the lack of these oxidants (Youxian and Baolin, 2006, Baloga and Earley, 1961).

2.2.2 Chromium(VI) Reduction

In most cases, the reduction of Cr(VI) is a much more prevalent process in the environment than oxidation of Cr(III) because Cr(VI) species are such strong oxidants. For example, chromic acid (H_2CrO_4) has been used in various industrial processes for bleaching cloth, and in the Jones' oxidation reactions to oxidise alcohols to carboxylic acids/ketones (Tojo and Fernandez, 2006). Consequently, Cr(VI) is readily reduced to Cr(III). Indeed, common electron donors such as Fe(II), Fe(II) containing minerals, OM, and sulfides can also reduce Cr(VI) (Rai *et al.*, 1989). Although biological processes can result in Cr(VI) reduction, chemical reduction is a much faster process. Therefore, the two most important environmentally relevant reductants are Fe(II) and OM.

Under reducing conditions, Fe(II) is an important reductant of Cr(VI) with complete reduction of Cr(VI) by Fe(II) within minutes (Fendorf, 1995, Rai *et al.*, 1989, Richard and Bourg, 1991, Xu *et al.*, 2017). Therefore, in reducing sediments which have low OM content the transformation of Cr(VI) to Cr(III) will be controlled by Fe(II) mediated reduction. In oxic soils and surface waters, Fe(II) is not stable and therefore the reduction of Cr(VI) is limited by the dissolution kinetics of Fe(II) minerals (Fendorf and Zasoski, 1992). The products of this reaction under acidic conditions (pH <4) are $Fe(III)_{aq}$ and $Cr(III)_{aq}$, but at pH >4 the solubility of Cr(III) decreases so the newly formed Cr(III) will precipitate as a mixed Fe - Cr hydroxide ($Cr_xFe_{x-1}(OH)_3$) (Papassiopi *et al.*, 2014). This is a rapid reaction which can result in the precipitation of (Cr_xFe_{x-1})$(OH)_3$. Therefore, in the environment, the formation of the Fe/Cr precipitate means this reaction has the potential not only to reduce Cr(VI) to a less toxic form but also to remove Cr from solution.

As mentioned above, another important reductant of Cr(VI) in the environment is OM (Kotaś and Stasicka, 2000, Rai *et al.*, 1989, Banks *et al.*, 2006). Soils with high OM content (>20%) have the capacity to reduce Cr(VI) at any pH (Kyziol *et al.*, 2006, Löv *et al.*, 2017). However, the reduction of Cr(VI) by dissolved OM (DOM) is pH dependent as the rate of reduction by DOM decreases with increasing pH and is minimal above pH 7 (Wittbrodt and Palmer, 1995). The rate of Cr reduction by OM decreases with time which suggests that the OM remains complexed to the newly formed Cr(III) (Elzinga and Cirmo, 2010). Since some of the OM can also be soluble, this process can lead to the Cr(III) formed by the reduction of Cr(VI) by OM being much more mobile than Cr(III) formed by Fe oxide reduction (Puzon *et al.*, 2005).

2.2.3 Environmental implications of chromium redox chemistry

In soils and sediments with elevated Cr concentrations, both the oxidation of Cr(III) and reduction of Cr(VI) can be thermodynamically feasible reactions (Figure 2-2). This means that changes in the speciation and/or concentrations of Fe and Mn along with changes in OM content have important impacts on the species of Cr present (Reijonen and Hartikainen, 2016, Wadhawan *et al.*, 2013). Wadhawan *et al.* (2013) investigated Cr inputs from COPR in an estuarine environment in Baltimore Harbour, an area known to be contaminated with COPR. Characterisation of surface sediment grab samples showed that Cr was mainly present as Cr(III) within the sediments, and there was not a significant amount of Cr(VI) detected in either the sediment or sediment porewaters. Laboratory experiments involving spiking sediment samples with Cr(VI) resulted in its reduction to Cr(III) under anoxic conditions. These were followed by experiments where anaerobic sediment samples were suspended in aerated waters. In these 1-15% of the newly formed Cr(III) was oxidised back to Cr(VI). Results from non-spiked control sediment samples, however, showed that none of the native Cr(III) was oxidised.

An investigation by Reijonen *et al.* (2016) found that when MnO_2 was added to soil and incubated for 47 days at 22°C net Cr(III) oxidation was observed, but no net Cr(III) oxidation was observed in soils without added MnO_2. They also reported that at lower pH the chemical availability of Cr(III) was lower and the amount of Cr(III) oxidised increased, however the net oxidation of Cr(III) was lower due to the increased reduction rate of Cr(VI) at lower pH (Reijonen and Hartikainen, 2016).

The composition of the soil/sediment, in particular the Mn oxide and OM content, is likely to be key in assessing the risk of net Cr(III) oxidation when both Cr(III) oxidation and Cr(VI) reduction reactions are considered. In aqueous environments if the interface between the sediment and surface water is at the boundary between oxic waters and anoxic sediments, this can lead to more complicated environmental chemistry where Cr can transfer between the aerobic water and the anaerobic sediment. The interactions of Cr at this interface are summarised in Figure 2-3. The processes described above are from estuarine environments which will have different chemistry to freshwater environments such as urban streams with a similar redox stratification. The difference in mineral phases formed due to changes in the chemistry may affect the stable species of Cr present and its behaviour in the urban stream system.

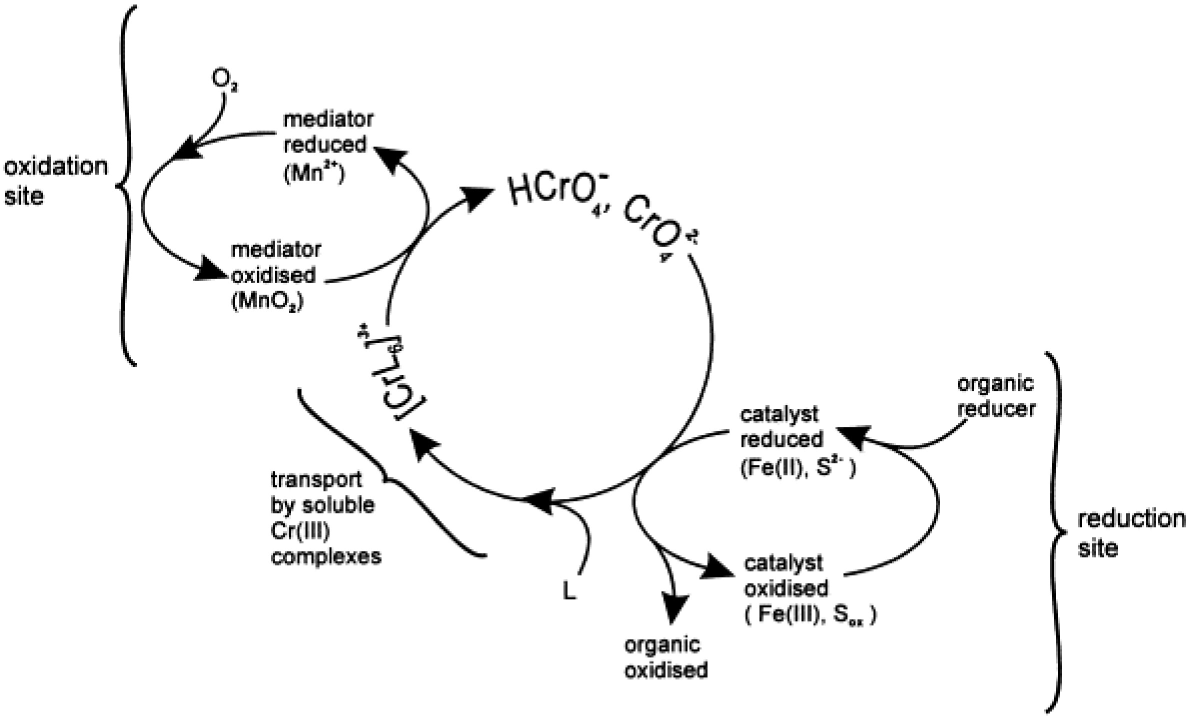

Figure 2-2: Chromium oxidation-reduction cycle in soils (Kotaś and Stasicka, 2000).

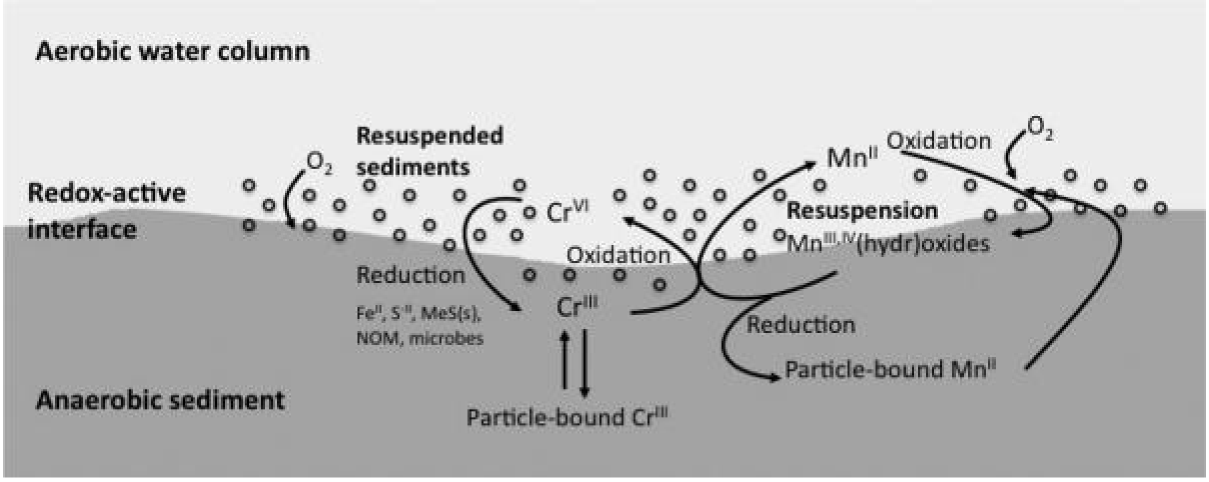

Figure 2-3: Schematic diagram of the water/sediment interface in an estuarine environment (Wadhawan et al., 2013). Note: NOM = natural organic matter

2.3 Adsorption, precipitation/dissolution and complexation processes

2.3.1 Adsorption to mineral surfaces

Many minerals found in soils and sediments exhibit pH-dependent surface charge as represented by equations 2.1 and 2.2. The point of net zero proton charge (pH_{PNZPC}) is the pH at which there is net zero charge on the mineral surface. At pH < pH_{PNZPC}, mineral surfaces have a net positive charge but when pH > pH_{PNZPC}, there is a net negative charge on the mineral surface (Drever, 1997).

$$\mathrm{Mineral-OH\ +\ H^{+} \leftrightarrow\ Mineral-OH^{2+}} \qquad \text{Equation 2.1}$$

$$\mathrm{Mineral-OH\ \leftrightarrow\ Mineral-O^{-}+\ H^{+}} \qquad \text{Equation 2.2}$$

The pH_{PNZPC} values are characteristic of individual minerals, e.g. clay minerals typically have values in the range 2-4 due to the substitution of differently charged cations in the clay lattice (such as Al^{3+} for Si^{4+}), whilst Fe oxides typically have values in the range 7-9 (Tschapek, 1974, Parks and Bruyn, 1962).

Adsorption of solution phase species, such as cationic species of Cr(III) and anionic species of Cr(VI), is therefore a pH-dependent process which is largely controlled by the pH_{PNZPC} of the mineral surface, but also by the presence of other ions in solution. As would be expected on the basis of their differing chemical characteristics, Cr(III) and Cr(VI) also differ in their sorption behaviour. In general terms, the former exhibits the typical sorption behaviour of a cation and its adsorption increases with pH, but decreases when competing cations are present. In contrast, Cr(VI) exhibits the typical sorption behaviour of an anion and its adsorption decreases with increasing pH and when competing dissolved anions are present (Richard and Bourg, 1991). Therefore, more detailed descriptions of their sorption behaviour will be covered separately in the sections which follow.

2.3.2 Adsorption processes for chromium(III)

As described in the preceding sections, Cr(III) is the stable form of Cr under reducing conditions and is typically present in cationic form under strongly acidic to near-neutral conditions. Hydrolysis occurs at relatively low pH and from pH 4 to 6, the first and second hydrolysis products, $CrOH^{2+}$ and $Cr(OH)_2^{+}$, dominate. Beyond pH 6, the main species in solution is $Cr(OH)_3^{0}$ (Figure 2-4). The onset of hydrolysis at such low pH values is important for the behaviour of Cr(III) since hydrolysis product formation is linearly related with the sorption, due to the disruption of the symmetric water co-ordination sphere of hydrolysable metal ions (Fendorf, 1995). Stumm (1987) showed that this disruption greatly enhanced ion reactivity, and so strong sorption to soil and sediment mineral phases would be predicted (Stumm, 1987). The propensity towards hydrolysis also imparts the low hydroxide solubility of Cr(III); the hydrolysis product, $Cr(OH)_3$, dominates when solution pH >6 but it is rapidly removed from solution by precipitation (see Section 2.4).

Chromium(III) is strongly and specifically adsorbed onto a range of different mineral phases in soils and sediments, including Fe oxides, Mn oxides, and clay minerals (Kotaś and Stasicka, 2000, Rai *et al.*, 1989). The extent of Cr(III) sorption increases with pH due to the increasing negative charge on the mineral surfaces (see Equations 2.1 and 2.2 above), but decreases in the presence of competing cations (Craik, 1886). The rate of sorption is usually rapid with ~90% of Cr(III) added sorbed by clay and Fe oxides (Richard and Bourg, 1991). The extent of sorption also increases with the OM content of the soil or sediment (e.g. Kotaś and Stasicka, 2000; Rai *et al.*, 1989), but decreases in the presence of dissolved OM (Whalley *et al.*, 1999). The specific interactions with OM are described below in Section 2.5.

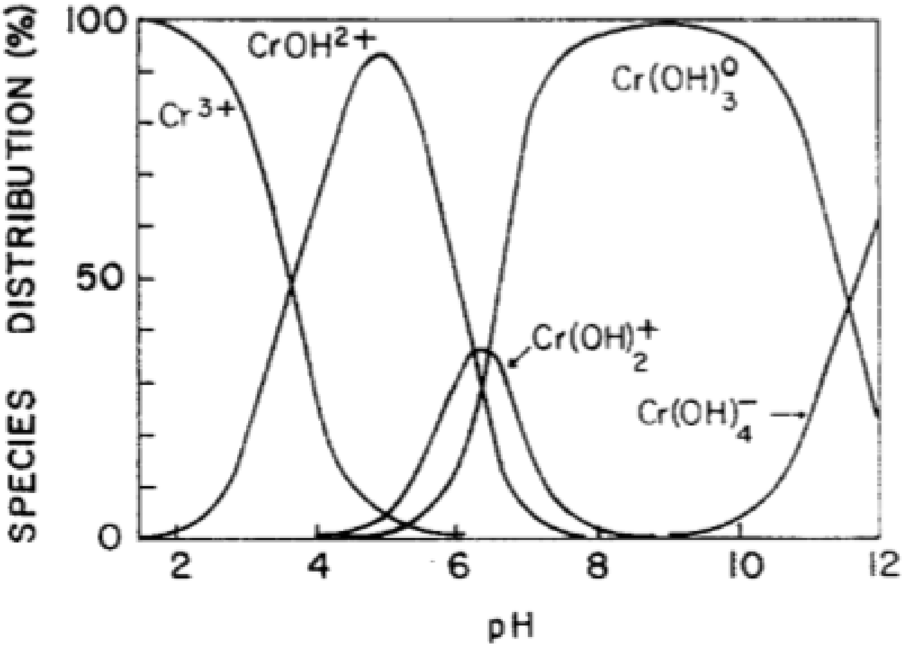

Figure 2-4: Speciation diagram showing hydrolysis of Cr(III) in aqueous solution (Richard and Bourg, 1991).

2.3.3 Adsorption processes for chromium(VI)

The sorption and desorption of Cr(VI) to soil/sediments can control Cr mobility although, in the main, the interactions between Cr(VI) and soil phases are generally weaker than those involving Cr(III). This weak electrostatic interaction with solid phases and the high aqueous phase stability of Cr(VI) anionic species explain why, in the absence of reducing agents, high Cr(VI) concentrations can be sustained in aqueous solutions. The adsorption of Cr(VI) is greatest at acidic pH and gradually decreases to a minimum adsorption at ~pH 8 (Rai *et al.*, 1989).

Chromium(VI) is adsorbed by minerals that have exposed surface inorganic hydroxyl groups, for example: Fe, Mn and Al (hydr)oxides, and clays. Indeed, It has been shown that Cr(VI) coordinates to 3-4 hydroxyl groups on the mineral surface (Benjamin and Bloom, 1981; Davis and Leckie, 1980). The general adsorption process can be represented by Equation 2.3 below (Rai *et al.*, 1989); where SOH is the inorganic hydroxyl site and $SOH_2^+ \cdots CrO_4^{2-}$ is the adsorbed complex.

$$SOH + H^+ + CrO_4^{2-} \leftrightarrow SOH_2^+ \cdots CrO_4^{2-} \qquad \text{Equation 2.3}$$

The extent to which Cr(VI) is adsorbed onto the soil is dependent on the $\mathrm{pH_{PNZPC}}$ of the mineral, the pH of solution, and the number of adsorption sites available. Decreasing the pH leads to a more positive charge on the mineral surface (see equations 2.1 and 2.2), which causes a greater attraction of the negatively charged Cr(VI) compounds to the soil/sediment. Studies have shown that Cr(VI) binds most strongly to Fe hydroxides, then to Al hydroxides, and least to clays such as kaolinite and montmorillonite, with greatest adsorption at acidic pH (Rai *et al.*, 1989, Ajouyed *et al.*, 2010). This is consistent with the $\mathrm{pH_{PNZPC}}$ values for these minerals which are typically highest for the Fe and lowest for the clay minerals.

The adsorption of Cr(VI) to Fe (hydr)oxides is independent of ionic strength showing that it forms inner sphere complexes with Fe hydroxides. By contrast, adsorption onto alumina was shown to depend on both pH and ionic strength, and it has been suggested that Cr(VI) bonding to Fe (hydr)oxides is specific (inner sphere) whereas the Cr(VI) bound to Al (hydr)oxides are non-specific columbic interactions (ion exchange mechanism). This ion-exchange process involving Al hydroxides is represented in Equation 2.4 below (Ajouyed *et al.*, 2010):

$$(\equiv \mathrm{Al-OH}) + \mathrm{H^+} + \mathrm{HCrO_4^{2-}} \leftrightarrow (\equiv \mathrm{Al-HCrO_4^-}) + \mathrm{H_2O} \qquad \text{Equation 2.4}$$

The presence of other major ions has been shown to significantly decrease Cr(VI) adsorption such as Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, $H_2PO_4^-$, and HPO_4^{2-}. This is due to competition for sorption sites between CrO_4^{2-} and the other anions which are preferentially adsorbed (Rai *et al.*, 1989). The extent of preferential adsorption depends, however, on the relative concentrations of Cr(VI) and the competing ions, on their relative affinities for the mineral surfaces, and on the properties of these surfaces (including surface site concentration) (Rai *et al.*, 1986). An additional effect of introducing competing ions is to shift the pH of the adsorption edge to lower values (Figure 2-5).

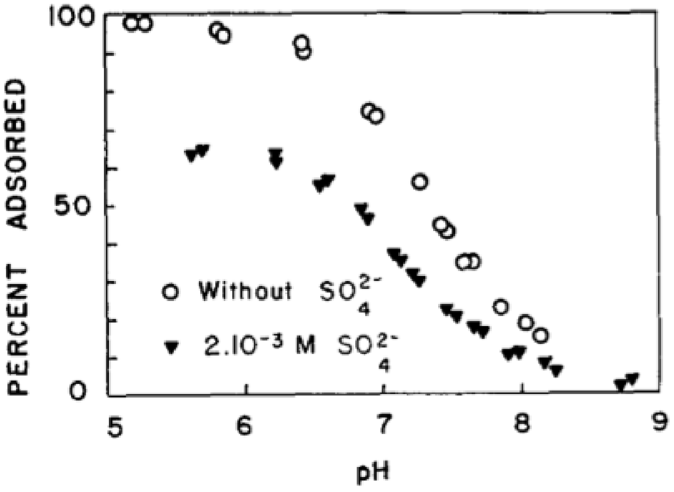

Figure 2-5: Competitive sorption between Cr(VI) and SO_4^{2-} onto amorphous Fe oxides (Cr(VI) = 5 x 10^{-6} M and Fe_{TOT} = 0.87 x 10^{-3} M) (from Rai et al., 1986).

The sorption of Cr(VI) from solution is not always a reversible process. It has been suggested that this may be because the removal of Cr(VI) from solution may not proceed through adsorption but through reduction to Cr(III) followed by subsequent precipitation to the soil/sediment surface (Richard and Bourg, 1991). This has implications for the speciation and mobility of Cr sorbed to soils and sediments. The section below discusses the precipitation of Cr to soils.

2.4 Precipitation/dissolution processes

The precipitation of Cr(VI) from solution is not thought to be an important mechanism for the removal of Cr(VI), due to the high solubility of Cr(VI) and the lack of stable Cr(VI) solid compounds under normal pH and Eh values found in the environment (Rai *et al.*, 1989). Only the formation and dissolution of solid phase Cr(III) compound is therefore considered in this section.

At pH <4 Cr(III) will be present as Cr^{3+}, which is readily soluble, but at higher pH it will form $Cr(OH)_3$, an insoluble species which will be removed from solution by precipitation (Richard and Bourg, 1991).

The insoluble nature of Cr(III) species and the strong binding of Cr(III) to soil phases results in low concentrations of Cr(III) in solution. Reduction of Fe in the Fe oxides as shown in Equation 2.5 below can lead to Cr(III) being released into solution. This is an acid consuming process resulting in an increase of pH which will most likely result in the precipitation of $Cr(OH)_3$.

$$\mathrm{Fe(OH)_3} + 3\mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{Fe^{2+}} + 3\mathrm{H_2O} \qquad \text{Equation 2.5}$$

The co-precipitation of Cr with Fe is another important mechanism for removing Cr from solution and often occurs after Cr(VI) reduction with Fe(II), resulting in the precipitation of a mixed Cr/Fe hydroxide with the general formula $Fe_xCr_{1-x}(OH)_3$. This complex is very stable as it is less soluble than $Cr(OH)_3$ precipitates (Papassiopi *et al.*, 2014).

2.5 Complexation processes

Although OM has been known to be important in the reduction of Cr(VI), there is still relatively little known about the binding of Cr to natural OM, and further studies are required to fully understand the mechanism of Cr-OM binding (Gustafsson *et al.*, 2014, Löv *et al.*, 2017). Like many other cations Cr(III) forms stable complexes with OM. However, Cr(VI) tends to form anionic species which do not complex with OM (Wen *et al.*, 2018). Many researchers have reported the trend of the immobilisation of Cr(III) in soil as OM content increases, and the reduction of Cr(VI) by OM is often followed by the formation of Cr(III)-OM complexes (Banks *et al.*, 2006, Jardine *et al.*, 2013, Jardine *et al.*, 1999).

The binding mechanisms of Cr(III) to OM, in order of binding strength, were summarised by Kyziol to be: i) weak polar interactions between negatively charged OM and positively charged Cr(III) cations; ii) cation exchange processes where Cr^{3+} replaces, for example Ca^{2+}, bound to OM and; iii) chelation of aromatic functional groups, chiefly carboxyl groups (-COOH) of humic acids, as shown by Equation 1.7 below (Kyziol *et al.*, 2006).

$$\mathrm{R-COOH} + Cr^{3+} \rightarrow \mathrm{R-COOCr^{2+}} + \mathrm{H^+} \qquad \text{Equation 1.7}$$

The complexation of Cr(III) to OM is often accompanied by a decrease in pH due to the displacement of H^+ ions from the OM as seen in Equation 1.7. Chromium bound to OM through carboxyl (-COOH) groups form octahedral Cr–O interactions with ligands (Gustafsson *et al.*, 2014). The study by Kyziol *et al.* (2006) found Cr to be sorbed to large molecular weight, insoluble organic molecules. They also discovered that the Cr(III)-OM complexes were very stable resulting in limited decomplexation, therefore low mobility of the Cr-OM molecules (Kyziol *et al.*, 2006).

At low pH, the rate of adsorption of Cr to OM is low due to the slow water exchange of Cr(III) (Gustafsson *et al.*, 2014). The reduction of Cr(VI) by OM can lead to the subsequent absorption of the newly formed Cr(III). This can lead to the removal of

Cr(VI) from solution and, due to the formation of stable Cr(III)-OM complexes, much reduced mobility of Cr (Jardine *et al.*, 2013, Banks *et al.*, 2006). Due to the formation of stable Cr(III)-OM complexes, the use of organic reducing barriers are one method which has been suggested for the removal of Cr from industrial effluent such as tanneries. Not only do these environments reduce Cr(VI) to Cr(III), they are also very successful in immobilising Cr(III) (Sultana *et al.*, 2014, Vymazal, 2014). In typical river settings the concentration of dissolved Cr(III) can be greatly overestimated due to the presence of Cr(III)-DOM complexes, and the formation of Cr(III)-DOM can increase the mobility of Cr in soils (Bolaños-Benítez *et al.*, 2018).

3 Sample collection and laboratory methods

3.1 Sample collection

3.1.1 Location of the sampling site

The sampling site for this PhD project was Polmadie Burn which is situated in south east Glasgow (Figure 3-1). The Polmadie Burn is a stream which flows around the perimeter of Richmond Park, above which it is culverted and these tributaries run around the perimeter of the site of the former chromium works and clay pits which were backfilled using COPR (Figure 3.2). Water, soil, sediment and porewater samples were taken from the area between the footbridge and where the stream flows into the River Clyde (Figure 3-3). This part of the stream had a narrow flood plain and steep sides which were vegetated with deciduous trees. The floodplain was densely vegetated during spring to autumn and bare during the winter (Figures 3.4 and 3.5).

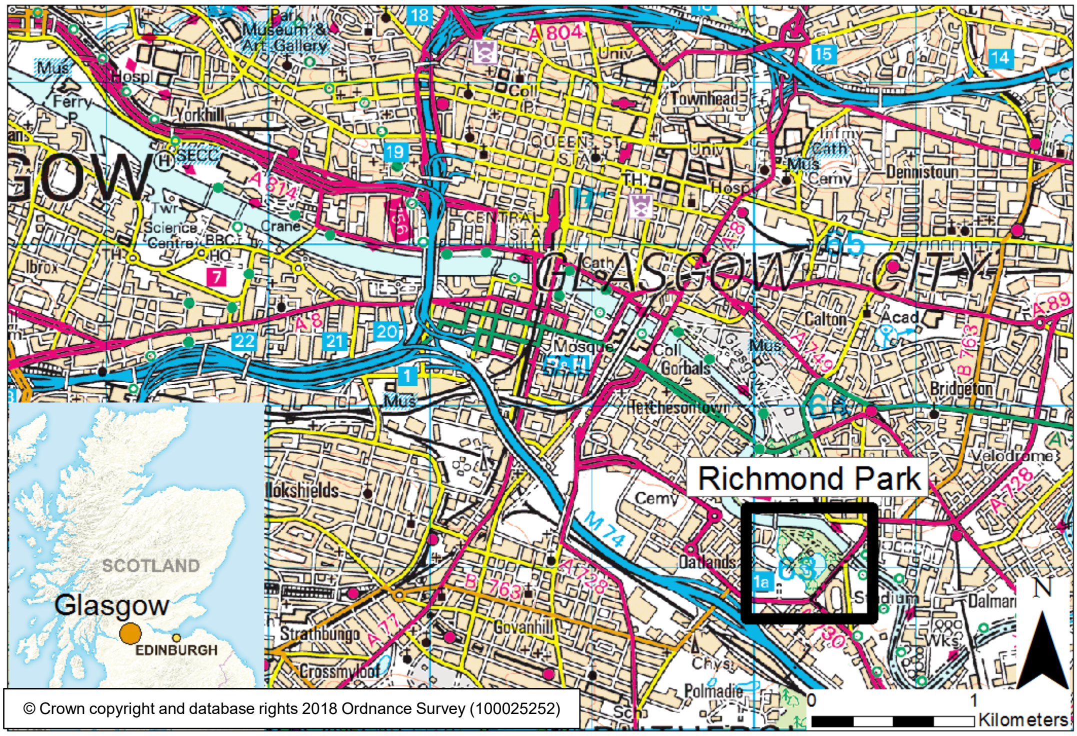

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Figure 3-1: Map showing the location of Richmond Park, Glasgow, with map of Scotland insert. The black rectangle shows the area which was sampled during this study.

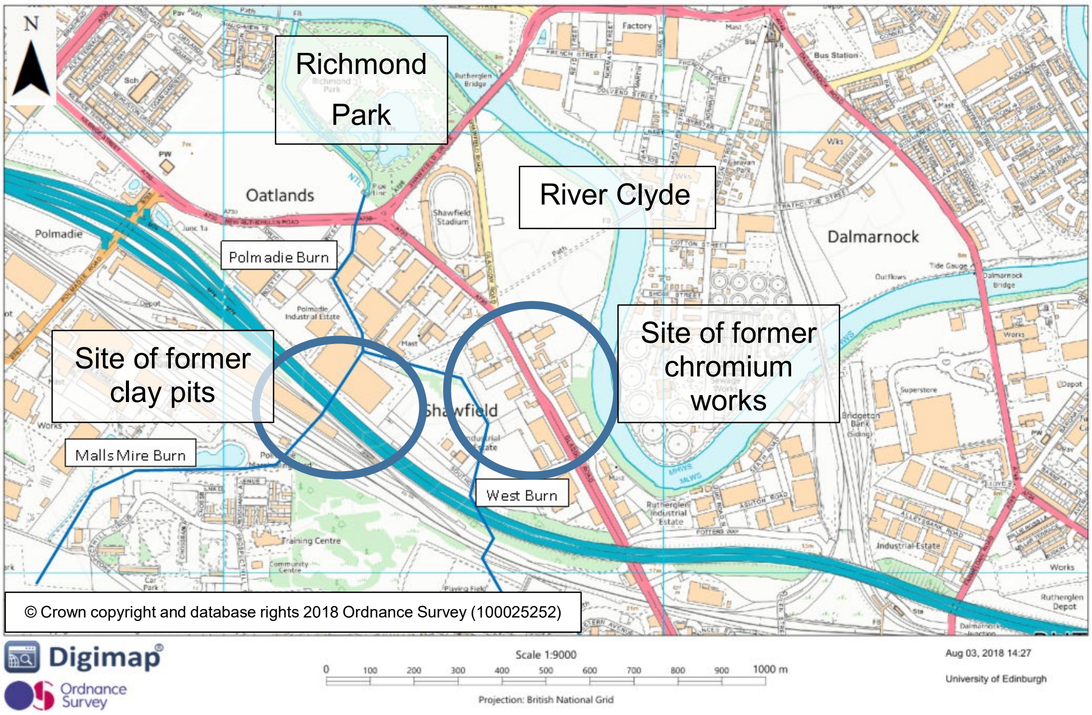

Figure 3-2: Route of culverted sections of the Polmadie Burn and its tributaries

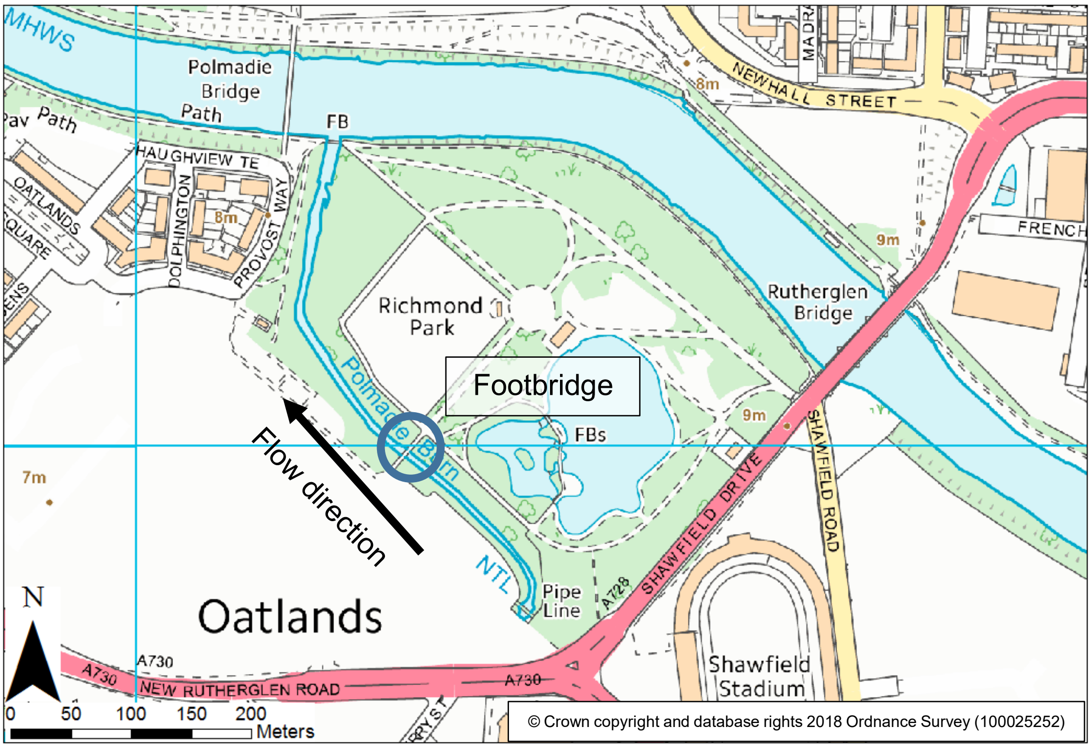

Figure 3-3: Map showing the location of Polmadie Burn along the perimeter of Richmond Park, south east Glasgow, Scotland.

Figure 3-4: Polmadie Burn during summer

Figure 3-5: Polmadie Burn during winter

3.1.2 Overview of sample collection throughout this PhD project

Water, soil and sediment samples were collected from the Polmadie Burn which were used to investigate the geochemistry of the area and also for laboratory experiments. Information and location of the water and porewater samples are shown in Table 3-1. The sediment sample information and locations can be found in Figure 3-7 and Table 3-2. The soil sample information and locations can be found in Figure 3-8 and Table 3-3.

Initial samples were collected on the 19th December 2014 to determine the concentrations of Cr and Cr(VI) in the soils. Two sediment cores on 17th May 2015 to investigate any changes in Cr deposited in the sediment with time. Two soil and sediment transects were taken on the 18th February 2016 and 27th October 2016 to investigate changes in Cr concentrations and associations along the burn and both of these sampling trips aimed to collect 7 and 5 samples, respectively, which were evenly spread between the footbridge and the mouth of the Clyde. Finally bulk soil and sediment samples were taken between September 2016 and April 2018 for laboratory experiments.

A long-term record of the organic, inorganic and other parameters which influence the water quality was provided by the Scottish Environment Protection Agency (SEPA). Due to the pervious published work on the Polmadie Burn and the limited variation of the water chemistry over time (see Chapter 4) only a limited number of water samples were collected over the duration of this project. These samples were used to establish a point of comparison with the SEPA dataset.

Both sediment cores and surface sediment samples were collected from the Polmadie Burn. The sediment cores were used to compare with previous work and to establish total Cr and Cr(VI) concentrations with depth along with porewater speciation. The surface sediment samples were collected along transects for determination of the concentrations of Cr(tot) along with other major elements (Fe, Mn, Al, Ca, Mg and S). Chromium(VI) concentrations were also determined, as were the Cr associations using sequential extraction schemes. Bulk sediment samples were collected for laboratory experiments to investigate changes in the leachable concentration of Cr in the sediment as the sediment dried in an oxic environment.

Banking soils are defined as the soils in the stream's floodplain and within 10 m of the edge of the stream. Banking soil samples were collected as either bulk or surface samples. The surface soil samples were used to establish total Cr and Cr(VI) concentrations, along with other major elements (Fe, Mn, Al, Ca, Mg and S). The associations between Cr and soil were investigated using sequential extraction. The bulk soil samples were used for laboratory experiments to investigate the changes in the leachable concentrations of Cr in the soil as it dried. Bulk soil samples were also used to determine the bioaccessibility of the 10 µm (PM_{10}) fraction of the soil.

Figure 3-6: Water and porewater sampling points

Figure 3-7: Sediment sampling points

Figure 3-8: Soil sampling points

Table 3-1: Water and porewater sample information

Sample Name	Grid Ref	Sample Point	Sample Type	Collection Date	Filter Size
Burn Water 1	NS 60135 63101	35	Water	04/11/2015	0.45 µm
Burn Water 2	NS 60147 63181	2	Water	12/09/2016	0.45 µm
Burn Water 3	NS 60135 63101	35	Water	24/10/2017	0.45 µm
Burn Water 4	NS 60143 63158	8	Water	24/10/2017	0.45 µm
Burn Water 5	NS 60147 63181	2	Water	24/10/2017	0.45 µm
Porewater 1	NS 60147 63181	2	Sediment Porewater	04/11/2015	0.45 µm

Table 3-2: Sediment sample information

Sample Name	Grid Ref	Sample Point	Sample Type	Collection Date	Sample Used for:					
					pH	OM	Acid Digestion	Alkali Digestion	Sequential Extraction	Laboratory Experiment
Core 1	NS 60216 62999	1	Sediment Core	17/05/2015	X	X	X	X		
Core 2	NS 60147 63181	2	Sediment Core	17/05/2015	X	X	X	X		
c1	NS 60179 63040	3	Surface Sediment	18/02/2016	X	X	X	X		
c2	NS 60165 63058	4	Surface Sediment	18/02/2016	X	X	X	X		
c3	NS 60151 63079	5	Surface Sediment	18/02/2016	X	X	X	X		
c4	NS 60137 63101	6	Surface Sediment	18/02/2016	X	X	X	X		
c5	NS 60137 63132	7	Surface Sediment	18/02/2016	X	X	X	X		
c6	NS 60143 63158	8	Surface Sediment	18/02/2016	X	X	X	X		
c7	NS 60144 63181	9	Surface Sediment	18/02/2016	X	X	X	X		

c8	NS 60162 63063	10	Surface Sediment	27/10/2016		X	X	X	X	
c9	NS 60144 63089	11	Surface Sediment	27/10/2016		X	X	X	X	
c10	NS 60134 63114	12	Surface Sediment	27/10/2016		X	X	X	X	
c11	NS 60143 63158	8	Surface Sediment	27/10/2016		X	X	X	X	
c12	NS 60144 63181	9	Surface Sediment	27/10/2016		X	X	X	X	
Bulk Sed 1	NS 60147 63181	2	Bulk Surface Sediment	12/09/2016		X	X	X		Column Leaching
Bulk Sed 2 [a]	NS 60147 63181	2	Bulk Surface Sediment	10/11/2017		X	X	X		Batch Leaching

[a]Sample used for gel electrophoresis

Table 3-3: Soil sample information

Sample Name	Grid Ref	Sample Point	Sample Type	Collection Date	Sample Used for:					
					pH	OM	Acid Digestion	Alkali Digestion	Sequential Extraction	Laboratory Experiment
s0	NS 60135 63095	13	Surface Soil	19/12/2014	X	X	X	X	X	
s1	NS 60175 63033	14	Surface Soil	18/02/2016	X	X	X	X		
s2	NS 60162 63054	15	Surface Soil	18/02/2016	X	X	X	X		
s3	NS 60146 63076	16	Surface Soil	18/02/2016	X	X	X	X		
s4	NS 60132 63098	17	Surface Soil	18/02/2016	X	X	X	X		
s5	NS 60131 63134	18	Surface Soil	18/02/2016	X	X	X	X		
s6	NS 60137 63160	19	Surface Soil	18/02/2016	X	X	X	X		
s7	NS 60138 63182	20	Surface Soil	18/02/2016	X	X	X	X		
s8a	NS 60158 63059	21	Surface Soil	27/10/2016	X	X	X	X	X	

s9a	NS 60137 63085	22	Surface Soil	27/10/2016	X	X	X	X	X	
s10a	NS 60129 63115	23	Surface Soil	27/10/2016	X	X	X	X	X	
s11a	NS 60137 63160	19	Surface Soil	27/10/2016	X	X	X	X	X	
s12a	NS 60138 63182	20	Surface Soil	27/10/2016	X	X	X	X	X	
s8b	NS 60169 63070	24	Surface Soil	27/10/2016	X	X	X		X	
s9b	NS 60151 63096	25	Surface Soil	27/10/2016	X	X	X		X	
s10b	NS 60143 63117	26	Surface Soil	27/10/2016	X	X	X		X	
s11b	NS 60146 63136	27	Surface Soil	27/10/2016	X	X	X		X	
s12b	NS 60150 63162	28	Surface Soil	27/10/2016	X	X	X		X	
s13	NS 60153 63061	29	Surface Soil	01/03/2017		X		X	X	
s14	NS 60142 63079	30	Surface Soil	01/03/2017		X		X	X	

s15	NS 60129 63121	31	Surface Soil	01/03/2017		X		X	X	
s16	NS 60137 63160	19	Surface Soil	01/03/2017		X		X	X	
s17	NS 60138 63182	20	Surface Soil	01/03/2017		X		X	X	
Bulk Soil 1	NS 60129 63102	32	Bulk Surface Soil	12/09/2016			X	X		Column Leaching
Bulk Soil 2	NS 60126 63106	33	Bulk Surface Soil	10/11/2017			X	X		Batch Leaching
Bulk Soil 3	NS 60131 63134	18	Bulk Surface Soil	09/01/2018			X	X		Bioaccessibility
Bulk Soil 4	NS 60129 63121	31	Bulk Surface Soil	09/01/2018			X	X		Bioaccessibility
Bulk Soil 5	NS 60130 63102	34	Bulk Surface Soil	09/01/2018			X	X		Bioaccessibility
Bulk Soil 6[a]	NS 60129 63102	32	Bulk Surface Soil	16/04/2018			X	X		Cr(VI) Loading

[a] Sample used for gel electrophoresis

3.1.3 Sample collection procedures

3.1.3.1 Polmadie Burn water samples

Water samples were collected in acid cleaned polyethylene bottles which were rinsed three times before being filled whilst taking care to remove all air bubbles. The samples were transported under ice back to the laboratory where they were filtered through 0.45 µm nitrocellulose membranes (Whatman, Sigma Aldrich). Chromium(VI) concentrations were determined using the diphenylcarbazide (DPC) colorimetric method (Section 3.7.2.2). Water samples used for determination of Cr(tot), Mn and Fe concentrations were acidified using nitric acid (Aristar, VWR International Ltd) to get 2 % v/v HNO_3 solution and were analysed using inductively couple plasma mass spectroscopy (ICP-MS) (Section 3.7.1.3). All samples were stored at 4°C in the dark before analysis.

3.1.3.2 Polmadie Burn sediment samples

3.1.3.2.1 Surface sediment samples

Surface sediment samples (0-20 cm) were collected using a metal spade. Samples were either bagged in ziplock plastic bags, for small samples (<1 kg), or contained in a clean, lidded bucket for larger samples (>1 kg) for transportation back to the laboratory. Reducing conditions were maintained by filling the sediment sample bags with helium in the field and then taping the bags closed before transportation.

3.1.3.2.2 Sediment cores

Two sediment cores were collected on 17th June 2015. These cores were collected using a 10-cm diameter plastic tube which was pushed into the bottom sediment of the Polmadie Burn to a depth of 41 and 36 cm for cores 1 and 2, respectively, and immediately capped at the top using a rubber stopper. The vacuum created by stoppering the top was used to extract the core intact and the bottom was capped using a rubber stopper. Once extracted the core was then inserted into a N_2-filled glove bag on a coring table (Figure 3-9). Each core was slowly extruded under N_2 and sliced into 1-cm depth sections. The total length of the cores 1 and 2 was 26 and 24.5 cm, respectively. Each depth section was transferred to a 50 mL centrifuge tube which was sealed within the glove box and then taped around the cap to minimise gas exchange during transport back to the laboratory. The centrifuge tubes were stored in an ice-filled cool box until return to the laboratory.

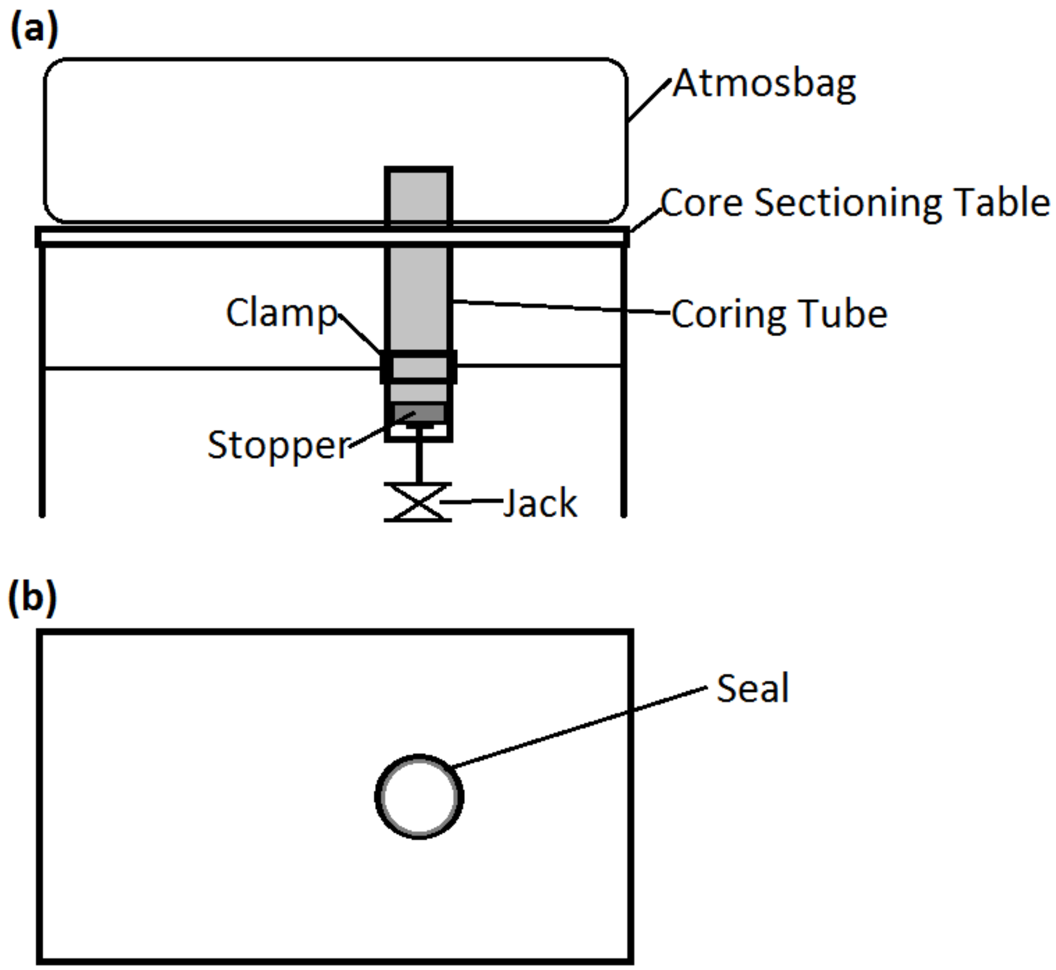

Figure 3-9: Schematic of the coring table (a) shows the side view and (b) a birds eye view of the top.

3.1.3.3 Polmadie Burn Banking Soil Samples

Banking soil surface samples (0-20 cm depth) were collected by taking 5 sub-samples within a 1 m x 1 m square, one from each corner and one from the centre using a soil auger (Figure 3-10). All 5 sub-samples were placed in the same plastic ziplock bag for transport back to the laboratory. For larger, bulk soil samples (> 1 kg) a spade was used to collect soil from 0-20 cm depth. These samples were transported in a clean, lidded bucket to the laboratory.

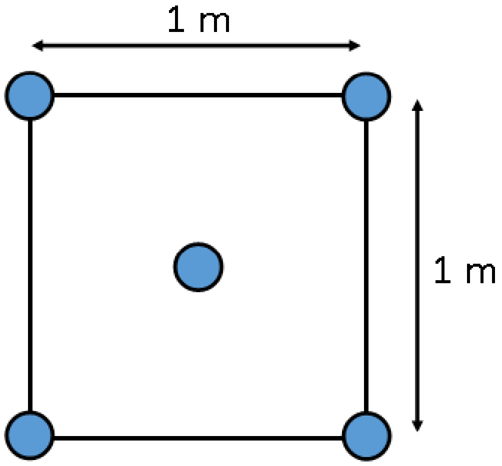

Figure 3-10: Soil sampling strategy

3.1.4 Porewater extraction

Porewater was separated from sediment core depth sections in the laboratory whilst they were still under N_2 using centrifugation and the porewater was decanted from the sediment under a N_2 atmosphere inside a glovebag. Porewater was extracted *in situ* from sediment in the field for Fe(II) determination using multilevel samplers; this was immediately filtered and reacted with the reagent in the field. The construction of these samplers is shown in Figure 3-11 and the pore water was extracted using a peristaltic pump at the following depth: 10, 20, 30 and 40 cm depth. Other sediment porewaters were extracted by collecting sediment and soil samples in the field which were transported back to the laboratory and the porewater extracted using centrifugation. The sediment was stored under a He atmosphere and extracted in a N_2 filled glove box. Soils were not kept under a He or N_2 atmosphere at any point. Material was packed into 50 mL centrifuge tubes and centrifuged at 5000 x g for 30 min. The porewater was then decanted from the material and filtered through a Millex-HA 0.45 µm syringe filter (Merck Millipore). The filtered porewater was acidified and stored at 4°C prior to inductively coupled plasma mass spectroscopy (ICP-MS) analysis, as described below.

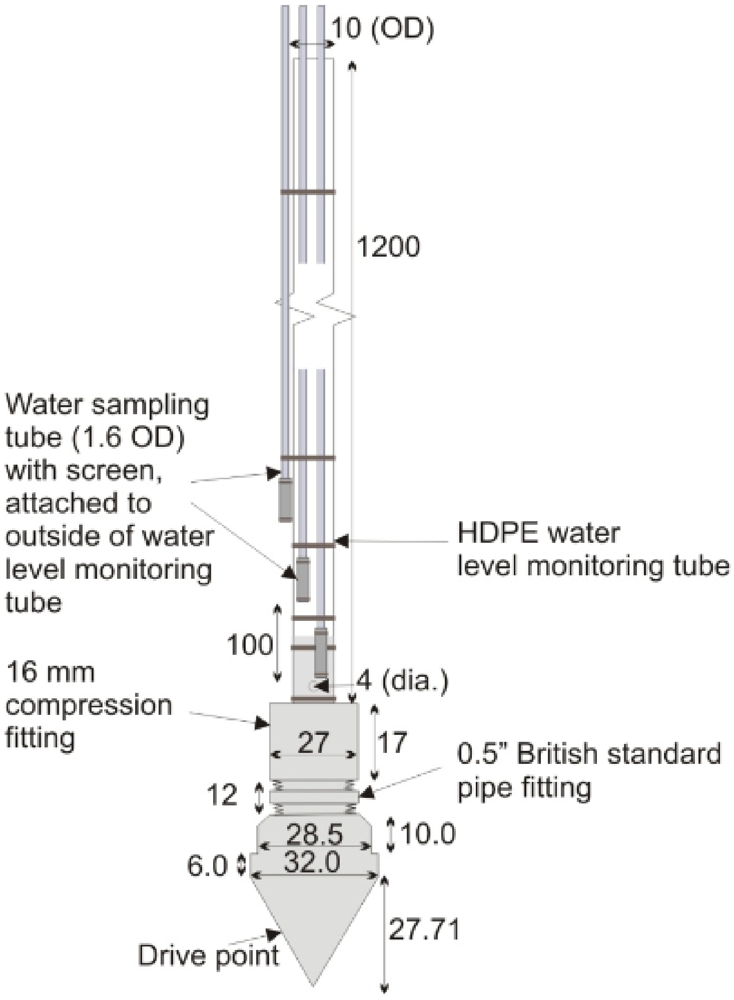

Figure 3-11: Schematic of the multi level samplers used for sediment porewater extraction. Not to scale, all measurements in mm (Dearden, 2010)

3.2 Soil/sediment sample preparation procedures

3.2.1.1 Safety precautions when handling dry soil and sediment

Due to the health hazards associated with Cr(VI) certain precautions were implemented for the storage and handling of the soils and sediments collected for this project. Material was dried in a room with controlled access and the samples were covered with paper towels to minimise dust disturbance. When handling the dry materials disposable coveralls were worn along with a respirator with a filter rating of P3 to minimise exposure to any dust formed. To dispose of any spilled material surfaces were damped to discourage dust formation before being swept up and disposed of through the appropriate waste stream.

3.2.1.2 Homogenisation of soil and sediment samples by dry sieving

Sieving removes material over a certain diameter, and was used to remove large material, such as large stones, plant material and cloth present in the soils and sediments and also helps to homogenise the samples. Once air-dried, each sample was sieved through a 2 mm sieve, unless stated otherwise. Soil and sediment samples collected for laboratory drying experiments were initially sieved through a 5 mm mesh to improve the homogeneity of the sample and were then sieved through a 2 mm mesh to further homogenise the sample before leaching.

3.2.1.3 Air drying of soil and sediment samples for digestion procedures

To prepare the sieved soil and sediment samples for digestions, they were air-dried in a drying cabinet at ambient temperatures until they reached a constant mass. Once dried the samples were stored in labelled plastic ziplock bags.

3.2.1.4 Air drying of soil and sediment samples for laboratory drying experiments

Material was pre-screened through a 5 mm mesh to homogenise the samples and remove any large twigs, stones and cloth before being spread out in large plastic trays in a ~5 cm layer to dry at 20°C. For the column experiment (Section 3.4.1) the soil/sediment was left to dry for 4 weeks with sub-samples taken at 0, 2 and 4 weeks of drying time. For the batch experiment (Section 3.4.2), samples were left to dry with sub-samples taken at 0, 1, 2, 5, 8, 12, 16, 21, 26, 35, 43, 50 and 62 days. These sub-samples were sieved through a 2 mm mesh before being used for the experiments.

3.2.1.5 Preservation of soil and sediment samples for sequential extraction and gel electrophoresis procedures

Field-moist soil samples were stored in plastic ziplock bags at 4°C in a fridge before use and were used within 2 weeks of collection.

3.2.1.6 Ball milling of soil and sediment samples for digestion procedures

To increase the homogeneity, air-dried and sieved soil and sediment samples were ball milled using a Retsch MM 200 ball mill until they formed a fine powder before digestion to improve precision of total elemental concentration data.

3.2.1.7 Determination of organic matter by the loss on ignition method

To remove organic matter from air-dried, sieved soil and sediment samples, 0.25 g aliquots (n= 3) were accurately weighed and then oven-dried at 105°C overnight. The oven-dried sample mass was recorded before they were placed in a muffle oven and ashed at 450°C for 4 h. Once cooled the ashed sample mass was recorded and the % organic matter in each of the samples was then calculated using Equation 3.1.

$$\%\ organic\ matter\ = \frac{oven\ dried\ mass - ashed\ mass}{oven\ dried\ mass} \times 100\% \qquad \text{Equation 3.1}$$

3.2.2 Glass/plasticware cleaning

All glassware used for trace analysis was first rinsed using tap water and scrubbed to remove any visible dirt. The glassware was then placed in a 5 M nitric acid (Analar) bath and boiled for 3 h. The glassware was removed from the acid bath, rinsed using deionised water and then submerged in a deionised water bath which was also boiled for 3 h. The washed glassware was rinsed as it was removed from the water bath using deionised water and then dried at 60°C in a clean drying cabinet.

Plasticware was rinsed with tap water to remove visible dirt before being submerged in a 5% nitric acid (Analar) bath where it was left for 24 h. On removal, the plasticware was rinsed using deionised water and then dried at 60°C in a clean drying cabinet.

3.3 Soil/sediment digestion and extraction procedures

3.3.1 Acid digestions for pseudo-total and total elemental concentration determination

3.3.1.1 Background

Before analysis of trace element concentrations using ICP-OES, the elements of interest must be in solution. This is typically achieved by dissolution of the metals in the soils/sediments using strong mineral acids. Common acids include concentrated (conc.) HNO_3 alone or conc. HNO_3 in combination with other mineral acids such as: (i) *aqua regia* (3:1 ratio, by volume, of conc. HNO_3 to conc. HCl); and (ii) conc. HNO_3: conc. HF acids (e.g. 9:1 ratio, by volume).

Boiling a*qua regia* will break down most minerals, but not silicates, making it suitable as a pseudo-total digestion method. *Aqua regia* digestions were used for digesting the residual phase of the BCR sequential analysis as stated in the BCR protocol (Rauret *et al.*, 1999). It was also used to obtain the pseudo-total metal concentrations so they could be compared to the sum of the fractions from the sequential extraction to evaluate the element recoveries (Bacon and Davidson, 2008). To obtain total digestion a mixture of HNO_3 and hydrofluoric acid (HF) is required to breakdown silicate minerals in the matrix. The United States Environmental Protection Agency (US EPA) Method 3052 was followed in order to digest soil and sediment samples using a Mars 6 microwave digestion system (CEM Corporation).

The concentrations of the following elements – Cr, Fe, Mn, Ca, Mg, Al and S – were measured in the soil and sediment samples collected during this project. Iron and Mn concentrations were analysed due to their importance in Cr oxidation and reduction reactions in the soils and sediments. Calcium, Mg, Al and S are prevalent in COPR so were analysed to investigate the influence of COPR in the samples.

Whilst handling strong acids and performing digestions certain safety precautions were followed to minimise the risk of injury. Minimal amounts of acid were used which was handled inside a chemical fumehood using chemical resistant gloves worn on top of disposable nitrile gloves. Due to the toxicity of HF, extra precautions were taken to minimise injury, including having the calcium gluconate gel nearby and performing all digestions with HF in sealed vessels within a Mars 6 microwave unit which reduced exposure. All waste acid was quenched and neutralised before disposal.

3.3.1.2 Hotplate aqua regia digestion method for pseudo-total elemental concentration determination in soils and sediments

Aqua regia digestions were used to determine the pseudo-total concentrations of Cr and other elements (Fe, Mn, Ca, Mg, Al and S) in the soils and sediments. Accurately weighed aliquots (n = 3) of soil/sediment samples, 0.25 g, were oven-dried in pyrex beakers at 105°C overnight, cooled and then reweighed before being dry-ashed in a muffle furnace at 450°C for 4 h. To the ashed samples, 15 mL of concentrated HCl (Aristar, VWR International Ltd) and 5 mL of concentrated HNO_3 (Aristar, VWR International Ltd) was added. Each beaker was covered with a watch glass and the mixture refluxed on a hotplate for 2 h (11466:1995, 1995). After cooling, the mixture was filtered using Whatman 420 hardened ashless filter paper into a clean beaker. The clean beaker was heated uncovered on the hotplate until the filtrate had been concentrated to approximately 1 mL, which was then transferred to a 25 mL volumetric flask, along with 2% v/v HNO_3 (Aristar, VWR International Ltd) washings. The solutions were made up to the mark with 2% v/v HNO_3 (Aristar, VWR International Ltd) and stored in a 30 mL Sterlin tubes at 4°C before ICP-OES analysis.

3.3.1.3 Microwave-assisted HF/HNO_3 digestion method for total elemental concentration determination in soils and sediments

Soil and sediment samples were digested using a modified version of the US EPA Method 3052. The modification involved ashing the samples to remove organic matter prior to microwave-assisted digestion. Replicate 0.25 g aliquots (n=3) of soil and sediments were oven-dried and ashed as described in section 3.2.1.4 and 3.2.1.7. The ashed samples were then transferred to polytetrafluoroethylene (PTFE) microwave vessels. To each vessel, 9 mL of conc. HNO_3 (Aristar, VWR International Ltd) and 1 mL of conc. HF (Aristar, VWR International Ltd) was added and the mixture was digested at 180°C for 9 min. After digestion, the microwave carousel was left to cool and then transferred into a fume cupboard. The vessels were carefully opened within the fume cupboard and each solution transferred to a PTFE beaker where it was evaporated to approximately 1 mL on a hotplate within the fume cupboard. These solutions were transferred, with washings using 2% v/v HNO_3 (Aristar, VWR International Ltd), into 25 mL volumetric flasks and made up to the mark using 2% v/v nitric acid (Aristar, VWR International Ltd). Each solution was filtered using Whatman 420 hardened ashless filter papers before storage in the fridge at 4°C in a 30 mL Sterlin tube prior to analysis.

3.3.1.4 Digestion quality control

For each set of digestions two reagent blanks and two replicates of a reference material were used. The reference materials used was a CRM 7002 Light Sandy Soil (with elevated analyte levels), ANALYTIKA Ltd. The certified values for total and pseudo-total (*aqua regia* digestions) concentrations of Cr in this reference material was 179 ± 8 and 147 ± 8 mg kg^{-1}, respectively. These quality control samples were digested in the exact same way as the samples.

3.3.2 Sequential extraction methods for determination of elemental associations in soils and sediments

3.3.2.1 Background

Whilst several different sequential extraction procedures exist (Tessier *et al.*, 1979, Tack and Verloo, 1995), inconsistency in the different methodology resulted in a harmonised method being produced by the Bureau Communautaire de Référence (BCR). This method was then further updated to produce the modified BCR sequential extraction which was used in this study (Ure *et al.*, 1993, Rauret *et al.*, 1999).

Sequential extractions uses selective extractants to selectively remove the elements of interest from different geochemical fractions from soils or sediments. This can provide useful information which improves our understanding of elemental interactions with soil/sediments and, when used in conjunction with other experiments, it can help to understand element remobilisation. The three target phases of the modified BCR sequential extraction are the exchangeable, reducible and oxidisable fractions (Table 3-4). Along with these three fractions, the residual material from Step 3 was digested using an *aqua regia* digestion as described above in Section 3.3.1.2. A summary of the three fractions and their target phases is shown in Table 3-4.

Table 3-1: BCR Sequential Extraction Summary of Target Phases

	Fraction	Reagent	Target phase
Step 1	Exchangeable	0.11 M acetic acid	Weakly absorbed to the soil – acid exchangeable
Step 2	Reducible	0.1 M hydroxylammonium chloride	Fe/Mn oxides
Step 3	Oxidisable	30 % v/v hydrogen peroxide followed by 1 M ammonium acetate	Organic matter/ sulfides
Step 4[a]	Residual	*Aqua regia* (3:1 conc. HCl and conc. HNO_3)	Mineral

[a]Evaluation of the residual phase is recommended, although not strictly part of the protocol, and was therefore included in this study

3.3.2.2 BCR sequential extraction method for determination of elemental associations in soils and sediments

The BCR sequential extraction used here followed the method outlined by Pueyo *et al.* (2001). In Step 1, fresh sample was sieved through a 2 mm mesh and then replicate 1 g aliquots (n=2) was weighed into a 50 mL centrifuge tube and 30 mL of 0.11 M acetic acid was added. A reagent blank was included for every 10 samples which was taken through the same extraction procedure. The samples were shaken for 16 h on an end-over-end shaker at ~20 rpm. After the shaking period, the tubes were centrifuged at 5000 x g for 10 mins, the supernatant was decanted and filtered through a Millex-HA 0.45 µm syringe filter (Merck Millipore) into a new container and stored at 4°C before analysis. The residue was washed using 20 mL of deionised water which was shaken for 20 min before being centrifuged at 5000 x g for 10 mins and the supernatant discarded.

For Step 2, 30 mL of 0.1 M hydroxylammonium chloride at pH 2 was added to the residue from Step 1. This was shaken for 16 h, separated and the residue washed as described in Step 1.

For Step 3, 10 mL of 30% v/v hydrogen peroxide was added to the residue from Step 2. The covered centrifuge tubes were left at room temperature for 1 h before being heated to 85°C for 1 h in a water bath. The liquid was evaporated down to ~ 1 mL before a further 10 mL of 30% v/v hydrogen peroxide was added, heated to 85°C for 1 h and then evaporated down to ~1 mL. Finally 50 mL of 1 M ammonium acetate solution was added and the tubes were shaken on an end-over-end shaker for 16 h. The slurry was separated using centrifugation and the residue was washed as described in Step 1.

The residual from Step 3 was digested using the *aqua regia* hotplate digestion method described in Section 3.3.1.2.

3.3.2.3 Quality control

For each batch two reagent blanks for each step and 1 g of certified reference material BCR-701 Lake Sediment (trace elements) were included. The recovery of selected certified elements in BCR 701 are shown in Table 3-5. The recovery of Cr from Step 3 of the sequential extraction was low (71%) and is likely to be related to the loss of material due to the violent reaction between the material with hydrogen peroxide during Step 3. Material lost during the washing stage may also have contributed to the low recovery in Steps 2, 3 and 4.

Table 3-2: Recovery of Cr from BCR 701 during sequential extraction. Values are mean ± one standard deviation

	Certified Value of Cr (mg kg^{-1})	Measured Value of Cr (mg kg^{-1})
Step 1	2.26 ± 0.16	2.62 ± 0.25
Step 2	45.7 ± 2	38.4 ± 0.94
Step 3	143 ± 7	102 ± 31
Step 4	63 ± 8	51.9 ± 7.6

3.3.3 Alkaline digestion for the determination of chromium(VI) concentrations in soils and sediments

3.3.3.1 Background

To selectively extract Cr(VI) from soils and sediments a procedure is required which will solubilise all forms of Cr(VI) without reducing Cr(VI) or oxidising Cr(III). The high pH of an alkaline digestion makes Cr(VI) reduction unfavourable and the addition of Mg^{2+} in a phosphate buffer will suppress Cr(III) oxidation. The alkaline digestion method used for this project followed the US EPA Method 3060A which was used in conjunction with colorimetric analysis using DPC for selectively determining Cr(VI) in the resulting solution.

Organic matter is a known reductant of Cr(VI) although this is only observed at low pH. The DPC colorimetric reaction occurs at acidic pH so the reduction of Cr(VI) during this stage can greatly reduce the concentration of Cr(VI) measured in the samples. To get around this problem it has been shown that ashing soil samples before digestion does not change the oxidation state of Cr making this a required step in Cr(VI) analysis (Broadway, 2008).

3.3.3.2 USEPA method 3060a for alkaline digestion of soils and sediments in preparation for chromium(VI) concentration determination

The digestion followed USEPA Method 3060A. The alkaline digestion fluid used was 0.5 M sodium hydroxide/0.28 M sodium carbonate which was prepared by dissolving 20 g of sodium hydroxide and 30 g of sodium carbonate in 1 L of deionised water. Soil and sediment samples (2 g wet mass) were dry-ashed at 450°C for 4 h before addition of 30 mL of the digestion fluid along with 0.5 mL of phosphate buffer (8.71 g of K_2HPO_4 and 6.80 g of KH_2PO_4 in 100 mL of deionised water) and approximately 0.4 g of magnesium chloride. The slurry was stirred for 5 min and then heated on a hotplate at 90 – 95°C for 1 h, with stirring every 15 min. After cooling, the slurry was filtered through a Whatman 542 hardened ashless filter paper into a 100 mL volumetric flask. The solution was then diluted, if required before analysis using the DPC colorimetric method (Section 3.7.2.2)

3.3.3.3 Quality control

Each set of digestions included two reagent blanks and a certified reference material (CRM041 Chromium VI – Sandy Loam, Sigma Aldrich) to assess the recovery of the digestion. The measured concentrations of the CRM041 Cr(VI) was 63.0 ± 6.1 mg kg^{-1} (n=11) (certified value 66.5 ± 5.51).

3.4 Simulated drying of soil and sediment in the laboratory

3.4.1 Column leaching of soil and sediments over drying period of 4 weeks

3.4.1.1 Background

The aim of the column experiments was to determine the changes in leachable Cr concentrations in soils and sediments over a drying period of 4 weeks, thus simulating conditions in the natural environment.

Glasgow is located on the West Coast of Scotland which has a relatively mild and wet climate. Historical rainfall data shows that the mean monthly rainfall is 93 mm and rain falls, on average, every second day. During periods of drying soil, pH can decrease due to the disruption and alteration of organic matter and the Eh can increase due to oxygen being able to diffuse through the soil more easily. The alteration of these factors may influence the leachability of Cr from soils after periods of dry weather. Sediments, unlike soils are better protected from drying as the Polmadie Burn was observed to flow on all sampling occasions over the duration of this project. However, dredging of material to deepen waterways, such as canals, to improve their navigability can lead to sediments with high concentrations of potentially toxic elements, including Cr, drying out. Since this change in environment can lead to drastic changes in metal leachability, sediment was also included in the simulated drying experiments to investigate the mobility of Cr in anoxic sediments upon drying in an oxic environment.

This section describes the experiments that were carried out to determine the effect of drying on the mobility of Cr in soils and sediments. For these experiments, bulk soil and sediment surface samples were collected which were air-dried for different time intervals (0, 2 and 4 weeks). Typically there is 1 mm of precipitation or more on 47% of the days per month in Glasgow so a drying period of up to 4 weeks was chosen as it was deemed unlikely for a dry period to last longer than this.

The bulk material was homogenised as described in Section 3.2.1.2, sub-sampled and uniformly packed into leaching columns. To determine the amount of Cr that could be leached by deionised water and synthetic rainwater, the different waters were fed in at the base and decanted at the top to stop compaction of the material during leaching. The synthetic rainwater was 0.01 M $CaCl_2$ solution (OECD, 2004) adjusted to pH 5, the mean pH of precipitation falling in South West Scotland (DEFRA, 2018). The design of the columns is outlined below.

3.4.1.2 Optimisation of column design

The original column design used gravity fed columns where the leachate was added to the top of the column on the material surface and collected from the base of the columns. Due to issues with compaction – especially with the sediment samples – it became clear that a different approach was required. The columns were redesigned so that they were again gravity fed, but the leachate was added to the base of the columns and travelled up the column before being decanted from the top (Figure 3-12). This reduced the effect of compaction on the material

The columns were constructed from a clear acrylic tube (internal diameter of 50 mm) and an acrylic plastic base which was milled to the specific dimensions (Figure 3-13 and Figure 3-14). The base was drilled to form the input for the column which was covered with a plastic mesh to disperse the leaching solution (Figure 3-15) and minimise the formation of preferential flow paths through the soil and sediment samples.

