Development of Methodologies for Determination of the Human Bioaccessibility of Chromium and Other Elements in Glasgow Soil

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Abstract

Physiologically based extraction tests (PBETs) have been developed over the last decade to predict the human bioavailability of soil-borne contaminants. The majority of these methods, which are essentially sequential extractions using simulated gastrointestinal biofluids, examine exposure via ingestion. Hitherto, most of the published research has focussed on the development and validation of PBETs to assess the bioaccessibility of Pb and As. In this project the Unified Bioaccessibility Method (UBM), a specific PBET, was not only used to examine Pb and As but, for the first time was applied to the assessment of Cr bioaccessibility in contaminated soils. Given the considerably greater toxicity of Cr(VI) relative to Cr(III), the ability to differentiate between chemical species during the application of a PBET was also assessed for the first time, using diphenylcarbazide colorimetric (DPC) analysis for Cr(VI). A combined chemical extraction and statistical technique, known as the Chemometric Identification of Substrates and Element Distributions (CISED) extraction, was used to assess the solid phase distribution, making it possible to identify the likely mineral sources of bioaccessible Cr, Pb and As within the soils. Since Cr(VI) is a known human lung carcinogen, the inhalation bioaccessibility was also determined in selected samples using a lung uptake simulation. These methods were used to assess the bioaccessibility of Cr, Pb and As in 27 contaminated soils from across Glasgow and the results incorporated into site specific risk assessment to determine the potential threats to human health. Glasgow was selected as a study area because between 1830 and 1968 the city was home to one of the world's largest producers of Cr-based chemicals. Chromite ore processing residue (COPR) arising from the factory was used as infill material across large areas of the city, resulting in widespread land contamination with Cr(VI).

The results of the UBM and CISED analyses demonstrated that in the majority of soils Cr was associated with Fe oxide mineral phases, resulting in a low bioaccessibility of only 5% of the total concentration. Two samples had a sizeable amount of Cr associated with clay and carbonate phases, the low acid stability resulting in larger bioaccessible fractions in the samples of 1156 ± 32 and 116 ± 2 mg/kg, respectively. This carbonate phase was unique to sites with a known history of COPR disposal, suggesting that it was derived from the waste material. Incorporating

Cr bioaccessibility into a site-specific risk assessment revealed that only one sample, from Rutherglen, exceeded assessment criteria and as such posed a potential risk to human health.

Although *in vivo* validation of the UBM method for Cr was beyond the scope of this study, limited validation was carried out with the TNO Gastrointestinal Model (TIM), which is widely accepted as a reliable simulation of the human gastrointestinal tract. The UBM was found to give similar results to the TIM method, therefore, indicating that the UBM is a suitable method for assessing the oral bioaccessibility of Cr in soil. In terms of Cr(VI) bioaccessibility, during the initial testing of the UBM, the low-pH, reducing conditions of the stomach simulation were found to be insufficient to convert all of a Cr(VI) spike to Cr(III) during the extraction. Thus the UBM, combined with a standard DPC analysis, was demonstrated to be capable of quantifying bioaccessible Cr(VI). These results are in contrast to the widely held view that Cr(VI) is completely reduced to Cr(III) in the stomach, with oral exposure posing little risk to human health. However, during the analysis of the actual soil samples, no bioaccessible Cr(VI) was detected, despite one containing almost 1500 mg/kg of Cr(VI). Through a combination of ultrafiltration gel electrophoresis and HPLC-ICP-MS it was found that Cr was present in the UBM extracts as Cr-humic complexes. This suggests that soluble organic matter, extracted by the UBM, is reducing soluble Cr(VI) rapidly to Cr(III). This indicates that soil geochemistry is critical in determining whether ingested Cr(VI) is bioaccessible. From these results it can be inferred that ingestion of soils with a low organic matter content is more likely to result in the presence of bioaccessible Cr(VI) in the gut than ingestion of soils with a high organic matter content. Results of the lung uptake tests in the present study revealed that Cr(VI) was bioaccessible in the <10 μm dust fraction in two samples.

In addition to Cr, the bioaccessibility of Pb and As was also assessed in the soils. Large amounts of Pb (average 52% of the total concentration) were found to be bioaccessible. Examination of $^{206}Pb/^{207}Pb$ ratios in the soils indicated that the majority of Pb present was deposited from a mixture of past industrial, domestic and vehicular sources. The $^{206}Pb/^{207}Pb$ ratio of bioaccessible Pb differed little from that in the whole soil, suggesting that the specific anthropogenic origin of Pb has little bearing on its bioaccessibility. Incorporating Pb bioaccessibility into a site-specific risk assessment

revealed that 15 of the 27 samples potentially posed a risk to human health and may require further investigation. Bioaccessible As averaged only 27% of the total As concentration. Incorporating As bioaccessibility into a site-specific risk assessment revealed that only two soils exceeded assessment criteria and posed a potential risk to human health.

This project has successfully demonstrated the application of the UBM to the determination of Cr bioaccessibility in contaminated soils. It has also shown that Cr(VI) may not be completely reduced by the conditions of the stomach prior to transit into the intestine. The standard DPC colorimetric method was shown to quantify Cr(VI) in the UBM extracts. The observation that the bioaccessibility of Cr, Pb and As was considerably less than the total concentration for respective elements suggests that the use of the latter in human health risk assessment will result in an overly conservative assessment. The relatively small bioaccessible fractions of Cr and As compared to those of Pb determined for the Glasgow soils also indicate that Pb poses a greater potential threat to health. However, the findings that Cr(VI) is bioaccessible via inhalation of dust is of interest and worthy of further investigation.

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Abbreviations

BARGE	BioAccessibility Research Group for Europe
BGS	British Geological Survey
CISED	Chemometric Identification of Substrates and Element Distributions
CLEA	Contaminated Land Exposure Assessment
COPR	Chromite Ore Processing Residue
DEFRA	Department for Environment, Food and Rural Affairs
DPC	Diphenylcarbazide
HPLC-ICP-MS	High Performance Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISC	Intrinsic Soil Constituent
PBET	Physiologically Based Extraction Test
SGV	Soil Guideline Value
SNIFFER	Scottish & Northern Ireland Forum For Environmental Research
SSAC	Site-Specific Assessment Criteria
TIM	TNO Gastrointestinal Model
UBM	Unified Bioaccessibility Method
USEPA	United States Environmental Protection Agency

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CHAPTER 1 INTRODUCTION

1.1 An Introduction to the Glasgow Study Area

Glasgow, with a population of around 740,000, is Scotland's largest city and has a long history of industrialisation and urbanisation. During the 19th Century a wide range of heavy industries thrived, especially shipbuilding, locomotive construction and engineering. Immigration from the Highlands in the 1820s and thousands fleeing from the potato famine in Ireland in the 1840s provided a vast pool of cheap, unskilled labour. At its height Glasgow ranked as one of the finest and richest cities in Europe, acclaimed as a model of an organised industrial society. Grand public buildings and a host of museums, galleries and libraries were built. Glasgow had more parks and open spaces than any other similar European city, along with a regulated telephone system, water and gas supplies. It was also widely considered to be 'the second city of the Empire'. Much of this wealth and expansion was unlikely to be felt by the working class, for whom industrialisation resulted in many human health and environmental problems, including contaminated land.

1.1.1 History of Glasgow's Chromium Industry

Between 1830 and 1968 J. & J. White's chemical works, located in Shawfield, Rutherglen, was one of the world's largest producers of Cr-based chemicals (Bewley *et al.*, 2001), especially potassium chromate (K_2CrO_4) and potassium dichromate ($K_2Cr_2O_7$). The industrial process involved the grinding of chromite ore, with the spinel structure $[(Cr,Fe,Al)_2O_3(Fe,Mg)O]$ (composition was approximately 35% Cr_2O_3, 20% Fe_2O_3, 15% Al_2O_3, 12% FeO and 12% MgO after World War I), into a powder, which was then mixed with an alkali carbonate before being roasted (oxidised) in a 1150 °C furnace. Prior to 1880, K_2CO_3 was the alkali carbonate of choice, after which Na_2CO_3 was increasingly used (Farmer *et al.*, 1999b).

One problem encountered during the roasting stage was that liquid chromate could create a barrier, preventing oxygen from reaching unreacted chromite. To avoid this, a diluent was added. Up until the 1950s the high-lime process was used, where the diluent was quicklime (CaO). After the 1950s the low-lime process was used, in which the diluent was dolomite ($CaMg(CO_3)_2$). In the final stages water was used to extract sodium chromate, which was later converted to potassium

chromate/dichromate (Farmer *et al.*, 1999b). A by-product of the high-lime process was insoluble $CaCrO_4$, which could not be extracted with water and so remained in the ore residue (Geelhoed *et al.*, 2003).

By the time that White's, which had first changed its name to British Chrome and Chemicals and then to Albright and Wilson, closed in 1968 it was producing approximately 30,000 tons of dichromate per year (McAvoy, 1992; Farmer *et al.*, 1999b). For every ton of dichromate produced by the high-lime process, 2.1 tons dry weight of waste was produced. The low-lime process was more efficient, only producing 1.15 tons of waste per ton of product. This waste came from many different stages of the industrial process. Only 30% (by weight) of the original ore was converted to dichromate, the rest, consisting mainly of Fe_2O_3, CaO and MgO, being used as landfiller. The alkali liquor, from which Na_2CrO_4 was extracted, was treated with acid to precipitate $Al(OH)_3$ and crystallise Na_2SO_4. This waste, which was still alkaline in nature, was then also sent to landfill (Farmer *et al.*, 1999b).

In 1921 the chemical works changed its manufacture process to yield chromic acid. The result was Cr-contaminated $NaHSO_4$ waste. This acidic by-product was able to react with the alkali furnace waste already in landfill, which in turn solubilised many chromates, i.e. $CaCrO_4$ and Na_2CrO_4 (Farmer *et al.*, 1999b). It has been estimated that, since no solids left White's, except for sale or as waste residues to landfill, the total amount of waste landfilled between 1830 and 1968 must have been around 2,500,000 tons dry weight (Farmer *et al.*, 1999b).

1.1.2 The Contamination Legacy

In 1989, a report by the Strathclyde Regional Council Public Analyst on the analysis of soils in Rutherglen stated "... our knowledge of this area of the city suggests that any fill area is likely to be contaminated by Cr waste from former Cr works" and "many of the Cr levels exceed the threshold level, even for open spaces" (Eizaguirre-García, 1996). The Environmental Health Department (EHD) of Glasgow District Council was approached in January 1991 by a company carrying out building work in Rutherglen with an enquiry into the possible existence of landfill sites in Glasgow licensed to receive Cr-contaminated waste. The issue became public knowledge after a local newspaper announced that the Health and Safety Executive had ordered a ban on earth removal at the building site (Eizaguirre-García, 1996).

Consequently the EHD carried out an investigation in order to assess the extent of Cr pollution. Soil samples from a range of sites were collected and analysed by the Regional Chemist. A preliminary report on the findings was made public in August 1991. The origin of the Cr was confirmed to be White's Factory in Rutherglen (Eizaguirre-García, 1996). The investigation identified fifteen sites where elevated concentrations of Cr(VI) extended below depths of 10 m. The average soil concentration of Cr(VI) across these sites was found to be 700 mg/kg, with a maximum of 15,600 mg/kg (Bewley *et al.*, 2001). The average value exceeded both the government soil guidelines at the time (ICRCL, 1987) and those in place today (see Section 1.7) for all residential land, whereas the maximum measured value is over three times greater than the guideline value for industrial land (DEFRA, 2002b).

As chromite ore processing residue (COPR) was used as infill material for land prior to development work, there was a high potential for human contact with Cr(VI). Indeed, as the MP for Glasgow Rutherglen said in 1992, "We are now discovering it [COPR waste] on sites adjacent to schools, playing fields, housing schemes and the spectators' area of a local junior football stadium. A nursing home in Rutherglen has been found to have been built on a site where White's dumped toxic Cr waste" (Herald, 1991a; McAvoy, 1992). Findings such as these have led to access being removed from many public areas to prevent exposure (Herald, 1991b, 2001).

Since 1991, when the first contaminated sites were cordoned off, there has been concern over adverse health effects. There has been anecdotal evidence of higher cancer rates in the Rutherglen and Cambuslang areas, where many of the contaminated sites are found (McAvoy, 1992). Indeed, it is known that there is a higher incidence of leukaemia, particularly of the childhood type, in the southeast of Glasgow (Eizaguirre-García *et al.*, 1999). The local media regularly prints articles and discussions concerning the situation (Herald, 2001, 2003, 2004). There is, however, little scientific evidence linking the contaminated sites with adverse human health effects. Eizaguirre-García *et al.* (1999) could not find a link between leukaemia rates and proximity to the contaminated sites, but concluded that further research is required. A seven year study into congenital anomalies in Glasgow equally could not find a relationship with proximity to Cr waste (Eizaguirre-García *et al.*, 2000), although another study has reported an increased risk of anomalies for people living

near waste (Dolk *et al.*, 1998). A significant increase in congenital anomalies was also found in a 1996 study. In addition, this work reported significant increase in eye irritation and a slight increase in upper gastrointestinal tract irritation around Rutherglen (Eizaguirre-García, 1996). The self-reported health of people living in Cambuslang, Carmyle and Rutherglen differed very little from those from a control area, with no Cr waste. It was noted, however, that there was a statistically significant poorer general health in the population from Cambuslang, Carmyle and Rutherglen. Within this group, the people who believed Cr adversely affected health showed worse results than those that did not (McCarron *et al.*, 2000).

1.2 Chromium in the Periodic Table

Chromium is a hard, silvery white metal located in the group VI-B of the periodic table. It is in the fourth period making it a transition element with various possible oxidation states between -2 and +6 (Barnhart, 1997). However, only +3 and +6 oxidation states are commonly found in nature (Rai and Eary, 1989). The trivalent species, which forms through loss of all *4s* electrons and one *3d* electron, is cationic and commonly known as chromite. The hexavalent species, which forms through the loss of all *4s* and *3d* electrons, is anionic due to strong association with oxygen and is commonly called chromate.

1.3 Chromium Occurrence in the Environment

1.3.1 Natural Sources of Chromium in the Environment

Chromium is a relatively common element, ranking the 7th most abundant element on earth, but only 21st in the crustal rock (McGrath and Smith, 1990). This makes it more plentiful than both copper and zinc (Gauglhofer and Bianchi, 1991). Chromium(III) is found naturally in several minerals, including copiapite, daubreelite, dietseite, fornacite, halotrichite, kaemmererite, lopezite, merumite, muscovite, phoeniocochroite, stichtite, barbetonite, uvarovite, vauquelinite and beidellite (Thayer, 1956). On the other hand Cr(VI) is rarely found in nature, its presence generally being due to anthropogenic inputs (Barnhart, 1997).

There are few mechanisms for Cr movement or enrichment in nature, therefore there are limited deposits around the world. This is highlighted by the fact that 95% of all economically viable reserves of Cr ore are located in southern Africa (Gauglhofer and Bianchi, 1991). Chromium is typically associated with basic and ultramafic igneous

rock. Soils derived from these rocks will be enriched with Cr. A study involving 2944 Scottish soil samples found Cr concentrations ranging from 0.5 to 10,000 mg/kg, with a median value of 62 mg/kg (Berrow and Reaves, 1986). The total Cr content in soils for England and Wales has been reported as ranging from 0.2 to 838 mg/kg with a median of 39.3 mg/kg (McGrath and Loveland, 1992).

1.3.2 Anthropogenic Sources of Chromium in the Environment

Chromium is used in a wide range of industries. In metallic form, Cr is used in alloy steels, in chrome plating and in the production of refractory bricks for lining furnaces. Chromium compounds have a variety of uses in the chemical industry, including as a tanning agent for leather, a pigment for paint, as a catalyst, as a wood and textile preservative and as coating for video/audio tape. Chromium is also found in phosphate fertilisers, where concentrations can range between 30 and 3000 mg/kg (McGrath and Smith, 1990).

Due to its use in a wide range of industries, chromium is released into air, water and soil systems. Disposal of fly ash is believed to be the largest single input of chromium into soils, while application of sewage sludge can also greatly increase soil concentrations (McGrath and Smith, 1990; DEFRA, 2002b). In a geochemical survey of 14 urban areas of the UK a median Cr concentration of 39 mg/kg was observed (Fordyce *et al.*, 2005). The highest concentrations were found in Glasgow, where the Cr content ranged from 38 to 4286 mg/kg (median 108 mg/kg).

1.4 Health Effects of Chromium

1.4.1 Trivalent Chromium

Chromium(III) is believed to be an essential element in the human diet, potentating insulin action in peripheral tissue and being essential for lipid, protein and fat metabolism. Deficiency causes changes in the metabolism of glucose and lipids and may be associated with maturity-onset diabetes, cardiovascular disease and nervous system disorders (USEPA, 1998a). The UK Committee on Medical Aspects of Food Policy has recommended a dietary intake of above 25 μg Cr(III) per day for adults and between 0.1 and 1 μg/kg bw/day for children and adolescents (DEFRA, 2002b).

It is widely considered that Cr(VI) has a significantly greater toxicity than Cr(III) and its effects on health have been well researched. For this reason there have been a very

limited number of studies into the toxicity of Cr(III) (USEPA, 1998a). However, most studies have revealed few significant side effects from oral exposure to Cr(III). Animal experiments (rats, mice, cats etc) found no significant respiratory, cardiovascular, gastrointestinal, hepatic, renal or neurological abnormalities following periods of regular Cr(III) ingestion (ATSDR, 2000).

It has been reported that this perceived lack of toxicity is due to the inability of Cr(III) to cross biological membranes (Pellerin and Booker, 2000; Qi *et al.*, 2000). Chromium(III) has been demonstrated to decrease the fidelity of DNA synthesis in *in vitro* studies and tests have shown that Cr(III) can potentially produce genotoxic DNA adducts that inhibit DNA replication and are mutagenic (Snow, 1991; Singh and Snow, 1998). In fact, Pellerin and Booker (2000) point out that the observed toxicity of Cr(VI) is a result of it acting as a "Trojan Horse", crossing the cell membrane before being reduced to Cr(III), which is then able to react with DNA. Animal tests, however, have shown no increase in the incidence of tumours (USEPA, 1998a; ATSDR, 2000). This discrepancy has led to the United States Environmental Protection Agency (USEPA) designating Cr(III) as a 'Group D-Not Classified' substance with respect to its human carcinogenicity (USEPA, 1998a). It is believed that, at high concentrations, Cr(III) is potentially harmful (Stewart *et al.*, 2003b).

1.4.2 Hexavalent Chromium

When considering the health effects of Cr(VI) it is useful to regard the routes of exposure as well. There are four main routes: (i) dermal absorption, (ii) inhalation, (iii) ingestion and (iv) ingestion secondary to inhalation.

1.4.2.1 Dermal Exposure to Hexavalent Chromium

Chromium is generally recognised as the second most common skin allergen in the general population after nickel, due to its ability to act as an oxidant directly on the skin surface (Polak, 1983; Haines and Nieboer, 1988). The main complaints reported after dermal exposure to Cr(VI) are dermatosis (skin ulceration) and dermatitis (allergic skin) (Bagdon and Hazen, 1991).

Absorption of Cr(VI) into the blood system through the skin has been reported but not extensively investigated. Once absorption has taken place there are antioxidants, such as ascorbate and glutathione, which can reduce Cr(VI) to Cr(III). Large doses of

Cr(VI) in blood can, however, still result in acute kidney and liver damage (DEFRA, 2002a).

1.4.2.2 Inhalation Exposure to Hexavalent Chromium

The largest particulates that can pass the nose and throat and enter the lungs are about 10 μm in diameter. This includes particles resulting from welding, ore roasting and from precipitative and thermal chemical processes involved in much of the Cr industry (Sheehan *et al.*, 1991). Unlike most other toxins, absorption is not the principal health concern for chromates. Instead the major concern is the direct effect on the bronchi of the lungs (IARC, 1990), whereby it is widely accepted to potentially result in respiratory cancer (USEPA, 1998b; ATSDR, 2000; DEFRA, 2002a). There is also some indication that exposure can cause cancer in the upper respiratory tract, i.e. the oesophagus, larynx and trachea. The International Agency for Research on Cancer (IARC) has concluded 'there is sufficient evidence in humans for the carcinogenicity of Cr(VI)' (DEFRA, 2002a). The USEPA has a similar view and both organisations have placed it in their highest cancer risk category (USEPA, 1998b; DEFRA, 2002a).

1.4.2.3 Oral Exposure to Hexavalent Chromium

Chromium can become incorporated into the gastrointestinal environment by direct ingestion of Cr-containing materials (e.g. water, food, soil, plant and animal products) or through particles cleared through the respiratory tract to the oesophagus (Wragner, 1980; Calabrese *et al.*, 1997; Paustenbach, 2000). It is believed, however, that the majority of Cr(VI) ingested will be quickly reduced in the acidic pH of the stomach and that only intakes that exceed the reducing capacity of the stomach will result in absorption of Cr(VI) across the gastrointestinal mucosa (Kerger *et al.*, 1996; Pellerin and Booker, 2000). For this to occur very large amounts of Cr(VI) need to be consumed, resulting in numerous toxic effects. Symptoms reported in humans following either accidental or deliberate ingestion of lethal doses of Cr(VI) include: haemorrhages in the gastrointestinal tract, generalised oedema, pulmonary oedema and severe liver and kidney damage (ATSDR, 2000; DEFRA, 2002a). The lethal oral dose is typically considered to be in the range 1-5 g Cr(VI), but lethal doses as low as 300 mg Cr(VI) have been reported (DEFRA, 2002a). Animal studies have also shown reproductive and developmental effects. Exposure to potassium dichromate in drinking water at 50 mg Cr(VI)/kg bw/day in pregnant mice caused severe

developmental effects, including embryo death, reduced litter size and gross congenital abnormalities (DEFRA, 2002a).

While the relationship between inhalation exposure to Cr(VI) and respiratory cancers is widely accepted, there are few data on the carcinogenic potential of oral exposure (ATSDR, 2000). Fore-stomach tumours have been reported in long term studies involving mice, but problems in data interpretation undermined their value (DEFRA, 2002a). In addition, epidemiological studies have highlighted a slightly elevated incidence of stomach cancer in populations exposed to Cr(VI) via inhalation. This could indicate that Cr reaches the stomach following clearance of the mucous membranes lining the lungs, but this is by no means definitive and it is not widely accepted that Cr(VI) is a carcinogen in the stomach (Alexeeff *et al.*, 1989; Lees, 1991)

1.5 Lead Occurrence in the Environment

1.5.1 Natural Sources of Lead in the Environment

Lead, the most common of the heavy metals, is generally found associated with igneous rocks, where it has an affinity for S forming minerals such as Galena (PbS). Sedimentary rock, such as shales and mudstones that result from the weathering of igneous rocks, are also known the contain Pb. A typical Pb content of shales and mudstones in the UK is 23 mg/kg. The total Pb content in soils for England and Wales has been reported as ranging from 3 to 16,338 mg/kg with a median of 40 mg/kg (McGrath and Loveland, 1992)

1.5.2 Anthropogenic Sources of Lead in the Environment

With a low melting point of only 327 °C, Pb can be easily worked resulting in it extensive use throughout history. Indeed Pb originating from the smelting of Pb ore in Britain prior to the Roman occupation has been found in Scotland (Cloy *et al.*, 2005). In addition to mining and smelting, there are several well-recognised anthropogenic sources of Pb in the environment, such as the use of sewage sludge in agriculture, aerial deposition from coal and petrol (leaded) combustion and the use of $PbAsO_4$ pesticides. The concentration of Pb in Scottish coals has been reported to range from 5.6 to 137 mg/kg, with a median of 17.8 mg/kg (Farmer *et al.*, 1999a). The combustion of coal will result in the aerial deposition of Pb. The vast amounts of coal used to power Britain's industrial cities in the past, along with other sources such as

leaded petrol, has resulted in elevated concentrations of Pb in urban areas compared to rural (Fordyce *et al.*, 2005). In a geochemical survey of 14 urban areas of the UK, a median Pb concentration of 40 mg/kg was observed (Fordyce *et al.*, 2005).

1.5.3 Health Effects of Lead

The effects of Pb on human health has been the subject of many studies, having been connected with adverse effects on the nervous system of children. Hearing impairment and disturbance of vitamin D metabolism have also been described as "critical effects" in children. While more obvious effects result from occupational exposure, public and scientific concern has been focussed on children. The developing foetus and child are considered to be at greater risk both because of "sources-pathways" (hand-to-mouth activity) and because of greater susceptibility (an increased dietary absorption of lead) (DEFRA, 2002h).

Lead has been connected with adverse effects on the behaviour and intelligence of children. In a study of 501 children aged 6 – 9 years old in Edinburgh, exposed primarily via drinking water, the mean blood Pb of the group was found to be 11.5 μg/dL (range 3.3–34 μg/dl). After adjustment for confounding variables, a significant inverse correlation was found between log blood Pb and scores for number skills and word reading (Fulton *et al.*, 1987). Another study of 309 children in Yugoslavia, from birth through to seven years old, found that a change in lifetime blood lead from 10 to 30 μg/dl was related to an estimated decrease of 4.3 full-scale IQ points (Wasserman *et al.*, 1997).

A Working Group of the IARC has classified inorganic lead compounds as "possibly carcinogenic to humans", whereas an assessment by USEPA considered a "probable human carcinogen" classification to be appropriate. These overall verdicts were based on a consideration of both human and animal data (DEFRA, 2002h).

1.6 Arsenic Occurrence in the Environment

1.6.1 Natural Sources of Arsenic in the Environment

Arsenic occurs in many minerals and, being the 12th most abundant element in the Earths crust, is widely distributed in rocks, soils and sediments. Arsenic is often found associated with Fe deposits in sedimentary rock, due to its co-precipitation with Fe and sulphides. As a result arsenopyrite is the most common arsenic-containing

mineral. Weathering of sedimentary bedrock can result in soils enriched with As. In the UK, Jurassic Ironstones have been connected with soil concentrations ranging from 19 to 102 mg/kg (Wragg *et al.*, 2007), although concentrations of 300 mg/kg have also been reported (Palumbo-Roe *et al.*, 2005).

1.6.2 Anthropogenic Sources of Arsenic in the Environment

As with Pb, As is commonly found enriched in coal, the combustion of which can result in widespread dispersion (Nriagu, 1994; Baird, 2000). Another principal source of anthropogenic arsenic is the processing of mineral ore and gangue, predominantly as a by-product of the extraction of Cu, Pb, Sn and Ag (DEFRA, 2002f). The atmospheric deposition from both Cu smelting and the burning of fossil fuels are important pathways for As input to soil (DEFRA, 2002f).

1.6.3 Health Effects of Arsenic

Oral exposure to low doses of As over extended periods of time has been linked to dermatological and cardiovascular effects. The dermatological effects include skin lesions of various kinds and skin cancer. The IARC and the USEPA have placed As in their highest cancer-causing category. The cardiovascular effects included peripheral vascular disease and myocardial damage due to the thickening of the inner layer of blood vessel walls (DEFRA, 2002g).

1.7 Contaminated Land and Human Health Risk Assessment

In 2002 guidance was published concerning the assessment of risks to human health from land contaminated with 10 inorganic substances, including Cr, Pb and As (DEFRA, 2002d). Toxicological information and Soil Guideline Values (SGVs) for each of the 10 contaminants were published as part of the Contaminated Land Exposure Assessment (CLEA) model. This model, developed for the Department for Environment, Food and Rural Affairs (DEFRA) and the Environment Agency, estimates contaminant intake from soil as a function of the contaminant concentration and the potential exposure of adults and children living, working and playing on contaminated land. It has been used to derive SGVs by comparing the calculated intake with the Tolerable Daily Intake for the respective contaminants. SGVs act as screening criteria for potentially contaminated site, where an exceedance indictates that there may be "significant possibility of significant harm" and further investigation should be performed (DEFRA, 2002e, 2002d). Prior to this, the

assessment of possible risk to human health from toxic elements present in soils was largely based on the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) trigger levels (ICRCL, 1987) or on the Risk Based Corrective Action (RBCA) model. Under the new guidelines, there is a need to consider whether the presence of the contaminant above the associated SGV justifies taking remedial action or whether a more detailed risk assessment is required.

There are three routes of exposure considered in terms of human health risk assessment for contaminants present in soil. These are the oral/ingestion, dermal and respiratory routes (Paustenbach, 2000). To pose an unacceptable risk to human health a potentially harmful element needs to be extracted from the soil and enter the human bloodstream. The use of total concentrations in risk assessment results in an overly conservative estimate of risk, as it assumes all of the contaminant present in the soil can enter the bloodstream. Determining the amount of a contaminant that can enter the bloodstream on a site-specific basis will reduce the exposure estimate, which will more realistically reflect the conditions at the given site (Kelley *et al.*, 2002).

In-vivo animal models are used to approximate the amount of a contaminant that may enter the bloodstream. Known as dosing trials, these involve test animals being fed the potentially harmful element in the form of a soluble salt, soil or foodstuff (Ruby *et al.*, 1999). The measurements of the contaminant in the animal's blood and urine are made regularly prior to death by slaughter. After necropsy, the organs, including the gastrointestinal tracts, are removed for analysis. The preferred animal species are immature swine as they have similar gastrointestinal tract characteristics to humans (Dodds and Hsu, 1982; Wragg, 2005).

Animal models have shown that contaminants bound in a soil are less likely to be absorbed and show fewer toxic effects when compared with those resulting from the same concentration of soluble salts administered from a food or liquid matrix (Freeman *et al.*, 1994; 1996; Casteel *et al.*, 1997). This indicates that the conservative assumption of many risk assessment models, i.e. that 100% of a contaminant reaches the bloodstream following soil ingestion, may not be appropriate.

Animal studies that determine the amount of a contaminant in the circulatory system produce data generally associated with the term bioavailability. Bioavailability is

defined as the fraction of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract (Paustenbach, 2000). The bioavailability of a range of inorganic contaminants, in numerous solid matrices, has been determined on a variety of animal species. Lead and As have received the most attention in this area of research (Ruby *et al.*, 1999), although other potentially harmful elements such as Cr have been studied (O'Flaherty, 1996; Febel *et al.*, 2001). The animal species used in dosing trials, where blood and urine samples have been collected for analysis, include juvenile swine (Casteel *et al.*, 1997), rats (Hamel *et al.*, 1999), rabbits (Ruby *et al.*, 1992; Ruby *et al.*, 1993) and monkeys (Freeman *et al.*, 1995). As a result of the physiological differences between humans and the experimental animals, it is difficult to interpret the data from *in-vivo* studies with respect to their relevance to human health. One problem associated with the lack of direct testing on humans is that the animal models used may produce a bioavailability that differs from those found in humans, because of the physiological differences between the species. In addition to this, animal dosing trials are time-consuming and expensive to carry out (Ruby *et al.*, 1999).

For human health risk assessment the ideal situation would be to have bioavailability data available for all contaminants present in all soil types. However, for ethical and financial reasons, as well as time constraints, this is not possible. As an alternative, a number of laboratory-based *in vitro* tests have been designed to assess oral bioaccessibility as a prediction of bioavailability (Ruby *et al.*, 1999). Bioaccessibility can be defined as the fraction of an administered dose that is soluble in the gastrointestinal environment and is available for absorption (Paustenbach, 2000). This differs from the definition of bioavailability by the omission of absorption into the bloodstream. At present the ability to simulate absorption from the gastrointestinal tract in the laboratory is very difficult (Rodriguez *et al.*, 1999). The amount of pollutant which is actually absorbed by an organism is generally considered to be less than, or equal to, the amount which is mobilised (Paustenbach, 2000). *In vitro* bioaccessibility methods use a variety of reagents, such as enzymes and organic acids, to simulate stomach and small intestinal fluids. The simulated systems have traditionally incubated various metal salts or soils at low pH for a period to mimic the residence in the stomach, followed by an increase in pH to mimic small intestinal conditions. The original *in-vitro* gastrointestinal systems were developed to study the

availability of Fe in foodstuffs for nutrition studies (Miller *et al.*, 1981). *In vitro* bioaccessibility tests are generally based around the gastrointestinal tract parameters of young children (0-3 yr), because it is thought that this age group is at the greatest risk from accidental ingestion of soil (Ruby *et al.*, 1999; Wragg and Cave, 2002). In addition to this, it is more applicable that this age group was chosen, because children generally absorb a higher percentage of nutrients/contaminants from the digestive system compared with adults. As a result, they are potentially susceptible to the adverse health effects of such exposure (Hamel *et al.*, 1998). It has since been recognised that this type of testing could provide "a rapid and significantly less expensive method to determine the amount of pollutant that can be dissolved out of a contaminated soil by the juices of the upper digestive tract" (DIN, 2000). As the cost and time required to perform *in vitro* bioaccessibility tests is small compared with those of *in-vivo* testing, there is a potential for a larger number of soils to be tested to fully characterise a site.

In this study an *in vitro* bioaccessibility test has been used to predict the oral ingestion bioavailability of Cr in industrially contaminated soils in Glasgow and its surrounding environs, focusing on Cr contamination originating from the disposal of COPR waste (Section 1.1.2). Release of Cr(VI) through disposal of COPR has led to major contamination problems in Glasgow, Scotland and Hudson County, New Jersey, USA (Geelhoed *et al.*, 2003). Unlike for Pb and As, both the subject of extensive study, there has been very limited research into the assessment of Cr bioaccessibility in soils. This is mainly because there are relatively few locations around the world where Cr(VI) poses an environmental health issue. Most of the research up to now has involved spiking otherwise uncontaminated soil with a soluble form of Cr (Skowronski *et al.*, 2001; Stewart *et al.*, 2003a; Stewart *et al.*, 2003b; Fendorf *et al.*, 2004). Very few, if any, studies have looked at Cr oral bioaccessibility in soils anthropogenically contaminated in 'real' environments opposed to uncontaminated soils spiked in the laboratory.

1.8 Aims and Objectives

The aim of this thesis was to investigate the bioaccessibility of soil Cr in the urban area of Glasgow, its relationship to mineral speciation and its implications for human

health. The bioaccessibilities of As and Pb were also determined to provide a more complete assessment of potentially harmful elements (PHE) in the urban soils.

The objectives were:

1. To review current bioaccessibility tests and their application to Cr-contaminated soil.

2. To identify sites where the selected PHE concentrations could be a potential risk to human health.

3. To optimise a Physiologically Based Extraction Test (PBET) with respect to assessing Cr-contaminated soils and apply it to the sites identified in 2.

4. To determine the solid phase distribution of Cr, Pb and As in the soils and assess how this relates to the bioaccessibility.

5. To use the bioaccessibility data to carry out human health risk assessment at each site.

1.9 Structure of Thesis

The thesis is organised into nine chapters, excluding the appendices and references, consisting of:

- Chapter 1 - the introduction, aims, objectives and structure of this project;
- Chapter 2 - a review of *in vitro* soil bioaccessibility methodologies;
- Chapter 3 - the sampling strategy and locations of each of the test sites;
- Chapter 4 - the analytical and statistical methodologies used in this thesis;
- Chapter 5 - the results of the chemical characterisation, total elemental composition, mineralogical characterisation and Cr speciation of the soil samples;
- Chapter 6 - the solid phase distribution of the analytes within the soil samples;

- Chapter 7 - the analyte bioaccessibility within the soils, including the application of speciation techniques to assess the nature of the Cr present;
- Chapter 8 - an integrated discussion of the results from Chapters 5, 6 and 7;
- Chapter 9 - the overall conclusions of this thesis.

CHAPTER 2 REVIEW OF BIOACCESSIBILITY METHODOLOGIES

2.1 Gastrointestinal Analogues

The human gastrointestinal tract consists of a number of different stages, where ingested material undergoes a series of reactions. During these reactions a number of parameters vary, including fluid composition, pH and reaction time. Table 2.1 summarises the order and conditions encountered in the gastrointestinal environment.

Table 2.1 Compartments of the human gastrointestinal tract (Oomen *et al.*, 2002).

Compartment Name	Residence Time	pH
Oral Cavity	Seconds to minutes	6.5
Stomach	8-15 min (fasting, half emptying time)	1-2
	0.5-3 hr (fed, half emptying time)	2-5
Small Intestine		
i) Duodenum	0.5-0.75 hr	4-5.5
ii) Jejunum	1.5-2 hr	5.5-7
iii) Ileum	5-7 hr	7-7.5
Colon	15-60 hr	6-7.5

Since the mid 1990s there has been a move towards developing *in vitro* methods that simulate the human digestive tract to provide a better estimate of bioavailability of potential harmful elements (PHEs). Oral bioavailability, in this case, can be defined as:

> "the fraction of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract" (Ruby *et al.*, 1996).

It is important to understand that these *in vitro* models do not simulate absorption of PHEs into the body and thus cannot directly measure bioavailability. Instead these *in vitro* methods measure the bioaccessibility, which is defined as:

> "the fraction that is soluble in the gastrointestinal environment and is available for absorption" (Ruby *et al.*, 1996).

Bioaccessibility therefore tends to be an overestimate of bioavailability. To date a wide variety of methods have been developed, employing combinations of one or more of the compartments shown in Table 2.1. Some simulate just the stomach, others

the stomach and small intestine. The inclusion or omission of one of these compartments will affect the measured bioaccessibility of contaminant metals in different ways. For example, As, which is primarily anionic and Pb, which is cationic in solution, will behave differently when extracted from the solid matrix under different pH regimes. In gastrointestinal extraction methods that employ more than one compartment, the bioaccessibility in each compartment may be determined. This can provide information on the relative amounts of PHEs being mobilised at each stage and represents a monitoring value that takes into account different chemical conditions as the extraction proceeds. For example, in a procedure that simulates the stomach and intestine phases, samples can be collected and analysed (i) after the stomach stage, but before the intestinal and (ii) after the intestinal stage. It is important to understand that results generated for the stomach and intestine phases must not be summed to give an overall bioaccessibility, since the intestine value is wholly dependent on the outcome of the stomach phase. Different PHEs will be mobilised to different degrees in the stomach and intestine stages, depending upon their chemistry. For the purposes of risk assessment, where a conservative approach is usually adopted, the higher of the values for the two stages is taken as the bioaccessible value.

Some *in vitro* models have attempted to take into account the inclusion of food in the stomach (Ruby *et al.*, 1999). Initially it was believed that fasting conditions would produce the most aggressive digestive condition, i.e. low stomach pH, maximising metal dissolution, which will provide the conservative estimate of bioaccessibility normally desired in risk assessment (Ruby *et al.*, 1996). Indeed, work has also shown that the presence of food can reduce the uptake of Pb (James *et al.*, 1985; Maddaloni *et al.*, 1998; Ruby *et al.*, 1999). Other workers (Dressman *et al.*, 1993; Rodriguez *et al.*, 1999; Oomen *et al.*, 2002), however, have found that the inclusion of food increases the bioaccessibility of As, Cd and Pb.

At present there is no simulation of the lower gut in any *in vitro* model. Metals contained within insoluble particles would eventually pass into the colon, where very different physico-chemical and biochemical conditions occur due to the presence of huge numbers of bacteria (Wragg and Cave, 2002). This could have an impact on the

soil particles and hence the mobilisation of toxic metals could take place (Rumney and Rowland, 1992).

The *in vitro* models can be divided into two categories: batch tests and flow-through reactor systems. Batch tests form the majority of the methods currently used as they are similar, quick and cost effective. A batch test is where the sample and reagents are reacted in a single container with additional chemicals being added and samples removed as stated in each specified protocol. A flow through reactor system on the other hand takes place under flowing conditions designed to simulate the transit characteristics of the gastrointestinal tract. Only two methods employing a flow through reactor system for soil bioaccessibility testing are currently being used. An overview of methods currently being used, based on their main features, is given in Table 2.2 and each is discussed individually in Sections 2.1.1 to 2.1.11.

2.1.1 The Physiologically Based Extraction Test (PBET)

The physiologically based extraction test (PBET) was developed in the early 1990s as a screening level test to assess the bioavailability of trace elements in soil. Based on a model originally used to determine available iron in foodstuffs, the PBET was designed around the paediatric gastrointestinal tract of a 2-3 year old child, because it is believed that this group is at the greatest risk from accidental soil ingestion (Ruby *et al.*, 1993). This test is essentially a two-stage sequential extraction using various acids and enzymes to simulate both gastric and the small intestine compartments, with extraction carried out at body temperature (37°C). Potentially contaminated soils are introduced into the simulated gastric solution to solubilise any bioaccessible metal present. The conditions are then modified, after a stomach aliquot has been collected, to simulate the small intestine. The reaction vessels for the extraction are argon-purged to keep the system under anoxic conditions (Ruby *et al.*, 1996).

This method has been shown to correlate Pb bioaccessibility with *in-vivo* Sprague-Dawley rat models ($r^2 = 0.93$, n=7). It was found, however, that the PBET tended to over-predict As bioavailability when compared with rabbit and primate models (Ruby *et al.*, 1996). All data collected at present indicates that the PBET is a "good predictor of oral Pb bioaccessibility" (Basta and Gradwohl, 2000).

Table 2.2 Summary of the main features of current gastrointestinal analogue extraction tests (Adapted from Wragg & Cave (2002))

Method	Type	Compartments	pH	T °C	Food	L/S ratio	Residence time	Analysis sample type	Elements tested	Validation status
PBET	Batch	Stomach	2.5	37	n	100/1	1 hr	Solution	As,Pb	V/swine,monkey (As, Pb)
		Small Intestine	7	37	n		4 hr	Solution (2)*		
SBRC	Batch	Stomach	1.5	37	n	100/1	1 hr	Solution	As,Cd,Pb	V/swine (Pb)
IVG	Batch	Stomach	1.8	37	y	150/1	nr	Solution	As	V/swine (As)
		Small Intestine	5.5	37	y		nr	Solution		
US P	Batch	Stomach	c.1	37	n	1000/1	2 hr	Solution	Pb, Cr, As, Cd, Ni	NV
MB & SR	Batch	Oral		37	n	160/1	5 s		Pb, Cr, As, Cd	C/human (Pb)
		Stomach	c.1	37	n	2160/1	2 hr	Solution		
		Small Intestine		37	n	4770/1	4hr	Solution +Solid		
DIN	Batch	Oral	6.4	37	y	15/1	0.5		As,Cd,Pb,Cr,Hg	V/swine (unpublished)
		Stomach	2	37	y	50/1	2 hr			
		Small Intestine	7.5	37	y	100/1	6 hr	Solution		
SHIME	Batch	Stomach	5.2	37	y	2.5/1	3 hr		As,Cd,Pb	C
		Small Intestine	6.5	37	y	4/1	5 hr	Solution		
RIVM	Batch	Oral	6.5	37	n	15/1	5 m		As,Cd,Pb	C
		Stomach	1.1	37	n	37.5/1	2 hr			
		Small Intestine	5.5	37	n	97.5/1	2 hr	Solution +Solid		
TIM	Flow-Through	Oral	5	37	n	5/1	5m		As,Cd,Pb	C
		Stomach	2	37	n	30/1	1.5 hr			
		Small Intestine	7.2	37	n	51/1	6 hr	Solution		
UBM	Batch	Oral	6.3	37	n	15/1	5 m		As, Cd, Pb	V
		Stomach	1.7	37	n	37.5/1	1 hr	Solution		
		Small Intestine	6.3	37	n	97.5/1	4 hr	Solution		

nr denotes not reported, * denotes two samples are taken
NV indicates no validation against other bioavailability or bioaccessibility methods
V indicates the method has been validated against a bioavailability model (human or animal)
C indicates the method has not been validated but has been compared with other bioaccessibility tests

2.1.2 The British Geological Survey (BGS) PBET

The procedure first described by Ruby *et al.* (1993) has several practical drawbacks. These include the difficulty in obtaining reproducible mixing of the extraction mixture with argon, whilst in a temperature controlled water bath and the time it takes to raise the pH to 7 for the intestine phase with a sodium carbonate solution contained within dialysis tubing. The latter can take more than the four hours that the intestine stage should last. The PBET has been adopted by the BGS with two modifications to account for these problems. Rodriguez *et al.* (1999) showed that instead of using dialysis tubing to raise the pH, direct titration with Na_2CO_3 or $NaHCO_3$ could be used, allowing much faster adjustment. Meanwhile Medlin (1997) demonstrated that anaerobic conditions were not necessary, thereby allowing the extraction to take place

in a screw-topped polypropylene vessel inserted into an end-over-end shaker in a water bath. This enables a more reproducible mixing of the soil solution.

The BGS PBET has been widely used in the UK to assess the bioaccessibility of PHEs. This work has mainly focussed on As and Pb (Cave *et al.*, 2002; Wragg, 2004; Palumbo-Roe *et al.*, 2005; Abrahams *et al.*, 2006; Palumbo-Roe and Klinck, 2007; Wragg *et al.*, 2007), as they represent major contamination problems across the UK. It has also been used to look at the bioaccessibility of Ce, Mg and Fe in Uganda (Smith *et al.*, 2000) and As in Thailand (Williams *et al.*, 1998). Interestingly, the method has also been used to assess As bioaccessibility in UK house dust (Rieuwerts *et al.*, 2006; Turner and Ip, 2007).

2.1.3 The Solubility/Bioavailability Research Consortium (SBRC) *In Vitro* Method

A simplified version of the PBET extraction procedure, the SBRC was developed specifically for Pb bioaccessibility measurements at the request of the USEPA (Medlin, 1997; Kelley *et al.*, 2002; Drexler and Brattin, 2007). Using few reagents in a single stage, short extraction, the SBRC is practically simple to carry out, making it ideal for large batches of samples. The extraction takes place at 37°C for one hour using a 0.4 M glycine solution adjusted to pH 1.5 with HCl. Constant end-over-end shaking (Kelley *et al.*, 2002) is used to simulate mixing within the stomach. Uptake is only considered from the stomach, the small intestine phase having been removed from the original PBET. The SBRC method has been shown to correlate well with a series of *in vivo* studies involving young swine, producing a correlation coefficient of 0.93 in an investigation with 15 soils (Medlin, 1997; Kelley *et al.*, 2002; Drexler and Brattin, 2007). This shows that the extent of Pb dissolution under the acidic stomach conditions was predictive of relative bioavailability in animal models. The choice of young swine for validation is preferred as they have closer physiologic, anatomic, nutritional and metabolic similarities with humans (Dodds and Hsu, 1982). The SBRC methodology is undergoing validation for other elements such as As, Cd, Cr and Be.

Compared with other *in vitro* methods, the SBRC produces slightly higher values for Pb bioaccessibility (Oomen *et al.*, 2002). This is a result of the SBRC method only including a stomach stage, whereas all of the other methods studied used both a stomach and intestine stage. Therefore, the soil in the SBRC method only experiences

acid conditions and not the near neutral pH conditions similar to the lower intestine, as in the other tested methods. This change in pH from low to neutral is likely to cause precipitation of some trace elements, including Pb, from solution and therefore give a lower bioaccessibility (Medlin, 1997).

The SBRC method has been used to investigate the bioaccesibility of Cr in soils. Stewart *et al.* (2003b) showed that bioaccessibility of Cr(III)-spiked soils decreased slightly over an ageing period of 1 to 100 days. It was also shown that the Cr bioaccessibility fraction could be modelled as a function of the inorganic carbon and clay content of the test soils. The same research group (Stewart *et al.*, 2003a) used the SBRC to investigate the bioaccessibility of soils spiked with both Cr(III) and Cr(VI) confirming the previous study that aging decreased bioaccessibility. It was also found that soils with high a organic carbon content had lower Cr bioaccessibility, as a result of enhanced reduction of Cr(VI) to Cr(III) by organic carbon. This study did not attempt to speciate the bioaccessible Cr, only measuring total Cr in the extracts.

More recently the SBRC has been used to assess the bioaccessibility of Ba in soils affected by mine dust (Shock *et al.*, 2007). It has also been used to assess As bioaccessibility in soil (Yang *et al.*, 2002) and Fe amended soil (Subacz *et al.*, 2007).

2.1.4 The *In Vitro* Gastrointestinal (IVG) Method

The *in vitro* gastrointestinal (IVG) method was developed to simulate the human gastrointestinal environment and to estimate the bioaccessibility of As in soil (Rodriguez *et al.*, 1999). The method was developed to address some of the limitations of the Ruby PBET, such as the ability to accurately predict As bioaccessibility (Section 2.1.1). The IVG simulates the gastric and small intestinal environments under anaerobic conditions at 37°C. The gastric solution differs from that of the PBET, being prepared in 0.15 M NaCl using different concentrations of reagents and a lower pH (pH 1.8 for the stomach phase and 5.5 for the intestine phase). Dough was also added to the gastric solution to simulate fed conditions. Comparison of results against those collected from an *in vivo* trial, using immature swine, showed that there was no statistical difference in the results produced (Rodriguez *et al.*, 1999).

Mixed results were reported for the addition of food. In some instances bioaccessibility increased relative to unfed conditions, while in others no change was observed (Rodriguez *et al.*, 1999). A later study by Schroder *et al.* (2003) reported that the addition of dough reduced the bioaccessibility of Cd in soil from 63.0 % to 39.1 % compared with an *in vivo* bioavailability of 63.4 %. More recently, Marschner *et al.* (2006) reported that simulating fed conditions with milk powder increased the bioaccessibility of Pb.

2.1.5 The US Pharmacopoeia (US P) Method

The US Pharmacopoeia (US-P) method was originally developed to simulate drug dissolution (USP XII, 1990), but has been applied to soil potentially harmful element (PHE) bioaccessibility testing by a number of workers (Hamel *et al.*, 1998). It is a single stage methodology using a synthetic gastric solution of NaCl, HCl and pepsin to extract PHEs from a given soil. The extraction takes place at 37°C for a period of two hours. The concentration of HCl used in the US-P method is much greater than that of other methods and of the human digestive system. The PBET methodology contains approximately 1 ml of HCl per litre, whereas this methodology contains 7 ml per litre. During the development of the method various solid to solution ratios were investigated, with the ratio of 1:1000 being found to be the most appropriate. This ratio is very large when compared with other methods (Table 2.2).

The US-P method was used to obtain bioaccessibility data for the National Institute of Standards (NIST) SRM 2710 and a New Jersey City composite soil for As, Cd, Cr, Pb and Ni (Hamel *et al.*, 1998). The results showed that, within the uncertainty of the measurement, only As in the New Jersey City soil showed a significant change in bioaccessibility, lowest in the highest gastric solid to fluid ratios, with an increase by a factor of ca. 5. However, it is difficult to put too much weight on the evidence of this work, as the high uncertainty in the measurement masked the effect of changing the solid to solution ratio. No results on how this method relates to bioavailability measurements have been presented (Wragg and Cave, 2002). The method was also used by Morrison and Gulson (2007) to investigate Pb bioaccessibility in slag waste from a Pb smelter. The samples were fractionated based on particle size, where 45 % of Pb in the <250 μm fraction was bioaccessible.

2.1.6 The Mass Balance & Soil Recapture (MB &SR) Method

In the development of the US-P method, Hamel *et al.* (1999) produced a three stage *in vitro* procedure. The method used artificial saliva, as described by Fusayama *et al.* (1963), gastric fluid (US-P formula) and a simple intestinal fluid (0.2 M Na_2CO_3) to sequentially extract the accessible soil metals at 37°C. Interestingly, the method measured not only the analyte concentration in the extract but also the final metal concentration in the residual soil after extraction. There was good agreement between the extracted analyte concentration and the decrease in soil analyte concentration. This approach provides numerous analytical advantages, including:

(i) matrix interferences associated with determining metal concentrations in complex bio-fluids are avoided; and,

(ii) in samples with a low bioaccessibility, the solution concentration is often close to the instrumental detection limit, whereas measurement of the difference between total metal content and non-bioaccessible metal content of the soil is likely to provide a more robust result.

Taking this approach, bioaccessibility experiments can be performed with considerably less analytical effort. It has the potential to incorporate more complex fluids and still provide a rapid estimation of bioaccessibility compared to other techniques, such as the PBET. However, the overall method has many steps and is quite complex in its design (Wragg and Cave, 2002).

This method was used in a study of the bioaccessibility of Pb, As, Cd and Cr in the USA (Hamel *et al.*, 1999). The sample for which the Cr bioaccessibility was determined consisted of contaminated slag material from Jersey City, USA. This material was believed to be contaminated with COPR and contained 2428 ± 357 mg/kg total Cr. Of this 34 ± 14 % was bioaccessible. Another important aspect to this study was that one soil had human bioavailability data for Pb (Maddaloni *et al.*, 1998), thus allowing direct comparison between bioavailability and bioaccessibility. The bioaccessible fraction of Pb was found to be 70 ± 11 %, which is significantly higher than the 26.2 ± 8.1 % bioavailability. This suggests that this method employs more aggressive extraction conditions than those found in the human gastrointestinal tract. This could be due to the high concentration of HCl used in the stomach phase.

2.1.7 The German DIN 00 19738 (DIN)

The DIN method, developed at the University of Bochum, Germany, has been applied to both anthropogenically contaminated and geologically elevated soils, as well as other materials, such as fly ash, blasting sand, sewage sludge, sediments and foundry waste (DIN, 2000). The sample under investigation is treated with a gastric solution (pH 2.0 ± 0.3) for two hours, followed by a six-hour small intestine phase (pH 7.5 ± 0.3). The synthetic bio-fluids employed contain both inorganic electrolytes and organic components. The use of nitrogen to create anaerobic conditions is optional for special purposes and the whole system is kept agitated at 37°C. It has been found that the addition of a saliva phase has only a negligible effect on the level of mobilisation for organics and is an optional step depending on the nature of the sample (DIN, 2000). The method has been partially validated for both organic and inorganic contaminants under standardised conditions that are physiologically close to humans (Hack and Selenka, 1996; DIN, 2000).

As with the IVG method, the influence of foodstuffs on bioaccessibility was investigated. Whole milk powder was used to simulate the average high fat and protein constituents in human food. Oomen *et al.* (2002) reported that the presence of milk powder increased the bioaccessibility of As, Cd and Pb. The DIN model does not, however, take into account the probable increase in pH caused by the presence of food in the human stomach and should therefore be assumed a worst-case scenario (Wragg and Cave, 2002). Without the addition of milk powder, the DIN method gave values within the range obtained by the other methods in a comparative study (Oomen *et al.*, 2002).

2.1.8 The Simulator of Human Intestinal Microbial Ecosystem of Infants (SHIME)

The University of Ghent and the Belgium-based VITO institute have designed a flow through *in vitro* digestion method that simulates the gastrointestinal microbial ecosystem of the human body (Molly *et al.*, 1993). The SHIME method incorporates both a stomach and small intestine phase with incubation at 37 °C for 3 and 5 hours, respectively. Similar to the DIN methodology, the SHIME involves the addition of cream to the gastric solution to simulate the nutrition of young children. The pH of the stomach is also considerably greater than that of other methods (Table 2.2), being

adjusted to pH 5.2. The pH of the small intestine phase is 6.5. The SHIME method has been compared with other bioaccessibility tests for As, Pb and Cd in soil (Oomen *et al.*, 2002), where the stomach conditions were adjusted to pH 4.0 (more realistic of fed conditions). The results obtained were considerably lower than those obtained by other methods for all metals. This is likely due to the relatively high pH of the stomach compared with that of the other methods. There are no validation data for this test against *in-vivo* studies for metals in soils, but the test has been successfully validated against human studies on polysaccharides (Molly *et al.*, 1994). The SHIME method has recently been used to assess As bioaccessibility in mine tailings (Laird *et al.*, 2007). This study reported that the addition of colon microbes into the bio-fluids increased the bioaccessibility.

2.1.9 The RIVM *In Vitro* Digestion Model

The National Institute of Public Health and the Environment (RIVM) in the Netherlands uses an *in vitro* method that was originally developed to assess bioaccessibility of organics in slag material (Rotard *et al.*, 1995). This was modified for soil samples (Sips *et al.*, 1998) and has been used to assess the bioaccessibility of organics and Pb (Oomen, 2000). The method is a three-stage sequential extraction, involving a five-minute saliva phase at pH 6.5, followed by a two-hour stomach extraction at pH 1.07 and a two-hour small intestine extract at pH 5.5 (Oomen *et al.*, 2002). The RIVM method was involved in a comparison with other bioaccessibility tests for As, Pb and Cd (Oomen *et al.*, 2002), where it produced results in the middle of the range found for the other methods. Mass balance measurements, however, gave recoveries significantly higher than 100% for some combinations of soils and metals. This problem most likely resulted from the total digestion procedure used by this laboratory, as it was shown to give low recoveries (Oomen *et al.*, 2002). This highlights a problem of reporting bioaccessibility values relative to the total metal concentration. If different laboratories use different total metal measurement techniques (e.g. aqua regia digest, HF digests, XRF analysis), the apparent relative bioaccessibilities will not be comparable (Wragg and Cave, 2002). There are no validation data for this test against *in-vivo* studies for metals in soils.

Recently, the RIVM has been used to investigate the bioaccessibility of Cd, Cr, Ni and Pb in soils collected from urban playgrounds in Sweden (Ljung *et al.*, 2007).

Chromium was shown to have on of the lowest bioaccessibility, being on average 4.2 % of the total concentration. The RIVM has also been used to assess Pb bioaccessibility in carbonate-rich soils (Denys *et al.*, 2007), where 40 % of Pb was found to be bioaccessible.

2.1.10 The TNO Gastrointestinal Model (TIM)

In contrast to the majority *in vitro* methods described here, the approach taken by TNO Nutrition at Zeist in the Netherlands, and more recently the Food Research Institute in Norwich UK, is a flow-through reactor system, rather than the more popular batch approach. It is a complex, dynamic method involving a number of gastrointestinal solutions, producing a number of fractions over a period of 6 hours. Transit through the gastrointestinal environment is computer controlled, using mathematical modelling of gastric and ileal delivery. After the initial saliva phase, the pH of the stomach extraction is reduced from 5 down to 2 over a period of 1.5 hours. The mixture from the stomach phase passes dynamically through three intestinal phases that represent the duodenum at pH 6.5, the jejunum at pH 6.8 and the ileum at pH 7.2. The model was shown to reproduce accurately the pre-set data on meal transit, pH and bile salt concentrations in the different gastrointestinal compartments. The model has been validated by comparing the dissolution profile of drugs *in-vivo* with and without food components (Minekus *et al.*, 1995). With respect to soils, the TIM method was compared to other *in vitro* tests for As, Pb and Cd (Oomen *et al.*, 2002). Results for As and Cd were similar to the other methods, while the Pb bioaccessibility was relatively low in comparison. The differences in Pb bioaccessibility were attributed to the dynamic nature of the TIM model or to the differences between the filtration methods used in the different tests. Other factors may also be involved and require further investigation.

The TIM method has been designed to be a much closer analogue of the human gastrointestinal tract than batch extraction tests. It can, therefore, be assumed to provide a better approximation of the true bioaccessibility than batch methods. The method is, however, very complex and not suited to the analysis of large numbers of samples. As a result it has been proposed that the TIM method may have a more appreciable role as a reference method for the validation of new and existing batch type procedures (Wragg and Cave, 2002).

2.1.11 Unified Bioaccessibility Method (UBM)

The BioAccessibility Research Group for Europe (BARGE) developed the UBM with the aim of producing a validated and standardised, physiologically based method of predicting bioavailability. BARGE has members from across the world, including the UK, Belgium, Denmark, France, Canada and the Netherlands. As RIVM was one of the foundering members of BARGE, its own method was used as the basis of the UBM. The composition of the digestive juices and the pH values are similar to the juices of the RIVM. The concentration of $NaHCO_3$ in the duodenal juice was changed in the UBM to increase the pH in the intestinal phase slightly. Other changes are that the gastric phase was reduced from 2 to 1 hour and the intestinal phase was increased from 2 to 4 hours (Oomen *et al.*, 2006).

The UBM presents a major step towards the harmonisation of bioaccessibility techniques and their use in human health risk assessment for contaminated soils. For this reason the UBM was used to assess the bioaccessibility of Cr, Pb and As in this project. One of the appeals of the UBM, over simpler methods such as the SBRC, is that the compositions of its extracting solutions are based on human physiology. In contrast to the SBRC (Section 2.1.3), which uses glycine as a buffer in the gastric solution, the UBM uses a combination of serum albumin and pepsin.

2.2 Lung Analogues

The airborne mobilisation of dust from contaminated land may also represent a significant pathway and risk to human health through particulate inhalation. The normal lung response to inhaled particulates is governed by a number of interrelated mechanisms that provide protection against particulate matter. Lehert (1990) identified the following specific mechanisms acting on deposited particles:

- Particle trapping in the tracheobronchial system, which consists of a network of airways, where the mucous lining is the main line of defence; and a muciliary transport system that removes the particles from the respiratory tract by means of the cilia. Soluble particles can undergo dissolution in the bronchial tree and solutes can pass into the vasculature and be transported to other body tissues by the blood (Lehert, 1993).

- Engulfment of particles by lung phagocytes providing protection to the underlying submucosa of the conducting airways.
- Particle clearance from the lung via the conducting airways mediated by alveolar macrophages that reside in the alveolar epithelial surface. Macrophages have the ability to precipitate several elements, which have been inhaled in water-soluble form, usually as phosphate (Galle *et al.*, 1992). Lehert (1990) demonstrated that it is possible to induce a particle overload condition on the macrophages by introducing a large burden of particulates. As a consequence, the alveolar macrophages become a sequestering compartment. It was suggested that, once established, the situation is irreversibly maintained and presumably lung function is diminished.