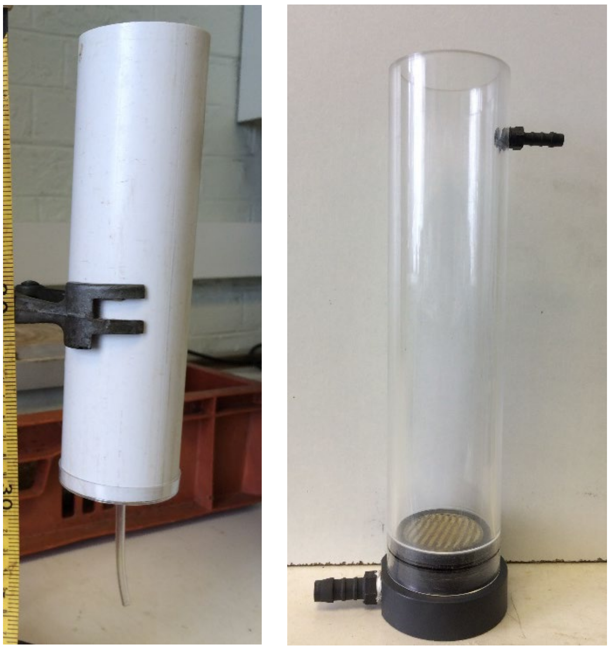

Figure 3-12: Original column design (a) and redesigned columns used for column leaching experiment (b)

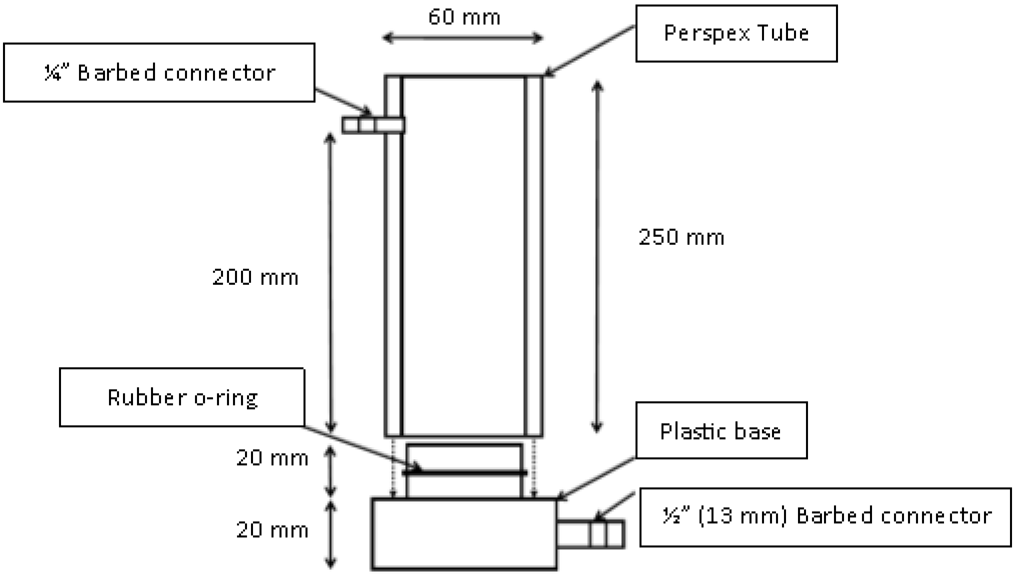

Figure 3-13: Side-on schematic of column and base giving approximate dimensions

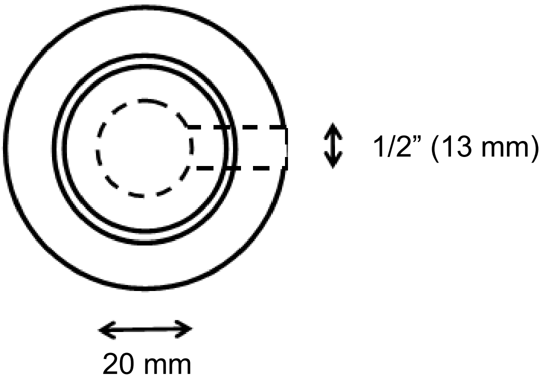

Figure 3-14: Input channels in column base

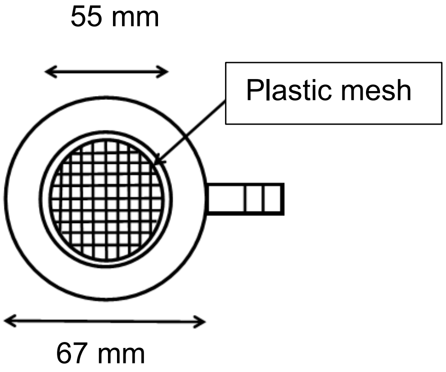

Figure 3-15: Top view of base giving approximate dimensions

3.4.1.3 Column leaching method

The two leaching solutions used in these experiments were deionised water (DIW) and synthetic rain water (SRW), a 0.01 M calcium chloride solution with a pH of 5.0 adjusted using dilute HCl (Aristar, VWR International Ltd). The columns (n=3) were packed by adding small amounts (~2-3 cm depth) of material which was gently shaken and tapped on the bench until a total of 20 cm of material had been added to the column. The columns were flooded with 120 mL of leaching solution for 1 h after which the columns were leached by adding 30 mL of leaching solution to the columns every 0.5 h for a total of 4 h, resulting in the collection of 8 fractions. Each fraction was equivalent to 1.5 weeks of rainfall, so in total the soil/sediment were leached with the equivalent of approximately 6 weeks of rainfall.

The leachates from each column were analysed for the following parameters: (i) Cr(total), Fe, Mn, Ca, Mg and S concentrations using ICP-OES/MS (see section

3.7.1); (ii) Cr(VI) concentration using the DPC colorimetric method (see section 3.7.2.2); and (iii) pH (see section 3.7.3.1). In addition, selected fractions were ultrafiltered to separate the colloidal fraction from the truly dissolved fraction as described below.

3.4.1.4 Ultrafiltration of column leachate samples

Ultrafiltration of 0.45 µm-filtered water samples and soil/sediment column leachates was achieved using Sartorius Vivaspin 3 kDa ultrafiltration units which contain a polyethersulfone membrane. An accurate mass (~10 g) of each water sample or leachate was transferred into the upper portion of these units which were then centrifuged at 3000 x g for 0.5 h which concentrated the liquid down to <1 mL. The accurate mass of the filtrate and retentate was recorded and the retentate was diluted with a known mass of deionised water. Both the filtrate and the diluted retentate were analysed for Cr(total), Fe, Mn and Al using ICP-MS (Section 3.7.1.3).To assess the accuracy results the recovery of the element was determined by comparing the concentration of the element, as measured by ICP-MS, in the aliquot of the sample which was not ultrafiltered. Adequate recovery was deemed to be between 80 -120%.

3.4.2 Batch leaching of soils and sediments over a drying period of 9 weeks

3.4.2.1 Background

The aim of the batch experiments was to determine the changes of leachable Cr concentrations in the Polmadie Burn banking soils and sediments over a drying period of 9 weeks.

To investigate the leachability of Cr from soils and sediments, batch experiments were used where a set mass of soil was shaken in a set volume of liquid to evaluate the release of Cr from the soil. These experiments were designed to obtain a more detailed view of the changes in Cr geochemistry during the drying process of the soils and sediments. The smaller sample size and time required for analysing the soil at different time brackets allowed for more frequent sampling and the ability to monitor the soil and sediment for a longer time period. This was deemed necessary to explain the trends seen from the column leaching experiment (see Chapter 5). From the column experiments it was observed that the first couple of weeks of drying had the largest impact on the soil and sediment where there was rapid water loss from the samples. Hence the simulated laboratory drying experiments were conducted over a period of 9 weeks with a more frequent sampling frequency during the first 3 weeks of drying and less frequently over the final 6 weeks. This allowed for a higher resolution than the column experiment which only examined limited time intervals during the drying period of 4 weeks.

The solid to liquid (S:L) ratio was 1:2 for this experiment. This low S:L ratio was used to simulate the infiltration of rainwater into soil rather than the suspension of material in water. Sediment was investigated using this experiment to examine the changes in Cr leachability if the sediment is dredged and allowed to dry in an oxic environment. From the column leaching experiments it was shown that there was no significant difference between the concentrations of Cr leached by the synthetic rain water compared to deionised water so the batch experiments used synthetic rain water (as described in section 3.4.1.1).

3.4.2.2 *Drying experiment*

Soil and sediment was collected, sieved through a 5 mm mesh to homogenise the sample and left to air dry. At certain time intervals (0, 1, 2, 5, 8, 12, 16, 21, 26, 35, 43, 50 and 62 days) sub-samples (n=3) were sieved through a 2 mm mesh and used for leaching. The leaching process used 10 g (field-moist) of the sieved material which was placed in a 50 mL centrifuge tube and to which 20 mL of synthetic rain water (0.01 M calcium chloride solution with a pH of 5) was added and the tubes were shaken at ~20 rpm on an end-over-end shaker for 1 h. After shaking, the samples were centrifuged at 5000 x g for 10 min and the supernatant was removed, filtered through a Millex-HA 0.45 µm syringe filter (Merck Millipore) and stored at 4°C before analysis. The following parameters were analysed: (i) Cr(VI) concentration using the DPC colorimetric method (see section 3.7.2.2); (ii) Cr(total), Fe and Mn concentrations using ICP-MS (see section 3.7.1.3); (iii) Ca, S and Mg concentrations using ICP-OES (see section 3.7.1.2); and (iv) pH (see section 3.7.3.1).

3.4.3 Investigation of the sorption of chromium(VI) to Polmadie Burn banking soil and its subsequent release

3.4.3.1 *Background*

The aim of these laboratory experiments was to investigate the sorption of Cr to the banking soil of the Polmadie Burn and then its subsequent release upon leaching.

To understand the role that the banking soil of the Polmadie Burn has as a Cr reservoir its ability to sorb and retain Cr needs to be quantified. Hence these laboratory experiments were designed to investigate: i) the speed of sorption of Cr to the soils and ii) the release of Cr that has been sorbed by the soil. There are three proposed pathways by which Cr can be immobilised by soils: i) the sorption of Cr(VI) species to the soil/sediment surface; ii) the Fe(II) reduction pathway followed by the precipitation of mixed Fe/Cr hydroxides; and iii) the reduction and then sorption by organic matter (Rai *et al.*, 1989, Barnhart, 1997, James *et al.*, 1997). By measuring the change in Cr concentrations in solutions which have been in contact with the soils for different lengths of time the speed of sorption/desorption can be measured.

Chromium(VI) is weakly absorbed to soil surfaces, however Cr(VI) reduced to Cr(III) forms insoluble species which are much less likely to re-dissolve. In the environment, at neutral pH the Cr(VI) concentration in solution is most likely to be controlled by adsorption/desorption reactions (Rai *et al.*, 1989). Examining the rate at which Cr is released from the soil will give an indication of the amount that is easily leachable and also of the stability of Cr in the material. If the soil is loaded with solution containing a known Cr concentration any decreases in Cr concentration in that solution must be due to sorption by the soil. The speed at which the Cr is removed from solution will depend on the adsorption kinetics of Cr to the soil. The order of the reaction was determined by modelling the removal of Cr(VI) from the solution using the following equations:

Zero Order: $$[Cr(VI)]_t = -kt + [Cr(VI)]_0$$ Equation 3.2

First Order: $$\ln[Cr(VI)]_t = -kt + \ln[Cr(VI)]_0$$ Equation 3.3

Second Order: $$\frac{1}{[Cr(VI)]_t} = kt + \frac{1}{[Cr(VI)]_0}$$ Equation 3.4

Where $[Cr(VI)]_t$ is the concentration of Cr(VI) in solution at time t, $[Cr(VI)]_0$ is the initial concentration of Cr(VI) at time t=0 and k is the reaction constant. Once modelled the adjusted R^2 value and the difference between predicted and actual $[Cr(VI)]_0$ were compared to determine how good the model was at predicting the kinetics of Cr(VI) removal from solution.

Once released into solution the speciation of Cr can change depending on the other species available (James *et al.*, 1997). If the material contains manganese oxides then Cr(III) can be oxidised to Cr(VI) whereas Fe(II) and organic matter will facilitate the reduction of Cr(VI) to Cr(III). The rate of the oxidation and reduction will depend on the environmental conditions, mainly pH, and the species of Cr and other metals/organic matter present.

The sections below outline the experimental procedures carried out to investigate: i) Cr(VI) sorption by the soil and ii) the subsequent release of Cr(VI) sorbed by the soil. These experiments were conducted using a batch equilibrium method to investigate the adsorption/desorption of Cr to the soils (OECD, 2000).

3.4.3.2 Chromium adsorption

Field-moist soil was sieved through a 2 mm mesh and stored in the dark at 4°C before use. In a 50 mL centrifuge tube, 10 g of field-moist soil was suspended in 20 mL of 0.01 M $CaCl_2$ solution which contained a known concentration of Cr(VI) and shaken for a set time. The time periods chosen for this experiment were 1, 2, 4, 8, 16, 24, 48 and 120 h. After shaking for the set time period the concentration of Cr(VI) in solution was measured using the colorimetric DPC method (described in section 3.7.2.2) and the concentration Cr(tot) was measured using ICP-OES (as described in section 3.7.1.2). The concentration of the loading solutions was 1.3 and 10 mg L^{-1}. Batch experiments were run in triplicate for each time period.

3.4.3.3 Chromium desorption

3.4.3.3.1 Control

Field-moist soil was sieved through a 2 mm mesh and stored in the dark at 4°C before use. To determine the background concentration of leachable Cr from the soil 10 g of field-moist soil was extracted with 0.01 M $CaCl_2$ solution made up in deionised water for the following time periods: 1, 2, 4, 8, 16, 24, 48, 96 and 120 h. After shaking for the set time period the concentration of Cr(VI) in solution was measured using the colorimetric DPC method (described in section 3.7.2.2) and the concentration Cr(tot) was measured using ICP-OES (as described in section 3.7.1.2). Batch extractions were run in triplicate for each time period.

3.4.3.3.2 Loading of chromium (VI) to soil

The soil was loaded with Cr by shaking 10 g of field-moist soil with 20 mL of 10 mg L^{-1} Cr(VI) solution which was shaken for 120 h after which over 95% of Cr(VI) had been adsorbed by the soil. The liquid was removed by centrifugation (5000 g for 15 min) after which it was leached using the same method as outlined in section 3.4.3.3.1 above.

3.5 Bioaccessibility of chromium(III) and chromium(VI) in the respirable fraction (<10 μm) of soils and sediments

3.5.1 Background

Chromium(III) is an essential nutrient but Cr(VI) is known to have adverse health effects where chronic exposure can lead to contact dermatitis when in contact with the skin, leading to skin irritation, rash or ulcers. Ingestion of Cr(VI) can lead to organ damage – specifically the liver and kidneys – and inhalation of airborne Cr can lead to respiratory irritation and also cancer of the lung and throat. Ingestion of Cr(VI) from soils which have a high OM content results in the reduction of Cr(VI) to Cr(III) in the acidic environment of the stomach by the organic matter. Once passed into the intestines the rise in pH results in the Cr(III) becoming insoluble and therefore precipitates and is passed out of the body (Broadway, 2008). The inhalation bioaccessibility of Cr(VI) is more poorly understood but, since Cr(VI) is a known carcinogen, it is important to quantify the risk associated with exposure to Cr containing soil to evaluate the potential uptake of Cr(VI) from dust.

Soil/sediment particles that are larger than 10 μm in diameter are too large to enter the lungs so any inhalation bioaccessibility study must use material which is smaller than this size fraction. Traditional methods to separate and isolate different particle size ranges involve passing soils/sediments through a sieve of a known aperture size, either as dry material or assisted by the addition of water. This method becomes problematic when trying to collect a large enough amount of <10 μm material for a series of bioaccessibility tests and so other methods had to be investigated. Laser particle size analysis, although useful for identifying the particle size distribution within soils and sediments, is not suitable for this purpose because size fractions cannot be isolated. Thus the available methods for isolating particles of <10 μm are narrowed to the use of gravity settling.

The Stokes equation can be used to determine how fast a particle of a certain diameter will travel through a medium (Equation 2.1):

$$V_t = \frac{gd^2(\rho_p - \rho_m)}{18\,\mu} \qquad \text{Equation 3.5}$$

where V_t is the terminal velocity of the particle (cm s^{-1}), g is the acceleration due to gravity (9.81 m s^{-2}), d is the diameter of the particle, ρ_p is the density of the particle, ρ_m is the density of the medium and μ is the viscosity of the medium.

Using Equation 2.1, a 10 µm particle with a density of 2650 kg m^{-3} (the mean density of soil particles) settling in methanol, which has a density of 792 kg m^{-3} and a viscosity of 0.000594 kg m^{-1} s^{-1}, will have a terminal velocity of 1.05 cm min^{-1}.

3.5.2 Isolation of <10 µm fraction from soil and sediment samples

Soil was collected from three sites (see Table 3-2) by the Polmadie Burn which was transported back to the laboratory where it was sieved through a 2 mm mesh and then air dried for 1 week. Aggregates in the material were gently broken up using a mortar and pestle and the material was dry-sieved sequentially through 2 mm, 90 µm, 53 µm and finally a 38 µm stainless steel sieve. Approximately 10 g of the <38 µm fraction from each sample was then suspended in ~280 mL methanol which was poured into a 250 mL measuring cylinder and left to settle for 1 h. The terminal velocity, as calculated in Equation 2.1 was 1.05 cm min^{-1} therefore the theoretical time for a particle to settle 20 cm is 19.0 min. To ensure all material greater than 10 µm was removed the suspension was left for 1 h to settle. After the settling period, the top 20 cm of liquid was decanted. The measuring cylinder was topped up to the original level, the material was re-suspended and the process was repeated a further two times to ensure that the maximum amount of the <10 µm fraction was recovered. The three fractions were combined and left to dry. From approximately 75 g of the <38 µm fraction approximately 3 g of <10 µm was recovered.

The extraction of potentially toxic elements from PM_{10} will depend on the extract used to simulate the lung fluid. The synthetic lung fluid used for this study was Gamble's solution which has a chemical composition that closely mimics the lungs Table 3-6 (Wragg and Klinck, 2007). This mixture of chemicals mimics the composition of the lungs and the surfactants and other ligands present in the fluid will influence sequestration of metals by the synthetic lung fluid.

3.5.3 Inhalation bioaccessibility method

Approximately 0.10 g of <10 µm material was accurately weighed and then suspended in 10 mL of Gamble's solution. The suspension was shaken on an end-over-end shaker for 2 h at 38°C before being centrifuged at 5000 x g for 2 min. The supernatant was decanted, the Gamble's solution was replaced and the process was repeated three more times to give a total of 4 fractions (0-2, 2-4, 4-6 and 6-8 h). For each fraction, the concentration of Cr(VI) was determined using the DPC colorimetric method (see section 3.7.2.2) and the concentrations of total Cr were determined using ICP-MS.

Table 3-3: Composition of Gamble's solution (Wragg and Klinck, 2007)

Chemical	Mass in 1 L (g)
Sodium chloride	6.779
Ammonium chloride	0.535
Sodium hydrogen carbonate	2.268
Glycine	0.375
Calcium chloride	0.022
Sodium citrate	0.059
L-Cysteine	0.121
Sodium hydrogen phosphate	0.187
Sulphuric acid	(5 mM)
Diethylenetriaminepentaacetic acid (DTPA)	0.080
Benzalkonium chloride (ABAC)	0.050

3.6 Gel electrophoresis

3.6.1 Background

To investigate the association of Cr with organic matter, gel electrophoresis was used to separate dissolved organic matter based on its size and charge. The gel electrophoresis principle works by creating an agarose gel bed which was submerged in a tris(trimethylsilyl) borate (tris borate) buffer solution with a well in which the soil extracted organic matter was added. An electric current was applied to the gel and the charged particles are drawn to the oppositely charged terminal. The speed, and therefore the distance, that the particle travels at will depend on their size and charge. Small highly charged colloids will travel further than large ones with less charge. By correlating the occurrence of Cr with organic matter in these bands it was possible to determine the association of Cr and organic matter.

3.6.2 Organic matter extraction from soils and sediments

To extract the organic matter from the soils and sediments a sodium hydroxide solution was used. To a centrifuge tube 10 g of soil/sediment was added to 20 mL of 0.1 M sodium hydroxide which was prepared by dissolving 0.4 g of sodium hydroxide in a 100 mL volumetric flask made up to the mark with deionised water. The mixture was shaken on an end-over-end shaker for 1 h and then the extractant was separated from the soil/sediment by centrifugation at 5000 g for 10 min. The extractant was then filtered through a Millex-HA 0.45 µm syringe filter (Merck Millipore) before being added to the gel electrophoresis well.

3.6.3 Gel electrophoresis method

The tris-borate buffer solution was prepared by dissolving 5.4 g of 2-amino-2-hydroxymethyl-propane-1,3-diol and 2.75 g of orthoboric acid in a 1 L volumetric flask which was made up to the mark using deionised water. The 1% w/v agarose gel was prepared by gently heating 1.5 g of agarose powder in 150 mL of tris-borate buffer. The mixture was then gently heated in a microwave oven (300 W for approximately 3 min) until the agarose dissolved. The hot gel was then poured into the gel tray where a well was created using a comb and left to cool for 30 min. The tank was filled with tris-borate buffer solution with the well closest to the negative terminal as the organic matter has a high negative charge. Approximately 2 mL of the soil or sediment extractant was added to the well and a fixed current of 20 mA was applied across the gel for 30 min. The gel was then cut into 10 strips of 1 cm width.

To extract the liquid from the gel the strips were frozen and defrosted and then centrifuged (5000 g for 20 min) to separate the liquid from the gel. The relative organic matter concentrations in each gel was determined by measuring the absorbance of the liquid at 254 nm (section 3.7.2.4) and the Cr, Fe, Mn and Al concentrations were measured using ICP-MS (section 3.7.1.3).

3.7 Analysis of water samples, extracts and digests

3.7.1 Inductively coupled plasma-optical emission spectroscopy (ICP-OES) and inductively coupled plasma-mass spectroscopy (ICP-MS)

3.7.1.1 Background

The concentrations of elements dissolved in an aqueous solution can be analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) or inductively coupled plasma-mass spectroscopy (ICP-MS). These techniques use an argon plasma which is created by passing argon gas through a high power radio frequency (RF) signal which causes it to ionise creating a gaseous mixture of positive ions and electrons which have a net neutral charge. The large amount of energy produced during this process creates temperatures of up to 10,000 K which atomises and ionises the samples (Figure 3-16). In ICP-OES the relaxation of electrons to lower energy states releases a photon which has a wavelength unique to that energy gap. This means different elements produce light of discrete values which identifies the element and, if the intensity of the light is measured, then the concentration of the element can be calculated.

For ICP-MS the plasma creates charged ions which can be selectively measured based on their mass over charge (m/z) ratio. By selecting a certain m/z ratio, individual elements can be quantified. The m/z was selected using a quadrupole mass analyser which has 4 poles arranged across for each other which have oscillating electric currents passing through them. This oscillating electrical current affects the trajectory of the ion therefore only focusing ions with a certain m/z on the detector. Due to interference of polyatomic species a collision cell was used for certain elements to increase the sensitivity of the instrument. The collision cell works by passing ions of the selected m/z through a reaction chamber filled with He_2. Due to the larger size of the polyatomic ions they are statistically more likely to collide with a He_2 molecule therefore removing them before entering the detector.

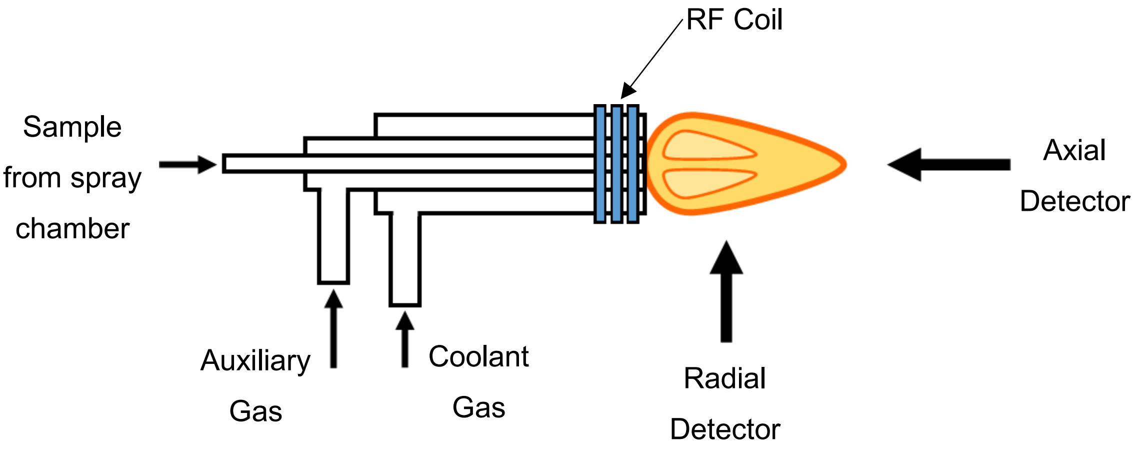

Figure 3-16: Schematic of ICP torch

3.7.1.2 ICP-OES

ICP-OES analysis was carried out using the following instruments: Perkin Elmer Optima 5300DV, Varian Vista Pro or Perkin Elmer Optima 5800 instrument. The LoD for the elements of interest is summarised in Table 3-7 and operating conditions in Table 3-8.

Regardless of the instrument used, calibration was achieved using Merck ICP multi-element standard IV (Merck M4), for Cr, Mn, Fe, Ca, Mg and Al and single element calibration standard for S (Merck). When used in axial detection mode, the following concentrations were used: 0.1, 0.5, 1, 5, 10, 20, 50, 100 and 200 mg L^{-1}. When radial detection was used the following standards were used: 10, 50, 100, 500 and 1000 mg L^{-1}. Two separate calibrations were used to determine the elemental concentration when using axial view: a low calibration of 0 to 10 mg L^{-1} and a high calibration of 0 to 200 mg L^{-1}. Independent checks, e.g. a x10 dilution of Merck ICP multi-element standard VI (Merck M6) and a x10 dilution of WavCal (Perkin Elmer) was used to test the accuracy at the beginning of each sample run. During analysis a calibration check (Merck M4) and a rinse (2 % v/v Aristar, VWR International Ltd HNO_3) was analysed every 10 samples to ensure there was no drift.

Table 3-4: Limit of detection from ICP analysis

Element	ICP-OES (mg L^{-1})	ICP-MS (µg L^{-1})
Cr	0.378	0.154
Fe	0.234	4.01
Mn	0.194	0.660
Al	0.901	5.14
Ca	0.557	-
Mg	0.565	-
S	0.248	-

Table 3-5: ICP-OES operating conditions

Parameter	Value
Nebuliser	Gem Tip cross flow
Spray Chamber	Scott Type
Plasma Gas Flow (Ar)	10 L min^{-1}
Auxiliary Gas Flow (Ar)	0.2 L min^{-1}
Carrier Gas Flow (Ar)	0.6 L min^{-1}
RF Power	1500 W
Pump Flow Rate	1.5 L min^{-1}
Plasma Mode	Axial and Radial[a]

[a]Radial view was only used for a select number of samples where concentrations were higher than 200 mg L^{-1}

3.7.1.3 ICP-MS

ICP-MS was carried out using an Agilent 7500ce instrument. The LoD of this instrument is summarised in Table 3-7 and it was used to analyse samples which had element concentrations lower than the LoD of the ICP-OES.

The instrument was calibrated using Merck M4 solution which was diluted using the same matrix as the samples, when possible, to the following concentrations: 0.1, 0.5, 1, 5, 10, 50, 100, 500, 1000 µg L^{-1}. The calibration was validated using Standard Reference Material 1640a Trace Metals in Freshwater (SRM 1640a) and, as with the ICP-OES analysis, drift checks and rinses were included after every 6 samples. When the sample matrix did not match the matrix of the standards an internal standard was used which had the closest first ionisation potential to that of the analyte. For Cr the internal standard used was scandium (Sc) and for Fe and Mn the internal standard used was rhodium (Rh). The approximate concentration of the internal standard was 100 µg L^{-1}. The operating conditions of the ICP-MS are summarised in Table 3-9.

Table 3-6: ICP-MS operating conditions

Parameter	Value
Nebuliser type	Glass Scott Type
Nebuliser uptake rate	0.02 mL min^{-1}
Plasma Gas Flow (Ar)	0.82 L min^{-1}
Axillary Gas Flow (Ar)	0.21 L min^{-1}
Carrier Gas Flow (Ar)	10 L min^{-1}
RF Power	1540 W
Analyser Pressure	3 x 10^{-6} Pa

3.7.2 Colorimetric Analysis

3.7.2.1 Background

Colorimetric analysis usually requires the analyte of interest to react with a reagent to produce a coloured complex which absorbs at a known wavelength in the ultraviolet or visible (UV-Vis) light spectrum. When light is passed through a coloured solution a proportion of the light at specific wavelengths will be absorbed by the solution. The amount absorbed is described by the Beer-Lambert law:

$$A = \varepsilon\, l\, c \qquad \text{Equation 3.6}$$

where A is the measured absorption of the solution, ε is the molar absorption coefficient, *l* is the path length of the cell and c is the concentration of the solution. Because the molar absorption coefficient and path length are kept constant, the absorbance is proportional to the concentration of the solution. By reacting known concentrations of the analyte with the reagent, a calibration curve can be constructed which can then be used to relate the absorbance of the unknown samples to the concentration of analyte.

3.7.2.2 Diphenylcarbazide chromium(VI) determination

Chromium(VI) can be selectively analysed by reacting it with 1,5–diphenylcarbazide (DPC) at an acidic pH to form a purple colour which has a maximum absorbance at 540 nm. The method used was a modified version of the USEPA Method 7196 Chromium, Hexavalent (Colorimetric). Instead of acidifying the solution before adding the DPC solution, the DPC solution was acidified using orthophosphoric acid to ensure that the final solution pH was that required for the complexation reaction to take place.

Acidified DPC solution was made by dissolving 0.095 g of DPC in 25 mL of acetone (Fisher Scientific, Reagent Grade), 30 mL of orthophosphoric acid (Fisher Scientific, Reagent Grade) and 70 mL of deionised water. Once made up the acidified DPC solution is light sensitive and rapidly degrades so fresh solution was made up as required and stored in a brown glass bottle for no more than 2 days. A Cr(VI) stock solution of 0.5 g L^{-1} was prepared by dissolving 0.141 g of potassium dichromate (Reagent Grade, Fisher Scientific) in 100 mL of deionised water. A working Cr(VI) stock solution of 5 mg L^{-1} was prepared by diluting 1 mL of this stock solution with 99 mL of deionised water in a 100 mL volumetric flask. The working stock solution was used to prepare Cr(VI) standards which had Cr(VI) concentrations of 0.02, 0.04, 0.1, 0.2, 0.4, 1, 2 and 5 mg L^{-1}. In a 25 mL volumetric flask 2.5 mL of acidified DPC solution was added to 5 mL of standard/sample, agitated and then left for 20 min for the colour to develop. Afterwards, the solution was made up to the mark with deionised water and then analysed at 540 nm using a Shimadzu UV-2700 UV-Vis spectrometer.

For each analysis at least 3 reagent blank samples were analysed and the concentration of the 5 mg L^{-1} Cr(VI) standard was checked using ICP-OES to ensure the accuracy of the calibration standards.

3.7.2.3 Ferrozine iron(II) determination

Iron(II) concentrations in porewater samples were determined using the ferrozine method (Viollier *et al.*, 2000). 100 µL of ferrozine solution (0.01 M of ferrozine in 0.1 M ammonium acetate solution) was added to 1 mL of porewater. The absorbance was measured at 562 nm using a UV/Vis spectrometer to determine the Fe(II) concentration in solution. The instrument was calibrated using the following $FeCl_3$ concentrations: 0.1, 0.5, 1 and 5 mg L^{-1} of Fe. An 800 µL aliquot of each of the standards was added to the ferrozine reduced using 150 µL hydroxylamine hydrochloride solution (1.4 M) made up in HCl (2 M) and 50 µL of 10 M ammonium acetate buffer, adjusted to pH 9.5 with a solution of ammonium hydroxide, before measuring the absorbance.

3.7.2.4 *Organic matter analysis*

The dissolved organic matter concentration (DOM) in waters has been shown to have a linear relationship with the absorbance at 254 nm due to the aromatic structures found in humic substances which are known to absorb UV light. To measure the relative concentration of DOM in each fraction separated using gel electrophoresis, the absorbance of each fraction between 550 - 200 nm was measured at 1 nm intervals at a medium scan rate using a Shimadzu UV 2700 UV-Vis spectrometer.

3.7.3 pH measurements

3.7.3.1 *Water samples*

The pH of aqueous samples was measured using a Jenway 33505 pH meter which had automatic temperature correction and was calibrated using pH 4 and 7 buffer solutions (Fisher Scientific). Calibration checks were made every 10 samples to ensure there was no drift in the measurements.

3.7.3.2 *Soil and sediment*

To measure the pH of soil and sediment samples 5 g of the soil/sediment was weighed into a 50 mL centrifuge tube along with 20 mL of 0.01 M $CaCl_2$ solution. This was mixed on an end-over-end shaker at 30 rpm for 15 min. The pH of the slurry was then left to settle for 10 min before being analysed using the same method as outlined above for water samples.

3.7.3.3 *Field pH and redox measurements*

Field pH and Eh measurements were taken using a Hannah HI98120 probe which was calibrated prior to use.

3.7.4 Statistical analysis

In order to aid the interpretation of the results, statistical methods were used to determine if there were significant differences or correlations between results. The normality of the data was checked by performing an Anderson-Darling normality test using Origin 2016. Data which was not normally distributed was $\log_{10}$ transformed and retested for normality. If, upon retesting, the $\log_{10}$ transformed data was not normally distributed an equivalent non-parametric test was selected. Statistical analysis was performed using Minitab 17 Statistical Software. Due to the large number of datasets which were not normally distributed, Spearman’s Rank correlation coefficient was used when testing the correlation between data. To determine statistical differences between soil and sediment in the column leaching test Student T-test or Mann-Whitney U (non-parametric) tests were used. The statistical significant level used was $p<0.05$ unless stated otherwise.

4 The temporal and spatial variations in chromium concentrations and associations in a sediment-water-banking soil system, Polmadie Burn, south east Glasgow, Scotland

4.1 Introduction

To understand changes in the mobility and speciation of Cr in the environment the geochemistry of the area must first be characterised. The speciation, and consequently the mobility, of Cr is largely influenced by pH and redox status as well as the presence of Fe, Mn and organic matter (OM). For industrially contaminated sites such as those in south east Glasgow, the mineralogical associations of Cr within the soil and sediment can also be important. This chapter characterises the geochemistry of the Polmadie Burn banking soils and sediments to help understand the changes that lead to Cr (in)mobilisation. The key questions that will be addressed in this chapter are:

i) What are the concentrations of Cr in the Polmadie Burn system including surface waters, soil and sediment porewaters along with the solid phase Cr concentrations in the banking soils and sediments?
ii) Are there any temporal trends in the concentrations of Cr in the Polmadie Burn?
iii) What impact does COPR have as a source of Cr on the system?
iv) What are the main associations of Cr in the banking soil and sediment and how does this impact its long-term fate?

This chapter first discusses the long-term data provided by SEPA collected from the Polmadie Burn water over the years 1967 to 2017 to identify long-term trends and evaluate the stream’s compliance with the European Union’s Water Framework Directive (WFD). The rest of the chapter presents data collected over the course of this project from samples taken from the Polmadie Burn water, banking soils and sediments to characterise system.

4.2 Evaluation of long-term trends in water quality and in the concentrations of chromium and other elements based on monthly sampling data (Polmadie-Malls Mire) provided by SEPA

Routine water quality monitoring was carried out by the Scottish Environment Protection Agency (SEPA) at the Polmadie Burn (NS 60238 62983) (Figure 4-1) from 1967 to the current time. A freedom of information request was made and monthly concentration data for the range of parameters, shown in Table 4-1 and Table 4-2, was provided for the period 25/01/1967 to 28/09/2017. Some parameters were only measured during part of this time period and the dates/numbers of measurements are also recorded in Table 4-1 and Table 4-2. The mean (± 1 s.d.), median, maximum and minimum values were calculated for each parameter over the entire time period and are summarised in Table 4-1 and Table 4-2. Non-metal, nutrient and other water chemistry data is summarised in Table 4-1 and metal and metalloid data is summarised in Table 4-2. The content of these tables will be explained in more detail below where the temporal trends are investigated.

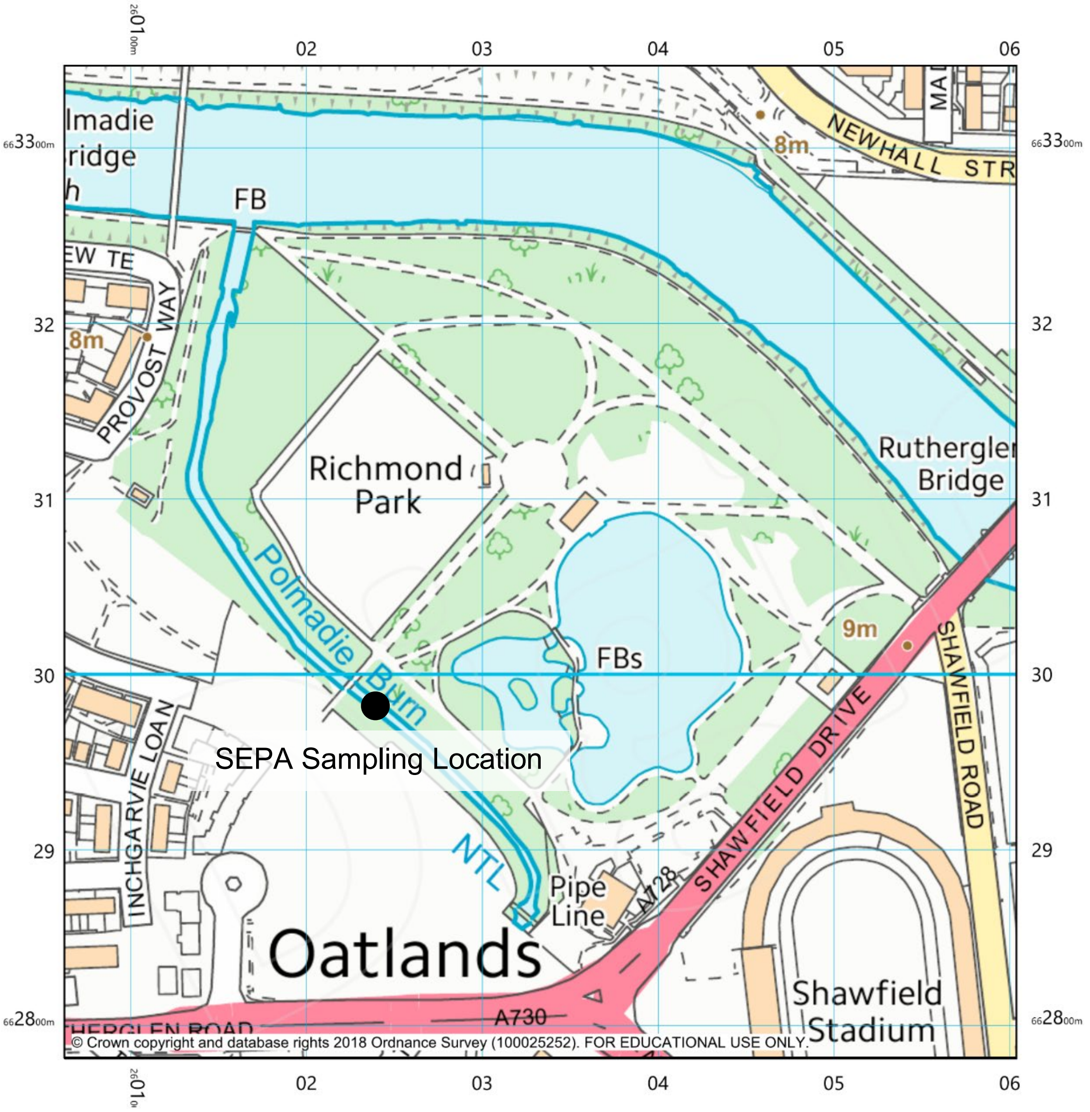

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Figure 4-1: Map showing the location of the SEPA surface water sampling point (●) over the period 1967-2017 (https://digimap.edina.ac.uk/)

Table 4-1: Non-metal, nutrient and other water chemistry data for Polmadie Burn measured by SEPA over the period 1967-2017

Parameter	Dates	Number of data points	Units	Mean value (± 1 s.d.)	Median	Max value	Min value
Alkalinity (carbonate)	25/01/1967-28/09/2017	267	mg L^{-1}	139±41	142	264	25.1
Ammonia (as N)	25/01/1967-28/09/2017	271	mg L^{-1}	0.71±1.1	0.41	10.7	0.03
Biochemical oxygen Demand	25/01/1967-28/09/2017	237	mg L^{-1}	6.48±15.1	3.1	140	0.5
Chloride	25/01/1967-28/09/2017	268	mg L^{-1}	75.2±144	55.5	2230	8.1
Dissolved Organic Carbon	20/10/2016-28/09/2017	11	mg L^{-1}	4.93±1.7	4.98	7.73	2.52
Electrical Conductivity	29/11/1978-28/09/2017	245	µS cm^{-1}	679±492	636	7220	6.9
Hardness	25/01/1967-28/09/2017	211	mg L^{-1}	187±60	188	380	34
Nitrate (as N)	25/01/1967-28/09/2017	262	mg L^{-1}	1.97±0.84	1.87	5.8	0.1
Nitrite (as N)	25/01/1967-28/09/2017	262	mg L^{-1}	0.09±0.12	0.06	1.5	0.01
Non-ionised ammonia	18/07/2005-28/09/2017	118	mg L^{-1}	0.0089±0.009	0.0058	0.058	0.0004
O_2-dissolved oxygen	25/01/1967-28/09/2017	268	mg L^{-1}	9.65±2.1	9.8	14.5	1.8
O_2-%saturation	25/01/1967-28/09/2017	266	%	84.0±14.1	86.9	118	13.5
pH	25/01/1967-28/09/2017	269	-	7.9±0.4	7.9	8.7	6.2
Soluble Reactive Phosphate (as P)	25/01/1967-28/09/2017	266	mg L^{-1}	0.46±1.3	0.15	17.2	0.02
Temperature	25/01/1967-28/09/2017	291	°C	9.90±3.9	9.8	22.5	1.0
Suspended solids	25/01/1967-28/09/2017	257	mg L^{-1}	23.1±38.7	10.0	331	2.0
Total Organic Nitrogen (as N)	25/01/1967-28/09/2017	271	mg L^{-1}	2.1±0.9	2.0	6.0	0.1

Table 4-2: Summary of metal and metalloid data for Polmadie Burn over the period 1967-2017

Parameter	Dates	Number of data points	Units	Mean value (± 1 s.d.)	Median	Max value	Min value	EQS[1]
Al total	02/02/2005-28/09/2017	54	μg L^{-1}	621±1140	222	5530	42.9	
Al dissolved*	02/02/2005-28/09/2017	70	μg L^{-1}	33.0±19.7	28.1	107	6.61	1[2]
As total	02/02/2005-28/09/2017	122	μg L^{-1}	5.13±12.0	2.02	117	0.33	
As dissolved*	02/02/2005-28/09/2017	106	μg L^{-1}	3.03±4.8	1.89	28	0.043	50
Ca	02/05/2011-28/09/2017	12	mg L^{-1}	75.2±25.4	74.2	132	38.7	
Cd total	02/02/2005-28/09/2017	115	μg L^{-1}	0.16±0.83	0.07	9.0	0.006	
Cd dissolved*	02/05/2011-28/09/2017	95	μg L^{-1}	0.06±0.05	0.03	0.25	0.004	0.25
Cr total	19/02/1982-28/09/2017	252	μg L^{-1}	2870±2170	2690	17300	2.49	
Cr dissolved*	12/03/1986-28/09/2017	211	μg L^{-1}	2810±2110	2650	15800	0.40	3.4 Cr(VI) (4.7 Cr(III))
Cu total	02/02/2005-28/09/2017	126	μg L^{-1}	6.5 ± 7.2	4.04	61.4	0.099	
Cu dissolved*	02/02/2005-28/09/2017	105	μg L^{-1}	2.18 ± 0.98	1.99	6.36	0.13	1[3]
Fe total	02/05/2011-28/09/2017	12	mg L^{-1}	1.71±1.7	0.996	5.65	0.41	
Fe dissolved*	11/04/2012-28/09/2017	31	mg L^{-1}	0.034±0.026	0.025	0.096	0.01	1
K	02/05/2011-28/09/2017	12	mg L^{-1}	6.57±2.6	6.92	11.2	3.35	
Mg	02/05/2011-28/09/2017	12	mg L^{-1}	11.2±2.3	11.9	14.5	6.96	
Mn total	02/05/2011-28/09/2017	12	mg L^{-1}	0.135±0.069	0.114	0.268	0.059	
Mn dissolved*	11/04/2012-28/09/2017	31	mg L^{-1}	0.072±0.035	0.067	0.158	0.019	0.123[3]
Na	02/05/2011-28/09/2017	12	mg L^{-1}	73.4±25.0	72.9	123	42.8	
Ni total	02/02/2005-28/09/2017	126	μg L^{-1}	3.69±1.9	3.45	12.5	0.20	
Ni dissolved*	02/02/2005-28/09/2017	102	μg L^{-1}	2.23±1.3	1.77	6.42	0.004	4[3]
Pb total	02/02/2005-28/09/2017	125	μg L^{-1}	4.33±6.4	2.00	30.6	0.043	
Pb dissolved*	02/02/2005-28/09/2017	106	μg L^{-1}	0.41±0.87	0.21	8.3	0.06	1.2
V total	02/02/2005-28/09/2017	104	μg L^{-1}	4.53±3.8	3.29	19.8	0.20	
V dissolved*	02/02/2005-28/09/2017	85	μg L^{-1}	2.54±1.5	1.96	6.66	0.20	
Zn total	02/02/2005-28/09/2017	125	μg L^{-1}	27.6±26.2	18.9	158	0.69	
Zn dissolved*	02/02/2005-28/09/2017	100	μg L^{-1}	10.4±10.0	7.73	77	0.37	10.9

*<0.45 μm water samples, [1]EQS for freshwaters [2]Reactive Al concentration, [3]Bioavailable concentration

4.2.1 Water classification for Polmadie Burn

The European Union (EU) water framework directive (WFD) was established in 2000 with the objective of improving the standard of water quality across Europe. The directive amalgamates existing legislation into one set of rules which applies to all waters within the EU. Through enforcement of river basin management strategies, >97% of waters have to have achieved a ranking of “good” or “high” for both the ecological and chemical status by 2027. As of 2016, 62% of Scottish water bodies achieved good or high classification. This is better than EU waters as a whole where on average 40% have achieved good or better classification in both ecological and chemical status (EEA, 2018, Priestley and Barton, 2018).

This section reviews the temporal changes in concentrations of elements and other parameters which define the quality of the Polmadie Burn water and evaluates the current water quality in the context of the EU WFD. Where data is available, the temporal variability in concentrations of metal species is also described and current values are compared with the relevant environmental quality standards (EQS).

4.2.1.1 Alkalinity

Alkalinity is an important measure of a waterbody’s ability to buffer addition of acids, e.g. from acid rain or from waste water discharged from industry. The mean alkalinity in the Polmadie Burn between the years 1967-2017 was 139 ± 41 mg L^{-1} with a median concentration of 142 mg L^{-1}. With respect to water quality, the mean alkalinity value for Polmadie Burn sits in the range 100 - 200 mg L^{-1} and the altitude is below 80 m so it fits the description of a river Type 5 in terms of alkalinity and elevation (Scottish Government, 2014). Thus, it is classed as a “lowland and high alkalinity” surface water body. A high alkalinity water body will have a higher buffering capacity against the acidification of the water. The values found in the Polmadie Burn are similar to those typically found in urban areas of the River Clyde catchment where the median value is 123 mg L^{-1} (Smedley, 2017).

There is some temporal variability in the data as exemplified by the range of values (~25 to ~264 mg L^{-1}) but there is no evidence of either a long-term increase/decrease (Figure 4-2A) or any seasonal trend (Figure 4-2B).

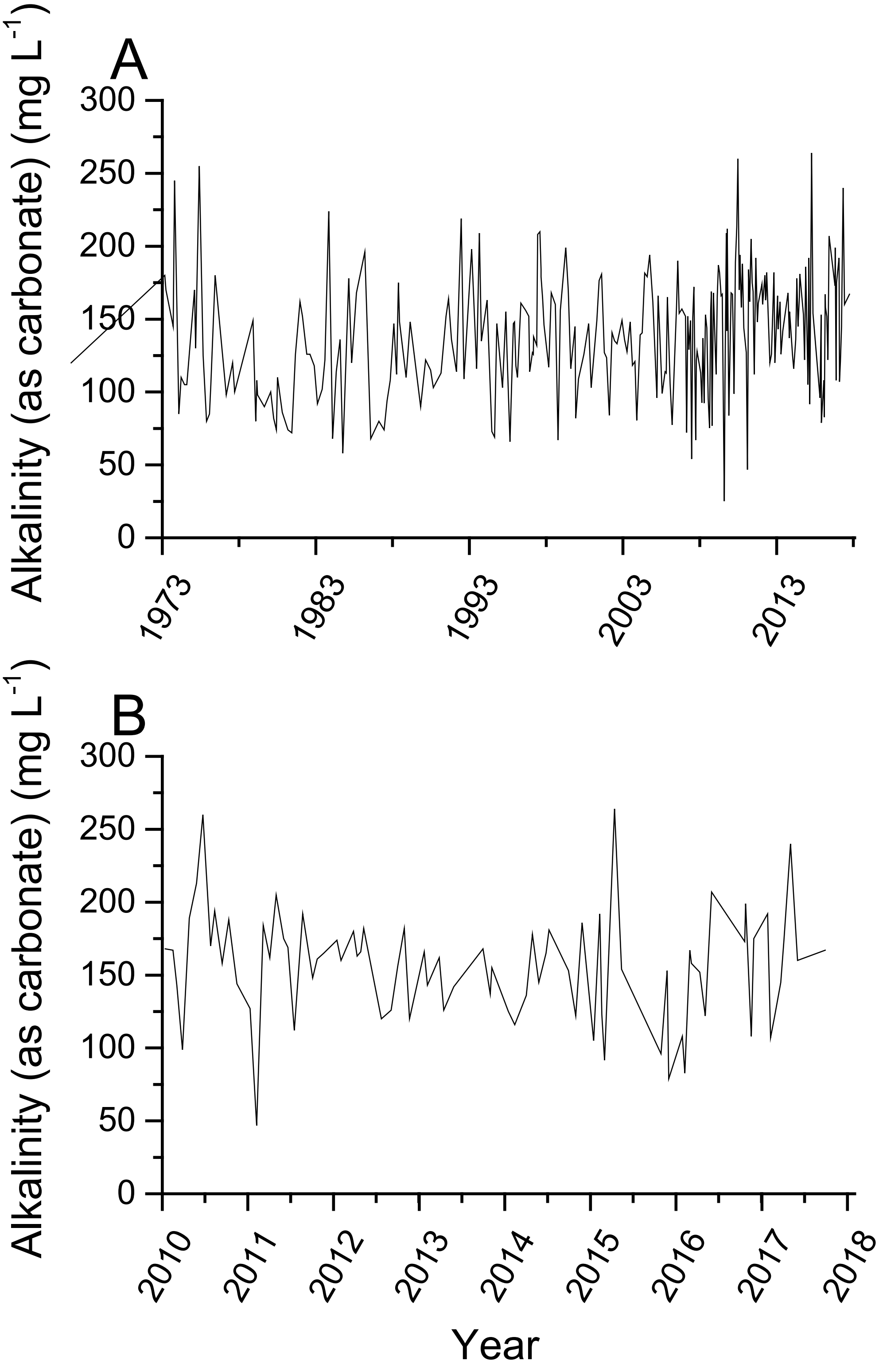

Figure 4-2: Alkalinity (as carbonate) in Polmadie Burn (A) 1967-2017 and (B) 2010-2017

4.2.1.2 Dissolved oxygen concentrations and temperature

Dissolved oxygen concentrations in a waterbody are important for sustaining aquatic life. Low oxygen concentrations indicate the formation of eutrophic conditions which occur due to the loss of oxygen which is used during the metabolism of organic matter by bacteria. Warm, stagnant water with high levels of nutrients favour the formation of eutrophic conditions. The mean dissolved oxygen concentration in the Polmadie Burn was 9.65 ± 2.1 mg L^{-1} (Figure 4-3). This value can be converted into the oxygen saturation level which gives an indication of how much oxygen is dissolved in the water compared to the theoretical maximum of 100%.

The Polmadie Burn is classed as a “lowland and high alkalinity” water so the dissolved oxygen levels (% saturation) should be >70% for high or 60-70% for good status under the EU WFD. Based on the entire data set, the mean dissolved oxygen (as % saturation) was 84.0 ± 14% but the 10th percentile value, which is used as the basis for classification, is only 67.3 % and so Polmadie Burn achieves good status. Based on the 2010-2017 data, the 10th percentile value is 71.4% and so now Polmadie Burn will be classified as achieving high status (Figure 4-4).

There is some evidence of seasonal variation with lowest dissolved oxygen levels typically occurring over summer into early autumn (June-September/October) (Figure 4-3). This is possibly due to the changes in the water temperature where warmer water promotes biological activity therefore increases the rate of oxygen consumption as indicated by the inverse relationship shown between water temperature and dissolved oxygen concentrations. The biological reduction of Fe(III) to Fe(II), which has been shown to reduce Cr(VI), may coincide with changes in the Cr speciation found in the burn with a higher percentage of Cr found in as Cr(III) during the summer months.

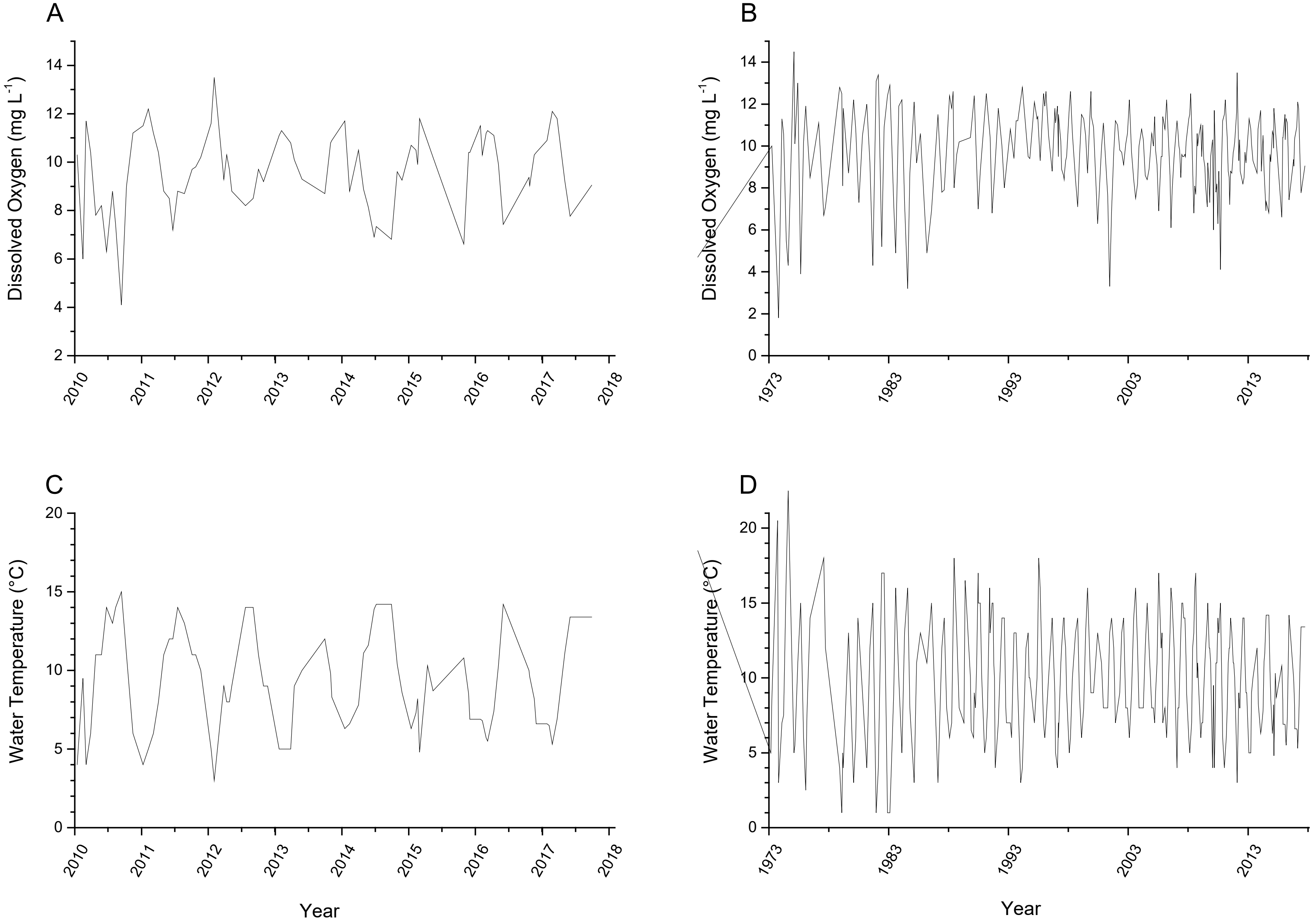

Figure 4-3: Temporal variations in (A) Dissolved oxygen (as mg L^{-1}) 2010-2017; (B) Dissolved oxygen (as mg L^{-1}) 1967-2017; (C) Temperature (°C) 2010-2017; (D) Temperature (°C) 1967-2017

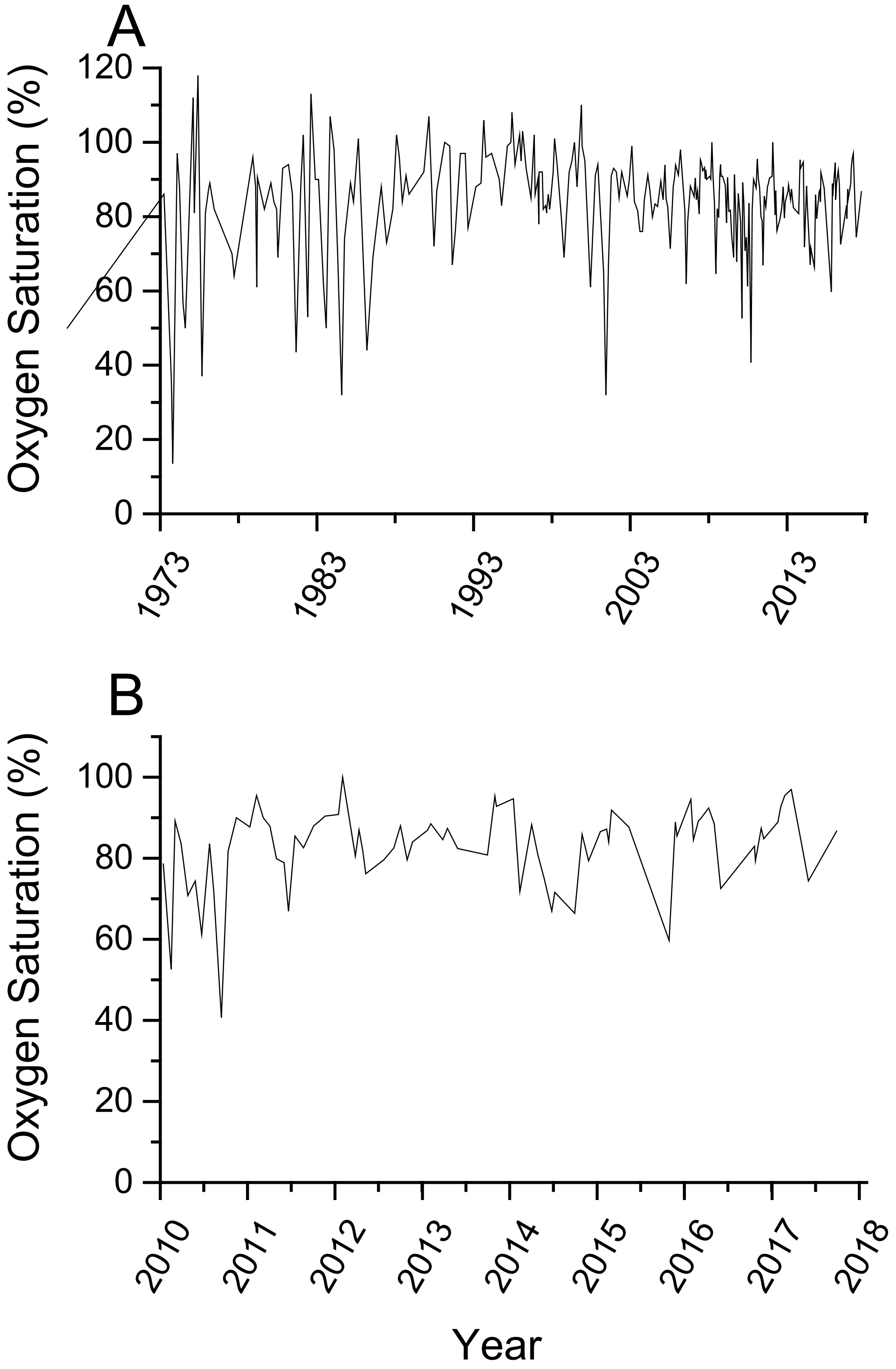

Figure 4-4: Dissolved oxygen (as % saturation) in Polmadie Burn (A) 1967-2017 and (B) 2010-2017

4.2.1.3 Biochemical oxygen demand

The concentration of oxygen used by microbes for the decomposition of organic matter is called the biochemical oxygen demand (BOD). In contrast with dissolved oxygen data, here it is the 90th percentile value that is used as the basis for classification because high values of BOD indicate poor water quality. The 90th percentile value for BOD in the Polmadie Burn between the years 1967-2017 was 9.12 mg L^{-1} which results in the water quality classification of poor (Figure 4-5). Between the years 2010-2017 the 90th percentile value was 9.33 mg L^{-1} which corresponds to poor water quality and between the years 2013-2017 the 90th percentile value was lower at 8.60 mg L^{-1} which falls into the category of moderate/poor. The BOD has spikes, such as in the winters of 2010-11 and 2016-17 which suggest isolated incidents, such as sewage overflow due to heavy rainfall, affects the BOD in the Polmadie Burn (Figure 4-5). Biochemical oxygen demand uses up DO and can cause anoxic conditions to form in the water column. These anoxic conditions may result in the production of reduced species, most notably Fe(II), which may influence the speciation of Cr in the burn by reducing Cr(VI) to Cr(III).

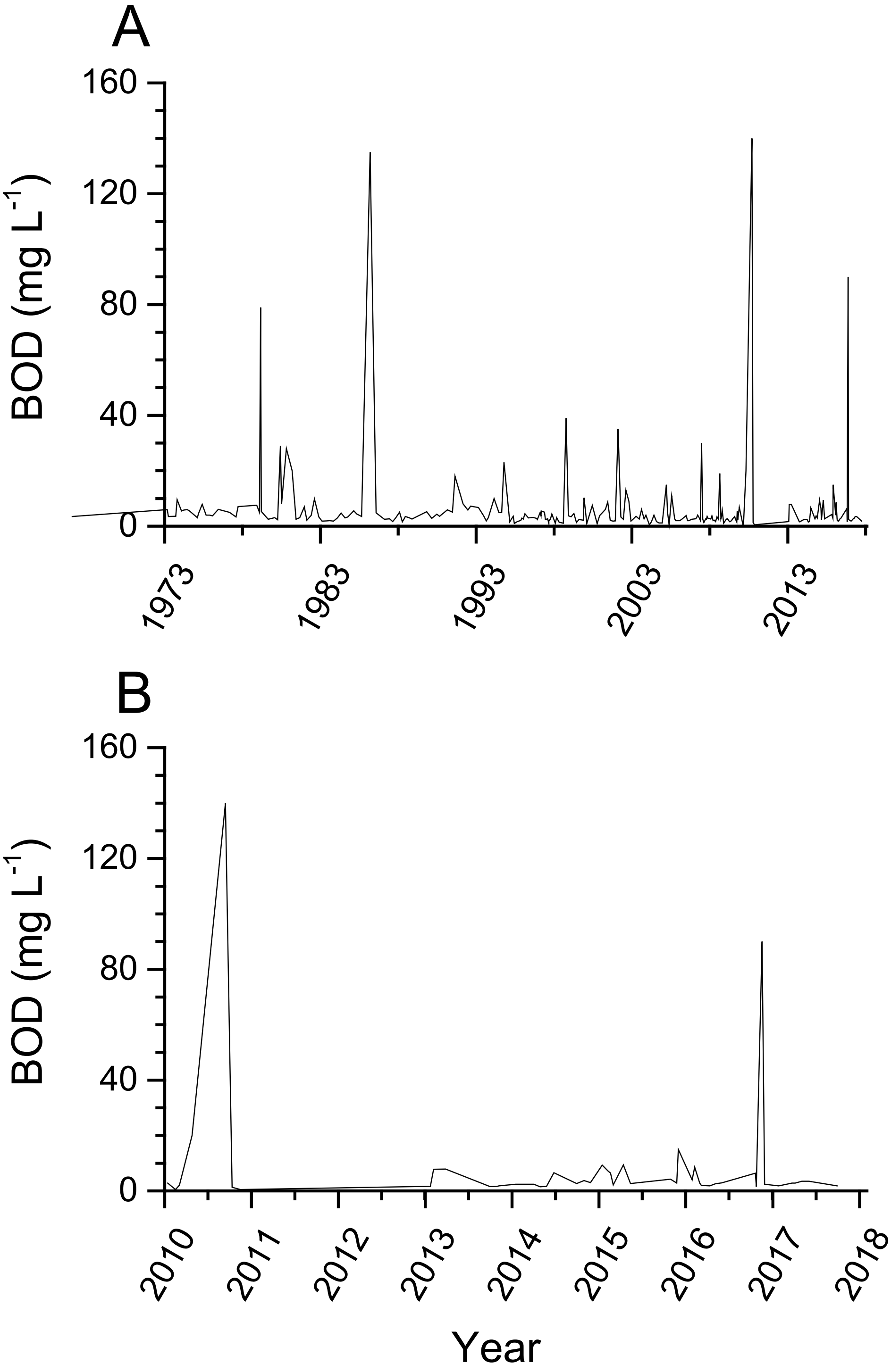

Figure 4-5: Temporal variations in biochemical oxygen demand (A) 1967-2017 and (B) 2010-2017

4.2.1.4 Water pH

The pH of a water body has a large influence on the solubility and indeed redox transitions of many elements. It can be an important control on the bioavailability of nutrients and also on the mobility of potentially toxic elements. The underlying geology of a stream as well as anthropogenic inputs, e.g. via rainwater, contaminated groundwater and effluent discharges, will influence its pH. In spite of its urban location and proximity to industrialised sites, the Polmadie Burn was classified as achieving high status in regard to pH as the 5th percentile and 95th percentile values (7.2 and 8.4, respectively) are well within the specified range (6 and 9, respectively). There has, however, been some temporal variability over the time period. Specifically, the burn water pH increased from approximately pH 7.5 in the 1970s to approximately pH 8.0 in the late 1990s (Figure 4-6). This could be in part due to changes in the input of the stream due to changes in industry and construction work in the area over the years. Although the pH of the Polmadie Burn is typical of those found in the Clyde catchment area, the pH of topsoils in the Polmadie area is much higher than the pH of the rest of Glasgow which is much more acidic (Figure 4-7) (Smedley, 2017). The high pH of the area can be attributed to the disposal of COPR in the area which is highly alkaline.