The final process of particle removal is either by ingestion or expulsion via coughing and swallowing or expectoration. According to a review of the kinetics of particle removal from the lung by Lehert (1993), half-times are about 24 hours for the tracheobronchial pathway and range from weeks to thousands of days for the alveolar phase. More recent numerical modelling by Hofmann and Asgharian (2003) suggests that about 10 to 15% of the initially deposited particles in the human bronchial tree were still present after 24 hrs. Lay *et al.* (1998) determined a long-term, clearance half-time of 110 days in human volunteers who had an intrapulmonary instillation of iron oxide particles. Other workers, who had used radiolabelled tracers, reported a range of 63 – 300 days for the clearance half-time. Consequently, any *in vitro* test needs to be able to assess reasonably long residence times and, furthermore, be able to track the evolution of the extraction profile of a particular contaminant in the lung with time.

The development of lung analogues for assessing human bioaccessibility is very much in its infancy, with very few methods having been reported. Twining *et al.* (2005) used a simulated lung fluid, comprising sodium chloride, sodium bicarbonate, calcium acetate, calcium chloride, magnesium acetate, magnesium chloride, potassium dihydrogen phosphate, dipotassium sulfate and citric acid with a pH of 7.19, to assess metal bioaccessibility in fly ash. The ash was mixed with the lung fluid (solid:fluid ratio 1:20) continuously in a hybridisation oven or 6 days.Wragg and Klinck (2007) used a method, originally employed to determine the half-times of yellowcake (the end product of uranium ore milling and processing) dissolution in the lung, to assess

Pb inhalation bioaccessibility in mine waste in Wales, UK. The simulated lung fluid used in the extractions was Gamble's solution, originally developed in 1942 (Eidson and Mewhinney, 1983). Gamble's solution (Table 4.7) is widely used to determine of solubility profiles in simulated lung surfactant fluids in *in vitro* studies and has been shown to reasonably reproduce uranium solubility profiles derived from *in vivo* tests on rodents (Damon *et al.*, 1984). The waste material was mixed with Gamble's solution (solid:fluid 1:40) using an end-over-end for 26 days (624 hr).

2.3 Conclusions

From this review it can be seen that there are a large number of *in vitro* methodologies available for predicting PHE bioavailability. The methods discussed all have similar fundamental characteristics, such as extraction at human body temperature, use of stomach and occasionally a small intestinal stage. However, differences such as stomach pH, intestinal pH and soil:solution used prior to analysis, can produce significantly different results (Oomen *et al.*, 2002). In addition there has been very limited validation of these methods against animal data (Table 2.2) because of the cost of animal testing.

This area of research, however, is still very much in its infancy. BARGE is still actively developing the UBM with the aim of incorporating it into ISO-standards. Producing a validated and approved procedure will be a huge step forward from the current situation, where different methods can give widely different results (Oomen *et al.*, 2002). Given its potential future acceptance, the UBM was used to assess bioaccessibility in this study. Much of the research conducted until now, however, has focused on As- and Pb-contaminated soils. In the UK, especially, the development of methods to assess As bioaccessibility has dominated this area of research. This is understandable since large parts of the UK have soil As concentration above the associated SGV (Rawlins *et al.*, 2002). Several studies have measured the bioaccessibility of Cr in soils, but there has been no attempt to validate a method. In addition, the methods used to measure Cr bioaccessibility have not featured an intestine stage and so its effect on Cr solubility is unknown.

CHAPTER 3 SAMPLING

This chapter describes the rationale for the selection of the soil sample sites across Glasgow for the present study, the methods of sample collection and a description of the sample sites as recorded during collection.

3.1 Sampling Procedure

3.1.1 BGS GSUE Samples

During 2001 and 2002, the British Geological Survey (BGS) collected 1381 urban soil samples at a density of 1 per 0.25 km^2 and 241 peri-urban samples at a density of 1 per 2 km^2 on a systematic grid across the Glasgow conurbation. The study was carried out as part of the BGS Geochemical Survey of Urban Environments (GSUE) project. The aim of the GSUE project was to provide an overview of the urban soil geochemistry of Glasgow and the immediate rural hinterland (Fordyce *et al.*, 2005).

Following the standard GSUE sampling methodology, within the sample area, each 1 kilometre national grid-square on 1:25 000 scale OS maps was subdivided into four sub-squares with 500 m x 500 m dimensions. A soil sample was collected as close as possible to the centre point of each 500 m square, accepting access and ground limitations. Common sites for collection included gardens, parks, road verges, open spaces, school yards, sports fields and waste ground.

At each site, two separate soil samples, a top and a deeper sample each of approximately 250 g of unsieved material were collected using a handheld Dutch auger. Each sample was a composite of five sub-samples collected from the corners and centre of a 20 x 20 m square. The top few centimetres of surface vegetation was discarded and sub-samples from standard depths of 5–20 cm (taking 0 as the top of the litter layer) for topsoils and 35–50 cm for deeper soils collected. The sub-samples were homogenised to form one top sample and one deeper sample from each site.

Observations of soil colour, depth and clast lithology and abundance were also recorded and the samples were classified into seven textural groups (gravel, sand, sandy-silt, silt, silty-clay, sandy-clay and clay). In addition, at each sample site, information on the location, geology, contamination, land use and other features

required for data interpretation was entered on a computer-compatible field data card in standard BGS format.

Following collection, the soils were air- and then oven-dried at < 30 °C to prevent the volatilisation of selenium. Samples were dry-sieved through nylon mesh to a < 2 mm size fraction. The samples were then homogenised, coned and quartered and sub-samples taken for analyses of total element concentrations (including Cr, Pb and As) by X-ray Fluorescence (XRF) Spectrometry.

Since the current project is concerned with human exposure risk to soils, only GSUE topsoils were selected for further investigation. On the basis of GSUE XRF total As, Cr and Pb data, 21 soils with concentrations of any of these elements that exceeded the current UK SGV and that were collected on land uses with a high possibility of contact with the human population (particularly children), were identified. Land uses included gardens, allotments and recreational land but not industrial sites.

Sub-samples of BGS GSUE archive < 2 mm top soil material were selected from these 21 sites for the present study.

3.1.2 Cr-Contaminated Site Samples

In addition to these BGS GSUE soils, a further six samples were collected for the study from locations identified during previous research into the Cr- contaminated sites around Rutherglen (Farmer *et al.*, 1999b; Farmer *et al.*, 2002). Six sites with, or in the vicinity of, locations with a known history of COPR disposal were selected. At each site a single composite sample was collected. A composite sample consisted of three individual 'flights' collected with a hand-held Dutch auger. The three flights were collected from the corners of a 2 m equilateral triangle (Palumbo-Roe *et al.*, 2005). As with the GSUE sampling procedure only the surface soils (0.05 to 0.20 m) were collected.

Once collected, all samples were returned to the laboratory to undergo preparation for analysis. The samples were dried in a fan-assisted oven, set at 35 ± 2°C, on plastic trays for at least 12 hours, until all moisture had been removed. Each dried coarse sample (including the 21 BGS GSUE samples) was gently disaggregated, by hand in a porcelain pestle and mortar, to ensure the breakage of aggregates but not clasts

(Wragg, 2005). This disaggregated sample was then sieved to <250 μm using a brass sieve (Calabrese *et al.*, 1997).

3.2 Sample Location and Description

Soil is a complex structure derived from the weathering of the rock and superficial deposit (drift) parent materials that underlie it. The geochemistry of soil is influenced by the type of geology and drift deposits from which the soil is derived as well as complex interactions with weather, climate, topography, vegetation, land use and atmospheric deposition. In addition to these natural processes, the geochemistry of soils is also affected by anthropogenic activities and contamination. For this reason a variety of observations about the geology, weather, land use, and the presence of any contamination or made ground were made in addition to a description of the soil type at each location. Site geology and drift were identified from British Geological Survey (1989; 1990; 1992a; 1992b; 1993; 1994) 1:50,000 Geological Maps.

Details of the locations sampled and descriptions of the soils used in the present study make up the remainder of this chapter. Table 3.1 gives the British National Grid (BNG) co-ordinates of, and Figure 3.1 the locations of, all samples.

Table 3.1 British National Grid references and locations of soil samples.

Sample number	Easting	Northing	Location	BGS GSUE Sample ID
1	239600	674790	Dumbarton	610368
2	240760	675170	Dumbarton	610417
3	252730	668740	Scotstoun	611011
4	253280	667750	Scotstoun	611021
5	260790	669250	Bishopbriggs	610390
6	261860	670150	Bishopbriggs	610370
7	254600	665230	Govan	610898
8	257750	666260	City Centre	611482
9	257920	665660	City Centre	611409
10	264340	667060	Hogganfield Park	610824
11	242370	662250	Johnstone	610184
12	245900	664110	Paisley	610452
13	248740	662170	Paisley	610522
14	258290	661720	Cathcart	610807
15	259028	662035	Cathcart	N/A
16	259146	662043	Cathcart	N/A
17	260105	662896	Oatlands	N/A
18	260388	662916	Oatlands	N/A
19	260855	662284	Rutherglen	N/A
20	260789	662012	Rutherglen	N/A
21	263650	662270	Shettleston	610943
22	264710	662730	Carmyle	611050
23	265380	662250	Carmyle	611094
24	257370	659680	Muirend	611261
25	262270	660700	Rutherglen	611396
26	263880	654680	East Kilbride	611234
27	261780	652210	East Kilbride	611118

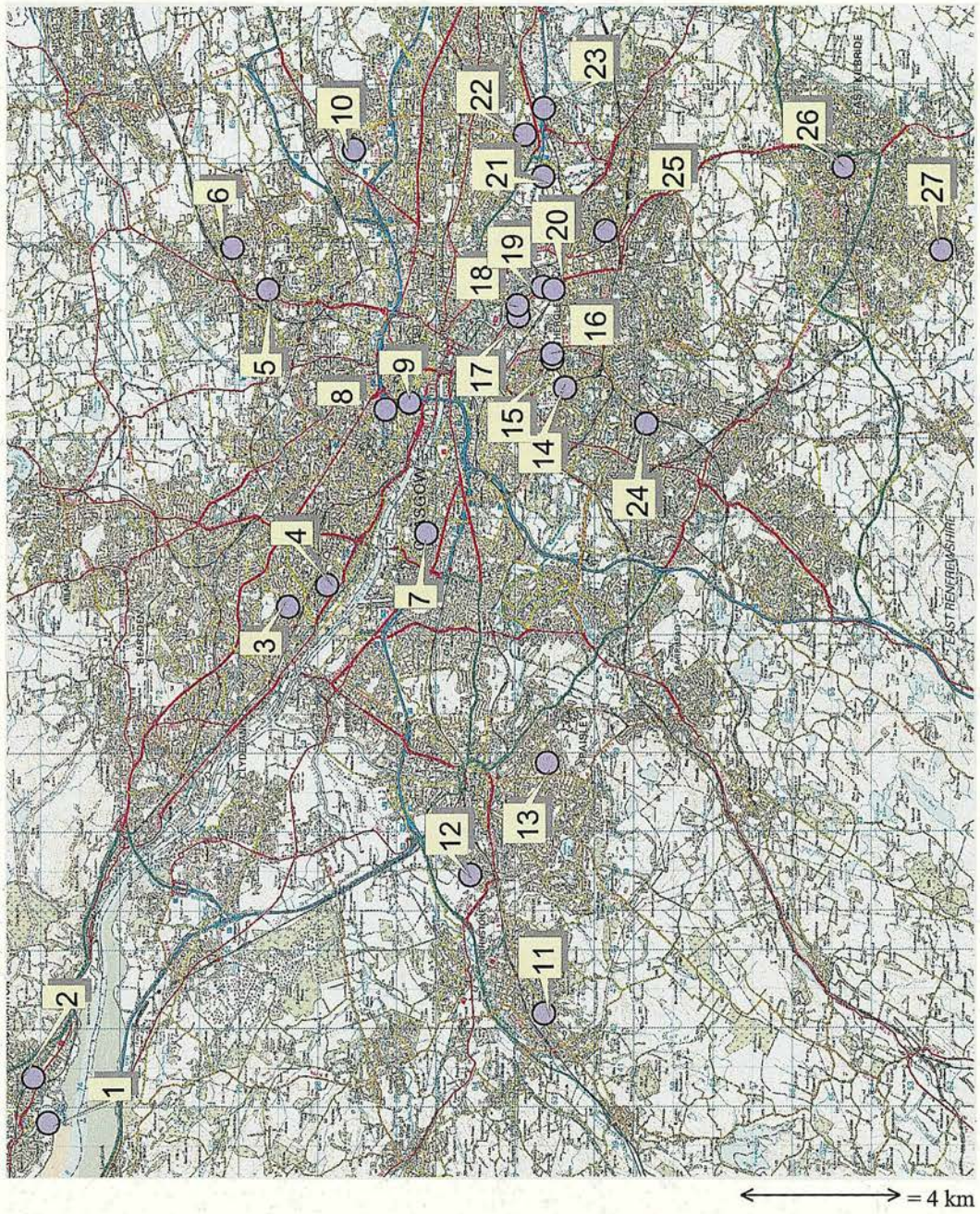

Figure 3.1 Sample locations across the Glasgow area.

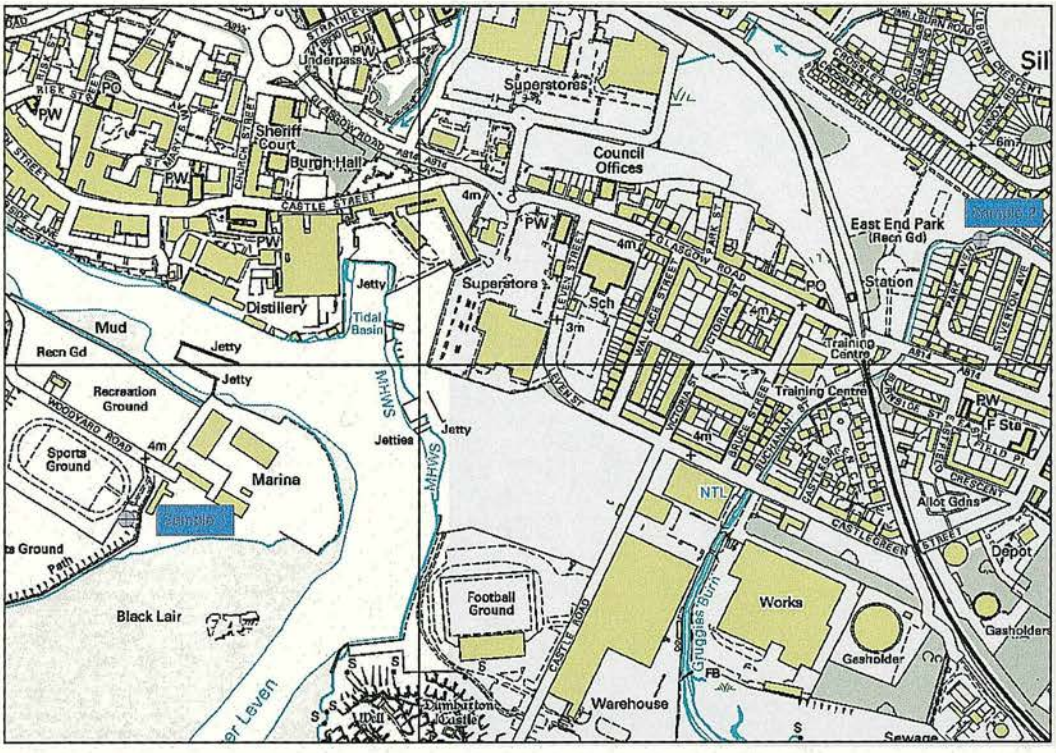

Figure 3.2 Location of Samples 1 and 2 in Dumbarton.

3.2.1 Dumbarton

Samples 1 and 2 came from Dumbarton, a town 22 km northwest of Glasgow city centre on the north bank of the River Clyde. Figure 3.2 shows the locations in more detail. The underlying geology of both sample sites is a structure known as the Kinnesswood Formation (a cross-bedded sandstone with siltstones and pedogenic limestone). Basaltic rock formations also occur within 200 m of Sample 1. Sample 1 came from a hockey pitch at the mouth of the River Leven. Geological maps indicate that the site is on made ground (fill of man-made or natural materials). The soil was dark brown in colour, had a silty texture, contained broken bricks, clear glass and coal waste but no natural clasts. Sample 2 was located approximately 1.2 km ENE of Sample 1, in the East End recreational park. The drift at this location varies from that at Sample 1 comprising raised beach and marine deposits. The soil was dark brown in colour, had a silty texture and contained broken bricks and coal waste. At the time that both samples were collected there had been no rain in the previous seven days.

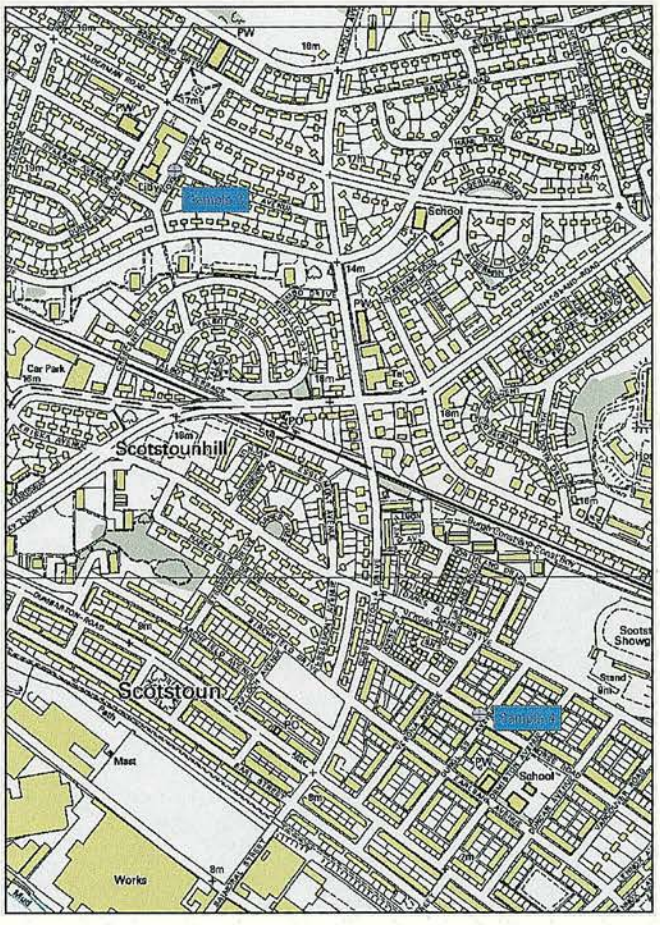

Figure 3.3 Location of Samples 3 and 4 around Scotstoun.

3.2.2 Scotstoun

Samples 3 and 4 were collected from the Scotstoun area of Glasgow, approximately 7.5 km northwest from the city centre. The underlying geology of both sample sites is the Limestone Coal Formation (a cyclic sequence of sandstones, siltstones, mudstones, coals, blackband and clayband ironstones and seatrocks). Sample 3 was taken from a grassy area outside the Knightswood Library, as shown in Figure 3.3. The drift at this site is indicated as deposits of intertidal and subtidal clays and silts. The soil was black, had a silty texture and contained broken bricks and coal waste. Sample 4 was collected approximately 1.3 km southeast of Sample 3, from a front garden on Norse Road (Figure 3.3). The drift map shows alluvial sand and gravel at this site. The soil was black, had a silty texture and contained coal waste and sandstone clasts. There had been heavy rain less than 24 hours before these samples were collected.

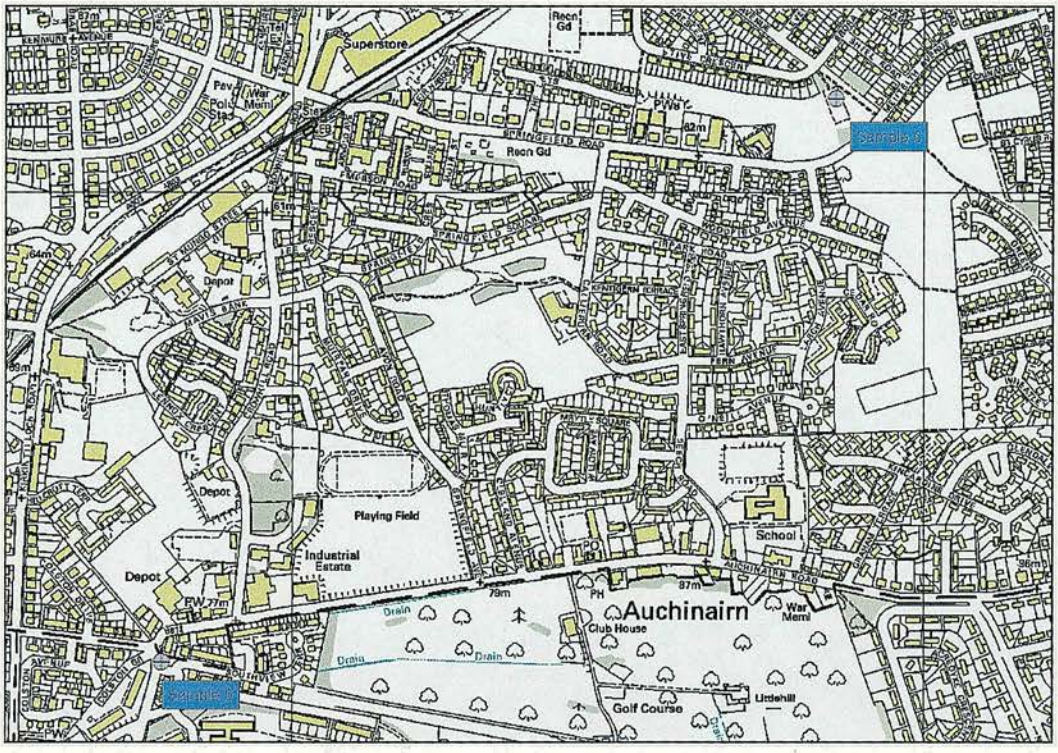

Figure 3.4 Location of Samples 5 and 6 in Bishopbriggs.

3.2.3 Bishopbriggs

Samples 5 and 6 came from Bishopbriggs, approximately 4.3 km north of Glasgow city centre. The underlying geology of both sample sites is the Upper Limestone Formation (a cyclic sequence of sandstones, siltstones, mudstones, marine limestones, coals and seatrocks). Sample 5 was collected from a patch of grass in front of houses on Southview Terrace (Figure 3.4). Geological maps show the drift on this site is glacial diamicton (poorly sorted sediment of boulders and stones in a hard to stiff sandy, silty, clay matrix), although within 100 m of this sample site there are large areas of made ground. The soil was dark brown, had a silty texture and contained broken bricks, clear glass, coal waste and sandstone clasts. Sample 6 was collected approximately 1.5 km northeast of Sample 5, from a city park surrounded by houses, as shown in Figure 3.4. Geological maps indicate that the drift at this site is alluvial sand and gravel. The soil was dark brown, had a silty-clay texture and contained broken bricks and coal waste. There had been no rain in the week leading up to when these samples were collected.

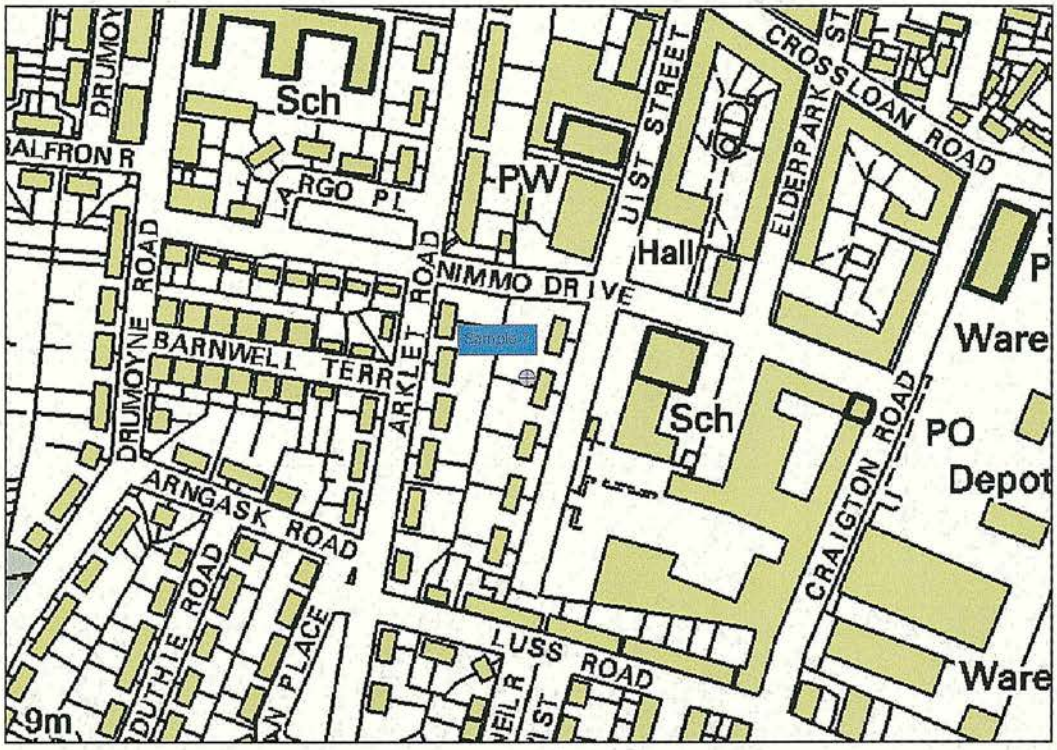

Figure 3.5 Location of Sample 7 in Govan.

3.2.4 Govan

Sample 7 came from Govan, approximately 4.7 km west of Glasgow city centre. The sample was taken from the back garden of a house on Uist Street (Figure 3.5). Geological maps of the local area show this site is underlain by the Limestone Coal Formation, while the drift map shows alluvial sand and gravel. The soil was dark brown, had a silty texture and there had been no rain in the previous week. The soil contained what seemed to be furnace waste but no clasts.

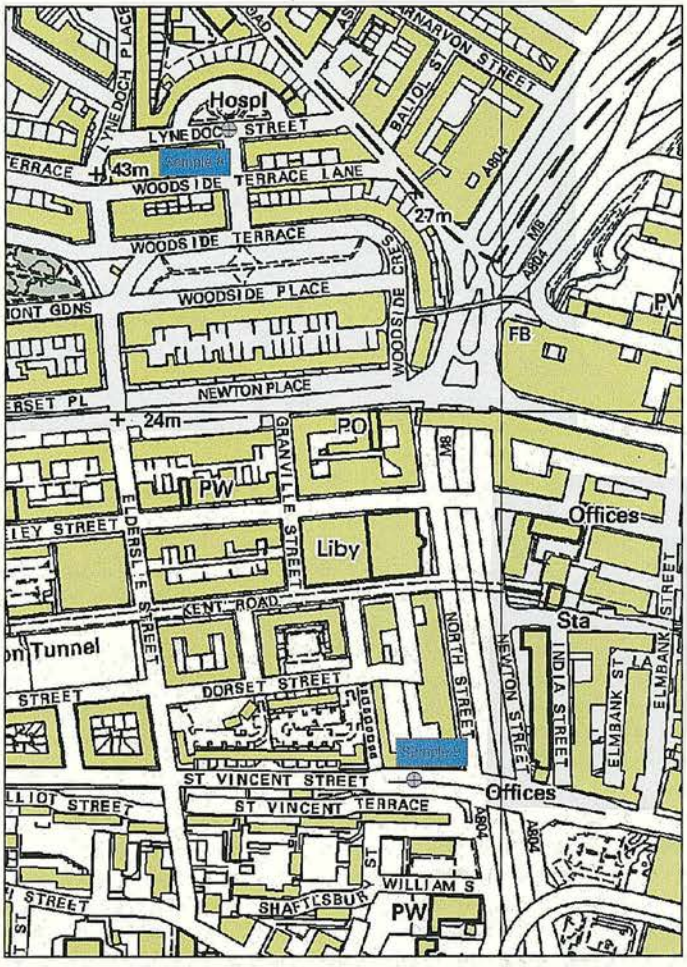

Figure 3.6 Location of Samples 8 and 9 in Glasgow City Centre.

3.2.5 City Centre

Samples 8 and 9 came from central Glasgow (Figure 3.6). Sample 8 was taken from the communal garden area serving tenement flats on Lynedoch Street, approximately 200 m from the M8 motorway. Geological maps of the local area show this site is underlain by the Limestone Coal Formation, while the drift map shows glacial diamicton. The soil was dark brown, had a silty texture and contained broken bricks and coal waste but no clasts. Sample 9 was taken from a front garden on St Vincent Street, approximately 60 m from the M8 motorway. Geological maps of the local area show this site is underlain by the Upper Limestone Formation, while the drift is glaciomarine deposits (deltaic and beach sand and gravel). The soil was dark brown, had a silty texture and contained coal waste and mudstone clasts. There had been heavy rain in the week leading up to when these samples were collected.

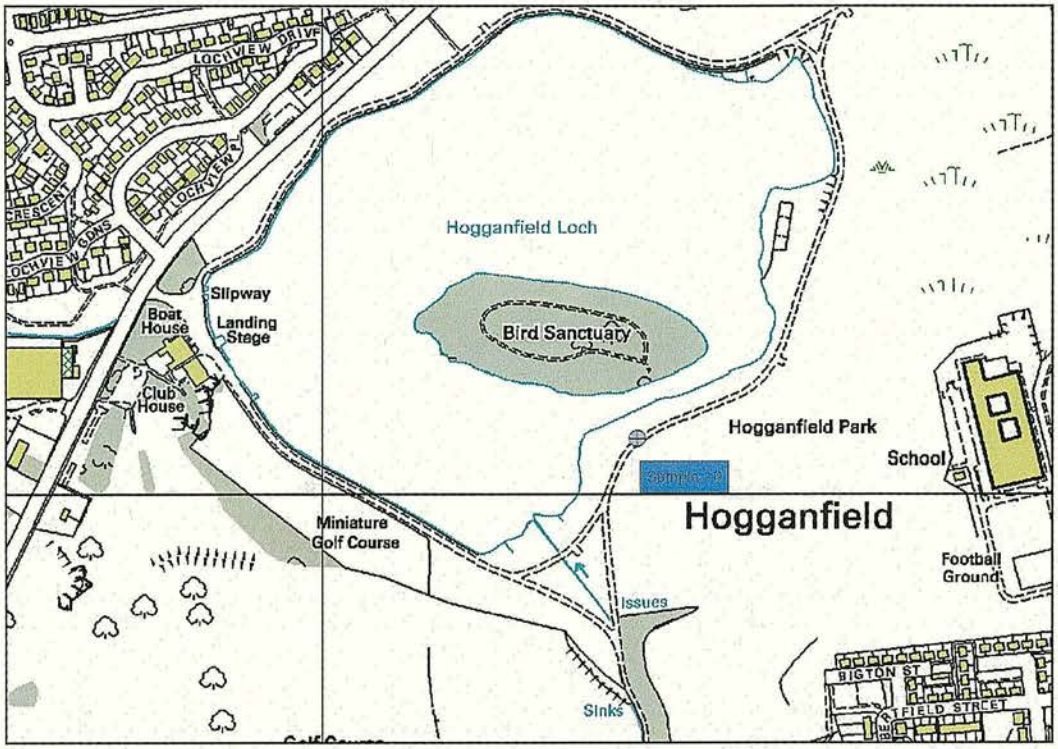

Figure 3.7 Location of Sample 10 at Hogganfield Loch.