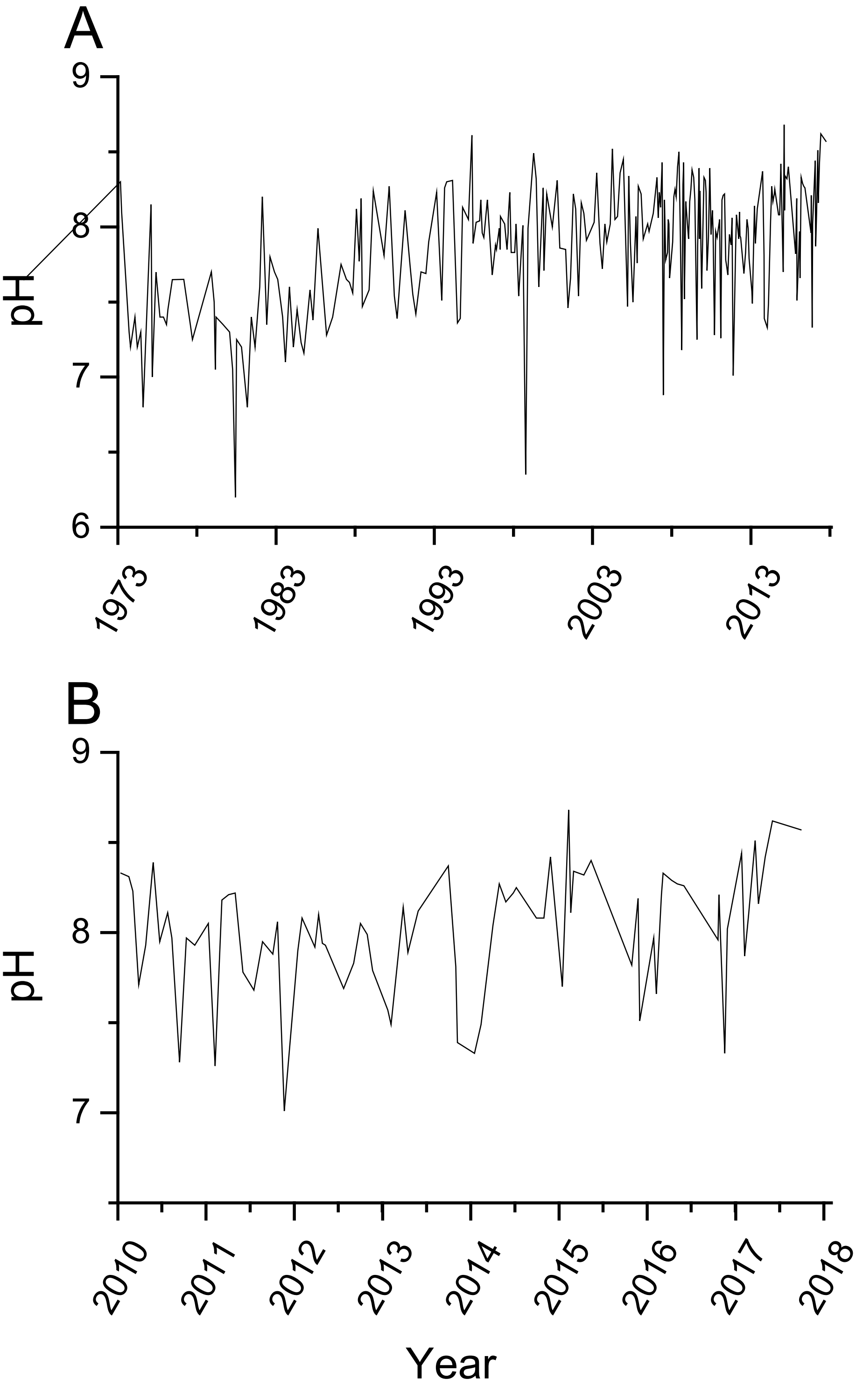

Figure 4-6: Temporal variations in water pH in Polmadie Burn (A) 1967-2017 and (B) 2010-2017

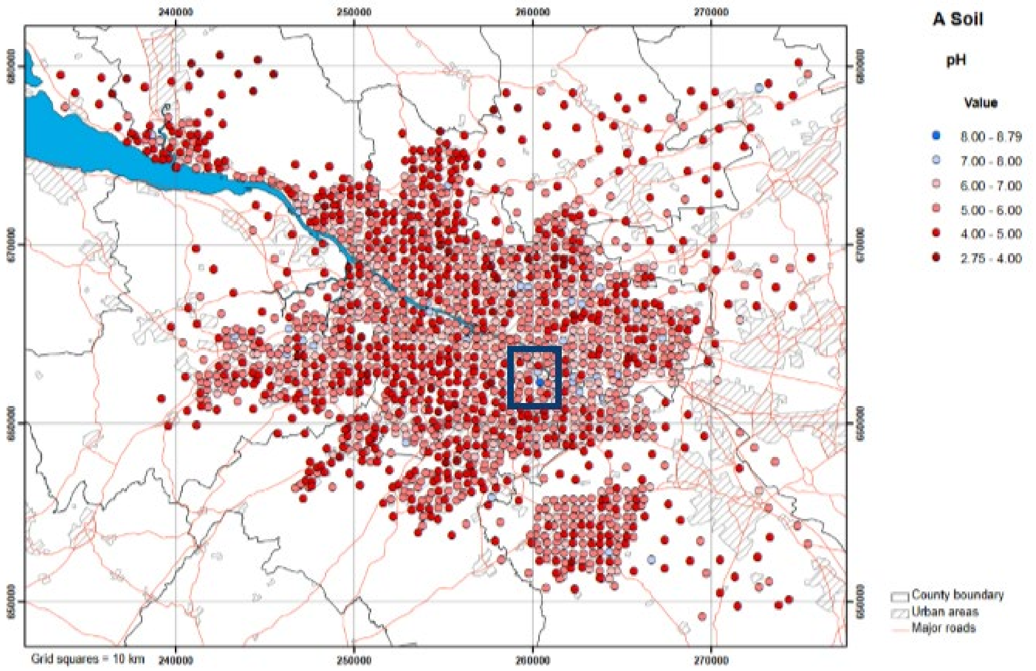

Figure 4-7: The pH of urban topsoils in Glasgow. The blue box shows the area of the Polmadie Burn (Fordyce, 2012)

4.2.2 Typical concentrations of major cations (calcium, magnesium, sodium, potassium) over the period 2016-2017, water hardness over the period 1967-2016 and Fe and Mn concentrations over the period 2012-2017

The mean Ca, Mg, K and Na concentrations in the Polmadie Burn were 72.7 ± 25, 10.9 ± 2.2, 6.14 ± 2.3 and 70.9 ± 24 mg L^{-1} respectively, between 2016 and 2017. Prior to the measurement of these elements individually the water hardness, in Ca carbonate equivalents, was determined. The mean water hardness between the years 1967-2016 was 187 ± 60 mg L^{-1}. There was no observable seasonal trend in the cation concentrations or hardness of the water. Soil Ca concentrations in the area are elevated compared to the rest of Glasgow which may be a source of the high alkalinity of the burn (Figure 4-8). The high concentration of Ca in the Polmadie Burn is likely to be related to the made ground in the vicinity of the site (Figure 4-9) which usually coincides with elevated Ca concentrations in Glasgow (Fordyce, 2012).

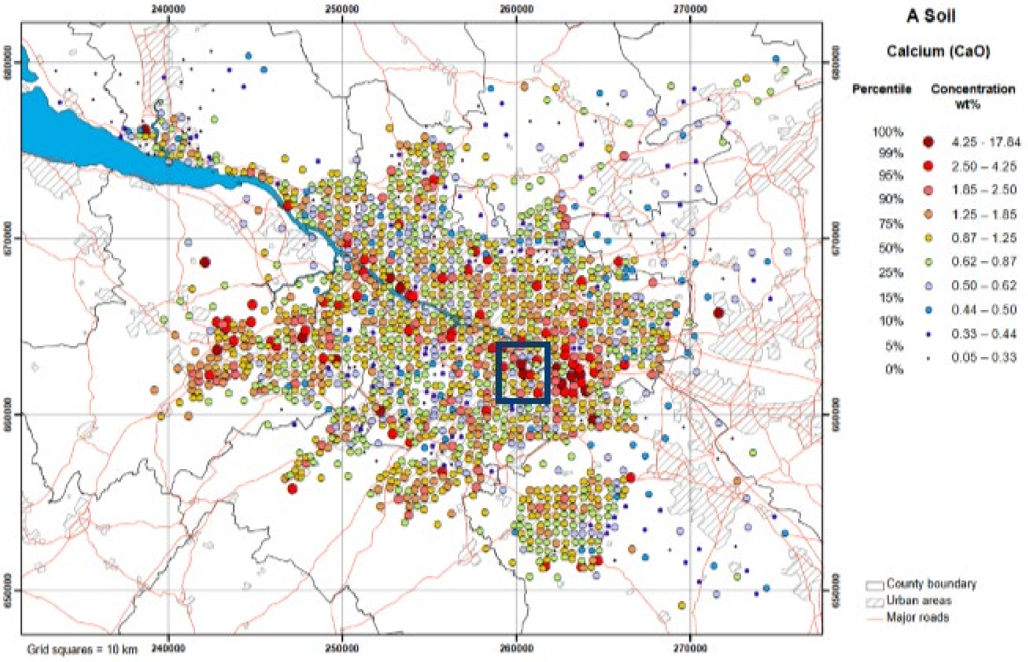

Figure 4-8: The CaO concentrations in urban Glasgow topsoils. The blue box shows the area of the Polmadie Burn (Fordyce, 2012)

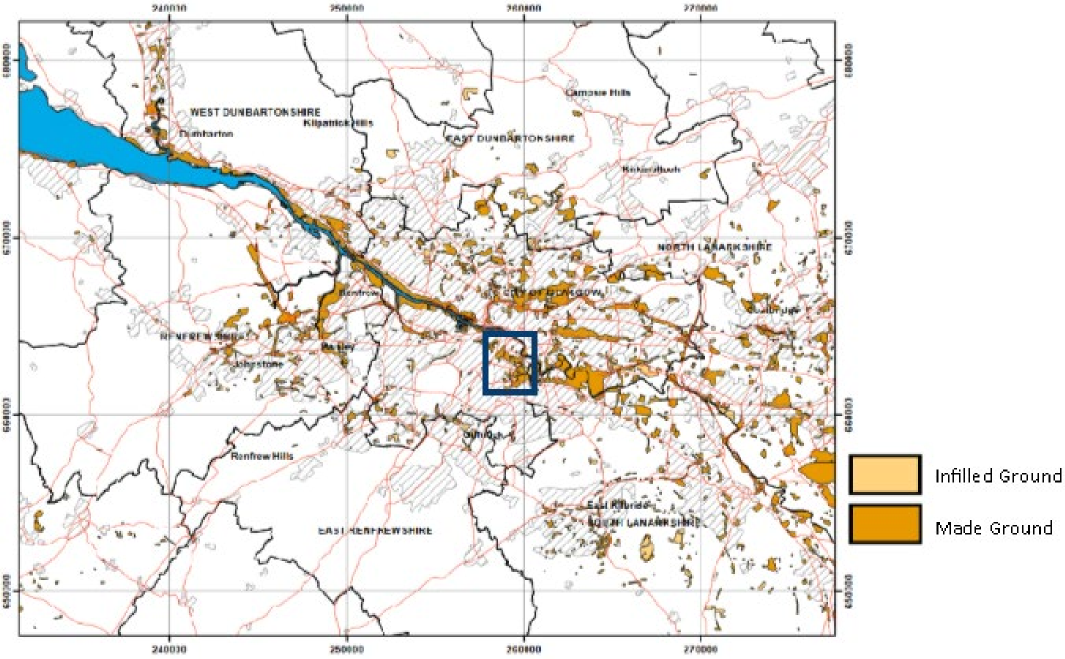

Figure 4-9: Made and infilled ground in Glasgow. The blue box shows the area of the Polmadie Burn. (Fordyce, 2012)

Monthly measurements of Fe and Mn in the Polmadie Burn have taken place since 2012. The mean concentrations of dissolved Fe and Mn in the Polmadie Burn were 337 ± 26 and 718 ± 35 µg L^{-1}, respectively. In general, Fe was predominantly found in suspended particulate form as only 3.7 ± 4% of Fe was in the dissolved phase (<0.45 µm). In slightly alkaline, well-oxygenated (based on the high O_2 saturation) waters, Fe would be present in the +III oxidation state as $Fe(OH)_3{}^0$ which is readily removed from solution (Figure 4-10: Eh-pH diagram for Fe in an idealised solution). The remainder would most likely be present in colloidal form within the <0.45 µm fraction. In contrast, dissolved Mn comprised 50 ± 25% of Mn present in the burn waters. As the pH range of the burn is overlaps the stability of $Mn(II)_{aq}$ and Mn(IV), which forms insoluble minerals, giving rise to the larger proportion of Mn in the dissolved fraction (50 ± 25%) compared to Fe (Figure 4-11). The Fe and Mn concentrations are elevated compared to riverwater concentrations found in urban areas of the Clyde catchment where the median concentrations of Fe and Mn were 134 and 81.1 µg L^{-1}, respectively. This is a reflection on the industrial history of the site (Smedley, 2017).

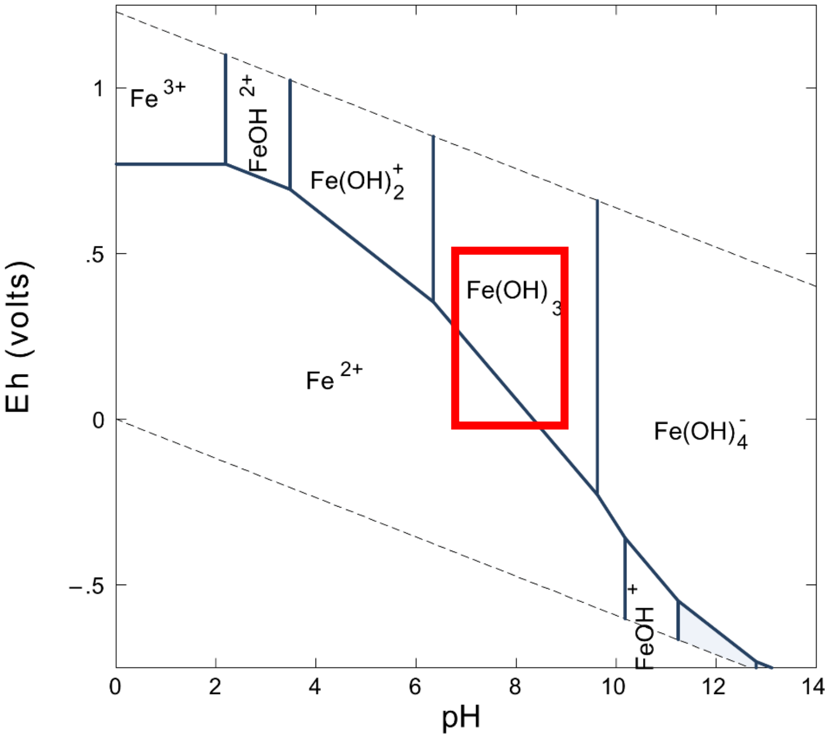

Figure 4-10: Eh-pH diagram for Fe in an idealised solution. The red box indicates the conditions found in the Polmadie Burn.

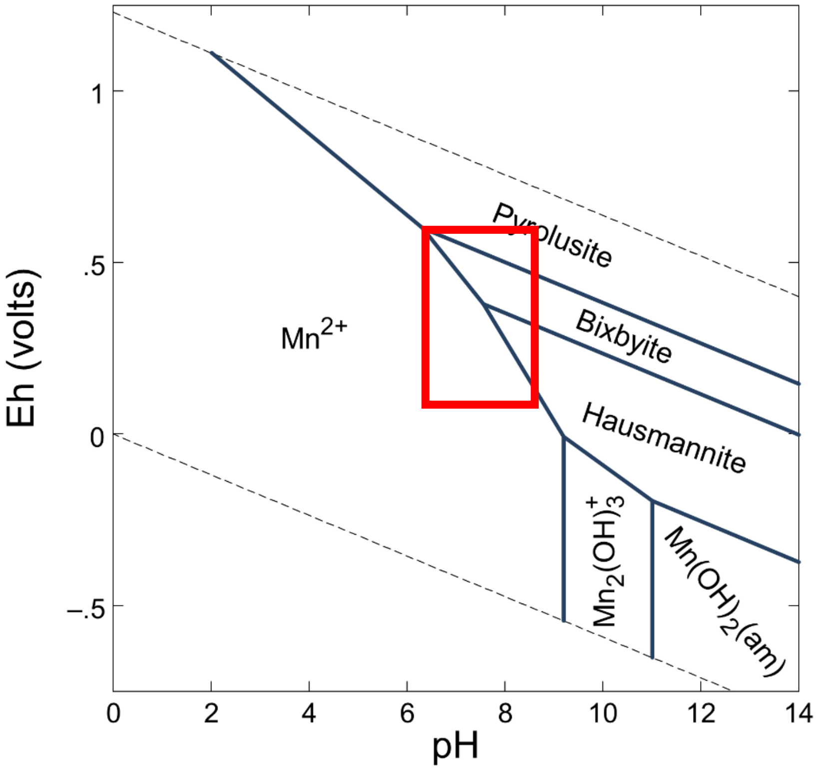

Figure 4-11: Eh-pH diagram for Mn in an idealised solution. The red box indicates the conditions found in the Polmadie Burn.

4.2.3 Temporal variations in trace element concentrations including chromium

The mean concentrations of As, Cd, Ni, Pb, V and Zn were all below the EQS values for fresh water (Table 4-2) and so these elements are not considered to be of concern for surface water quality. The Cr concentrations were, however, consistently higher than the EQS values for freshwater with only 4 sampling dates where the concentration of dissolved Cr was <4 μg L^{-1} (n=212). The median total Cr concentration over the monitoring period of 1967-2017 was 2.69 mg L^{-1}. Overall, there appear to be three main trends in the long-term Cr data set. In the pre-1997 period higher concentrations of predominantly dissolved Cr occurred compared with the post-1997 period. The period between 1997 to ~2010 appeared to account for a higher proportion of the total particulate Cr, as seen by the larger variability in the % of dissolved Cr compared to the total Cr (Figure 4-13C), but there were fewer exceedances of total Cr of 5 mg L^{-1} (Figure 4-13A). Between the years 2010-2017, there was no apparent decrease in mean total Cr concentration, but an increasingly significant relationship between Cr and pH in both the concentrations of total Cr and dissolved Cr.

The dissolved Cr concentrations are highly correlated with the total Cr concentrations, however post-1997, there were more instances where the dissolved Cr fraction made up a small part of the total Cr (Figure 4-13C). In the same period there were more spikes in the total suspended solids concentration (Figure 4-13D) which could be contributing to the Cr concentration in the particulate phase. This could be due to high rainfall events which transported COPR particulate material into surface waters including the Polmadie Burn. The Cr concentration in topsoils in the vicinity of the Polmadie Burn is elevated compared to the rest of Glasgow so increased particulate loading in the burn is likely to be the reason for increased Cr concentrations during increased suspended solids (Figure 4-12).

There was no obvious seasonal trend in Cr concentrations (Figure 4-14). There was, however, a significant positive correlation between pH and dissolved Cr concentrations (Spearman's Rho = 0.492, $p < 0.01$). Leaching of Cr(VI) is greatest at pH 8 leading to the desorption of Cr(VI) from particles and is likely to be the reason for the correlation between pH and dissolved Cr concentrations. Figure 4-15 shows the Eh-pH diagram for Cr with the red box indicating the pH range of the stream along with typical Eh concentrations found in well-oxygenated waters. The DO cannot be directly converted to Eh but, given the high O_2 saturation percentage, it can be presumed that the water body is well-oxygenated. This range straddles the boundary between CrO_4^{2-} and $Cr(OH)_3$ suggesting that a slight drop in the Eh may result in the transformation of Cr(VI) to Cr(III) and as a consequence lower the solubility of Cr in the stream waters. Such a change in oxidation state is not spontaneous and requires a reducing agent to mediate the reduction of Cr(VI). Conversely, the oxidation of Cr(III) requires the presence of a suitable oxidising agent. Without these oxidising and reducing agents present there is unlikely to be a change in the oxidation state of Cr in the stream (Richard and Bourg, 1991).

There were also significant positive correlations between Cr (n=11), Ca (n=12) and Mg (n=12) between the years of 2010 to 2018. (Appendix 1). All of these elements are major constituents of COPR. There is significant correlation between dissolved Cr and dissolved Al (n=11) and, although no significant correlation, a trend of increasing Ca and Mg with increasing dissolved Al concentrations. The poor correlation may have been due to the low number of sample points available. As discussed above, high Ca concentrations in the surrounding soils in this area are indicative of the presence of COPR and so it is likely from the correlations and trends that Cr in the stream originated from COPR which has been released as ground water passes through the waste sites. The elements Ca, Mg and Cr (as Cr(VI)) are very soluble and so will stay in solution once leached from COPR, leading to the high concentrations of these elements found in the stream water. In contrast, the solubility of Al is at its lowest at slightly acidic to near neutral pH values which results in the much lower dissolved Al concentrations found in the Polmadie Burn water in contrast to the Cr(VI), Ca and Mg.

Figure 4-14 shows that there is variability in both total Cr and dissolved Cr concentrations over the time period 2010-2017. During this period a major remediation project was carried out at the nearby Shenkin Site (Figure 4-16). This involved CaS_x reduction of Cr(VI) to Cr(III) and its subsequent precipitation as $Cr(III)(OH)_{3\,(s)}$ (Bewley and Sojka, 2013) by direct injection of CaS_x into the ground. It was demonstrated that <1% Cr(VI) remained in the solid phase and Cr(VI) concentrations of <30 μg L^{-1} were measured in groundwater leaving the site after remediation. It is clear from Figure 4-14 that this remediation has had little or no impact on the Cr concentrations of the Polmadie Burn. Figure 4-16 shows the route of the Polmadie Burn and its tributaries and also the location of the remediation site. Although it has previously been suggested that waters leaving the remediation site enter the Burn, it is more likely that waters drain directly into the Clyde which flows adjacent to the side of the site. Thus it is not surprising that there is no obvious decline in Cr(VI) concentrations in the Polmadie Burn post-2013.

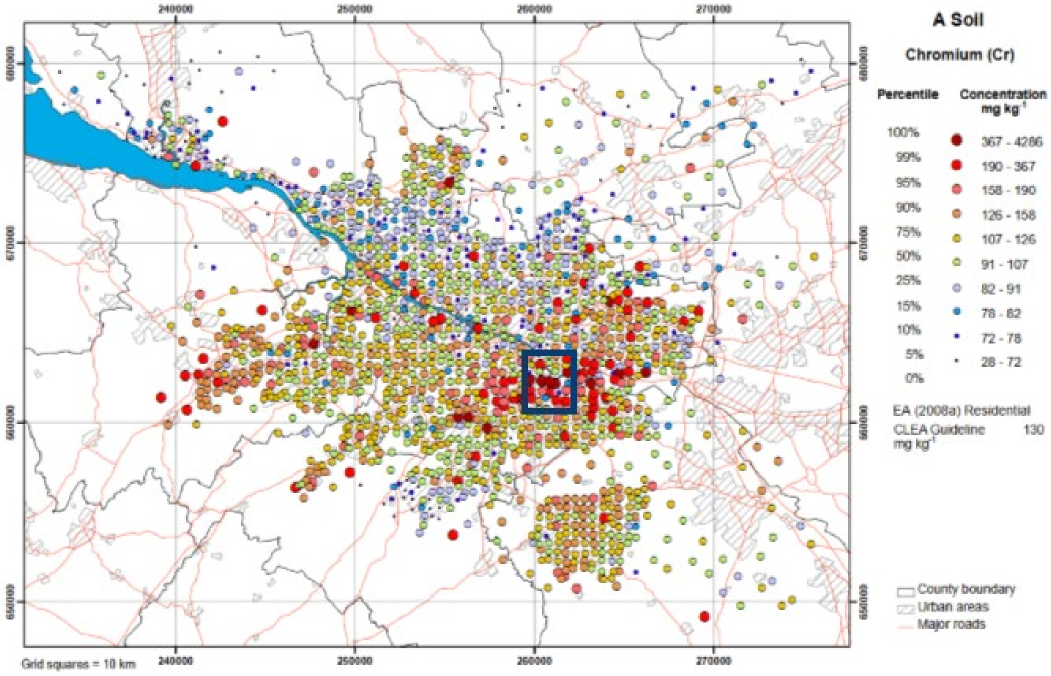

Figure 4-12: The Cr concentrations in urban Glasgow topsoils. The blue box shows the area of the Polmadie Burn (Fordyce, 2012)

From the data set provided by SEPA from the long-term monitoring of the Polmadie Burn, it can be seen that Cr is the only major inorganic pollutant that is consistently present above its EQS. The correlation between dissolved concentrations of Cr with dissolved concentrations of Ca, Mg and Al in the surface waters suggests that COPR is a source of Cr in the water. Although there was a trend which suggested Cr concentrations decreased in the stream in the 1990s, between 2010-2017 the median dissolved Cr concentration was 2.26 mg L^{-1}, exceeding the EQS for both Cr(III) and Cr(VI) of 4.7 and 3.4 µg L^{-1}, respectively, by 3 orders of magnitude. The speciation of Cr in the burn was not measured so it is not known if it is present as Cr(III) or Cr(VI). Determining the species of Cr present in the surface water will influence the toxicity and fate of Cr in the stream so it is critical that this is understood along with the influence that the banking soils and sediment have on Cr sequestration and release. The chemistry of the banking soils and bottom sediments will dictate the Cr complexes formed and this in turn will influence the fate of Cr in the system. So not only is it important to understand the water chemistry the interaction of Cr with the banking soils and bottom sediments must also be investigated. The rest of this Chapter characterises the banking soils and bottom sediments of the Polmadie Burn to get a fuller understanding of the fate of Cr in the system as a whole.

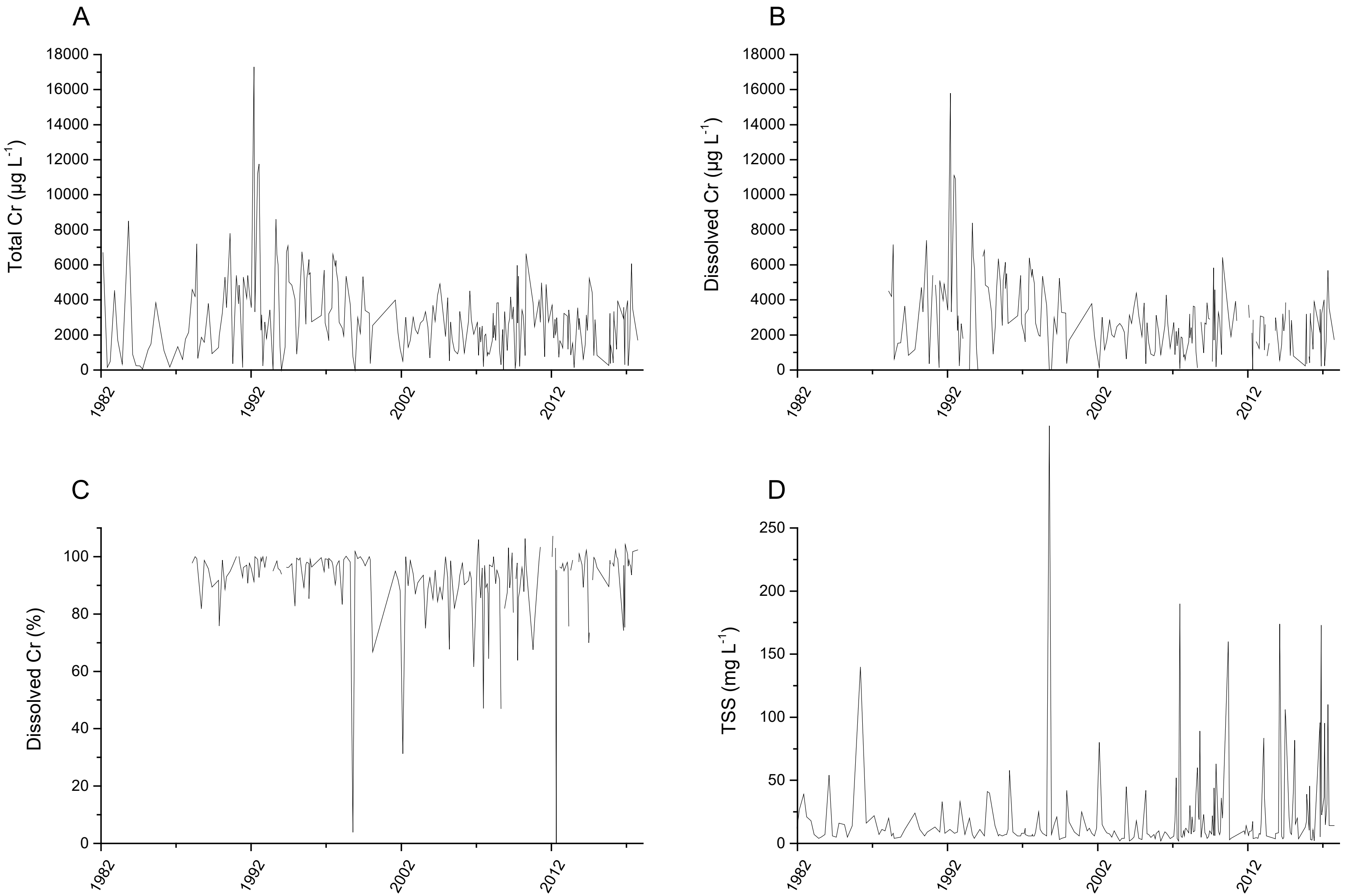

Figure 4-13: Temporal variations in Cr concentration in Polmadie Burn (A) 1967-2017 total Cr (mg L^{-1}); (B) dissolved Cr (mg L^{-1}); (C) percentage of Cr as dissolved Cr (%) and (D) total suspended solids (mg L^{-1}).

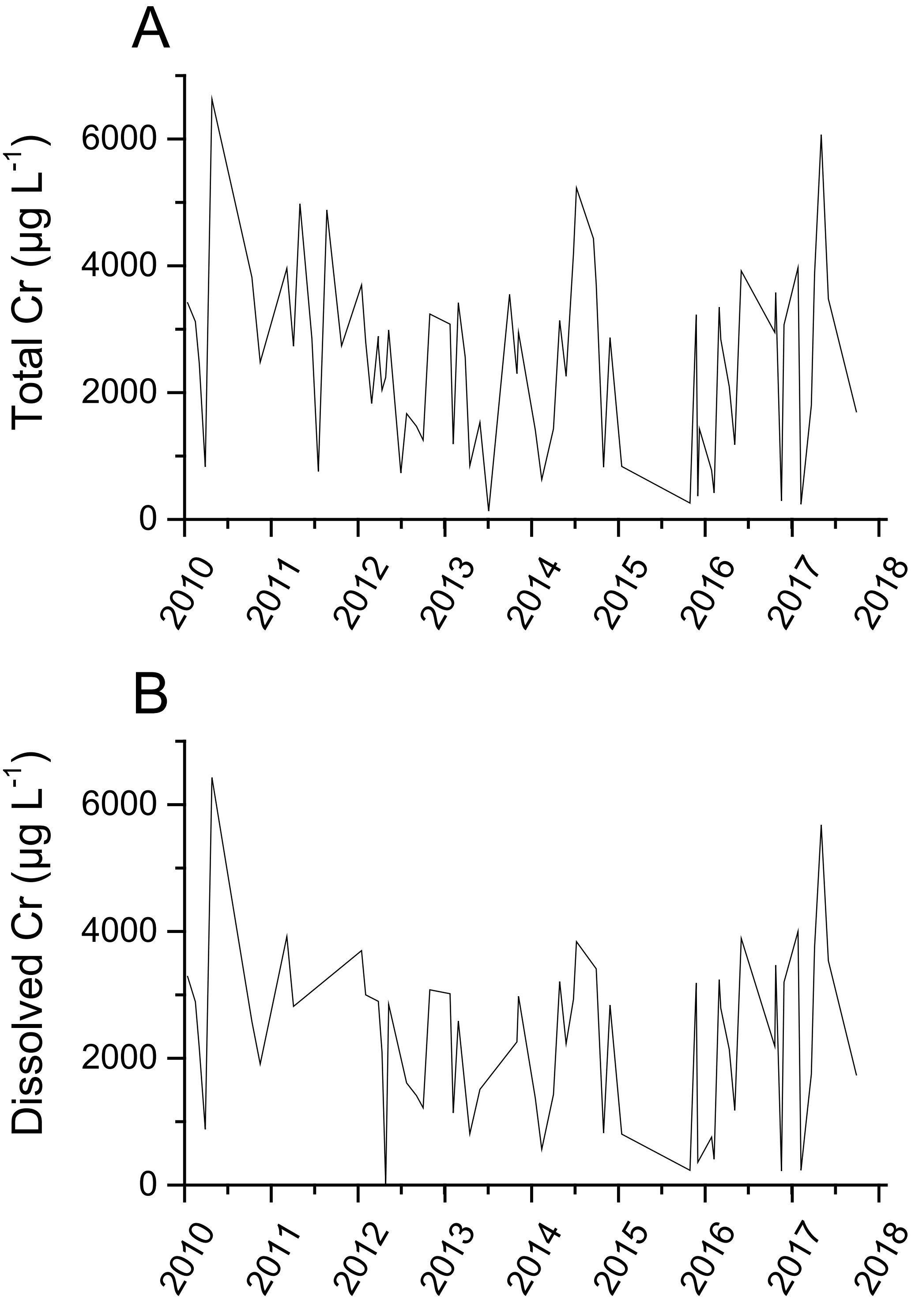

Figure 4-14: Temporal variations in Cr (mg L^{-1}) concentration in Polmadie Burn between 2010-2017 (A) total Cr and (B) dissolved Cr

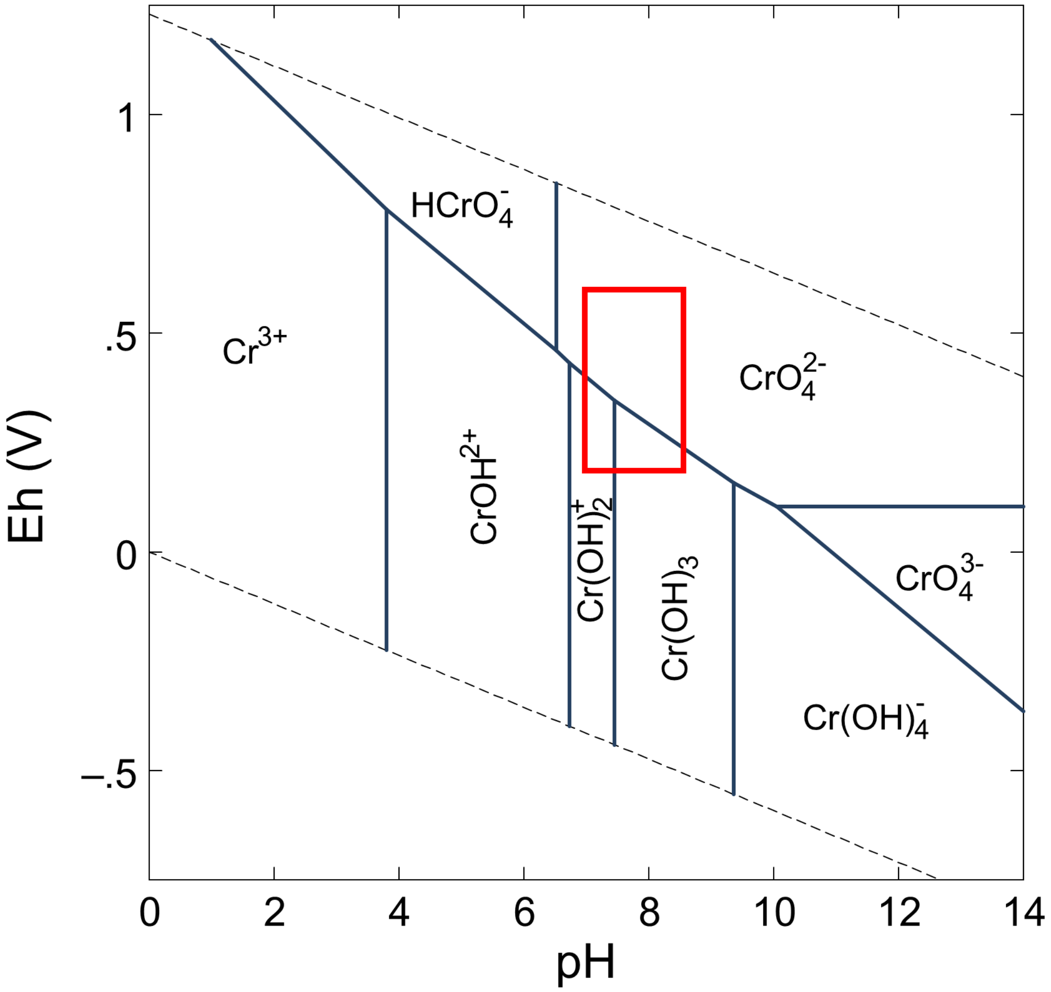

Figure 4-15: Eh-pH diagram for Cr in an idealised solution, the red box shows the pH range found in the Polmadie Burn and the typical Eh expected in a a well oxygenated water

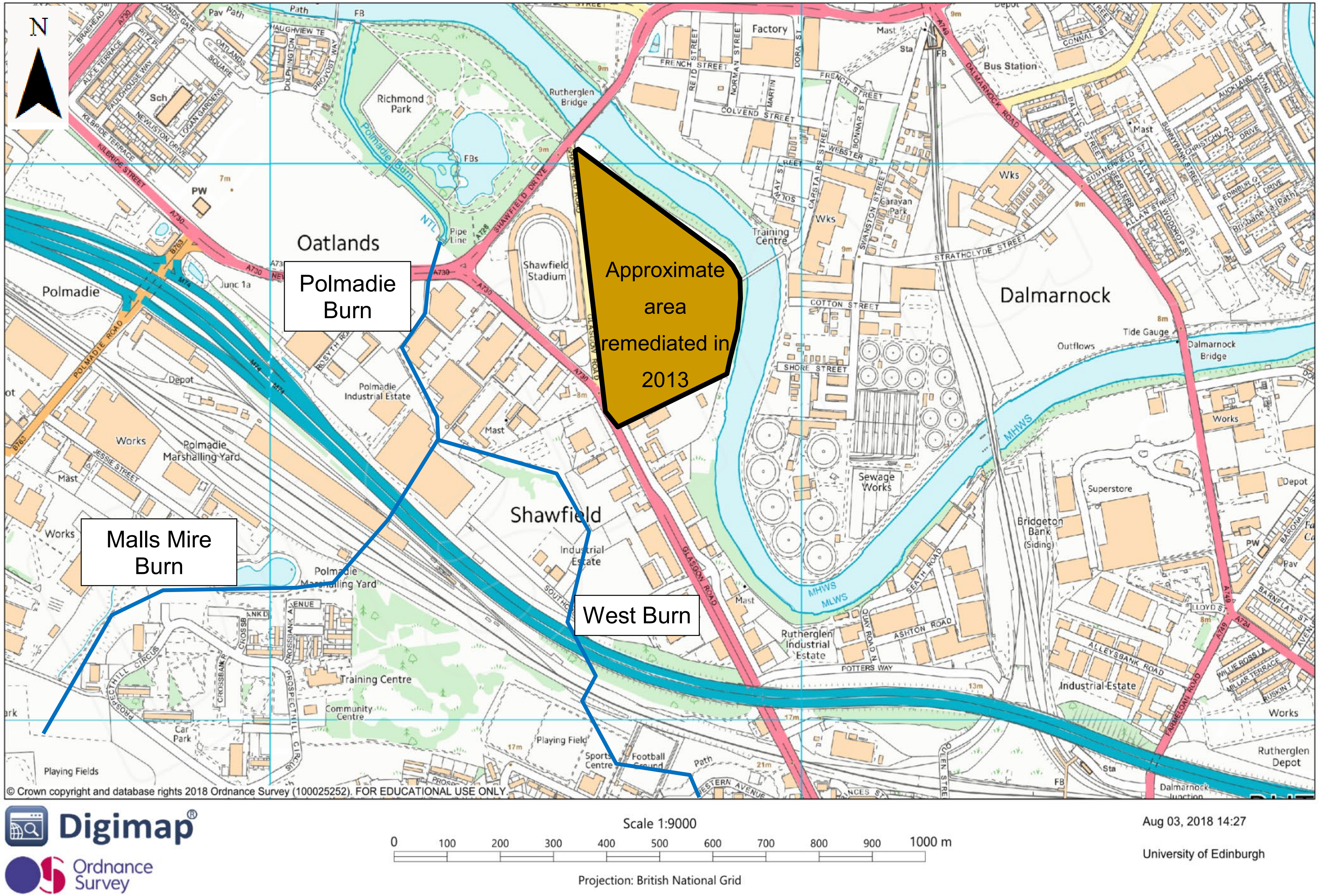

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Figure 4-16: Route of the Polmadie Burn, its tributaries and the area of land remediated in 2013 with calcium polysulfide

4.3 Characterisation of water, sediment and banking soils from the non-culverted section of the Polmadie Burn

From the evaluation of the dataset provided by SEPA in Section 4.2 it is apparent that the only inorganic pollutant of interest in the Polmadie Burn is Cr. Therefore to understand the impact that Cr has on the Polmadie Burn banking soils and sediment the concentration of Cr along with Fe and Mn concentrations as well as the OM content of the soils were determined due to their importance in the redox cycling of Cr. The concentrations of Ca, Mg and Al, which are major constituents of COPR, were also determined.

The remainder of this chapter will therefore examine the water and soil phase elemental composition, along with sequential extraction and mineralogical data, to identify potential sources of Cr in the banking soils and sediments. The data is presented in Sections 4.3-4.6 followed by a discussion of the results in Section 4.7.

4.3.1 Elemental concentrations and pH of surface water samples from Polmadie Burn

Polmadie Burn water samples (n=3) were collected in Nov 2015, Sept 2016 and March 2017. More information on the location of the samples and the sampling strategy can be found in Sections 3.1.2 and 3.1.3.1. The mean pH of the burn was 7.64 ± 0.35. The mean Cr concentration in the dissolved (<0.45 µm) fraction of the stream water was 2.36 ± 1.5 mg L^{-1}. This is very similar to the SEPA long-term (2010-2017) mean dissolved Cr concentration of 2.29 ± 1.4 mg L^{-1}. The mean Cr(VI) concentration in the dissolved fraction was 2.24 ± 1.5 mg L^{-1} which was equivalent to 94 ± 4 % of total dissolved Cr present in the burn. There was no speciation data provided by SEPA so the oxidation state of Cr present is not known. From the results of the Cr speciation it is suggested that Cr is found predominantly in streamwater as Cr(VI) species.

Mean Fe and Mn concentrations in the Polmadie Burn were 197 ± 160 and 45.0 ± 25 µg L^{-1}, respectively.

4.3.2 Elemental concentrations in porewaters isolated from soil and sediment samples

Porewaters were isolated using the method described in Section 3.1.4 from (i) bulk sediment samples (n=6) collected on 11th November 2015 which were analysed for Fe(II) concentrations and (ii) banking soil (n=3) and burn sediment (n=2) samples collected on the 27th October 2016 which were analysed for Cr, Cr(VI), Fe and Mn concentrations. The locations of these soil and sediment samples are shown in Section 3.1.1. The concentrations of Cr, Fe and Mn in the 0.45 µm-filtered porewaters were determined by ICP-MS (see Section 3.7.1.3), the Cr(VI) concentration was determined using the DPC method described in Section 3.7.2.2 and the concentration of Fe(II) was determined using the ferrozine method as described in Section 3.7.2.3.

The mean Cr concentration in soil and sediment filtered porewaters was 91.1 ± 23 and 1.49 ± 0.34 µg L^{-1}, respectively. Chromium(VI) was not detected in any of the porewaters. The Fe concentrations in soil and sediment filtered porewaters taken on the 27th October 2016 was 655 ± 130 and 2540 ± 570 µg L^{-1}, respectively. In the soil porewaters Fe(II) concentrations were <LoD and the sediment porewaters taken on the 11th November 2015 contained 4540 ± 670 µg L^{-1} of Fe(II). The mean concentration of Mn in soil and sediment porewaters was 87.9 ± 82 and 1020 ± 830 µg L^{-1}, respectively.

The concentration and speciation of Cr was ~3 orders of magnitude lower in the sediment porewater compared to the concentrations found in the stream water and porewater Cr(VI) concentrations were <LoD whereas it was the dominant species in the stream water. Opposite trends were seen for Fe and Mn which were found in larger concentrations in the sediment porewater (2540 ± 570 and 1020 ± 830 µg L^{-1}, respectively) compared to the stream water (197 ± 160 and 45.0 ± 25 µg L^{-1}, respectively). The high concentration of Fe(II) found in the sediment porewater (4540 ± 670 µg L^{-1}) indicates the contrast between the reducing sediments and the more oxic water, as reflected by the high DO concentrations reported by SEPA.

4.3.3 Organic matter content, pH and Eh of banking soils, surface sediments and sediment cores from Polmadie Burn

4.3.3.1 Banking soils

Surface banking soils were collected on several occasions and from multiple locations (see Section 3.1.1). The mean organic matter content was 22.4 ± 4.7% (w/w) (n = 23) and the mean soil pH was 6.63 ± 0.33 (n=18). The range of pH values was 6.11 to 7.21. From previous work, the mean organic matter content for Glasgow top soils was 9.5% (Fordyce, 2012), approximately half of the organic matter content of the Polmadie Burn banking soils. This could be due to the fast growing, dense vegetation which grows along the bank, and which dies during the winter. There are also deciduous trees which overhang the site and provide an additional input of organic matter. The mean pH of Glasgow soils is 5.31 which was approximately 1.3 units lower than the mean pH of the Polmadie banking soils. The slightly elevated pH of the soils could be due to the presence of COPR which has a high pH and a large buffering capacity (Farmer *et al.*, 1999, Farmer *et al.*, 2002). The Eh of the bulk soil sample taken on the 12th September 2016 was 230 mV which was mildly oxidising.

4.3.3.2 *Bulk sediments samples*

Surface burn sediments were collected on several occasions and from multiple locations (see Section 3.1.1). The organic matter content of the sediment was 8.78 ± 6.2% (n = 12) and the mean pH was 6.97 ± 0.32 and it ranged between pH 6.53 and 7.43 (n= 7). The OM content of the sediments was lower than the OM content of the banking soils by approximately a factor of 2 and the pH of the sediments was approximately 0.4 units higher than the soils.

Sediment samples taken from Sample Point 10 (Section 3.1.1) in October 2016 had the highest OM content of 23.8 ± 0.35, approximately 5 times higher than the sediment sample taken at Sample Point 4 which was 4.67 ± 0.29 %. It must be noted that the banking soils between Sample Point 1 and Sample Point 10 had been disturbed shortly before the sampling in October 2016 potentially resulting in soil material being transported into the sediment and contributing to the high OM content in the sample taken at Sample Point 10. The Eh of the bulk surface sediment taken on the 12th September 2016 was -134 mV highlighting its reducing nature.

4.3.3.3 *Sediment core profiles*

Sediment cores were collected on the 17th May 2015 from locations shown in Section 3.1.1 in order to determine the changes in elemental composition with depth. The OM content and pH of Cores 1 and 2 did not show similar trends (Figure 4-17A and Figure 4-18A). In Core 1, the OM was 10.2 ± 1.6% dry weight (dwt) for the 0-4 cm depth sections before decreasing to 4.18 ± 0.83% dwt over the 4-12 cm depth sections. The OM content then increased to 11.6 ± 3.1% dwt over the rest of the core (12- 18 cm depth) (Figure 4-17A). In Core 2, the top 0-2 cm had an OM content of 4.74 ± 2.4% dwt which then increased to a maximum of 27.0 ± 2.6% dwt at 10-11 cm depth before decreasing again. There was a decrease in OM between 9 and 10 cm depth (Figure 4-18A).

The pH of the sediment porewater of Core 1 tended to increase with depth whereas the pH of Core 2 increased sharply from pH 8.22 to pH 8.49 between the surface and 2 cm depth. The pH then decreased to a minimum of pH 8.16 at 6 cm depth before rising with depth again (Figure 4-17B). The pH then tended to increase with depth to pH 7.0 at 7 cm and pH 7.47 at 15 cm depth. For Core 2 the pH increased from 8.22 at depth 0-1 cm to 8.49 at 2-3 cm depth. There pH then decreased with depth until 5-6 cm depth to 8.16 before increasing again with depth until 8-9 cm depth where the pH was 8.50 (Figure 4-18B).

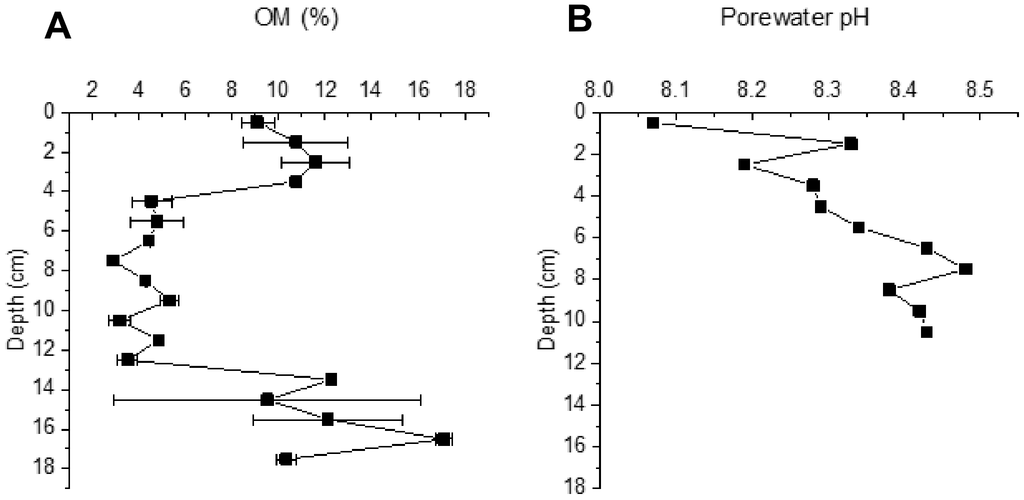

Figure 4-17: Mean ± 1 s.d. of (A) organic matter concentrations and (B) porewater pH with depth for Core 1

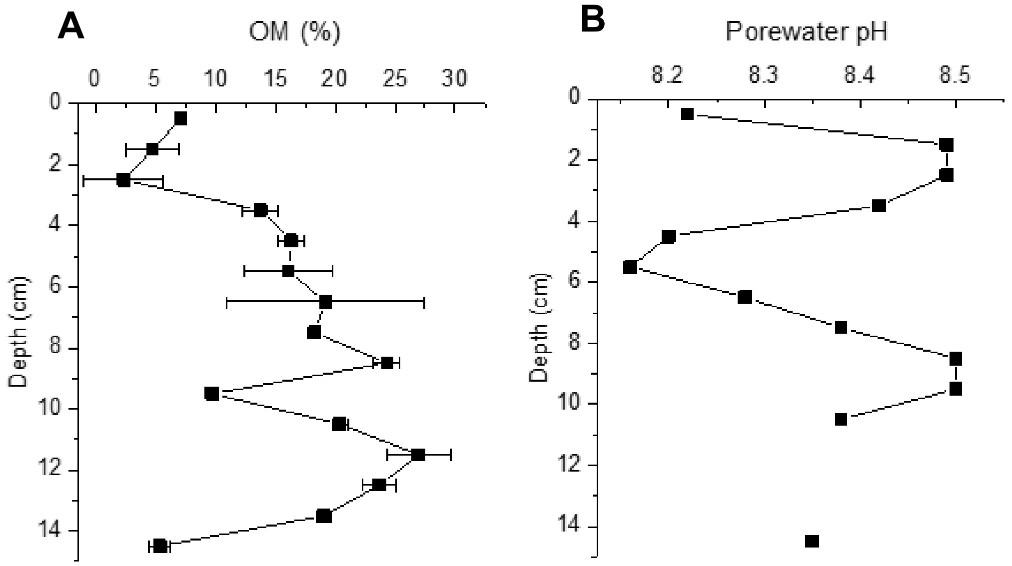

Figure 4-18: Mean ± 1 s.d. of (A) organic matter concentrations and (B) porewater pH with depth for Core 2

4.3.4 Elemental concentrations in surface banking soils, surface sediments and sediment cores from Polmadie Burn

4.3.4.1 Elemental concentrations in banking soils

The mean Cr concentration in banking soil was 1710 ± 1300 mg kg^{-1} (n = 19). This was greatly elevated compared to the mean concentration of Cr reported in Scottish and Glasgow soils which are 44.7 and 125 mg kg^{-1}, respectively (Fordyce, 2012, Paterson, 2011). The maximum Cr concentration of 6310 ± 140 mg kg^{-1} was measured in the soil sample collected at Sample Point 21 in October 2016 (Figure 4-20A). This soil had been recently disturbed by construction work before sampling which could have contributed to the high Cr concentration which may have exposed deeper soil with higher Cr concentrations (Figure 4-19). There did not appear to be any spatial trend in the banking soil Cr concentrations when considering location of the samples and the concentrations of Cr found in them. The mean Cr(VI) concentrations in banking soils was 427 ± 520 mg kg^{-1} (n = 19) which represented ~19 ± 10% of the total Cr in the soil. The maximum concentration of Cr(VI) was 2190 ± 130 mg kg^{-1} which was also found in the soil sample taken from Site 21 in October 2016 (Figure 4-20B).

Figure 4-19: Earthworks showing disturbance of banking soil

The mean Fe (n=19) and Mn (n=19) concentrations were 4.41 ± 0.93% (w/w) and 1040 ± 320 mg kg^{-1}, respectively (Figure 4-20C and Figure 4-20D). The mean Al (n=19), Ca (n=9) and Mg (n=9) concentrations were 2.61 ± 0.75, 1.56 ± 0.36, 0.72 ±0.32% (w/w), respectively (Figure 4-21). Like Cr, there was no trend in the concentration these elements in the banking soils.

The Cr concentration in the soils was significantly positively correlated with the OM content, Al, Ca and Mg concentrations in the soil (Spearman's Rho, $p < 0.05$). The Cr(VI) concentration in the soil was significantly positively correlated with the Fe concentrations and Cr(III) concentrations were significantly correlated with Ca and Mg concentrations, (Appendix 1). The mean Mg concentration was 7180 ± 3100 mg kg^{-1}. The Fe, Al and Mn concentrations were significantly positively correlated in the soils (Spearman's Rho, $p < 0.05$) (Appendix 1).

4.3.4.2 Elemental concentrations in sediments

The mean Cr concentrations in the Polmadie Burn sediment was 2420 ± 790 mg kg^{-1} (n = 12) which was elevated compared to the mean geochemical baseline of Cr in sediments in Great Britain which is 125 ± 190 mg kg^{-1} (Fordyce, 2012). The maximum Cr concentration was 3880 ± 310 mg kg^{-1} (Figure 4-20A). The mean Cr(VI) concentration was 113 ± 48 mg kg^{-1} (n = 7) which was 5.2 ± 1% of Cr in the sediment (Figure 4-20B). The Cr concentrations in the sediment had a significantly positive correlation with the OM content of the sediment and Cr(III) concentrations had a significantly positive correlation with Al concentrations (Spearman's Rho, $p < 0.05$) (Appendix 1).

The mean Fe (n=12) concentrations in the sediment was 3.31 ± 0.64% (w/w) and the mean Mn (n=12) concentration was 472 ± 160 mg kg^{-1}(Figure 4-20C and Figure 4-20D). The sediment concentration of Mn in sediment was lower than the soils. The reducing conditions of the sediments will result in Mn being lost over time by Mn(II) leaching into the overlying water. This will leave non-redox cyclable forms of Mn in the solid phase. These were lower than the geochemical baseline concentrations of Fe and Mn in British sediments which are 5.0 ± 2.4% and 3400 ± 7700 mg kg^{-1}, respectively (Fordyce, 2012). The mean Al (n=12), Ca (n=7) and Mg (n=7) concentrations in the sediments were 1.23 ± 0.15, 2.39 ± 0.4 and 0.79 ± 0.079 % (w/w), respectively. Iron and Mn were significantly positively correlated but Mn and Fe were both significantly negatively correlated with the OM content. The Mn and Mg concentrations had a significant positive correlation and Ca a significant positive correlation with pH (Appendix 1).

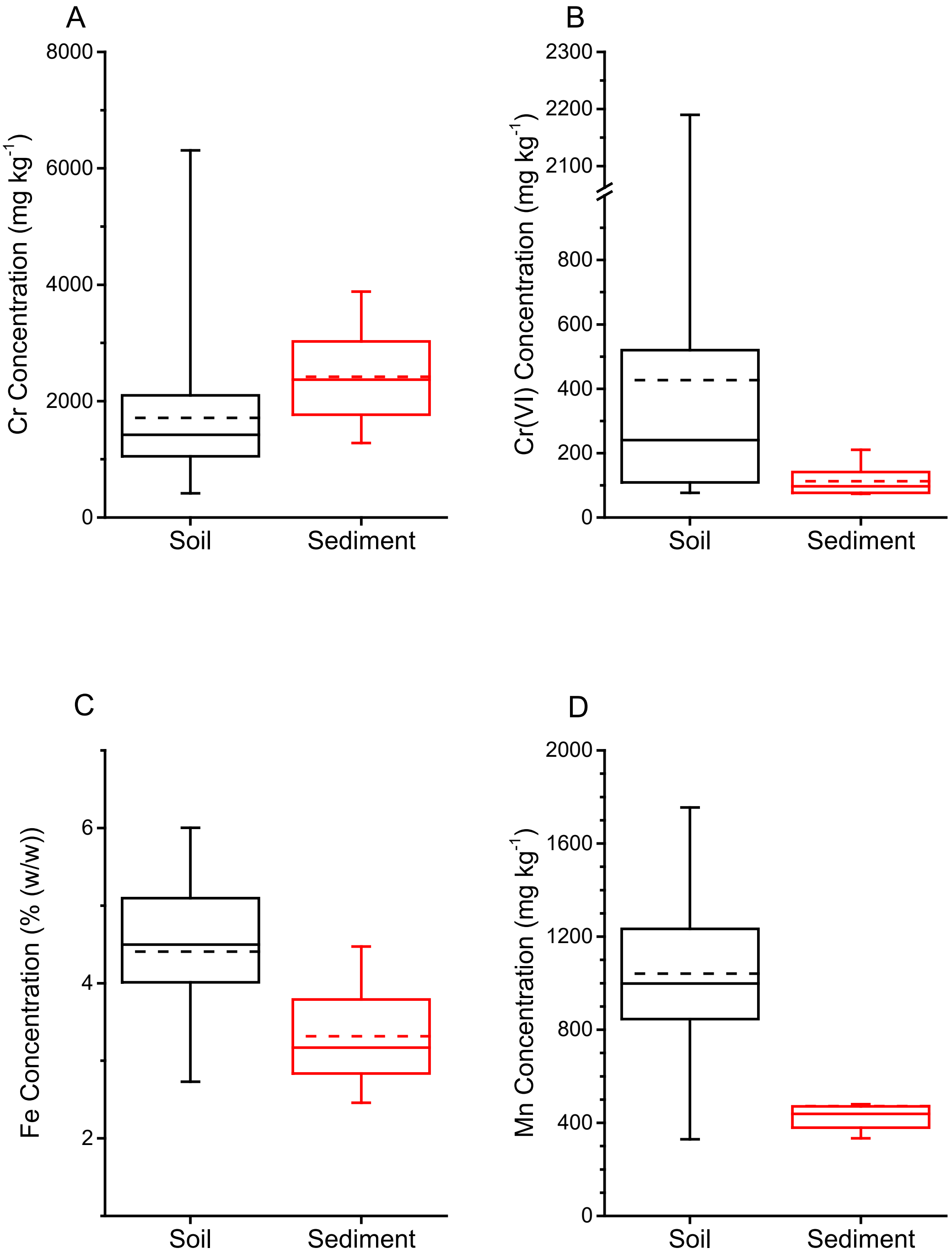

Figure 4-20: Box and whisker plots to describe the range of concentrations of: (A) Cr; (B) Cr(VI); (C) Fe and (D) Mn in Polmadie soils and sediments. The box shows the 25th (lower line), 50th (middle line) and 75th (upper line) quartiles with the mean as a broken line. The lower and upper whiskers show the minimum and maximum concentrations, respectively.

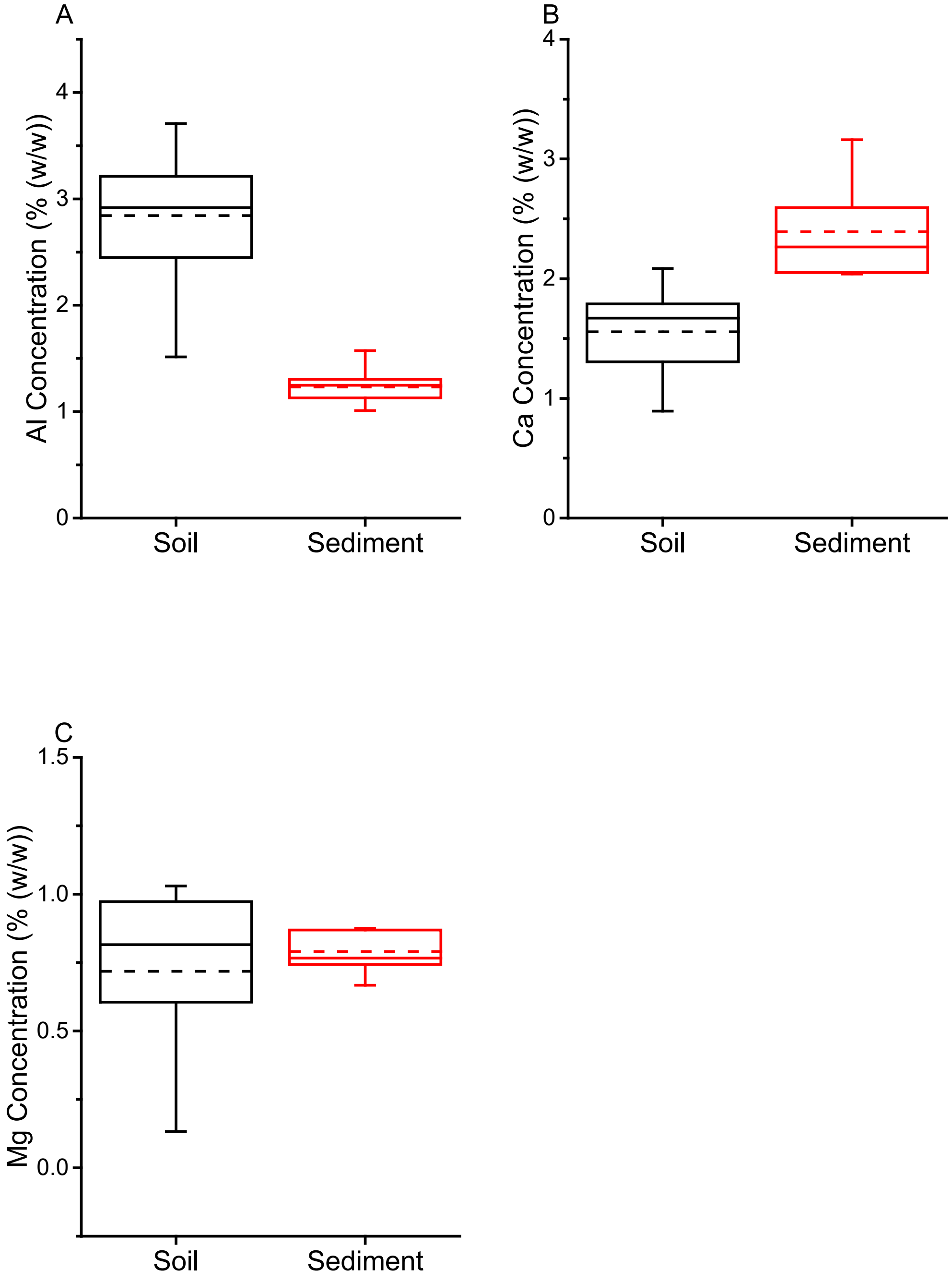

Figure 4-21: Box and whisker plots to describe the range of concentrations of: (A) Al; (B) Ca; (C) and Mg in Polmadie soils and sediments. The box shows the 25th (lower line), 50th (middle line) and 75th (upper line) quartiles with the mean as a broken line. The lower and upper whiskers show the minimum and maximum concentrations, respectively.

4.4 Elemental concentrations profiles for sediment cores collected from Polmadie Burn

Two sediment cores, Core 1 and Core 2, were taken at Sample Points 1 and 2, respectively (Section 3.1.2). These cores were sectioned into 1 cm sections and then digested using an HF/HNO_3 digestion followed by ICP-OES analysis to determine the vertical distribution of Cr, Fe, Mn, Al, Ca and Mg (Sections 3.3.1.3 and 3.7.1.2). Sediment from selected depths was also digested using an alkali digestion to determine the Cr(VI) concentration using DPC complexation (see Sections 3.3.3 and 3.7.2.2).The results from these core profiles are described in this section.

4.4.1 Core 1

The mean Cr concentration in Core 1 was 2080 ± 240 mg kg^{-1} and the Cr concentration remained relatively constant with increasing sediment depth (Figure 4-24A). The Cr(VI) sediment concentrations was measured at depths 0, 3, 5, 6, 9 and 12 cm depth. The surface Cr(VI) concentration was 484 ± 0.71 mg kg^{-1} which decreased slightly with increasing depth to 210 ± 50 mg kg^{-1} at 13 cm depth (Figure 4-24B). The percentage of total Cr present as Cr(VI) was 19 ± 7%. The surface Cr concentration ~10 m upstream of Core 1's location was 1280 ± 8.0 mg kg^{-1}, lower than the mean concentration in the top 0-4 cm of Core 1 which was 2240 ± 230 mg kg^{-1}, probably due to the heterogeneous nature of the sediments. This was reflected in the large variation in the elemental concentrations of Cr, Fe and Mn which had relative standard deviation (RSD) values of 33, 19 and 34% along with the OM content which had an RSD of 71% in the surface sediments taken at various locations along the stream.

The Fe concentration ranged between 2.32 and 4.36% (w/w) and did not vary much with depth (Figure 4-24C). The Mn concentration range was 346 - 873 mg kg^{-1}. The concentrations in the top 0 – 5 cm were more variable but, below 5 cm depth, remained constant (Figure 4-24D).

The Al and Ca concentrations ranges were 0.95 – 1.76 and 0.92 – 1.67% (w/w), respectively. Both the Al and Ca concentrations decreased with depth. The Mg concentration range was 5070 – 7080 mg kg^{-1} and tended to decrease with depth (Figure 4-23). The Al and Ca concentrations had a strong positive correlation (Spearman's rank correlation $\rho = -1.00$, $p < 0.01$) and both Al and Ca were significantly negatively correlated with pH (Spearman's rank correlation $\rho = -0.82$, $p < 0.01$).

4.4.2 Core 2

The Cr concentration in the surface 4 cm of Core 2 was 3130 ± 840 mg kg^{-1} after which it increased to a maximum of 14900 ± 2100 mg kg^{-1} at 7 cm depth, before decreasing to a 4020 ± 80 mg kg^{-1} at 11 cm depth. Between 11 – 15 cm depth the range of Cr concentrations was 3510 – 4540 mg kg^{-1} (Figure 4-24A). The Cr(VI) concentration was also measured at depths

0, 3, 5, 6, 9 and 12 cm and tended to follow the same pattern as total Cr where there was a peak of 1130 mg kg^{-1} at 7 cm depth (Figure 4-24B). The percentage of Cr(VI) in Core 2 was lower than Core 1 as the mean Cr(VI) % (of the total Cr) was 11 ± 9%. Although the maximum Cr(VI) concentration at 6-7 cm of 1130 ± 38 mg kg^{-1} coincided with the peak in total Cr, the largest percentage of Cr(VI) was at 12 -13 cm depth which contained 25 ± 0.4% (of total Cr). It should also be noted that at 0-1 cm the percentage of Cr as Cr(VI) as 18 ± 0.1%. The mean surface 0-4 cm Cr concentration of 3130 ± 840 mg kg^{-1} was slightly higher than the surface Cr concentration of 2360 ± 49 mg kg^{-1} from the transects but this variation is probably due to the heterogeneity of the site, as discussed above.

The Fe concentration increased from 3.64 ± 0.018% (w/w) at the surface to 4.40 ± 0.43%(w/w) at 4 cm, below which it decreased to 3.07 ± 0.063%(w/w) at 12 cm depth, before increasing again slightly (Figure 4-24C). The Mn concentrations tended to increase with depth, from 583 ± 46 mg kg^{-1} at the surface and reaching a maximum at 928 ± 350 mg kg^{-1} at 13 cm depth (Figure 4-24D).

The Al concentration ranged between 0.45 – 1.71% (w/w) and the Al concentration was significantly positively correlated with the Cr concentration (Spearman's rank correlation $\rho = 0.73$, $p < 0.01$). The range of Ca and Mg concentrations were 1.25 – 2.21% (w/w) and 660 – 4550 mg kg^{-1}, respectively (Figure 4-25). Magnesium concentration decreased with depth and was significantly negatively correlated with Al concentrations (Spearman's rank correlation $\rho = -0.74$, $p < 0.01$).

4.4.3 SEM-EDS analysis of Core 1 sediment samples

Sediment samples from depths 0-1 cm and 6-7 cm depth in Core 1 were analysed using SEM-EDS to gain an insight into the forms of Cr occurring in the sediment. These depths were chosen due to high concentration of Cr in the 6-7 cm depth to compare it to the Cr phases in the surface (0-1 cm) layer. The images taken were back-scattered electron (BSE) images which showed the relatively heavier elements Fe and Cr as white areas. Chromium was found in what appeared to be surface coatings and small discrete grains. The Cr coatings were found on quartz (SiO_2) and feldspar ($KAlSi_3O_8$) minerals in both the 0-1 and 6-7 cm depths (Figure 4-26, Figure 4-27 and Figure 4-28). Quartz and feldspar minerals are not typically found in COPR waste and so it is more likely that these surface coatings have formed within the sediment. There were also small discrete grains observed which contained Ca, Mg, S and O, which could be residual COPR material (Figure 4-29). The minerals found in COPR are calcite, brucite, periclase, aragonite and ettringite which contain large concentrations of Ca, Mg, S and O (Hillier *et al.*, 2003). Overall, SEM-EDS analysis showed that Cr was generally found alongside Fe, Ca, S, and Al in the surface coatings which suggests the precipitation of Cr minerals contributes to the formation of the Cr phases observed in the sediment, however the exact mechanism could not be identified through SEM-EDS.