3.2.6 Hogganfield Park

Sample 10 was taken from Hogganfield Park, next to Hogganfield Loch (Figure 3.7), approximately 5.5 km from the city centre. The site has several major roads nearby, with the M8, M80 and A80 approximately 800 m, 1.2 km and 500 m away, respectively. Geological maps of the local area show this site is underlain by an igneous intrusion of ophitic alkali olivine-dolerite, which may contain naturally occurring Cr. Meanwhile the drift map indicates till (rock fragments in a stiff to hard clay and silt matrix). The soil was grey, had a clay texture and there had been no rain in the previous seven days. The soil contained coal waste and sandstone clasts.

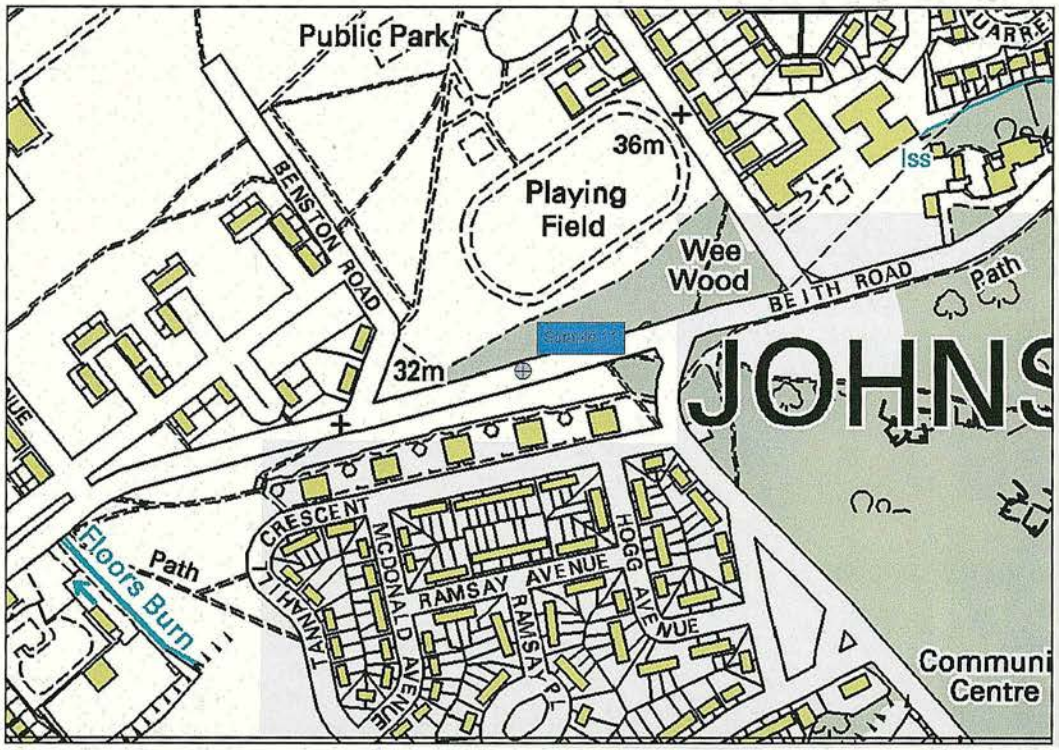

Figure 3.8 Location of Sample 11 at Johnstone.

3.2.7 Johnstone

Sample 11 came from Johnstone, approximately 17 km west of Glasgow city centre. The sample was taken from a grassy area beside a running track (Figure 3.8). Geological maps of the local area show this site is underlain by the Lawmuir Formation (mainly sandstone with siltstones, mudstones, marine and non-marine limestones, coals and seatstones) although the sample location appears to fall on a zone known as the Paisley Ruck (a southwest–northeast trending, broad fault zone consisting of highly shattered rocks). The drift map of the area shows glaciomarine deposits, although this area also contains made ground at the surface. The soil was dark brown, had a silty-clay texture and there had been no rain in the previous seven days. The soil contained broken bricks but no clasts.

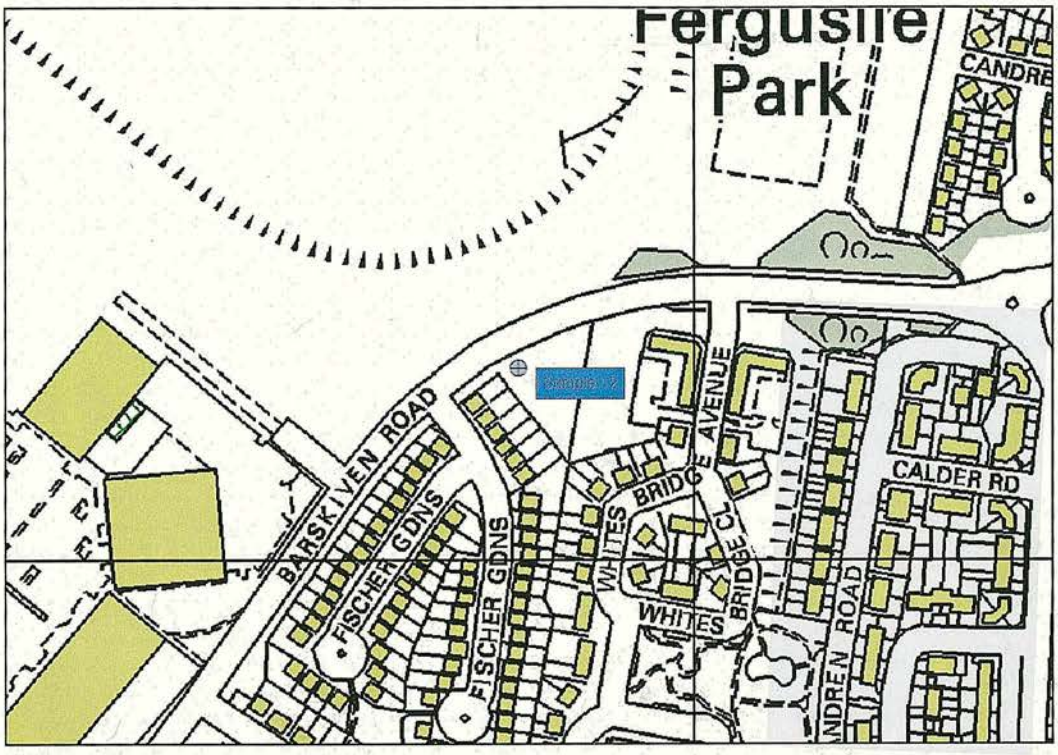

Figure 3.9 Location of Sample 12 in Paisley.

3.2.8 Paisley

Sample 12 came from Paisley, approximately 4 km northeast of Sample 11. The sample was taken from a grassed area behind houses on Barskiven Road (Figure 3.9). The site is close to two dual carriageways, the A761 and the A737, which are approximately 450 and 900 m away, respectively. Geological maps of the local area show this site is underlain by the Paisley Ruck where it divides three geological formations, those being the Lawmuir, Limestone Coal and Upper Limestone Formations. The drift map of the area shows glaciomarine deposits, although this area also contains made ground at the surface. The soil was dark brown, had a sandy silt texture and there had been no rain in the previous seven days. The soil contained broken bricks and coal waste but no clasts.

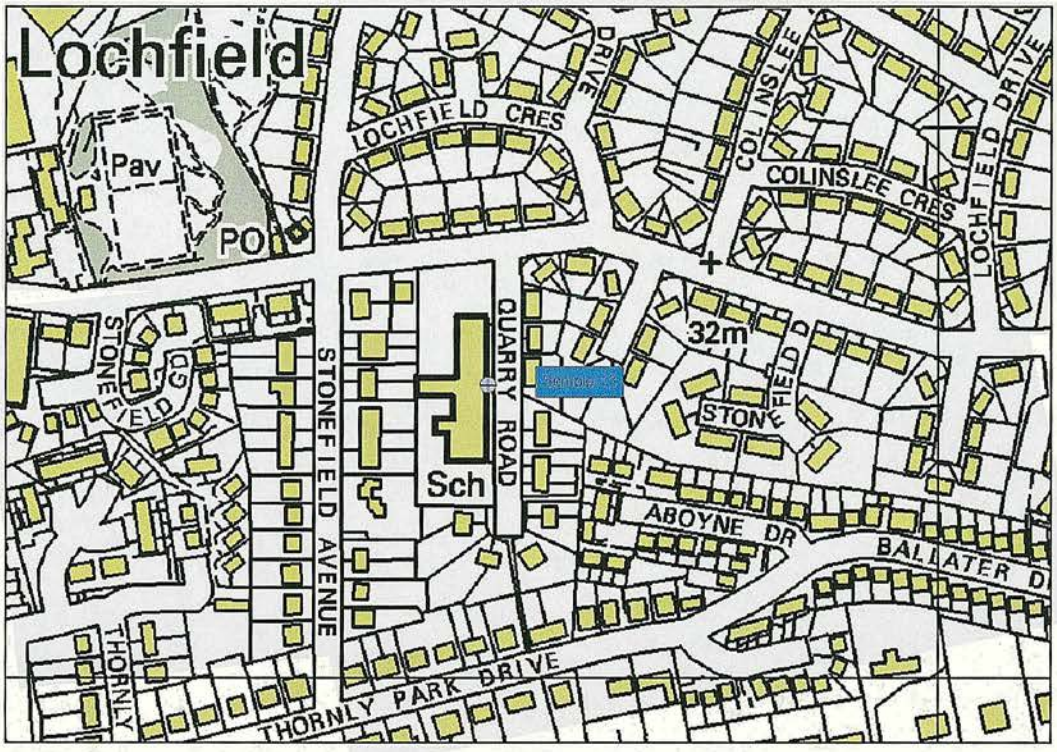

Figure 3.10 Location of Sample 13 in Paisley.

Sample 13 also came from Paisley, approximately 3.5 km southeast of Sample 12, from a grass area in front of Lochfield Primary School on Quarry Road (Figure 3.10). Geological maps of the local area show this site is underlain by the Lawmuir Formation, while the drift map of the area shows glacial diamicton deposits, although the bedrock is close to the surface. The soil was dark brown, had a silty-clay texture and there had been heavy rain in the previous 24 hours. The soil contained coal waste and sandstone, limestone, siltstone and mudstone clasts.

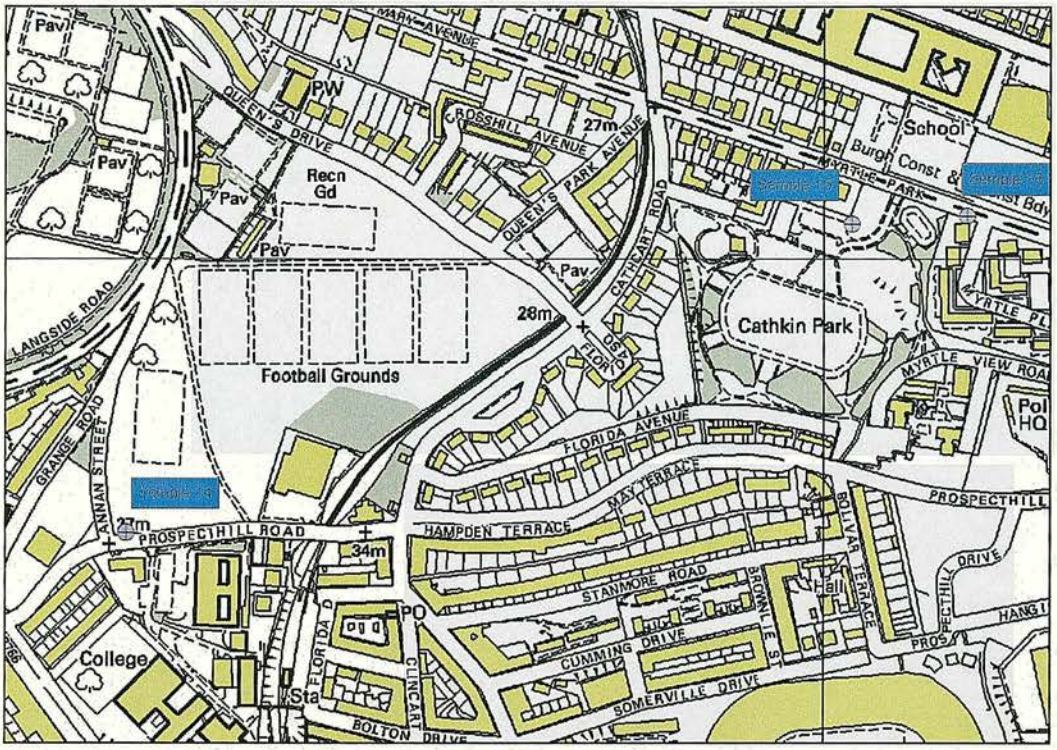

Figure 3.11 Locations of Sample 14, 15 and 16 in Cathcart.

3.2.9 Cathcart

Samples 14, 15 and 16 came from Cathcart, approximately 3.6 km south of the city centre (Figure 3.11). Sample 14 was taken from Queen's Park, where several football pitches are located, next to The Victoria Infirmary. Geological maps of the local area show this site is underlain by the Upper Limestone Formation, while the drift map of the area shows glaciomarine deposits. The soil was dark brown, had a silty texture and contained broken bricks and coal waste but no clasts. There had been no rain in the week prior to collection of this sample.

Samples 15 and 16 were located approximately 800 m northeast of Sample 14, in Cathkin Park. This area contains a football pitch and running track. Geological maps show that underlying these sites is a boundary between the Middle (sandstones, siltstones, mudstones, coals and seatrocks) and Upper (sandstones and mudstones, mainly reddened) Coal Measures, while the drift map shows glaciomarine deposits, although the surrounding area (<50 m) has large amounts of made ground, both buried and at the surface. Cathkin Park has a known history of COPR disposal. Sample 15 was taken from the edge of the park and was a dark brown colour and had

a silty texture. Sample 16 was taken from the front garden of a house on Myrtle Park, approximately 120 m east of Sample 15. This garden was elevated and supported by a brick wall, which had yellow stains permeating it, possibly from chromate leaching through the brickwork from the soil behind. The soil was dark brown and had a silty texture. There had been heavy rain in the 24 hours preceding collection of these two samples.

3.2.10 Oatlands

Samples 17 and 18 came from Oatlands, approximately 1.3 km northeast of Sample 16, in the area around Richmond Park (Figure 3.12). Both sample sites are underlain by the Upper Coal Measures, while the drift map shows alluvial deposits, although the surrounding area has large amounts of made ground. Sample 17 was taken from an area of grass next to houses on Toryglen Street. The site is adjacent (~100 m) to Roseberry Park, which has a known history of COPR disposal (Farmer *et al.*, 1999b) and as such has been closed to the public to reduce exposure. The soil was dark brown and had a silty texture. Sample 18 was collected, approximately 280 m east of Sample 17, in Richmond Park. The soil was dark brown and had a silty-clay texture. There had been heavy rain in the 24 hours prior to collection of the sample.

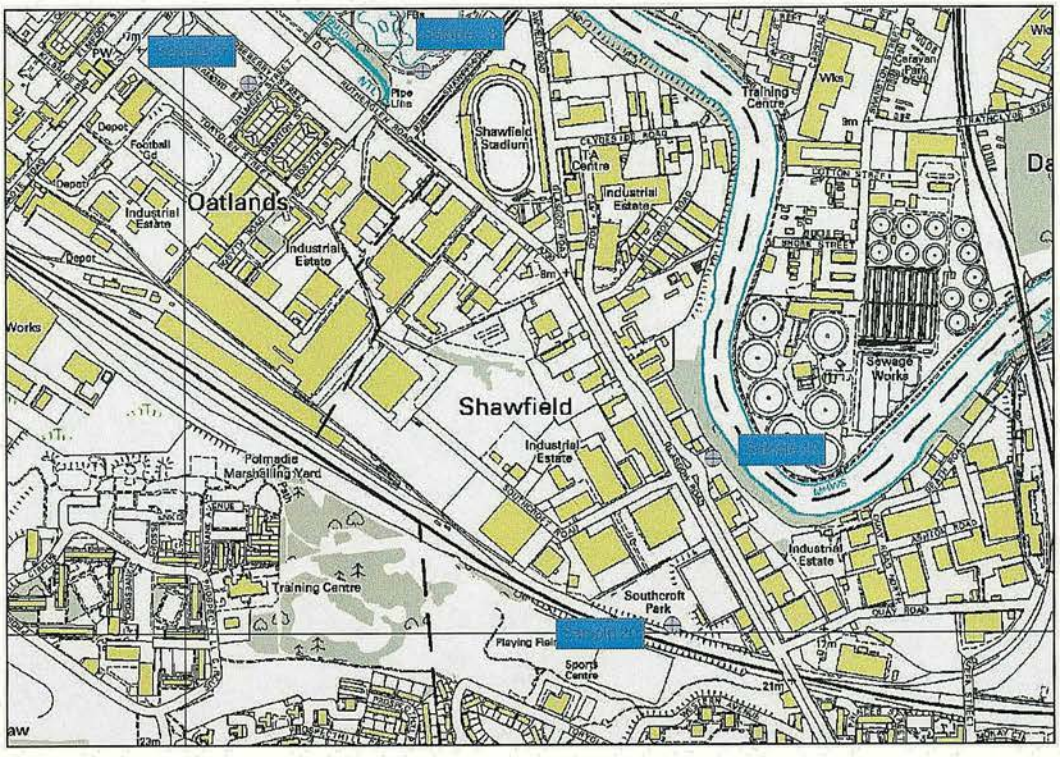

Figure 3.12 Locations of Samples 17, 18, 19 and 20 in Oatlands and Rutherglen.

3.2.11 Rutherglen

Samples 19, 20 and 25 came from Rutherglen, approximately 4.7 km southeast of the city centre. Sample 19 was collected approximately 800 m southeast of Sample 18 from a patch of scrubland at the entrance to Shawfield Industrial Estate (Figure 3.12). This is very close to the former site of the J & J White's chemical works (Section 1.1.1). Geological maps of the local area show this site is underlain by the Upper Coal Measures, while the superficial deposits are made ground. The soil was dark brown and had a sandy texture. The soil also contained large amounts of gravel.

Sample 20 was taken from a patch of disused land immediately next to Rutherglen Glencairn football ground, approximately 280 m south of Sample 19 (Figure 3.12). This is a site with a known history of COPR disposal (Farmer *et al.*, 1999b). The underlying geology and drift is the same as for Sample 19. The soil was dark brown and had a silty texture. The soil also contained a white, yellow tinted, pumice like material that was easily broken up to form a powder, and was possibly COPR. There had been heavy rain in the 24 hours leading up to when Samples 19 and 20 were collected.

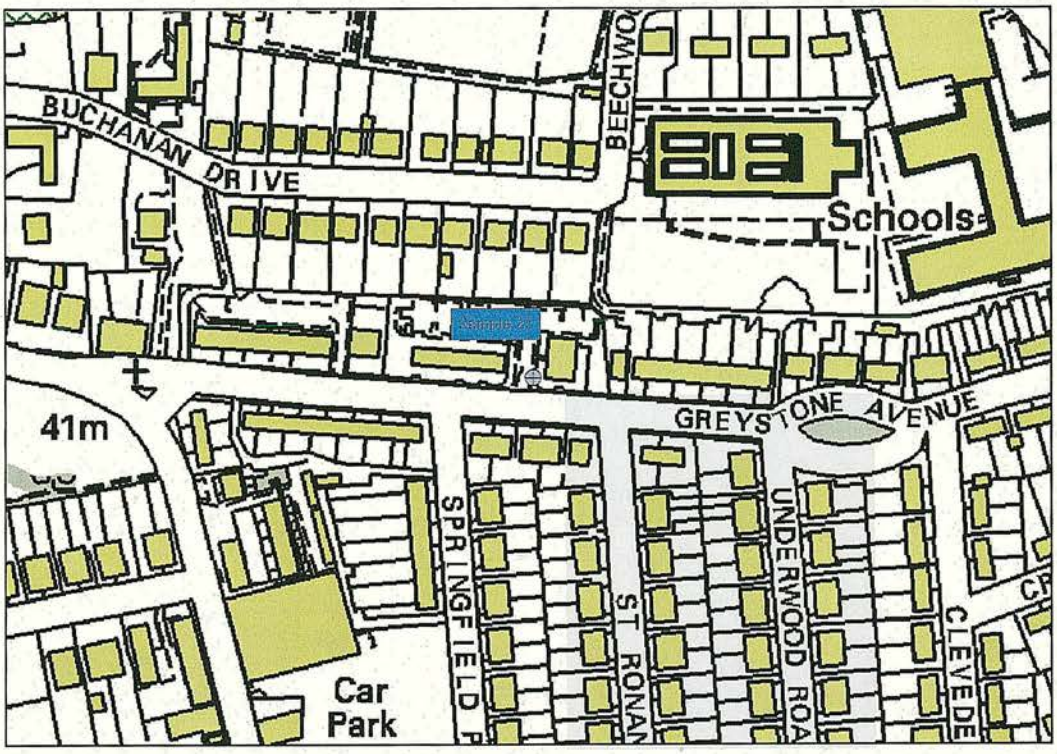

Figure 3.13 Location of Sample 25 in Rutherglen.

Sample 25 was collected, approximately 2 km southeast of Sample 20, from a patch of grass in a residential area on Greystone Avenue (Figure 3.13). Geological maps of the local area show this site is underlain by the Middle Coal Measures, while the drift of the area is till. The soil was dark brown, had a silty-clay texture and there had been no rain in the previous seven days. The soil contained broken bricks and coal waste as well as sandstone clasts.

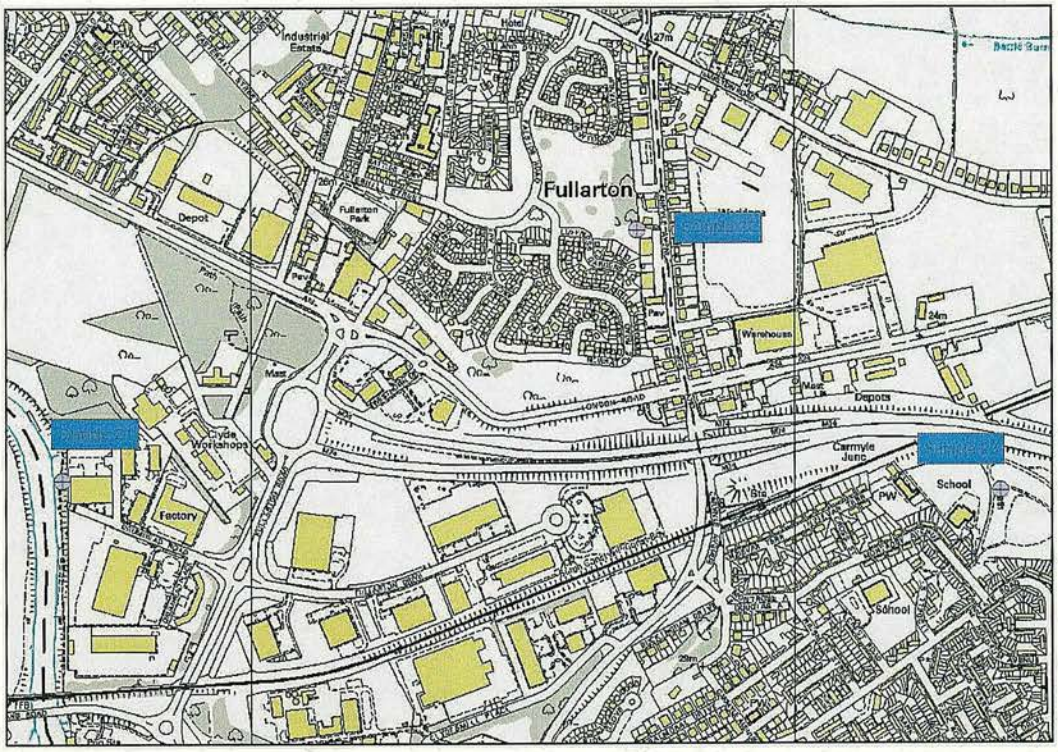

Figure 3.14 Location of Samples 21, 22 and 23 in Shettleton and Carmyle.

3.2.12 Shettleston and Carmyle

Sample 21 came from Shettleston, approximately 2.3 km east of Rutherglen and 450 m west of the end of the M74. The sample was taken from a verge on the side of the River Clyde footpath. Geological maps of the local area show this site is underlain by the Middle Coal Measures, while the surface deposits are made ground. The soil was dark brown, had a silty texture and contained broken bricks, coal waste and sandstone clasts.

Sample 22 was collected from Fullarton Park, approximately 1.2 km northeast of Sample 21 and 400 m north of the M74. The underlying geology was the same as Sample 21, but the drift differed being raised beach marine deposits (deltaic beach sand a gravel). The soil was dark brown, had a silty texture and contained what seemed to be furnace slag but no clasts.

Sample 23 came from a park off Montrose Avenue, approximately 800 m southeast of Sample 22 and 80 m south of the M74. The site is next to a local school. The underlying geology was the same as Samples 21 and 22, but the surface deposits are made ground. The soil was dark brown, had a silty-clay texture and contained iron

wire, broken bricks and glass but no clasts. There had been no rain in the week prior to collection of these three samples.

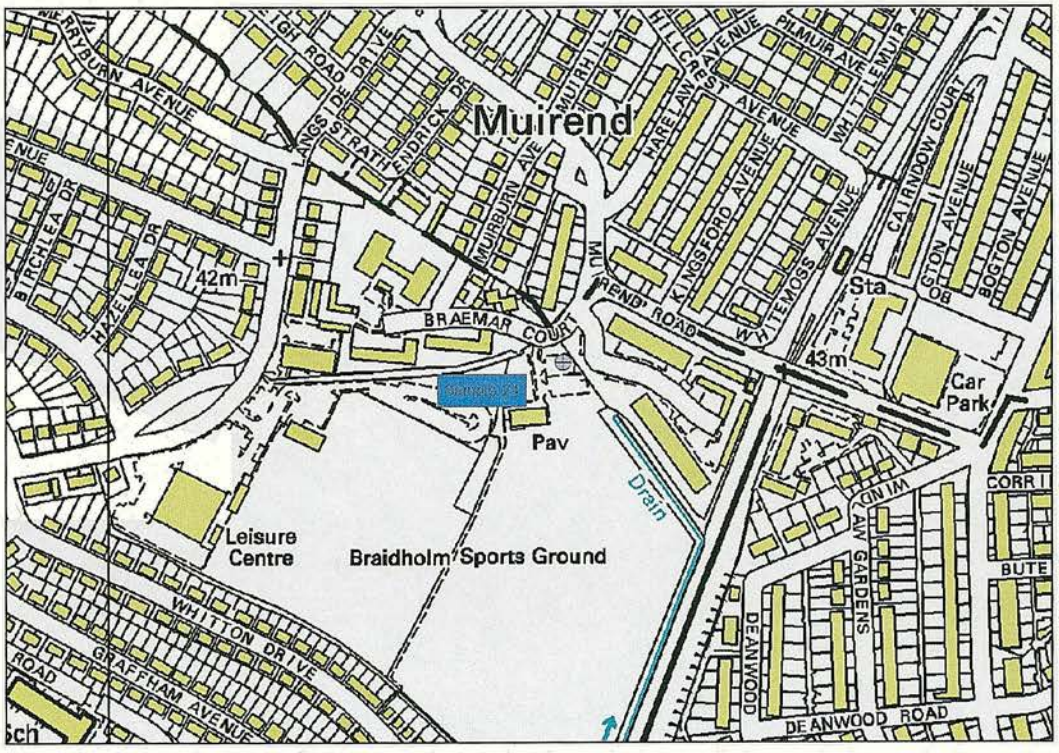

Figure 3.15 Location of Sample 24 in Muirend.

3.2.13 Muirend

Sample 24 also came from Muirend, approximately 5.8 km south of Glasgow city centre and 4.5 km southwest of Rutherglen. The sample was taken from the Braidholm playing fields (Figure 3.15), an area with a documented history of COPR disposal (SEPA, 2001). Geological maps of the local area show this site is underlain by the Upper Limestone Formation, while the drift is alluvial, although made ground does occur along the eastern side of the playing fields. The soil was red, had a silty texture and there had been no rain in the previous seven days. The soil also contained broken bricks but no clasts.

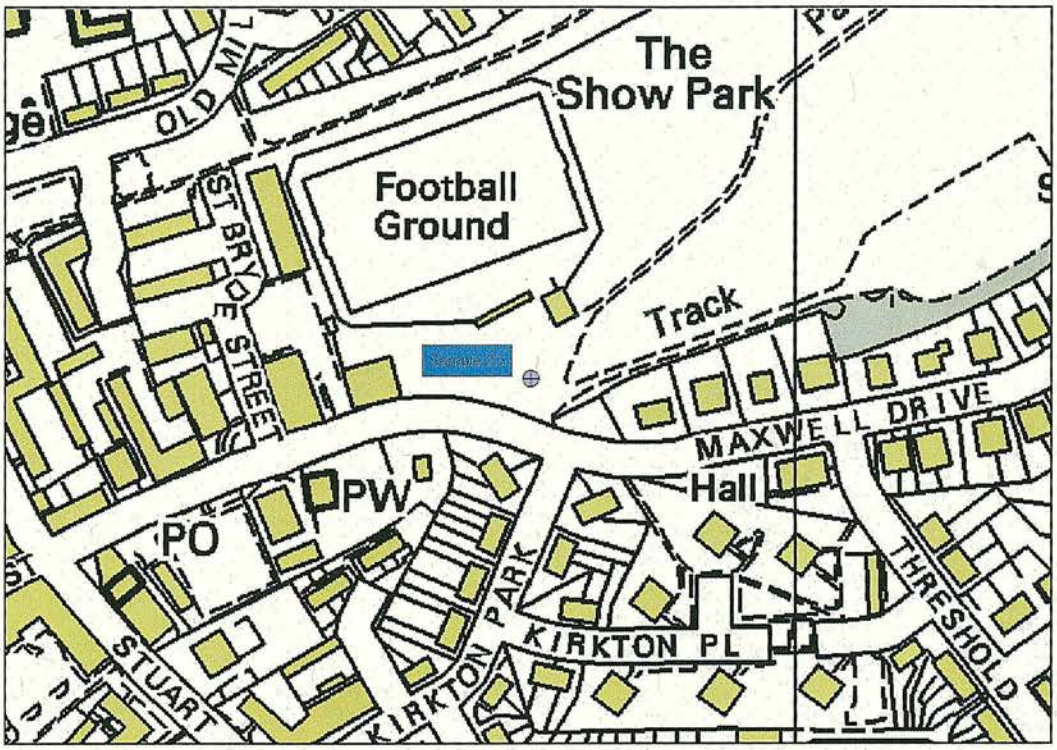

Figure 3.16 Location of Sample 26 in East Kilbride.