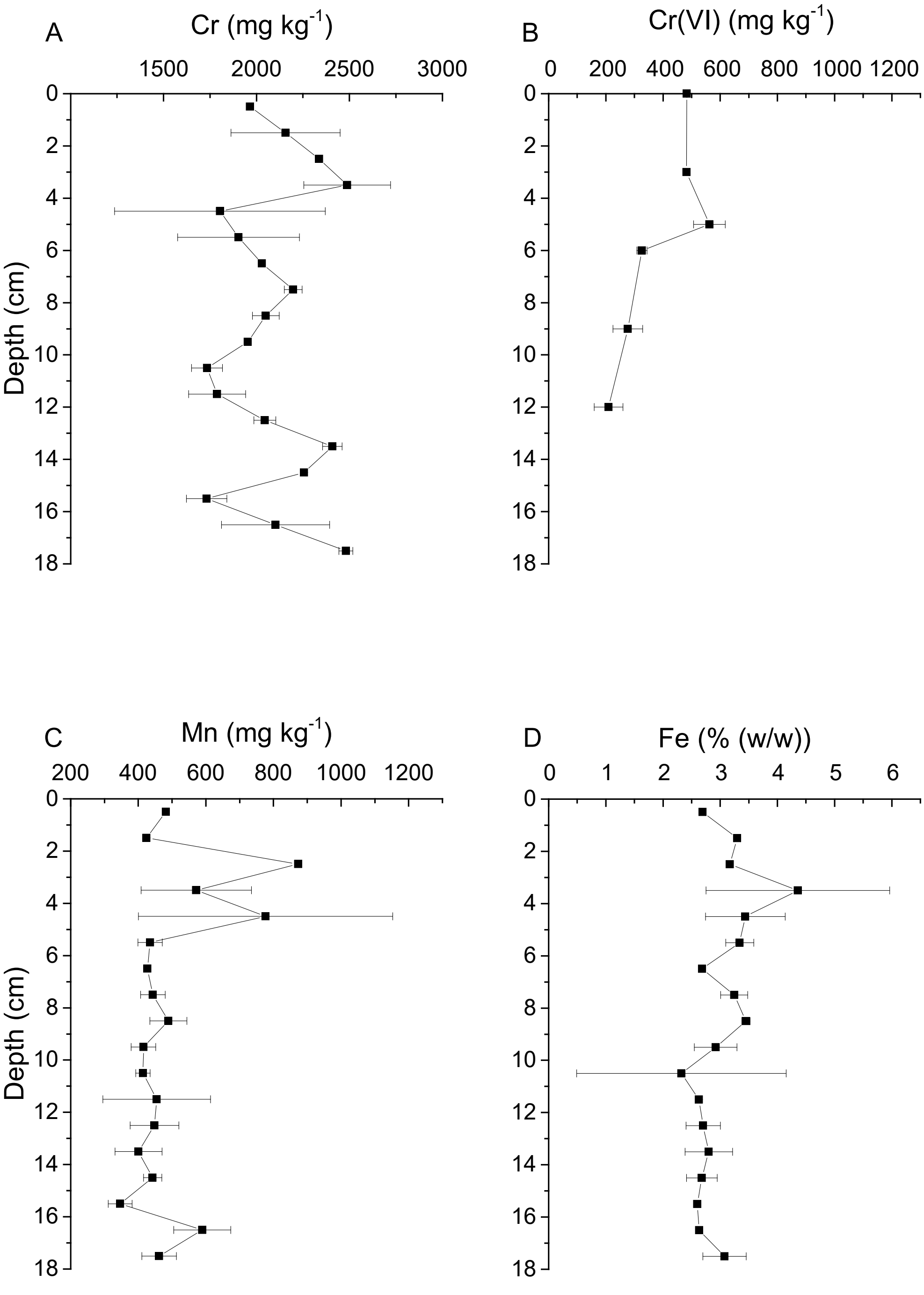

Figure 4-22: Mean ± 1 s.d. of (A) Cr(tot); (B) Cr(VI); (C) Fe and (D) Mn concentrations with depth in Sediment Core 1

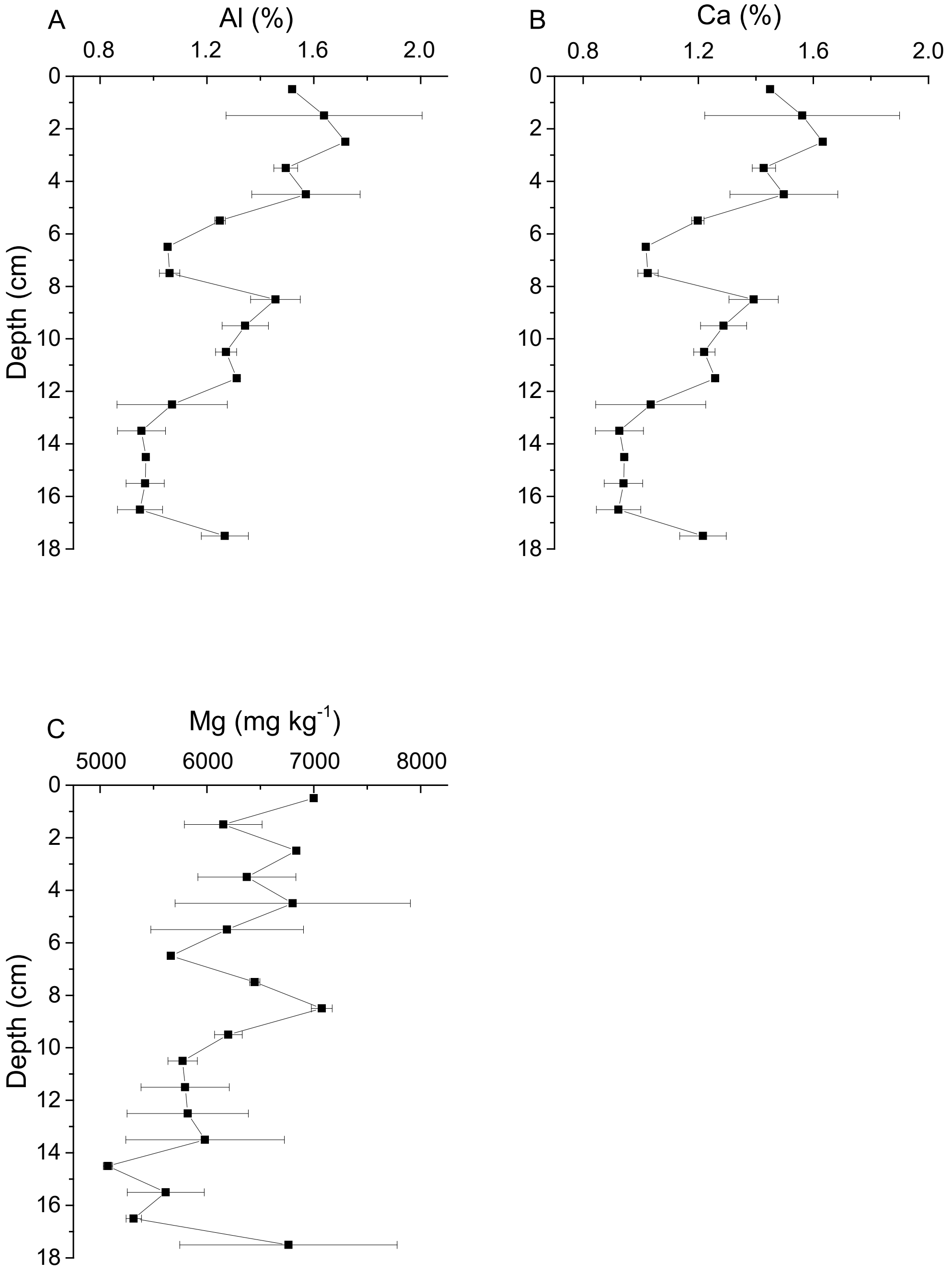

Figure 4-23: Mean ± 1 s.d. of (A) Al; (B) Ca and (C) Mg concentrations with depth in Sediment Core 1

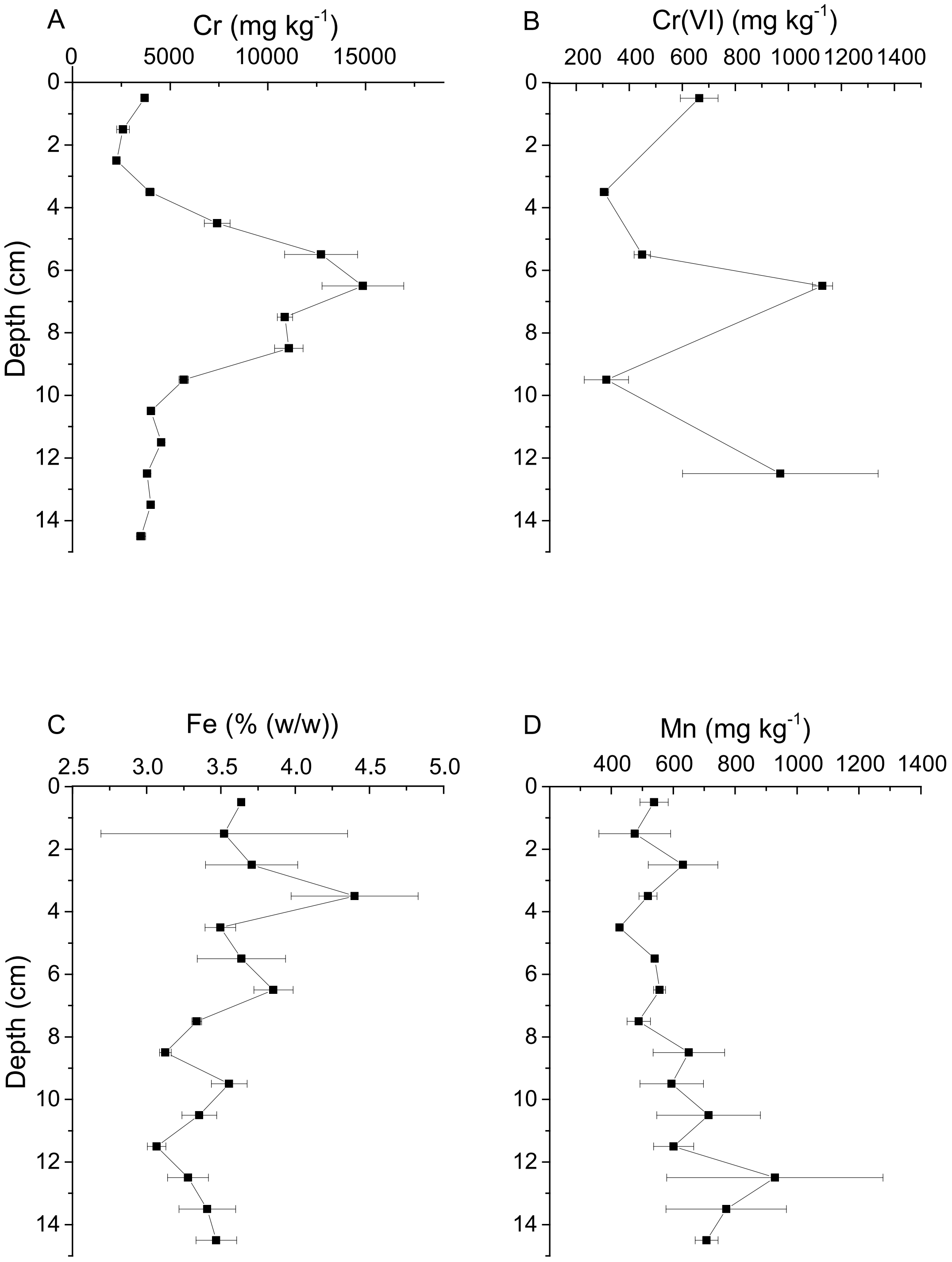

Figure 4-24: Mean ± 1 s.d. of (A) Cr(tot); (B) Cr(VI); (C) Fe and (D) Mn concentrations with depth in Sediment Core 2

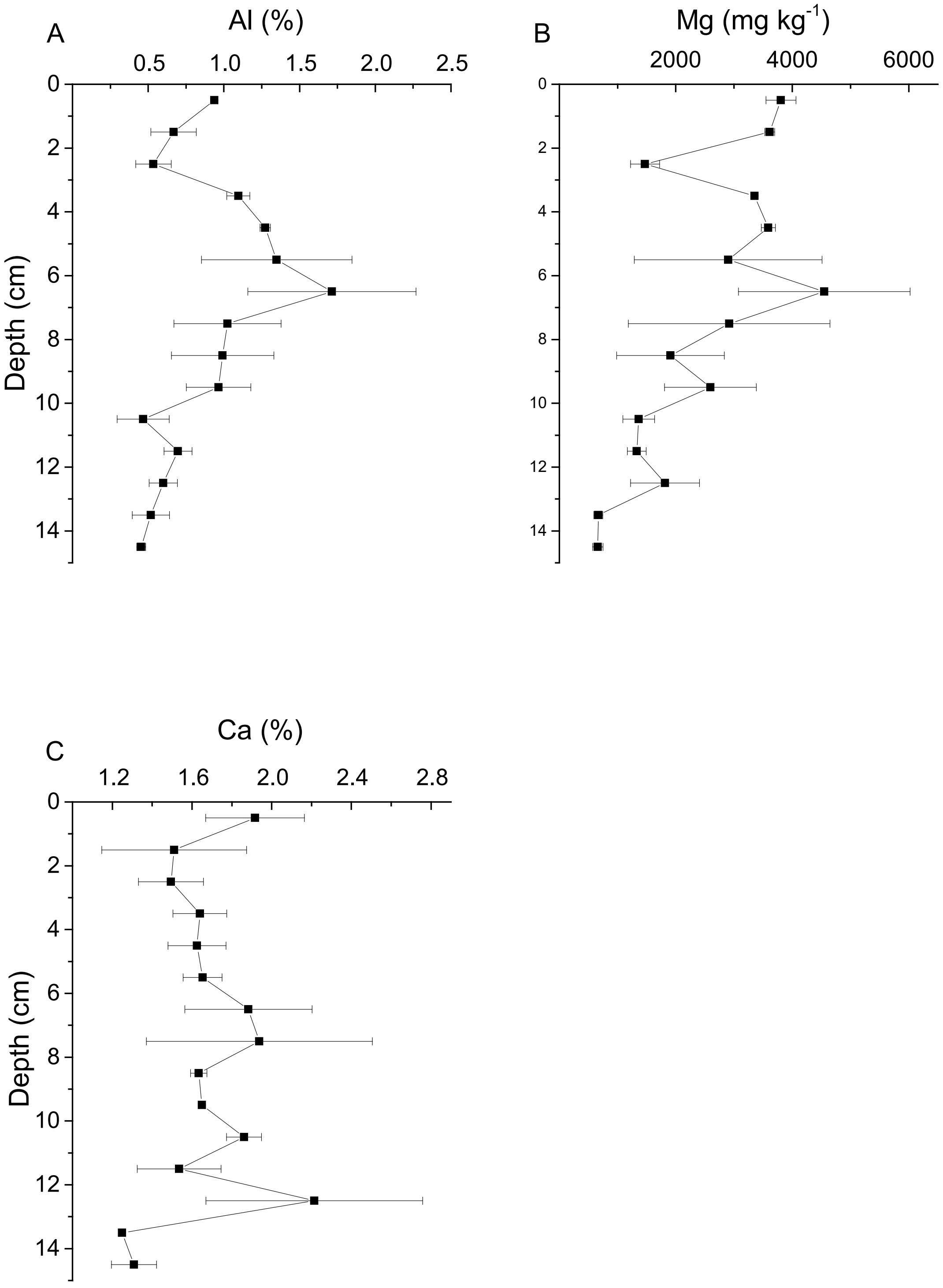

Figure 4-25: Mean ± 1 s.d. of (A) Al; (B) Ca and (C) Mg concentrations with depth in Sediment Core 2

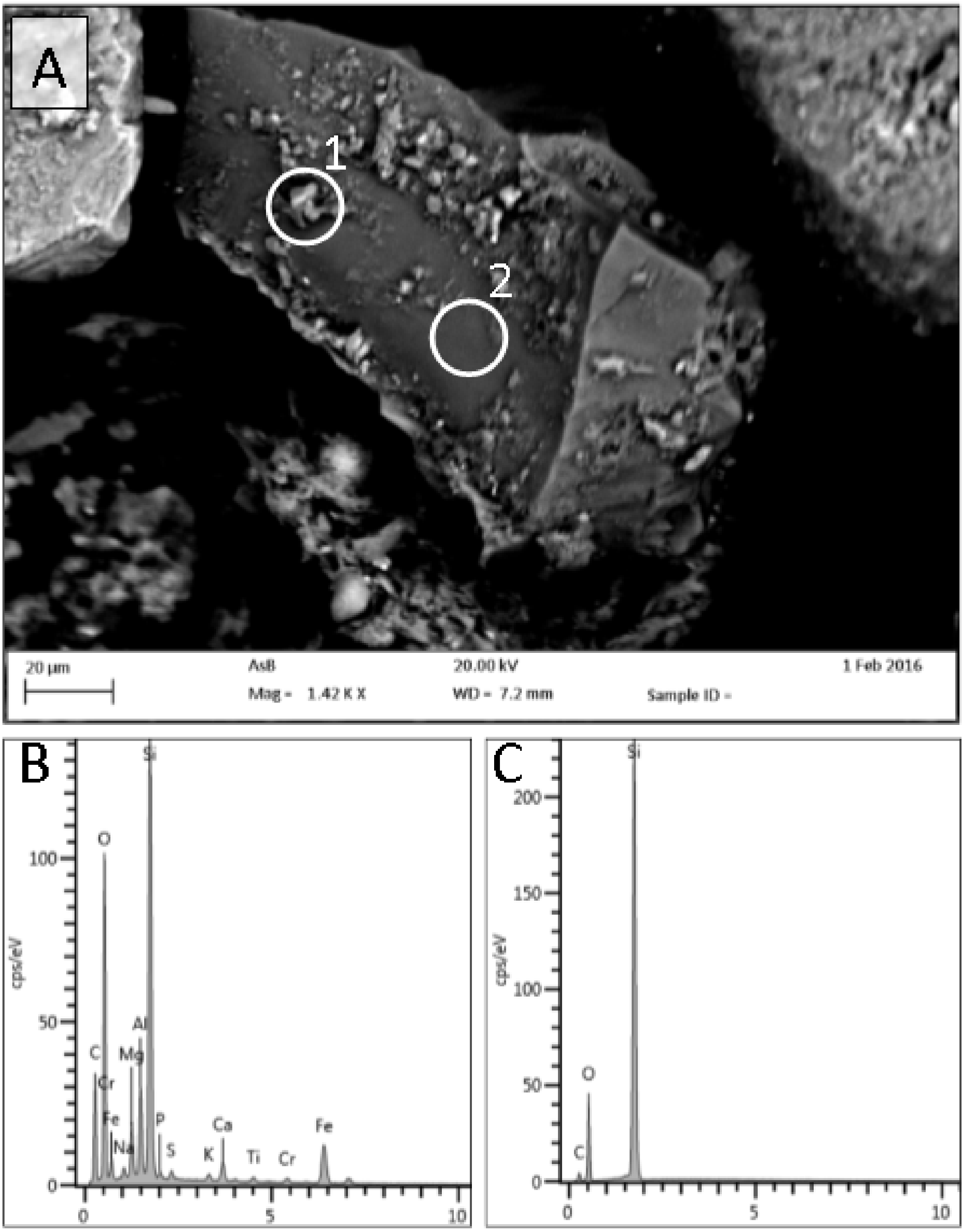

Figure 4-26: (A) A BSE SEM image showing quartz grain with a surface coating; (B) the typical elemental concentration of a surface coating from Site 1and (C) the elemental content of the grain at Site 2.

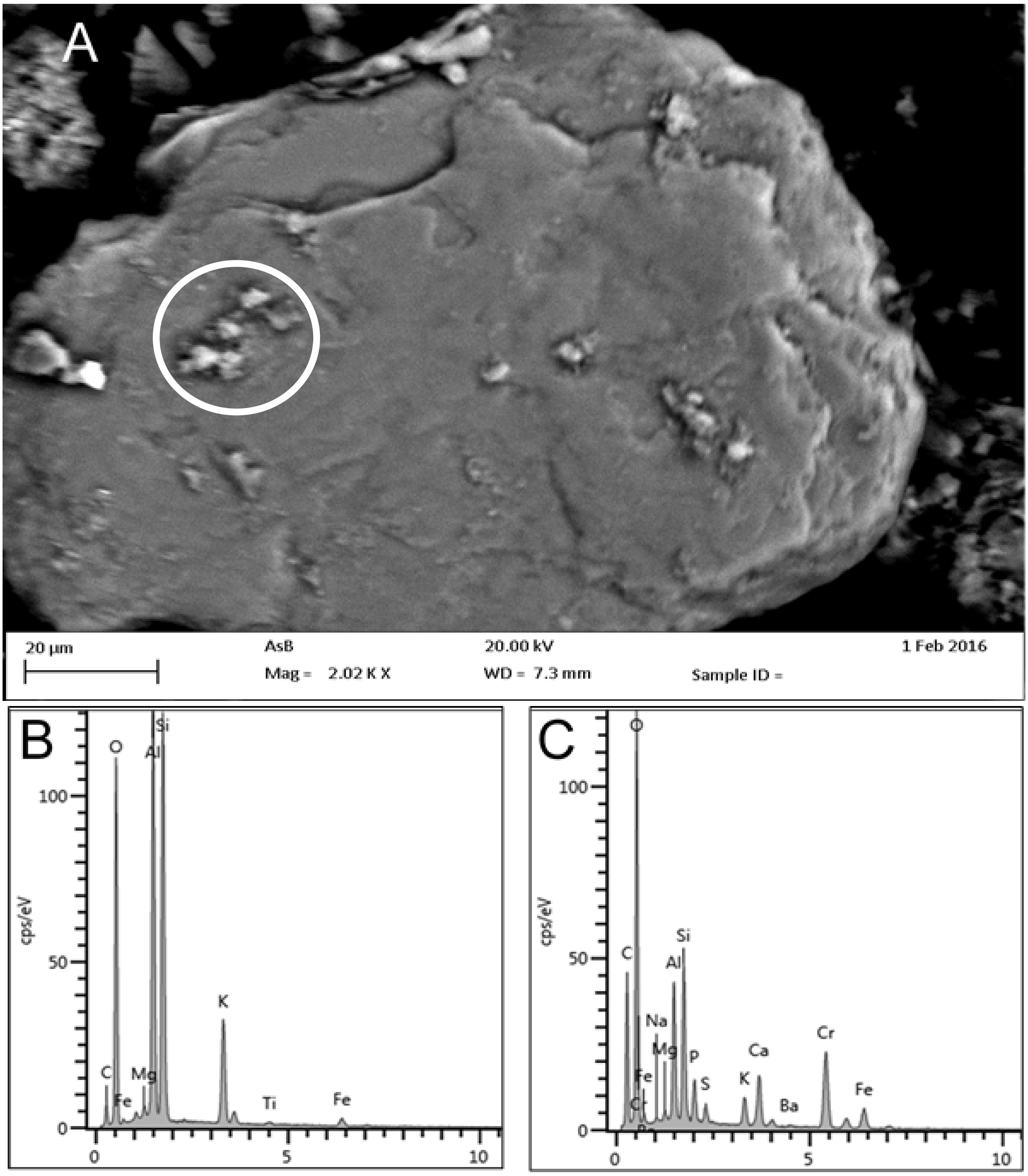

Figure 4-27: (A) A BSE SEM image of feldspar mineral with surface coating. (B) The composition of the mineral grain and (C) the surface coating highlighted by the white circle.

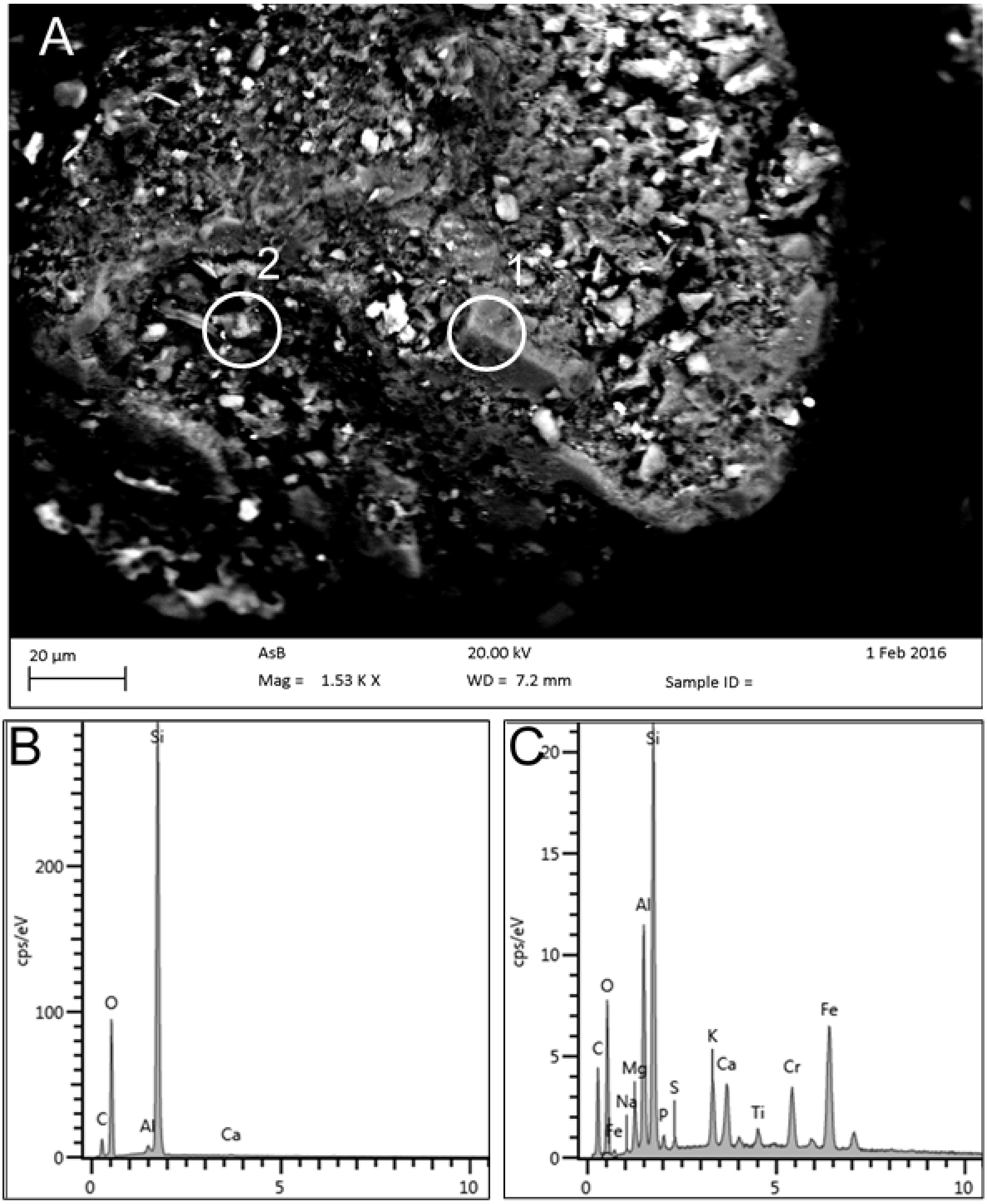

Figure 4-28: (A) A BSE SEM image showing the presence of aggregates. (B) The composition of the mineral at Site 1 and (C) the composition of mineral at Site 2.

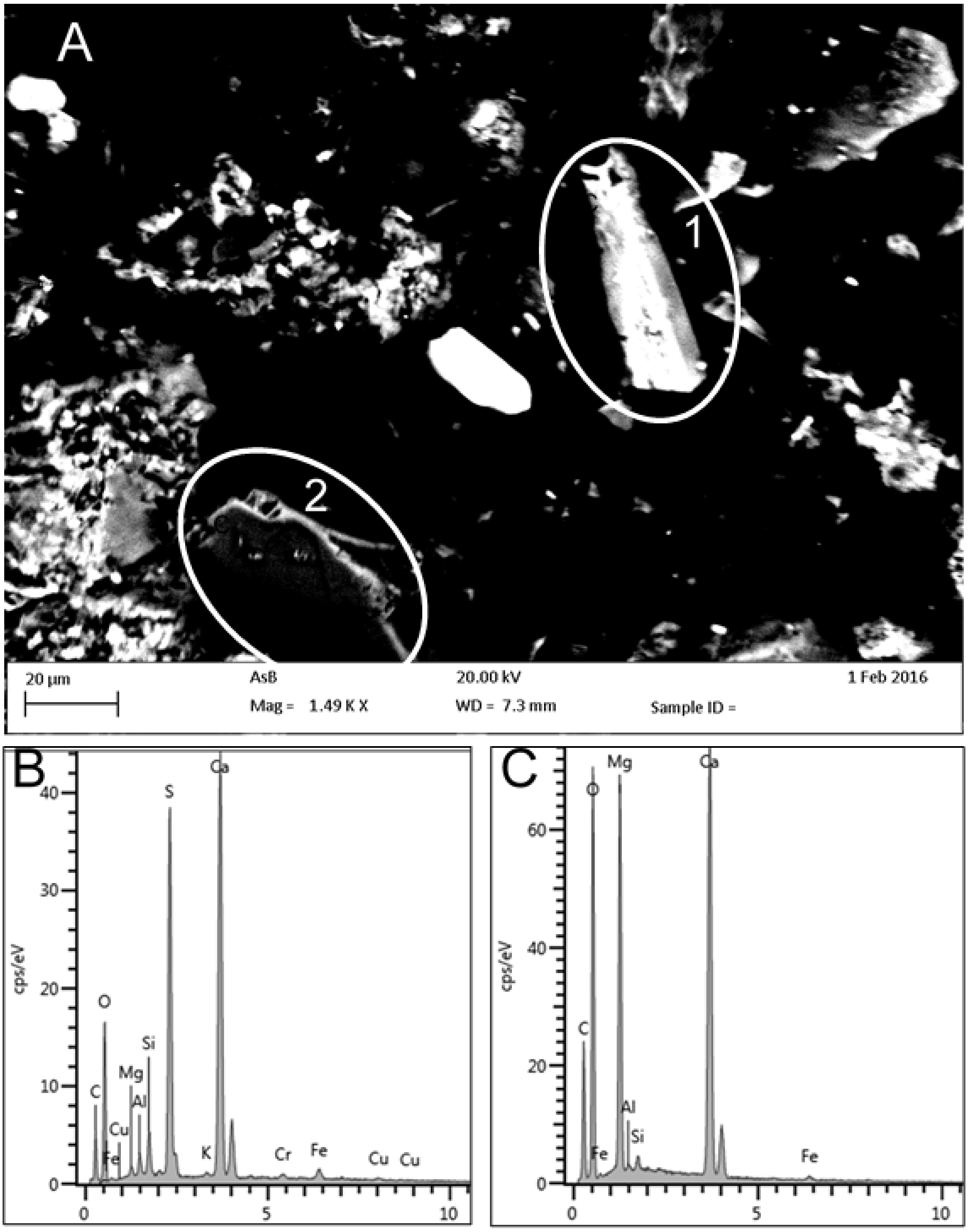

Figure 4-29: (A) A BSE SEM image showing small individual grains. (B) The elemental composition of 1 is shown in and (C) the composition of 2 is shown in.

4.5 BCR sequential extraction of surface soils and sediments

To gain insight into the associations of Cr in different fractions of the Polmadie soils and sediments, a BCR sequential extraction was used to determine the percentage of Cr in the weakly absorbed, reducible (Fe/Mn oxides), oxidisable (OM/sulfides) and the residual phase in field-moist samples. Ten soil samples were taken from banking soil, five from each side of the burn. Five sediment samples were also taken approximately in line with the soil samples. The sampling locations are shown in Section 3.1.2. Information on the sampling methods and BCR procedure can be found in Sections 3.1.3 and 3.3.2, respectively. The recovery of the elements from the BCR sequential analysis was 87 ± 16%.

4.5.1 Elemental distribution within the banking soil

There was no significant difference between the distribution of the elements in Steps 1-4 of the BCR sequential extraction between the banking soils taken from opposite sides of the stream (Two Sample T-Test, $p= 0.05$). Therefore, the results of the BCR sequential extraction for all the soils were combined. The values stated below are the mean of these 10 samples ± one standard deviation and are summarised in Appendix 3.

Little Cr was released in the acid exchangeable step (1.02 ± 0.33%). The majority of Cr was removed in the reducible and oxidisable steps (25.9 ± 8.5 and 63.2 ± 14%, respectively) and 9.82 ± 4.4% in the residual phase (Figure 4-30A). These results suggest that the majority of Cr in the banking soils is associated with Fe/Mn hydroxides and OM.

As for Cr, there was a low percentage of Fe extracted in the acidic exchangeable step (0.13 ± 0.23%). However, the percentage of Fe extracted in the reducible and oxidisable steps was 26.2 ± 5.6% and the 11.1 ± 4.1%, respectively (Figure 4-30B), and the majority (62.6 ± 6.7%) of Fe was found in the residual phase. The percentage of Mn extracted in the acid exchangeable step was 26.6 ± 7.4%. The greatest proportion of Mn was removed during the reducible step (42.3 ± 9.2%) and there was 9.41 ± 11% extracted in the oxidisable step along with 21.7 ± 7.2 % found in the residual phase (Figure 4-30C). There was 0.53 ± 0.25, 15.0 ± 2.7 and 8.37 ± 2.7% of Al extracted in the acid exchangeable, reducible and oxidisable steps, respectively. The highest percentage of Al occurred in the residual phase (76.0 ± 4.5%) (Figure 4-30D).

Approximately half of Ca (49.8 ± 14%) was extracted in the exchangeable fraction with relatively low amounts being removed in the reducible and oxidisable fractions (14.6 ± 2.5 and 8.63 ± 1.7%, respectively). The second highest fraction was the residual fraction which contained 27.0 ± 18% of Ca extracted. There was 22.7 ± 7.5% of Mg extracted in the exchangeable phase and, like Ca, relatively low amounts of Mg were extracted in the reducible and oxidisable fractions (4.32 ± 0.48 and 18.7 ± 1.4%, respectively). As for Al, the majority of Mg was associated with the residual phase (54.2 ± 9.4%).

4.5.2 Elemental distributions within the burn sediments

As for the elemental distributions within the soils, there did not seem to be any spatial trend in the data and so the mean result for each element in each sequential fraction was taken for the five sediment samples. These results are summarised in Appendix 2. The values stated below are the mean ± one standard deviation of the results from the five sediments. The distribution of Cr in sediments showed a similar trend to that described for the soil samples with 3.55 ± 1.9, 37.6 ± 3.9, and 52.3 ± 9.5% extracted in the acid exchangeable, reducible and oxidisable fractions, respectively. 6.58 ± 3.6% of Cr was present in the residual phase (Figure 4-30A). The Fe/Mn oxide fraction contained a higher proportion of Cr in the sediments compared to the soils.

Iron distribution in the sediments was also similar to that in the soils with 1.77 ± 0.60, 25.8 ± 7.2 and 5.18 ± 2.2% found in the acid exchangeable, reducible and oxidisable fractions, respectively. The majority (67.2 ± 8.6%) of Fe was again present in the residual phase (Figure 4-30B). The percentage of Mn extracted in the acid exchangeable step was 24.8 ± 5.7%. The percentage of Mn extracted in the reducible step was 19.2 ± 2.3% which was approximately half that found for the soils (Figure 4-30). The percentage extracted in the oxidisable step was 7.37 ± 0.93% and the majority of Mn occurred in the residual phase (48.6 ± 6.3%). The proportion of Mn found in the residual phase of the sediments was approximately double that found in the soil residual phase. This is probably due to reducible Mn being lost in the sediments due to the highly reducing environment, and hence the increase in the Mn in the residual phase which will be non-redox cyclable Mn. The loss of reducible Mn has likely contributed to the lower overall concentrations of Mn in the sediment compared to the banking soils. The distribution of Al in sediment was similar to the distribution of Al in the soils, even though the sediment Al concentration was approximately half the concentration of Al in the banking soil. For Al 2.26 ± 1.8, 20.9 ± 3.6 and 9.05 ± 4.4% occurred in the acid exchangeable, reducible and oxidisable fractions, respectively, and 67.8 ± 8.8% was found in the residual phase (Figure 4-30D).

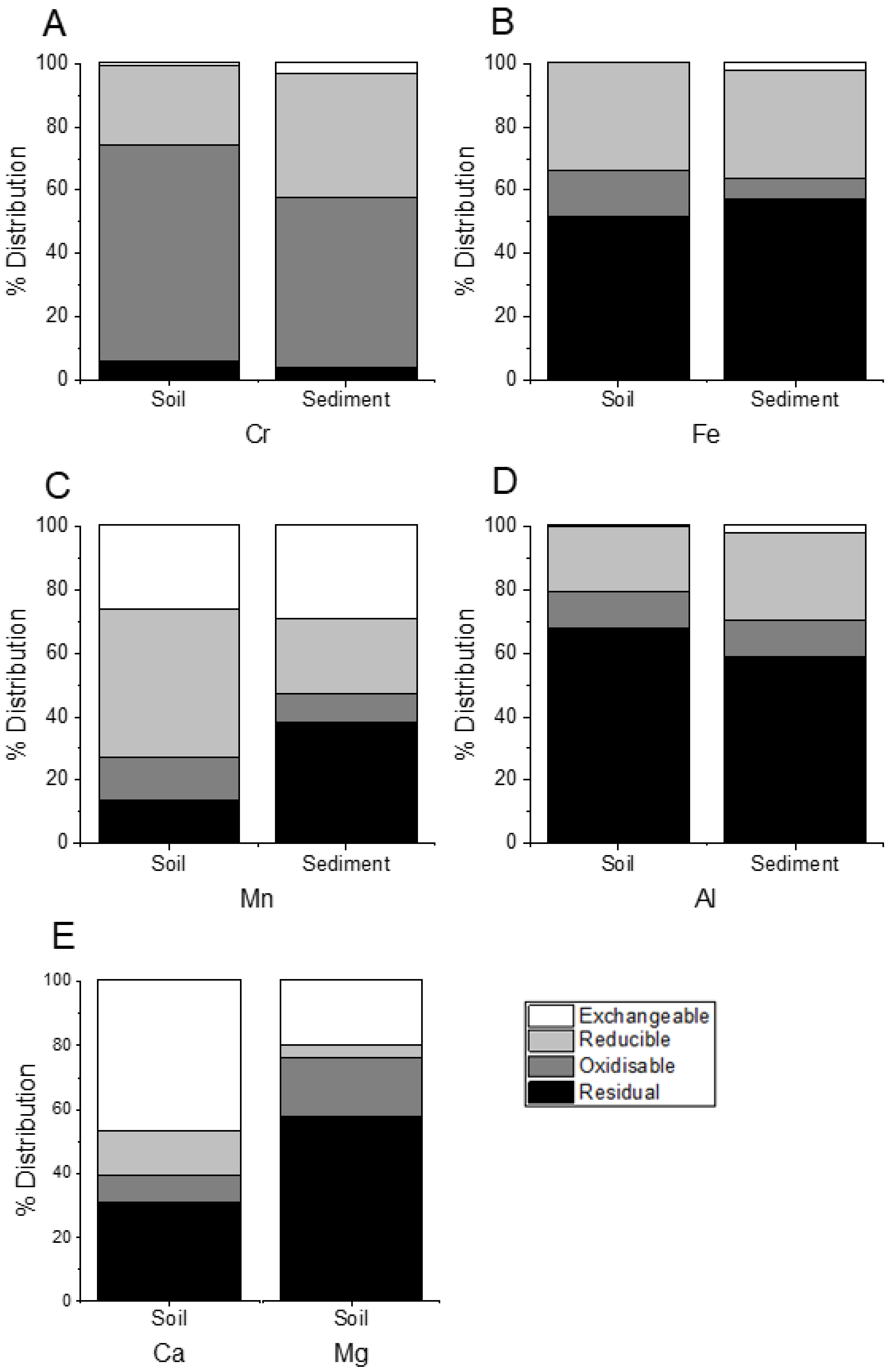

Figure 4-30: Distribution of: (A) Cr; (B) Fe; (C) Mn and (D) Al in soils and sediments along with (E) distribution of Ca and Mg in soils

4.6 Gel Electrophoretic fractionation of organic matter extracted from the Polmadie Burn banking soils and bottom sediments

Gel electrophoresis has been successfully shown to separate OM extracted from soils based on their molecular weight and charge (Graham *et al.*, 2008). The principle works by applying difference in potential (voltage) across a gel which is filled with a buffer solution and to which the soil OM is added to a well. This potential difference separates the material based on its charge density and size and therefore can be useful for determining the associations of metals to different types of OM. Since sulfides can also be removed in the oxidisable step of the sequential extraction methods, this technique was used here to confirm the association of Cr and OM that was suggested by the BCR sequential extraction for both banking soils and stream sediments.

Organic matter was extracted using a 0.1 M NaOH extraction from dried soil, field-moist soil, dried sediment and field-moist sediment to investigate the differences in Cr/OM interactions as banking soil and sediments dry. The dried soil and sediment used for this experiment were air-dried for 4 weeks. The electrophoresis gel was prepared as described in Section 3.6.3 and the wells of the horizontal bed electrophoresis unit were filled with 0.045 M Tris-borate buffer (Graham *et al.*, 2008). Approximately 2 mL of the extracted OM was transferred to the gel well and the electrophoretic procedure was run using conditions of fixed current (20 mA) for 30 min (Graham *et al.*, 2008). All of the organic material emerged from the gel well and a brown band was observed. Under UV light, a white band was observed ahead of the brown band. The gel was then cut into ten 0.5 cm strips, fraction 1 the closest 0.5 cm section to the well and fraction 10 the furthest, each was placed in a separate centrifuge tube, frozen and then thawed. Centrifugation (5000 x g for 20 min) was used to isolate the dissolved OM (DOM) from the gel. An aliquot of leachate recovered from each strip was analysed using ICP-MS to determine the Cr, Fe and Mn concentration. The absorbance of the leachate was measured using UV-Vis spectrometer over the wavelength 200 – 550 nm. The ratio of the slope of the natural logarithm of the absorbance between 275 and 295 nm to the slope of the natural logarithm of the absorbance between 350 and 400 nm was taken. This value gives an indication of the molecular weight and source of the OM extracted (Helms *et al.*, 2008). Although the DOM concentration was not directly measured in the solution released after a freeze-thaw method, the UV absorbance at 254 nm was used as a proxy to obtain the relative DOM concentrations (USEPA, 2009).

4.6.1 Electrophoretic fractionation of banking soil organic matter

A brown colour was observed in electrophoretic fractions 4 and 5, i.e. 1.5-2 and 2-2.5 cm from the gel well, in the OM extracted from both the field-moist and dried soil samples. Fractions 5 and 6 also showed fluorescence under UV light. The maximum absorbance at 254 nm (corrected for dilutions which were made before the spectra were obtained) was ~3.6 in F5 of the extractant from field-moist soil and ~3.7 in F4 of the extractant from dried soil, matching well with the visual observations. The slope ratio initially decreased to a minimum value at the position of the OM bands (F4-6) for both the air-dried and field-moist samples. The mean slope ratio for the field-moist and air-dried OM in F4-6 was 0.644 ± 0.14 and 0.722 ± 0.13, respectively (Figure 4-31 and Figure 4-32).

The maximum concentrations of Cr were 239 and 314 μg L^{-1} in F4 in the extractant from field-moist and dried soil, respectively. This coincides with the position of the brown band observed visually and confirmed by the absorbance at 254 nm. The same distribution was observed for Fe which had a maximum concentration of 1410 and 981 μg L^{-1} in F4 in the extractant from field-moist and dried soil, respectively. Thus, both Cr and Fe co-migrate with OM in the gel electrophoresis system, indicating that they are in some way associated, Both Cr and Fe may be directly bound to the negatively charged OM or Cr may be bound to Fe which is intimately associated with the OM. It may indeed be a mixture of both of these associations, which would be highly consistent with the sequential extraction results.

The Mn concentrations in the gel fractions were generally a lot lower than those for Cr and Fe, as expected both from the sequential extraction results and from previously published work which shows that Mn does not associated strongly with OM. In addition, the electrophoretic distribution pattern for Mn was not the same as for Cr and Fe, as Mn concentrations peaked in F3. Maximum Mn concentrations of 49.9 and 32.6 μg L^{-1} were found in F3 of the extractant from field-moist and dried soil, respectively. Thus it appears that the small amount of Mn associated with extracted OM was associated with a less mobile component. The significance of the difference between the Cr/OM associations from DOM extracted from dried and field-moist soils is discussed in a later chapter.

4.6.2 Sediment

A brown colour was observed in F2 and 3 in the OM extracted from field-moist sediment and so the sediment OM was less electrophoretically mobile than that in the soil. A pale brown colour was also observed in F2 and 3 of the OM extracted from dried sediment. The maximum absorbance at 254 nm was ~2.1 in F4 of the OM extracted from field-moist sediment but only ~0.3 in F3 of the OM extracted from dried sediment. The mean slope ratio for OM extracted from the field-moist and air-dried sediments in F2-4 was 1.26 ± 0.095 and 1.32 ± 0.032 respectively. This was higher than the soil slope ratio implying that the type of OM differs between the soil and sediment. This is possible due to the soils having a greater input of leaf litter from the vegetated banks whereas OM in the sediment may be derived more from sewage overflows.

The maximum Cr concentrations were 271 µg L^{-1} in F4 of the field-moist sediment extractant and 30.6 µg L^{-1} in F6 of the extractant from dried sediment. Maximum Fe concentrations were 1420 µgL^{-1} in F3 of the field-moist sediment extractant and 38.4 µg L^{-1} in F3 of the extractant from dried sediment. The maximum concentrations of Mn were 49.1 µg L^{-1} in F4 of the field-moist sediment extractant and 6.04 µg L^{-1} in F2 of the extractant from dried sediment. This shows that in the field-moist sediments Cr is bound to OM complexes which compliments the results shown in the BCR sequential extraction. The significance of the difference between the Cr-OM interactions in the field-moist and air-dried sediments will discussed in a later chapter.

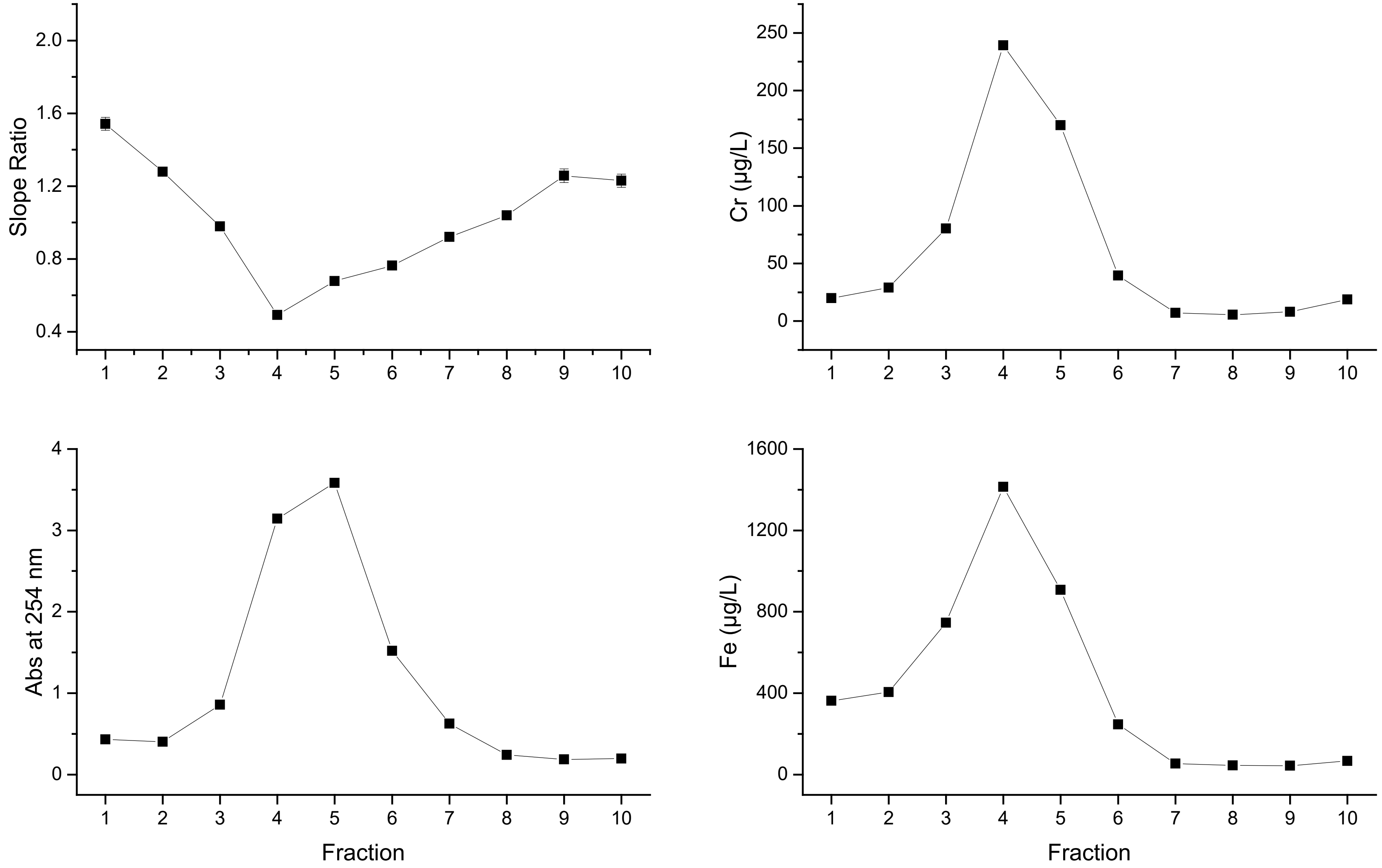

Figure 4-31: Gel electrophoresis data for organic matter extracted from field-moist soil

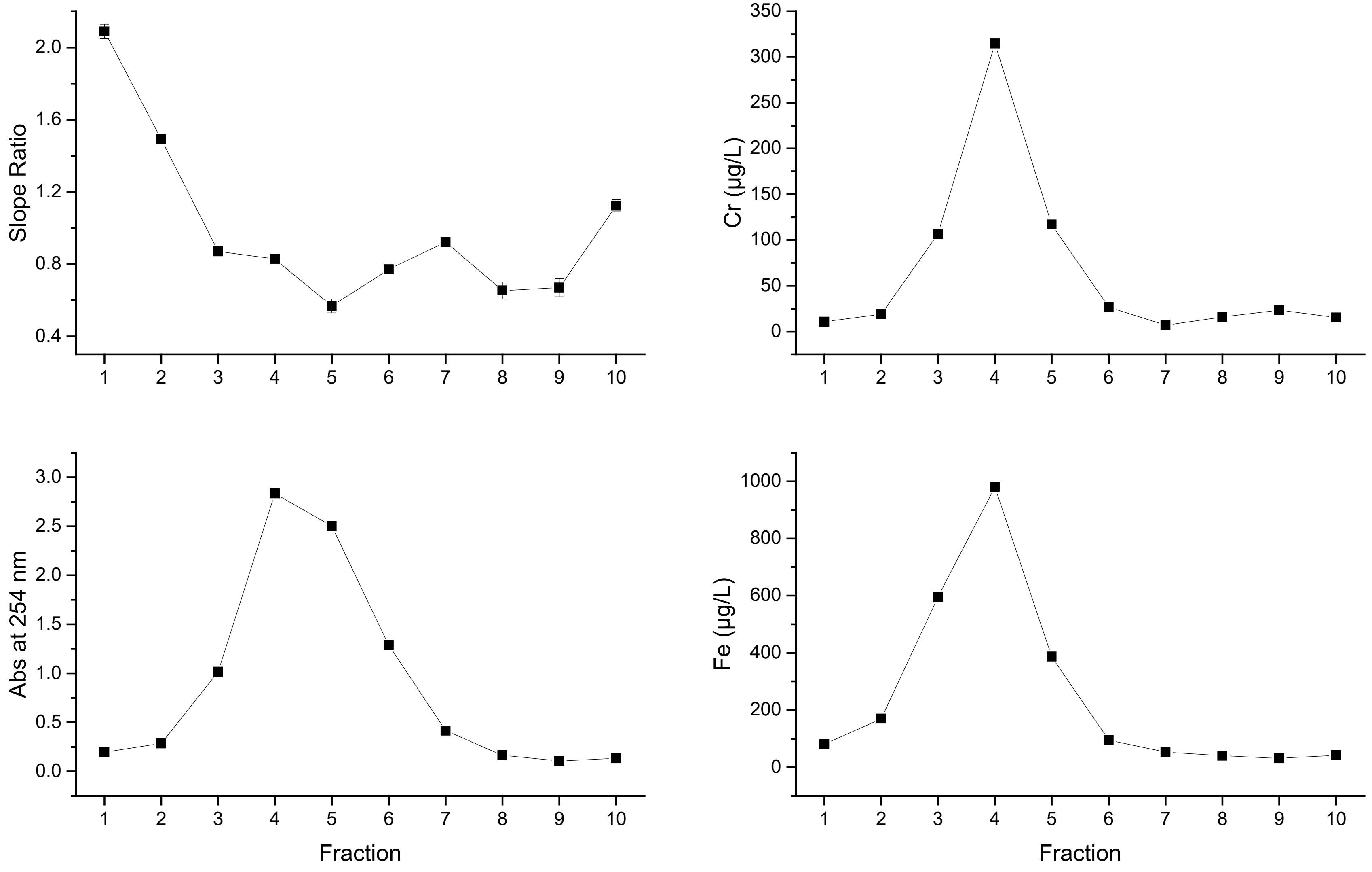

Figure 4-32: Gel electrophoresis data for organic matter extracted from air-dried soil

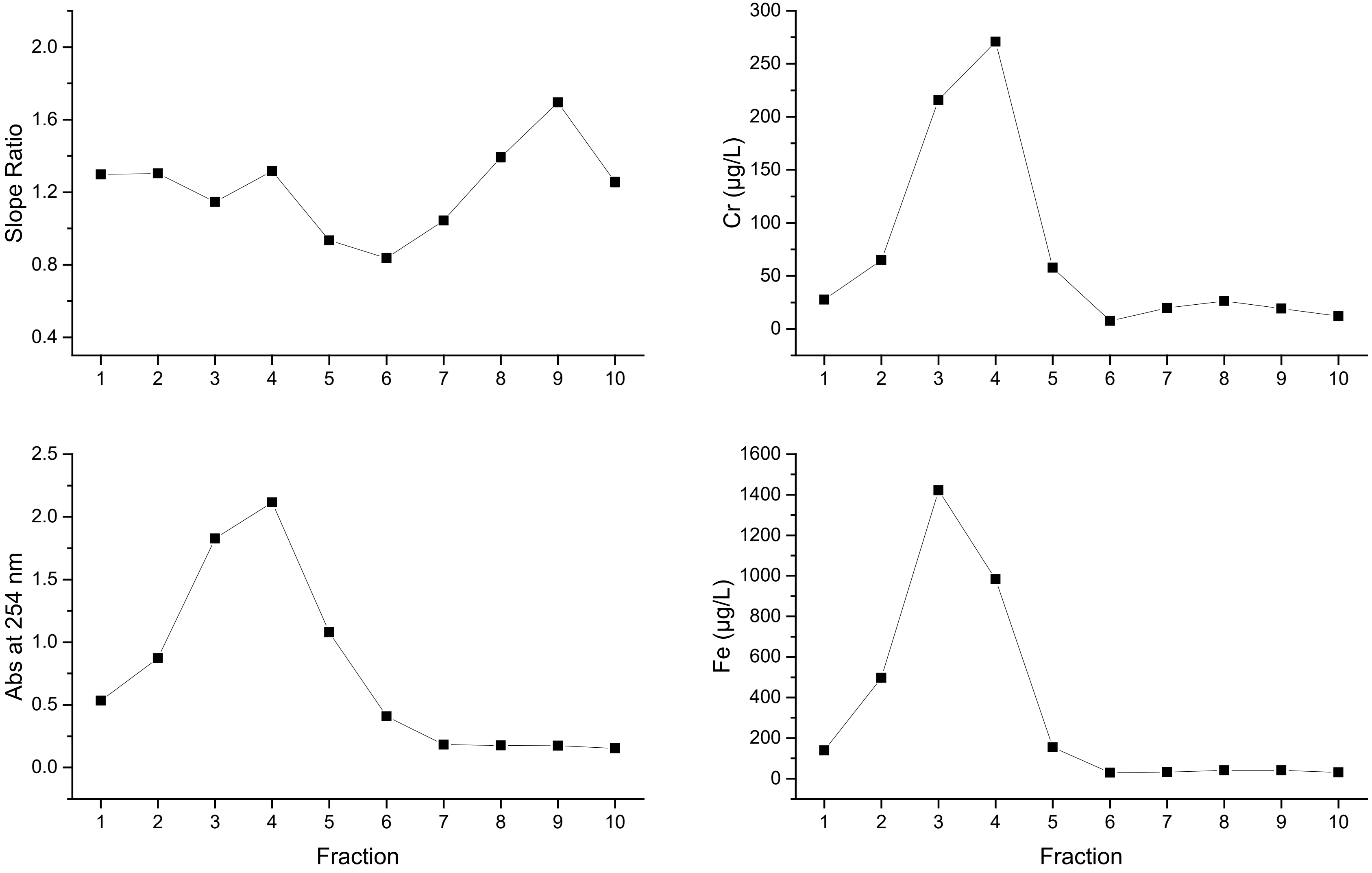

Figure 4-33: Gel electrophoresis data on field-moist sediment

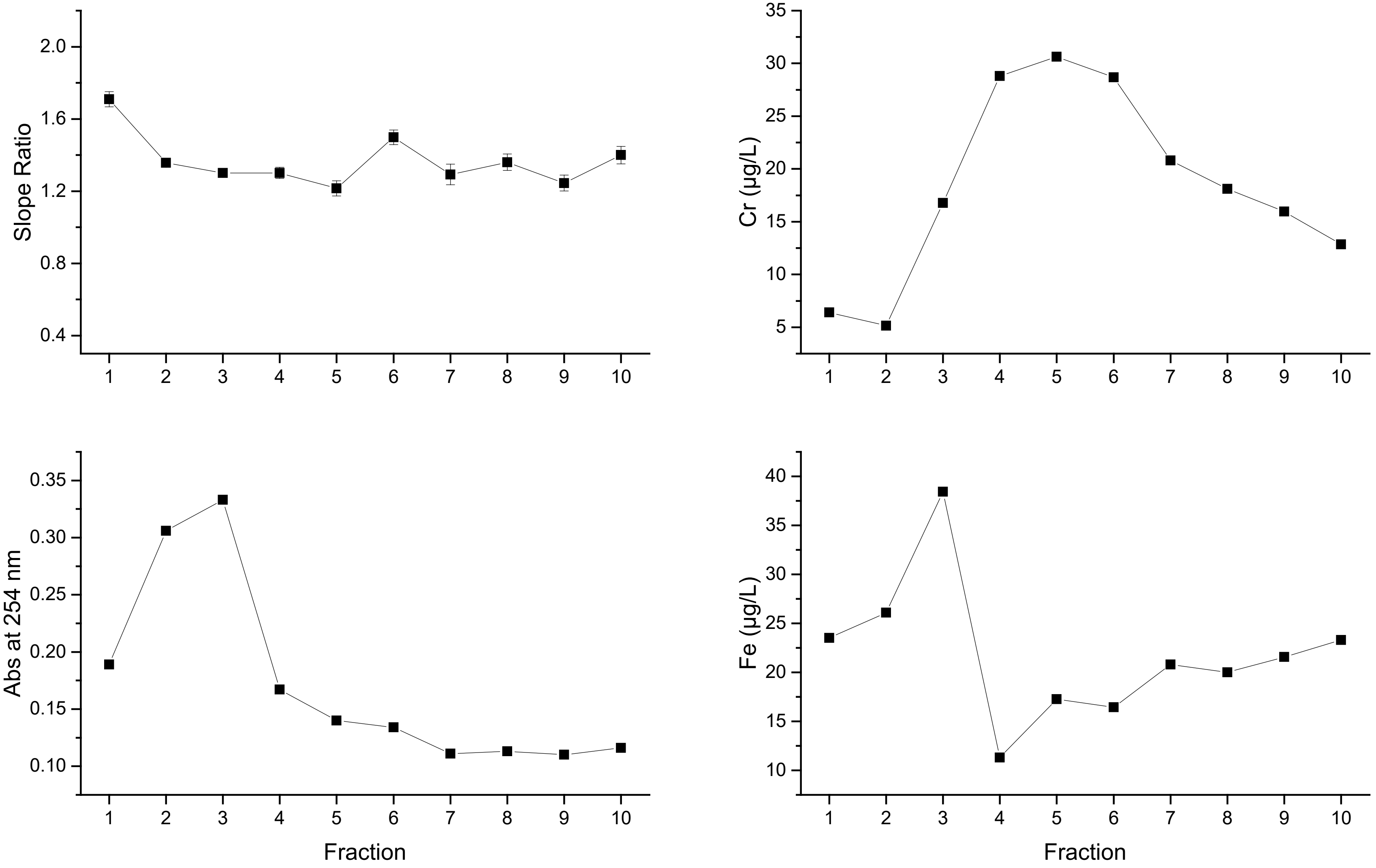

Figure 4-34: Gel electrophoresis data on air-dried sediment

4.7 Discussion of results

4.7.1 Occurrence of chromium in the Polmadie Burn sediments and banking soils

When the outlier of 6310 mg kg^{-1} was removed (Grubbs' test, G=3.52, p<0.01) there was significantly more Cr in the sediments (2420 ± 790 mg kg^{-1}) compared to the banking soil (1460 ± 703 mg kg^{-1}) (T-test, T= -3.41, p<0.01). The catchment of the Polmadie Burn flows through areas which have been impacted by COPR which originated from the J&J White Chromium Chemical Works (Farmer *et al.*, 2002). Previous work has shown that detrital COPR particles are present in the Polmadie Burn sediment which contribute to their high concentrations of Cr (<8800 mg kg^{-1} in the 150 µm fraction) (Palumbo-Roe *et al.*, 2017). The same study showed that mineral coatings containing Cr were present in the Polmadie Burn sediment. Similar material was found using SEM-EDS analysis of the sediments in this project. The surface coatings on quartz grains and feldspar minerals are unlikely to have originated from COPR waste indicating the formation of these coatings in the sediment. This is consistent with Cr(VI) having been reduced by Fe(II) which has been observed to precipitate as a mixed Fe/Cr hydroxide (Papassiopi *et al.*, 2014).

A slight decrease in Cr concentrations in the Polmadie Burn between the culvert and its entrance to the River Clyde was observed by Palumbo-Roe *et al.* (2017). This suggested that Cr(VI) is attenuated by precipitation and/or adsorption reactions to the sediment surface although the exact mechanism was not determined (Palumbo-Roe *et al.*, 2017). The same study reported minimal penetration of burn water into the sediment indicate the large variation of Cl concentrations in the stream water but limited response in the sediment porewater. This suggests that, although the sediment is effective in immobilising Cr(VI), there is limited exchange between the surface water and sediment porewater allowing Cr(VI) to remain in solution (Palumbo-Roe *et al.*, 2017).

The highly reducing conditions indicated by the presence of Fe(II) coupled with the lack of Cr(VI) in the sediment porewaters strongly support the hypothesis that Cr(VI) is unstable under the prevailing conditions and is removed onto the surfaces of sediment particles. Indeed, there was also significantly less Cr(VI) in the surface sediments (113 ± 48 mg kg^{-1}) compared to the soils (427 ± 520 mg kg^{-1}) (Mann-Whitney, U=240, p=0.01). Also, the percentage of total Cr as Cr(VI) was significantly lower in the surface sediments compared to the banking soils (Mann-Whitney, U=294, p=0.03). The observed behaviour is also consistent with previously published studies which show that reducing sediments which contain high concentrations of Fe(II) will result in the rapid reduction of Cr(VI) to Cr(III). It has been shown that the rate of Cr(VI) reduction by Fe(II) decreases as pH increases up to pH 4.5 and then increases as pH rises above pH 5.5 (Pettine *et al.*, 1998). In the sediment porewater which has pH > 8 this reaction will rapidly reduce all soluble Cr(VI) in the sediment to Cr(III) which will then precipitate as an insoluble mixed Fe/Cr hydroxide to form surface coatings.

In this study, it has also been observed that both Cr(III) and Cr(VI) can be present in the sediments even when the pH and redox conditions indicate that Cr(III) should be the thermodynamically stable species (Figure 4-15). For example, the percentage of Cr in the form of Cr(VI) found in the surface 0 – 1 cm of the sediment cores 1 and 2 was 24.6 ± 0.036 and 17.9 ± 2.0%, respectively, which tended to decrease with depth in both cores with depth to 14.2 ± 2.7 and 5.50 ± 1.5% at 9-10 cm depth. The persistence of Cr(VI) in the Polmadie sediment has been documented before and has been attributed to the weathering of COPR minerals which forms a crust protecting the Cr(VI) inside these minerals from weathering (Hillier *et al.*, 2003). The process of ball milling to break up these particles and the use of an alkaline digestion will release Cr(VI) from the internal surfaces within the sediment and soil.

As well as Fe(II), OM is also important in the reduction of Cr(VI). At circumneutral pH the reduction of Cr(VI) by DOM is not a favourable process but the reduction of Cr(VI) by solid OM is (Kyziol *et al.*, 2006, Löv *et al.*, 2017). The oxic soils, have high concentrations of OM (22.4 ± 4.7%) but Fe(II) is thermodynamically unstable and will rapidly oxidise to Fe(III), as shown by the absence of Fe(II) in the soil porewaters (Figure 4-10). Thus it is hypothesised that the mean rate of Cr(VI) reduction in the banking soils will be much lower than in the sediments due to low concentrations of Fe(II). The results of this study are consistent with such a hypothesis; in the surface soils 18.9 ± 15% of Cr was Cr(VI) compared to 5.17 ± 1.3% in the surface sediments. The reduction of Cr(VI) in the soils is a less favourable process due to the limited abundance of Fe(II) and the low rate of DOM reduction at circumneutral pH.

4.7.2 Associations of chromium in Polmadie Burn Banking soils and sediments

Sequential extraction of Polmadie soils and sediments suggested that Cr is mainly associated with OM and Fe/Mn oxides in both the banking soil and sediment. The results from the gel electrophoretic fractionation of OM extracted from field-moist soils and sediments further confirms that Cr present in the Polmadie banking soils and sediments is associated with OM by the positive correlation observed between OM and Cr in each of the fractions. This is consistent with literature which suggests that OM complexes with Cr(III) to form stable complexes and often acts as a sink for Cr (Kyziol *et al.*, 2006). The association between Fe, Cr and OM shown by the gel electrophoresis data was also seen by Löv *et al.* 2017 who used EXAFS to investigate the speciation of Cr and Fe in soil and colloids. They found that Fe and Cr were not directly bound, and they hypothesised that Cr bound to OM which coated Fe minerals was the reason for their association (Löv *et al.*, 2017). It is likely that this mechanism is present in the Polmadie banking soils and sediments, explaining the positive correlation between Cr, Fe and OM.

A study by Elzinga and Cirmo 2010 who used sequential extractions to investigate the associations of Cr in soil found a similar distribution of Cr in COPR derived soils when using the BCR sequential extraction procedure. This was combined with x-ray absorption spectroscopy data which showed that Cr in their soil was present as the mineral chromite, bound to OM and mixed Cr/Fe hydroxides (Elzinga and Cirmo, 2010). The mobility of an Cr(III) can be increased if it is bound to OM in the soil. Elements bound to suspended or dissolved OM will increase its solubility and leads to the supersaturation of Cr(III) in waters (Banks *et al.*, 2006).

Another important phase that Cr is associated to in the soils and sediments was Fe/Mn hydroxides as shown by the large proportion of Cr extracted in the reducible fraction of the BCR sequential extraction. The reduction of Fe minerals will release metals which are associated with these complexes and is the process which is utilised by Step 2 in the BCR sequential extraction (Rauret *et al.*, 1999). The sequential extractions showed that more Cr was held in the Fe/Mn fraction in the sediments (37.5 ± 3.9%) compared to the banking soils (25.9 ± 8.5). This attributed to the reduction of Cr(VI) by Fe(II) in the sediment leading to the formation of mixed Fe/Cr hydroxide precipitates which coat the surface of sediment particles.

The same process is not thought to be as important in the banking soils as Fe(II) is unstable and will rapidly oxidise to form insoluble Fe(III) compounds in the soils. The higher Fe(II) concentrations in the sediment which reduces Cr(VI) will result in a higher proportion of Cr being found in the Fe/Mn (hydr)oxide fraction of the sequential extraction. This is supported by the significantly larger proportion of total Cr occurring as Cr(VI) in the banking soils compared to the sediments.

In banking soils, the presence of Cr(III) containing minerals from COPR, such as brownmillerite, and other weathering products from COPR minerals may contribute to the Cr concentrations released during the reducible step of the BCR sequential extraction. Adsorption of Cr(VI) to soil has been shown to be a mechanism which can lead to the immobilisation of Cr(VI), although competition for the sorption sites can greatly reduce Cr(VI) adsorption (Rai *et al.*, 1989, Richard and Bourg, 1991, Choppala *et al.*, 2018). Charged mineral surfaces, such as Al, Fe and Mn hydroxides can adsorb anionic species and at pH 6-7 the adsorption of chromate to these Fe and Al (hydr)oxides is a favoured process (Rai *et al.*, 1989). This may account for some of the Cr found in the Fe oxide phase in the soils although it is not possible from the data here to determine its contribution to the soil Cr concentration.

In the banking soil, Cr was positively correlated with Al, Ca and Mg suggesting they come from the same source. The main elements found in COPR are Ca, Mg, Al and Cr which make up 18.1, 12.6, 12.0 and 4.0% (w/w) of the material, respectively (Geelhoed *et al.*, 2002, Hillier *et al.*, 2003). From the sequential extraction data, the proportion of Cr in the exchangeable fraction was 0.96 ± 0.33 and 3.72 ± 1.9% in the soils and sediments, respectively. Although the proportion of Cr extracted in the exchangeable fraction was low, the proportion of Ca and Mg extracted in the exchangeable fraction was 49.8 ± 14 and 22.7 ± 7.5%, respectively. The use of acetic acid in this step will dissolve carbonates, such as $CaCO_3$ and $MgCO_3$ contributing to the high concentration of Ca and Mg in this fraction. The low proportion of Cr released in the exchangeable step compared to Ca and Mg is likely to be due to the weathering of COPR to form secondary minerals, such as Fe/Cr oxides, and also the incorporation of any leached Cr into OM. Chromium(VI) held in the COPR minerals is easily leached and therefore would be expected to be seen in Step 1 of the BCR sequential extraction along with Ca and Mg (Geelhoed *et al.*, 2003). In the Polmadie soils the mean Ca concentration of 1.56 ± 0.32% was elevated compared to the mean Glasgow soil concentrations of 0.82%. Elevated concentrations of Ca have been found in Glasgow soils around the vicinity of the Cr chemical works due to the use of lime in the extraction process.

As mentioned, there was a low proportion of Cr associated with the residual phase, with 5.64 ± 4.4 and 3.87 ± 3.6% of Cr occurring in the residual phase of the soils and sediments, respectively. Elements released in the residual phase are usually associated with silicate minerals which are resistant to weathering and therefore are likely to persist in the soils (Davidson *et al.*, 1998). The absolute concentration of Cr in the residual phase was 89.5 ± 58 and 108 ± 38 mg kg^{-1} for the banking soils and sediments. These values were not too dissimilar to the baseline Cr concentrations in Glasgow top soils which had a median value of 108 mg kg^{-1} (Fordyce, 2012). The persistence of chromite ($FeCrO_3$) from COPR is to be expected in the residual phase as it is a stable mineral which is resistant to chemical weathering. This may provide a source for of Cr extracted in the residual step of the sequential extraction, however, due to the similar concentration of Cr in the residual phase to the baseline concentration of Cr in Glasgow soils, the contribution of chromite to the overall Cr concentrations in the Polmadie banking soils and sediments is not known (Elzinga and Cirmo, 2010).