3.2.14 East Kilbride

Sample 26 came from East Kilbride, approximately 12 km southeast of Glasgow city centre, taken from the edge of East Kilbride Thistle football pitch (Figure 3.16). Geological maps of the local area show this site is underlain by the Limestone Coal Formation, while the drift is till. The soil was red, had a gravel texture and there had been no rain in the previous seven days. The soil also contained broken bricks and coal waste as well as sandstone clasts.

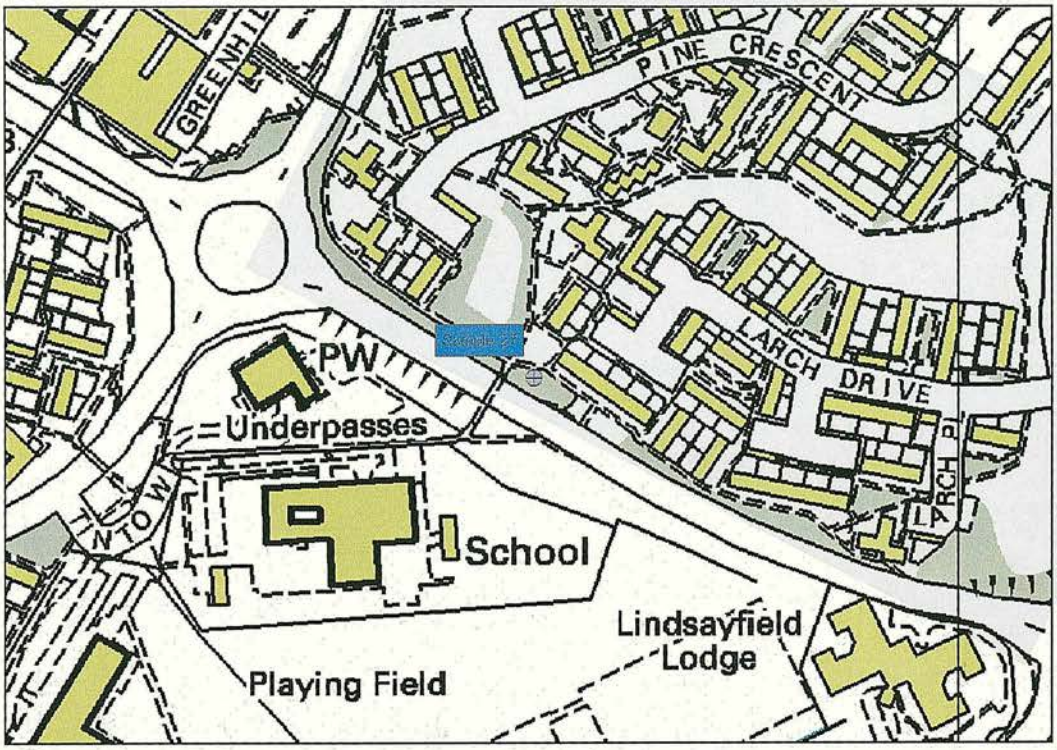

Figure 3.17 Location of Sample 27 in East Kilbride.

Sample 27 also came from East Kilbride, approximately 3.2 km southwest of Sample 26, taken from a grass verge in a residential area on Greenhills Road. Geological maps of the local area show this site is underlain by the Lower Limestone Formation, while the drift is till. The soil was light brown, had a silty-clay texture and there had been heavy rain in the previous 48 hours. The soil also contained broken bricks and coal waste as well as limestone clasts.

CHAPTER 4 ANALYTICAL AND STATISTICAL METHODOLOGIES

A number of analytical and statistical techniques were used to assess the samples in this project. These techniques and methods are described in this chapter. Figure 4.1 shows how the different methods were used together, i.e. which instrumental methods followed which extraction/digestion methods. The theory of the analytical techniques, descriptions of the instrumentation used and standard operating conditions are presented. The quality control and quality assurance procedures applied to the analytical techniques and the data acquired from them are also described, along with detection limits and reference materials recoveries.

4.1 HF/HNO_3 Digestion

4.1.1 Background

The total concentrations of a range of trace and major elements, in addition to Cr, Pb and As, were required to aid identification of any relationships between soil geochemistry (Section 4.14.3) and bioaccessibility. Prior to inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis (Section 4.8), preparation of the soil samples was required in order to bring the elements of interest into a suitable form for introduction into the instrument. ICP-OES, like the majority of trace element analytical techniques, requires the sample to be in solution before analysis can take place. This is typically achieved using wet digestions with selected concentrated mineral acids. Examples include: cold and hot nitric acid dissolution, *aqua regia* (three parts HCl + one part HNO_3) and nitric acid combined with hydrofluoric acid. Hot nitric acid is capable of partially leaching elements from non-silicate minerals. *Aqua regia* will leach most elements from soils but, as elements present in the silicate matrix (e.g. quartz) are not fully released, it is considered a pseudo-total method. An HF/HNO_3 mixture, on the other hand, is able to completely break down silicate minerals present in soils allowing total concentrations of trace elements to be determined. This makes HF/HNO_3 the preferred digestion procedure in geochemical laboratories, although Si and B are volatilised in the digestion process and as a result cannot be determined by this method.

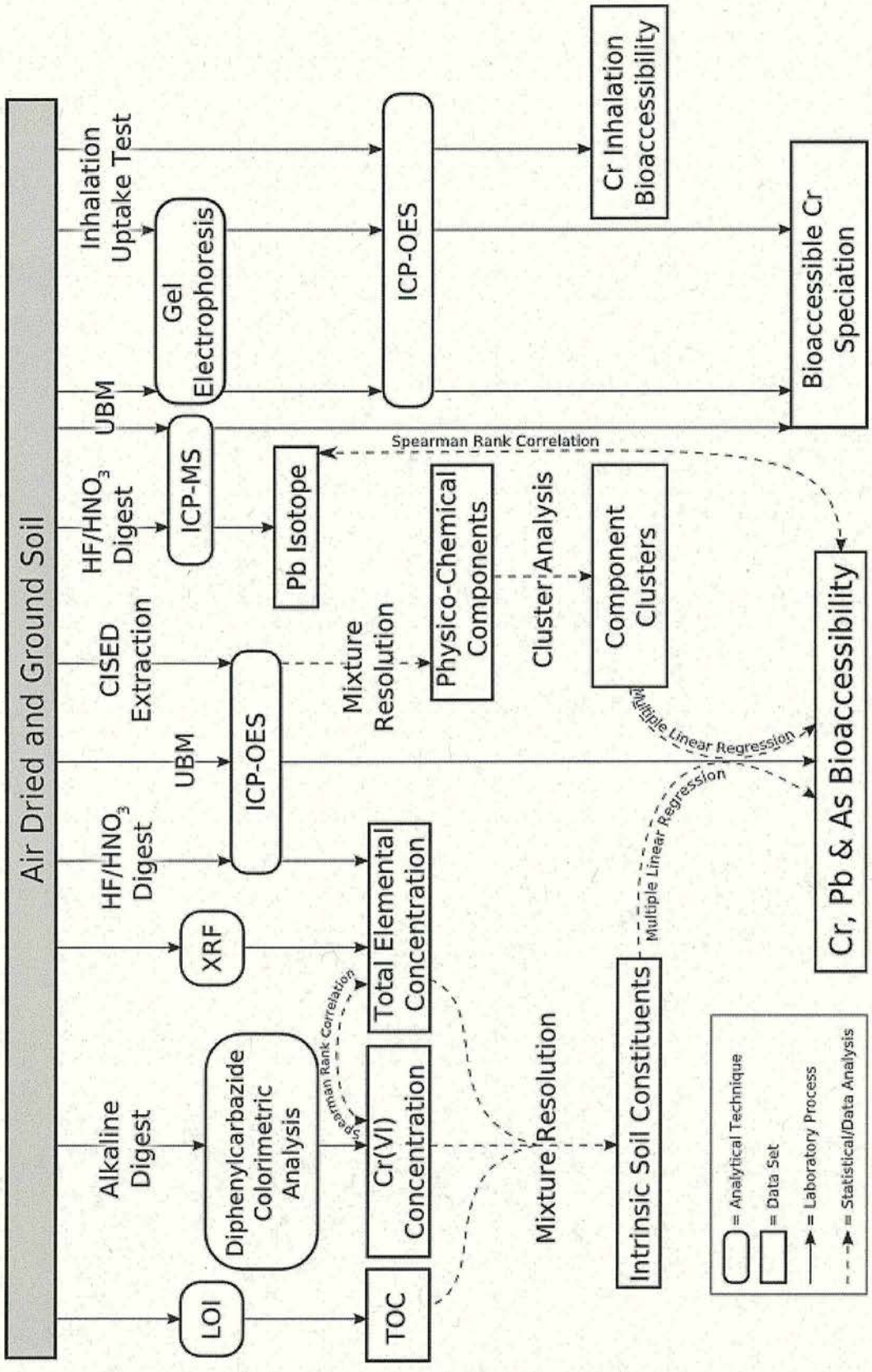

Figure 4.1 Analytical and statistical methods used in this study.

This research project is concerned with assessing the bioaccessibility of heavy metals in urban soils. It is useful to relate the bioaccessible analyte concentration to its total concentration in an original sample, which makes the method of assessing total concentrations very important. If, for example, an *aqua regia* procedure is employed, the total concentration will tend to be slightly underestimated, making it appear that a greater proportion is bioaccessible (Oomen *et al.*, 2002). For this reason an HF/HNO_3 procedure was used in this project.

4.1.2 Digestion Procedure

A modified version of the USEPA Method 3052 was used to digest the sample soils (USEPA, 1996b). 0.250 ± 0.001 g of oven-dried soil was transferred into a Teflon® microwave sample vessel. To this 9.0 ± 0.1 ml of concentrated HNO_3, 1.0 ± 0.1 ml of concentrated HF and 1.0 ± 0.1 ml of 30% H_2O_2 was added in a fume hood. The addition of H_2O_2 was to aid the oxidation of soil organic matter. Once any effervescing had finished the vessels were sealed and irradiated for 15 minutes in a CEM MARS5 microwave digester (CEM, UK). The heating programme raised the vessel temperature to 180°C in less than 5.5 minutes and maintaining it for a further 9.5 minutes. The pressure throughout was controlled at 7.5 ± 0.7 atm. Following irradiation the vessels were left to cool for at least 5 minutes before removal from the microwave. Once they had cooled to room temperature, each vessel was uncapped in a fume hood and the sample transferred to a Teflon® beaker. To remove any remaining HF the sample solutions were evaporated on a hot plate down to approximately 1 ml. This concentrated solution was then made up to 25 ml with 2 % v/v HNO_3.

One digestion run consisted of six samples in duplicate, one reagent blank and one certified reference material (CRM) (Czech Metrological Institute, number 7002, a Light Sandy Soil with elevated analyte levels). The digestion solutions were stored at 4 °C prior to analysis for a range of major (Mg, Mn and Na) and trace (As, Cr, Cu, Ni, Pb and Zn) elements by ICP-OES (Section 4.8). The recoveries and detection limits for each element are given in Table 4.1.

Table 4.1 Elemental recoveries and detection limits for HF/HNO_3 digestion of CMI 7002 soil reference material

	As	Cr	Cu	Mg	Mn	Na	Ni	Pb	Zn
Measured (mg/kg)	35 ± 5	170 ± 7	22 ± 1	12670 ± 993	538 ± 74	10360 ± 1570	41 ± 8	64 ± 1	66 ± 5
Certified (mg/kg)	32.4 ± 1.9	179 ± 8	29.3 ± 0.6	11460[1]	587 ± 37	10760[1]	42.0 ± 1.7	58.9 ± 4.9	69.0 ± 7.7
Recovery %	108	95	75	111	92	96	98	109	96
Detection Limit (mg/kg)[2]	0.14	0.01	1.0	27	1.0	42	11	0.04	8.4

[1] Value not certified. n = 5

[2] 5 x Reagent Blank SD. Five blanks analysed.

4.2 Alkaline Digestion for Extraction of Hexavalent Chromium

4.2.1 Background

Given the relationship between Cr toxicity and its speciation (Section 1.4), it was important to determine the Cr(VI) concentration of each soil sample. Prior to analysis with the diphenylcarbazide (DPC) colorimetric method (Section 4.6), Cr(VI) had to be extracted from the soil. It has been reported that a heated carbonate-hydroxide solution is capable of extracting operationally defined total Cr(VI) from soils (Vitale *et al.*, 1994; James *et al.*, 1995; Vitale *et al.*, 1997). A standard method employing a carbonate-hydroxide reagent has been published by the USEPA (1996a), which is capable of extracting soluble, insoluble, precipitated and sorbed forms of Cr(VI) from soils, sludges, sediments and similar waste material. Any method being used for speciation analysis must not allow inter-conversion of analyte species, in this case Cr(III) and Cr(VI). To minimise the potential oxidation of Cr(III) to Cr(VI), Mg^{2+} and a phosphate buffer are added to the carbonate-hydroxide reagent. As seen in Figure 4.2, reduction of Cr(VI) to Cr(III) is unlikely due to the highly alkaline conditions (pH > 11.5).

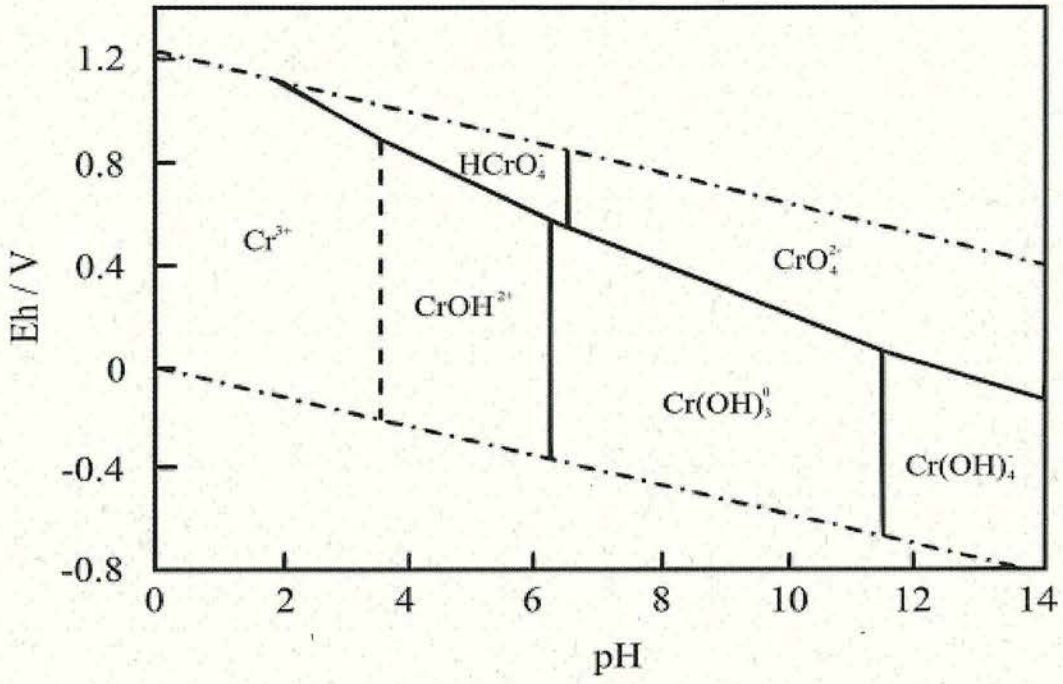

Figure 4.2 Eh-pH diagram showing the dominant Cr species at varying pH (adapted from Rai and Eary (1989)).

4.2.2 Digestion Procedure

A modified version of the USEPA method 3060A was used to extract Cr(VI) from soil in this project. Initial investigations using the unmodified USEPA method produced spike recoveries of between 0 and 7 %. This is most likely due to the presence of humic matter, which is readily leached into solution under the strongly alkaline conditions of the extraction. This can cause numerous analytical problems, including: (a) rapid reduction of Cr(VI) under the acidic conditions of the DPC colorimetric method (see Section 4.6) and (b) absorption by humic matter at 540 nm, which is the wavelength for quantifying the DPC–Cr coloured complex (Pettine and Capri, 2005). By ashing the samples beforehand it is possible to remove any organic matter before digestion, thus removing the associated interferences. Quality control was achieved through digestion of a certified reference material and sample spike recoveries, for which an additional sample was weighed out and spiked with between 0.010 and 0.020 g of $PbCrO_4$ (a water-insoluble salt). The recovery for this spike was required to be within 80 and 120 %. A reagent blank, consisting of just the digestion reagents, was also processed.

The modified method involved ashing, at 450 °C for 4 hours, 2.50 ± 0.10 g of each oven-dried soil in duplicate. The samples were then transferred to a 250 ml beaker, to

which 50 ml of digest reagent was added. The digest reagent comprised 0.28 M Na_2CO_3 and 0.5 M NaOH, with a characteristic pH between 11.8 and 12.3. In addition to the digest reagent, approximately 400 mg of $MgCl_2$ and 0.5 ml of 1.0 M phosphate buffer (0.5 M K_2HPO_4 and 0.5 M KH_2PO_4) were added to suppress any method-induced oxidation of Cr(III) to Cr(VI). The mixture was then stirred unheated for 5 minutes, before being heated to 90-95 °C for 60 minutes. During this time the samples were stirred every 15 minutes. Once the samples had cooled they were filtered into a 100 ml volumetric flask, with washings, using a Whatman 542 filter (ashless filter paper, pore size ~ 2 μm). The flask was then made up to the mark with deionised water. Chromium(VI) was then quantified by colorimetric UV/Visible spectrometry (see Section 4.6).

It is important to confirm that the ashing of the sample soil has no effect on the speciation of Cr. If ashing resulted in the oxidation or reduction of either Cr species it would not be an acceptable pre-digestion step. To test this a CRM, certified for Cr(VI), was obtained from Resource Technology Corporation (RTC Soil Product Number SQC-012). This reference material was digested using the method described above, both with and without ashing. Table 4.2 shows the recoveries obtained. It can be seen that when the CRM is not ashed the recovery for Cr(VI) is only 8 %. This increases greatly when ashing is used as a pre-digestion step to 91 %. This validates the modified USEPA method for determining Cr(VI) concentrations in soil.

Table 4.2 Recoveries of Cr(VI) for alkaline digestion of RTC SQC-012 soil reference material, both ashed and unashed (n = 5).

	Certified Cr(VI) Value (mg/kg)	Measured Cr(VI) Conc. (mg/kg)	Recovery
Unashed	245 ± 98	19.9 ± 0.3	8 %
Ashed	245 ± 98	223 ± 20	91 %

4.3 Physiologically Based Extraction Test (PBET)

4.3.1 Background

The background to the Unified Bioaccessibility Method (UBM), used during this project, and the other available tests is discussed in Chapter 2.

4.3.2 UBM Procedure

The four simulated fluids (saliva, gastric, duodenal and bile) were prepared individually one day prior to carrying out the extraction, thus ensuring that all of the reagents were thoroughly dissolved. The individual fluids were prepared by making-up a 500 ml solution of organic reagents and a 500 ml solution of inorganic reagents. The organic and inorganic phases were then combined, with some additional solid phase chemicals added, in a 2 l HDPE screw top bottle. The chemical composition of the inorganic, organic phases and the solid chemical reagents required to prepare 1000 ml of each fluid are given in Table 4.3, Table 4.4 and Table 4.5, respectively. The following day, the pH of each fluid was measured to ensure it fell within required limits, which were: saliva 6.5 ± 0.5, gastric 0.9 – 1.0, duodenal 7.4 ± 0.2 and bile 8.0 ± 0.2. If required, the pH was adjusted with either 1.0 M NaOH or 37% HCl. In addition, the pH of the combined fluids was checked. The combined saliva and gastric fluids (1 ml of saliva and 1.5 ml of gastric) required a pH of 1.2-1.4, while the mixed gastro-intestinal fluid (1.0 ml of saliva, 1.5 ml of gastric, 3.0 ml of duodenal and 1.0 ml of bile) required a pH of 6.3 ± 0.5. If the mixture was not within specification, the pH of the gastric or duodenal fluid was adjusted with either 1.0 M NaOH or 37% HCl before being rechecked.

Table 4.3 Organic constituents of the four simulated fluids in the UBM. Amounts per 500 ml.

Reagent	Saliva	Gastric	Duodenal	Bile
Urea	200 mg	85.0 mg	100 mg	250 mg
Glucose	-	650 mg	-	-
Glucuronic acid	-	20.0 mg	-	-
Glucosamine hydrochloride	-	330 mg	-	-

Table 4.4 Inorganic constituents of the four simulated fluids in the UBM. Amounts per 500 ml.

Reagent	Saliva	Gastric	Duodenal	Bile
KCl	896 mg	824 mg	564 mg	376 mg
NaH_2PO_4	888 mg	266 mg	-	-
KSCN	200 mg	-	-	-
Na_2SO_4	570 mg	-	-	-
NaCl	298 mg	2752 mg	7012 mg	5259 mg
NaOH	1.80 ml of 1.0 M	-	-	-
NH_4Cl	-	306 mg		
HCl	-	8.3 ml of 37% HCl	180µl of 37% HCl	180µl of 37% HCl
$CaCl_2$	-	400 mg	-	-
$NaHCO_3$	-	-	5607 mg	5785 mg
KH_2PO_4	-	-	80 mg	-
$MgCl_2$			50.0 mg	

Table 4.5 Additional solid phase constituents of the four simulated fluids in the UBM. Amounts per 1000 ml.

Reagent	Saliva	Gastric	Duodenal	Bile
Amylase	145 mg	-	-	-
Mucin	50.0 mg	3000 mg	-	-
Uric Acid	15.0 mg	-	-	-
Bovine Serum Albumin	-	1000 mg	1000 mg	1800 mg
Pepsin	-	1000 mg	-	-
$CaCl_2$	-	-	200 mg	222 mg
Pancreatin	-	-	3000 mg	-
Lipase	-	-	500 mg	-
Bile	-	-	-	6000 mg

In the UBM procedure 0.6 g of each soil sample was accurately weighed into a HDPE extraction vessel, capable of undergoing centrifugation. To this 9 ml of simulated saliva was added and the resulting suspension was shaken manually, to ensure thorough mixing, before being left for 5 – 15 minutes. After this time 13.5 ml of simulated gastric solution was added and the extraction vessels placed in an end-over-end shaker, in a thermostatically controlled water bath set at 37 °C, thus simulating the stomach. After one hour the vessels were removed and the pH measured. If the pH was not between 1.2 and 1.7, the sample was re-extracted with an additional spike of 37 % HCl (up to 1 ml) as required. If the pH of the suspension was within the required limits, the stomach solution was collected by centrifuging the suspension at

3000 rpm for 5 minutes. 1.0 ml of the supernatant was collected and made up to 10 ml with 0.1 M HNO_3 and stored at <8 °C prior to analysis. To simulate the intestinal phase, the above procedure was repeated except, after the pH of the stomach phase had been checked, 27 ml of duodenal and 9 ml of bile solutions were added and the vessels returned to the water bath for a further 4 hours. The pH of the soil suspension at the end of the 'stomach + intestinal' phase was required to be 6.3 ± 0.5. If this was not the case the sample was re-extracted with an additional spike of 37 % HCl (up to 1 ml) as required. The end-over-end shaker can hold up to 20 vessels at one time, thus a single run consisted of eight samples in duplicate, two reference materials, one blank and one spiked blank. The reference materials used were BGS 102 (BGS, UK) and NIST 2710 (National Institute of Standards and Technology, USA), both of which are in the process of being assigned consensus bioaccessibility values for the UBM procedure.

Bioaccessibility values for the 'stomach' and 'stomach + intestine' phases were both reported from the UBM procedure. The value used for further data interpretation, however, was the higher of the two numbers, as this provides the most conservative prediction for human health risk assessment, as discussed in Chapter 2.

4.3.3 UBM Validation

The reference material recoveries for Cr, Pb and As are shown in Table 4.6. Poor recoveries were obtained for both Cr and Pb in the stomach+intestine extraction compared with the stomach alone.

As was discussed in Chapter 2, it is important that *in vitro* procedures are validated against *in vivo* data. The UBM is currently undergoing validation against animal models for As, Cd and Pb, but not Cr. In fact it appears that none of the PBETs developed so far (Chapter 2) have been validated to measure Cr bioaccessibility. Ellickson *et al.* (2001) reported the bioavailability of selected elements for NIST 2710, but Cr was not included. It was not possible to perform any bioavailability validation of the UBM for Cr as part of this project. Instead one sample was sent to TNO Nutrition in Zeist, Netherlands, for analysis with the TIM *in vitro* method (Minekus *et al.*, 1995). As discussed in Section 2.1.10, this dynamic model represents a close analogue of the human gastrointestinal tract and it has been suggested that it could be used to validate batch *in vitro* methods (Wragg and Cave, 2002). Since the

TIM method always incorporates an intestinal stage, the data were compared with the stomach+intestine data from the UBM. For the analysed sample the TIM method gave a Cr bioaccessibility of 41 ± 2 mg/kg, while the UBM gave 52 ± 1 mg/kg. Whilst not validating the UBM method for Cr, since it is based on a single sample (in duplicate), it does give some confidence to the accuracy of the data produced by the present study.

Table 4.6 UBM reference material recoveries and detection limits.

	BGS 102			NIST 2710		
	Cr	As	Pb	Cr	As	Pb
Stomach						
Consensus (mg/kg)	41 ± 1	4.8 ± 1.5	16 ± 2	1.7 ± 0.4	251 ± 13	2966 ± 227
Measured (mg/kg)	39 ± 2	4.8 ± 0.3	12 ± 2	1.5 ± 0.3	316 ± 30	3691 ± 416
Recovery (%)	95	100	75	88	126	124
Detection Limit (mg/kg)	2.6	5.8	3.0	2.6	5.8	3.0
Stomach+Intestine						
Consensus (mg/kg)	5.8 ± 3.8	4.4 ± 1.4	-	0.5 ± 0.2	219 ± 31	1184 ± 152
Measured (mg/kg)	3.2 ± 2.5	4.3 ± 0.3	0.9 ± 0.7	1.5 ± 0.8	230 ± 78	846 ± 663
Recovery (%)	55	98	-	300	105	71
Detection Limit (mg/kg)	5.0	5.2	4.0	5.0	5.2	4.0

4.4 Respiratory Uptake Test

4.4.1 Background

As discussed in Section 1.4.2.2, Cr(VI) is a known lung carcinogen. Given current plans for a major development around Rutherglen (Herald, 2008), with the possibility of dust generation, an assessment of Cr inhalation bioaccessibility was also undertaken. The method used was that of Wragg and Klinck (2007) who had used it to assess Pb inhalation bioaccessibility in mine waste in Wales, UK. The method was based on a procedure originally employed to determine the dissolution fractions and half times of yellowcake, the end product of uranium ore milling and processing, in simulated lung fluids. The simulated lung fluid used in the extractions was Gamble's solution, which was originally developed in 1942 (Eidson and Mewhinney, 1983). Gamble's solution is widely used for the determination of solubility profiles in simulated lung surfactant fluids in *in vitro* studies and has been shown to reasonably reproduce uranium solubility profiles derived from *in-vivo* tests on rodents (Damon *et al.*, 1984).

4.4.2 Procedure

To obtain enough <10 μm material, the particle size of most interest in terms of the respiratory exposure, additional soil material needed to be collected. A further 0.93 kg of soil was collected from the same location as Sample 20, whilst 1.0 kg and 0.99 kg of Samples 22 and 24, respectively, were also collected in October 2006. From the additional material, 10 g was separated and milled to <250 μm for total digestion, leaving 0.92, 0.90 and 0.98 kg of Samples 20, 22 and 24, respectively. This material was then sieved to separate the <10 μm fraction, of which between 1 and 3 g was obtained for each sample.

The Gamble's solution (composition given in Table 4.7) was prepared and pH-adjusted to 7.3 with 10 % HCl. 0.5 g of the <10 μm fraction of each sample was accurately weighed into a 30 ml polyethylene centrifuge tube and 20 ml of Gamble's solution was added. The tubes were capped and placed in an end-over-end shaker within a temperature controlled room set at 37 °C. After two hours, the samples were removed from the extractor and centrifuged for five minutes at 3000 rpm. The supernatant was decanted for analysis without filtration and fresh Gamble's solution added to the tube. In total twelve extraction fluids were collected per sample, at 2, 4, 6, 8, 10, 24, 48, 76, 96, 168, 326 and 624 hours from the start of the test. Prior to the addition of each subsequent aliquot of Gamble's solution the pH was checked, if the pH had increased above 7.3 it was adjusted back down by the drop wise addition of 10 % HCl. All samples were stored without further preservation at 4-8°C prior to analysis.

Due to the nature of the lung simulation (i.e. at each collection interval the entire supernatant is decanted for analysis and replaced with fresh lung fluid) the Cr extracted at each stage was summed together, to obtain the complete inhalation bioaccessibility for a sample. This information is displayed as an extraction profile, showing how the rate of Cr solubilisation changes throughout the extraction. If the Cr content of the extract was below the detection limit (6.0 mg/kg), a value of half the detection limit (3.0 ± 3.0 mg/kg) was applied to take account of the fact that undetectable amounts of Cr may be leached at each stage. This is the approached followed by Wragg and Klinck (2007).

Table 4.7 Composition of Gamble's Solution (Wragg and Klinck, 2007).

Salt	Mass per litre	Molar Concentration
NaCl	6.779	0.116
NH_4Cl	0.535	0.010
$NaHCO_3$	2.268	0.027
Glycine	0.375	0.005
Na_3 Citrate	0.059	0.0002
$CaCl_2$	0.022	0.0002
L-Cysteine	0.121	0.001
H_2SO_4	0.004 ml	0.0005
NaH_2PO4	0.187	0.0012
DTPA[a]	0.2 ml	0.0002
ABAC[b]	0.050	-

[a] Diethylenetriaminepentacetic acid, not present in blood serum. [b] Alkylbenzyldimethylammonium chloride, added as an antibacterial agent

4.4.3 Quality Control

There are no reference materials known to exist with a certified inhalation bioaccessibility. A blank Gamble's solution, spiked with a Cr ICP-OES standard to give a concentration of 1 mg/l, was included with the sample run. At the end of each stage, the spiked blank was collected and replaced with fresh blank solution, which was also spiked to 1 mg/l. The change in Cr concentration observed in the spiked Gamble's solution is shown in Figure 4.3. The concentration was generally lower than 1 mg/l, indicating that Cr is possibly being lost, the average being 0.73 ± 0.06 mg/l. Due to time constraints further investigation and refinement of this method was not possible.

4.5 Sequential Extraction

The solid phase distribution of Cr, Pb and As was determined to provide further understanding of the factors controlling bioaccessibility. The Chemometric Identification of Substrates and Element Distributions (CISED) sequential extraction scheme was used to determine the solid phase distribution in the soil samples.

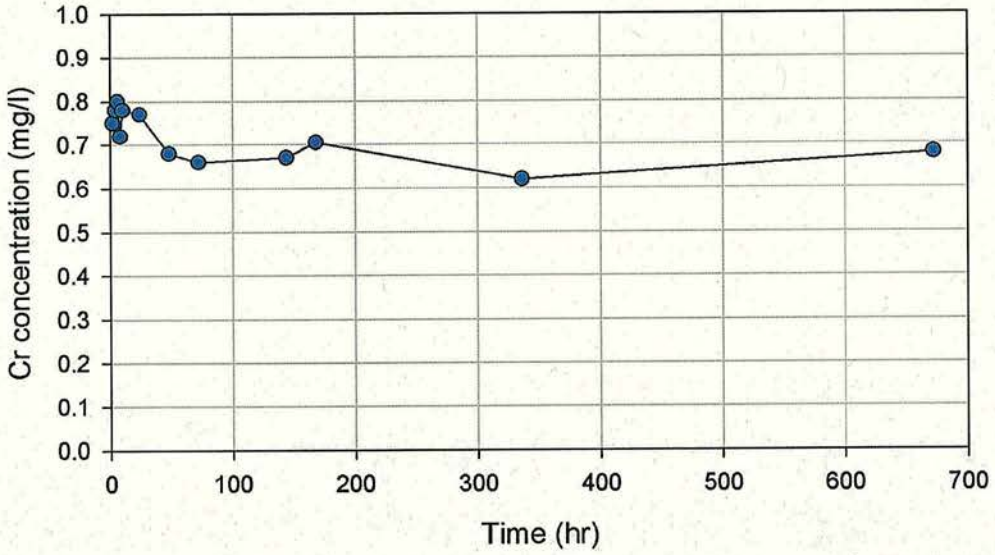

Figure 4.3 Fluctuation in Cr concentration observed in the 1 mg/l spike Gamble's solution

4.5.1 Background

Sequential extraction is a widely used method for characterising the distribution of elements in soils and sediments. Elements of interest can be distributed among several physico-chemical phases within a soil that act as reservoirs or sinks (Cave *et al.*, 2004). These phases are generally defined as combinations of the exchangeable fraction, the specifically adsorbed fraction and those associated with carbonates, Fe and Mn-oxides, organic matter and sulphides and the mineral lattice or residual (Cave and Wragg, 1997; Cave *et al.*, 2004). Extraction schemes normally involve carefully chosen reagents that are used to selectively dissolve specific phases of a given soil. As the extraction schemes progress the reagents used to remove each successive phase become more aggressive.

Sequential extractions are generally used to characterise pollution sources, to evaluate metal mobility and bioavailability and to identify binding sites of metals for assessing metal accumulation, pollution and transport mechanisms (Filgueiras *et al.*, 2002). The more easily extractable phases (e.g. exchangeable and carbonates) are often equated to bioavailability fraction (Kavanagh *et al.*, 1997), although it is more likely that this is referring to phytoavailability and not animal or human bioavailability.

4.5.1.1 Tessier Extraction Schemes

The basis of a large proportion of the extraction schemes currently available is that first described by Tessier *et al.* (1979). This test has been used for a wide variety of applications (Cave and Wragg, 1997) and has also undergone a number of modifications over the years. The Tessier method is a 4-step extraction scheme, thus allowing separation of 4 fractions. These fractions are exchangeable, acid soluble, reducible (or Fe and Mn bound), oxidisable (organic bound) and residual. Table 4.8 shows the procedure followed.

While the original Tessier method was developed for use on sediment samples, it has been successfully applied to soils as well. It has been reported that good reproducibility is found for the acid soluble, reducible and residual phases, but the exchangeable and oxidisable phases are less satisfactory (Filgueiras *et al.*, 2002). With respect to the exchangeable phase, this observation is believed to be due to insufficient extraction or interferences from the $MgCl_2$ reagent if analysed by atomic spectrometry techniques. For the oxidisable fraction, poor reproducibility is likely to result from insufficient selectivity during extraction, or to undissolved organic matter (Filgueiras *et al.*, 2002). Modifications have been made to the Tessier method in an attempt to completely dissolve the target phase, for example, by increasing the time and the amount of H_2O_2 used in the oxidisable extraction.

4.5.1.2 Bureau Communautaire de Reference (BCR) Type Extraction Schemes

One of the major limitations of the Tessier method is a lack of comparability between laboratories. The literature contains many examples of slightly modified schemes, which give different results (Cave *et al.*, 2004). In light of this problem, the European Standard Measurement and Testing Programme proposed a standardised leaching scheme, commonly known as the BCR method. The method defines the extraction of exchangeable, reducible and oxidisable fractions (Ure *et al.*, 1993). With the inclusion of some modifications, throughout its development, this method has been successfully used to generate reproducible inter-laboratory data for reference materials (Rauret *et al.*, 1999). Table 4.8 shows the extraction scheme.

4.5.1.3 Problems associated with Sequential Extraction

Despite the widespread use of sequential extraction schemes, a number of fundamental weaknesses in the methodologies have been exposed. One important limitation is that the reagents used are not specific to a target phase (Cave and Harmon, 1997; Cave and Wragg, 1997). It has also been shown that during the leaching process liberated trace metals can re-sorb onto the sample soil, again compromising the interpretation of metal distribution (Rakasataya *et al.*, 1996; Gray *et al.*, 1998; Bunzl *et al.*, 1999; Ho and Evans, 2000; Cave *et al.*, 2004).

Table 4.8 The Tessier and BCR sequential extraction schemes (Tessier *et al.*, 1979; Rauret *et al.*, 1999; Filgueiras *et al.*, 2002)

Operationally-defined phase	Reagent	Operating conditions
Tessier method		
Exchangeable	8ml of 1M $MgCl_2$, pH 7	1h at 25°C
Acid soluble	25ml of 1M NaOAc pH 5	5h at 25°C
Reducible	20ml of 0.04M $NH_2OH.HCl$ in 25% w/w HOAc	6h at 96°C
Oxidisable	3ml of 0.02M HNO_3 + 5ml of 30% w/v H_2O_2	2h at 85°C
	3ml of 30% w/v H_2O_2	3h at 85°C
	5ml of 3.2M NH_4OAc	30min at 25°C
BCR method		
Acid soluble	40ml of 0.11M HOAc	16h at 25°C
Reducible	40ml of 0.5M $NH_2OH.HCl$	16h at 25°C
Oxidisable	10ml of 30% w/w H_2O_2	1h at 25°C (covered)
	10ml of 30% w/w H_2O_2	1h at 85°C (uncovered)
	50ml of 1M NH_4OAc	1h at 85°C
		16h at 25°C

The choice of reagents used in sequential extraction methods can also cause problems for modern analytical instruments. Analysis of the extraction solutions is generally carried out by atomic spectrometric methods, with the use of ICP-OES and inductively coupled plasma mass spectrometry (ICP-MS) being the most common. For these techniques the high salt content of the extraction solutions can cause a number of problems, including blockages in the sample introduction system and de-stabilisation of the ICP source (Cave *et al.*, 2004; Hill *et al.*, 2004). In addition, non-spectroscopic suppression of the analyte signal can occur (Belazi *et al.*, 1995; Stead *et al.*, 2000). This suppression is caused by large concentrations of easily ionised elements drawing energy away from the plasma, making harder to ionise other elements. For example, it has been shown that, during ICP-OES analysis a 0.05 M

$MgCl_2$ solution can reduce the emission intensity of Zn by 11% (Vandercasteele and Block, 1997). This can be problematic because $MgCl_2$ is used in the Tessier method to extract the exchangeable phase, where trace elements are generally low in concentration and any reduction in signal intensity would lead to detection problems.

A practical consideration that cannot be overlooked when using sequential extraction schemes is the amount of time required for their completion. This can range from 18 hours for the Tessier extraction to 51 hours for the standard BCR extraction scheme (Filgueiras *et al.*, 2002). However, this problem has begun to be addressed by research into the application of ultrasound to reduce extraction times, although further work is still required before the methods can be applied fully (Davidson and Delevoye, 2001).

4.5.1.4 The Chemometric Identification of Substrates and Element Distributions (CISED) Extraction Scheme

To overcome some of the methodological and practical problems associated with sequential extractions, the British Geological Survey has developed a non-specific extraction method utilising chemometric data processing to measure trace element distributions in soils and sediments. This method is known as the Chemometric Identification of Substrates and Element Distributions, or CISED (Cave and Harmon, 1997; Cave and Wragg, 1997; Cave *et al.*, 2004). Since no extraction reagent can be assumed totally specific for a target phase, this method employs a single non-specific extractant in increasing concentration, where each extracted solution can be considered mixtures of different physico-chemical phases/components. These mixtures of the different dissolved phases are then resolved using a chemometric approach, which is based on a multivariate self-modelling mixture resolution procedure (Cave *et al.*, 2004). This approach assumes that:

(i) the material under study consists of a mixture of discrete physico-chemical components with distinct major element compositions and that the trace metals of interest are distributed amongst these components (Cave *et al.*, 2004).

(ii) under increasing acid strength, the different physico-chemical components will have different degrees of solubility, thus in a sequential series of extracts

of increasing acid concentration, each solution will contain differing proportions of each of the components of the test material (Cave *et al.*, 2004).

(iii) within any given physico-chemical component all of the elements are dissolved congruently (Cave *et al.*, 2004).

4.5.2 CISED Procedure

Extraction in the CISED method (used in this study) involves the sample being supported on a cellulose acetate filtration membrane in a centrifuge tube, through which the successive extractants are passed under centrifugal force. A diagram of the centrifuge arrangement is shown in Table 4.2.

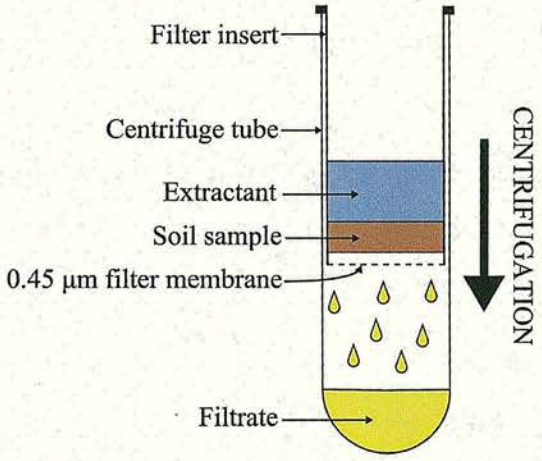

Figure 4.4 Diagram of centrifuge arrangement used for the CISED extraction.

Approximately 2.0 g of the soil sample was accurately weighed onto the filter tube inserts. A 10 ml aliquot of extractant was added above the soil. The tube was then centrifuged at 1034 g for 10 minutes and the filtrate collected. The process was then repeated sequentially with all extractants. Seven extractants were used, de-ionised water (DI), 0.01, 0.05, 0.1, 0.5, 1 and 5 M aqua regia (70 % HCl: 30 % HNO_3), which were all performed in duplicate, giving 14 extractions per sample. For the 0.1, 0.5, 1 and 5 M acid extract, 0.25, 0.50, 0.75 and 1 ml, respectively, of H_2O_2 was added to the soil, before making up to 10 ml volume. This was done to oxidise soil organic matter and prevent its precipitation. The extracts were then analysed by ICP-OES for the following elements: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, P, S, Se, Sr, V and Zn (Cave *et al.*, 2000; 2002; 2004).

4.5.2.1 Chemometric Data Processing

For each extracted soil a data matrix is produced, consisting of 14 extraction solutions by 23 elements. Figure 4.5 shows a simplification of the chemometric procedure.

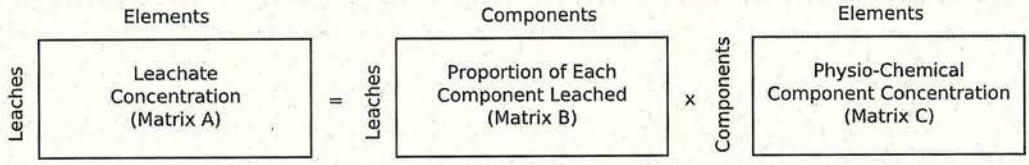

Figure 4.5 Simplified CISED Algorithm (Cave *et al.*, 2004)

Matrix A, measured using ICP-OES, is the concentration of each element in the 14 leachates. This forms the basis of the chemometric resolution of Matrices B and C. The proportion of each component in a given leachate (Matrix B) is known as the profile data for any given soil extraction, i.e. it describes where in the extraction scheme (extraction number 1-14, DI water increasing to 5 M acid strength) a given component is leached. The profile concentration data (Matrix B) also gives an indication of the extractable mass of the solid/soil sample from each individual derived component. The component concentration data (Matrix C) is known as the composition data, i.e. the elemental composition of a given component. The combination of the information provided by the composition and the extraction profile of a given component can be used to provide an interpretation of the geochemical source of that component. For example, if a component is dominated by Fe and is extracted at the final stages of the methodology (high acid strengths), it could be assumed that a likely source of this component is an Fe-oxide containing material. However, if the component is dominated by Ca and removed during the early stages of the extraction (extraction point 3 or 4, 0.01 M acid, the first addition of acid), the component is likely to be a Ca-carbonate derived component (Cave *et al.*, 2004; Wragg, 2005).

The CISED mixture resolution algorithm is implemented in the Matlab computer programme and is broken down into a number of stages according to Cave *et al.* (2004). The different stages of the CISED algorithm are summarised in Table 4.9.

Table 4.9 Summary of the stages involved in the CISED mixture resolution algorithm (reproduced from Wragg (2005)

Stage	Summary of CISED mixture resolution stages
1	The extraction Matrix A is scaled to its maximum and subjected to principal component analysis (PCA) to estimate the number of components present. This is implemented within the Matlab programme.
2	Varimax rotation (within Matlab) of the scores from the PCA (0-1) gives the first approximation of the shape of each of the extraction profiles of each component.
3	To estimate the relative proportion of each of the leached components needed to make up the leachate concentration data (Matrix A), a multiple linear regression (MLR) is carried out within Matlab. The dependant variable is the sum of each row in the leachate concentration matrix (scaled to 1) and the independent variable is the scaled score matrix from the PCA in stage 2. The columns of the scaled score matrix are multiplied by their corresponding MLR coefficients, creating a new matrix that has its rows scaled to 1. This new matrix is a first approximation of the proportion of the extraction profiles (scaled Matrix B).
4	The composition of each component (Matrix C) can be calculated as a first approximation, once both scaled data matrices A and B are known, using the equation A = BC, or in its pseudoinverse form $C = AB'[B'B]^{-1}$, where B' is the transpose of B.
5	As in the first approximation of Matrix C some values are negative values they are corrected to 0 and a second approximation of Matrix B is required within Matlab using the equation $B = [C'C^{-1}]\ C'A$. This second approximation and subsequent iterations are used to refine the approximation of the proportions and compositions of each of the components until no further significant changes to the proportions or compositions information for each component is made.
6	At this stage an input from the operator, to interpret the number of components determined by the CISED algorithm to enable completion of the mixture resolution process, is required. The algorithm provides a graphical plot (an iteration and average fit plot), an example of which is shown in Figure 4.6. This shows, the modelled number of components present in the extracted soil sample and how many iterations of the data set were carried out to achieve a close fit between the actual and modelled data. The modelled number of components generally ranges from 2-15, with differing degrees of closeness of fit.
7	The iteration and average fit plot (Figure 4.6) is split into two halves. The upper half identifies the number of iterations completed by the algorithm to determine the number of components present (blue line) and the fit of the modelled data compared to the actual input data (green line) for that number of components. The lowest point on the fit line (green) gives the first indication of the number of acid extractable components present in the test soil that gives a good fit between the actual and modelled data.

Stage	Summary of CISED mixture resolution stages
8	The lower half of the iteration and average fit plot (Figure 4.6) summarises the average difference between the actual extraction and the modelled extraction data. The lowest point on this plot tells the operator how many components are present in the test soil. This value is then required as an input into the mixture resolution algorithm implemented by Matlab.
9	Once the number of components (as determined using the iteration and average fit plot) is inputted into the mixture resolution algorithm, the final component composition, the concentration of each component in each stage of the CISED extraction (profile concentration data) and information on the distribution of each of the input elements are calculated and provided as graphical or tabular outputs resulting in completion of the mixture resolution algorithm.

Cave *et al.* (2004) have reported the application of the CISED extraction method to the certified reference material NIST 2710. The mineralogical phase information produced by the methodology was favourably compared against mineralogical data produced by backscattered scanning electron microscopy and that previously reported by other extraction methods for this material.

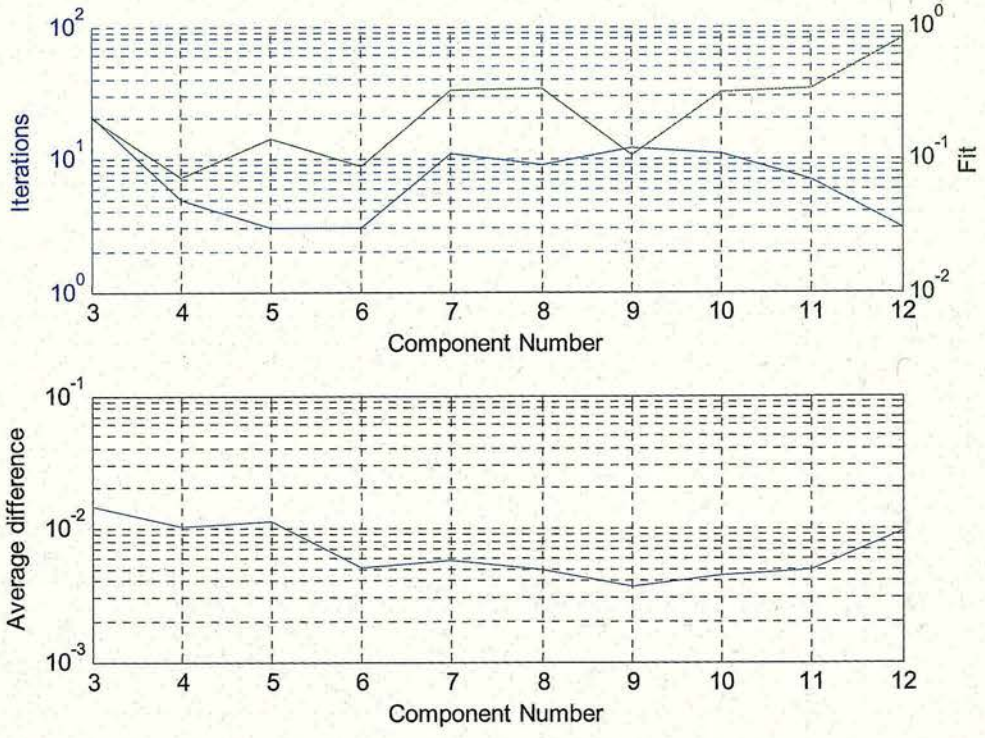

Figure 4.6 Matlab CISED mixture resolution iteration and average fit plot

4.6 Diphenylcarbazide Colorimetric Procedure

The most common method for determining Cr(VI) in aqueous solutions is that based on its reaction with diphenylcarbazide (DPC) in acidic solution (Pettine and Capri, 2005). The addition of an excess DPC yields the pink-violet coloured product of unknown composition. The absorbance of this product was measured, using a spectrophotometer, at 540 nm. The method is very sensitive, the absorbency index per gram atom of Cr being about 40,000 at 540 nm (USEPA, 1992).

A modified version of USEPA method 7196A was used to determine Cr(VI) concentrations in the alkaline digests (Section 4.2.2), UBM (Section 4.3.2) and Respiratory Uptake extraction (Section 4.4.2). This procedure involved 2.5 ml of DPC reagent (prepared from 0.38 g 1,5-diphenylcarbazide dissolved in 100 ml acetone, 120 ml H_3PO_4 and 280 ml H_2O) being added to 5.0 ml of sample. Due to the presence of H_3PO_4, the resulting solution had a pH <2, as required. The solution was agitated gently, covered and left for 20 min to allow the colour to develop. The solution was made up to 25 ml and the absorbance of the complex measured at 540 nm using a Unicam UV2-100 spectrophotometer (ThermoSpectronic, UK). Calibration standards (0.04, 0.2, 0.4, 1.2 and 2 mg/l) were prepared from a 1000 mg/l stock solution of $K_2Cr_2O_7$ and were reacted with the DPC reagent in the same way as the samples. Reagent blanks from the alkaline digestion were also included with each sample batch, from which a detection limit of 0.04 mg/l was calculated (five times the standard deviation of five reagent blanks). This relates to a detection limit of 1.8 mg/kg in the solid samples.

4.7 X-Ray Fluorescence Spectrometry

X-Ray fluorescence (XRF) was used to determine the total concentration of Si in the solid soil sample, due to its loss as a volatile fluoride during HF/HNO_3 digestion. In addition, the total concentrations of selected major elements (Al, Ba, Ca, Fe, K, P and V) were also determined due to unsatisfactory recoveries encountered when using HF/HNO_3 with ICP-OES analysis.

4.7.1 Background

X-Ray fluorescence (XRF) spectrometry is a non-destructive analytical technique used to measure elements present in samples, normally in the solid form (Vandercasteele and Block, 1997). This means that a minimum of sample preparation

is required prior to analysis, in comparison to the total digestion method described in Section 4.1.2. When an atom is exposed to short-wavelength radiation, such as X-ray or gamma, ionisation can occur. Furthermore, X-ray and gamma radiation can be energetic enough to eject electrons from an inner shell of an atom. The removal of an electron in this way leaves the electronic structure of the atom unstable and the vacancy is immediately filled by an electron from a higher energy level. In dropping down to a lower energy level, a photon is produced, the energy of which is equal to the energy difference of the two orbitals involved. These photons have a narrow energy bandwidth and are specific for the particular electron transition and are characteristic of the ionised element.

4.7.2 Analytical Method

Wavelength-dispersive (WD) X-ray fluorescence spectrometry was used to determine the selected major and trace elements (Al, Ba, Ca, Fe, K, P and V) in the Glasgow soil samples. The wavelength-dispersive instrument used was Panalytical PW2404 wavelength-dispersive sequential X-ray spectrometer, fitted with automatic sample changers. The instrument was fitted with a 3kW Rh-anode, end-window X-ray tube. Table 4.10 shows the instrument configuration used in this project.

All major and trace elements in the test soils were determined on pressed powder pellets. The pellets were prepared by grinding the sample to <100 μm in an agate mortar and pestle. The ground sample was then ashed at 450 °C for 4 hours to remove any organic matter. Of this ground and ashed sample 8.0 g was combined with 10 drops of binder (EMU120FD, a styrene copolymer) and pressed at a 25 tonne load into 40 mm diameter pellets.

Both instruments were calibrated using multi-element international reference materials. A CRM from the Czech Metrological Institute (number 7002, a Light Sandy Soil with elevated analyte levels) was included with each run for quality control purposes.

Table 4.10 Configuration of the wavelength-dispersive XRF instrument

Model	PW2400
Tube	3 kW Rhodium Super Sharp
Tube Rating	Max 60 kV / 125 mA
Detectors	Gas Flow Proportional Counter (2µm window)
	Scintillation Counter
	Sealed Xenon Gas Counter
Gas	Argon / Methane (P10)
Crystals/	LiF220(lithium fluoride)
2d spacing Å:	LiF200(lithium fluoride)
	GE111 (germanium)
	PE002 (pentaerythritol)
	TlAP (thallium acid phthalate)
	PX-1 (multi-layer)
	PX-6 (multi-layer)
	TlAp 100 (coated)
Beam filters/	Brass 100 µm and 300 µm
Thickness	Aluminium 750 µm
	Lead 1000 µm
Channel masks (diameters)	6 mm, 27 mm, 37 mm
Collimator spacing	700 µm, 300 µm, 150 µm
Sample Changer	Panalytical PW2540 VRC 168-position

4.8 Inductively Coupled Plasma Optical Emission Spectrometry

The analyte concentrations in the soil digests (Section 4.1.2), UBM (Section 4.3.2), CISED (Section 4.5.2) and Respiratory Uptake (Section 4.4.2) extracts were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). This is a multi-elemental technique utilising an argon plasma, with a temperature up to 10,000 K, allowing complete sample vaporisation and near complete atomisation. The electrons of these atomised elements become excited moving to a higher energy level. These atoms however return to a ground state at a certain spatial position in the plasma, emitting energy at an element-specific wavelength. The intensity of this emission is measured by a photomultiplier and is directly proportional to concentration (Vandercasteele and Block, 1997).

4.8.1 Instrumentation

Two ICP-OES instruments were used in this project. A Perkin Elmer Optima 5300 DV was used to determine the concentration of the major and minor elements in the total digests and the Respiratory Uptake extracts, while a Varian Vista AX CCD was

used to determine the concentration of major and minor elements in the UBM and CISED extracts. The operating conditions of each instrument are given in Table 4.11.

Table 4.11 ICP-OES Operating Conditions

Parameter	Instrument	
	Perkin Elmer Optima	Varian Vista
Forward Power	1.4 kW	1.3 kW
Coolant Gas Flow	15 l/min	18 l/min
Auxiliary Gas Flow	0.2 l/min	1.5 l/min
Nebuliser Gas Flow	0.80 l/min	0.75 l/min
Integration Time	Average of 3 x 10 s measurements	Average of 3 x 10 s measurements
Pump Speed	1.5 ml/min	15 rpm for 1.01 mm bore sample intake tube
Sample Uptake Rate	1 ml/min	1 ml/min
Rinse Time	50 s	10 s
Uptake Delay	30 s	30 s
Stabilisation Delay	15 s	15 s

4.8.2 Analysis of Total Digests and Respiratory Uptake Extracts

As stated in Section 4.8.1, the Perkin Elmer Optima ICP-OES was used to determine the concentration of major and trace elements in the total digests and the Respiratory Uptake extracts. To ensure that the effects of either instrumental drift or matrix interferences were kept to a minimum a Rh internal standard was used. This was applied manually with 1 ml of a 1 mg/l Rh internal standard being added to a 2 ml aliquot of each standard and sample. The ICP-OES was calibrated with 11 multi-element standards, the concentrations of which are given in Table 4.12. Two internal quality control standards were routinely analysed with each run to ensure the accuracy of the calibration. Reagent blanks from the total digestion were also included with each sample batch, from which detection limits (standard deviation multiplied by five) were calculated. Detection limits for individual elements are given in Table 4.1.

4.8.3 Analysis of CISED and UBM Extracts

As stated in Section 4.8.1, a Varian Vista AX CCD ICP-OES was used to determine the concentration of major and trace elements in the CISED extracts and Cr, Pb and As in the UBM extracts. In both cases, the sample solutions were run along with a 1% $CsCl_2$ solution to increase the linear dynamic range of the calibration, which reduced the need for diluting samples. The ICP-OES was calibrated with 16 mixed standards, the concentrations of which are given in Table 4.12. To ensure that the calibration was

accurate and that instrument drift was kept to a minimum, two quality control standards were analysed every 10 samples throughout a sample run. Reagent blanks from the CISED and UBM extractions were also analysed, from which detection limits were calculated. Detection limits for individual elements are given in Table 4.13.

Table 4.12 Concentration of major and trace elements in the multi-element ICP-OES standards. Only standards 1 to 11 were used when calibrating for total digests.

All concentrations are in mg/l

	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Std 1					10						5	0.1	10			50		0.5		5					
Std 2					50						10	0.2	50			100		1.0		10					
Std 3					100						25	0.4	100			500		5.0		50					
Std 4					500						50	0.5	500			1000		10		100					
Std 5	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1	0.1				0.1	0.1		0.1		0.1		0.1		0.1	0.1	0.1
Std 6	0.5	0.5	0.25	0.2		0.5	0.5	0.5	0.5	0.5				0.5	0.5		0.3		0.2		0.5		0.25	0.5	0.5
Std 7	1.0	1.0	0.5	0.4		1.0	1.0	1.0	1.0	1.0				1.0	1.0		0.5		0.4		1.0		0.5	1.0	1.0
Std 8	5.0	5.0	1.0	0.5		5.0	5.0	5.0	5.0	5.0				5.0	5.0		1.0		0.5		5.0		1.0	5.0	5.0
Std 9	10	10	5.0	1.0		10	10	10	10	10				10	10		5.0		1.0		10		5.0	10	10
Std 10	50	100		5.0		25				50				50			10		10				10		25
Std 11	100			10		50		50	100	100				100			20		50				25		50
Std 12																						0.5			
Std 13																						1.0			
Std 14																						5.0			
Std 15																						10			
Std 16																						25			

Table 4.13 ICP-OES detection limits for CISED extraction.

Analyte	Detection Limit (µg/l) *	Analyte	Detection Limit (µg/l) *
Al	76	Mn	4
As	11	Mo	45
B	30	Na	717
Ba	3	Ni	3
Ca	332	P	16
Cd	1	Pb	13
Co	3	S	342
Cr	7	Se	22
Cu	5	Si	239
Fe	157	Sr	5
K	847	V	11
Li	1	Zn	7
Mg	221		

* 5 x reagent blank standard deviation. n = 71.

4.9 Inductively Coupled Plasma Mass Spectrometry

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to determine the Pb isotope ratios for each soil and the speciation of Cr in the UBM extracts, for which it was coupled with a liquid chromatography system.

There are four stable isotopes of Pb, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. The amount of ^{206}Pb, ^{207}Pb, and ^{208}Pb gradually change with time due to the supply from the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively. The ratio of these Pb isotopes in minerals/ores will, therefore, differ depending on when the ore was formed and its geological condition. As such, the isotope ratio of Pb ores varies with geographical location, e.g. a $^{206}Pb/^{207}Pb$ of 1.04 for Broken Hill, Australia, 1.17 for Leadhills, Scotland, and 1.39 for Mississippi Valley, USA (Farmer *et al.*, 2000). Lead sources retain this characteristic isotopic signature from the ore from which they are derived. As such, it is possible to distinguish sources of Pb pollution using Pb isotope ratios (Shirahata *et al.*, 1980; Hopper *et al.*, 1991). For example the alkyllead anti-knock additives, formerly used in UK petrol (drivied from Pb ores from Australia and Canada), had a $^{206}Pb/^{207}Pb$ of 1.07 compared to a $^{206}Pb/^{207}Pb$ of 1.18 in British Coal (Farmer *et al.*, 1999a; 2000). Lead isotopes were determined in this project to assess whether the isotopic signature of a soil was related to the observed Pb bioaccessibility.