4.8 Summary

4.8.1 Concentrations of chromium in the Polmadie Burn waters, banking soils and sediments

The Polmadie Burn water-soil-sediment system contains elevated concentrations of Cr compared to baseline concentrations. Chromium(VI) concentrations of <4180 µg L^{-1} were found in the Polmadie Burn waters which exceeded the EQS value of 3.4 µg L^{-1} for freshwaters by 3 orders of magnitude. Total Cr concentrations in the banking soil and sediment were <6310 and <14900 mg kg^{-1}, respectively. This was much larger than the mean Cr concentrations found in Scottish soils and sediments of 44.7 and 125 mg kg^{-1}, respectively. Concentrations of Cr(VI) of <2190 and <1200 mg kg^{-1} were found in the banking soils and sediments respectively. However, Cr was found in low concentrations in the soil and sediment porewaters, <115 and <25 µg L^{-1}, respectively, and was exclusively Cr(III).

The highly reducing nature of the sediment was evident by the large concentrations of Fe(II) present in the sediment porewater. This will promote the reduction of Cr(VI) leading to a short half-life of Cr(VI) in the porewater and lowering the concentration of Cr(VI) in the sediment. Evidence for this process was provided by the significantly lower percent of total Cr present as Cr(VI) in the sediments (5.17 ± 1.3%) than banking soils (18.9 ± 15%). Reduction of Cr(VI) in the banking soils will be by solid OM due to the absence of Fe(II). At circumneutral pH values found in the soils, the reduction of Cr(VI) by DOM will also be a slow process which is not likely to significantly contribute to the reduction of Cr(VI).

4.8.2 Temporal trends in the concentrations of chromium in the Polmadie Burn

The long-term monitoring data provided by SEPA showed that a large proportion of Cr in the Polmadie Burn surface water is in the dissolved fraction. The dissolved Cr concentrations were significantly positively correlated with the dissolved Ca, Mg and Al concentrations. The burn drains an area which is known to contain COPR which contains these four elements in large concentrations, so this confirms that dissolution of COPR minerals is a major source of Cr in the Polmadie Burn. From the results of Cr speciation in the Polmadie Burn in the current project it was concluded that Cr(VI) was likely to be the main species present in the Polmadie Burn in the data provided by SEPA, however Cr speciation was not determined. The Cr concentrations also had a significant positive correlation with pH which is hypothesised to be related to low adsorption of Cr(VI) at pH 8 leading to the increased adsorption, and therefore slight reduction in Cr(VI) concentrations as the pH decreases.

Between 1990 and 2000 Cr concentrations in the Polmadie Burn appeared to decrease. The mean pre-2000 total Cr concentration was 3.57 ± 2.8 mg L^{-1} and the post-2000 mean Cr concentration was 2.38 ± 1.4 mg L^{-1}. Chromium concentrations over the period of 2010-2017 did not show any decrease and the Cr remediation works carried out at a nearby site in 2013 has not appeared to influence the Cr concentrations in the stream, although it is not known if the remediated area drained into the Polmadie Burn.

4.8.3 Evidence of COPR in the Polmadie Burn waters, banking soils and sediments

Due to the high concentration of dissolved Cr(VI) in the Polmadie Burn and its correlation with Ca, Mg and Al it is most likely the source of Cr is due to the dissolution of COPR material in the stream's catchment area. The slow dissolution kinetics of Cr(VI) from COPR and the large amount of COPR in the area suggests it is likely that the high streamwater Cr concentrations will persist.

From the SEM-EDS data the small discrete grains containing Ca, Mg, S and O indicate that detrital COPR material has been transported into the sediment. The input of COPR material into the stream is likely to be the reason for the large peak of Cr at 6-7 cm depth in sediment core 2. There was evidence of Cr in surface coatings of quartz and feldspar minerals which indicate *in situ* formation of Cr/Fe precipitates. In the soils, no direct evidence of COPR minerals was found, however there was a significant positive correlation between soil Cr concentrations with Ca and Mg, although these elements were extracted in different fractions of BCR sequential extraction. There was also a significant positive correlation between Cr and OM concentrations in the banking soils. This suggests that the COPR has been weathered and Cr(VI) associated with the material has been leached and has formed secondary minerals and/or been reduced then incorporated into OM.

4.8.4 The associations of chromium in the banking soil and sediment and the impact on its long-term fate

Associations of Cr were investigated using BCR sequential extraction which showed that the majority of Cr, 63 ± 9.5 and 52 ± 5%, is associated with OM in the soils and sediments, respectively. This was confirmed by the gel electrophoresis which confirmed a significant positive correlation between OM and Cr. The other major phase was Fe hydroxides, which contained 25.0 ± 8.5 and 38.8 ± 3.9% of Cr in soils and sediments, respectively. Little Cr was present in the exchangeable and residual phases, again suggesting that COPR present in the material has been weathered releasing Cr which has been incorporated into Fe/Cr hydroxides, sorbed to Fe/Mn surfaces or incorporated into OM.

The formation of mixed Fe/Cr hydroxides, as hypothesised to be happening in the sediments, results in the formation of stable insoluble compounds resulting in the immobilisation of Cr. Literature suggests that formation Cr-OM complexes are stable but the lability of the OM can influence the mobility of Cr bound to OM. The next chapter will investigate the leachable concentrations of Cr from banking soils and sediments to investigate its mobility.

5 Mobility of chromium in the Polmadie Burn banking soils and bottom sediments under changing environmental conditions

5.1 Overview and chapter structure

Chapter 3 demonstrated that: (i) both banking soils and bottom sediments contained elevated concentrations not only of total Cr but also Cr(VI); and (ii) in both banking soils and bottom sediments, a large proportion of Cr was associated with OM and most of the remainder was associated with Fe/Mn oxides. There were, however, distinct differences between the soil and sedimentary environments, namely: (i) OM content, which was approximately a factor of 2 higher in soils; (ii) pH which was about 0.5 units higher in the sediment; (iii) redox conditions, which were typically strongly reducing in the sediments but oxidising in the soils. These differences may mean that the soils and sediments respond differently to environmental changes, e.g. prolonged dry periods followed by intense wet periods. Such scenarios are likely to be of wide global relevance over coming decades due to climate change. However, these may have imminent local significance for the behaviour of Cr at the Polmadie Burn site because of the proposed diversion of waters as part of two schemes:

(i) the culverting and diversion of the West Burn to avoid the Cr-waste contaminated area. This scheme is in progress but has not been switched on yet (SEPA Pers. comm.).

(ii) a further scheme that is being considered is the realignment of the Richmond Park Combined Sewer Overflow (CSO) which joins the Polmadie burn at the north end of the culverted section. The plan is to screen and reroute the discharge so that it directly discharges into the Clyde which will reduce the water flow in the Polmadie Burn (SEPA Pers. Comm.,).

Both the West Burn and the Richmond Park CSO are connected to the Polmadie Burn and so diversion of water through these new schemes will reduce water flow and lead to increased exposure of banking soils and bottom sediments, especially in warmer summer periods in the Polmadie Burn. There are concerns about the impact of the lower flow and increased sediment exposure to oxygenated conditions on Cr mobility.

This chapter considers these issues and will start with a focused review of the literature on impacts of wetting and drying cycles on Cr speciation and mobility in contrasting environmental settings. Thereafter, the results for a series of laboratory experiments investigating the changes in leachable Cr concentrations as banking soil and bottom sediments dry over different time periods will be presented. This will be followed by discussion on the likely impacts of wet/dry cycles on the release of Cr(VI) from Polmadie Burn banking soils and bottom sediments to the burn waters which flow into the River Clyde. Following the discussion on drying, the sorption of Cr to soil during periods of flooding during heavy periods of rain, should the proposed water diversion schemes not go ahead, is considered by simulating the loading of Cr(VI) to soils through a series of batch experiments.

5.2 Review of literature on impacts of wet/dry cycles on chromium speciation and mobility in soils and sediments

There is a growing body of evidence which demonstrates that wetting and drying cycles can alter the speciation of many redox-sensitive elements including Cr in soils and sediments. In rice paddy soils it was found that when the soil was kept waterlogged the soil Cr(VI) porewater concentrations decreased by between 10 and 47% over the duration of the 120 day study period (Xiao *et al.*, 2015). In the same study, however, Cr(VI) porewater concentrations fluctuated with changes in soil redox potential, and wet/dry cycles lead to an overall increase in Cr(VI) concentrations, also attributed to changing redox potential. This study did not rewet the constantly (120 day) waterlogged soils and did not offer any mechanisms to account for the changes in speciation of Cr.

Several studies used laboratory experiments to investigate the leaching of potentially toxic elements from dredged sediments placed in a highly oxidising environment. These reported an increase in the leachability of potentially toxic elements, including Cr (Cappuyns *et al.*, 2006, Stephens *et al.*, 2001). Release of Cr from sediments was strongly associated with the pH of the leachate. As leachate pH dropped from slightly alkaline (pH 7.8) to acidic (pH 3.5) over the drying period the concentration of Cr released from the sediment increased by three to four orders of magnitude. This is probably due to the release of Cr(III) which becomes soluble at pH<4.5 (Rai *et al.*, 1989). Stephens *et al.* (2001) observed a change in the sediment associations of elements as the sediments dried out over time. This was postulated to be due to the dissolution of metal sulfides as the sediments dry and the Eh increases, leading to the release of metals into solution as the sulfides oxidise, and then rapid re-adsorption of the metals by the sediment OM. Upon further drying, changes in OM structure release the metals bound to them leading to the initial decrease and then increase in metals released from sediment as drying time increases (Stephens *et al.*, 2001). Changes in pH due to the oxidation of sulfides appears to be an important control of Cr solubility in sediments due to the release of Cr(III) which become soluble at pH<4.5 (Rai *et al.*, 1989).

Soils typically have a higher redox potential than sediments found in slow moving waters, such as canals. Thus, Cr(VI) is likely to be more stable in soils compared to the sediments. Similarly, to sediments, however, the speciation of Cr leached from soil has been found to be pH-dependent. A study by Geelhoed *et al.* (2002) showed that at pH<4.5 Cr leached was in the Cr(III) oxidation state but as the pH increases above 4.5, Cr leached is almost exclusively found as Cr(VI) (Geelhoed *et al.*, 2002). This change in Cr speciation with pH is due to the reduction of Fe(III) to Fe(II) at low pH and the faster rate of Cr(VI) reduction by OM and Fe(II) at low pH. The concentration of Cr leached from soil has also been shown to be influenced by OM, a known reducer of Cr(VI). Weng *et al.* observed a 5-fold increase in Cr concentrations leached from soils from which the OM had been removed prior to leaching compared to the original soil (Weng *et al.*, 1994). Studies have shown that the addition of OM amendments to soils is effective in reducing the concentrations of leachable Cr (Banks *et al.*, 2006). This was attributed to the reduction of Cr(VI) and its subsequent immobilisation by precipitation or adsorption by OM. In summary, for soils it appears that OM concentration and soil pH are the most important factors which control the leachability of Cr.

From the review of the literature, it is clear that the release of Cr from soils and sediments depends on the source of Cr, pH, OM content along with the presence of Mn and Fe. Taking account of the contrasting environments of the Polmadie banking soils and bottom sediments the hypothesised changes in Cr mobility and speciation upon drying and rewetting were:

H_1: The release of Cr from banking soils will be greater than that released from bottom sediments.

H_2: The speciation of Cr released from the banking soils will be dominated by Cr(VI) species whilst that for Cr released from the bottom sediments will be dominated by Cr(III) species.

H_3: For the bottom sediments, if released sulphate concentrations are high enough to decrease the pH below pH 5, then the concentration of Cr(III) released will increase significantly.

5.3 Column experiments to investigate the leachability of chromium from banking soils and sediments which have been dried for different time periods

As discussed in the section above, as soils and sediments dry out, changes in their chemical and physical properties can lead to the release of elements which were previously stable within the solid phase. As demonstrated in Chapter 3, the concentration of COPR-derived Cr is greatly elevated in the banking soils and bottom sediments taken from multiple locations along the Polmadie Burn, and so there is the potential for environmentally significant amounts of Cr to become remobilised during drying. To investigate the extent of Cr remobilisation as banking soil and bottom sediment dry out, column experiments were designed to investigate Cr release upon rewetting after selected drying periods. This section gives a brief outline of the sample treatment and the column design before going on to describe and discuss the results from these column experiments.

5.3.1 Overview of sampling and sample treatment

The full experimental design for the column leaching experiments is described in detail in Section 3.4.1 but a brief overview is given below. Approximately 5 kg of banking soil was collected on the 10th April 2016 and approximately 5 kg of sediment was collected on 12th September 2016. The sampling locations of the soils and sediments are shown in Figure 3-8. Once transported back to the laboratory the soil/sediment was screened through a 5 mm sieve to homogenise the material and to remove components, such as large stones, plant material and rags (that are commonly found in this stretch of urban sediment). The sieved material was left to air dry for a set period (0, 2 or 4 weeks). These drying time periods were relevant to the local conditions based on rainfall data for the West of Scotland which showed that between 2016 and 2017 there were three instances of between 8-14 days with no rainfall and one where there was a 22-28 day period with only 0.2 cm of rain. After each time period, a sub-sample was removed from the bulk material and sieved through a 2 mm sieve to further homogenise the sub-sample. The columns were packed to a depth of 20 cm with either 2 mm sieved fresh soil or sediment or with 2 mm sieved soil or sediment which had been dried for a period of either 2 weeks or 4 weeks. After packing, the columns were left for 16 h to settle under gravity before rewetting with one column volume (120 mL) of one of two different eluents, de-ionised water (DIW) or synthetic rainwater (SRW). The pH of these eluents was 4.5 and 5.0, respectively.

The extent of replication and elution conditions used in this experiment is summarised in Table 5-1 and an example of the packed columns is shown in Figure 5-1.

Table 5-1: Summary of the experimental design for column leaching experiments for Polmadie Burn banking soils and bottom sediments

Drying Period	Column Settling Period	Matrix	Eluent		Rewetting Volume/Time	Elution Volume
			DIW	SRW		
0 weeks	16 h under gravity	Soil	2 columns	2 columns	>120 mL (>1 column volume) / 1 h	8 x 30 mL = 240 mL ~6 weeks Glasgow rain *
		Sediment	3 columns	3 columns		
2 weeks		Soil	3 columns	3 columns		
		Sediment				
4 weeks		Soil	3 columns	3 columns		
		Sediment				

* typically, monthly rainfall in Glasgow is 93 mm; 1 mm rainfall = 1 mL cm^{-2}, so 93 mm = 9.3 mL cm^{-2}; column surface area = 19.6 cm^{2} and so 9.3 cm equates to ~180 mL eluent

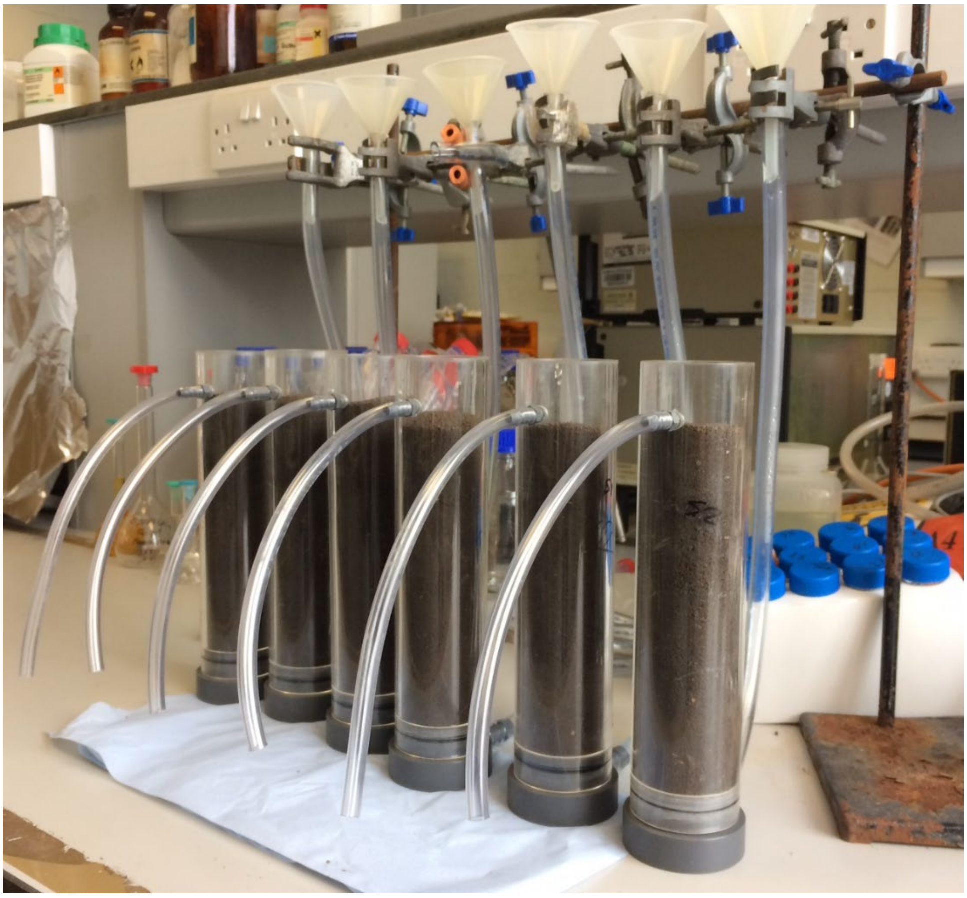

Figure 5-1: Filled columns prior to leaching

5.3.2 Solid phase elemental concentration

The concentration of Cr in the leaching column banking soil and bottom sediment was 2050 ± 31 and 3290 ± 66 mg kg^{-1}, respectively, which was typical of the concentrations reported in Chapter 4. The other element concentrations were also similar to those found in the Polmadie banking soil and bottom sediment in Section 4.3.4. Again, the organic matter content of the banking soils was greater than that of the bottom sediment. In this case, the OM content was ~six fold greater in the banking soils (Table 5-2).

Table 5-2: Mean ± standard deviation of the solid phase concentrations of the soil and sediment used for batch experiments

	Unit	Soil	Sediment
Cr	mg kg^{-1}	2050 ± 31	3290 ± 66
Fe	% w/w	3.39 ± 0.021	2.43 ± 0.006
Mn	mg kg^{-1}	1540 ± 4.7	636 ± 12
Al	% w/w	3.45 ± 0.11	1.08 ± 0.45
Ca	% w/w	1.96 ± 0.0003	1.92 ± 0.14
Mg	mg kg^{-1}	7880 ± 220	4470 ± 1600
S	mg kg^{-1}	2260 ± 26	3150 ± 99
OM	% w/w	27.0 ± 0.50	4.38 ± 0.32

5.3.3 Results for the column leaching experiments for Polmadie Burn banking soils and bottom sediments

For each parameter, the initial consideration will be identification and explanation of changes in leachate composition with increasing elution volume and in the following section, the parameter values, except for pH, were converted to mass of element leached per kg dry soil/sediment. These mass-normalised values will then be used to identify key differences between the banking soil and bottom sediment and to identify statistically significant changes that have occurred with increased drying time before the rewetting and column leaching took place.

5.3.3.1 Leachate pH in 30 mL fractions collected from soil and sediment columns which had been rewetted and leached after different drying periods.

The first point to note is that the pH of the eluents was ≥2 units higher than that of the initial leachate solutions and this is in line with the typical pH of soil and sediment suspensions of between pH 6.5 to 7.5. Moreover, there was generally good agreement between the pH in DIW and SRW leachates across the entire elution volume for both soils and sediments. Initially (Week 0), the pH of the soil leachates remained approximately constant as leaching progressed (~7-7.5) but after two weeks drying, the pH of the leachates from the rewetted soils increased from ~7.2 to ~7.7 and after four weeks of drying, a similar pattern was observed with even lower initial values for the SRW leachate (~6.7) increasing to 7.7 by the end of column elution (Figure 5-2). For the sediments, the values for the leachates only showed this trend of increasing pH with increasing elution volume after 4 weeks of drying prior to rewetting and elution. Here the leachate pH increased from 6.2 to 6.7 over the course of elution (Figure 5-2).

A potential reason for these initially lower pH values could be that drying of the soil/sediment increases the acidity of surfaces through processes such as oxidation of Fe(II) to Fe(III) (Erich and Hoskins, 2011):

$$Fe^{2+} + 3H_2O \rightleftharpoons Fe(OH)_3^0 + 3H^+ + e^- \qquad \text{Equation 5.1}$$

Since such acidity may then influence the solubility of major cations and anions (Erich and Hoskins, 2011), the resulting leachate pH is impossible to predict. A further explanation of the difference between the pH results for banking soil and bottom sediment is that the sediments were originally under significantly more reducing conditions and so it is not surprising that the effect on pH is evident only after the 4-week drying period.

5.3.3.2 Mean pH in soil and sediment column leachates

Since the “during-leaching” differences, i.e. between the 8 x 30 mL aliquots, were often smaller than the “between-drying time-period” differences, a mean leachate value and standard deviation was calculated (Figure 5-3 and Figure 5-4). In addition, since the results for DIW and SRW were not statistically different (Man-Whitney-U test, $p = 0.551$), the results for all columns for a given time period were combined. Thus, there were four mean leachate concentrations for each of the banking soil columns for Week 0 and 6 values for each banking soils for Week 2 and Week 4 and for bottom sediment in Week 0, Week 2 and Week 4 (Table 5-1). These were then combined to give the overall mean ± 1 standard deviation of these values which are described below. The same approach will be taken for the other parameters in the sections which follow.

The mean soil column leachate pH at time zero was 7.34 ± 0.12 which increased to 7.67 ± 0.17 after Week 2 of drying. The soil column leachate in Week 4 of drying then decreased to 7.37 ± 0.28. The initial sediment column leachate at Week 0 was 7.80 ± 0.11 was significantly higher than that for the soil column leachates (Mann-Whitney test, $p<0.01$). After the two-week drying period, however, unlike soils the sediment pH decreased to 7.68 ± 0.21 which was similar to the soil pH at Week 2. After the four-week drying period the sediment column leachate pH, like the soil pH, decreased to 7.29 ± 0.27 (Figure 5-5).

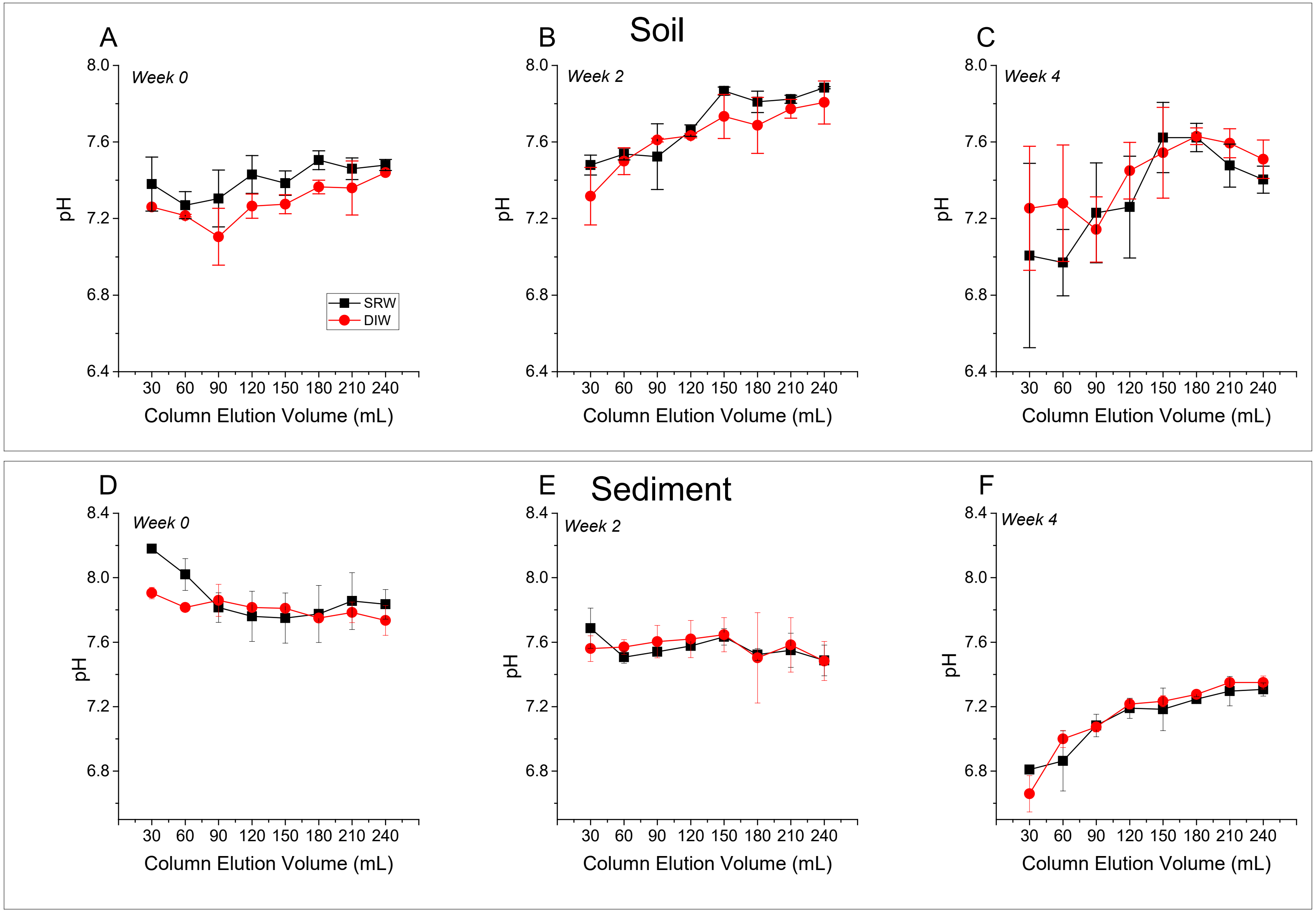

Figure 5-2: Mean pH values (± 1 s.d.; n =3 except for week 0 soil) of soil and sediment column leachate fractions

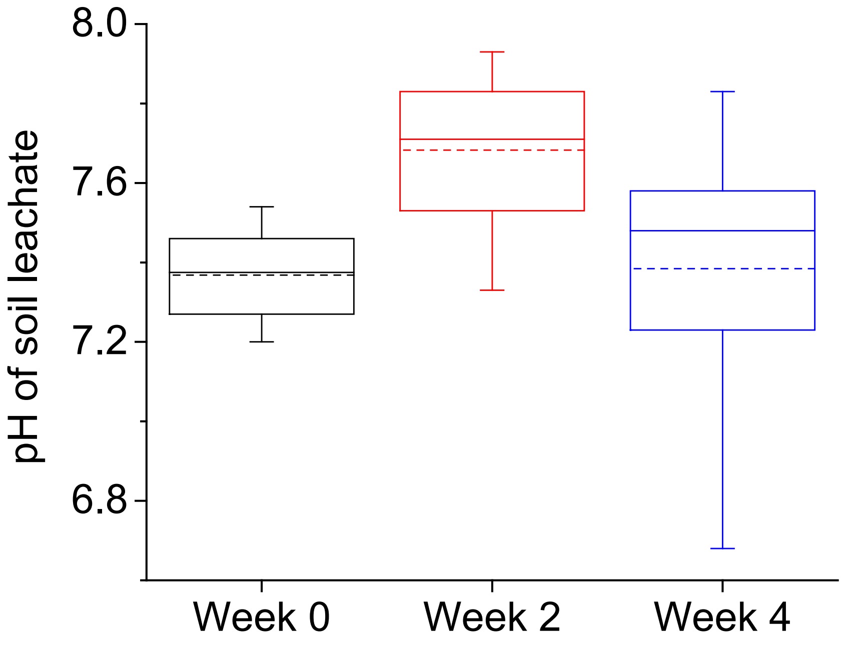

Figure 5-3: Range of pH of column leachate from soil column experiments. The box shows the 25th (lower line), 50th (middle line) and 75th (upper line) quartiles with the mean as a broken line. The lower and upper whiskers show the range of the values.

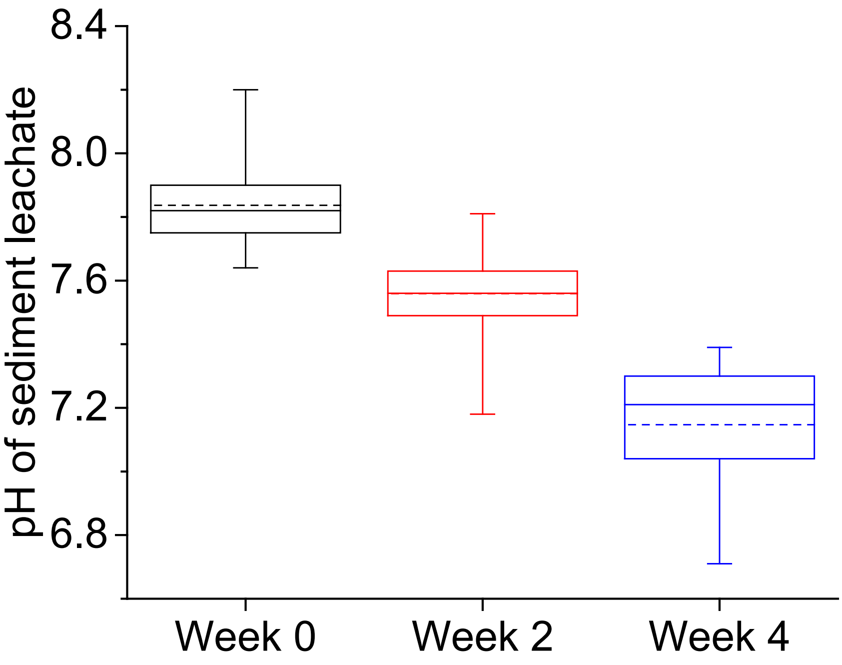

Figure 5-4: Range of pH of column leachate from sediment column experiments. The box shows the 25th (lower line), 50th (middle line) and 75th (upper line) quartiles with the mean as a broken line. The lower and upper whiskers show the range of the values.

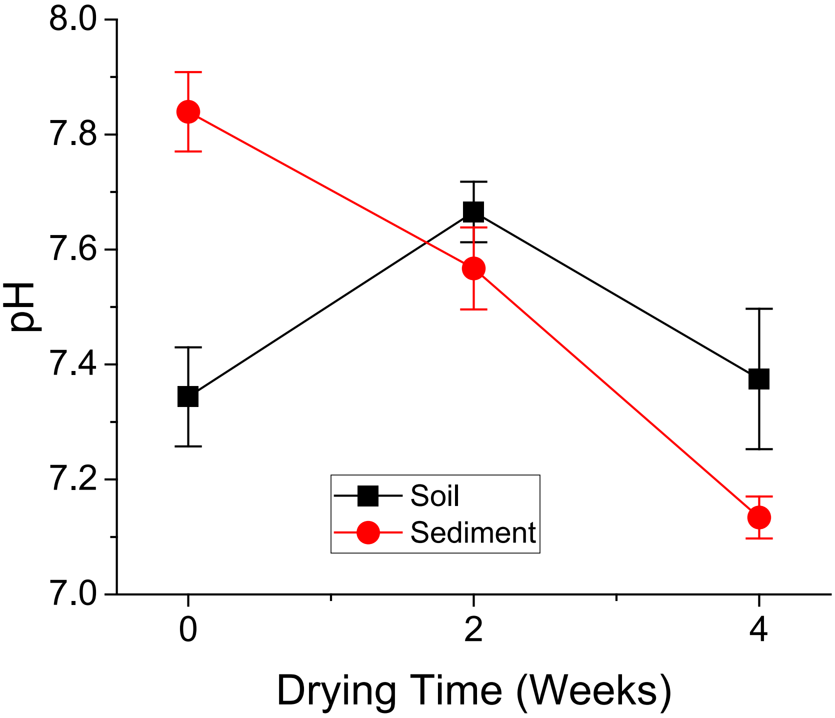

Figure 5-5: Mean leachate pH in soil and sediment columns ± 1 standard deviation

5.3.3.3 Leachate chromium concentrations in 30 mL fractions *columns which had been rewetted and leached after different drying periods*

In this section, total leachate Cr refers to the concentration measured by ICP-OES in 0.45 µm filtered column eluates so it comprises Cr(III) and Cr(VI) which are indistinguishable by this method. For the soil, the concentration of total leachate Cr remained almost constant as elution progressed whilst for the sediment, the total leachate Cr concentration either decreased to a constant level or remained the same (Figure 5-6). A portion of each 30 mL leachate fraction was subjected to Cr(VI) analysis following DPC complexation (see Section 3.7.2.2) and, as might be expected, based on the results presented in Chapter 4, Cr(VI) was only detected in the leachates from the soil.

For the Week 0 and Week 2 columns, the %Cr(VI) (relative to total leachate Cr) remained relatively constant as elution progressed. However, for the Week 4 columns, the % values were lower at the beginning of elution and there as a small increase from 17% to 26% for the synthetic rainwater leachate and from 28 to 41% for the DIW leachate (Figure 5-7). The final values were similar to those observed for the Week 2 columns. The concentrations of Cr(III) (= Cr total – Cr(VI)) remain near-constant as elution progresses and so the reasons why Cr(VI) might be released more slowly need to be explored further. At this stage, however, there was no obvious relationship with pH and so other factors will be considered.

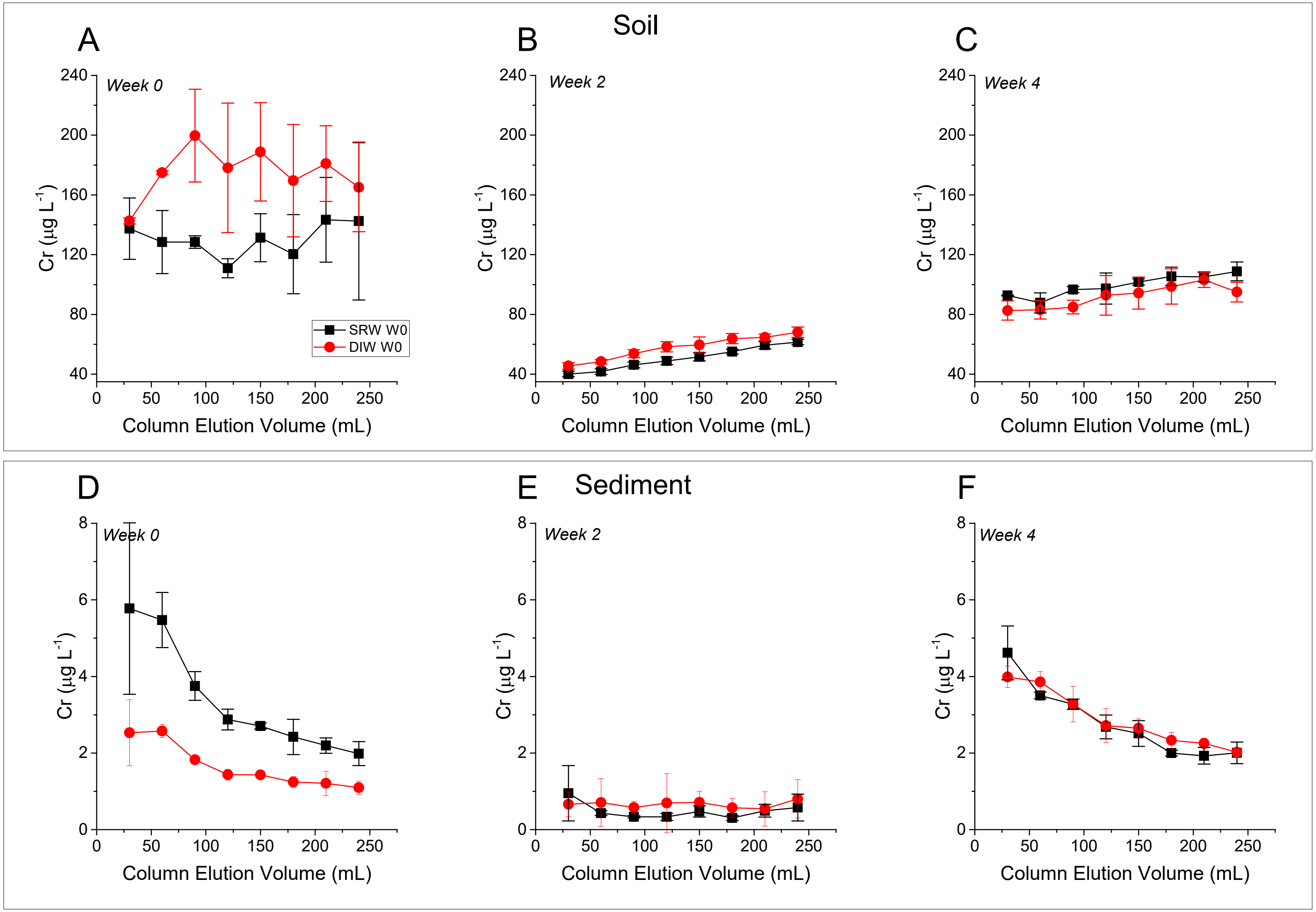

Figure 5-6: Concentrations of total Cr in soil and sediment column leachate fractions

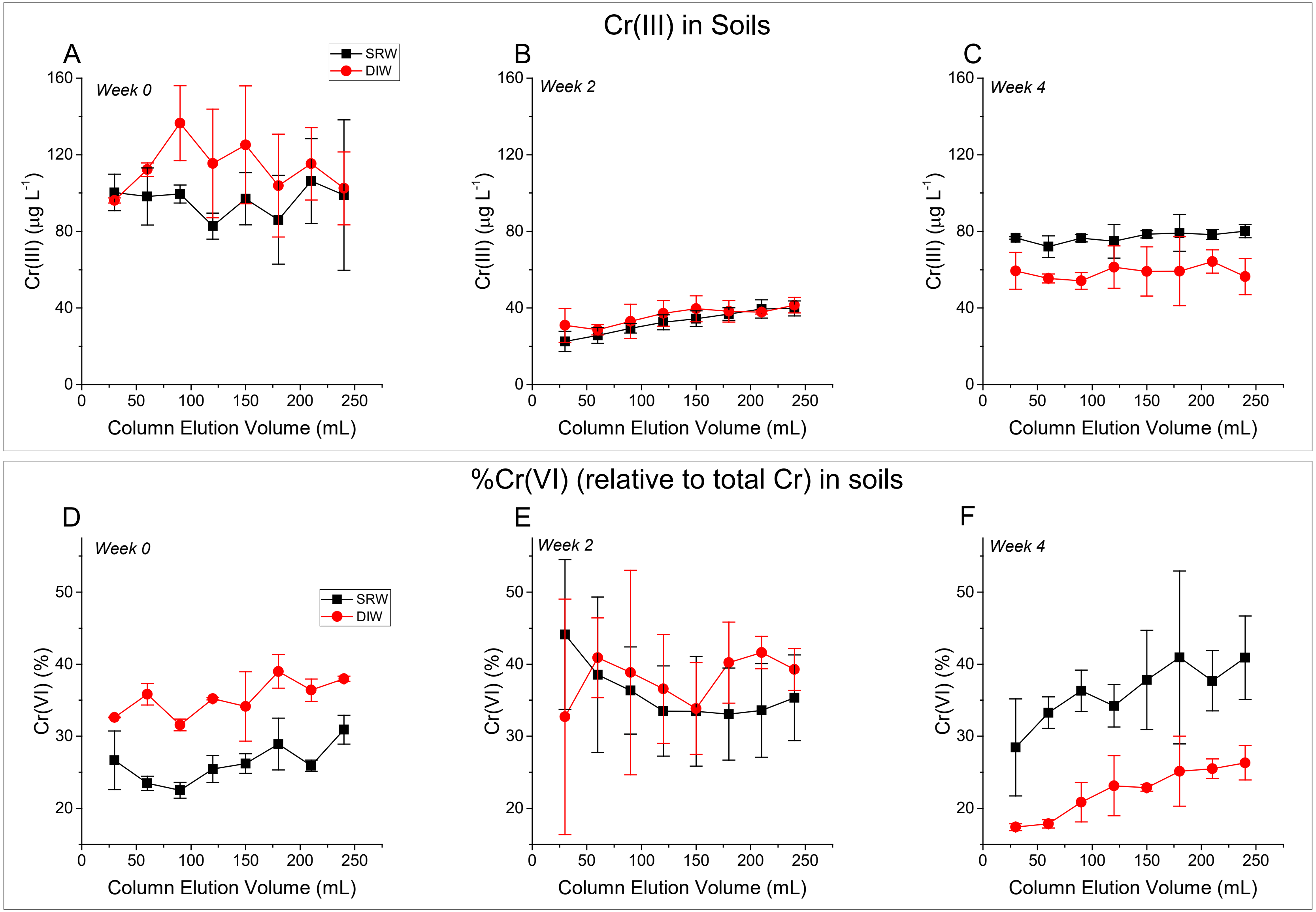

Figure 5-7:Cr(III) concentrations and %Cr(VI) (relative to total Cr) in soil column leachate

5.3.3.4 Mean chromium total for sediments and mean chromium(III) and chromium(VI) concentrations for banking soils

There was no significant difference between the total Cr concentration data for the synthetic rain water and the deionised water leachate concentrations (Mann-Whitney, U=287, p=0.73) and so, for each matrix, the data for all columns were combined (4 columns for Week 0 and 6 columns for each of weeks 2 and 4). Before combining the data, the concentrations were converted to mass of element leached per kg dry weight of soil/sediment. The errors were calculated as described in section 4.3.2.2 above.

The amount of total Cr leached from both the soil and the sediment was lowest after 2 weeks of drying time (Figure 5-8A). The mean mass of Cr leached from soil were 268 ± 64 (n=4), 94.2 ± 17 (n=6) and 183 ± 18 (n=6) µg kg^{-1} after drying times of 0, 2 and 4 weeks, respectively, whilst those from the sediment were much lower, at 1.86 ± 0.76 (n=4), 0.340 ± 0.17 (n=6) and 2.47 ± 0.22 (n=6) µg kg^{-1} for the same drying times. No Cr(VI) was leached from the sediments but the mean mass of Cr(VI) leached from the soil were 47.9 ± 5.3 (n=4), 20.0 ± 5.3 (n=6) and 27.8 ± 8.0 (n=6) µg kg^{-1} after the drying times of 0, 2 and 4 weeks, respectively (Figure 5-8B).

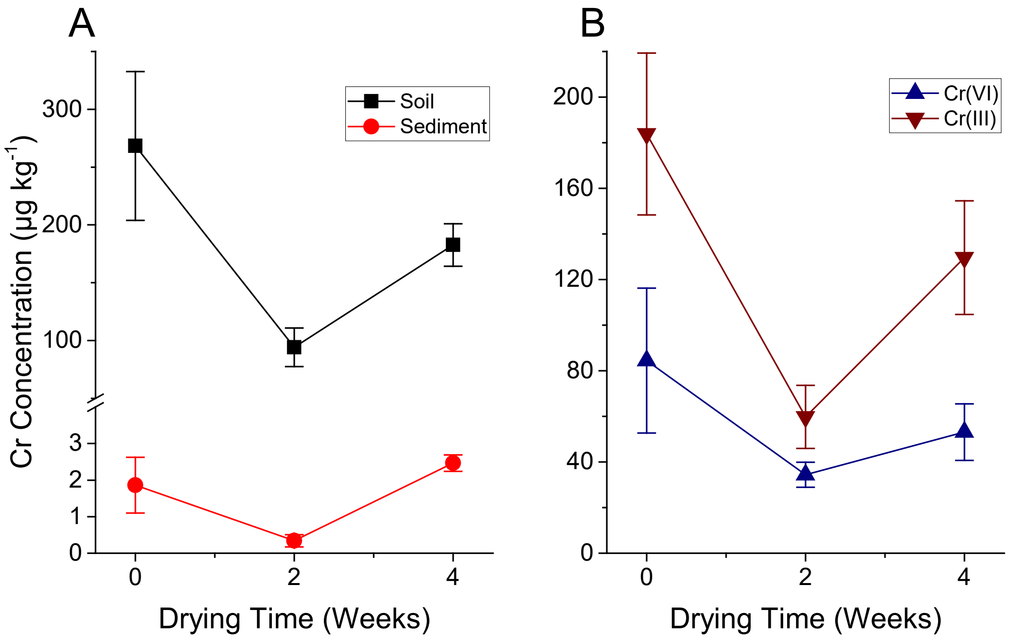

Figure 5-8: (A) Mean ± 1 standard deviation of Cr mass leached from soil and sediment columns and (B) mean ± 1 standard deviation of Cr(III) and Cr(VI) mass leached from in soil columns.

5.3.3.5 Iron, manganese and aluminium concentrations in 30 mL leachates from soil and sediment columns which had been rewetted and leached after different drying periods

In the Week 0 columns, the soil leachate Fe concentrations were in the range ~1600-3000 µg L^{-1} (equivalent to 28.6-53.6 µM). The concentrations were typically higher and increased more rapidly when DIW was used to leach the columns. For the sediment columns, the reverse trend was true and SRW released more Fe compared with DIW (Figure 5-9). The concentrations were typically higher and increased more rapidly as elution progressed when DIW was used to leach the columns. The trend was also different with decreasing Fe concentrations towards the end of the column elution. As for the Week 0 columns, the Fe concentrations leached from the Week 2 soil columns increased as elution progressed whilst those for the sediment columns decreased. There was little difference between the results obtained using the two leaching solutions, DIW and SRW. For the Week 4 soil columns, there was a very slight increase in leachate Fe concentrations as elution progressed but almost no change for the sediment columns. There was very good agreement between the DIW and SRW leachate data for both soil and sediment columns in the Week 4 column.

There was no obvious relation between total Cr or %Cr(VI) and Fe concentration in leachates as between Weeks 0, 2 and 4. Although both %Cr(VI) and Fe concentration did increase slightly for the Week 4 soil columns, there was a more substantial increase with increasing elution volume for the Week 2 columns but this was not accompanied by an increase in %Cr(VI). For the Week 4 data, if a relationship between %Cr(VI) and Fe were to be invoked, it would most likely be caused by dissolution of Fe phases to which Cr(VI) was adsorbed rather than by an oxidation (Cr(III)/Cr(VI))/reduction (Fe(III)/Fe(II)) mechanism since only Mn(IV) has been shown to be capable of Cr(III) oxidation in natural systems (Fandeur *et al.*, 2009).

The trends for Mn concentration in soil and sediment leachates appear quite similar to those described above for Fe (Figure 5-10). The relationship between Mn and Fe is quite different for the soil compared with the sediment leachates. For the soil, there was no single relationship to describe the Mn and Fe data over all time periods whilst for the sediment, there was a significant strong positive correlation (Spearman's rank correlation, $p<0.01$) (Figure 5-12).

For the soil columns, leachate Al concentrations were very closely related to those of Fe over all time periods (Figure 5-11). Taken together with the Mn data, this suggests that a similar mechanism of release is involved in the release of Fe and Al but there may be a different process or processes involved in the release of Mn from the soil. This will be explored further in the section which follows.

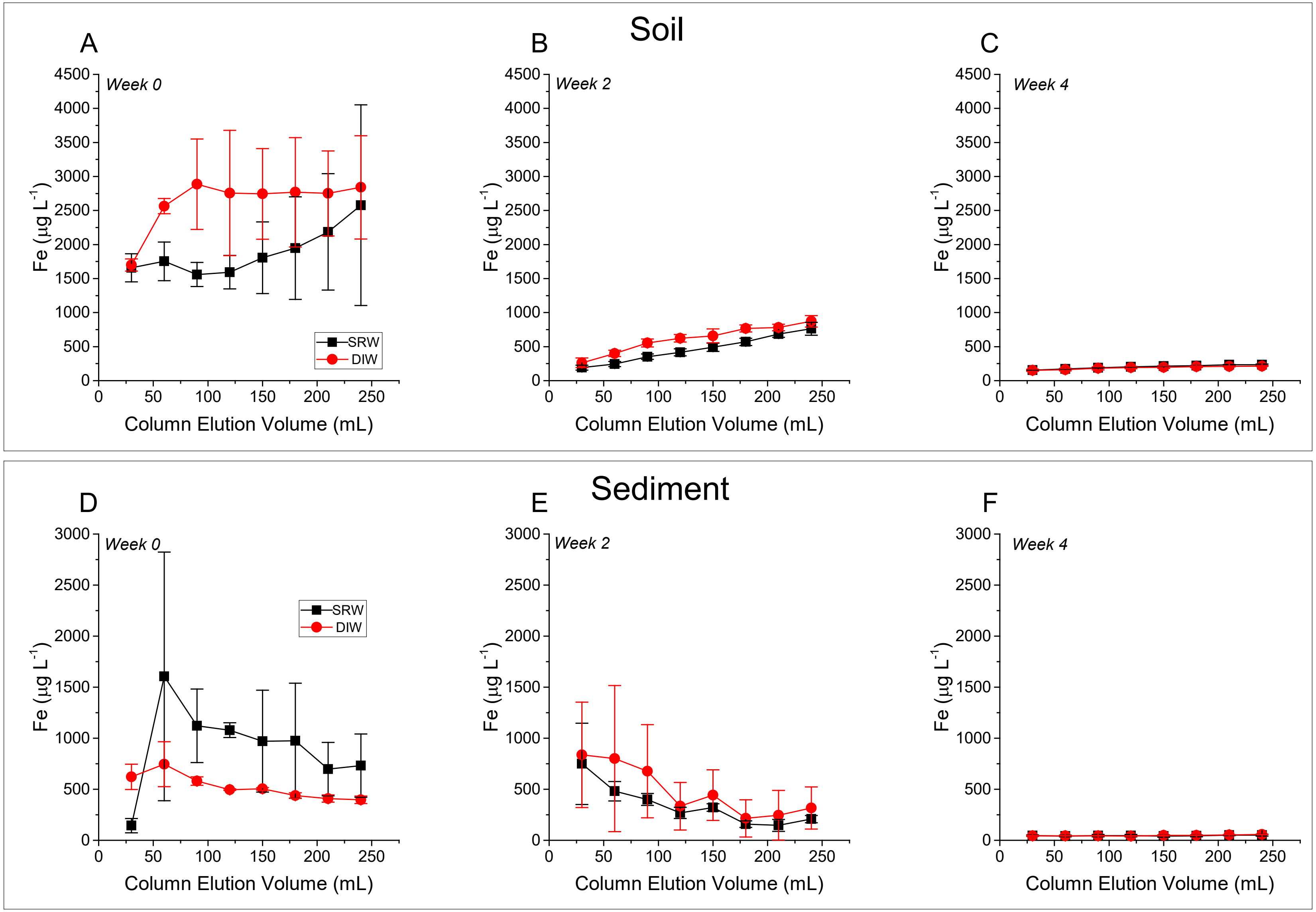

Figure 5-9: Mean ± 1 standard deviation of Fe concentrations in soil and sediment leachate fractions

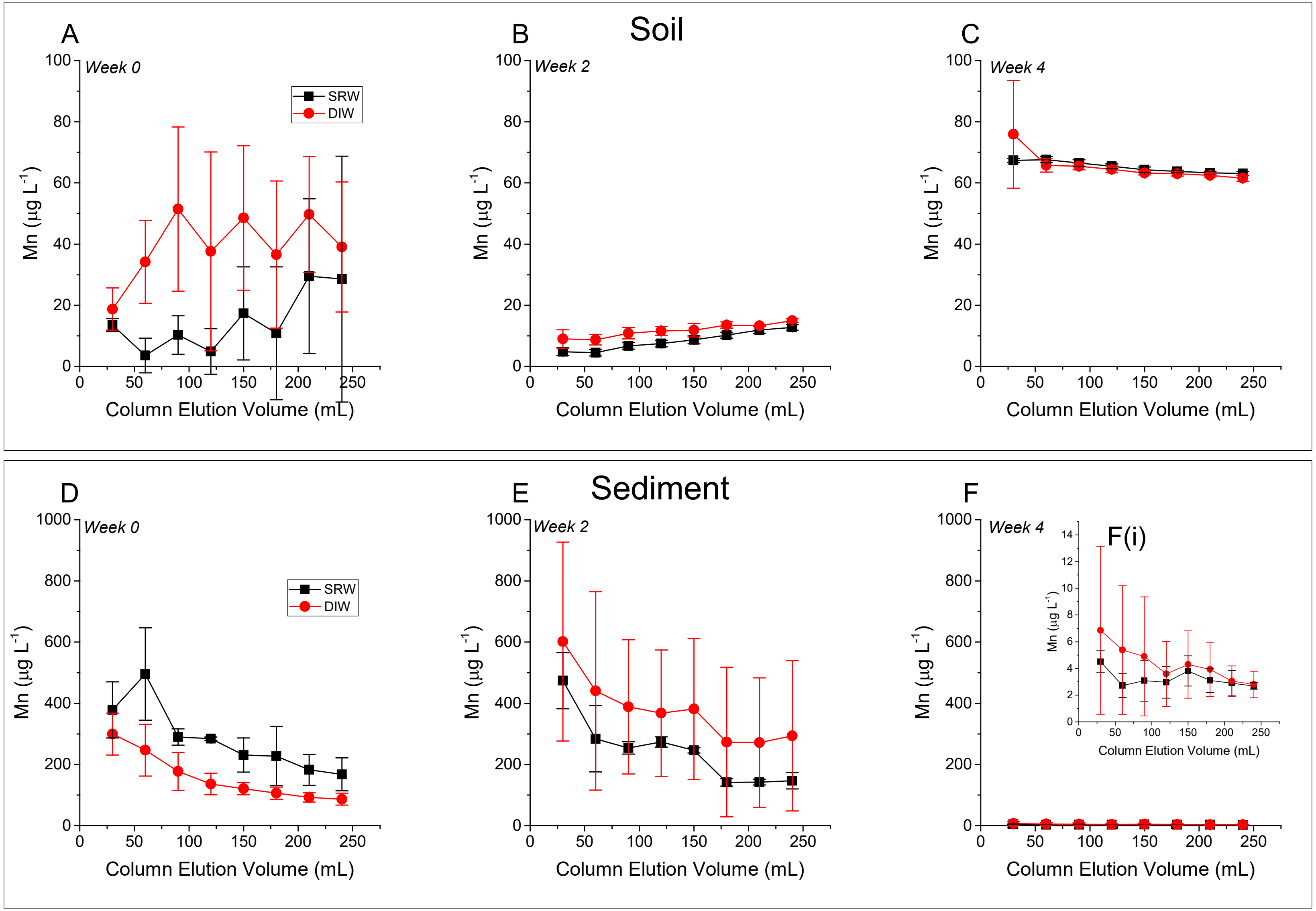

Figure 5-10: Mean ± 1 standard deviation of Mn concentrations in soil and sediment leachate fractions

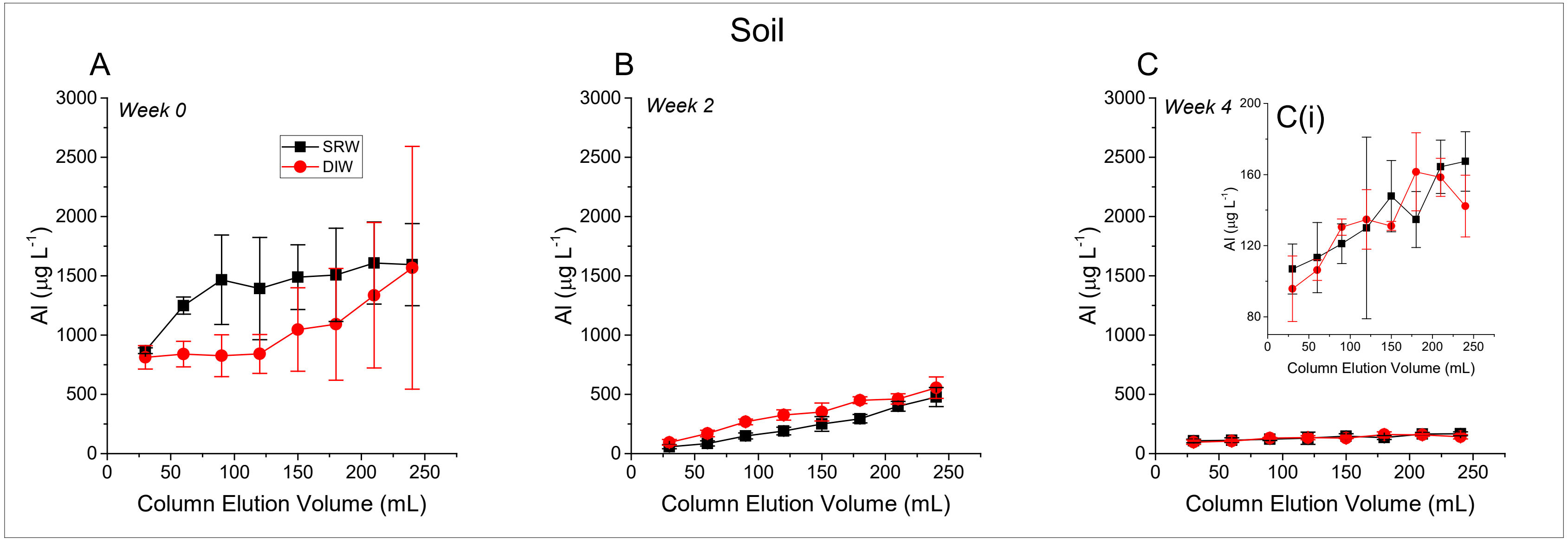

Figure 5-11: Mean ± 1 standard deviation of Al concentrations in soil leachate fractions. Aluminium was not measured in the sediment leachate.

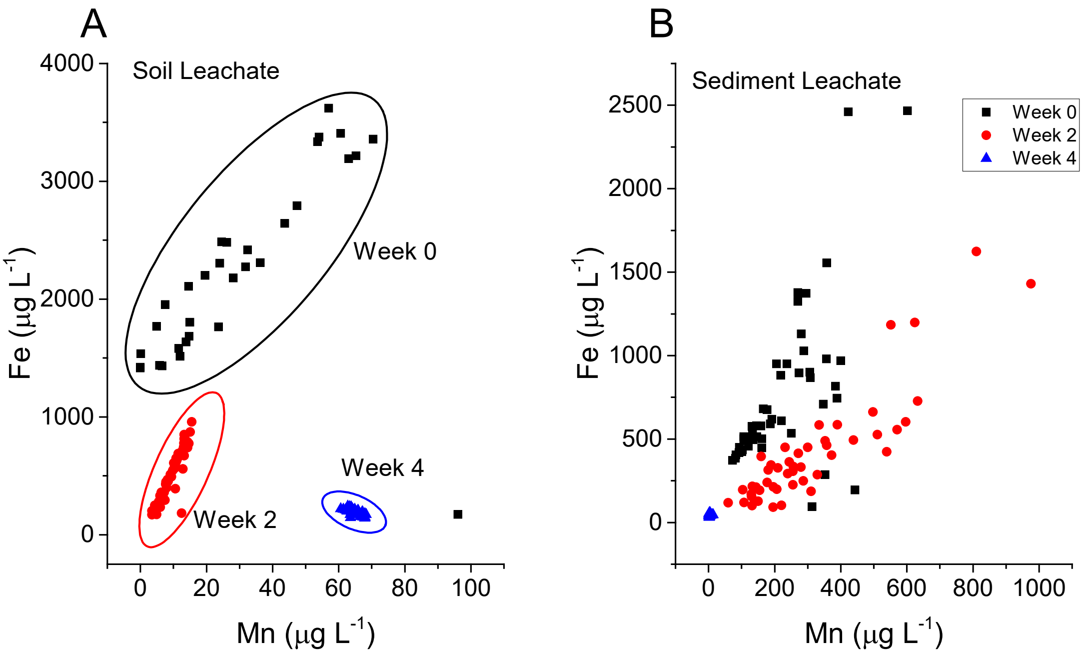

Figure 5-12: Relationship between Fe and Mn concentrations in leachates from (A) soil and (B) sediment columns

5.3.3.6 Mean leachable iron, manganese and aluminium concentrations for the soil and sediment columns

For both the soil and sediment, the mean leachable Fe concentrations decreased over the drying period. The mean soil leachate Fe concentrations were 3980 ± 1200, 936 ± 210 and 374 ± 35 µg kg^{-1} after the drying times of 0, 2 and 4 weeks, respectively, and the equivalent values for the sediment were 528 ± 170, 245 ± 150 and 40.1 ± 6.1 µg kg^{-1}. As expected from the relationship identified between soil leachate concentrations of Fe and Al, the mean leachable Al concentrations followed a similar trend to Fe and had concentrations 2150 ± 650, 499 ± 140 and 256 ± 23 µg kg^{-1} after the drying times of 0, 2 and 4 weeks, respectively. By contrast, however, the patterns for mean leachate Mn concentrations were somewhat different, especially for the soil leachates where there was a distinct increase upon rewetting in Week 4. The mean values for the soil leachates were 101 ± 35, 17.5 ± 5.2 and 125 ± 11 µg kg^{-1} whilst those for the sediment leachates were 159 ± 52, 185 ± 110 and 3.25 ± 1.7 µg kg^{-1} for the 0-, 2- and 4-week drying periods, respectively. Although both mean soil leachate Mn and Cr concentrations show similar trends across the three drying time periods, a mechanistic interpretation is not immediately obvious since both mean leachate Cr(III) and Cr(VI) concentrations are higher for the final time period. For example, oxidation of Cr(III) to Cr(VI) and the concomitant reduction of freshly formed Mn(IV)O_2 would only account for the increase in Mn and Cr(VI) concentrations in the leachate from the Week 4 columns but not the increase in the mean Cr(III) concentration.

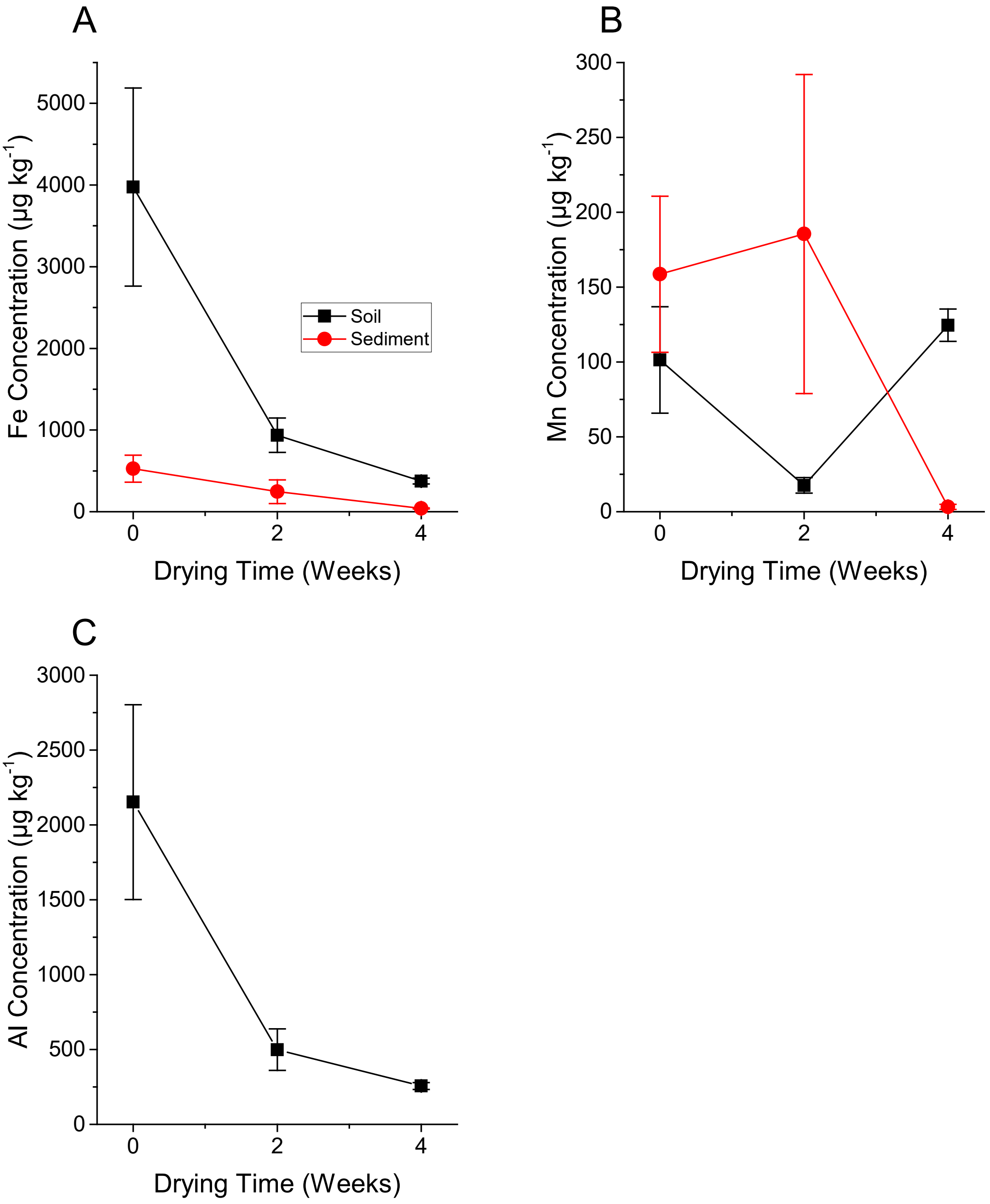

Figure 5-13: Mean ± 1 standard deviation (A) Fe and (B) Mn concentrations in soils and sediments column leachate along with (C) Al concentrations in soil column leachates.

5.3.3.7 Calcium, magnesium and sulfur concentrations in 30 mL leachates columns which had been rewetted and leached after different drying periods

The Ca concentrations were high (40-100 mg L^{-1}) in the early leachate fractions and then decreased over the course of column elution to ~20-40 mg L^{-1}. The exception to this was the Week 4 sediment data for which there was little change with increasing elution volume and concentrations were ~60 mg L^{-1}. It must be noted that the maximum Ca concentration was equivalent to ~2.5 mM but it is not possible to calculate the extent of over- or under-saturation of calcium carbonate phases because the carbonate content of the leachates is unknown.

Although the leachate concentrations were typically lower, the trends for Mg were very similar to those described above for Ca. There is a positive linear relationship between the leachate concentrations of the Ca and Mg elements, albeit there are some deviations for the different drying periods (Spearman's rank correlation, r_s=0.99 (soil), r_s=0.91 (sediment)). In particular, the Week 4 sediment data stands out as being different – here there were near-constant concentrations of both Ca and Mg over the entire column elution volume but there was relatively more Mg relative to Ca in comparison with the leachates for the Week 0 and Week 2 columns (Figure 5-14).

As for both Ca and Mg, leachate S concentrations were typically highest in the early stages of elution (e.g. up to ~30 mg L^{-1} and up to ~100 mg L^{-1} in the soil and sediment column leachates, respectively; corresponds to ~0.31 and 1.0 mM with respect to sulphate). The exception was again the Week 4 sediment data for which near constant S concentrations of ~60 mg L^{-1} were obtained. In terms of solubility, the leachate solutions would be undersaturated with respect to $CaSO_4$ as the K_{SP} value for $CaSO_4$ is 2.4×10^{-5} and the maximum ion activity product (IAP) would be in the range 7.8×10^{-7} to 2.5×10^{-6}.

For the soil leachates, there is a very strong positive relationship between S and Ca concentrations which holds for all of the data from all of the drying time periods (Spearman's rank correlation, r_s=0.98) whilst for the sediment leachates, there are clearly different relationships which relate to the different drying periods (Figure 5-14).

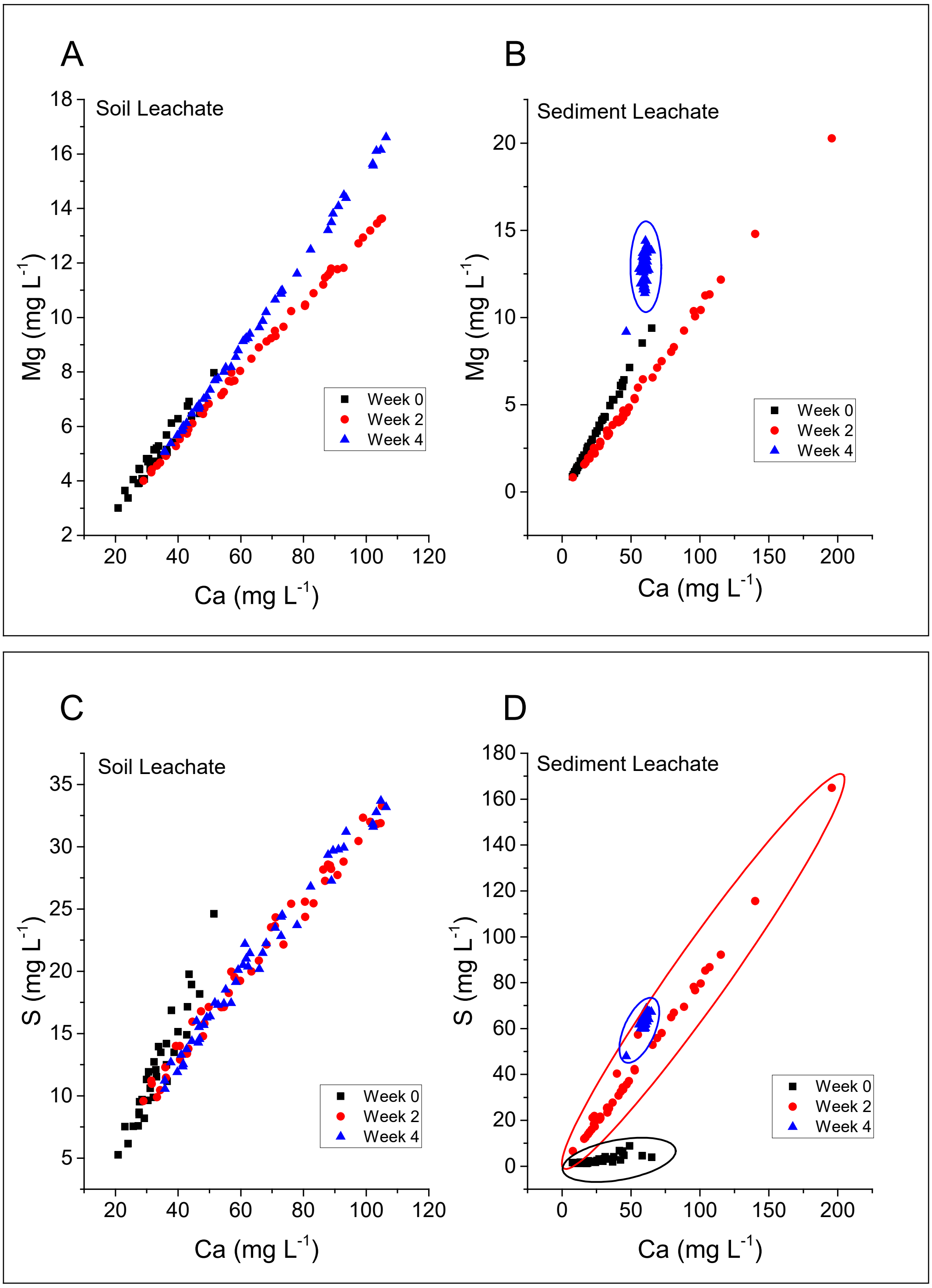

Figure 5-14: Relationship between Mg and Ca in (A) soil and (B) sediment leachate and the relationship between S and Ca in (C) soil and (D) sediment leachate.