As with ICP-OES, ICP-MS is a sensitive multi-elemental technique utilising an argon plasma, which allows complete sample vaporisation, near complete atomisation and

ionisation. The ionised sample is carried by a stream of argon though several sampling cones into a mass spectrometer, which separates the ions based on their mass to charge ratio.

4.9.1 Instrumentation

An Agilent 7500ce (with octopole reaction system) ICP-MS was used in this project. A Mira mist nebuliser was used to aspirate the sample into plasma and both the skimmer and sample cones were made of nickel. The ICP-MS was coupled with an Agilent 1200 Series LC System to analyse the UBM extracts. The instrument conditions for the two methods can be seen in Table 4.14.

Table 4.14 Operating conditions of the ICP-MS for Pb isotope analysis and when coupled to the HPLC

	Pb Isotope Ratios	HPLC-ICP-MS
RF power	1.5 kW	1.5 kW
RF matching	1.74 V	1.85 V
Reflected power	1 W	1 – 2 W
Carrier gas	0.8 l/min	0.7 l/min
Make-up gas	0.2 l/min	0.12 l/min
Reaction cell gas	N/A	6.3 l/min He
Nebuliser pump	0.3 rps	1.2 ml/min
Spray chamber Temperature	15°C	-5°C

4.9.2 Lead Isotope Method

The $^{206}Pb/^{207}Pb$ ratio was determined in the soil digests (Section 4.1.2) and the UBM extracts (Section 4.3.2). To determine the Pb isotopic ratio, in the sample solutions, the Agilent 7500ce ICP-MS was set-up in isotope analysis acquisition mode. Each isotope was determined in a fully quantitative mode, at three points per unit mass. ^{206}Pb and ^{207}Pb were integrated for 2 s per point, giving a total integration time of 6 s per unit mass and ^{208}Pb for 1 s per point, giving a total integration time of 3 s. Ten replicate runs per sample were employed. To ensure good crossover between pulse counting (P) and analogue counting (A) mode, a P/A factor was determined across the mass range 206-208 amu at the start of each analysis day. All samples, however, were diluted to ensure that they fell into the pulse count mode. In addition, the instrument was slightly detuned in sensitivity. NIST SRM981 was used for mass bias correction. Tabulated $^{206}Pb/^{207}Pb$ is shown in Appendix 1.

4.9.3 Chromatography Method for Assessing Chromium Speciation

High Performance Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS) was used to investigated the form of Cr(III) present in the UBM extracts. The chromatography method used in this project was based on that reported by Woelki *et al.* (1997). It involved an acetonitrile/H_2O mobile phase and a ZORBAX Eclipse XDB-C18 column (5 µm particle size, 4.6 x 150 mm I.D (80Å pore size)). The composition of the mobile phase was varied over time with a stepwise gradient programme, which enhanced separation and allowed the sample to be eluted in 20 minutes. The profile of the gradient programme can be seen in Figure 4.7.

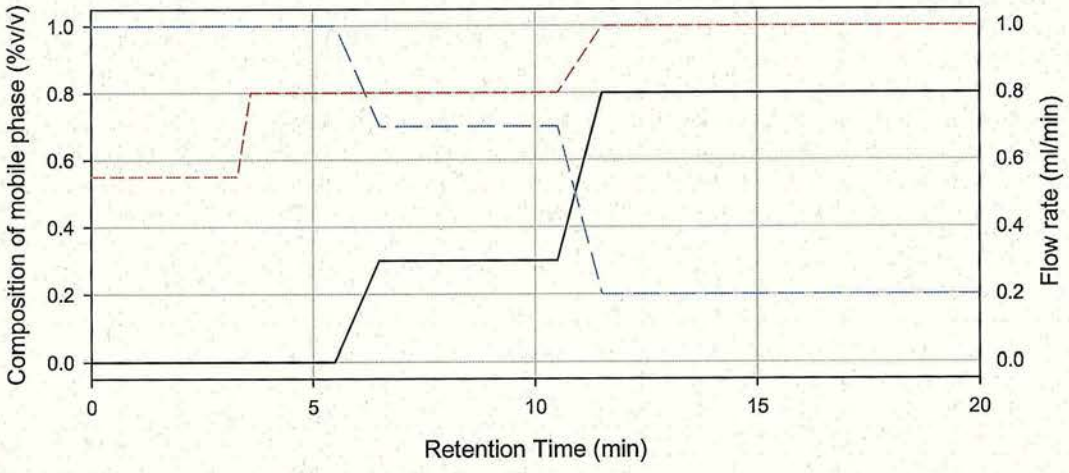

Figure 4.7 Gradient programme for HPLC-ICP-MS.
— = acetonitrile, — = water, - - = flow rate

The ICP-MS conditions (shown in Table 4.14) were set to cope with the most extreme conditions that would be experienced throughout the HPLC run (80% Acetonitrile / 20% water at a pump speed of 1.0 ml/min). At this point the RF matching power was set at 1.85 V to maintain a reflected power of 1-2 W; however, the reflected power varied through out the separation programme up to a max of 7 W. The carbon build-up on the sampling cones from acetonitrile was regulated by adding an 80:20 mix of argon:oxygen at a rate of 17 % into the aerosol.

The analysis of Cr with ICP-MS has potentially many interferences, with every isotope having several polyatomic interferences known to form in the plasma (Table 4.15). These polyatomic, or molecular ions, can be removed from the plasma through

the use of a collision cell. This involves accelerating the ions (produced by the plasma) with the magnetic field of the mass spectrometer, giving them a high kinetic energy in the associated vacuum. These high-energy ions are then allowed to collide with inert gas, in this case helium. If the colliding species is a molecular ion, kinetic energy is transferred to the molecular bonds, resulting in bond breakage and the fragmentation of the molecular ion into smaller fragments. Hence, He was added to the gas flow to allow more accurate measurement of Cr concentration.

Table 4.15 Polyatomic interferences associated with Cr analysis by ICP-MS

Isotope	Abundance	Associated Polyatomic Ions
^{50}Cr	4.35	$^{34}S^{16}O^+$, $^{36}Ar^{14}N+$, $^{35}Cl^{15}N^+$ $^{36}S^{14}N^+$, $^{32}S^{18}O^+$, $^{33}S^{17}O^+$
^{52}Cr	83.76	$^{35}Cl^{16}O^1H^+$, $^{40}Ar^{12}C^+$, $^{36}Ar^{16}O^+$, $^{37}Cl^{15}N^+$, $^{34}S^{18}O^+$, $^{36}S^{16}O^+$, $^{38}Ar^{14}N^+$, $^{36}Ar^{15}N^1H^+$, $^{35}Cl^{17}O^+$
^{53}Cr	9.51	$^{37}Cl^{16}O^+$, $^{38}Ar^{15}N^+$, $^{38}Ar^{14}N^1H^+$, $^{36}Ar^{17}O^+$, $^{36}Ar^{16}O^1H^+$, $^{35}Cl^{17}O^1H^+$, $^{35}Cl^{18}O^+$, $^{36}S^{17}O^+$, $^{40}Ar^{13}C^+$
^{54}Cr	2.38	$^{37}Cl^{16}O^1H^+$, $^{40}Ar^{14}N^+$, $^{38}Ar^{15}N^1H^+$, $^{36}Ar^{18}O^+$, $^{38}Ar^{16}O^+$, $^{36}Ar^{17}O^1H^+$, $^{37}Cl^{17}O^+$, $^{19}F_2{}^{16}O^+$

4.10 Gel Electrophoresis

Gel electrophoresis, in addition to the HPLC-ICP-MS (Section 4.9.3,) was used to investigate the form of Cr(III) present in the UBM extracts. The method used was adapted from that reported by Farmer *et al.* (2002) The individual UBM extracts were filtered using a 0.2 μm hydrophilic membrane (Whatman). Approximately 3 ml of this filtrate was transferred to the upper compartment of a 3 kD Vivaspin (polyethersulfone membrane) ultrafilter tube. This tube was centrifuged at 6000 rpm (MSE Mistral 3000, Sanyo Gallenkamp plc, UK) for 20 minutes, or until the retentate volume was ~0.3 ml. The retentate and a 0.3 ml aliquot of the filtrate were recovered, to each of which 0.2 ml 0.05 M Tris/HCl was added. The retentate and filtrate were then transferred to separate sample wells of a MbP Horizontal Mega-Gel System 8300 Series 19 *6* 25 cm gel electrophoresis system (Molecular Bio-Products Inc., USA) containing agarose gel (1.5 g agarose in 150 ml 0.045 M Tris–borate). The running buffer was 0.045 M Tris–borate and the system was operated at 20 mA fixed current (150 V, 3 W) for 30 minutes.

Visual observations of the separation were recorded under both ordinary and UV light, the latter at 302 nm using a Transilluminator Model M-20 UCP Bio-Doc-It

System (UVP, USA). The gels were then sectioned on the basis of observed colour and fluorescence characteristics into approximately ten 0.5 cm-wide strips. These strips were labelled F1, F2, F3 etc with increasing distance from the sample well. The strips were digested with a minimal amount of 2% Aristar HNO_3 on a hotplate for 2 h. After digestion the volume was diluted to 3 ml with 2% v/v Aristar HNO_3 for subsequent analysis by ICP-OES.

4.11 X-Ray Diffraction

X-ray diffraction (XRD) is a versatile, non-destructive solid-state analytical technique that can be used for the identification and quantitative determination of the various crystalline compounds that make up a powdered or solid sample (USGS, 1997). In fine-grained rocks rich in clay minerals, X-ray diffraction is an essential characterisation tool. In this study it was important that the soil mineralogy, with particular interest in the clay mineralogy, was identified to aid in the interpretation of the CISED data (Section 4.5.2.1).

4.11.1 Analytical Method

To aid in the assessment of soil clay mineralogy the fine material was isolated from the bulk soil samples. This was achieved by mixing approximately 1 g of soil in a measuring cylinder containing 8 cm of deionised water. The cylinder was inverted and left to stand for 2 minutes, at which time the solution was transferred to a centrifuge tube and centrifuged at 3000 rpm for 5 minutes. The supernatant was discarded and the pellet dried in a 30°C oven. Prior to analysis the isolated fine material was disaggregated with an agate mortar and pestle, to which acetone was added to form a slurry. This slurry was then pipetted on to a glass disk and left to dry, ready for analysis.

The XRD analysis was carried out using a Bruker-AXS D8 Advance with Cu K_α X-ray tube. The soil samples were scanned from 4-60° 2θ at 0.02° 2θ per second. The resulting diffraction data were analysed using DIFFRAC^{plus} EVA software.

4.12 Soil pH

Given the relationship between Cr speciation and pH (Figure 4.2), the pH of each soil was assessed. The soil pH was determined with a recognised standard protocol (Rowell, 1994) using a glass slurry electrode and Jenway 3350 meter. The pH meter

was calibrated to 4 and 7 or 7 and 9 depending on the pH of the slurry to be measured. To 10.0 g of the <250nμm sample 25 ml of 0.01 M $CaCl_2$ (1.1098 g AnalaR® $CaCl_2$ made up to 1 l with deionised water) was added and the mixture was manually stirred for one minute and then left to settle for 15 minutes. Prior to analysis the samples were stirred to reform the suspension. Buffer check solutions were analysed before and after every ten soil mixtures and all samples were analysed in duplicate.

4.13 Loss on Ignition

In this project loss on ignition (LOI) was used as an estimation of the total organic carbon content of the soils. The procedure is gravimetric, assuming that any weight lost following heating of a soil to 450°C is due to decomposition of organic matter to CO_2. However, this is only an estimate as weight loss can also arise from the volatilisation of substances other than organic matter, such as H_2O, structural OH, CO_2 from carbonates and incomplete oxidation of carbonaceous materials.

The procedure followed involved drying a beaker in an 110°C oven to drive off any moisture and recording its weight. Into this beaker approximately 2.5 g of soil was accurately weighed and then heated to 450°C in a muffle furnace for 4 hours. Once cooled, the beaker and soil was re-weighed and LOI calculated as the difference in soil mass after heating.

4.14 Statistics

To aid interpretation of the results from the outlined analytical methods a variety of statistical methods were used. These methods are outlined here.

4.14.1 Pearson's Product-Moment and Spearman Rank Correlation Coefficients

To identify correlations between variables (such as the Cr(VI) concentration and other major element concentrations in the samples) and therefore the degree to which any two variables are related, a series of Pearson's product moment and Spearman correlations were performed. In the former, the coefficient, r, is calculated using Equation 4.1 and can take any value between –1 and +1. A value of -1 implies a perfect negative correlation between variables. Similarly an r of +1 is a perfect positive correlation, but an r of 0 means that there is no relationship between the values (Miller and Miller, 2000).

$$r = \frac{n\sum(xy) - \left(\sum x\right)\left(\sum y\right)}{\sqrt{\left[n\sum x^2 - \left(\sum x\right)^2\right]\left[n\sum y^2 - \left(\sum y\right)^2\right]}}$$

Equation 4.1 Calculation of the Pearson's Product-Moment Correlation Coefficient, r, for two variables, x and y, when n is the number of data points (Miller and Miller, 2000).

One of the assumptions made by the Pearson method is that the data set is normally distributed. Much of the concentration data generated in this project was not normally distributed, thus making the Pearson's method inappropriate. The Spearman Rank Correlation method, however, makes no assumptions concerning the distribution of data (Miller and Miller, 2000). The coefficient, r_s, is calculated by first ranking the two variables, x and y, in order of magnitude, with the largest being ranked 1. Thus, for n number of samples with variables x and y, the ranked variables X and Y will both range from 1 to n. The difference between ranks, X and Y, for each sample is then used to calculated r_s using Equation 4.2.

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

Equation 4.2 Calculation of the Spearman Rank Correlation Coefficient, r_s, when n is the number of data points and d is the difference between ranks (Miller and Miller, 2000).

4.14.2 Two-Sided *t* Test

A t test was used to assess whether the $^{206}Pb/^{207}Pb$ ratio of bioaccessible Pb differed significantly from that in the soil. The value of t is calculated using Equation 4.3 and is compared with tabulated values for a two-sided test at 95% confidence. Taking the null hypothesis that there is no correlation between the two data sets, if the calculated value of t is greater than the tabulated value, the null hypothesis is rejected and it can be concluded that the correlation is significant (Miller and Miller, 2000).

$$t = \frac{|r|\sqrt{n-2}}{\sqrt{1-r^2}}$$

Equation 4.3 t value for assessing the significance of an identified correlation.

4.14.3 Mixture Resolution Data Processing

A multivariate statistical approach using predictive modelling was used to identify the intrinsic soil constituents that make up the Glasgow samples. An intrinsic soil

constituent (ISC) is defined as an assemblage of soil particles from a common biogenic, geogenic or anthropogenic input, with a consistent chemical composition, present at varying concentrations in a number of similarly developed soils (Wragg, 2005). Figure 4.8 shows the relationship between ISCs and soil composition. The mixture resolution algorithm used to identify ISCs is the same as that used in the CISED procedure (Section 4.5.2.1). In the case of ISC resolution, a matrix of total elemental and TOC concentrations (i.e. Al, As, Ba, Ca, Cr, Cr(VI), Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, V, Zn and TOC) was inputted into the algorithm, as opposed to the acid extractable element concentrations used to resolve physico-chemical components in the CISED. This matrix can be seen in Appendix 2.

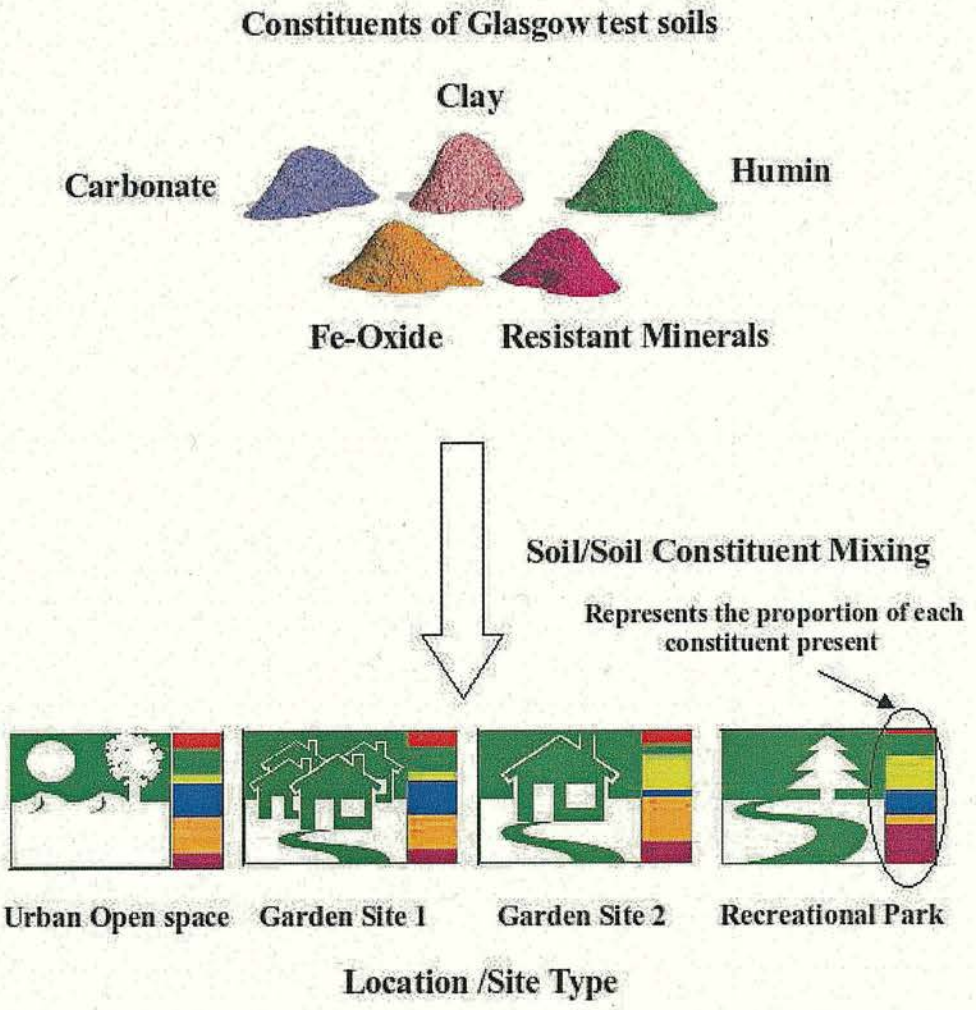

Figure 4.8 Diagram showing the relationship between intrinsic soil constituents and soil composition. Adapted from Wragg (2005).

This approach assumes that the soil samples were derived from similar geological or anthropogenic sources and as such consisted of similar particulate components. The distribution of Cr within these ISCs was used to determine the probable sources of bioaccessible Cr in the Glasgow soils. This was based on the assumption that Cr associated with the more easily extractable constituents, such as carbonates, was more bioaccessible than Cr held in less soluble phases, such as Fe oxides.

4.14.4 Cluster Analysis

The CISED data processing (described in Section 4.5.2.1) identifies a number of geochemically distinct acid extractable components that are unique for each soil sample. Since the soils in this study were collected from geochemically similar locations across Glasgow, it was beneficial for the identified components to be classified into a common set of physico-chemical groups, thus allowing comparison between samples.

To do this, a component data matrix was made containing all the components identified by the CISED method for every sample. Each component was described by its major element chemical composition (Al, Ca, Fe, K, Mg, Mn, Na, P, S and Si) and the amount of leached material in each of the 14 extracts. Before the clustering procedure was carried out the information in the component data matrix was mean centred and scaled on each variable, so that all variables contributed the same weighting to the clustering method. This process is summarised in Table 4.16. The data matrix of components was then subjected to a hierarchical clustering procedure to identify any clusters of similar components.

Table 4.16 Stages involved in mean centre and scaling for cluster analysis

Stage	Mean Centre and Scaling Stages
1	Construct a data matrix with the column headings: sample name, the component name, the major elements (Fe, Al, P, Si, Mn, Ca, K, S, Na, Mg) and finally the total extracted solids in each of the 14 extracts. Thus the matrix has 26 columns.
2	For each of the data columns calculate the mean and the standard deviation.
3	Create a new data matrix by subtracting the mean of each column from each individual value in that column so that the values are centred around zero and divide the mean centred value by the standard deviation. The data set is then ready for use in the hierarchical cluster analysis technique.

The hierarchical cluster analysis algorithm starts with each acid extracted component in its own individual cluster. In the first step, the two objects closest together are joined. In the next step, either a third object joins the first two, or two other objects join together into a different cluster. Each step results in one fewer cluster than the step before, until, at the end, all objects are in one cluster. The distance metric used in this application was euclidean distance and the linkage method, to determine how the clusters are combined, was Ward's method (Wragg, 2005). A binary tree, called a dendrogram, represents the hierarchy of the clusters. This is shown in Figure 4.9. The final assignment of each component to a cluster was achieved using a colourmap. This is a visual presentation of the data matrix, reordered by the dendrogram groupings, in which the previously mean centred and scaled data is represented by different colour shading, depending on magnitude. An example of a colourmap can also be seen in Figure 4.9. The colourmap can be divided in two by a vertical line, one side showing the major elemental compositions and the other indicating where in the extraction scheme the components were removed from the soil. High concentrations are associated with yellow and white colours, medium concentrations are associated with red blocks of colour and the dark red and blacks indicate that low concentrations are being extracted. This allows visualisation of both the major element composition of individual components and where in the CIESED extraction they were removed. Clusters are assigned manually by identifying groups of components with a similar major element composition, extracted at a similar stage of the CISED. For example it can be seen that the initial components are all dominated by the presence of Ca and extracted relatively early in the scheme, suggesting a cluster of carbonates components. There are, however, two discrete windows of extraction. The initial set of components tending to be extracted between stages 5 and 7, while a second set was extracted between stages 3 and 5. This indicates that there are two geochemical distinct sets of carbonate components and therefore two carbonate clusters (C1 and C2) were identified. The same situation can be seen with Fe-dominated components, which have been divided into three clusters based on the stage of the CISED procedure they were extracted.

4.14.5 Multiple Linear Regression

Multiple Linear Regression (MLR) is a technique used to establish a quantitative relationship between a series of predictor variables and a response (Miller and Miller,

2000). In this study the predictor variable used is the concentration of an analyte in each identified cluster (as part of the CISED methodology) or intrinsic soil constituent for the Glasgow soils and the response is the analyte bioaccessibility. Using MLR, a better understanding of which predictors control bioaccessibility should be gained. This should be achieved by identifying which, if any, geochemical factors linearly model the measured bioaccessibility.

A stepwise MLR was used to assess these relationships. This involves adding predictor terms into the MLR on a step-by-step basis, beginning with the most statistically significant (in this case p-value <0.05). The most statistically significant predictor is identified within the MLR programme by completion of a regression. Following this the next most significant predictor that models the response is added, after which the next most significant factor that models the residual dependent factor is added. The process is continued until the addition of predictors has no significant effect.

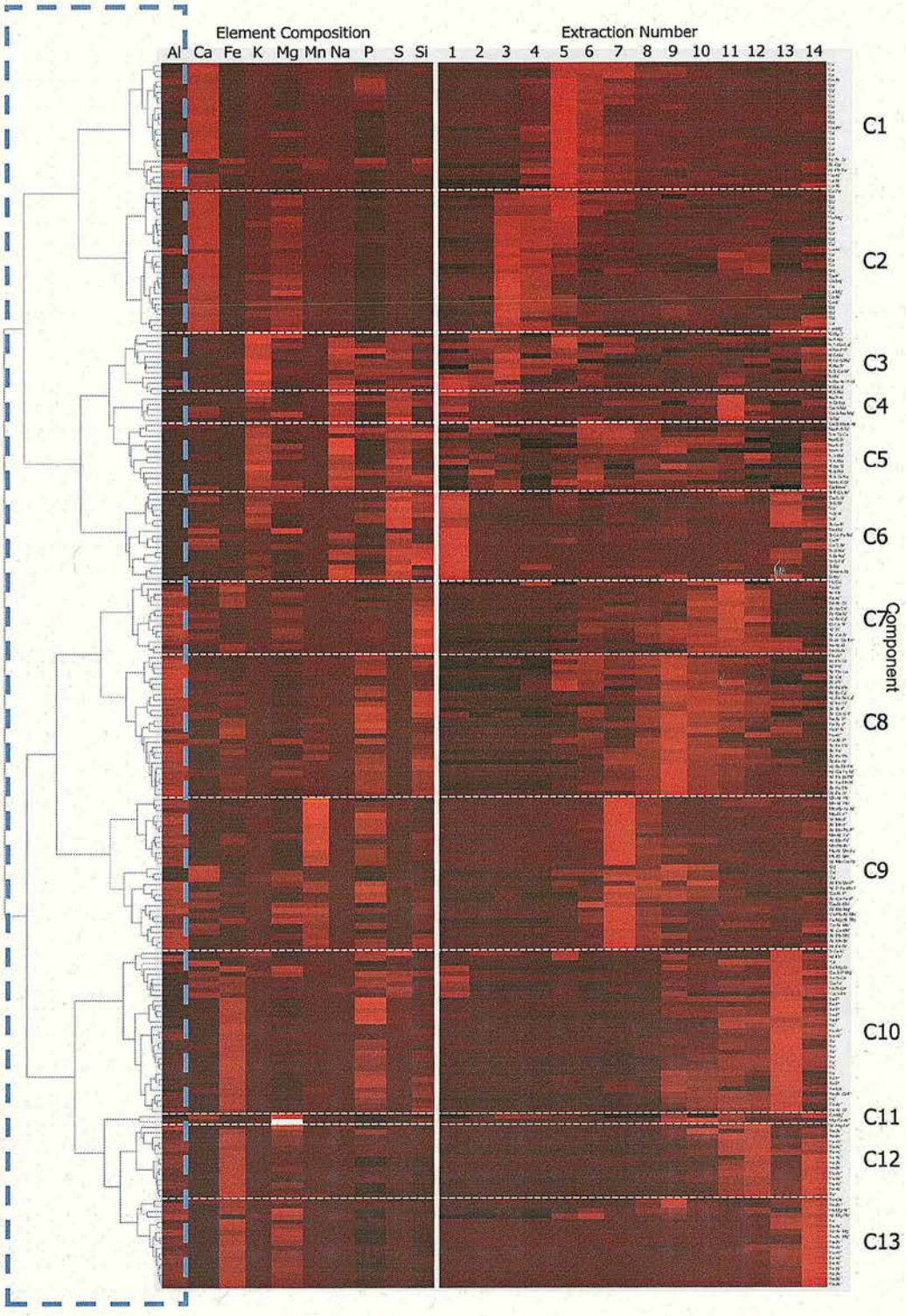

Figure 4.9 Dendrogram and colourmap produce from CISED competent data. The blue box shows the dendrogram. Horizontal white dashed lines separate the 13 identified clusters.

CHAPTER 5 ELEMENTAL AND MINERALOGICAL COMPOSITION OF GLASGOW SOIL SAMPLES

5.1 Elemental Composition of Glasgow Soils

The total elemental composition of the 27 Glasgow soils was determined using acid digestion with ICP-OES analysis (Section 4.1.2 and 4.8.2). Chromium(VI) was determined using alkaline digestion and colorimetric analysis (Section 4.2.2 and 4.6), while the ICP-MS (Section 4.9.2) was used to assess the Pb isotope ratio. Total Cr, Pb and As concentrations for each of the 27 Glasgow soil samples (Table 3.1), along with corresponding Cr(VI) concentrations and $^{206}Pb/^{207}Pb$, are listed in Table 5.1. The concentrations are also summarised in box plots (Figure 5.1).

Table 5.1 Total concentrations of Cr, Pb and As, Cr(VI) concentrations and $^{206}Pb/^{207}Pb$ ratio in the Glasgow soil samples.