5.3.3.8 Mean leachable calcium, magnesium and sulfur concentrations for the soil and sediment columns

Combining the data in the way that was described above in Section 5.3.2.3 the mean soil leachate concentrations of Ca, Mg and S increased with drying time. Initial concentrations of Ca, Mg and S of 59.0 ± 5.7, 8.83 ± 0.85 and 21.5 ± 3.1 mg kg^{-1}, respectively, for the Week 0 columns which increased to 124 ± 22, 18.5 ± 3.5 and 40.1 ± 7.1 mg kg^{-1}, respectively for the Week 4 columns (Figure 5-15).

As for the soil columns, the mass release of Ca, Mg and S into sediment leachate also tended to increase with drying time. Initial mass release of Ca, Mg and S were 17.0 ± 5.9, 2.32 ± 0.87 and 1.80 ± 0.53 mg kg^{-1}, respectively, for the Week 0 columns which increased to 51.6 ± 1.8, 11.1 ± 0.48 and 55.0 ± 2.3 mg kg^{-1}, respectively, for the Week 4 columns. As anoxic sediments dry out, transformation of Fe sulfides by oxidants such as O_2 releases Fe(II) and S(VI), most likely in the form of sulphate (Equation 5-2). There is a concomitant release of protons and so there should also be a decrease in the pH. A greater decrease in pH might be expected if Fe(III) is the oxidant (Equation 5-3) (Rimstidt and Vaughan, 2003).

$$FeS_2 + 3.5O_2 + H_2O \rightleftharpoons Fe^{2+} + 2H^+ + 2SO_4^{2-} \qquad \text{Equation 5-2}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightleftharpoons 15Fe^{2+} + 16\,H^+ + 2SO_4^{2-} \qquad \text{Equation 5-3}$$

This provides an explanation for the increase in S mass release from 1.80 ± 0.53 to 55.0 ± 2.3 mg kg^{-1} between Week 0 and Week 4. In further support of this explanation, Palumbo-Roe *et al.* (2017) previously identified Fe sulfide in the Polmadie Burn sediments and, over the drying period, there was an observed change in colour of the sediment from black to grey, consistent with the oxidation of Fe sulfides. Finally, the release of sulphate should be accompanied by a reduction in leachate pH as was previously shown in Figure 5-5 and supported by a significant negative correlation between S and pH (Spearman's rank correlation, ρ=-0.74).

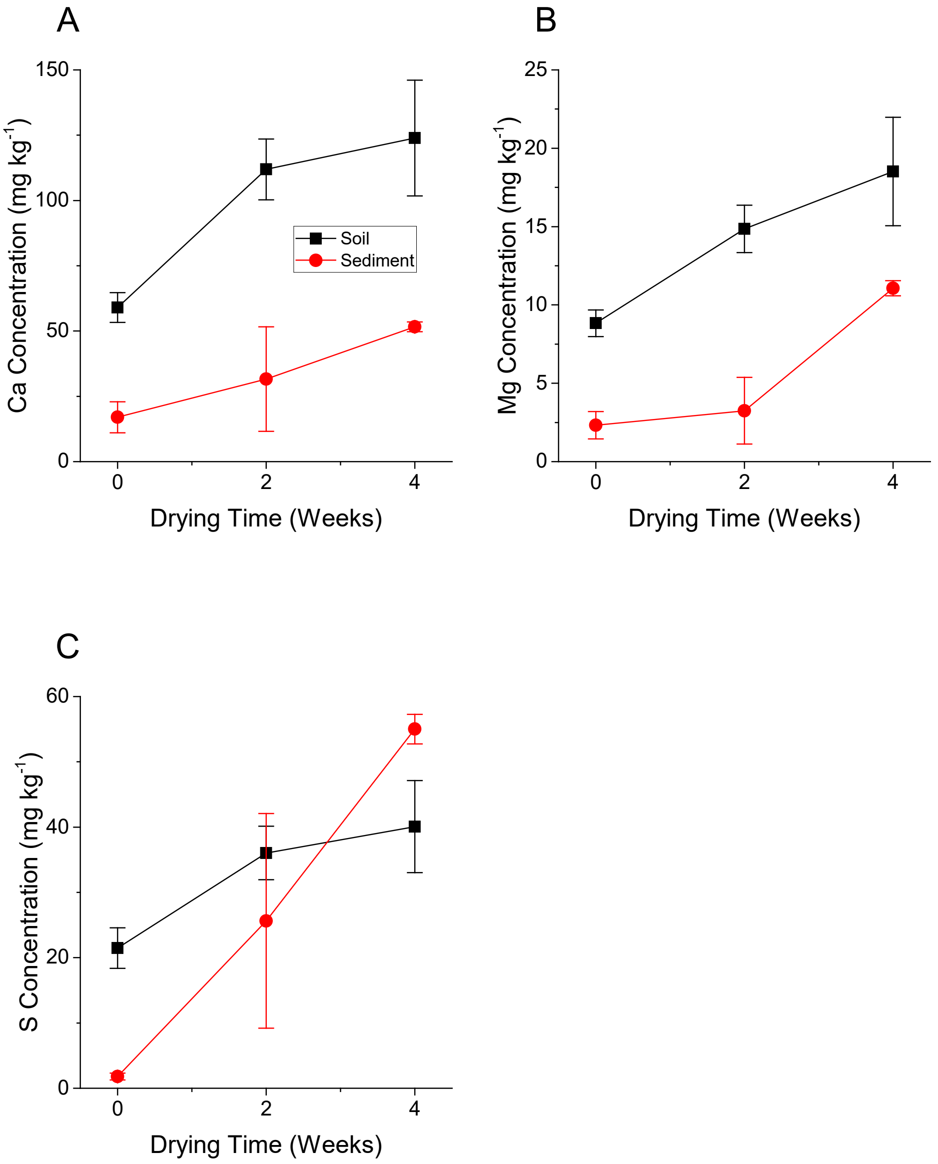

Figure 5-15: Mean ± 1 standard deviation of the mass release of (A) Ca, (B) Mg and (C) S from the soil and sediment column leachate.

5.3.4 Ultrafiltration of leachate from the 120-150 mL fraction from soil and sediment columns

To determine the concentrations of Cr, Mn and Fe in the colloidal and truly dissolved fraction of the column leachates, 0.45 µm filtration (also carried out prior to non-fractionated leachate analysis) was followed by ultrafiltration using a 3 kDa membrane to isolate the two fractions. In this section the colloidal fraction describes the concentration of metal in the leachate that did not pass through the 3 kDa membrane, but is smaller than 0.45 µm, and the dissolved fraction is the concentration of metals in the leachate which passed through a 3 kDa membrane. Leachate used for ultrafiltration was taken from the 120-150 mL fraction from Week 2 and Week 4 from both banking soil and bottom sediment.

The results were determined using the 3 kDa ultrafiltrate concentration and total elemental concentration in the leachate fraction 6 for each column (6 per drying period). Importantly, a generally very consistent pattern emerges when comparing the results for the 6 columns for a given matrix and given drying period

5.3.4.1 *Cr, Fe and Mn Speciation in Soil Column Leachates*

Ultrafiltration of the 0.45 µm-filtered soil column leachates showed that ~30-40% Cr was present in the truly dissolved (<3 kDa) fraction and so 60-70% was in the colloidal (3 kDa-0.45 µm) fraction in the leachates relating to both the 2- and the 4-week drying periods (Figure 5-16). This is remarkably similar to the proportions of Cr(VI) and Cr(III) in the same leachates, which were ~30-40% Cr(VI) and ~60-70% Cr(III). Chromium(VI) is highly soluble and usually present as the free CrO_4^{2-} ion whereas Cr(III) is typically insoluble and readily forms $Cr(OH)_3^0$ which is readily removed from solution. The first step to removal is often colloid formation and so it would be expected that Cr(VI) would be present in the truly dissolved fraction while Cr(III) would be present in the colloid fraction.

For both the week 2 and 4 drying periods, soil leachate Mn and Fe are both primarily present in the colloid fraction as would typically be expected for an oxidised soil system. During Week 4, however, there was a measurable proportion in the truly dissolved fraction (Figure 5-16). This could suggest that there has been some reduction of freshly precipitated Mn as a result of Cr(III) oxidation to Cr(VI). Further work was, however, need to explore this hypothesis and is expanded on in the soil and sediment drying batch leaching experiment in Section 5.4, below.

5.3.4.2 *Cr, Fe and Mn Speciation in Sediment Column Leachates*

Ultrafiltration of the 120-150 mL fraction of the sediment column leachate showed that 93.7 ± 12 and 82.7 ± 5.2% of Cr was present in the dissolved fraction in Week 2 and Week 4, respectively (Figure 5-17). The percentage of Fe and Mn in the dissolved fraction was similar in Week 2 and Week 4. The percentage of Fe in the dissolved fraction of the 120-150 mL fraction of the column leachate was 25.9 ± 8.6 which increased to 75.2 ± 11% in Week 2 and Week 4, respectively. The percentage of Mn in the dissolved fraction was 95.5 ± 4.3% in the dissolved fraction in Week 2 which dropped to 13.2 ± 11% in Week 4 (Figure 5-17). In the sediment leachates, the distribution of colloidal and truly dissolved forms changed between Weeks 2 and 4 for Fe and Mn although for Cr, there was no change. The change in colloidal and dissolved fractions of Fe and Mn is reflective of the change in speciation of the elements as their reduced forms (Fe(II) and Mn(II)) are more soluble than the oxidised versions which are generally insoluble. This is also shown by the reduction of the total concentrations of Mn and Fe in the leachate.

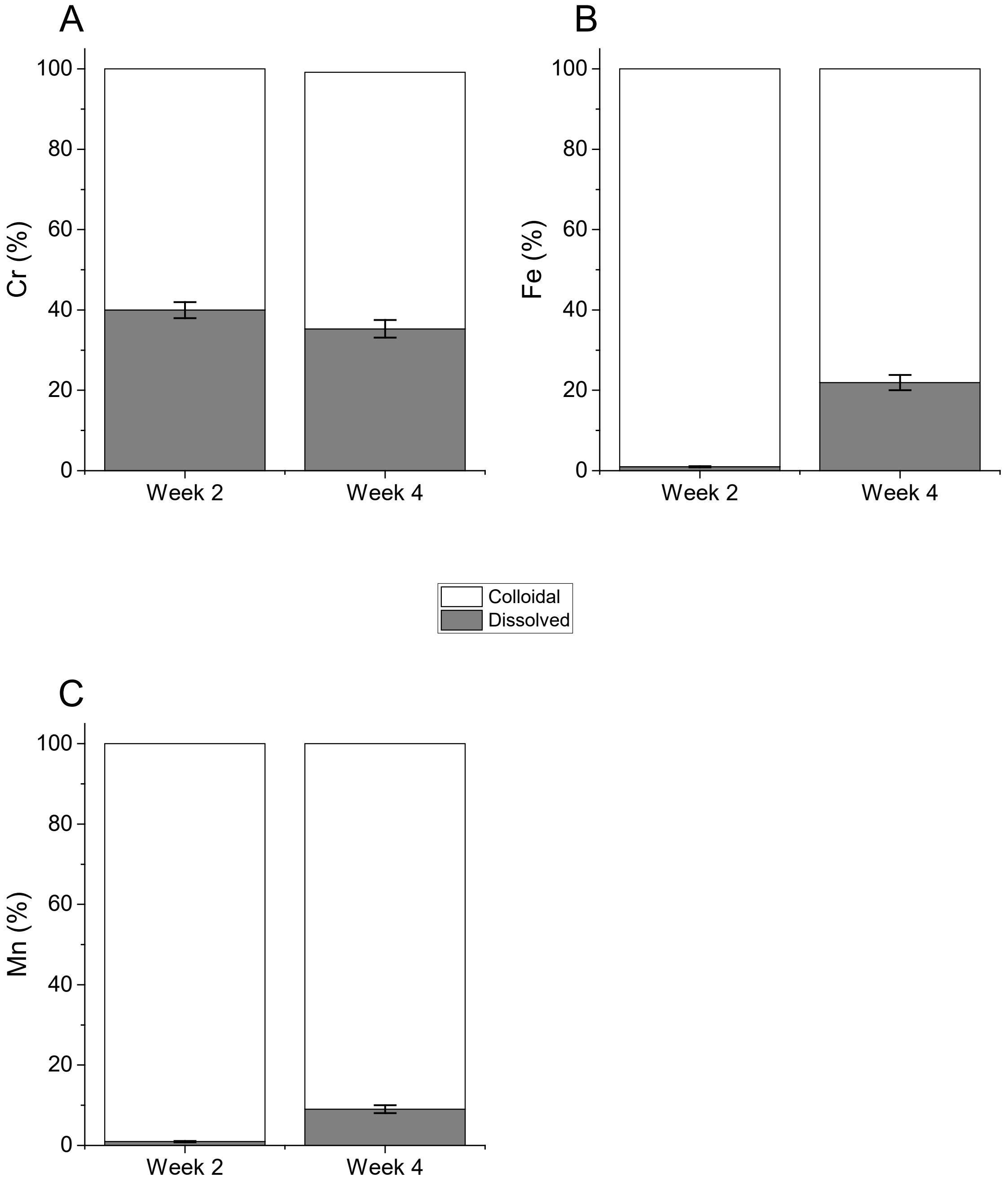

Figure 5-16: Percentage of colloidal and dissolved fraction of (A) Cr, (B) Fe and (C) Mn in the 120-150 mL fraction of the soil column leachate.

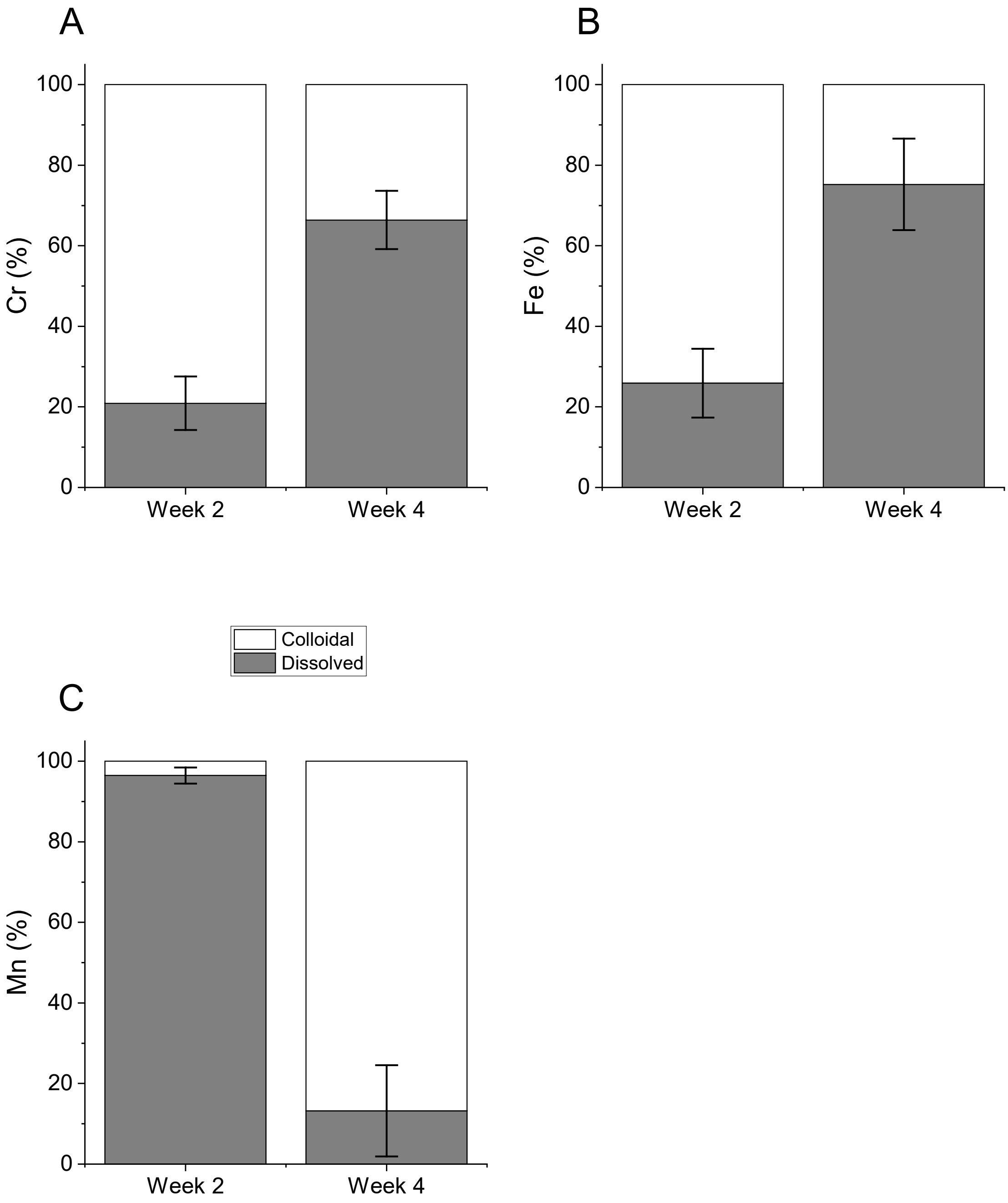

Figure 5-17: Percentage of colloidal and dissolved fraction of Cr (A), Fe (B) and Mn (C) in the 120-150 mL fraction of the sediment column leachate

5.3.5 Discussion of chromium release from soil and sediments during column leaching

5.3.5.1 *Comparison of chromium and chromium(VI) concentrations in soil and sediment column leachates*

The range of Cr mass leached from soil columns, 79.5 - 349 µg kg^{-1}, was significantly greater than the Cr concentration leached from sediment columns which was in the range of 0.20 – 2.86 µg kg^{-1}. The Cr(VI), as a percentage of total Cr leached from the soil columns, was in the range 20.7 – 42.8%. However no Cr(VI) was detected in any of the sediment leachates (Table 5-3). For total Cr, both the soil and sediment column results followed the same trend with the lowest concentrations leached after a 2-week drying period.

Previously published results for leaching of COPR material where 3 years of Glasgow rainwater were passed through the column showed that after initially higher concentrations were released, Cr(VI) continued to be released at a near-constant level over the entire time period (Geelhoed *et al.*, 2003). After 3 years of rainfall, only 7 mmol Cr(VI) kg^{-1} (0.36 g Cr(VI) kg^{-1}) which was equivalent to 3% of the total Cr present in the COPR had been removed (Geelhoed *et al.*, 2003).

Scaling the results of this study up from 1 month (240 mL leachate ~ 1 month of Glasgow rain) to 3 years, the amount of Cr(VI) leached would be equivalent to 0.2-0.4% of the Cr(VI) content in the banking soils. For total Cr in the leachate, the values would be equivalent to 0.06-0.28% of the total Cr content of the banking soils. For the sediment, 3 years of leaching would release 0.000005-0.0008% of Cr in the sediment which, based on this experiment, suggests a significantly lower Cr remobilisation potential from sediment compared with soil. This difference in mobility can be explained only in part by the presence of Cr(VI) in the soil.

The reducing conditions which prevailed within the Polmadie Burn bottom sediments meant that Cr(VI) had been efficiently converted to Cr(III), likely at least in part due to Fe(II) oxidation which leads to the immobilisation of Cr in the form of insoluble mixed Cr/Fe hydroxides. Sequential extraction results showed that although the proportion of Cr bound to Fe (hydr)oxides was greater than that for soils, some 60% was still associated with OM. Reduction and subsequent complexation of Cr(III) by organic matter may also lead to Cr sequestration and this form is not easily observed using SEM-EDX. Organic matter has been reported in the literature to form stable complexes with Cr(III) (Gustafsson *et al.*, 2014, Banks *et al.*, 2006, Elzinga and Cirmo, 2010).

For COPR collected from several locations in SE Glasgow/N Lanarkshire, the Cr(VI) containing minerals were determined to be: Cr(VI)-substituted ettringite ($Ca_6Al_2(OH)_{12}(CrO_4)_3.26\ H_2O$), hydrocalumite ($Ca_4Al_2(OH)_{12}CrO_4.6\ H_2O$) and hydrogarnet ($Ca_3Al_2((Cr/Si/H_4)O_4)_3$) (Geelhoed *et al.*, 2002). Based on this earlier work, it might be expected to see Ca and Mg concentrations to increase slightly as Cr concentrations increase in the leachate but there are competing reactions which may remove some components from solution. Since there is no evidence to support the release of Cr from COPR dissolution, and the sequential extraction data for banking soils showed that Cr was associated mainly with OM and Fe (hydr)oxides the binding of Cr to these phases must be considered.

The binding of Cr to labile OM complexes will result in the solubility forms of Cr(III) which are mobile. Both Cr(III) and Cr(VI) species are adsorbed to Fe hydroxide surfaces with the latter forming weaker interactions. The desorption of Cr(VI) from these surfaces is one mechanism that may result in the release of Cr(VI) into solution. The sections below discuss the influence that Fe hydroxides and OM have on the change in mobility of Cr leached from the soil and sediment column between fresh material and that which had been dried for 2 and 4 weeks.

Table 5-3: Comparison of soil and sediment column parameters and leachable Cr concentrations

Parameter	Soil	Sediment
Mean Cr	1480 ± 410 mg kg^{-1}	3870 ± 400 mg kg^{-1}
Mean Cr(VI)	174 ± 30 mg kg^{-1}	195 ± 12 mg kg^{-1}
Mean %Cr(VI)	11 ± 3.6%	5.0 ± 1.3%
Leached Cr - range	79.5 - 349 μg kg^{-1}	0.200 – 2.86 μg kg^{-1}
Leached Cr(VI) - range	20-48 μg kg^{-1}	-
Leached Cr(VI) (as %)	20.7 – 42.8%	-

5.3.5.2 *Mobility of chromium in leachate from soil and sediment columns*

As discussed at the beginning of this chapter (Section 5.2) many studies have suggested that leaching of Cr(III) or Cr(VI) from soils and sediments is heavily influenced by the leachate pH (Geelhoed *et al.*, 2002, Weng *et al.*, 1994). In brief, at pH <4.5 dissolution of Cr(III) leads to high concentrations of Cr in the leachate however at pH >4.5 Cr(VI) was found to be the dominant species in solution. In this series of column experiments the pH of the soils and sediments were quite similar (mean values in the range 7.1-7.9). Although the sediment leachate pH was often slightly lower than that of the soil leachates, it did not drop below pH 6.5 and so Cr(III) is unlikely to be present in truly dissolved form, i.e. Cr^{3+} and its hydrolysis products such as $Cr(OH)_2^+$. There was, however, a difference in the concentration of Cr(VI) between the soil and sediment column leachate but, as mentioned above, that alone cannot explain the greater leachability of Cr from soils than sediments. The higher than expected concentrations of Cr(III) in the leachate has been attributed to colloidal Cr species which will be explained further below.

5.3.5.2.1 Organic matter complexation of Cr

As the drying time increased Fe (and Al) become increasingly less leachable. However, gel electrophoretic fractionation of OM extracts (pH 8.5) confirmed the presence of negatively charged, moderately large Cr-Fe-OM colloids, even after prolonged drying of the soil, and it is proposed that a proportion of these are present in the leachates (pH 7-8). Indeed, ultrafiltration data confirms that 60-70% of Cr and 75-100% Fe is present in colloidal form in the soil column leachates (Figure 5-16).

The gel electrophoretic fraction of OM extracted from fresh sediment also demonstrated the presence of Cr-Fe-OM complexes which had similar mobility to those observed for the extracts from both fresh and dried soil. This is in agreement with the findings of Löv *et al.* (2017) who demonstrated using extended X-ray absorption fine structure (EXAFS) spectroscopy that Cr is bound to OM coated ferrihydrite colloids. It may be, therefore, that the extractable sediment OM is a relatively small portion of the total sediment OM pool and so Cr-Fe-OM complexation may be an effective sink in the sedimentary environment. For the sediment, the gel electrophoresis and ultrafiltration data suggest, again to a small extent, that OM is present in the form of low molecular weight Cr(III)-OM complexes, which are small enough to be present in the truly dissolved fraction (Löv *et al.*, 2017).

The gel electrophoretic fraction of OM extracted from sediment that had been air-dried for 4 weeks revealed some major differences in the OM-Cr associations between the dried sediment and field-moist sediment (Section 4.6). There was: (i) a decrease in the amount of OM extracted as reflected in the lower absorbance (254 nm) values (~10-fold); (ii) a decrease in mobility of the main band (F2-F3 compared with F3-F4); (iii) a ~10-fold decrease in extracted Cr and a ~40-fold decrease in extracted Fe; (iv) an increased proportion of the extracted Cr and Fe is found in the higher mobility fractions (F7-F10). Clearly, over time, the extractable OM becomes an even smaller portion of the pool of total sediment OM. The extractable OM appears to have a relatively higher proportion of highly mobile molecules which bind both Cr and Fe. Manganese, which does not form strong complexes with OM, appears to be unaffected by this process. Although Mn speciation was not determined for the sediment, it is likely that the high concentrations of Mn initially released from the sediment were due to the presence of Mn(II) which is stable in mildly reducing conditions, such as that found in drying sediment (Figure 5-13).

The gel electrophoresis results for the OM extracted from the dried sediment may initially seem difficult to explain because: (i) there was no Cr(VI) in the sediment leachates and so colloidal Cr(III) would be expected to be the main form of Cr; (ii) the sediments have been drying out and oxidising and so colloidal Fe(III) might also be expected to be the main form of Fe resulting in lower mobility of. However, other changes occurring during drying can include alteration of OM. Gel electrophoretic fractionation of OM extracted from sediments which had been air-dried for more than one month showed that Cr(III) was not only associated with relatively large organic colloids but was also associated with small, highly mobile organic molecules (Figure 5-18). It is therefore hypothesised that Cr is being leached in the form of complexes with highly soluble, low molecular weight organic molecules. The Cr observed in the dried sediment gel electrophoresis is not Cr(VI) as chromate, which is small and highly mobile, will have travelled significantly further from the well than even the small organic molecules (Farmer *et al.*, 2002). Such an association was not observed for similarly dried soil samples where the shape of OM and Cr patterns are more in sync (Figure 5-19). It must be noted that the OM extracts used in the gel electrophoresis contain higher concentrations of OM than would be present in the sediment column leachates but the results provide evidence in support of the species of which can be mobilised from the dried sediments. In support of the association between Cr and dissolved OM, other studies, using EXAFS to analyse soil leachates, showed that Cr(III) was bound to both colloidal and dissolved OM (Löv *et al.*, 2017).

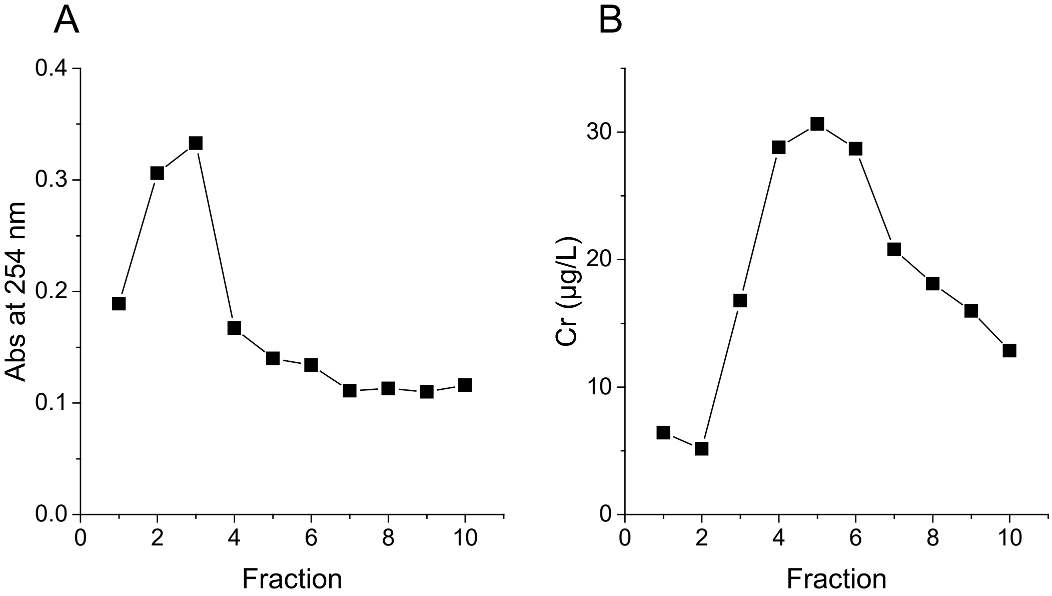

Figure 5-18: Gel electrophoretic patterns obtained for (A) organic matter extracted from air-dried Polmadie sediment for OM and (B) Cr concentrations in fractions 1-10.

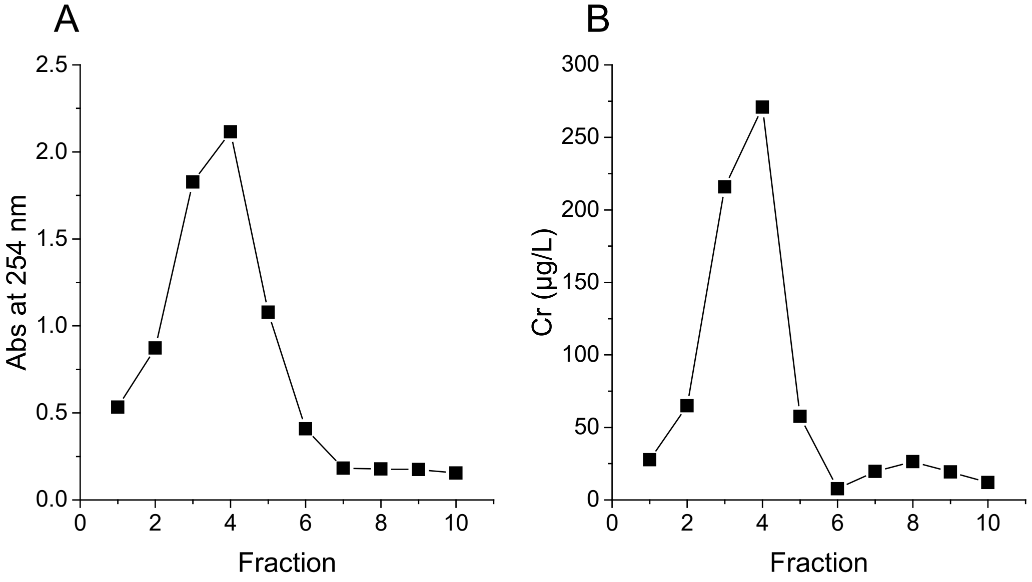

Figure 5-19: Gel electrophoretic patterns obtained for organic matter extracted from (A) fresh Polmadie Burn sediment for OM and (B) Cr concentrations in fractions 1-10.

5.3.5.2.2 Oxidation of Cr(III) by Mn

For both soil and sediment, there was a slight increase in the amount of Cr leached after the 4-week drying period compared with the 2-week drying period (Figure 5-8). Over the same time period this was accompanied by an increase in the amount of Mn leached from soils but for the sediment, it was accompanied by a significant decrease in the amount of Mn leached. Manganese is the only known oxidant which is environmentally relevant for the oxidation of Cr(III) to Cr(VI) (Rai *et al.*, 1989). However, for this reaction to take place there must be a "clean" Mn(IV) oxide surface as, although this reaction is initially fast, the rate will decrease as the active sites on the catalytic surface become occupied (Pan *et al.*, 2017). It is these newly formed Mn oxide surfaces that can oxidise Cr(III) to Cr(VI) on rewetting of the soil, leading to the production of Mn(II) and Cr(VI) which is seen in the leachate. For the soil, it is proposed that, to a small extent, Cr(III) is being oxidised to soluble Cr(VI) whilst freshly formed Mn(IV)O_2 is reduced to Mn(II). This is supported by the ultrafiltration data which shows the presence of truly dissolved Mn only for the 4-week leachate data. The reaction can be shown as:

$$Cr^{3+}{}_{(aq)} + 2MnO_{2(s)} \rightarrow CrO_4^{2-}{}_{(aq)} + 2Mn^{2+}{}_{(aq)} \qquad \text{Equation 5.4}$$

From this it can be seen that oxidation of Cr(III) by Mn(IV) oxides will result in the production of soluble forms of both Cr and Mn. To explain why this may be occurring only to a limited extent it is important to remember that this process is dependent on the pH, initial Cr(III) concentration and initial MnO_2 surface area. Although this process occurs over the pH range of 3 – 10, it is kinetically limited by the solubility of Cr(III) at pH > 5 (Pan *et al.*, 2017). Oxidation is fast within the first 30 min after which the reaction is greatly inhibited due to surface alteration of the MnO_2 surfaces, probably due to precipitation of Cr(III) onto the Mn oxide surface (Fendorf and Zasoski, 1992, Świetlik, 2002). This means that there must be a fresh source of Mn surfaces in these soils to facilitate this reaction. Manganese(II) oxidised to Mn(IV) which precipitates on surfaces will provide a new surface for Cr(III) oxidation to occur.

When the Eh increases as the sediment dries there will be a point where Mn(II) is no longer stable and it will precipitate as Mn(IV) oxide, resulting in the significant decrease in the leachable Mn concentrations in Week 4. It is this precipitation of Mn(II) which results in the decrease of Mn leachate concentrations observed in the sediment column leachate as drying time increases. This is significant because freshly precipitated Mn(IV) oxides may provide a surface for the oxidation of Cr(III) to Cr(VI) leading to leachable Cr(VI) in the leachate. Whilst this was not observed in this experiment, if the sediment had dried for longer Cr(VI) may have been observed in the leachate. It is therefore hypothesised that the alteration of OM is the reason for changes in the leachable Cr concentrations found in the column leachate.

5.3.6 Summary

The results from the column experiments have shown that there is a significant difference between the mobility of Cr in the Polmadie Burn banking soil and bottom sediments. The leaching experiment was equivalent to 6 weeks of Glasgow rainfall and the maximum percentage of Cr released over the experiment from the banking soils and bottom sediments was <0.023 and <0.00008%, respectively, based on the maximum concentration of Cr leached from the mean Cr concentration in the banking soils and sediment. Even though the total Cr concentration in both the soils and sediments are significantly elevated compared with the baseline Cr concentrations in Glasgow these results show that the amounts of Cr that would be released after 4 weeks drying and then 4 weeks of rainfall would indeed be very small.

The lower Cr concentration in sediment column leachates is due largely to the highly reducing nature of the Polmadie Burn sediments resulting in the reduction of Cr(VI) by Fe(II) to precipitate as stable Cr/Fe hydroxides. Although as shown in Section 4.3.3 the oxic banking soils provide an environment where Cr(VI) is stable, the relatively high concentrations of Cr(III) in soil leachate did not agree with literature which suggested that Cr(VI) would be the dominant species leached at pH>5. Ultrafiltration data demonstrated, however, that Cr released from soil was associated with colloidal particles as well as in the truly dissolved fraction. Combining the ultrafiltration results with those for gel electrophoretic fractionation of extracted soil organic matter, leached Cr was (i) most likely associated with Fe/OM in the colloid fraction or (ii) present as Cr(VI) in the truly dissolved fraction. The presence of "truly dissolved" (<3 kDa) Cr(III) in the sediment leachates, where no Cr(VI) was detected, was initially harder to explain but gel electrophoresis showed that, especially after 4 weeks of drying, there was the formation of small, mobile OM-Cr(III) complexes which may pass through a 3 kDa membrane.

More generally, it is possible that the decrease in Cr, Fe and Al leachate concentrations as drying time increases is due to the changing in the leachability of OM. Interestingly, the leachate concentrations of Cr from both soils and sediment columns decreased between Week 0 and Week 2 then increased between Week 2 and Week 4. This trend was also observed for Mn concentrations in the soil column leachates, suggesting that the oxidation of Cr(III) to produce soluble Cr(VI) and Mn(II) may be occurring. To further investigate the changes in Cr concentrations and its relationship with Mn batch experiments were carried out. These experiments allowed the changes in the elemental concentrations leached to be sampled more frequently over the duration of the drying period, and over a longer time period, to gain a more detailed understanding of the mechanisms of Cr release from Polmadie Burn banking soils and bottom sediments upon rewetting after drying.

5.4 Batch Experiments to investigate the leachability of chromium from soils and sediments which have been dried for different time periods

To investigate the changes in elemental concentrations, with especial focus on the Cr and Mn concentrations, found in the column leachate a study was required which had shorter time intervals between subsamples over the drying period. Due to the large mass of banking soil and bottom sediment required to fill the columns (>20 kg of soil and sediment) and the large costs associated with analysis and consumables, it was not feasible to expand the column experiment described in the section above to the required resolution. It was therefore decided to use batch leaching experiments which reduced the mass of material required along with the number of samples to analyse (one rather than eight solutions per time step) but still provided the information about the changes in the leachate composition when banking soil and bottom sediments are rewetted after set drying periods. The drying time periods used for these batch experiments were: 0, 1, 2, 5, 8, 12, 16, 21, 26, 35, 43, 50 and 62 days with all time step replicates in triplicate. Due to the non-significant difference in the elements leached from banking soils and bottom sediments by SRW and DIW in the column leaching experiments, only SRW was used as the leaching solution.

Section 5.4.1 below gives a brief overview of the sampling and batch leaching method. This is followed by the results from the batch leaching experiments (Section 5.3). This section then compares the batch and column leaching experiments before finally discuss the results from the batch leaching, leading to an improved mechanistic understanding of Cr release from the Polmadie Burn banking soil and bottom sediment.

5.4.1 Overview of sampling and sample treatment

Approximately 5 kg of surface banking soil and surface sediment was collected on the 10th November 2017 (Section 3.1.2). The material was passed through a 5 mm sieve to remove debris, as described in Section 5.3.1, and then left to dry. After set time intervals a sub-sample of the soil or sediment was removed, passed through a 2 mm sieve to further homogenise the sample. Triplicate portions (10 g) of the homogenised material were weighed into 50 mL centrifuge tubes. To each of the tubes 20 mL of SRW (Section 5.3.1), was added and the tubes were shaken at 20 rpm on an end-over-end shaker for 1 h. This time period was chosen to coincide with the 1 h rewetting time of the columns so that the results would be comparable to the first aliquot of the column leaching experiments. After centrifugation at 5000 x g for 10 min the supernatant was removed and filtered through a 0.45 µm filter and stored at 4°C in the dark before analysis.

5.4.2 Moisture content and pH of soils and sediments

The moisture content of the soil decreased linearly from 63.3 ± 0.24% to 11.1 ± 0.21 % during 43 days of drying, after which it decreased at a much lower rate reaching 6.64 ± 0.19 % after 62 days of drying (Figure 5-20A). The sediment moisture content decreased linearly from 26.7 ± 0.44 % to 3.40 ± 0.19 % over the first 21 days of drying. After day 21 the moisture content remained constant at 2.68 ± 0.42 % until day 62, showing that the sediment had already reached a steady state with respect to moisture content (Figure 5-20B). The slower moisture loss by the soils can be attributed to their higher OM content. The dry mass of the material was used to determine the mass of element leached.

The pH of the soil leachate decreased from an initial value of 7.84 ± 0.015 to 7.46 ± 0.17 after 8 days of drying. Between days 8 and 62 the mean pH of the leachate was 7.53 ± 0.076 (Figure 5-20C). The steady decrease in pH over the first 15 days of drying did not follow the trend shown by the column experiments where the leachate pH of the fresh sample (Week 0) was 7.34 ± 0.12 which increased between Week 0 and Week 2 before decreasing between Week 2 and Week 4. The pH of the soil column leachate in Week 2 and Week 4 was similar to the pH observed in the batch leachate of 7.38 ± 0.23 and 7.61 ± 0.0051 for soils dried for 16 and 26 days, respectively.

The sediment leachate pH decreased from 7.97 ± 0.081 to 6.63 ± 0.22. After this minimum the pH increased and levelled off at 7.35 ± 0.054 between days 26 to 62 of drying, (Figure 5-20D). This was similar to the trend observed in the column leaching experiment where the pH decreased linearly over the drying period from 7.80 ± 0.11 at Week 0 to 7.29 ± 0.27.

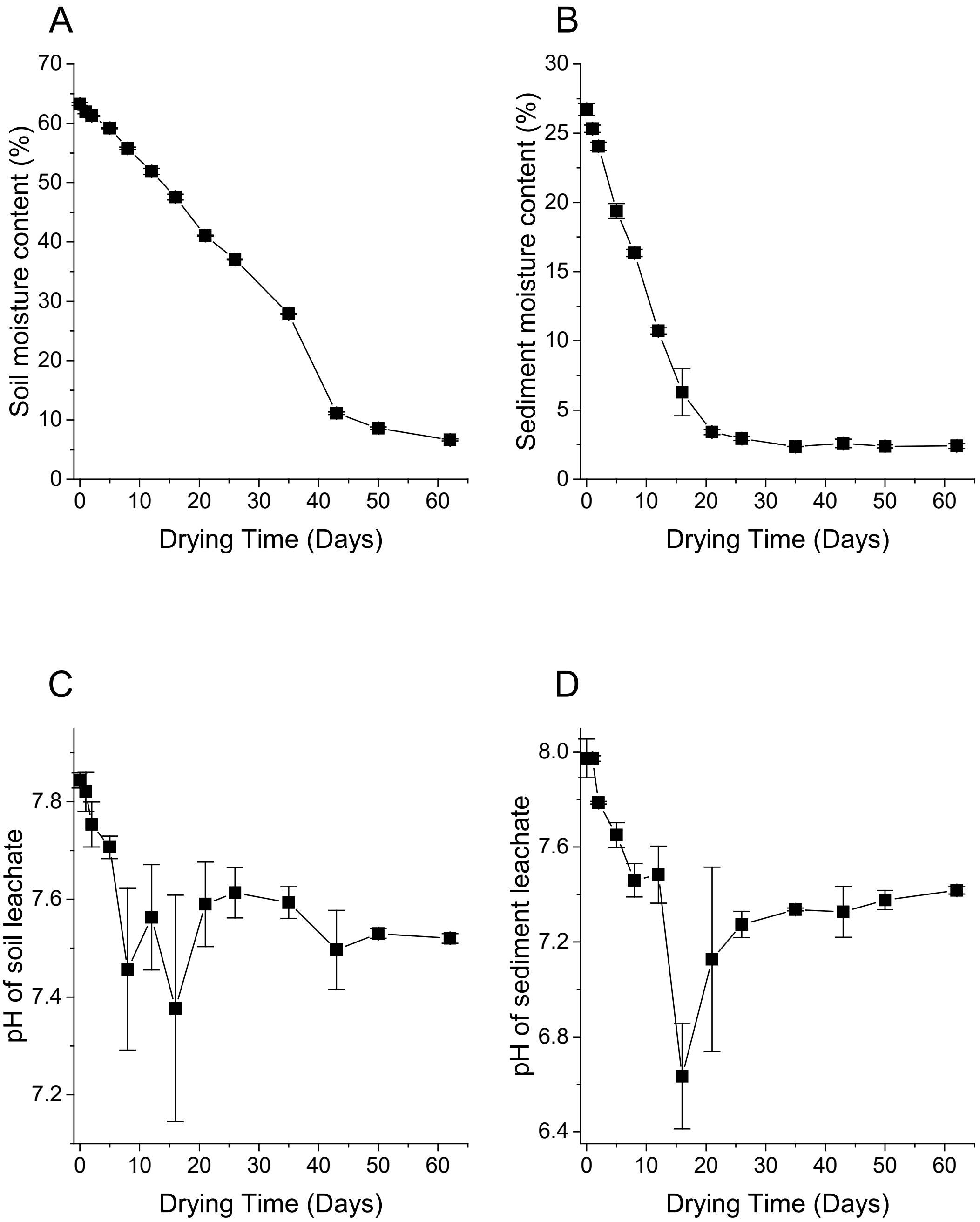

Figure 5-20: Mean ± 1 standard deviation values of the moisture content of (A) soil and (B) sediment along with pH of (C) soil and (D) sediment leachate with increasing drying period (n=3).

5.4.3 Elemental release from soil during rewetting with increasing drying time

The soil leachate Cr, Mn, Fe, Al, Ca, Mg, and S concentrations for different drying time periods of up to 62 days are shown in Figure 5-21 and Figure 5-22. While leachate Cr(III) concentrations peaked at 2310 ± 83 µg L^{-1} after 2 days of drying, additional drying time decreased the leachable Cr concentration which fell to a minimum value of 19.6 ± 1.4 µg kg^{-1} after 43 days of drying. Between 43 and 62 days of drying the leachable Cr(III) concentration was 23.5 ± 3.4 mg kg^{-1}. Leachate Cr(VI) concentrations peaked after 5 days drying at 469 ± 110 µg kg^{-1} and then decreased to 31.6 ± 9.0 µg kg^{-1} after a drying time of 43 days. Between days 43 and 62 the leachate Cr(VI) concentration increased slightly to 36.4 ± 2.1 µg kg^{-1}.

The leaching profiles of Fe, Mn and Al were very similar to that of the concentration of Cr(III). The leachate Fe concentration peaked at 27.5 ± 0.98 µg kg^{-1} and then decreased to 0.116 ± 0.011 µg kg^{-1}. Between days 43 and 62 the average Fe concentration was 0.104 ± 0.016 µg kg^{-1}. The leachate Mn concentration peaked at day 2 at 1000 ± 46 µg kg^{-1} and decreased to 2.40 ± 0.43 µg kg^{-1} after 43 days of drying. Between days 43 and 62 the Mn concentrations increased slightly to 10.9 ± 0.65 µg kg^{-1}. Aluminium leachate concentrations were measured between day 0 and day 26 rather than up to day 62 like the other elements due to analytical oversights. The maximum concentration of Al in the leachate was 14.7 ± 0.63 µg kg^{-1}, after which it decreased to 1.20 ± 0.11 µg kg^{-1} on day 26.

The Ca leachate concentrations decreased from 155 ± 7.8 to 111 ± 12 mg kg^{-1} between days 0 and 1, respectively. The Ca concentrations leached between days 1 and 16 was 109 ± 5.9 mg kg^{-1} on day 21 the Ca concentration increased to 165 ± 24 mg kg^{-1} and the mean Ca concentration between days 21 and 62 was 157 ± 7.9 mg kg^{-1}. The Mg concentration, like Ca, decreased from 23.5 ± 0.75 to 17.9 ± 0.36 mg kg^{-1} between days 0 and 1, respectively. The Mg concentration continued to decrease until it reached 13.7 ± 1.3 mg kg^{-1} on day 21. The Mg concentration then increased between days 21 and 50, the mean Mg concentration between days 50 and 63 was 23.6 ± 0.039 mg kg^{-1}. The concentration of S leached from the soil, in general, increased with drying time. The initial S concentration was 32.2 ± 1.4 mg kg^{-1} and increased linearly until day 21 where it reached 57.0 ± 18 mg kg^{-1}. After decreasing to 48.5 ± 1.9 mg kg^{-1} the S concentration increased to its maximum value of 62.2 ± 7.1 mg kg^{-1} on day 52.

5.4.3.1 *Comparison of batch leaching results of Cr, Fe and Mn with those for column leaching of Polmadie Burn Banking Soils*

One of the trends observed in the column experiments was the tendency for leachate Cr(III) and Cr(VI) concentrations to decrease between Weeks 0-2 and then increase between Weeks 2-4.This was not observed for the soil batch leachate over the same time period. The initial concentration of leachable Cr(III) was 1763 ± 160 µg kg^{-1} and the Cr(III) concentration leached after 16 and 26 days of drying was 725 ± 42 and 193 ± 11 µg kg^{-1}, respectively, and continued to decrease until Day 62. The Cr(VI) concentration in the batch leachate showed an increase in the amount of leachable Cr(VI) over the first 5 days of drying before decreasing over the rest of the drying period although there is a very slight increase in the Cr(VI) concentration leached on Day 62 (36.4 ± 2.1 µg kg^{-1}) compared to Day 50 (32.4 ± 2.5 µg kg^{-1}).

The Mn concentration in the soil column leachable showed the same trend as Cr described in the paragraph above and the column leachate Fe concentration decrease over the drying period. In the batch leachate both Fe and Mn were highly correlated with Cr(III) concentrations which supports the hypothesis that Cr(III) in the leachates is associated with colloids, since Fe and Mn, as shown by the ultrafiltration data in Section 5.3.2.10, were found mainly in the colloidal fraction.

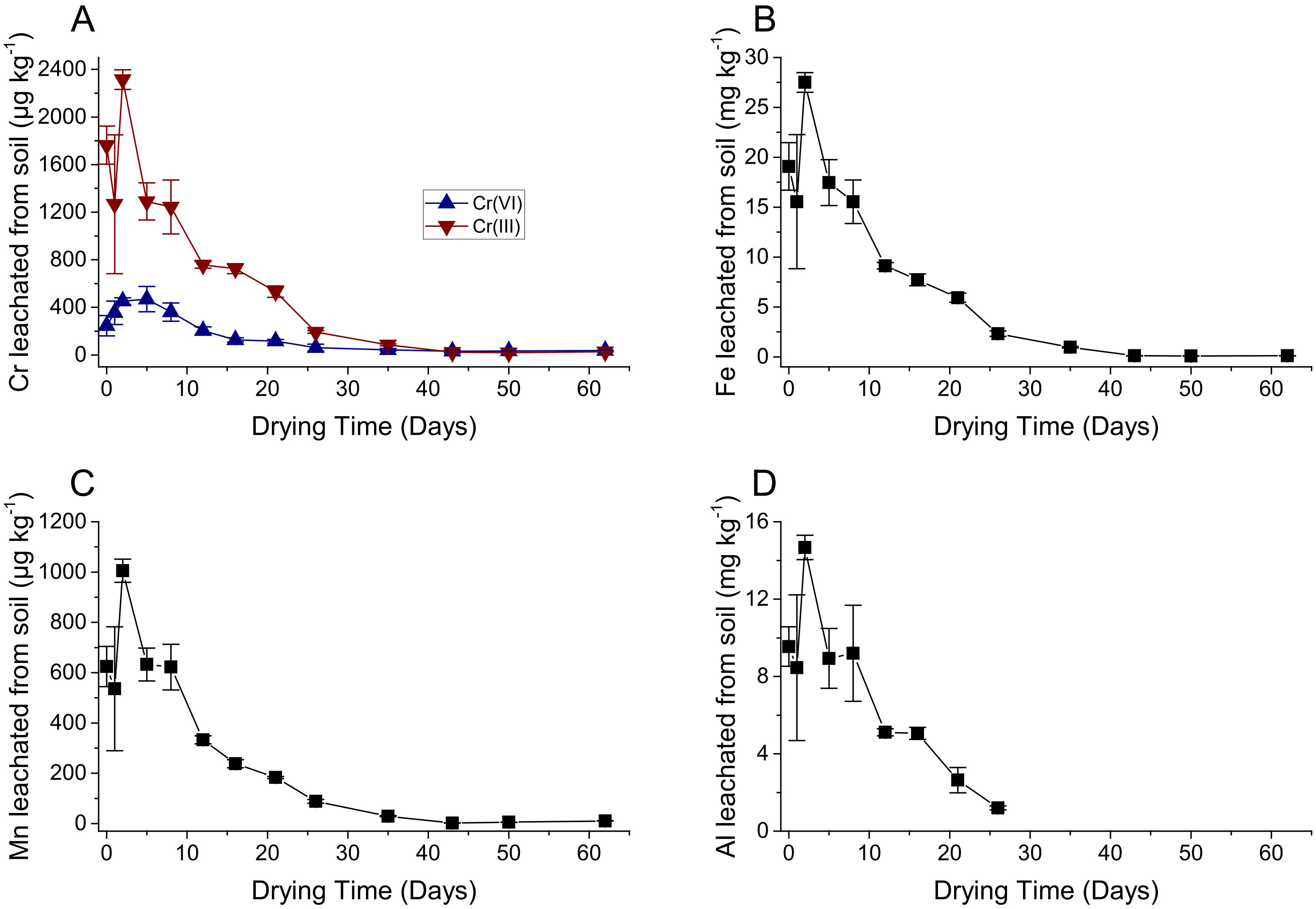

Figure 5-21: Concentration of (A) Cr, (B) Fe, (C) Mn and (D) Al leached from soil over a drying time of 62 days.

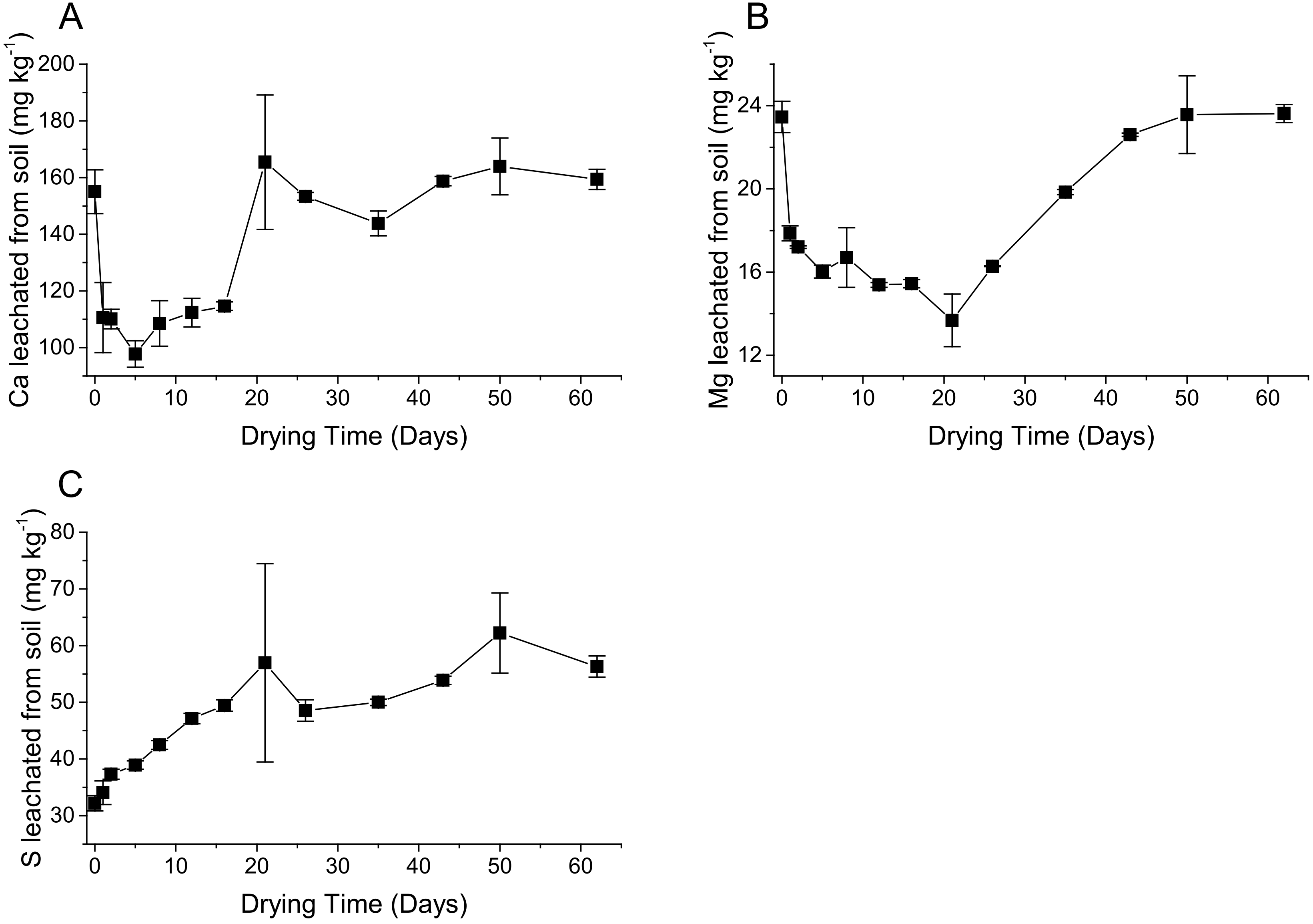

Figure 5-22: Concentration of (A) Ca, (B) Mg and (C) S leached from soil over a drying time of 62 days.

5.4.4 Elemental release from sediment during rewetting with increasing drying time

The change in leachable Cr, Fe, Mn, Al, Ca, Mg, and S concentrations in sediment over the period of 62 days as it dried are shown in Figures 5-23 and 5-24. Leachate Cr concentrations decreased from 266 ± 41 μg kg^{-1} to 17.4 μg kg^{-1} between days 0 and 2, respectively. The Cr concentration continued to decrease until it reached 4.66 ± 0.31 μg kg^{-1} on day 16. Between days 16 and 43 the Cr concentration increased and the mean concentration of leachable Cr was 36.3 ± 2.9 μg kg^{-1} between days 43 and 62. Between days 35 to 62 Cr(VI) was detected in the leachate (Appendix 2). The Cr(VI) was 150 and 121 % of the total Cr in the leachate in days 35 and 43, respectively. This is probably due to the uncertainties associated with the measurements of Cr and Cr(VI) at low concentrations but show there was a change in the speciation of Cr released after day 35 from exclusively Cr(III) to Cr(III) and Cr(VI).

The concentration of Fe released from the sediment decreased from 254 ± 41 μg kg^{-1} to 3.58 ± 0.26 μg kg^{-1} on day 12. The Fe concentration between days 12 to 62 remained low with a mean concentration of 2.42 ± 0.67 μg kg^{-1}. The leachable Mn concentration increased from 198 ± 20 μg kg^{1} on day 0 to 711 ± 1.6 μg kg^{-1} on day 2. The Mn concentrations decreased from 681 ± 46 μg kg^{-1} on day 5 to 37.1 ± 2.5 μg kg^{-1} on day 12. The Mn concentration then increased slightly to 66.0 ± 3.9 μg kg^{-1} on day 21 before increasing between days 21 and 35 to 259 ± 10 μg kg^{-1}. The mean concentration of Mn between days 35 and 62 was 271 ± 16 μg kg^{-1}. The leachable Al concentration was monitored between days 0 and 16. Over this period the Al concentration decreased from 275 ± 2.9 μg kg^{-1} to 149 ± 15 μg kg^{-1}.

The leaching of Ca, Mg and S followed a similar general trend where the leachable concentration of the element increased linearly over a period before reaching, and remaining at, constant concentration for the duration of the remaining time. The leachable Ca concentration increased from 49.9 ± 2.9 mg kg^{-1} on day 0 to 1030 ± 41 mg kg^{-1} on day 8. Between day 8 and day 62 the mean Ca leachable concentration was 1060 ± 60 mg kg^{-1}. The leachable Mg concentration increased from 6.82 ± 0.061 mg kg^{-1} to 48.0 mg kg^{-1} on day 5. Between days 5 and 62 the mean Mg concentration was 48.2 ± 2.1 mg kg^{-1}. The leachable concentrations of S increased from 20.4 ± 1.2 mg kg^{-1} on day 0 to day 12 where it reached a maximum of 1170 ± 68 mg kg^{-1}. It then decreased slightly and the mean leachable S concentration between day 16 and 62 was 907 ± 35 mg kg^{-1}.

5.4.4.1 *Comparison of batch leaching Cr, Fe and Mn results with those for column leaching of Polmadie Burn Bottom Sediments*

In the sediment batch leachate Cr concentrations was significantly lower than in the soil batch leachate. This was also observed for Cr concentrations in the column experiments. The sediment column Cr concentration followed the same trend as the soil Cr concentration with a decrease in Weeks 0-2 and then increase between Weeks 2-4 which was also observed in the leachable Cr in the sediment batch experiment (Figure 5-21A and Figure 5-23A). The initial sediment batch Cr concentration on Day 0 was 226 ± 41 µg kg^{-1} which decreased rapidly to 4.66 ± 0.31 µg kg^{-1} on Day 16 and then increased to 15.9 ± 2.7 µg kg^{-1} after 26 days of drying. After a drying time of 26 days Cr(VI) was observed in the sediment batch leachate. No Cr(VI) was detected in the sediment column leachate.

The trend observed in the sediment column leachate was Fe concentration to decrease as drying time increased. This was also observed in batch sediment leachates over the same time intervals but at different rates. Initial Fe concentrations in the sediment batch leachate was 254 ± 41 µg kg^{-1} which decreased to 1.21 ± 0.20 and 2.47 ± 1.0 µg kg^{-1} after the drying times of 16 and 26 days, respectively. The sediment column Mn leachate concentration did not follow the same trend as in the sediment batch leachate. In the sediment column leachate the Mn concentration increased between Week 0 and Week 2 and then decreased between Week 2 and Week 4, however the sediment batch Mn leachate concentration decreased from 198 ± 1.8 on Day 0 to 58.6 ± 5.21 µg kg^{-1} on Day 16 and then increased to 191 ± 11 µg kg^{-1}.

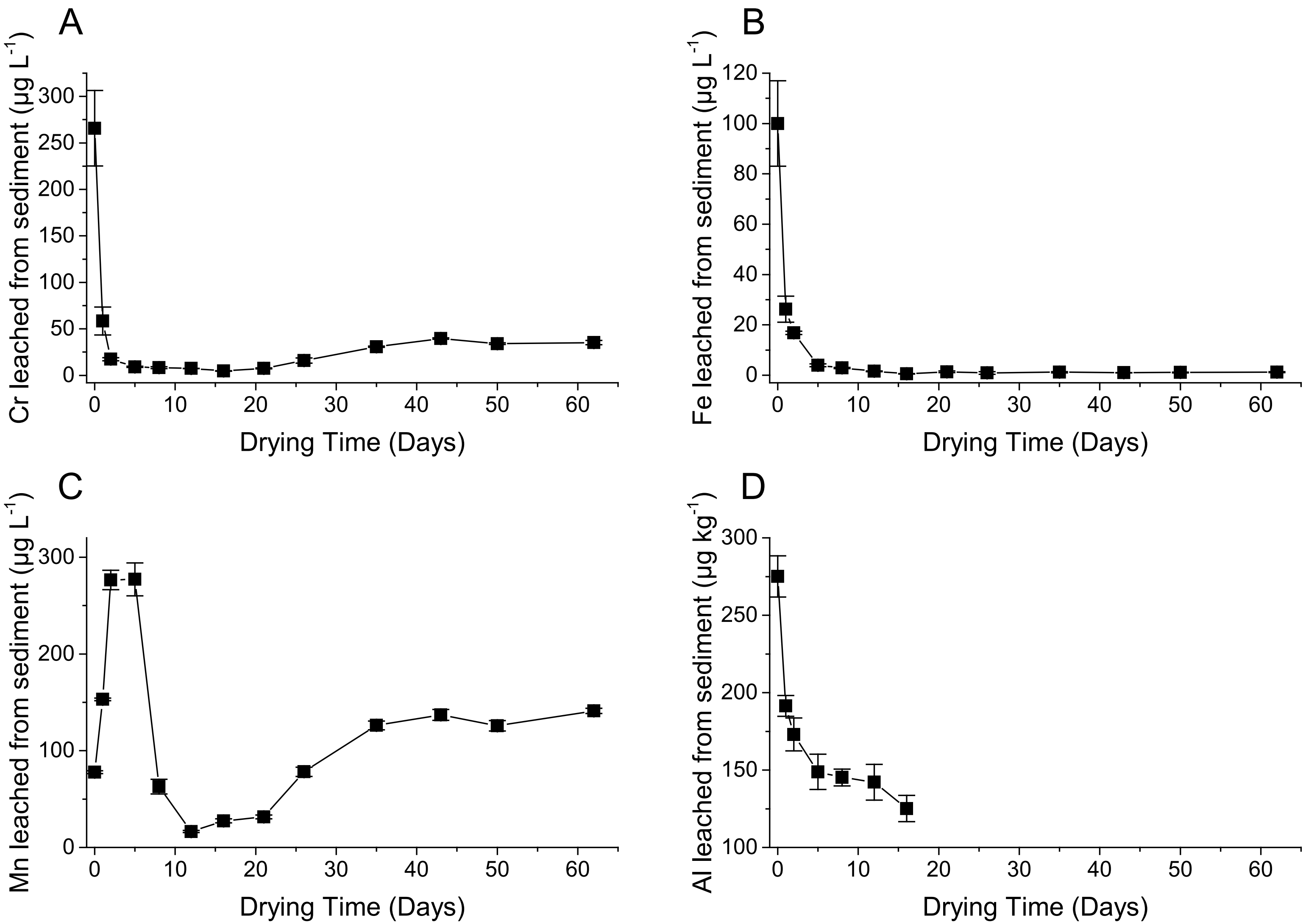

Figure 5-23: Concentration of (A) Cr, (B) Fe, (C) Mn and (D) Al leached from sediment over a drying time of 62 days

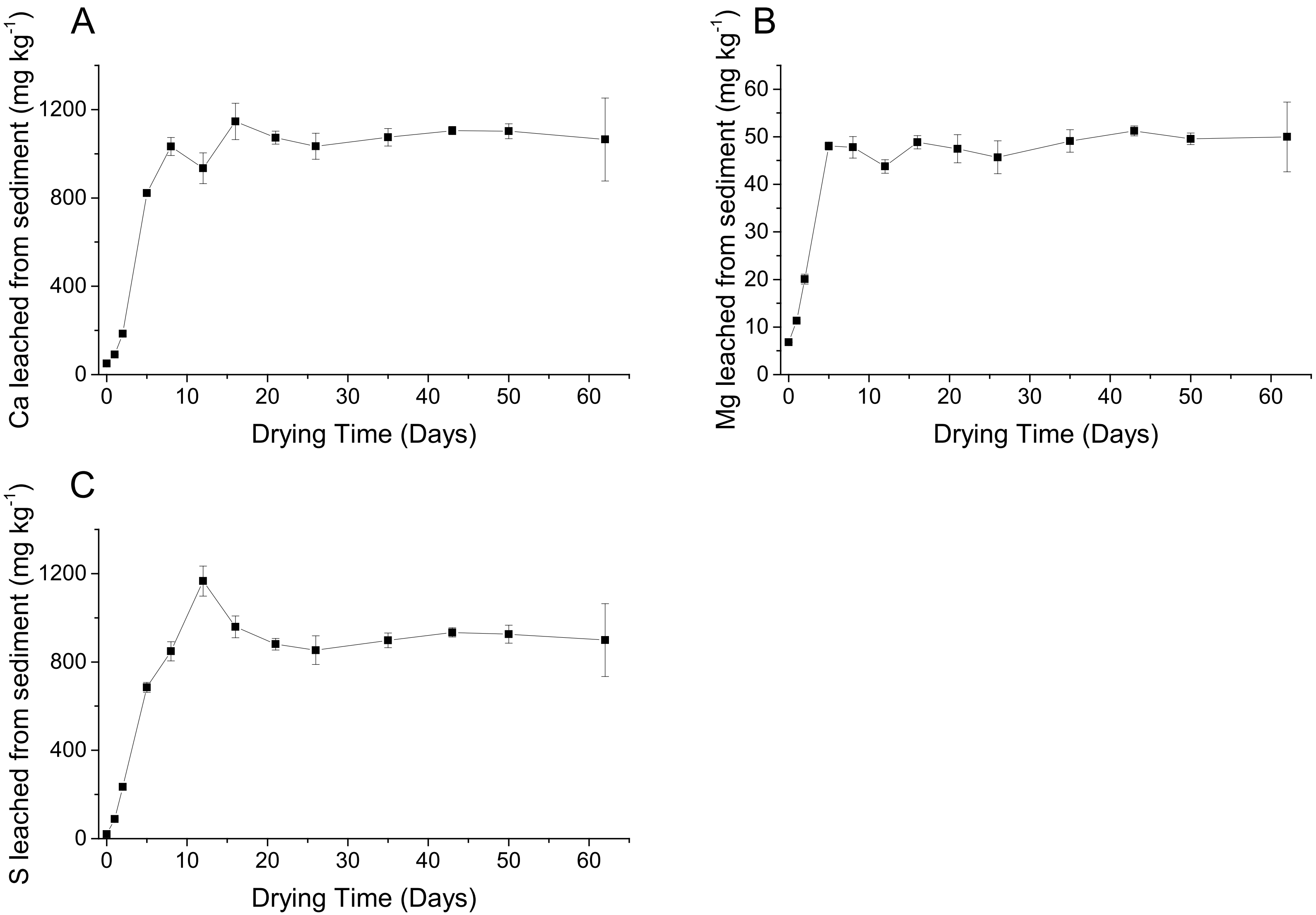

Figure 5-24: Concentration of (A) Ca, (B) Mg and (C) S leached from sediment over a drying time of 62 days

5.4.5 Discussion of batch leaching results for Polmadie Burn Banking Soils and Bottom Sediments

5.4.5.1 Moisture content of soils and sediments

The moisture retained in the soil was approximately double that of the sediment after the initial sieving to remove large stones, plant material and rags. This is due to the higher OM content of the banking soils allowing them to retain water much more effectively than the bottom sediment consequently, the soil did not reach a constant moisture content until air-drying for 62 days. The sediment, on the other hand, reached a constant moisture content after 21 days of drying.

Drying of soils and sediments can lead to changes in their physical and chemical properties. An example of changes in the physical properties of soils is the formation of aggregates during drying along with the disruption of organic matter. A review by Kaiser *et al* reports that air-drying of soil can result in organic matter sticking to aggregates. As the water content decreases in the soil the water tension decreases resulting in charged particles being able to interact more easily leading to deposition of these particles on other surfaces (Kaiser *et al.*, 2015). They also found that air-drying of soils can result in a strengthening of the interactions between the organic matter and the surfaces to which it is bound. This is due to the change in bonding from outer-sphere to inner-sphere bonding as the moisture content decreases. Since Cr and Fe have been shown to be associated, using gel electrophoresis, the immobilisation of labile organic matter will result in lower concentrations of these metals in the leachate (Gu *et al.*, 1995).

Chemical changes in the banking and bottom sediments usually involved the precipitation or dissolution of metals due to changes in the oxidation state. The banking soil, which are already mildly oxic, were not affected as much by the change in redox potential as the bottom sediments. The sediments, which were originally black in colour, changed to a grey colour which can be attributed to the oxidation of Fe sulfide to Fe hydroxides. An increase in leachable S concentrations and decrease in leachate pH also occurred as drying time increases. The increase in redox potential will also affect the speciation of other redox sensitive metals, such as Fe and Mn. The oxidation of these metals and their influence on leachable Cr concentrations is discussed below.

5.4.5.2 Oxidation of chromium in drying soil and sediment

The column leaching experiments showed that the Cr(III) associated with colloidal material was important in the mobility of Cr in the Polmadie banking soil and bottom sediments. This was also observed in the soil batch leachate with the positive correlation of Cr(III), Fe, Mn and

Al which are hypothesised to be in the leachate associated with colloidal material, for the reasons discussed in Section 5.3.3.2.

The main trend observed in the column leaching experiment was the decrease followed by the increase in the Cr and Mn leachate concentrations as the soil drying time increased (Figure 5-8 and Figure 5-13B). The same trend was observed for Cr in the sediment column leachate. Due to the relatively large time gaps between drying time the exact mechanism could not be determined. The higher resolution of the batch leaching experiment due to the more frequent sampling allowed a better insight into this mechanism. When considering the sediment batch experiment leachate concentrations of Cr, Fe and Mn, there appear to be three different responses during the drying process (Figure 5-25). Initially, in Stage 1 over the first 12 days of drying leachable Cr and Fe concentrations rapidly decreased to a constant level. This is probably due to the reduction of leachable OM as the sediment dries, resulting in the much lower concentrations of Cr and Fe observed in the batch sediment leachate as drying time increases as shown in Section 5.3.3.2.1. (Gu *et al.*, 1995, Dultz *et al.*, 2018, Arce *et al.*, 2017) Manganese(II), which is stable in moderately oxidising conditions, and does not strongly bind to organic matter, will persist longer in the sediment hence the longer drying period required to reach the minimum leachable Mn concentrations. In Stage 2, between days 12 and 21 the leachable concentrations of Cr, Fe and Mn remain low and the moisture content of the sediment reaches its minimum.

In Stage 3 the concentration of leachable Cr and Mn concentrations increase along with a change in the speciation of Cr in the leachate from Cr(III) to Cr(VI). This provides evidence for the mechanism proposed in Section 5.3.3.2.2 where freshly precipitated Mn(IV) oxides oxidise Cr(III) to Cr(VI) on rewetting. During Stage 3 the Fe and moisture content of the sediment remain constant indicating that the re-release of Cr-Fe-OM complexes, from dissolution of Fe phases which contain Cr or the release of Fe-Cr colloids, is not the reason for the increase in Cr leachability.

The same trends were not observed in the soil batch experiment leachate with increasing drying time. This could be due to the difference in moisture content of the two matrices, although soils which have a high OM content and low Mn concentrations, such as the banking soils, generally have much lower Cr(III) oxidising potential than soils/sediments with low OM content and high Mn concentrations. The water holding and retention capacity of the banking soil is much greater than the bottom sediments, due to the reasons discussed above, which required a longer drying time before the soil to reach a constant moisture content. When considering the drying period of 43 to 62 days of drying there was an increase in the Cr(VI) and Mn concentrations in the soil batch leachate but not in Cr(III) or Fe leachate concentrations. A longer period of drying would be required to confirm this trend but the oxidation of Cr(III) in dried bottom sediments is more likely that in the highly organic banking soil.

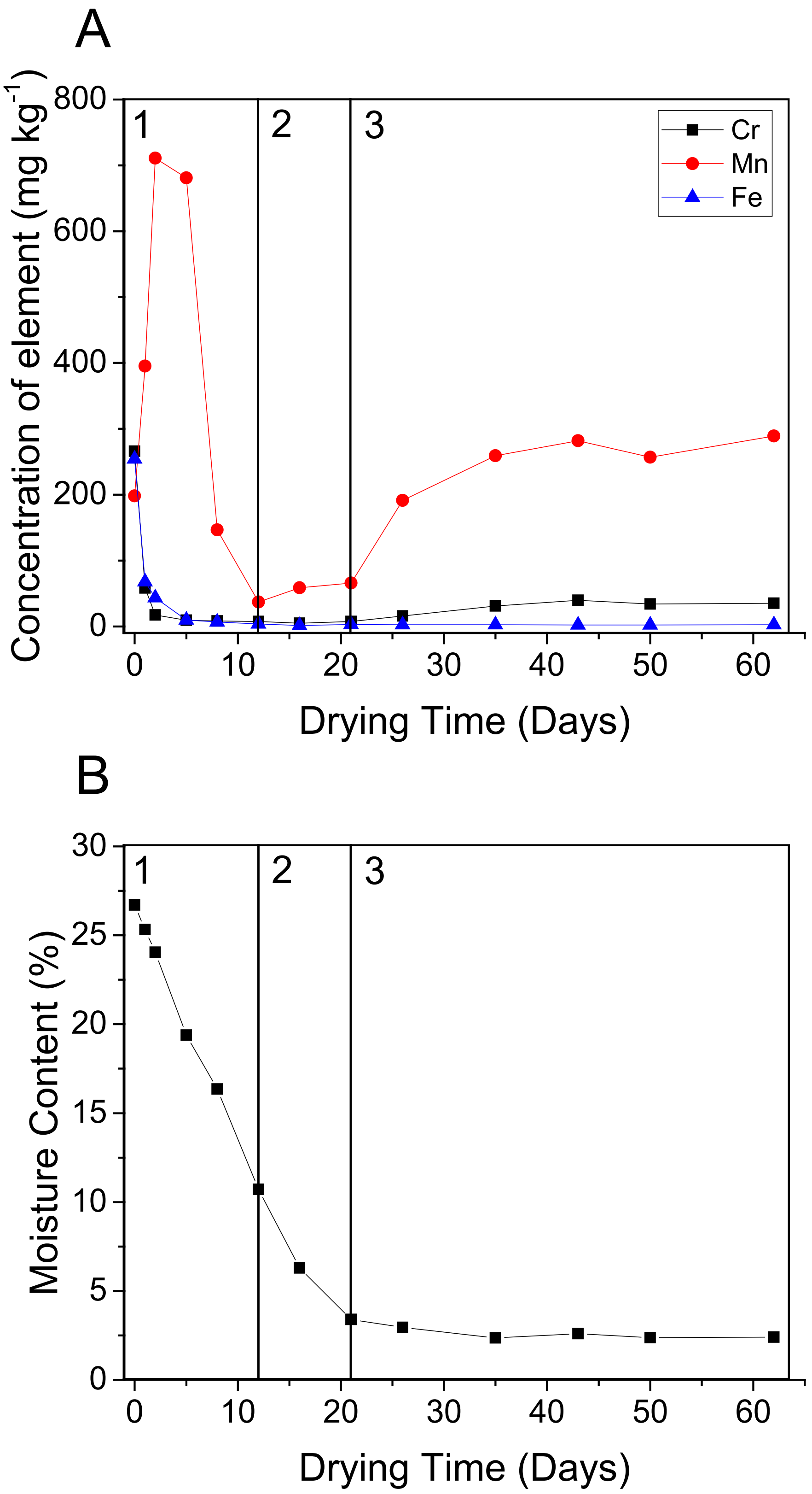

Figure 5-25: (A) Leachable Cr, Fe and Mn concentrations and (B) moisture content of sediment as drying time increases

5.4.6 Summary

Like the column drying experiment there was a significant larger concentration of Cr leached from the banking soil compared to the bottom sediment. As drying time increased the concentration of Cr(III) and Cr(VI) in the leachate upon rewetting tended to decrease. The soil batch leachate Cr(III) concentrations were positively correlated with Fe, Mn and Al. At pH > 5 Cr(III) is very insoluble, therefore its presence in the leachate is due associations with colloidal material and OM. As soil dries the disruption of OM and the formation of aggregates will decrease the leachability of Cr(III). Leachate Cr(VI) concentrations also tended to decrease as drying time increased, leading to an overall reduction of Cr released upon rewetting as drying time of soil increases.

The release of Cr upon rewetting of sediment dried for different lengths of time showed a different trend to the soils. The increase in redox potential as the sediment dries leads to the oxidation of Fe and Mn which precipitate to form Fe and Mn(IV) oxides. The freshly precipitated Mn(IV) oxides oxidise Cr(III) upon rewetting resulting in the release of Cr(VI) and Mn(II). This process was not seen in the air-dried soils which contained high OM content and low Mn concentrations which have been shown in the literature to have a low oxidation potential for Cr(III).

5.5 Chromium(VI) removal from solution by banking soil

As discussed in Section 5.1 above, there are proposals to divert the flow of water from the Polmadie Burn which may result in the banking soils experiencing increasingly drier conditions as the water level in the Burn drops. . However, the more severe weather conditions including more violent storms predicted under most climate change scenarios may lead to flooding of low lying areas. Indeed SEPA has identified several areas within the Clyde Valley Basin which are already vulnerable to flooding and these include the study area for this project (Figure 5-26). If severe storms do occur, the banking soils, which are typically at an elevation of only 15 m above mean sea level, may become flooded. Since there is much COPR contamination of the surrounding area and typically ~25% Cr in COPR is in the form of Cr(VI), the banking soils may be impacted by Cr(VI)-contaminated flood waters. This section explores the fate of Cr(VI) in waters that flood the banking soil by simulating the exposure of banking soil to Cr(VI) solutions of various concentrations. The aim of this section is to determine the amount of Cr(VI) that can be adsorbed by the Polmadie banking soil and to investigate the rate as well as the reversibility of the adsorption process.

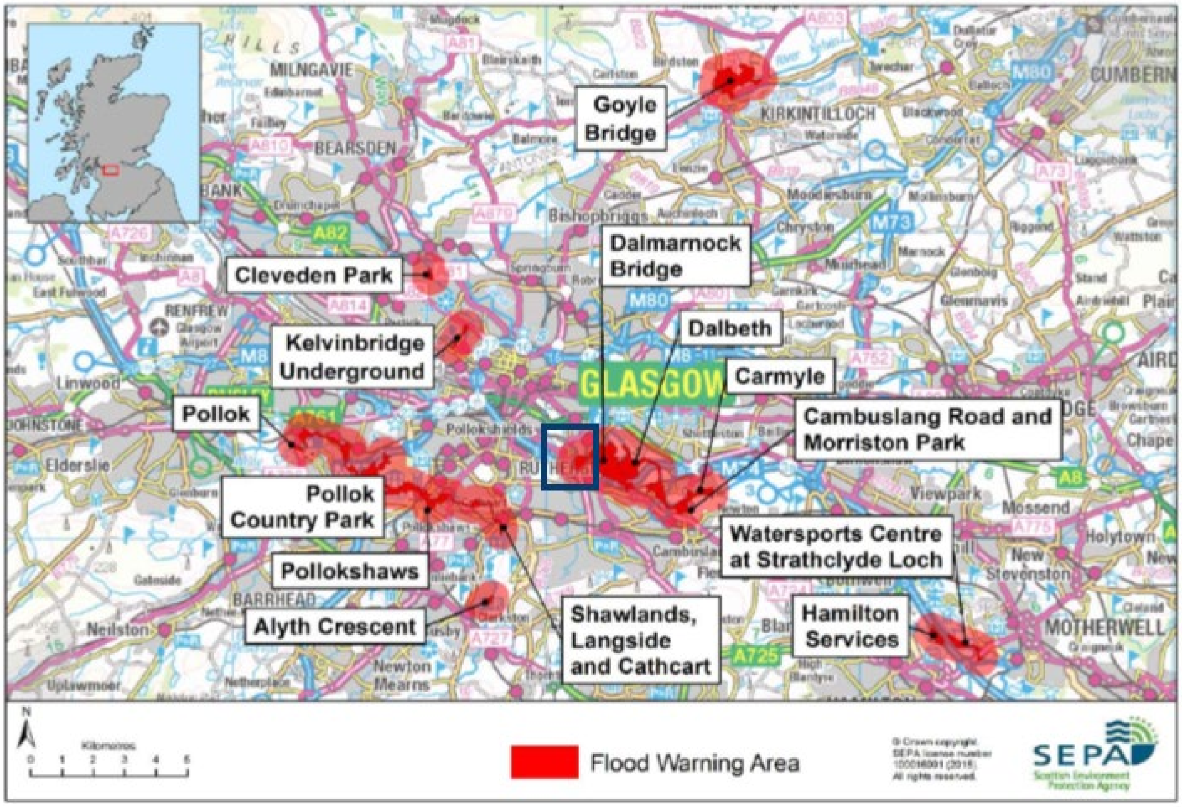

Figure 5-26: Areas at risk of flooding in Glasgow. The blue box shows the Polmadie Burn. (http://apps.sepa.org.uk/FRMStrategies/pdf/lpd/LPD_11_Sources.pdf)

From the data presented so far it has been shown that Cr is not readily released from the banking soil. In these experiments, banking soils were exposed to “flood simulation solutions” containing different concentrations of Cr(VI) and it was hypothesised that a low proportion of the added Cr(VI) would be adsorbed to the soil because of the near-neutral to slightly alkaline pH which does not favour Cr(VI) retention. If, however, Cr(VI) were to be removed from solution, the main reason would be reduction of Cr(VI) to Cr(III) by organic matter. Retention in the solid phase would then occur either through complexation by organic matter or precipitate as Cr/Fe hydroxides.

5.5.1 Overview of sampling and method

Approximately 5 kg of soil was collected on the 16th April 2018 and then passed through a 2 mm sieve. To investigate the loading of Cr onto soil, 10 g portions of the field-moist sieved soil were weighed into a series of 50 mL centrifuge tubes. As a control, one set of tubes simply contained the soil in 20 mL of 0.1 M $CaCl_2$ leaching solution which were shaken for different time periods (1, 2, 4, 8, 16, 24, 48, 96 and 120 h; three tubes per time period). To gain an insight into the capacity of the soil to sorb Cr(VI), 10 g of field-moist soil was shaken with a Cr(VI) spiked 0.1 M $CaCl_2$ “flood simulation” solution for different time periods. The concentrations of Cr(VI) loading solutions used were 1.4, 10, 50 and 100 mg L^{-1} and the shaking periods were 1, 2, 4, 8, 16, 24, 48 and 120 h. No samples were shaken for 96 h in this experiment due to an oversight during tube labelling in the preparation for this experiment. To investigate the reversibility of the sorption of Cr(VI) to soil, Polmadie Burn banking soil was loaded by shaking 10 g of soil in a 10 mg L^{-1} solution for 48 h before being leached using the same method described for the baseline experiment.

5.5.2 Results for the control experiment (0.01 M calcium chloride only)

To establish the baseline concentrations of Cr released into solution as the shaking time increased the soils were leached with a control solution of 0.01 M $CaCl_2$. The pH of the leachate decreased with shaking time from 7.60 ± 0.032 after 1 h of shaking to 7.03 ± 0.0058 after 96 h of shaking. The pH of the leachate after 120 h of shaking increased to 7.37 ± 0.025 (Figure 5-27).

The Cr(III) concentration released from the banking soil increased with time from 197 ± 32 µg kg^{-1} (dwt) after 1 h of shaking up until 16 h of shaking when 508 ± 70 µg kg^{-1} of Cr(III) was released from the soil. Thereafter, the concentration of Cr in the leachate decreased in a linear fashion until it reached 176 ± 160 µg kg^{-1} after 120 h (Figure 5-28). The release of Cr(VI) concentration followed a similar trend with 139 ± 25 µg kg^{-1} released after 1 h of shaking, increasing to 517 ± 81 µg kg^{-1} after 8 h of shaking. The Cr(VI) concentration then decreased with time to 163 ± 140 µg kg^{-1} after 120 h of shaking (Figure 5-29).

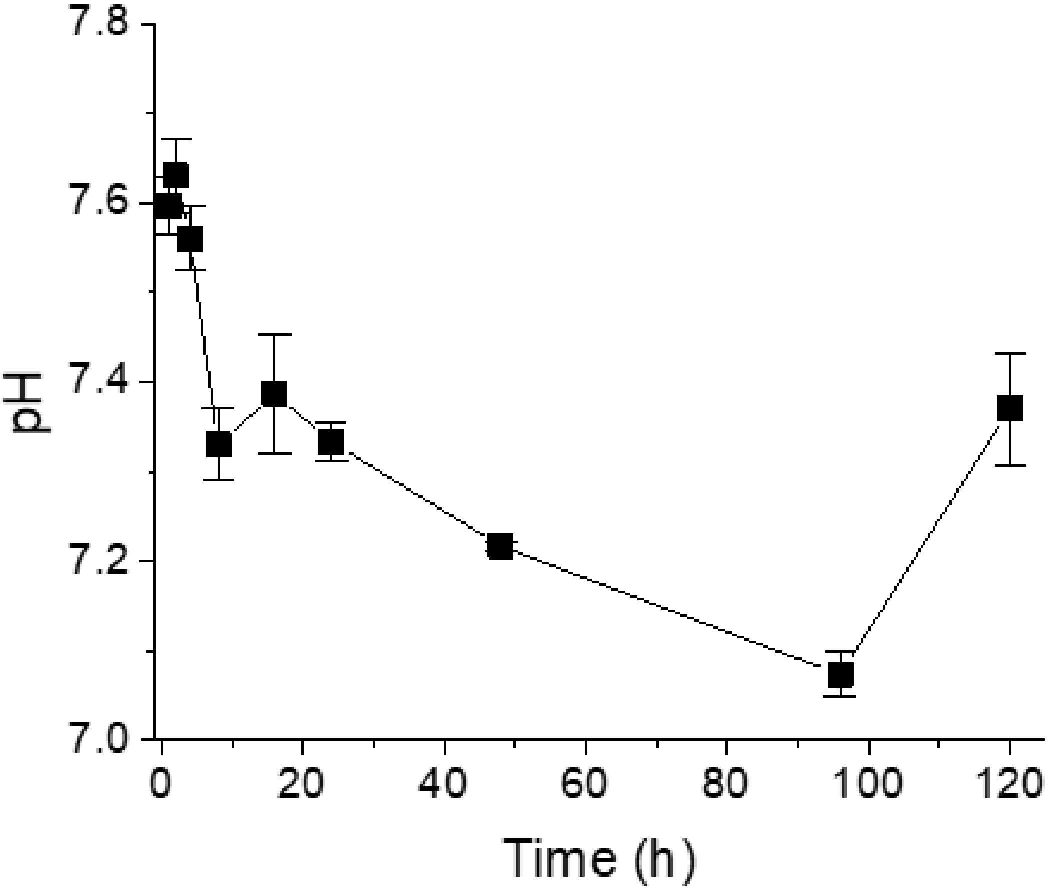

Figure 5-27: Baseline leachate pH variation with shaking time

The same trend described for Cr was observed for Fe, Mn and Al which were directly correlated (Appendix 1) with the (total) Cr concentration released from the soil (Figure 5-30). The concentrations of Ca, Mg and S released from the soil increased with shaking time but did not follow the same trend as Cr, Fe, Mn and Al. Although the concentrations of each of Ca, Mg and S increased over most/all of the experimental period (100 h for Ca, 120 h for Mg and S), there was a stronger correlation between the concentrations of Ca and Mg (Figure 5-31).

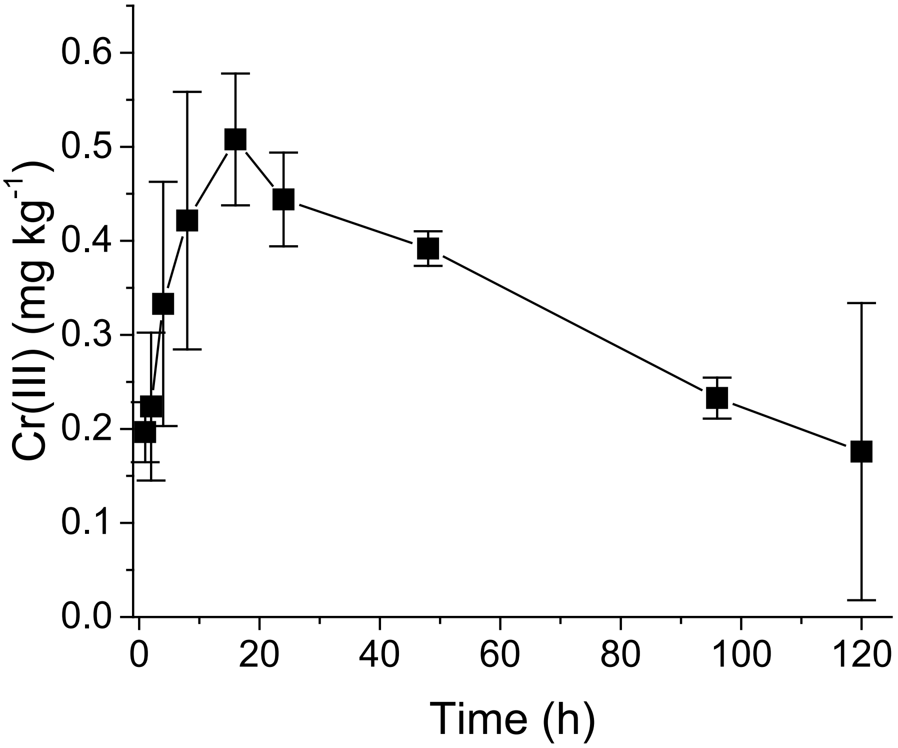

Figure 5-28: Baseline leachate Cr(III) concentration variation with shaking time

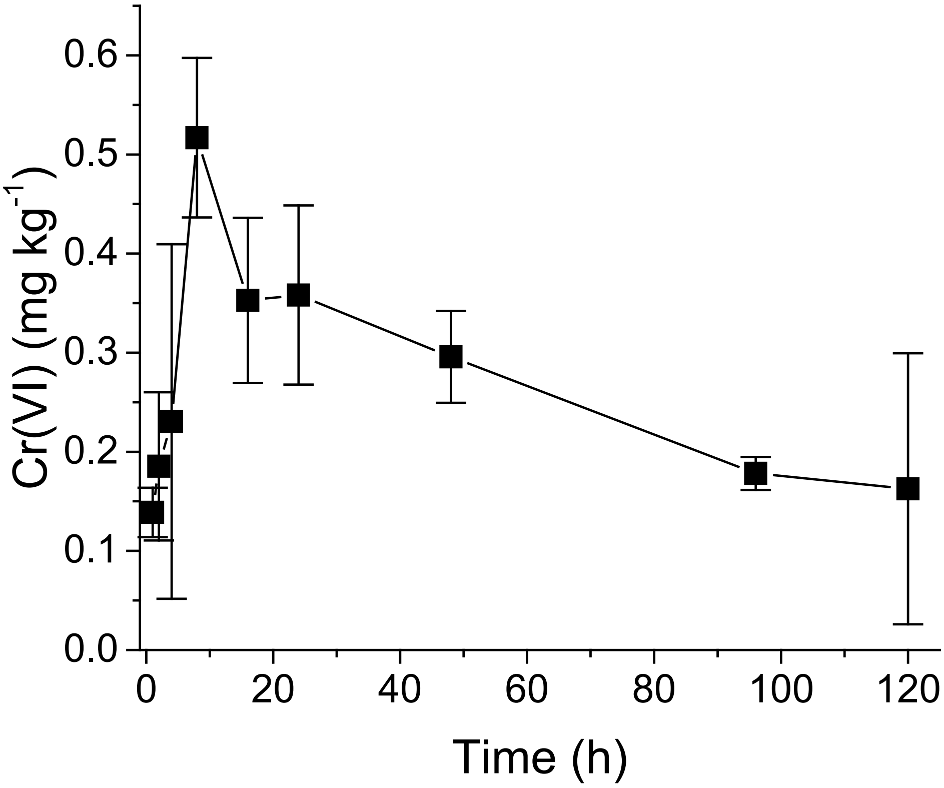

Figure 5-29: Baseline leachate Cr(VI) concentration variation with shaking time

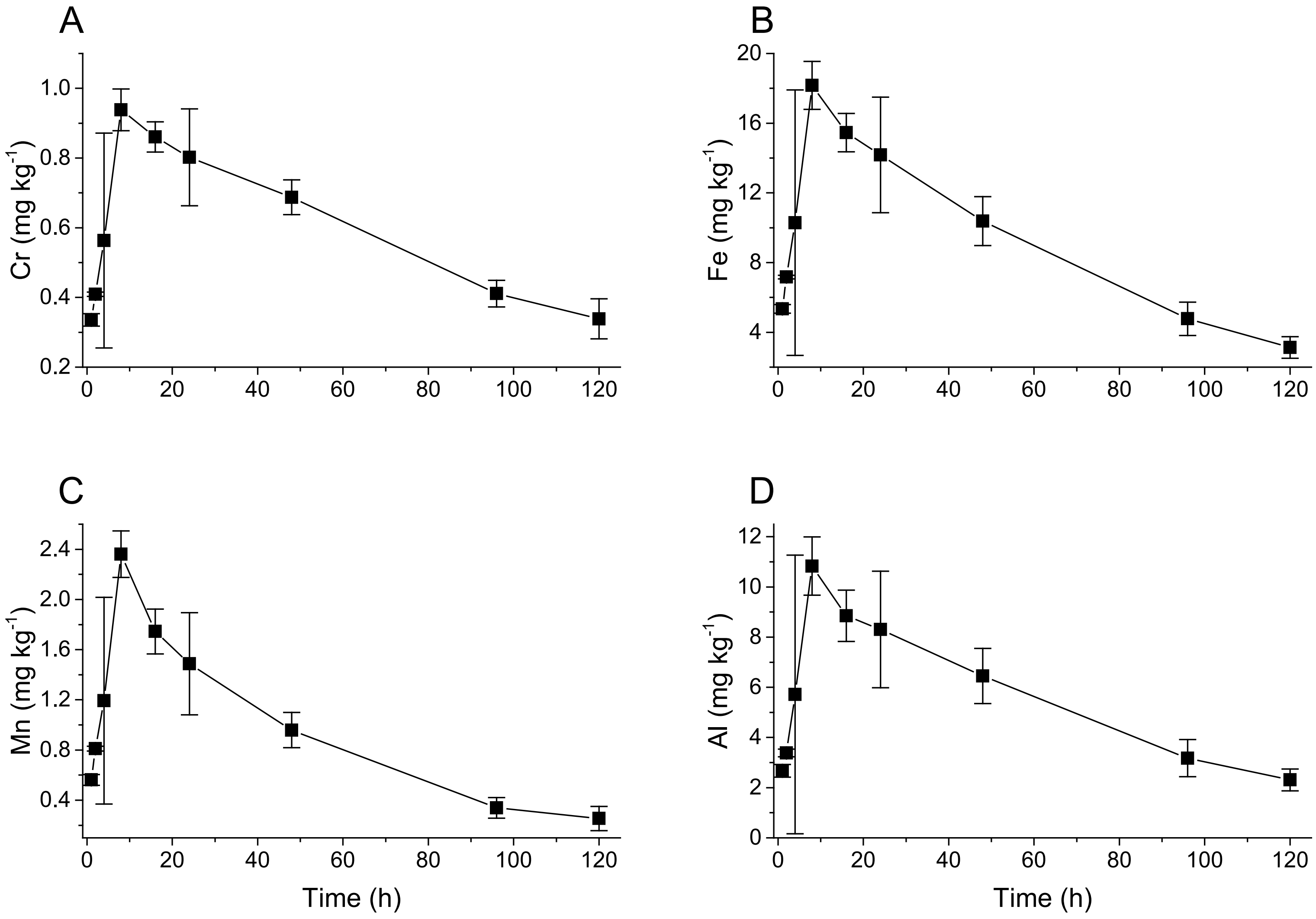

Figure 5-30: Leachate (A) Cr, (B) Fe, (C) Mn and (D) Al concentration variation with shaking time

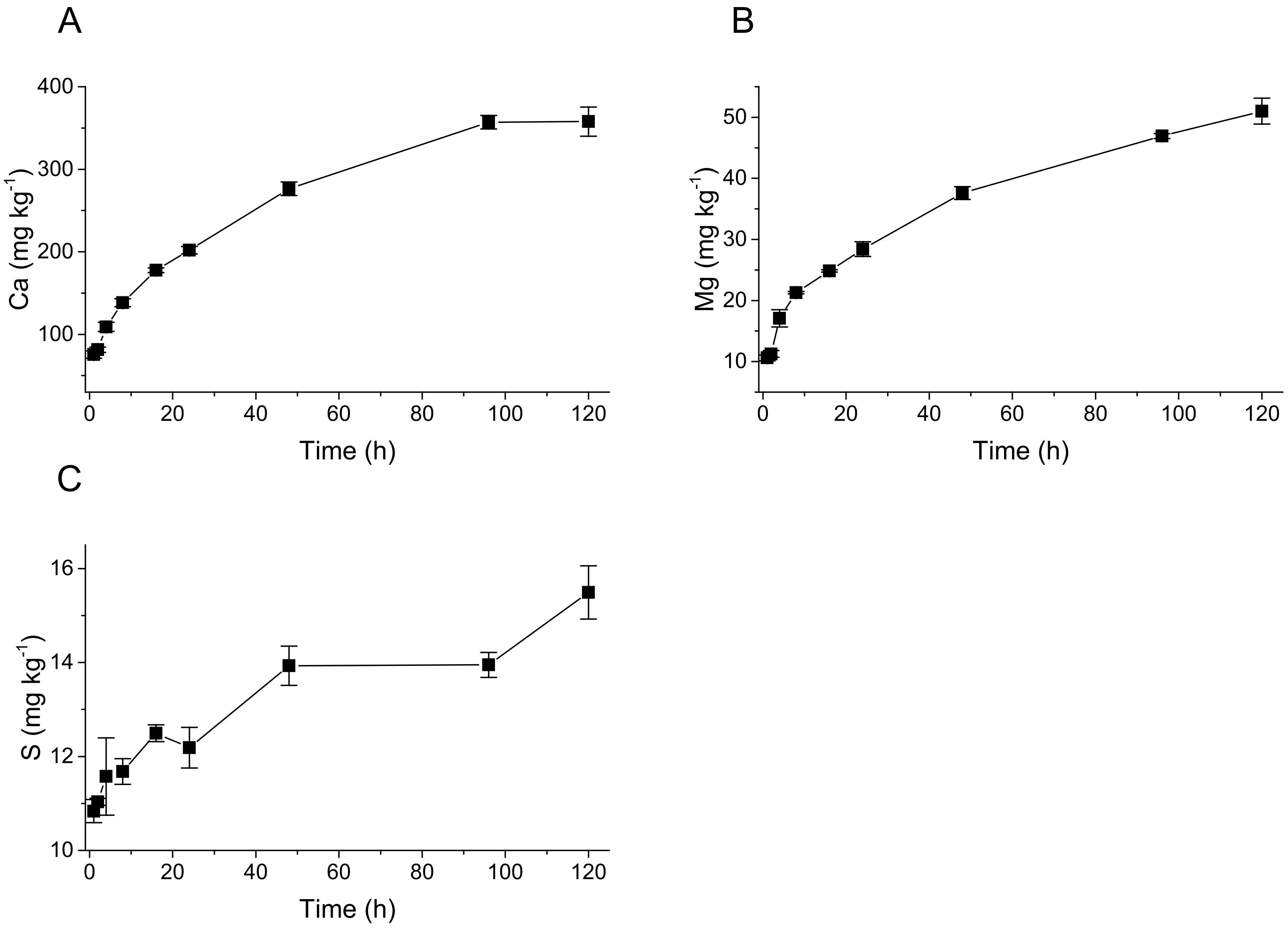

Figure 5-31: Leachate (A) Ca, (B) Mg, and (C) S concentration variation with shaking time

5.5.3 Chromium adsorption and subsequent release

5.5.3.1 *Chromium sorption*

When the Polmadie Burn banking soil was shaken in a 0.01 M $CaCl_2$ solution spiked with various concentrations of Cr(VI), the concentration of Cr(VI) sorbed increased almost exponentially. After shaking Polmadie banking soils for 48 h in a 1.4, 10, 50 and 100 mg L^{-1} Cr(VI) solution, 97.1 ± 0.30, 95.4 ± 2.51, 66.8 ± 6.9 and 60.7 ± 5.6% of the Cr(VI), respectively, was adsorbed by the soil. This increased to 97.9 ± 0.25, 99.6 ± 0.054, 93.5 ± 3.7 and 83.7 ± 3.0% of the Cr(VI) removed from solution in the 1.4, 10, 50 and 100 mg L^{-1} Cr(VI) solutions, respectively, after 120 h (Figure 5-32). The leachate pH and the concentration of Fe, Mn, Al, Ca, Mg and S followed the same patterns seen in the baseline.

5.5.3.2 *Chromium release*

To examine the reversibility of Cr sorption to the soil, soil was shaken with a 0.01 M $CaCl_2$ solution spiked with 10 mg L^{-1} of Cr(VI) for 48 h as the majority of Cr(VI) had been removed by this time. After 48 h the liquid was separated from the soil using centrifugation, as described above, and the soil was subsequently leached following the same procedure outlined for the baseline.

The mean concentration of Cr(VI) loaded onto the soil was 40.0 ± 1.6 mg kg^{-1}. Over the leaching period of 1 – 120 h, the leaching pattern for Cr(III) and Cr(VI) followed the same trend as the control Cr(III) and Cr(VI) concentrations (Figure 5-33 and Figure 5-34). There was a small increase in the leachable Cr(VI) concentrations (0.789 ± 0.093 mg kg^{-1} compared to 0.231 ± 0.18 mg kg^{-1} for the control) from soil that had been loaded with ~40 mg kg^{-1} of Cr(VI) suggesting that only a small amount of Cr(VI) that had been removed to the soil solid phase could be re-released. Thus the majority (>98%) of added Cr(VI) was held irreversibly by the soil. For both the control and the spiked soils, the maximum released occurred after ~120 h of shaking. The decrease in the amount leached over the longer time periods suggests that the Cr(VI) that was initially released was then returned to the soil solid phase. In contrast with the Cr(VI) results, there did not appear to be an increase in Cr(III) released from the loaded soil (Figure 5-33). Thus the additional Cr released from the loaded soil was all in the form of Cr(VI). The mean difference in Cr(VI) released from the spiked compared with the control soil was 298 ± 170 µg kg^{-1}. This corresponded to 0.74 ± 0.4% of the Cr(VI) adsorbed to the soil.

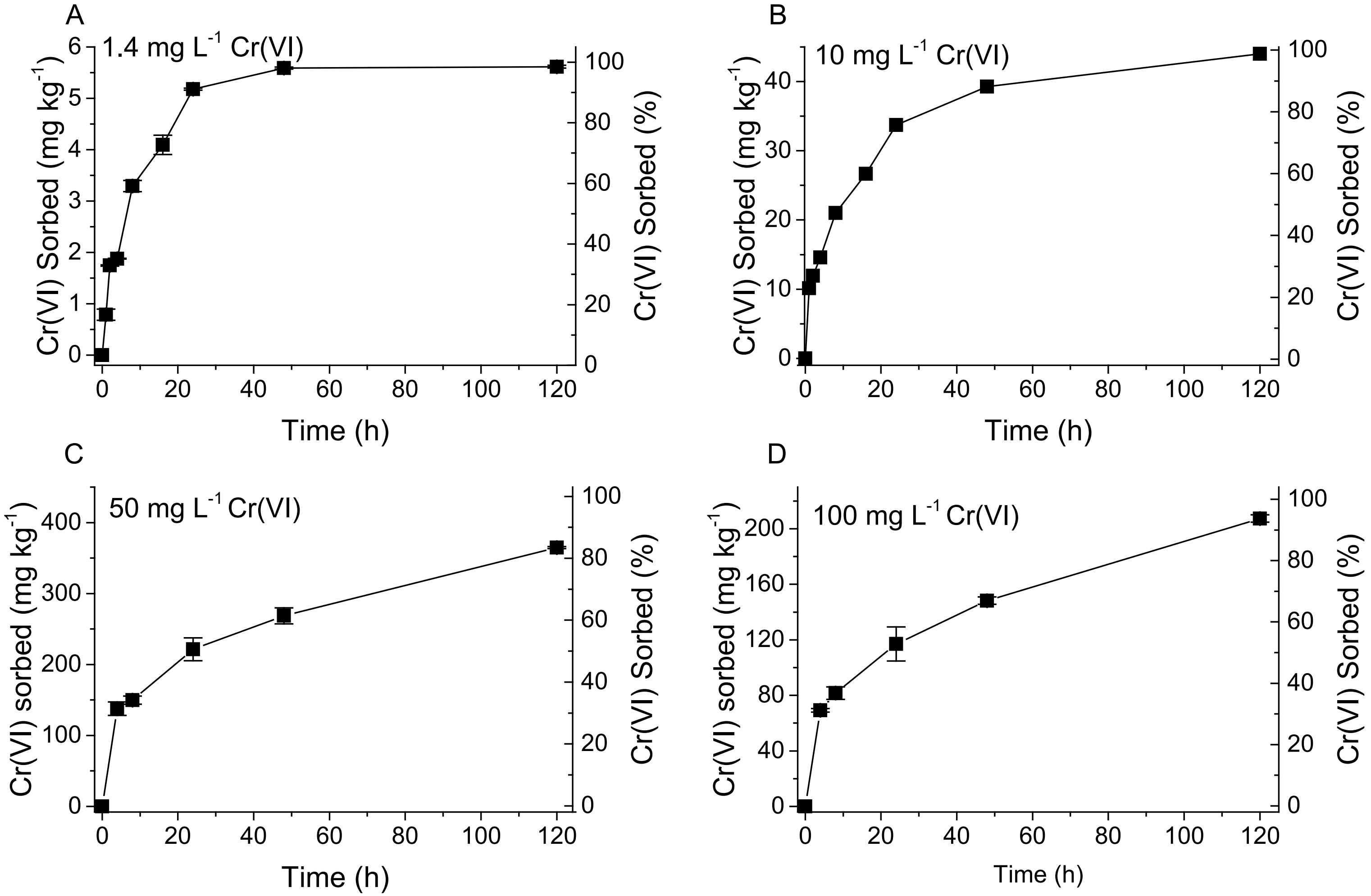

Figure 5-32: Cr(VI) sorption to soil shaken in (A) 1.4, (B) 10, (C) 50 and (D) 100 mg Cr(VI) L^{-1} loading solution

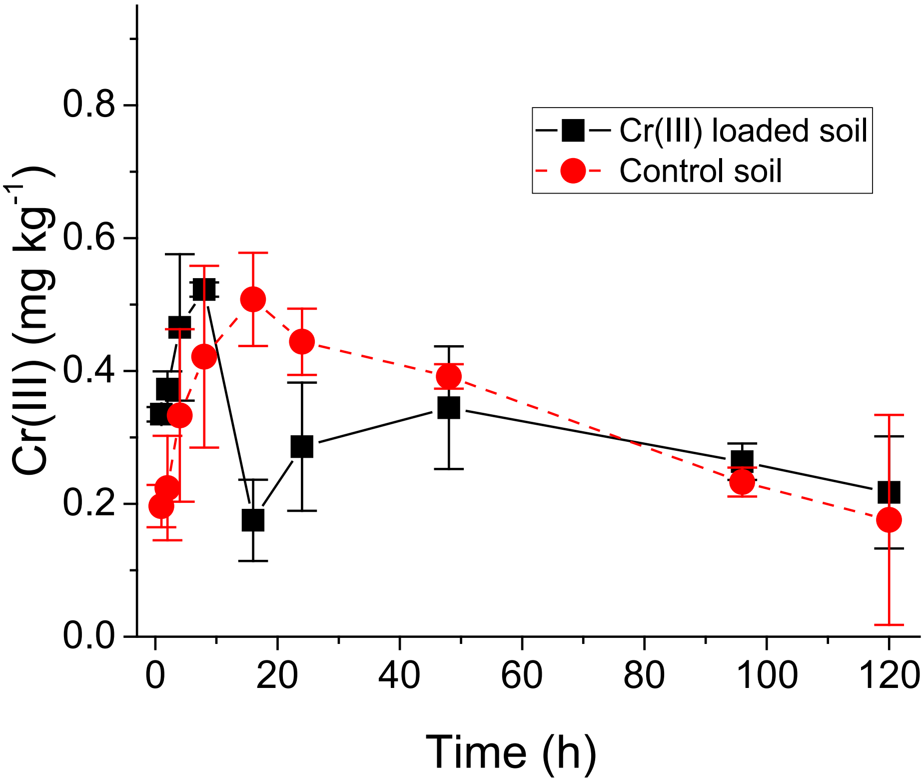

Figure 5-33: Cr(III) release from Cr(III) loaded soil and control soil

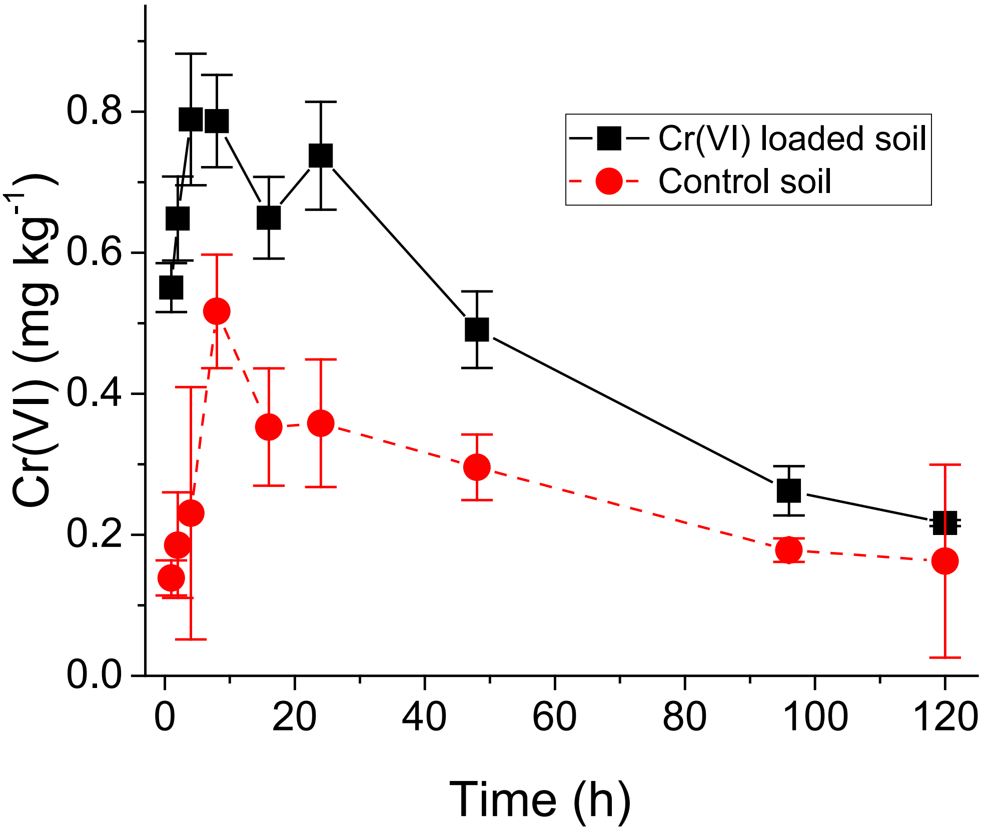

Figure 5-34: Cr(VI) release from Cr(VI) loaded soil and control soil

5.5.4 Kinetic modelling

The removal of Cr(VI) from solution can be described in simple terms in Equation 5.5 and the rate of this reaction can be described in Equation 5.6 where $Cr(VI)_{aq}$ is dissolved Cr(VI), $Cr(VI)_{sorbed}$ is Cr(VI) sorbed onto the soil surface, $\frac{d[Cr(VI)]}{dt}$ is the change in Cr(VI) concentration with time (reaction rate), k is the reaction constant, $[Cr(VI)_{aq}]$ is the Cr(VI) concentration in solution and x is the order of reaction with respect to Cr(VI).

$$Cr(VI)_{aq} \rightarrow Cr(VI)_{sorbed} \qquad \text{Equation 5.5}$$

$$\frac{d[Cr(VI)_{aq}]}{dt} = -k[Cr(VI)_{aq}]^{x} \qquad \text{Equation 5.6}$$

To model the rate of removal of Cr(VI) from solution, zero, first and second order rate (x = 0, 1 or 2, respectively) simple mathematical models can be used as described in Equations 5.7, 5.8 and 5.9 below where $[Cr(VI)]_t$ is the concentration of Cr(VI) in solution at time t, $[Cr(VI)]_0$ is the initial concentration of Cr(VI) in solution at time t=0 and k_0, k_1 and k_2 are the reaction constants for the zero, first and second order reactions, respectively. The control values of $[Cr(VI)]_t$ were subtracted from the $[Cr(VI)]_t$ for the 1.4, 10, 50 and 100 mg L^{-1} Cr(VI) solutions to correct for Cr(VI) released from the soil.

Zero Order: $$[Cr(VI)]_t = -k_0 t + [Cr(VI)]_0 \qquad \text{Equation 5.7}$$

First Order: $$\ln[Cr(VI)]_t = -k_1 t + \ln[Cr(VI)]_0 \qquad \text{Equation 5.8}$$

Second Order: $$\frac{1}{[Cr(VI)]_t} = k_2 t + \frac{1}{[Cr(VI)]_0} \qquad \text{Equation 5.9}$$

To determine the contribution of the control concentration to $[Cr(VI)]_t$ Equation 5.10 was used to quantify the percentage of the Cr(VI) in solution which was attributed by the baseline where $[Cr(VI)]_{control}$ is $[Cr(VI)]_t$ of the control at time t and $[Cr(VI)]_{loading}$ is $[Cr(VI)]_t$ of the loading solution at time t.

$$\%Contribution\ of\ control = \frac{[Cr(VI)]_{control}}{[Cr(VI)]_{loading}} \times 100\% \qquad \text{Equation 5.10}$$

From this it was shown that for $[Cr(VI)]_t$ at t = 8 – 120 h of the 1.4 mg L^{-1} loading solution and $[Cr(VI)]_t$ at t =120 for the 10 mg L^{-1} loading solution, the control concentrations accounted for more than 20% of Cr(VI) in solution so were therefore excluded from the modelling due to the large uncertainties associated with the "corrected" Cr(VI) concentration. The remaining data was then modelled using Equations 5.7, 5.8 and 5.9 and the fit of the model to the data was evaluated using the adjusted R^2 and the difference between the predicted and the measured $[Cr(VI)]_0$ value. The adjusted R^2 gives an indication of how well the curve fitted the data and ranges between 0 and 1, with 1 representing perfect agreement.

Overall, the 1st order model appeared to best fit the 10 and 50 mg L^{-1} loading solutions whilst the 2nd order model appeared to be the best fit for the 100 mg L^{-1} loading solution (Table 5-4, Table 5-5 and Table 5-6). However, due to the nature of the rate equation described in Equation 4.4, the rate constant, k, should be independent of starting concentration. Based on this data set, the 1st order rate constant values decreased as $[Cr(VI)]_0$ increased (10, 50 and 100 mg L^{-1}) and therefore the first order model cannot be used to describe the removal of Cr(VI) from solution. Thus the processes accounting for removal of Cr(VI) from solution to the soil solid phase are more complicated than the simple adsorption of Cr(VI) on to mineral surfaces. The reduction of Cr(VI) by OM is likely playing a key part in Cr(VI) removal and the kinetic mechanism of this reaction must be understood before this can be modelled, which was outside of the scope of this project due to time constraints.

Table 5-4: Summary of zero order kinetics parameters from zero order model

Initial Cr(VI) Concentration (mg L^{-1})	Adj. R^2	k_0 (mg L^{-1} s^{-1})	$[Cr(VI)]_0$ predicted	% difference of true $[Cr(VI)]_0$
10	0.577	0.174 ± 0.029	7.60 ± 0.59	22
50	0.743	0.315 ± 0.080	37.3 ± 4.3	26
100	0.702	0.538 ± 0.15	73.7 ± 8.1	25

Table 5-5: Summary of first order kinetics parameters from first order model

Initial Cr(VI) Concentration (mg L^{-1})	Adj. R^2	k_1 (s^{-1})	$[Cr(VI)]_0$ predicted	% difference of true $[Cr(VI)]_0$
10	0.987	0.0635 ± 0.0027	8.98 ± 0.22	8.1
50	0.981	0.0211 ± 0.0013	41.5 ± 0.79	17
100	0.939	0.0134 ± 0.0015	76.1 ± 1.4	23

Table 5-6: Summary of second order kinetics parameters from second order model

Initial Cr(VI) Concentration (mg L^{-1})	Adj. R^2	k_1 (L mg^{-1} s^{-1})	$[Cr(VI)]_0$ predicted	% difference of true $[Cr(VI)]_0$
10	0.817	0.0480 ± 0.0084	-8.83 ± 13	190
50	0.909	0.00236 ± 0.00033	541 ± 5200	975
100	0.977	0.000416 ± 0.000029	92.3 ± 13	6.1

5.5.5 Discussion of the sorption and release of chromium(VI) from solution by Polmadie banking soil

In contrast with the initial hypothesis, the results for the Cr(VI) adsorption batch experiments show that Cr(VI) is effectively removed from solution when it was shaken with Polmadie banking soil but the rate of this reaction could not be accurately modelled using zero, first or second order kinetics.

There are two mechanisms described in the literature which are important for Cr(VI) removal from solution by soils: i) the adsorption of Cr(VI) by exposed hydroxyl groups on metal hydroxides and ii) the reduction of Cr(VI) and the subsequent precipitation or complexation of Cr(III). Although in the environment Cr(VI) is adsorbed to mineral surfaces which have exposed hydroxyl groups including Fe and Al oxides, this process is limited by the number of adsorption sites and pH. Above pH 6 the adsorption of Cr(VI) to soil minerals decreases sharply to a minimum around pH 8 (Rai et al., 1989). The mean pH of the leachate was 7.36 ± 0.19 so Cr(VI) adsorption is likely to play a minimal part in the removal of Cr(VI) from solution. Mpouras *et al*. (2017) found that the adsorption of Cr(VI) adsorption to soil was constant in the pH range of 4-7 with ~50% of added Cr(VI) adsorbed but this fraction sharply decreased above pH 7 to almost 0 at pH 8.5. The small increase in Cr(VI) released from the Cr(VI) loaded soil compared to the control soil does, however, show that there must have been a small amount of Cr(VI) adsorption. However, it is unlikely that this process plays a major role in the removal of Cr(VI) from solution over the duration of the shaking experiment. It is more likely that a reduction/precipitation reaction is removing Cr(VI) from solution.

The reduction to Cr(III) by Fe(II) would result in the precipitation of mixed Fe/Cr hydroxides which have very low solubility at pH >4.5 (Rai et al., 1989, Papassiopi et al., 2014). However the low concentrations of Fe(II) found in the soil porewater (Section 4.3.2) makes this process unlikely to account for the removal of significant quantities of Cr(VI) from solution. This leaves reduction of Cr(VI) by organic matter as the mechanism which is most likely to lead to the removal of Cr(VI) from the loading solutions. From the literature, this mechanism is especially prevalent in soils with high organic matter content and low Mn concentrations (Kožuh et al., 2000, Reijonen and Hartikainen, 2016). Although many researchers have reported that the reduction of Cr(VI) by dissolved OM is a slow process at neutral pH, Kožuh *et al*. demonstrated that at neutral pH solid organic matter was very effective at reducing Cr(VI) (Kožuh et al., 2000). Their results show that all Cr(VI) in solution was removed after 10 days when up to 50 mg kg^{-1} of Cr(VI) was loaded onto a soil with a high OM content. Chromium(VI) reduced by OM can precipitate as insoluble Cr(III) hydroxides, which will remove Cr from the solution, or be incorporated into OM. Evidence for Cr association with OM complexes in the Polmadie banking soils was already demonstrated by the co-migration of Cr and OM during gel electrophoretic experiments (Section 4.6). Although Cr(III) bound to labile OM may be released back into solution leading to the remobilisation of Cr, the low percentage of Cr(III) leached compared to the soil Cr(III) concentrations in both the column and batch leaching experiments suggests that this is unlikely to result in the remobilisation of significant concentrations of Cr(III). This was further demonstrated by the low concentrations of Cr(III) released during the leaching of loaded soil as there was no difference between the loaded and the control soil (Figure 5-33). Further work investigating the fate of the Cr(VI) which was loaded on the soil is recommended. Alkaline digestion of control and Cr(VI) loaded soil and a HF/HNO_3 digestion would determine the amount, along with the species, of Cr that is sorbed by the soil. Extraction and subsequent analysis of the OM using gel electrophoresis may also give a further insight into the role of OM on sequestering Cr(VI) from solution.

Although no quantitative kinetic data could be gained from the modelling of the removal of Cr(VI) from solution by the soil, it is still important to consider why. This is likely to be due to the complex nature of the process of Cr(VI) reduction by OM. The reaction rate of Cr(VI) with soil fulvic acids (SFA) was determined by Wittbrodt and Palmer (1995) to be dependent on Cr(VI) concentration, SFA concentration, initial Cr(VI) concentration and pH. Although the rate equation described by Wittbrody and Palmer (1995) was for the reduction of Cr(VI) with DOM rather than solid phase soil OM, it indicates that the reaction has many variables and is likely a reason why simple models do not fit the data (Wittbrodt and Palmer, 1995).

In spite of the lack of elucidation of the kinetics of the removal process, it is clear that the soil has a large sorption capacity due to the almost complete removal (>95%) of Cr(VI) from solution after 48 h in the 1.4 and 10 mg L^{-1} loading solutions. These concentrations are comparable to the concentrations that are found in the Polmadie Burn waters (Chapter 4.3.1) and demonstrates that Cr(VI) is not only removed from solution, it is also immobilised by the soil due to the low release of Cr from soils loaded with ~40 mg kg^{-1} of Cr(VI). The maximum amount of Cr(VI) sorbed to the soil was 369 ± 1.5 mg kg^{-1} after 120 h in the 100 mg L^{-1} Cr(VI) loading solution. This value does not reflect the true sorption potential of the soil in the environment which may be much higher than these laboratory suggest. These results show that the soils play an important part in immobilising Cr(VI) in groundwater that flows through them alluding to the possible role of these soils as a natural barrier to reduce and immobilise Cr(VI) in groundwater.

5.6 Conclusions

This chapter has explored the mobility of Cr in Polmadie banking soils and bottom sediments: (i) during prolonged drying spells followed by intense rainfall; and (ii) the adsorption of Cr by the banking soil from stream water during flood events. Banking soil and bottom sediments were air-dried for up 62 days and the mobility of Cr was analysed during rewetting after different drying periods using both column and batch leaching laboratory experiments. To investigate the adsorption of Cr(VI) to banking soil, batch shaking experiments were designed where Cr(VI) loading solutions were used to simulate the immersion of the banking soil by stream water.

5.6.1 Mobility of chromium during rewetting of air-dried banking soil and sediments

From the column and batch leaching experiments it has been established that Cr is not readily released from the soil or sediments upon drying. The maximum percentage of Cr released from soils and sediments was <0.023 and <0.00008%, respectively, of the solid phase concentration and, in general, as drying time increases the leachable Cr(III) and Cr(VI) concentrations decrease. Chromium(III) forms stable complexes with OM and the labile concentration of OM in the soil is important in the release of Cr(III) from the banking soil. As drying time increases the concentration of leachable Cr(III) decreases which is likely to be related to the alteration of OM with drying time. Chromium(VI) was present in all the soil leachates but it is not the dominant species released into solution from the banking soils.This agrees with the literature which reports that the mobility of Cr(III) is dominated by thermodynamically stable Cr(III)-OM complexes in pH neutral soils.

Less Cr was released from bottom sediments compared to Cr from soils. The highly reducing environment of the sediment with high Fe(II) concentrations has a large reduction capacity for Cr(VI) to Cr(III) which is likely to precipitate as insoluble mixed Fe/Cr hydroxides and also be bound to OM. The lower concentrations of labile OM in the sediment results in the lower leachability of Cr from the sediments, but, by using gel electrophoresis, Cr(III) was shown to be associated with small highly mobile organic molecules. During drying, once the sediments reached a constant moisture content, the oxidation of Mn(II) and its subsequent precipitation to form Mn(IV) oxides allowed the oxidation of Cr(III) to Cr(VI) upon rewetting which is seen by the increase in Cr and Mn released from air-dried sediment. This was also accompanied by a change in the Cr speciation released, from exclusively Cr(III) in fresh sediment, to Cr(VI) after reaching constant moisture content.

5.6.2 Removal of chromium(VI) form solution by banking soil

The banking soils have shown the ability to irreversibly remove Cr(VI) from solution when they were shaken in Cr(VI) loading solutions of up to 100 mg L^{-1}. This experiment showed that after 120 h over 93% of Cr(VI) was removed from 1.4, 10 and 50 mg L^{-1} Cr(VI) loading solutions and over 83% of the Cr(VI) was removed from a solution containing 100 mg L^{-1} Cr(VI). The sorption of Cr(VI) from solution could not be modelled using zero, first or second order kinetics suggesting that the process is more complex than a simple adsorption of Cr(VI) to the soil surface. Up to 2% of Cr(VI) adsorbed during the loading of 40 mg kg^{-1} of Cr(VI) to banking soil was released during leaching with 0.01 M $CaCl_2$ solution. The Cr(VI) that was released appeared to be re-adsorbed by the end of the 120 h shaking period. This suggests that the removal of Cr(VI) from solution was not a simple adsorption process. It is therefore hypothesised that the main Cr(VI) removal mechanism was through the reduction of Cr(VI) by organic matter. The fate of the reduced Cr(VI) is most likely to be incorporation into OM to form Cr(III)-OM complexes or by the precipitation of Cr(III) hydroxides.

The rate equation for the reduction of Cr(VI) by DOM has been shown to be dependent on multiple factors, such as the Cr(VI) concentration, DOM concentration, initial Cr(VI) concentration and the pH. The results of this study show that the removal of Cr(VI) could be explained by a simple zero, first or second order rate model and further work is needed to more fully characterise the likely role of solid phase soil organic matter in this process.. Although kinetic data could not be obtained, the maximum sorption capacity of the soil observed was 369 ± 1.5 mg kg^{-1} but the true maximum sorption capacity is certainly larger than this although impossible to predict from the data. This shows the potential of the Polmadie banking soil to act as a natural barrier which is able to remove Cr(VI) from groundwater. Therefore it is likely these soils play a part in reducing the Cr(VI) concentrations entering the Polmadie Burn rather than acting as a source.

6 Bioaccessibility of chromium in the <10 µm fraction of banking soils

6.1 Background

The toxicity of Cr(III) is vastly different from Cr(VI) as Cr(III) is an essential micronutrient whereas exposure to Cr(VI) can result in a number of health effects as described in Section 1.5. Although acute exposure to Cr(VI) is relatively rare, chronic exposure to Cr(VI) can cause contact dermatitis, skin irritation and the development of cancer, most notably lung cancer (WHO, 2000). This is because Cr(VI) has the ability to efficiently cross the cell membrane where it is subsequently reduced to Cr(III). The product Cr(III) can interact with DNA to cause mutation along with the Cr(VI) reduction which produces the reactive intermediates, Cr(V) and Cr(IV), causing further damage to tissue and DNA (USEPA, 1998).

Although the people who are most at risk from chronic health effects are those who work with Cr and its chemicals, chronic exposure to low environmental concentrations of Cr(VI) has the potential to increase an individual's lifetime risk of cancer (WHO, 2000). Exposure may result from "contact" with Cr-containing industrial materials/wastes/contaminated soils, Cr(VI)-contaminated water, or food contaminated with Cr(VI). In the UK, contact with Cr-containing materials/waste and, in particular, exposure to contaminated soil, is typically the most important exposure pathways and is generally the most likely risk for people who live near industries that use or produce Cr-containing materials, or who live near Cr waste disposal sites. Exposure to Cr(VI) in contaminated soils can occur in three was: i) dermal contact; ii) ingestion; and iii) inhalation. Dermal contact can occur through activities such as gardening and playing. Children are likely to experience greater exposure than adults because play activities bring them into greater contact with soil (Science Communication Unit, 2013, Nielsen and Kristiansen, 2004). For this reason also, children are known to consume more soil than adults, via hand to mouth contact. In addition, ingestion can occur in adults and children by inadvertent swallowing of dust and by soil stuck to food produce as well as by eating vegetables grown on contaminated land (Environment Agency, 2009b). The inhalation of dust can happen via the breathing in of suspended soil dusts. An important factor to consider is also the track back of soil into homes where it dries making the resuspension of Cr contaminated soil more likely (Environment Agency, 2009c).

It is important to recognise that the concentrations of Cr(VI) found in environmental matrices such as dusts, soils/sediments and water do not necessarily reflect the percentage of Cr absorbed by the body (Broadway *et al.*, 2010, Jardine *et al.*, 2013). In order to determine the health risks for those living in, working in and visiting areas which contain elevated concentrations of Cr(VI), the exposure route must be considered along with the threshold concentrations, which result in detrimental health. Once the level of unacceptable risk has been determined, tests to determine the potential exposure to contaminants, such as Cr(VI), can be carried out to evaluate if an area is safe to be used for its specified purpose. This section discusses the methods used to assess the health risks of contaminants in soils, before evaluating the inhalation bioaccessibility of Cr in the Polmadie banking soils. Finally, the results from the bioaccessibility experiment are discussed with respect to the current guidelines and the health of those living in and visiting this area of Glasgow.

6.2 Risk assessment of soils in the UK

6.2.1 Definition of contaminated land

As set out in the Environmental Protection Act 1990 Part IIA, land is defined as contaminated in the UK if: i) it poses a significant risk to human health, property or protected species: ii) there is significant pollution of water (surface or ground); or iii) it will cause harm due to radioactivity. Once land has been identified as potentially contaminated it must be remediated to lower the risk to acceptable levels before the site can be developed for its intended use. Most land that is deemed to be potentially contaminated is remediated during the planning process and there are relatively few sites in the UK that are classed as contaminated land. To determine if the risk is significant, socio-political judgement is required and this takes into account the overarching effects of the pollution and defines what society believes is acceptable risk (Environmental Protection Act, 1990, Environment Agency, 2009c).

6.2.2 Assessment of soils for contamination

In UK soils, risk to human health is assessed via the Contaminated Land Exposure Assessment (CLEA) model, which was developed by the Environment Agency (EA) (Environment Agency, 2009c). In Scotland, the Scottish Environment Protection Agency (SEPA), the regulatory body tasked with protecting and improving the environment, has broadly adopted the CLEA model for assessing land contamination. The approach to assessing land contamination is based on the source-pathway-receptor concept. This considers the quantity of a contaminant in the soil (the source) and who is exposed to the contaminant (the receptor). Both need to be linked by a mechanism by which the receptor is exposed to the contaminant in concentrations that pose an unacceptable risk (pathway) (Figure 6-1). This method of risk assessment has three steps: i) preliminary risk assessment; ii) generic quantitative risk assessment; and iii) detailed quantitative risk assessment (Environment Agency, 2004). The preliminary risk assessment seeks to develop a conceptual model of the site and to establish any potentially unacceptable risks that may be present. This is usually a desk-based exercise and, if any potential pollutant linkages are identified, the site will be investigated further by carrying out the generic quantitative risk assessment. This involves measuring the soil pollutant concentration and comparing it to a soil guideline value

(SGV). For the generic assessment criteria (GAC), soil guideline values (SGVs) have been produced to assist with assessing the risk associated with long-term exposure to chemical contamination in the soil. These values should be considered as “trigger values”. If the GAC SGV is not exceeded, the land is considered not to pose an unacceptable risk. If the GAC SGV is exceeded, this does not mean that the land is contaminated, rather that further investigation is required to determine if the risk is indeed unacceptable. The detailed quantitative risk assessment is site-specific and looks at the pollution linkages that have been identified in the previous steps to assess their risk. If at this point there is an unacceptable risk, the site must be remediated (Environment Agency, 2009c).

The GAC SGV values have been derived based on the toxicological evidence for specific potentially harmful substances and likely soil exposure from the available literature. This information has been compiled into a series of reports that provide technical guidance to regulators. The toxicological reports typically define a health criteria value (HCV), which represents a tolerable, or minimal risk, to human health from long-term exposure to the contaminant in soil and are used as the basis of the SGV (Environment Agency, 2009b).

To aid the risk assessment of soils in the UK the EA has developed the CLEA software, a Microsoft Excel-based tool, which derives generic assessment criteria values for soils based on the characteristics of the contaminants and the receptors. It can also be used to derive site specific soil assessment criteria and the risk posed by a contaminant to human health under given circumstances (Environment Agency, 2009a).

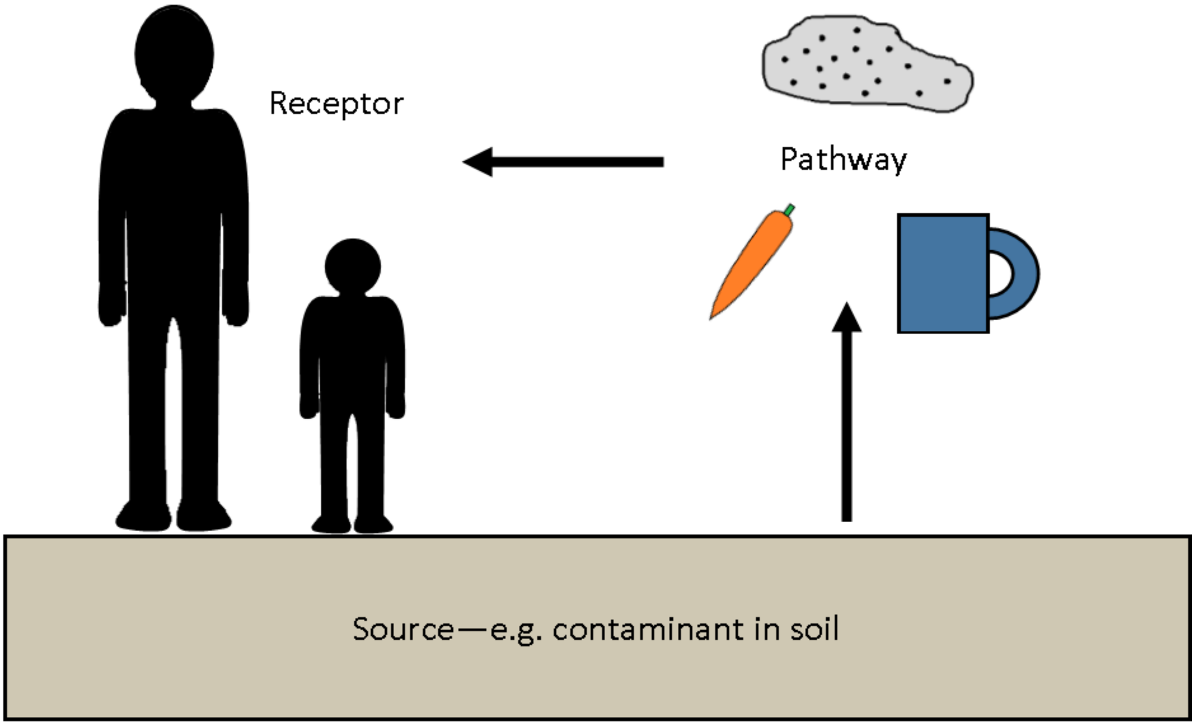

Figure 6-1: Schematic of source-receptor-pathway model

6.2.3 Category 4 Screening Level soil guideline values as trigger values

In 2014, an update to the SGV GAC for England and Wales was released by the UK Department for Environment, Food and Rural Affairs (DEFRA). It was based on taking a low, rather than minimal, level of health risk (as was previously the case for the existing EA SGVs). In the updated guidance, there are 4 categories set by DEFRA to classify the severity of pollution. Soils classified as Category 4 present an acceptably low hazard whereas Category 1 soils have a risk that is clearly unacceptable to human health (DEFRA, 2014b). The category 4 screening levels (C4SL) are to be used similarly to the GAC SGVs as a screening tool to assess whether a more detailed investigation is required. The revised DEFRA GAC SGVs have not been adopted officially by SEPA in Scotland but they are widely used in practice. Both the CLEA SGVs and DEFRA C4SLs are land use-based guidelines, with different values for various land use types reflecting the different levels of likely human interaction with soil in diverse settings (Table 6-1).

Bearing in mind the UK approach to assessing land contamination risk and the SGV and C4SL screening values, the sections below will evaluate the possible risks from Cr in soil in the Polmadie area.

Table 6-1: Summary of the generic assessment criteria (GAC) soil guideline value (SGV) for Cr and the category 4 screening level (C4SL) for Cr(VI) across different land uses

Land Use	SGV[a] value for total Cr (mg kg^{-1})	C4SL[b] value for Cr(VI) (mg kg^{-1})
Residential (with consumption of homegrown produce)	130	21
Residential (without consumption of homegrown produce)	200	21
Allotments	130	170
Commercial	5000	49
Public open space beside housing (POS$_{resi}$)	-	21
Public open space away from housing (POS$_{park}$)	-	250

[a]Environment Agency (2002), [b]DEFRA (2014a)

6.3 Comparison of Polmadie Banking soils to current trigger values

To carry out a preliminary assessment of possible human health risks from exposure to the banking soil from the Polmadie Burn, the total Cr and Cr(VI) concentrations in 19 surface soils collected from both banks of the Burn were compared to the UK GAC SGVs and C4SL values. The Burn is bounded on the east side by Richmond Park and on the west side by housing developments (Figure 3-3). Given the proximity of housing to the burn, for the purposes of a preliminary risk assessment the most precautionary SGVs for residential land use with plant uptake were used for comparison. The range of total Cr concentrations in the banking soil, from both sides of the Burn, was 416 – 6310 mg kg^{-1} which exceeded the CLEA residential GAC SGV of 130 mg kg^{-1}. Similarly, concentrations of 76.7 – 2019 mg kg^{-1} of Cr(VI) were found in banking soils from both sides of the stream, which exceeded the GAC C4SL for Cr(VI) for public open spaces close to housing of 21 mg kg^{-1} (Table 6-1). Due to the concentration of Cr(VI) in the banking soil exceeding the SGV and C4SL values, it was decided to investigate the inhalation bioaccessibility of the soil to determine the risk associated with inhaling Cr(VI) containing dust originating from the banking soil. The reason for focussing on the inhalation exposure route is explained in the following section.

6.4 Bioaccessibility testing

The bioaccessibility of a chemical is defined as the fraction of the chemical that is soluble and available for absorption by the human body (Semple *et al.*, 2004). Although bioaccessibility tests are not mandatory, they are recommended as part of phase two site specific risk assessments (DEFRA, 2014b). Bioaccessibility tests were developed by Ruby *et al.* (1993) to provide an *in vitro* approach to predict the oral ingestion bioaccessibility of metals from solid matrices. The method has since been optimised to help refine the assessment of human exposure to soil via ingestion and inhalation route (Ruby et al., 1993). Bioaccessibility tests are *in vitro* tests which mimic conditions of the human stomach and gastrointestinal tract or the lungs to simulate absorption of pollutants on ingestion or inhalation, respectively. They are a cost-effective alternative to expensive *in vivo* animal studies and are also ethically more sound (Wragg et al., 2011). Before measuring the inhalation bioaccessibility fraction of soil, the size of particles that can be inhaled into the lungs must be considered. It is generally accepted that the largest diameter of particle that can be inhaled into the lungs is 10 µm therefore the <10 µm fraction (PM10) of soils must be isolated and used for the inhalation bioaccessibility testing. The bioaccessibility risk assessment in this study focused on the inhalation rather than the oral exposure route for three reasons:

(i) Public access to the Polmadie Burn is restricted, and the banking soils are not likely to form the substrate for growing vegetables/direct soil contact etc. in the future that may be of concern for oral bioaccessibility. However, as outlined in Section 5.1, there are plans to divert water inputs away from the Burn, which will lead to lower flow rates in the future and potentially greater drying out of the banking soil, especially during prolonged dry spells. This could lead to greater resuspension of soil dust from the banking soil and possible risk of human exposure via inhalation.

(ii) Previous studies close to the Polmadie area of Glasgow (Broadway et al., 2010) and from other parts of the world have shown that the oral ingestion bioaccessibility of Cr(VI) in soils is low because Cr(VI) in the stomach is reduced to Cr(III) due to the presence of dissolved organic matter from the soil in the acidic environment (pH = 1) of the stomach. This facilitates the reduction of any ingested Cr(VI) and the Cr(III) formed will then precipitate once it moves into the intestines. Here the pH rises to above pH 6, and Cr(III) is mainly excreted from the body (Broadway *et al.*, 2010, Ljung *et al.*, 2007, Morman *et al.*, 2009). Indeed, Broadway *et al.* quantified the oral bioaccessibility of Cr in 27 Glasgow soils and found that the Cr(VI) was converted to Cr(III) and therefore only the bioaccessibility of total Cr in the soils could be determined as the fate Cr(VI) and Cr(III) could not be differentiated. The bioaccessible fraction of Cr in these soils ranged from <3 to 1156 mg kg^{-1} and all of were below the site-specific assessment criteria (SSAC) for the individual sites except one. Low bioaccessibility of Cr in soils has also been reported by other researchers who found the bioaccessible fraction of Cr was <5% in soils (Morman *et al.*, 2009, Ljung *et al.*, 2007). These studies did not take into account the speciation of Cr in the soils but it can be presumed that any Cr(VI) will be reduced to Cr(III) in the stomach, minimising the uptake of Cr(VI) by the body.

(iii) Very limited studies have been carried out on Cr inhalation bioaccessibility compared to oral ingestion bioaccessibility. A few studies have looked at the inhalation bioaccessibility of Cr from ferrochromium dust, which contains a mixture of Cr(III) and elemental Cr (Hedberg *et al.*, 2010, Midander *et al.*, 2010). The most relevant study by Broadway *et al.* (2010), mentioned above, quantified the inhalation bioaccessibility of the PM10 fraction of three Glasgow soils. They found that the 24 h inhalation bioaccessibility of Cr in the PM10 fraction of Glasgow soils was <296 ± 32 and 18 ± 4 mg kg^{-1} for total Cr and Cr(VI), respectively. This corresponded to a bioaccessibility fraction for total Cr of <14% (Broadway et al., 2010).

The soils selected for inhalation bioaccessibility in the Broadway *et al.* 2010 study were from an area in Glasgow near the Polmadie Burn which was made-ground using COPR. The Polmadie banking soils that were analysed in the current study were not as heavily impacted with COPR but contained elevated concentrations of Cr (and Cr(VI)) in the soil which was associated with OM and Fe hydroxides.

In this study, the Cr inhalation bioaccessibility of three bulk soil samples (Section 3.1.2) was determined by first isolating the PM10 fraction from the soils using gravity settling before determining the concentration of Cr and Cr(VI) leached using Gamble's solution (Sections 3.5.3 and 3.7, respectively). Gamble's solution was developed to mimic the fluid found in lungs and has been used in numerous studies to determine the *in vitro* inhalation bioaccessibility of metals (Boisa et al., 2014, Wragg and Klinck, 2007, Wiseman et al., 2018).

Before measuring the bioaccessibility of Cr(VI) in these soils preliminary experiments were conducted to optimise the bioaccessibility procedure used by Wragg and Klinck (2007) and the optimisation of the procedure looked to determine the ideal solid to liquid (S:L) ratio. The procedure of Wragg and Klinck (2007) used an S:L ratio of 1:67 but literature has suggested that in the lungs the solid to liquid ratio is likely to be between 1:500 and 1:50,000 (Julien et al., 2011, Wragg and Klinck, 2007). To explore the difference in bioaccessibility of different S:L ratios, the amount of bioaccessible Cr(VI) removed from the material was compared using S:L ratios of 1:67 and 1:500.

The results below describe the outcome of the preliminary experiment and the justification for using the method chosen to determine the bioaccessibility of Cr in the PM10 fraction of the Polmadie banking soils. It then goes on to document the bioaccessibility of Cr found in the Polmadie banking soils and compares these values to the current relevant soil guidelines to assess the implications of these results for the risk assessment of the site.

6.5 Bioaccessibility of chromium from soil dusts

6.5.1 Trial experiment comparing solid to liquid ratios

A preliminary experiment was carried out to determine whether the bioaccessibility of Cr(VI) could be precisely measured using an S:L ratio of 1:500 due to the low concentrations of Cr(VI) released from the dusts. This experiment compared the S:L ratios of 1:67 (n=3) and 1:500 (n=3). This size fraction used for this initial test was the <38 μm fraction of the soil rather than PM10 due to the difficulty of separating large enough quantities of PM10 from soil samples. The results showed that over an 8 h time period the bioaccessibility of Cr(VI) in the banking soil was above the detection limit only for the 0-2 h extraction for the S:L ratios of 1:67 (Table 6-2).

6.5.2 Conclusions from trial experiment

The technique available to analyse Cr(VI) was not sensitive enough to accurately determine Cr(VI) concentrations released by the S:L ratio of 1:500. It was therefore decided to continue using the S:L ratio of 1:67 as described in the method stated by Wragg and Klinck (2007). From this trial experiment it was noted that the majority of Cr(VI) was released from the 0-2 h extraction so it was decided to carry out the bioaccessibility experiment for a total of 8 h rather than the 24 h suggested by literature. This was similar to the results generated by the study which had previously determined the inhalation bioaccessibility of Cr(VI) in Glasgow soils (Broadway, 2008). It is therefore a recommendation that a more sensitive method for analysing Cr(VI) is used when studying the inhalation bioaccessibility of Cr(VI) in dust in the future but due to the time frame and instruments available this was not possible for this project.

Table 6-2: Bioaccessibility of Cr(VI) from banking soil after different time sampling intervals in different S:L ratios. Values are mean ± 1 standard deviation

S:L Ratio	Bioaccessibility of Cr(VI) from the 38 µm fraction of banking soil (mg kg^{-1})			
	0-2 h	2-4 h	4-6 h	6-8 h
1:67	12.3 ± 0.61	<LoD*	<LoD	<LoD
1:500	<LoD	<LoD	<LoD	<LoD

* LoD refers to the Cr(VI) concentrations in SLF which was 0.059 mg L^{-1}

6.5.3 Bioaccessibility of chromium from Polmadie soil samples

6.5.3.1 Total chromium

The results from the bioaccessibility experiment are summarised in Table 6-3. The mean 8 h lung bioaccessibility fraction of total Cr from the PM_{10} fraction of the three soils investigated was 47.0 ± 33.1, 26.5 ± 4.3 and 104 ± 8.7 mg kg^{-1}, respectively (Figure 6-2). The PM10 total Cr concentration in the soils 1, 2 and 3 PM10 was 373 ± 13, 377 ± 42 and 429 mg kg^{-1}, respectively (Table 6-3). Due to the very small quantities of PM_{10} separated from the soil, replicates were not possible for soil 3 Cr concentration as there was not enough material for duplicate measurements. The percentage of bioaccessible Cr in the PM_{10} fraction of soils 1, 2 and 3 was 13 ± 9, 7.0 ± 1 and 24 ± 2%, respectively.

The concentration of Cr found in the 2 mm fraction the soil at sample point 23, which was within 20 m of the soils analysed in the bioaccessibility study, was 416 ± 50 mg kg^{-1}. Therefore the PM_{10} concentrations of 373 – 429 mg kg^{-1} are similar to those measured in the 2 mm soil fraction (Figure 3-8)

6.5.3.2 Chromium(VI)

The lung bioaccessible fraction of Cr(VI) in the PM_{10} was 14.4 ± 6.6, 14.7 ± 2.8 and 19.7 ± 0.82 mg kg^{-1} in soils 1, 2 and 3, respectively (Figure 6-2). The PM_{10} total Cr(VI) concentration was 67.7, 125 and 64.4 mg kg^{-1}, respectively. Due to the very small quantities of PM_{10} that were separated from the soil, replicates were not possible for the Cr(VI) concentration as there was not enough material for duplicate measurements. The % of bioaccessible Cr(VI) in the PM10 of soils 1, 2 and 3 was 21 ± 10, 12 ± 2 and 31 ±1%, respectively (Table 6-3).

The Cr(VI) concentration in the 2 mm fraction at sample point 23 was 83.9 ± 5.9 mg kg^{-1}, similar to the concentration of Cr(VI) in the PM10 fraction which ranged from 64.4 – 125 mg kg^{-1}.

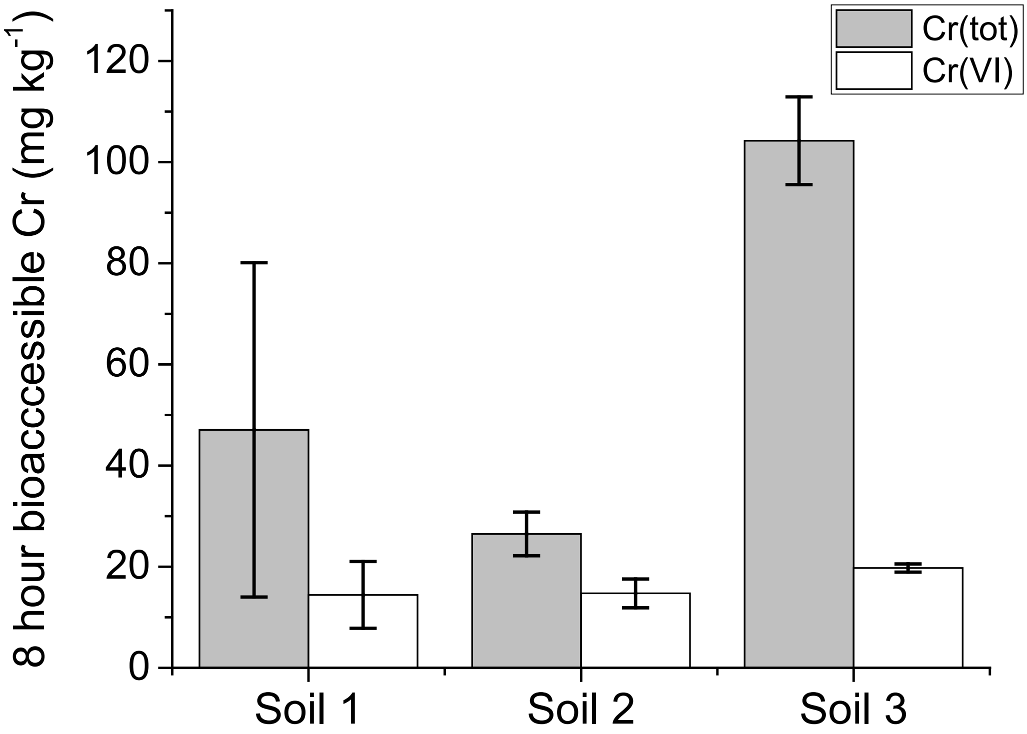

Figure 6-2: Bioaccessible chromium from the soil samples

Table 6-3: Summary of inhalation bioaccessibility of Polmadie Burn banking soils PM10 material

	Total Cr (mg kg^{-1})	Cr(VI) (mg kg^{-1})	Lung Bioaccessible total Cr (mg kg^{-1})	Lung Bioaccessible Cr(VI) (mg kg^{-1})	Lung Bioaccessible Fraction total Cr (%)	Lung Bioaccessible Fraction Cr(VI) (%)
Soil 1 PM10	373 ± 13	67.7	47.0 ± 33	14.4 ± 6.6	13 ± 9	21 ± 10
Soil 2 PM10	377 ± 42	125	26.5 ± 4.3	14.7 ± 2.8	7.0 ± 1	12 ± 2
Soil 3 PM 10	429	64.4	104 ± 8.7	19.7 ± 0.82	24 ± 2	31 ± 1

6.6 Evaluation of the bioaccessibility of Polmadie Burn banking soils

6.6.1 Comparison of PM10 chromium concentrations to soil guideline values and category 4 screening levels.

As mentioned, land use can influence the pathway of exposure and the receptor of a contaminant, therefore the SGV and C4SLs have different values depending on the land use. The most appropriate SGV for total Cr was residential without produce of 130 mg kg^{-1} and the most appropriate land use for the C4SLs to describe the Polmadie banking soils is public open space (POS) which is split into two categories. Public open space with residential (POS$_{res}$) takes into account backtrack of soil to residential properties, for example through transport on shoes and clothing, whereas public open spaces non-residential (POS$_{park}$) presumes there is a low possibility of soil being transported back to residential properties (Enviromnent Agency, 2009a). As mentioned in Section 6.2, the proximity of housing to the POS will influence the exposure pathway. The most appropriate land use for the Polmadie Burn is POS$_{res}$ which has a C4SL Cr(VI) value of 21 mg kg^{-1}.

The Cr PM$_{10}$ concentrations of all three soils exceed the GAC SGV value of 130 mg kg^{-1} and the Cr(VI) PM$_{10}$ concentrations of all three soils exceed the GAC C4SL value of 21 mg kg^{-1} for POS$_{res}$ land use. However, it should be noted that this only takes into account the Cr and Cr(VI) concentrations in the PM$_{10}$ size fraction whereas the GAC values refer to < 2 mm whole soil. Since most metals are concentrated in the fine fraction of soil, it would be expected that values in the PM10 fraction are likely to be higher than in the < 2 mm whole soil (Alloway, 2013). When considering the bioaccessible fractions of Cr and Cr(VI) in the soils, these values did not exceed the SGV or C4SLs. However, these guidelines are for all exposure routes, including soil ingestion, so the SGV/C4SL value must reflect the exposure route which causes the most harm to the receptor. Therefore the individual exposure routes must be considered to determine if it is the inhalation or oral bioaccessibility that will cause the most harm. The bioaccessible fraction of Cr(VI) in soils will be lower than 100% and therefore the total concentration of a contaminant in the soil is hard to relate to the concentration that is soluble and available for uptake by the body.

6.6.2 Comparison of the PM$_{10}$ bioaccessible fraction to the CLEA model soil assessment criteria value

Using the CLEA model, a SSAC for Cr(VI) for inhalation and oral bioaccessibility can be derived. This value gives the site specific C4SL value which estimates the concentration of Cr(VI) which poses an unacceptable risk. The banking soil SSAC, with respect to inhalation bioaccessibility of Cr(VI), determined by the CLEA model for soils 1, 2 and 3 was 55.0, 96.2 and 37.2 mg kg^{-1}, respectively, for POS$_{res}$ land use. The fraction of oral bioaccessible Cr(V) from the soils was presumed to be 5%, based on the results of Broadway *et al.* (2010). This gave a SSAC of 2090 mg kg^{-1} for the oral bioaccessibility of Cr(VI) in the Polmadie banking soils

These results suggest that the inhalation bioaccessibility of the Polmadie banking soils is indeed more important than the oral bioaccessibility. The SSAC for inhalation bioaccessibility was lower than the total Cr(VI) PM10 concentrations in the banking soils analysed in this study which were 67.7, 125 and 64.4 mg kg^{-1}, for soils 1, 2 and 3, respectively. This suggests that the Polmadie banking soils may pose an unacceptable risk to those visiting and living nearby. This should, however, be interpreted cautiously as other factors, such as access to the banking soil and the number of visitors, due to the secluded nature of the burn, should be considered before classifying the soils.

6.6.3 Suspension of Polmadie banking soil dusts and its potential health effects

6.6.3.1 Defining risk

To determine the risk posed by a contaminant, a threshold value must be identified below which there is acceptable risk, as described above in Section 6.2. The threshold value represents the concentration above which there is the potential of significant harm to human health. This value is usually based on a no observed adverse effect level (NOAEL) which is determined by animal or epidemiological studies. Carcinogens, such as Cr(VI), are considered non-threshold chemicals as they can originate from a single mutation in a single cell meaning that theoretically exposure to any concentration can result in significant harm, i.e. cancer. Since these contaminants technically do not have a NOAEL, they require a different approach to determining a health-based guideline value. The common practice is to apply the principle of “as low as reasonable practicable” and what is determined as “reasonably practicable” is determined by the remediation /risk management decision (Environment Agency, 2009b).

To assist in the assessment of carcinogens, the excess lifetime risk associated with a concentration of contaminant, the index dose, is used to determine acceptable levels of risk. The excess lifetime risk is defined as the ratio of the point of departure to the estimated human exposure for a carcinogen. The point of departure in this case is determined by using the benchmark dose lower confidence limit. The index dose is the daily intake of the chemical expressed as mass of contaminant per kg of body weight per day (g kg^{-1} bw day^{-1}) which is associated with a pre-defined excess lifetime risk (Environment Agency, 2015).

To determine acceptable risk of a carcinogen, margins of error have been proposed which describe the level of risk. In general, an excess lifetime risk of <1 in 10,000 is considered as “may be a concern”, between 1 in 10,000 and 1 in 1,000,000 is considered “unlikely to be a concern”, and >1 in 1,000,000 is “highly unlikely to be a concern” (Environment Agency, 2009b). For the purpose of C4SL, the pre-defined excess lifetime risk, based on socio-political judgment, of dying from lung cancer due to the exposure of Cr(VI) is 1 in 50,000. This is lower compared to the excess lifetime risk of 1 in 100,000 adopted by the minimal risk approach of the former 2002 SGV guideline values (CL:AIRE, 2014, Environment Agency, 2002).

If the airborne concentration of a contaminant is known for a set excess lifetime risk, the index dose i.e. the uptake of contaminant per body weight per day, can be calculated for minimal risk concentrations. The index doses used for the Cr(VI) C4SL values are based on guidance from the World Health Organisation (WHO) who related the airborne Cr(VI) concentrations to excess lifetime risk from the available epidemiological reports on workplace Cr(VI) exposure. Their conclusion was that if exposed to an air concentration of 1 µg m^3 Cr(VI), the risk factor for developing cancer was 0.04 (i.e. an excess lifetime risk of 1 in 25). By extrapolating this value, assuming a linear dose-response relationship, the concentrations of Cr(VI) related to an excess lifetime risk of 1 in 50,000 and 1 in 100,000 are 0.52 and 0.25 ng m^{-3}, respectively (WHO, 2000). The index dose used by DEFRA and the EA was calculated based on these values and assumes a 70 kg adult breathing 20 m^3 of air per day. The mass of Cr(VI) that an adult needs to be exposed to daily in order to have a 1 in 50,000 or 1 in 100,000 chance of dying from cancer due to Cr(VI) exposure is 0.15 and 0.71 ng kg^{-1} bw day^{-1} respectively.

6.6.4 Amount of Polmadie banking soil PM_{10} required to exceed index dose

Using the index values it is possible to calculate the amount of airborne PM_{10} from Polmadie banking soil needed to be suspended in air to exceed the guideline air concentrations of 0.52 and 2.5 Cr(VI) ng m^3. This can be done using the following equation:

$$PM_{10}\ conc. (\mu g\ m^{-3}) = \frac{Guideline\ Cr(VI)\ conc. (ng\ m^{-3})}{Soil\ Cr(VI)\ conc. (mg\ kg^{-1})} \times 1000 \qquad \text{Equation 6.1}$$

where the PM_{10} conc. is the amount of PM_{10} material required to be suspended to exceed the guideline Cr(VI) concentrations. The suspended airborne PM_{10} amounts required are summarised in Table 6-4. The suspended airborne PM_{10} materials required to exceed the guideline value of 0.52 ng m^{-3} were 26.4 - 36.0 µg m^3 based on the PM_{10} bioaccessible Cr(VI) and 4.12 – 8.08 µg m^3 for the PM10 total Cr(VI) concentrations (Table 6-4). The mean PM_{10} concentrations measured at Glasgow Townhead monitoring centre between 2008 and 2018 was 12 ± 6 µg m^3 (UK-air, 2018) which highlights that the required amounts of suspended PM_{10} to exceed the airborne Cr(VI) guidelines are not unreasonable values for the local area.

In a consultation document looking at the concentrations of metals and metalloids in ambient air with regards to human health, DEFRA recommend a maximum ambient air annual mean Cr(VI) concentration of 0.2 ng m^{-3} (DEFRA, 2008). This translates to 12.5 ± 2.1 and 2.55 ± 0.83 µg m^3 of PM_{10} with respect to bioaccessible Cr(VI) and total Cr(VI) concentrations in the

Polmadie banking soils, respectively. However, without knowing the current Polmadie Cr(VI) airborne concentration and the contribution to airborne dust from the banking soil, it is not possible to comment further on the significance of this value.

Table 6-4: Amount of Polmadie soil PM_{10} required to exceed airborne Cr(VI) concentration of 0.52 ng m^{-3} as recommended by the C4SL soil quality risk assessment and 0.2 ng m^{-3} as recommended by the DEFRA air quality guidelines

	Cr(VI) concentration (mg kg^{-1})		Concentration of suspended PM_{10} required to exceed C4SLs guideline Cr(VI) concentration (µg m^{-3})[a]		Concentration of suspended PM_{10} required to exceed DEFRA air quality guideline Cr(VI) concentration (µg m^{-3})[b]	
	PM_{10}bio	PM_{10}tot	PM_{10}bio	PM_{10}tot	PM_{10}bio	PM_{10}tot
Soil 1	14.4	67.7	36.0	7.68	13.9	2.95
Soil 2	14.7	125	35.3	4.15	13.6	1.60
Soil 3	19.7	64.4	26.4	8.08	10.1	3.11

[a] Based on the index dose of 0.001 µg kg^{-1} bw day^{-1} and a 70 kg adult breathing 20 m^3 of air per day which requires a Cr(VI) concentration of over 0.52 ng m^{-3} to exceed the soil C4SL guideline values (CL:AIRE, 2014)

[b] Based on the DEFRA Cr(VI) air quality annual mean concentration value of 0.2 ng m^{-3} (DEFRA, 2008)

PM_{10}bio = based on bioaccessible concentration of Cr(VI) in the PM_{10} soil fraction

PM_{10}tot = based on the total concentration of Cr(VI) in the PM_{10} soil fraction

6.6.5 Comparison of bioaccessible concentrations with solid phase chromium concentrations in the banking soil PM_{10}

The current approach by DEFRA is to use a conservative method which presumes that all Cr(VI) in dust is bioaccessible (DEFRA, 2014b). In the case of the Polmadie banking soil the inhalation bioaccessibility of Cr(VI) was 21 ± 9% therefore there is approximately a 5-fold difference in the concentration of suspended PM_{10} required to exceed the guideline value depending on whether the bioaccessible fraction or total concentration of Cr(VI) is used. Since the index values are calculated using airborne Cr(VI) concentrations, the exposure to soil PM_{10} required should be based on the bioaccessible Cr(VI) concentrations rather than the solid phase Cr(VI) concentration. This means the current method used taking the total concentration of Cr(VI) in dusts is not necessarily the best value when determining the exposure to Cr(VI). It also shows that the current conservative approach by the CLEA model that assumes that all airborne Cr(VI) is absorbed by the body will overestimate the true concentration of Cr(VI) absorbed.

The soil guidelines also state that the inhalation of soil derived dusts for public open space and parks is estimated to contribute to 0.03% of the total exposure to Cr(VI); however, the amount of dust produced should be considered on a site by site basis. The factors influencing the production of dust are: the climate and coverage of the site; vehicle movements on the site; and whether Cr(VI) is present in a dusty form (DEFRA, 2014a, Envrionment Agency, 2002). As shown here, Cr(VI) is present in the PM_{10} fraction of the Polmadie banking soil and the vegetation coverage is minimal in places resulting in bare soil – especially during winter months. However, under current conditions the Polmadie banking soil is unlikely to dry completely considering the banking soil's large water holding capacity and the wet climate of Glasgow. Due to these reasons it is likely that the banking soil will produce a limited amount of dust. If the burn is diverted and there are prolonged dry spells the dust produced by the soil is likely to increase. Additionally, the amount of soil that is transported into nearby homes is unknown but important to assess when considering the exposure to Cr(VI) of local residents.

6.7 Summary

The mean PM_{10} Cr(VI) bioaccessibility fraction of three banking soils was 16.3 ± 3 mg kg^{-1} which corresponded to 19.0 ± 8.3% of the PM_{10} total Cr(VI). The bioaccessible fraction of Cr(VI) did not exceed the C4SL value for POS_{res} land use, but the solid phase Cr(VI) concentration of 85.8 ± 34 mg kg^{-1} did. This highlights a discrepancy between the bioaccessible and solid phase concentrations of a contaminant, and challenges the current practice of presuming 100% bioaccessibility when carrying out a soil risk assessment. The question remains as to whether or not this is the best practice. The methods used to derive C4SL screening values are highly conservative and act as a guideline prompting further investigation if exceeded. This project investigated the bioaccessible fraction of total Cr and Cr(VI) in PM_{10} fraction of Polmadie soils. The PM_{10} total Cr(VI) concentrations exceeded the site-specific assessment criteria value provided by the CLEA model, however the secluded nature of the soil may reduce exposure to the soil to acceptable levels. To gain a better understanding of the risk posed, the actual airborne concentration of Cr(VI) in the area is required. An assessment of this was outside the scope of this project but is highly recommended to be determined if the true exposure to Cr(VI) by the local population is to be measured. The bioaccessibility should also be measured on this dust to determine the fraction of Cr(VI) that is potentially available to be absorbed by the body as this is unlikely to be 100% as assumed by the CLEA model.

7 Summary, conclusions and further work

7.1 Fate of chromium in the Polmadie Burn surface water

7.1.1 Chromium in the Polmadie Burn

Long-term monitoring data was provided by SEPA which included concentrations of nutrients and inorganic constituents in the Polmadie Burn waters over the period 1967 to 2017. The Polmadie Burn is classified as a lowland (<80 m altitude) and high alkalinity (>50 mg L^{-1}) surface water body. This categorisation is then used to determine the water quality with respect to several other parameters such as dissolved oxygen concentrations. At the current time, the water is neutral/slightly alkaline with a pH range (5th to 95th percentile) of pH 7.2 -8.4 which is consistent with high status. However, for BOD, Polmadie Burn is classified as moderate/poor suggesting that anoxic conditions may result in the formation of anoxic conditions Metal and metalloid concentrations with the exception of Cr, were typically below their respective EQS values. The median Cr concentration over the monitoring period of 1967-2017 was 2.69 mg L^{-1} exceeding the EQS value for Cr(VI) of 3.4 μg L^{-1} by ~3 orders of magnitude. Although SEPA did not determine Cr speciation, analysis of 0.45 μm-filtered Burn water in this PhD project showed that it was almost exclusively present as Cr(VI). This is a concern because exposure to Cr(VI) can lead to a variety of human health effects, ranging from contact dermatitis to lung cancer.

The long-term temporal trends in the Cr concentrations were analysed which suggest that there had been a decrease in the Cr concentrations during the 1990s, with pre and post 2000 median values of 2.46 and 2.17 mg L^{-1}, respectively. However, the concentration over the time period 2010-2017 has been relatively stable at 2.26 mg L^{-1}. Over this period, it was evident that the dissolved Cr concentrations were directly correlated with pH. Glasgow COPR is a highly alkaline material which has been shown to impact upon the pH and Cr concentrations in groundwater and surface water (Farmer et al., 2002, Geelhoed et al., 2003) and this may well still be an importance source of Cr to the Polmadie Burn waters. In addition, however, banking soil leaching experiments revealed a positive correlation between leached Cr concentration and Ca and Mg concentrations. This had previously been observed by Geelhoed et al. (2002) in leaching studies of COPR and so runoff from banking soils may also continue to be a source of COPR-derived Cr in these surface waters (Geelhoed et al., 2002).

7.1.2 Removal of chromium from surface water by the banking soil during flood events

7.1.2.1 Chromium(VI) removal from simulated flood waters by Polmadie banking soil

The mean total Cr concentration in the banking soils was 1710 ± 1300 mg kg^{-1} and Cr(VI) comprised 18.9 ± 15% of the total soil. Sequential extraction showed that most of the Cr was associated with organic matter which comprised ~22.4 ± 4.7% of the dry soil mass. Most of the remainder of the Cr was associated with Fe/Mn (hydr)oxides. In support, gel electrophoresis showed that Cr and Fe were intimately associated with the soil organic matter. It was therefore hypothesised that Cr(III) was present as Cr(III)-organic complexes of Cr(III)-Fe(III)-OM ternary complexes and that Cr(VI) may be adsorbed to Fe(III) oxides. Sorption studies showed that the banking soils could retain significant additional amounts of Cr (added in the form of dissolved Cr(VI)). At least an additional 350 mg kg^{-1} could be sorbed by the banking soils and only <2% was re-released upon leaching with 0.01 M $CaCl_2$ solution. Although the speciation of Cr in the solid phase could not be determined, the results suggest that OM may play an important role in the removal of Cr from the aqueous phase by reducing Cr(VI) to Cr(III). The rationale for this interpretation is summarised as follows: under oxic conditions Fe(II) will spontaneously and rapidly (within minutes) oxidise to Fe(III) to form insoluble hydroxide precipitates so therefore it is not considered to be important for the reduction of Cr(VI) in the Polmadie banking soils which are mildly oxidising. Chromium(VI) may, however, be adsorbed by these insoluble (hydr)oxides but this process occurs only to a very limited extent under the prevailing conditions (Rai et al., 1989, Richard and Bourg, 1991). Therefore for the circumneutral pH, oxic banking soils it is most probable that the solid phase OM reduces Cr(VI) and retains it either directly (complexation) or indirectly (bridging Fe) (Banks et al., 2006, Kyziol et al., 2006, Löv et al., 2017).

7.1.3 Chromium(VI) removal from surface waters by Polmadie bottom sediments

The removal of Cr(VI) from surface waters by the reduction of Cr(VI) by Fe(II) bottom sediments was shown by Palumbo-Roe *et al*. (2017). This was also indicated in this PhD project by the high concentrations of Cr(VI) in the surface water which contained no detectable Fe(II), however the opposite (high Fe(II) concentrations with no detectable Cr(VI)) was found in the sediments. The Polmadie Burn water is generally slow flowing and events causing sediment re-suspension are considered to be rare. Debris such as rags cover a significant proportion of the bed sediment and this may play an additional role in limiting the contact between the bottom sediments and the Cr(VI)-containing Burn waters. Nevertheless, within the anoxic bottom sediments, Fe(II) is stable and, in this highly reducing environment, Cr(VI) will be quickly reduced to form Cr(III) which precipitates to form surface coatings (Hillier et al., 2003, Palumbo-Roe et al., 2017). Supporting evidence for Cr-Fe-containing surface coatings was obtained using SEM-EDX in this project. Although the sediment's ability to effectively remove Cr(VI) from the aqueous phase is considered to be high, as shown by the high concentrations of Fe(II) and limited concentrations of Cr(III) found in the sediment porewaters, the limited infiltration of surface water to the sediment is a physical constraint limiting its effectiveness to remove Cr(VI) from overlying waters.

7.2 Complexation of chromium with organic matter and its release from banking soil and bottom sediment during drying

7.2.1 Chromium complexation with organic matter in banking soils and sediments

Sequential extraction analysis of banking soil and bottom sediments showed that the majority of Cr was associated with OM and Fe/Mn hydroxides. These associations between Cr and OM were confirmed further using gel electrophoresis. Although these were observed for field-moist soils and sediments and air-dried soils, there was a distinct difference in: i) the type of organic molecules Cr was associated with and ii) the amount of OM extracted from air-dried sediment. Chromium associated with OM extracted from air-dried sediment was bound to smaller, more mobile organic molecules as demonstrated by the greater distance travelled during the gel electrophoresis compared to the OM extracted from field-moist sediment. In the field-moist sediment there is small proportion of Cr associated with small organic molecules also, but the majority is bound to larger organic molecules which closely resembles the interactions of Cr with OM extracted from field-moist and air-dried banking soil. This has implications because any change in labile OM concentrations will affect the mobility of Cr in the soils and sediments due to the large proportion of the overall Cr concentration in this fraction.

7.2.2 Influence of air-drying on the release of chromium from Polmadie banking soils and sediment upon rewetting

The drying of banking soil and sediment due to prolonged dried spells was simulated in the laboratory through a series of experiments that monitored the release of Cr from the banking soils and bottom sediments upon rewetting after increasing drying time. Column leaching experiments monitored the release of Cr from fresh banking soil and bottom sediment and from material which had been air-dried for the time periods of 2 and 4 weeks. In addition to the column leaching experiments, batch leaching experiments were conducted which monitored the changes in leachable Cr concentrations from fresh banking soil and bottom sediments and from material which had been air-dried for 1, 2, 5, 8, 12, 16, 21, 26, 35, 43, 50 and 62 days.

7.2.2.1 Leachate chromium concentration and speciation upon rewetting

The first thing that must be noted from the leaching experiments was the contrast in Cr concentrations leached from banking soils and bottom sediments. Specifically, concentrations of Cr leached from banking soils were in general an order of magnitude higher than those leached from bottom sediments. This contrast is mainly due to the larger OM content of the banking soils compared to bottom sediments. As discussed above, Cr forms complexes which contain Fe and OM so when soil is rewetted, the mobilisation of these molecules and the formation of colloids will result in the release of Cr into solution. For both the banking soil and bottom sediments, the Cr leachate concentrations tended to decrease as the drying time increased. This is most likely due to the reduction in the mobility of OM-Cr-Fe complexes as drying time increased due to the immobilisation of these species.

Although the concentration of leachable Cr decreased after Week 2 and 4 of drying, as shown by the column experiments results, leachable Cr concentrations decreased over the initial 2-week drying period but then increased between Weeks 2 and 4. This was observed for the leachable Cr concentrations upon rewetting of both banking soils and bottom sediments and for leachable Mn concentrations in the banking soil, but not for any other element or parameter analysed. This was hypothesised to be due to the oxidation of Cr(III) by Mn(IV) which will subsequently release Cr(VI) and Mn(II) into solution during rewetting. More frequent sampling intervals allowed greater detail to be gained on changes in leachable Cr concentrations as drying time increased and can be explained from the results from the batch drying experiment of the bottom sediment which are discussed in detail in the section below.

7.2.3 Oxidation of chromium(III) by manganese oxides upon drying and rewetting Polmadie bottom sediments

During the batch drying and rewetting of bottom sediments (Section 5.4.4) it was clear that there were two processes occurring. Over the first 21 days of drying, leachable Cr concentrations decreased with drying time until the sediment reached a constant moisture content. After day 21 of drying the leachable Cr concertation increased with Cr(VI) being detected in the leachate. This process is illustrated in the schematic shown in Figure 7-1. During the initial drying phase, leachable Cr is hypothesised to be complexed to dissolved and colloidal OM in the leachate, as implied by the ultrafiltration data from the leaching column data. The redox potential is also sufficiently low so that Mn(II) is stable. As the sediment dries, the immobilisation of the Cr-Fe-OM fraction results in the decrease in Cr(III) leached upon rewetting and the rise in redox potential results in the oxidation of Mn(II) which precipitates as Mn(IV) oxides. The freshly formed Mn(IV) oxides will oxidise Cr(III) in the sediments to form soluble Cr(VI) and subsequently be reduced to Mn(II), which will also be released into solution. This is an important consideration if Polmadie bottom sediment is allowed to dry for long periods of time. Currently the rain-free periods in Glasgow are 1-2 weeks (3 instances between November 2017 and November 2018) and only one instance where there was a 2-4 week dry period between November 2017 and November 2018.

Although the increase in leachate Cr(VI) and Mn concentrations as drying time increased was not seen as clearly in the batch leaching experiment of the banking soils, the soil column experiment showed that this was most likely occurring in the soils also. The higher OM content and lower Mn concentrations in the soils is likely to reduce any Cr(VI) formed, as shown by the rapid removal of Cr(VI) from solution discussed in Section 5.5.

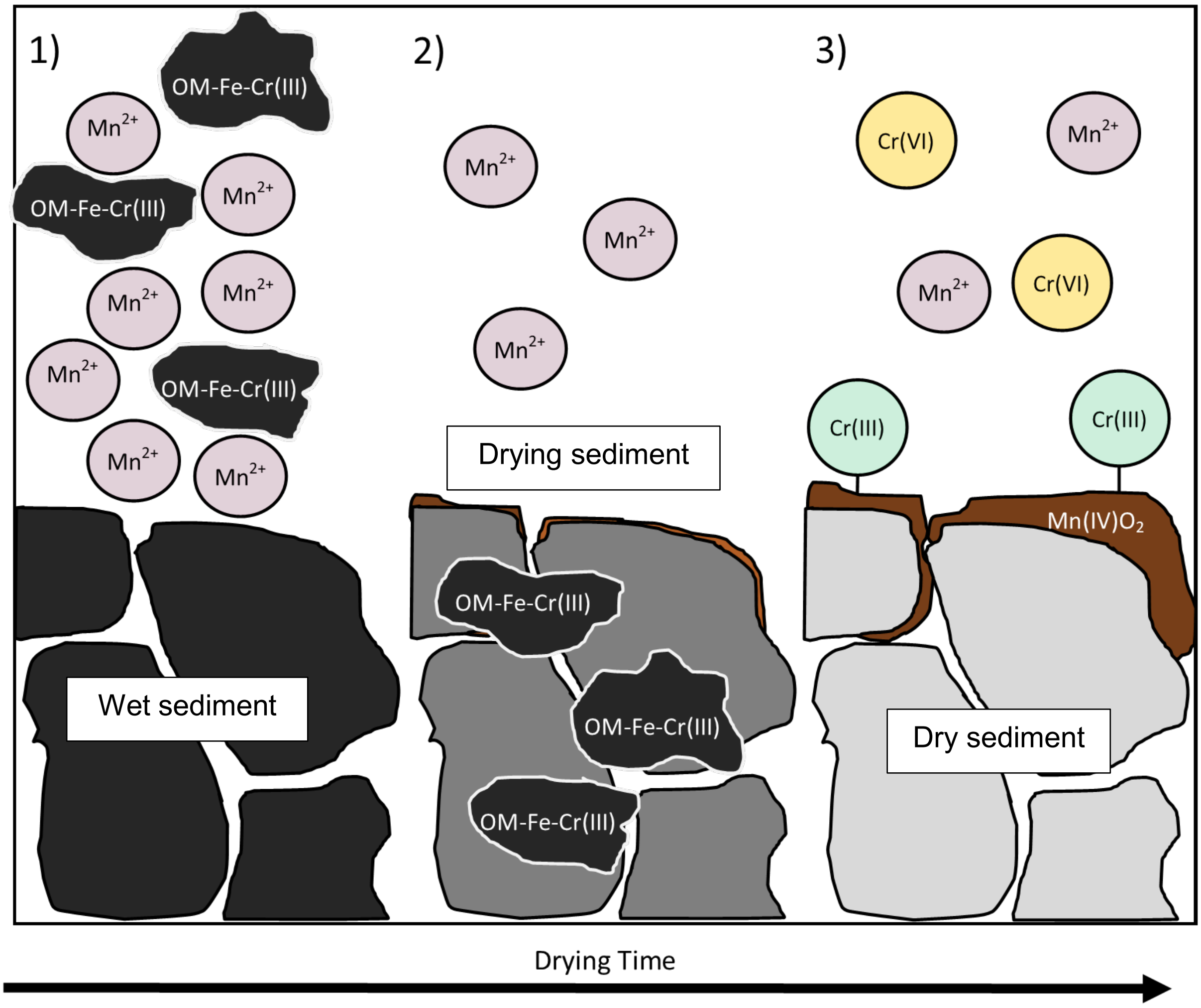

Figure 7-1: Schematic showing the change of leachate concentration as sediment dries. Period 1 shows the wet sediment which has low redox potential, high Mn^{2+} concentrations and suspended OM-Fe-Cr(III) complexes. Period 2 shows the sediment during the drying period where the redox potential increase leading to the oxidation of Mn^{2+} to form Mn(IV) oxide surface coatings. During this period the OM-Fe-Cr(III) complexes become less soluble. In period 3 the sediment is fully dry and upon rewetting Cr(III) is oxidised by the freshly formed Mn(IV) oxides resulting in the release of Cr(VI) and Mn^{2+} into the leachate.

7.3 Mobilisation of chromium from banking soil dust in the lungs – an inhalation bioaccessibility study

7.3.1 UK soil risk assessment overview

To protect people from exposure to contaminants in soil, the UK Environment Agency (EA) developed the Contaminated Land Exposure Assessment, a three-step risk assessment method, for assessing potentially contaminated land. This method first considers the site history to identify potential risks to human health. Once this has been carried out, a generic risk assessment uses predefined trigger values to determine whether further investigation is required and, if needed, the final step is a detailed risk assessment which determines if the risk to human health is acceptable or not. The current trigger values in use are the category 4 screening levels (C4SLs) set out by DEFRA. These values have been developed by considering the available literature on the health effects of contaminants, the concentrations required before detrimental health affects occur and what society deems to be unacceptable risks. The Scottish Environment Protection Agency (SEPA) has largely adopted the same methods that the DEFRA use as described here.

Due to the history of COPR disposal in the surrounding area and high concentrations of Cr in the Polmadie Burn water, an investigation into the Cr concentrations in the banking soils and sediment was needed to quantify the amount of Cr in the proximity of a public park and new housing development. The banking soil analysed over the course of this project (n=19) showed a range of total Cr concentrations of 418 – 6310 mg kg^{-1} and the Cr(VI) concentration of 76.7 – 2190 mg kg^{-1}. For all soils they exceed the Cr(VI) C4SL of 21 mg kg^{-1} for public open space beside residential areas land use. Although the concentrations of Cr(VI) found in the soils are above the trigger value, it does not necessarily mean that the soil poses an unacceptable risk to human health as the soil concentrations do not necessarily reflect how much Cr(VI) is bioaccessible which is the important aspect with regards to health. As demonstrated above, the quantities of Cr leached from the soil is a very small fraction of the concentrations present in the soils. To estimate the risk to human health created by inhalation of dust from the Polmadie banking soil, the inhalation bioaccessibility of the banking soils was measured.

7.3.2 Bioaccessible concentrations of chromium in Polmadie banking soil <10 µm fraction

The largest particle size that can enter human lungs is considered to be 10 µm and so the bioaccessibility of the PM_{10} fraction (particles of up to 10 µm) of the soil must be used before considering the inhalation bioaccessibility. The bioaccessible fraction of total Cr and Cr(VI) in the banking soil PM_{10} fraction was 59.2 ± 40 and 16.3 ± 3.0 mg kg^{-1}, respectively. This corresponded to 15.1 ± 10 and 19.0 ± 8.3% of the total Cr and Cr(VI) concentration, respectively. The mean PM_{10} total Cr(VI) concentration of 85.8 ± 34 mg kg^{-1}, was above the C4SL trigger value of 21 mg kg^{-1} however the PM_{10} bioaccessible fraction was below this value. The site-specific assessment criteria was determined for each site and the PM total Cr(VI) exceeded this value for each site. However, due to the secluded nature of the site, with limited access it is recommended that further studies investigating the concentration of Cr(VI) in airborne dust in the site are conducted to gain a better understanding of the exposure to those who live in the area. A detailed evaluation of the inhalation bioaccessibility of the Polmadie banking soils can be found in Chapter 6.

Although the oxidation state of Cr was determined in the inhalation bioaccessibility leachate, there was no further investigation into the associations of Cr in the PM_{10} fraction or in the leachate. From the results of the soil leaching experiments it is however possible to predict the factors affecting the Cr mobilisation in the lungs. Chromium mobilisation in the lungs is likely to be due to: i) the mobilisation of Cr(III)-OM complexes and ii) the desorption of Cr(VI) adsorbed to PM_{10}. The most important mobilisation of Cr from Polmadie banking soils is the complexation of Cr(III) with labile OM. As shown by the leaching experiments, the species of Cr extracted in the inhalation bioaccessibility assessment of Cr was predominantly in the Cr(III) form. This was due to the mobilisation of OM which was an important mechanism influencing the concentration of bioaccessible Cr(III). Since Cr(VI) does not form stable complexes with OM, the release of Cr(VI) adsorbed by the soil is likely to be a source of bioaccessible Cr(VI).

From the results of the bioaccessibility test it could be seen that there was much larger variation in the bioaccessible Cr(III) concentrations (RSD = 68%) compared to the Cr(VI) (RSD = 18%). The variation of the PM_{10} total Cr(III) concentration was relatively low (RSD = 8.0%) this suggests that there is a variable in the PM_{10} which is controlling the bioaccessibility of Cr(III). This could be due to the variations in the composition of OM between the sites but further work investigating the Cr-OM complexes, for example using gel electrophoresis, is needed to identify if this is the case.

It was also noted that the release of Cr from the PM_{10} fraction during the inhalation bioaccessibility was much larger than the concentration of Cr leached from the banking soil by the batch and column leaching experiments. This is due to the small size fraction of the PM_{10} which has a much larger surface area per mass than the whole soil, leading to higher capacity to adsorb Cr(VI). The lower S:L ratio will also increase the desorption kinetics and the chelating agents in the Gamble's solution will promote the solubility of Cr.

7.4 Wider implications of this study

Former urban-industrial environments are becoming more valuable due to the increased demand for development land to support the continued migration of people to urban centres. Therefore, the behaviour of pollutants in urban waterways and soils needs to be understood to predict the exposure pathways resulting in detrimental effects on human health. To aid with the risk assessment of potentially contaminated land this PhD project has shown that the total Cr concentrations in the soil is not an appropriate parameter as it does not reflect the risk of exposure to toxic species of Cr or its release to ground/surface water. This PhD project has explored the processes that lead to the interconversion of Cr(III)/Cr(VI) in the sediments and highly vegetated banking soils of urban streams. The results show that the reduction and immobilisation of Cr(VI) in these soils and sediments was a more predominant process than the Cr(III) oxidation making these sediments and soils a sink for Cr(VI). The drying of highly organic banking soils resulted in the decrease of leachable Cr concentrations when the soil was rewetting, suggesting that the rerelease of Cr back into ground/surface water was minimal. The high capacity of these organic soils for immobilising Cr suggests that some urban soils could potentially be used as a natural barrier to reduce Cr(VI) concentrations from industrial effluents, such as tannery waste. In Cr impacted waterways, the banking soils may contain inhalation bioaccessible Cr(VI) and this risk will need to be quantified on an individual site basis.

The main hazard identified by this PhD project is the potential risk of increased leachable Cr(VI) concentrations from dried sediments. This may have implications for the disposal of dredged sediments which have high Cr concentrations as the oxidation and subsequent release of Cr(VI) may result in the release of Cr back into the environment. This may be also applicable to soils with low organic matter content. The results of the drying experiments have shown that drying/wetting cycles of exposed sediments and soils are an important natural process that governs Cr(VI) release. This has particular relevance for areas of the world, such as India which still produces COPR and has regular and distinct wet and dry seasons (in the form of the Monsoon) where they may be seasonal releases of Cr(VI) from soil. This is particularly true as it has been reported that COPR is increasingly being used as road aggregate, which will dramatically increase its prevalence in the environment.

7.5 Conclusions

- From the dataset provided by SEPA Cr in the Polmadie Burn surface waters was identified to be the only inorganic pollutant which constantly exceeded its EQS. The mean concentration of Cr between the years of 1982 and 2017 was 2.88 ± 2.2 mg L^{-1} which was approximately 3 orders of magnitude higher than the EQS for Cr(VI) in freshwaters. The species of Cr in the surface water was not determined by SEPA but the majority of Cr (91 ± 15%) was in the <0.45 µm fraction suggesting that it was Cr(VI). From the analysis of the Polmadie Burn surface water it was shown that the majority of Cr is present as Cr(VI)

- Surface water Cr and Cr(VI) concentrations of <4.03 and <3.94 mg L^{-1}, respectively, were found in the Polmadie Burn. Banking soil concentrations contained <6310 mg kg^{-1} of total Cr and <2190 mg kg^{-1} of Cr(VI). The majority of Cr was associated with (OM 63.2 ± 9.5%) and Fe hydroxides (25.9 ± 8.5%). Burn sediment concentrations were <14,900 mg kg^{-1} of total Cr and < 1200 mg kg^{-1} of Cr(VI) were found in the sediment. Like the soils, the majority of Cr was found associated with OM (52.2 ± 5.4%) and Fe hydroxides (37.6 ± 3.9%). Gel electrophoresis of OM extracted from Polmadie banking soils and sediments suggested that Cr was predominately bound to OM and Fe complexes were found

- Overall there were low leachable Cr concentrations in both soils and sediments as the maximum amount of Cr released was < 0.023% of Cr from the banking soil and <0.00008% of Cr from sediment after the material was leached with the equivalent of 6 weeks of rain. Chromium leached from soils contain between 30-40% or Cr(VI) whereas Cr released from sediments was almost exclusively Cr(III).

- The drying of Polmadie Burn banking soil and sediment generally resulted in a decrease in the leachable total Cr and Cr(VI) concentrations which was attributed to the alteration of OM as the material dried. Upon drying the Cr concentrations decrease and then increased again along with leachable Mn concentrations. This was shown to be due to the oxidation of Mn(II) to form Mn(IV) oxides when the material dries, resulting in the oxidation of Cr(III) along with the reduction of Mn(IV) to form soluble Cr(VI) and Mn(II).

- Both soils and sediments showed the potential to act as a sink for Cr(VI). The proposed mechanism for the immobilisation of Cr(VI) in sediments is reduction by Fe(II) followed by the precipitation of Fe/Cr hydroxides. In soils the reduction of Cr(VI) by solid OM is likely to be followed by the incorporation of Cr into OM.

- The banking soil showed the ability to remove over 99% of Cr(VI) from a 1.4 and 10 mg L^{-1} Cr(VI) solution over a period of 120 h. The rate of removal of Cr(VI) from solution by the banking soils did not follow zero, first or second order kinetics suggesting that this process was not a simple adsorption reaction and that the reduction of Cr(VI) by OM was the main driving force for Cr(VI) removal. It was demonstrated that the banking soil has the potential to sorb over 365 mg kg^{-1} of Cr(VI) suggesting that these soils may be a natural barrier in the removal of Cr(VI) from groundwater.

- The removal of Cr(VI) from the Polmadie Burn surface water by the sediment is thought to be limited due to the low hydraulic exchange between the surface water and the sediment porewater.

- The inhalation bioaccessibility of Cr(VI) from the PM10 fraction of three banking soil samples was found to be 14.4 – 19.7 mg kg^{-1}. The PM10 total Cr(VI) concentrations ranged between 64.4 and 125 mg kg^{-1} which exceeded the CLEA C4SL Cr(VI) concentration of 21 mg kg^{-1} for POS_{res} land use. The site specific Cr(VI) concentrations were determined using the bioaccessibility data and the Cr(VI) concentrations of the PM10. In all three soils the PM_{10} total Cr(VI) concentrations exceeded the site specific Cr concentration. However, due to the secluded nature of the Polmadie Burn and the high moisture content of the soils, which will result in low dust formation, the true risk is likely to be lower.

7.6 Further work

This study has determined the speciation and mobility of Cr in a water-soil-sediment system. To build on this research, future work looking at effective remediation strategies of Cr(VI) using soils with a high OM content to provide low cost barriers which remove Cr(VI) from groundwater. To understand how these "organic barriers" work, OM-Cr complexes should be understood better to identify the important functional groups on the OM. This could be done using size exclusion chromatography to gain a better understanding of the OM characteristics that bind to Cr species. This technique can provide information on the molecular size characteristics that are associated with Cr species both in sediments and soils. Furthermore, these fractions can then be characterised using advanced techniques such as Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and UV-Vis spectral parameters e.g. spectral slope ratios; E2:E3. This can glean information on molecular character, (e.g. aromatic, aliphatic) of the OM and the dominant functional groups present in the OM fraction. Fourier-transform ion cyclotron resonance mass spectroscopy (FTICR-MS) will give an insight to the characteristics and relative composition of OM in the system, allowing use to gain fine scale information on OM bound Cr.

The fate of Cr in soils that have a low OM content should also be understood since COPR has been produced in various places around the world all of which will have different soil characteristics. Based on the results of this study, the addition of OM ammendments may help reduce Cr mobility in soils and further tests should be carried out to investigate its suitability as a low cost remediation strategy for Cr(VI).

To get a better understanding of the Cr species present in the Polmadie Burn soils and sediment the use of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) will give ultrafine speciation data of Cr in the soils and sediments. This will give a better understanding of the species of Cr that is bound to soils and sediments, and allow us to better understand what phases dictate Cr species availability. Using time resolved XANES will offer an opportunity to quantify the effect OM has on the sorption kinetics of Cr species on banking soils.

The method used for the inhalation bioaccessibility of Cr(VI) containing dusts still needs refined. Future work improving the LoD of the analytical methods would allow the lower solid to liquid ratios, which are more representative of the lungs, to be used which may affect how the risk is determined in the future. Future work investigating the inhalation risk of bioaccessible Cr(VI) in the ambient PM10 concentrations of Richmond Park will help determine the risk of Cr(VI) exposure to those living in the new housing development at the site. Quantification of PM10 in the Richmond Park air is required to accurately model the Cr inhalation risk. Following this, the PM10 total Cr(VI) concentrations along with the bioaccessible Cr(VI) concentrations can be measured to understand the flux of PM10 associated Cr. Given the low concentration of Cr(VI) associated with PM10 fractions, the use of high performance liquid chromatography coupled with ICP-MS will give a greater sensitivity to detecting Cr(VI) in the inhalation bioaccessibility fractions.

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Appendix 1 Correlation Matrices

All numbers quoted are Spearman’s Rank Correlation coefficients. ***Significant correlations are indicated by the numbers in bold and italic.***

Table A-1: Correlations in banking soil

	Cr	Cr(VI)	Cr(III)	OM	pH	Fe	Mn	Al	Ca
Cr(VI)	***0.727***								
Cr(III)	***0.873***	0.424							
OM	***0.498***	-0.140	0.433						
pH	0.140	0.422	0.13	-0.415					
Fe	0.340	***0.798***	0.363	***0.493***	0.039				
Mn	0.342	0.349	0.284	0.375	-0.044	0.547			
Al	***0.556***	0.495	0.503	***0.723***	-0.147	***0.735***	***0.718***		
Ca	***0.783***	0.683	***0.783***	0.35	0.633	***0.75***	***0.783***	0.633	
Mg	***0.750***	0.033	***0.750***	0.417	0.400	0.333	0.483	0.650	0.633

Table A-2: Correlations in bulk sediment

	Cr	Cr(III)	Cr(VI)	OM	pH	Fe	Mn	Al	Ca
Cr(III)	***1.000***								
Cr(VI)	***0.821***	***0.821***							
OM	***0.594***	0.750	0.571						
pH	0.000	0.000	0.321	-0.393					
Fe	-0.524	-0.607	-0.357	***-0.636***	0.464				
Mn	-0.224	-0.429	-0.357	***-0.678***	0.071	***0.664***			
Al	0.413	***0.929***	0.643	0.035	-0.214	-0.049	0.133		
Ca	-0.071	-0.071	0.429	-0.429	***0.857***	0.500	0.214	-0.357	
Mg	-0.464	-0.464	-0.500	-0.750	-0.143	0.607	***0.893***	-0.536	0.036

Table A-3: Correlations in sediment core 1

	Cr	Fe	Mn	Al	Ca	Mg	OM
Fe	0.414						
Mn	0.296	0.432					
Al	0.011	***0.530***	***0.521***				
Ca	0.011	***0.530***	***0.521***	***1.000***			
Mg	0.230	***0.723***	***0.542***	***0.682***	***0.682***		
OM	0.411	-0.109	0.042	-0.112	-0.112	-0.181	
pH	-0.232	-0.314	-0.633	***-0.815***	***-0.815***	-0.515	***-0.802***

Table A-4: Correlations in sediment core 2

	Cr	Fe	Mn	Al	Ca	Mg	OM
Fe	-0.100						
Mn	-0.175	-0.421					
Al	***0.729***	0.382	***-0.661***				
Ca	0.382	-0.004	-0.118	0.414			
Mg	0.261	***0.532***	***-0.782***	***0.739***	0.475		
OM	***0.582***	***-0.657***	0.386	0.136	0.314	-0.218	
pH	-0.306	-0.193	0.281	-0.387	-0.302	-0.334	-0.105

Table A-5: Correlations in soil column leachate

	Cr	Fe	Mn	Ca	Mg	S
Fe	-0.039					
Mn	0.112	***0.823***				
Ca	0.3	***-0.437***	-0.261			
Mg	***0.481***	***-0.539***	-0.367	***0.943***		
S	0.182	***-0.464***	-0.296	***0.943***	***0.91***	
pH	0.01	***0.718***	***0.656***	***-0.637***	***-0.671***	***-0.762***

Table A-6: Correlations in sediment column leachate

	Cr	Fe	Mn	Ca	Mg	S
Fe	-0.039					
Mn	0.112	***0.823***				
Ca	0.3	***-0.437***	-0.261			
Mg	***0.481***	***-0.539***	-0.367	***0.943***		
S	0.182	***-0.464***	-0.296	***0.943***	***0.91***	
pH	0.01	***0.718***	***0.656***	***-0.637***	***-0.671***	***-0.762***

Table A-7: Correlations in soil batch leachate

	Cr	Cr(VI)	Cr(III)	Fe	Mn	Al	Ca	Mg	S	pH
Cr(VI)	***0.945***									
Cr(III)	***1.000***	***0.945***								
Fe	***0.995***	***0.934***	***0.995***							
Mn	***0.984***	***0.978***	***0.984***	***0.973***						
Al	***0.950***	***0.833***	***0.950***	***0.950***	***0.950***					
Ca	***-0.703***	***-0.824***	***-0.703***	***-0.709***	***-0.747***	-0.517				
Mg	-0.335	-0.434	-0.335	-0.352	-0.374	***0.667***	0.341			
S	***-0.901***	***-0.819***	***-0.901***	***-0.907***	***-0.852***	***-0.800***	***0.731***	0.110		
pH	***0.588***	0.456	***0.588***	0.582	0.527	0.467	-0.198	0.066	***-0.632***	
Moisture Content	***0.956***	***0.885***	***0.956***	***0.967***	***0.918***	***0.850***	***-0.648***	-0.308	***-0.923***	***0.615***

Table A-8: Correlations in sediment batch leachate

	Cr	Fe	Mn	Al	Ca	Mg	S	pH
Fe	0.264							
Mn	***0.599***	0.324						
Al	***1.000***	***1.000***	0.643					
Ca	-0.286	***-0.973***	-0.330	***-0.964***				
Mg	-0.022	***-0.797***	0.071	***-0.857***	***0.824***			
S	-0.434	***-0.819***	-0.500	***-0.964***	***0.786***	***0.643***		
pH	0.470	***0.872***	0.498	***0.955***	***-0.889***	***-0.586***	***-0.652***	
Moisture Content	0.055	***0.835***	0.137	***1.000***	***-0.819***	***-0.813***	***-0.676***	***0.707***

Table A-9: Correlation between Ca, Cr and Mg concentrations found in the Polmadie Burn from long-term monitoring data provided by SEPA

Element	Mg	Cr
Cr	0.906	
Ca	0.841	0.954

Appendix 2: Soil and sediment data

Table A-8: Elemental concentration, pH and OM content of soils

Sample Point	Cr (mg/kg)	Cr(VI) (mg/kg)	Cr(III) (mg/kg)	(%)Cr(VI)	OM (%)	pH	Fe (mg/kg)	Mn (mg/kg)	Al (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
s0	817	127.8	689	15.6	20.8	6.22	46036	1233	24483	14871	3531	-	470
s1	529	109.2	420	20.6	15.8	6.35	43701	846	15153	8934	1327	-	409
s2	1059	114	945	10.8	22.6	6.97	50960	998	22570	16748	6057	-	-
s3	1384	116	1268	8.4	22.5	6.58	46354	1191	29163	17898	10303	-	-
s4	1685	135	1550	8.0	29.1	6.66	51752	1380	33091	18352	9723	-	-
s5	2099	241	1858	11.5	29.3	6.38	45188	1367	33603	20842	8783	-	-
s6	1421	76.7	1345	5.4	23.0	6.45	44697	1108	28273	16710	10076	-	-
s7	1421	89.6	1331	6.3	36.9	6.17	44972	1162	32112	13053	8157	-	-
s8a	832	98.4	734	11.8	24.6	6.34	44426	915	28633	12679	6644	-	-
s9a	6310	2190	4120	34.7	22.1	7.2	50754	1067	27877	-	-	371	558
s10a	1830	520	1310	28.4	24.9	6.85	56108	877	30921	-	-	241	501
s11a	416	83.9	332	20.2	21.6	6.87	43595	771	23721	-	-	245	289
s12a	3080	661	2419	21.5	23.1	6.66	52976	954	37080	-	-	332	702
s8b	1550	949	601	61.2	25.0	6.79	60033	1396	35599	-	-	273	577
s9b	1170	-	-	-	20.7	6.94	32558	905	21104	-	-	186	424
s10b	2650	-	-	-	21.0	7.15	40121	1755	29903	-	-	365	692
s11b	1050	-	-	-	18.2	6.78	27311	759	13232	-	-	136	315
s12b	1110	-	-	-	20.3	7.21	28488	757	13714	-	-	136	332
s13	2130	-	-	-	25.2	6.11	27524	329	15648	-	-	157	388
s14	-	353	-	-	17.3	-	-	-	-	-	-	-	-
s15	-	346	-	-	14.8	-	-	-	-	-	-	-	-
s16	-	391	-	-	20.7	-	-	-	-	-	-	-	-
s17	-	371	-	-	20.1	-	-	-	-	-	-	-	-

Table A-9: Mean elemental concentration, pH and OM content of surface sediments

Sample	Cr (mg/kg)	Cr(VI) (mg/kg)	Cr(III) (mg/kg)	% Cr(VI)	OM (%)	pH	Fe (mg/kg)	Mn (mg/kg)	Al (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
c1	1278	1205	73.5	5.8	5.0	6.53	37103	480	11255	20510	8691	-	-
c2	1614	1537	76.8	4.8	4.30	7.1	44707	609	11328	22646	8750	-	-
c3	1575	1484	90.9	5.8	4.60	7.3	33851	395	10367	25923	7664	-	-
c4	1923	1782	141	7.3	5.1	7.43	38698	419	12398	31604	7429	-	-
c5	3880	3669	210	5.4	8.5	6.93	33237	433	12991	24951	8575	-	-
c6	2699	2601	98.7	3.7	12	6.74	29652	364	12672	21411	7539	-	-
c7	2779	2682	97.3	3.5	17	6.77	26655	333	13152	20388	6673	-	-
c8	3010	-	-	-	24	-	24597	336	10104	-	-	418	220
c9	3040	-	-	-	10	-	29013	461	13081	-	-	87	314
c10	2040	-	-	-	4.2	-	42428	931	15725	-	-	93	216
c11	3170	-	-	-	8.4	-	30121	456	12135	-	-	122	280
c12	2020	-	-	-	2.7	-	27685	445	12567	-	-	256	1088

Table A-10: Mean elemental concentration, pH and OM content of Core 1

Depth (cm)	Cr (mg/kg)	Cr(VI) (mg/kg)	(%)Cr(VI)	Fe (mg/kg)	Mn (mg/kg)	Al (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	OM %	pH porewater
0	1965	484	25	2.69	482	1.52	1.45	7001	7.9	8.07
1	2156			3.30	424	1.64	1.56	6153	10.7	8.33
2	2338			3.17	873	1.72	1.63	6838	11.6	8.19
3	2488	482	19	4.36	571	1.50	1.43	6374	10.2	8.28
4	1804			3.44	777	1.57	1.50	6803	4.5	8.29
5	1904	562	30	3.34	435	1.25	1.20	6188	4.8	8.34
6	2030	326	16	2.68	427	1.05	1.02	5663	4.4	8.43
7	2197			3.25	443	1.06	1.02	6447	2.9	8.48
8	2051			3.45	489	1.46	1.39	7075	4.3	8.38
9	1954	277	14	2.92	415	1.34	1.29	6200	5.3	8.42
10	1734			2.32	414	1.27	1.22	5773	3.1	8.43
11	1788			2.63	454	1.31	1.26	5797	4.8	-
12	2045	210	10	2.70	448	1.07	1.03	5820	3.5	-
13	2408			2.80	401	0.95	0.93	5982	12.3	-
14	2256			2.68	443	0.97	0.94	5073	9.5	-
15	1732			2.60	346	0.97	0.94	5615	12.1	-
16	2103			2.63	589	0.95	0.92	5315	17.1	-
17	2481			3.08	462	1.27	1.22	6763	10.3	-
18	2091			3.15	653	1.76	1.67	6236	8.2	-

Table A-11: Mean elemental concentration, pH and OM content of Core 2

Depth (cm)	Cr (mg/kg)	Cr(VI) (mg/kg)	(%)Cr(VI)	Fe (mg/kg)	Mn (mg/kg)	Al (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	OM %	pH porewater	pH Sediment
0	3701	664	18	3.64	538	0.936	1.92	3806	7.11	8.22	7.5
1	2589			3.52	476	0.668	1.51	3612	4.77	8.49	7.51
2	2249			3.71	632	0.535	1.49	1472	2.34	8.49	7.51
3	3969	306	8	4.40	519	1.10	1.64	3355	13.8	8.42	7.16
4	7406			3.50	426	1.27	1.63	3588	16.3	8.2	7.32
5	12726	449	4	3.64	540	1.35	1.65	2899	16.1	8.16	6.48
6	14867	1129	8	3.85	556	1.71	1.88	4549	19.2	8.28	7.01
7	10872			3.34	489	1.02	1.94	2917	18.3	8.38	7.05
8	11079			3.13	650	0.991	1.63	1909	24.3	8.5	7.07
9	5700	314	6	3.56	595	0.965	1.65	2593	9.73	8.5	7.26
10	4021			3.35	714	0.467	1.86	1364	20.4	8.38	7.27
11	4540			3.07	601	0.697	1.54	1329	27.0	-	7.05
12	3820	970	25	3.28	928	0.600	2.21	1817	23.7	-	7.22
13	4006			3.41	771	0.518	1.25	669	19.0	-	7.29
14	3510			3.47	708	0.454	1.31	660	5.39	8.35	7.47

Appendix 3 BCR Sequential Extraction Data

Table A-12: Distribution of elements in soils (%) as determined by BCR sequential extraction

Element	Distribution in soil fraction (%)			
	Exchangeable	Reducible	Oxidisable	Residual
Cr	0.956 ± 0.33	25.0 ± 8.5	68.4 ± 9.5	5.64 ± 4.4
Mn	26.8 ± 7.4	46.7 ± 9.2	13.5 ± 11	13.0 ± 7.2
Fe	0.153 ± 0.23	34.2 ± 5.6	14.6 ± 4.1	51.1 ± 6.7
Al	0.702 ± 0.25	20.5 ± 2.7	11.5 ± 2.7	67.3 ± 4.5
Ca	49.8 ± 14	14.6 ± 2.5	8.63 ± 1.7	27.0 ± 18
Mg	22.7 ± 7.5	4.32 ± 0.48	18.7 ± 1.4	54.2 ± 9.4

Table A-13: Concentration of elements in soils (mg kg^{-1}) extracted by BCR sequential extraction

Element	Concentration in soil fraction (mg/kg)			
	Exchangeable	Reducible	Oxidisable	Residual
Cr	15.2 ± 8.6	396 ± 210	1087 ± 1000	89.5 ± 58
Mn	293 ± 94	512 ± 240	148 ± 270	143 ± 34
Fe	40.4 ± 62	9050 ± 2200	3860 ± 1700	13500 ± 2100
Al	102 ± 34	2980 ± 700	1680 ± 670	9810 ± 3400
Ca	5630 ± 400	1680 ± 320	991 ± 160	3600 ± 3300
Mg	494 ± 170	101 ± 56	443 ± 260	1390 ± 1100

Table A-14: Distribution of elements in sediments (%) as determined by BCR sequential extraction

Element	Distribution in sediment fraction (%)			
	Exchangeable	Reducible	Oxidisable	Residual
Cr	3.72 ± 1.9	38.8 ± 3.9	53.6 ± 5.4	3.87 ± 3.6
Mn	29.8 ± 5.7	23.4 ± 2.3	8.96 ± 0.93	37.8 ± 6.3
Fe	2.39 ± 0.60	34.1 ± 7.2	6.81 ± 2.2	56.7 ± 8.6
Al	2.84 ± 1.8	27.4 ± 3.6	11.4 ± 4.4	58.3 ± 8.8

Table A-15: Concentration of elements in sediments (mg kg-1) extracted by BCR sequential extraction

Element	Concentration in sediment fraction (mg/kg)			
	Exchangeable	Reducible	Oxidisable	Residual
Cr	104 ± 68	1090 ± 310	1500 ± 380	108 ± 38
Mn	143 ± 27	112 ± 22	42.8 ± 6.1	181 ± 52
Fe	493 ± 180	7030 ± 1600	1400 ± 520	11700 ± 2300
Al	255 ± 170	2460 ± 87	1020 ± 300	5230 ± 1600