Sample ID	Total Cr (mg/kg)	Cr(VI) (mg/kg)	Total Pb (mg/kg)	$^{206}Pb/^{207}Pb$	Total As (mg/kg)
1	144 ± 2	9.1 ± 0.4	298 ± 21	1.156 ± 0.0012	63 ± 1
2	65 ± 3	3.2 ± 0.4	602 ± 47	1.131 ± 0.0014	15 ± 5
3	188 ± 2	4.1 ± 1.0	1344 ± 32	1.175 ± 0.0008	135 ± 6
4	105 ± 1	11 ± 1	482 ± 8	1.151 ± 0.0014	14 ± 5
5	102 ± 2	<1.8	965 ± 140	1.133 ± 0.0012	14 ± 1
6	65 ± 4	3.5 ± 0.2	709 ± 30	1.169 ± 0.0008	25 ± 1
7	84 ± 2	3.5 ± 0.4	1152 ± 9	1.156 ± 0.0010	23 ± 4
8	72 ± 3	<1.8	555 ± 7	1.159 ± 0.0010	17 ± 1
9	113 ± 3	7.3 ± 0.5	1200 ± 23	1.146 ± 0.0008	24 ± 8
10	92 ± 0	3.2 ± 0.3	618 ± 41	1.161 ± 0.0008	13 ± 1
11	178 ± 9	6.1 ± 1.9	441 ± 13	1.137 ± 0.0014	23 ± 2
12	156 ± 32	3.9 ± 0.4	1318 ± 11	1.128 ± 0.0007	48 ± 10
13	91 ± 6	2.7 ± 0.4	508 ± 41	1.155 ± 0.0022	13 ± 0
14	86 ± 1	4.7 ± 0.8	663 ± 34	1.168 ± 0.0017	8.1 ± 6.0
15	79 ± 6	7.5 ± 0.7	157 ± 2	1.152 ± 0.0017	2.0 ± 2.9
16	97 ± 3	15 ± 3	152 ± 4	1.156 ± 0.0016	4.9 ± 1.0
17	70 ± 2	4.2 ± 0.1	147 ± 0	1.162 ± 0.0010	6.5 ± 0.5
18	128 ± 2	7.6 ± 1.9	363 ± 13	1.164 ± 0.0019	15 ± 0
19	229 ± 2	23 ± 1	227 ± 3	1.142 ± 0.0011	2.1 ± 0.2
20	3680 ± 23	1485 ± 24	399 ± 16	1.117 ± 0.0011	33 ± 2
21	122 ± 6	3.1 ± 0.1	1107 ± 4	1.165 ± 0.0008	26 ± 3
22	223 ± 8	9.0 ± 0.5	210 ± 8	1.130 ± 0.0011	18 ± 1
23	98 ± 5	7.0 ± 0.3	856 ± 194	1.094 ± 0.0015	15 ± 2
24	658 ± 23	171 ± 5	126 ± 11	1.146 ± 0.0014	<0.1
25	83 ± 0	4.4 ± 0.2	2157 ± 18	1.057 ± 0.0016	7.1 ± 1.2
26	152 ± 1	<1.8	539 ± 14	1.164 ± 0.0005	26 ± 5
27	106 ± 1	14 ± 1	500 ± 50	1.100 ± 0.0015	0.4 ± 1.9

Mean ± SD. n=2

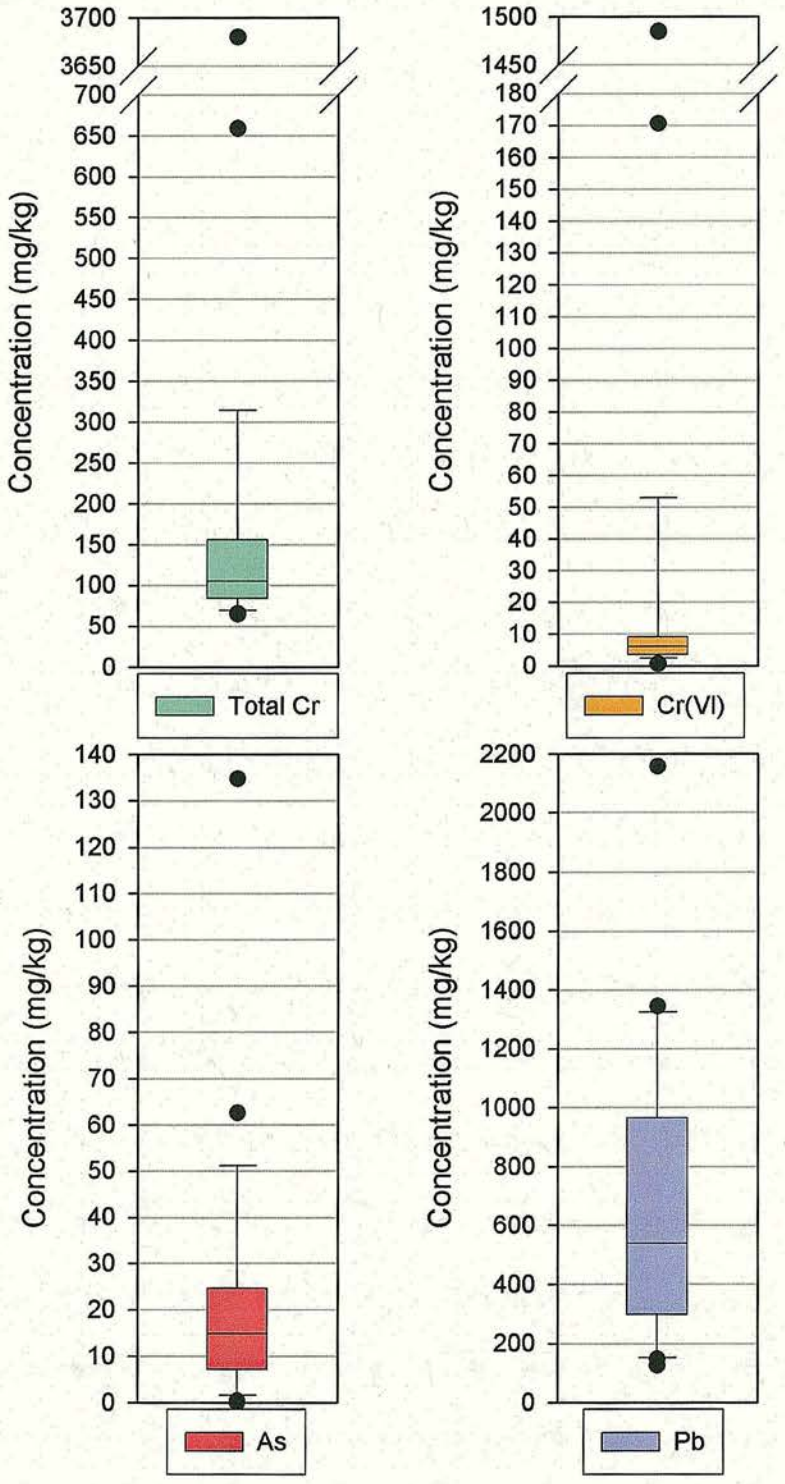

Figure 5.1 Box and Whisker plots showing the range of Cr, Cr(VI), As and Pb concentrations found in the 27 Glasgow soils.

Box and whisker indicates the 10^{th}, 25^{th}, 50^{th}, 75^{th}, 90^{th} percentiles, while points indicate an outlier.

5.1.1 Chromium Distribution

The geographical distribution of total Cr concentrations in the Glasgow soils is displayed in Figure 5.2.

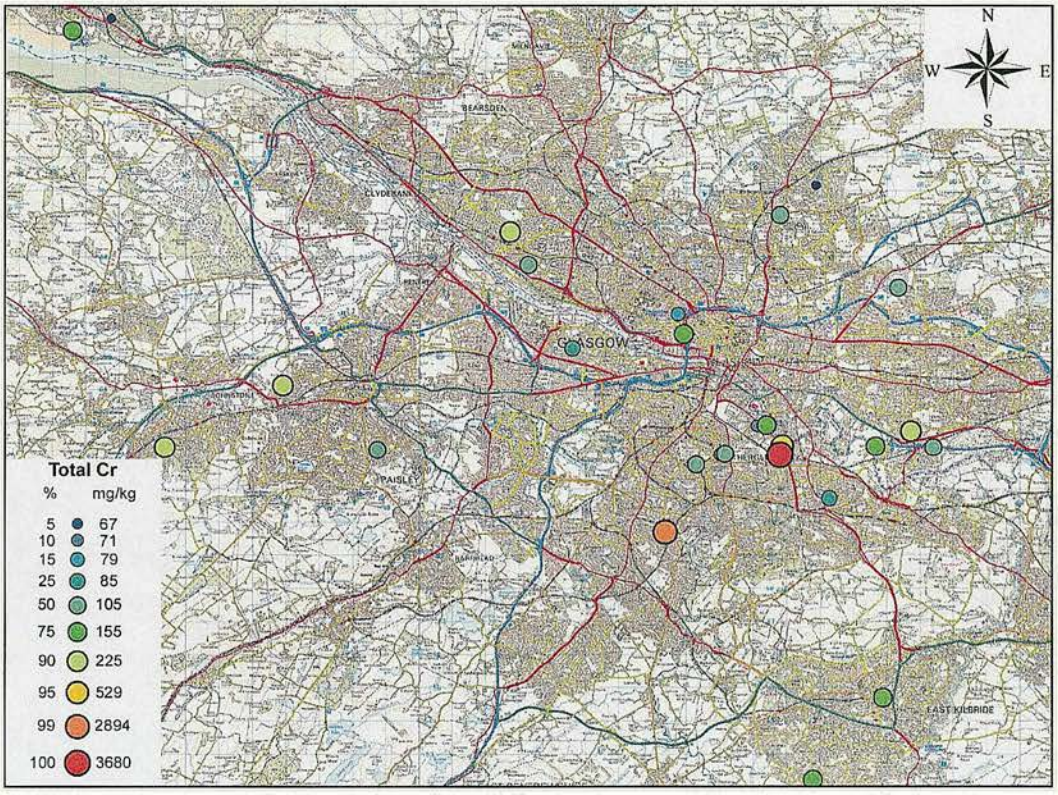

Figure 5.2 Geographical distribution of total Cr concentrations in the 27 soils across Glasgow.

The concentration of total Cr in the selected Glasgow soils ranged from 65 to 3680 mg/kg, although in 90% of soils it was less than 225 mg/kg (Figure 5.1). In total, nine samples exceeded the Cr soil guideline value (SGV) for residential land with plant uptake (130 mg/kg) (DEFRA, 2002b). These came from a wide area, spread out across the city, from Dumbarton in the northwest to East Kilbride in the southeast. Of these, four samples also exceeded the SGV for residential land without plant uptake (200 mg/kg) (DEFRA, 2002b), all located in a relatively small geographical area (23 km^2) in the southeast, around Rutherglen. The highest Cr concentration was found in this area; Sample 20 collected from land adjacent to Rutherglen Glencairn Football Ground, contained 3680 ± 23 mg/kg. This site, as discussed in Section 3.2.11, is very close to the former site of the chemical factory that generated the COPR waste. The other site with a Cr content in considerable excess of the SGV was Sample 24. This sample, collected from the Braidholm sports fields in Muirend, had a Cr concentration

of 658 ± 23 mg/kg. The remaining two samples both had a Cr content approximately 26 mg/kg over the 200 mg/kg SGV. Sample 19, collected from scrubland in Rutherglen close to Sample 20, had a total Cr concentration of 229 ± 2 mg/kg. Sample 22, from Fullarton Park in Carmyle, had slightly less Cr at 223 ± 8 mg/kg. Under the CLEA risk assessment regime, all nine soils with Cr concentrations >130 mg/kg would merit further investigation to determine source-pathway-receptor linkages and the bioavailability of the Cr present. The geographical distribution of Cr(VI) in the soils is displayed in Figure 5.3. While the Cr(VI) content ranged from <1.8 to 1485 mg/kg, the majority of soils contained little Cr(VI), with 90% containing less than 18 mg/kg (Figure 5.1). Once again, and perhaps not surprisingly given the history of COPR disposal, Samples 20 (1485 ± 24 mg/kg) and 24 (171 ± 5 mg/kg) had the highest Cr(VI) concentrations. The next highest (23 mg/kg) was Sample 19.

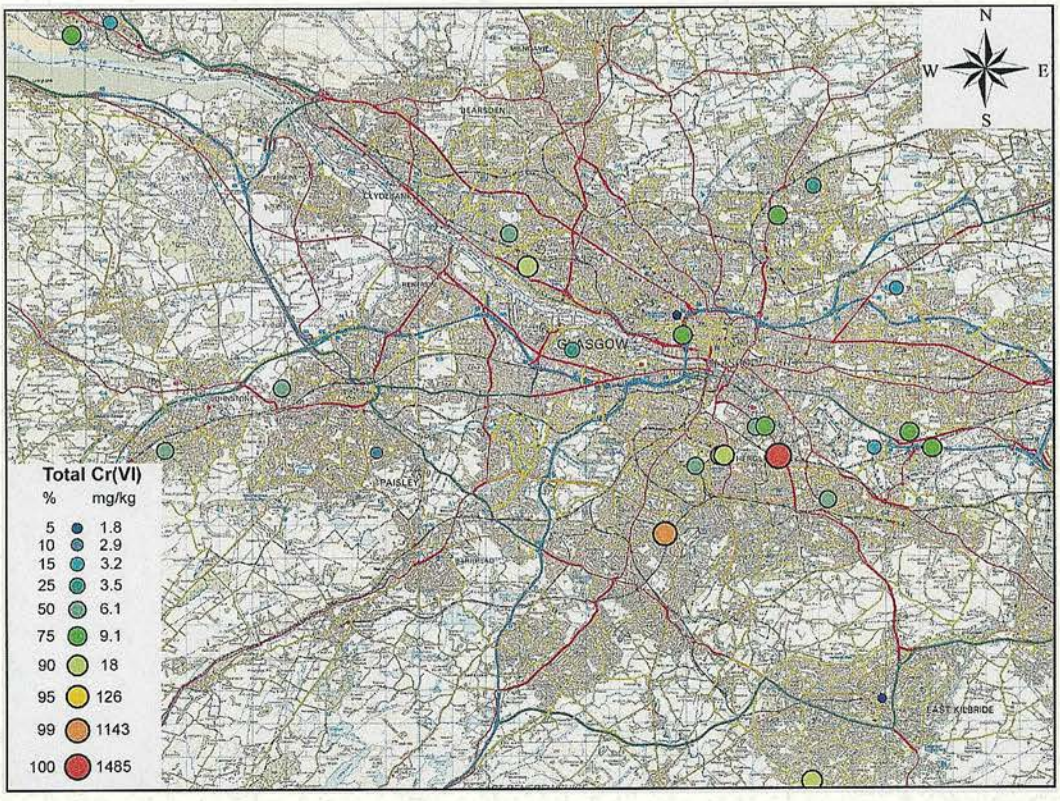

Figure 5.3 Geographical distribution of Cr(VI) concentrations in the 27 soils across Glasgow.

Samples 1, 3, 11, 12, 22 and 26 all showed high concentrations (>130 mg/kg) of total Cr, yet all contained low levels (<10 mg/kg) of Cr(VI) (Figure 5.4). This could imply that the Cr present is mostly naturally occurring. It is not possible to come to a definitive conclusion on the basis of total Cr and Cr(VI) concentration data alone.

Information on the solid phase distribution and leachability of Cr is also required. These issues are discussed in Chapter 6.

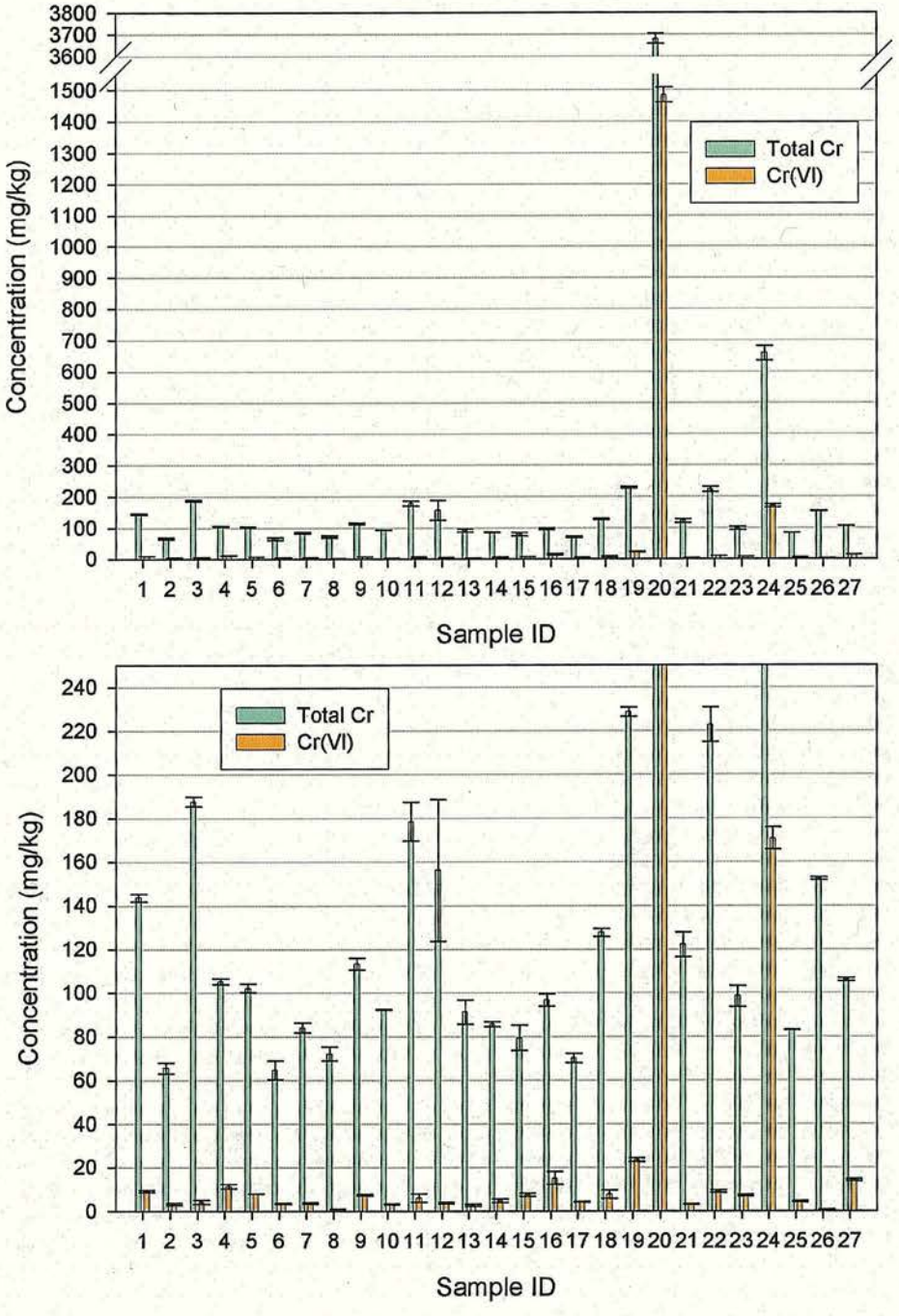

Figure 5.4 Concentration of Cr and Cr(VI) in the 27 Glasgow soil samples.

5.1.2 Lead Distribution

The concentrations of Pb in the Glasgow soils ranged from 126 to 2157 mg/kg (Table 5.1), with 50% of samples above 539 mg/kg (Figure 5.1). In total, 17 samples had a Pb concentration greater than the 450 mg/kg SGV for residential land (DEFRA, 2002c). Of these 17 samples, eight had a Pb content greater than the 750 mg/kg SGV for industrial land (DEFRA, 2002c). Elevated concentrations of Pb were expected given Glasgow's industrial past and the widespread use of tetra ethyl Pb petrol in the past.

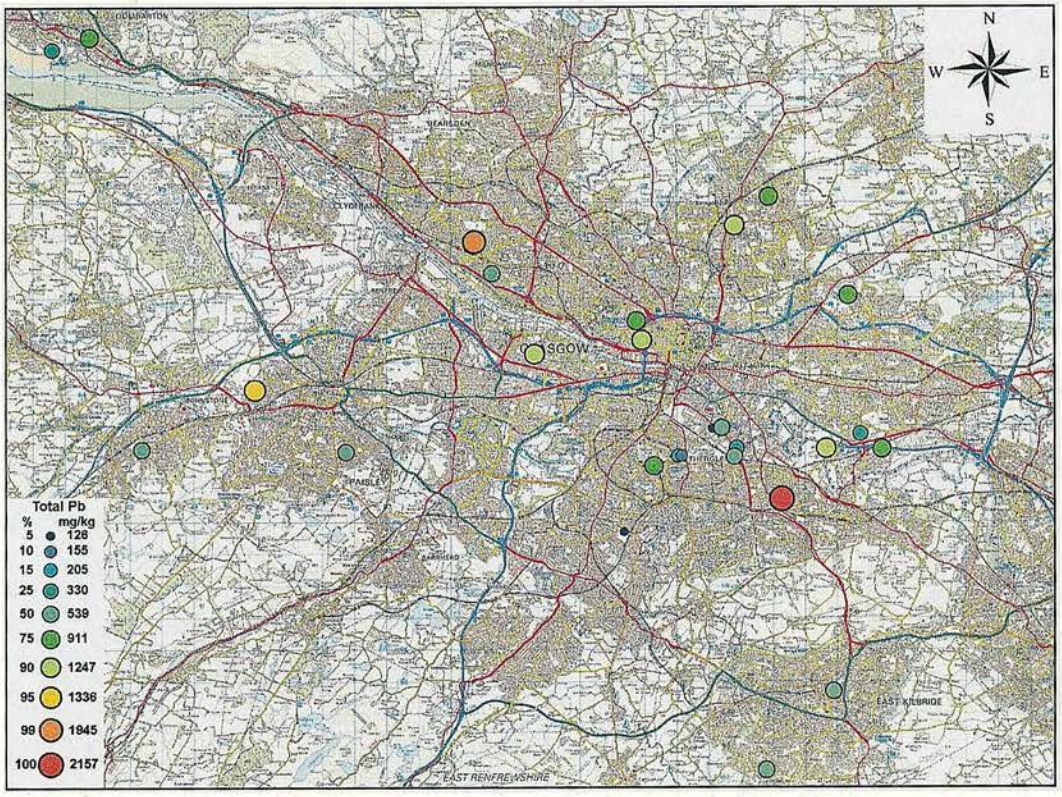

Figure 5.5 Geographical distribution of total Pb concentrations in the 27 soils across Glasgow.

The $^{206}Pb/^{207}Pb$ isotope ratio in the soils ranged from 1.057 to 1.175 (Figure 5.6), although the majority of soils (65%) had a ratio between 1.132 and 1.166. This is similar to the $^{206}Pb/^{207}Pb$ ratio (1.151 ± 0.042) reported in rainwater in the Central Belt area of Scotland during the late 20th century (Farmer *et al.*, 2000).

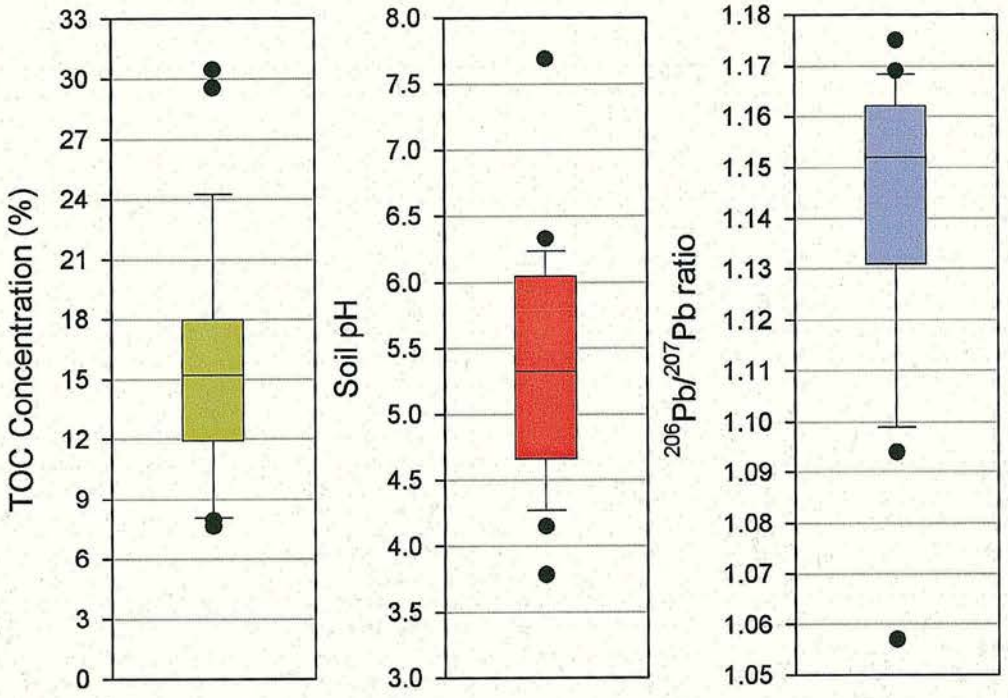

Figure 5.6 Box and Whisker plots showing the range of TOC concentrations, soil pH and $^{206}Pb/^{207}Pb$ isotope ratios found in the 27 Glasgow soils.

Box and whisker indicates the 10th, 25th, 50th, 75th, 90th percentiles, while points indicate an outliner.

Figure 5.7 shows that the $^{206}Pb/^{207}Pb$ ratios tend to be between those reported in leaded petrol (1990s mean of 1.076 ± 0.011) and Scottish coal (1.181 ± 0.011). The range of $^{206}Pb/^{207}Pb$ ratios observed indicates that the Pb content of the samples represents an accumulation of Pb deposited over decades from a variety of sources. The majority of samples have a ratio closer to that observed in coal than to petrol. This is perhaps to be expected given Glasgow's long industrial past, compared to the relatively short period that leaded petrol was in use. In addition, coal waste was noted in 16 (Samples 1, 2, 3, 4, 5, 6, 8, 9, 10, 12, 13, 14, 25, 21, 26 and 27) of the 27 samples at the point of collection (Chapter 3).

Sample 25, which had the highest total concentration of Pb (2157 ± 18 mg/kg), also had the lowest $^{206}Pb/^{207}Pb$ ratio (1.057 ± 0.0016). This total concentration is more than 10 times the SGV for residential land (DEFRA, 2002c) and the $^{206}Pb/^{207}Pb$ ratio is so low that it is almost equal to that of leaded petrol (1.061 ± 0.0071) in Scotland in 1989 (Farmer *et al.*, 2000). Sample 25 came from a grassed area in residential Rutherglen, around 200 m from a main road (A749), perhaps explaining the elevated Pb content and low isotope ratio observed. Two other samples had a $^{206}Pb/^{207}Pb$ ratio

similar to that of leaded petrol. Sample 23 (856 ± 194 mg/kg, 1.094 ± 0.0015) came from a park 80 m south of the M74, while Sample 27 (500 ± 50 mg/kg, 1.100 ± 0.0015) came from a residential area of East Kilbride. No major roads were located in this part of East Kilbride, although numerous small local roads did surround the site.

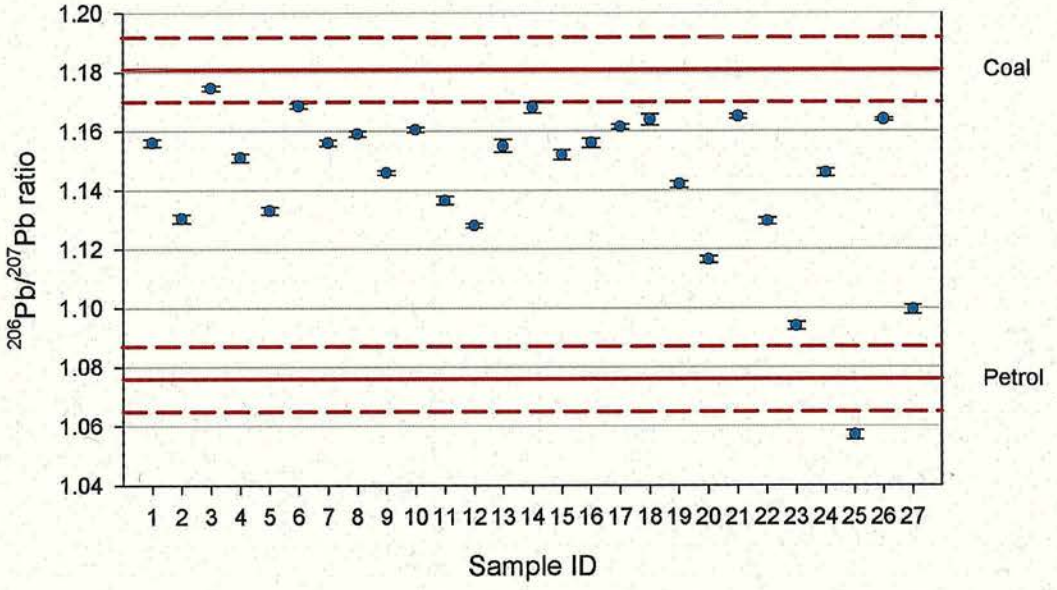

Figure 5.7 $^{206}Pb/^{207}Pb$ isotope ratios found in the 27 Glasgow soils. The $^{206}Pb/^{207}Pb$ ratio (mean ± SD) reported in Scottish coal (Farmer *et al.*, 1999a) and petrol (Farmer *et al.*, 2000) is also shown.

5.1.3 Arsenic Distribution

The concentration of As in the Glasgow soils (Table 5.1) ranged from <0.1 to 135 mg/kg, with 75% of samples having less than 25 mg/kg (Figure 5.8). In total, 10 samples had an As concentration greater than the 20 mg/kg SGV for residential land (DEFRA, 2002f). The soils with the highest concentration of As (i.e. those above the 90th percentile) were all located in the NW of the study area. The highest concentration found was 135 ± 6 mg/kg in Sample 3, which was collected from a grassy area outside the Knightswood Library in Scotstoun. This is considered to result from localised contamination due to coal waste, which was noted in the sample description.

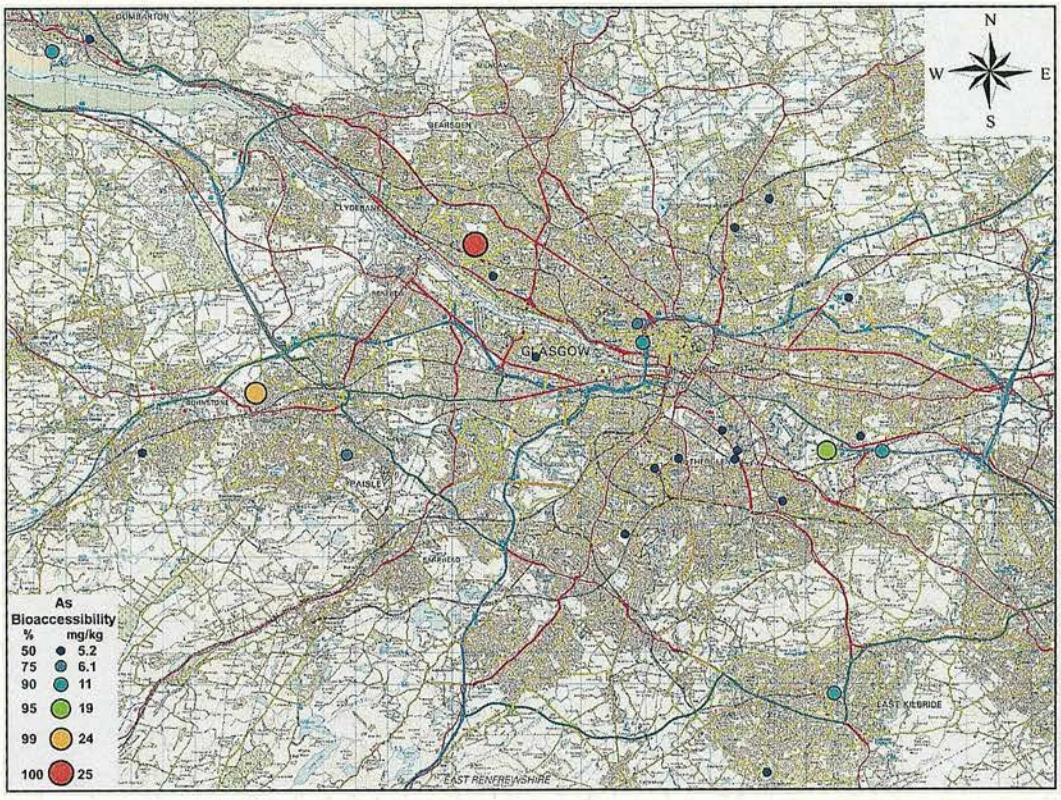

Figure 5.8 Geographical distribution of the total As concentrations in the 27 soils across Glasgow.

5.2 Soil TOC and pH

The TOC and pH of each soil are listed in Table 5.2. The TOC content ranged from 7.7 to 30.5% (w/w) (Figure 5.6), although most samples (65%) were between 12.3 and 21.9%. Samples 11 and 18 have a TOC of around 30%. As typical soil organic carbon content is between 4 and 10% TOC (Ashman and Puri, 2005), the content of the selected Glasgow soils appears to be relatively high.

The pH of the Glasgow soils ranged from 3.8 to 7.7, with 50% of soils having a pH between 4.7 and 5.9 (Figure 5.6). The highest pH was recorded in Sample 20, which was collected from near Rutherglen Glencairn Football ground, a known disposal site of COPR, a high pH industrial waste product (as discussed in Chapter 1) that can lead to increases in soil pH. The soil pH of Sample 20 is noticeably lower than that reported by Farmer *et al.* (1999b), who observed a soil pH between 10.9 and 11 (n=3) for the same site. This apparent discrepancy could arise from remediation having taken place at the site in the intervening six years (there was evidence of new top soil having been applied to the site) or reflect the greater sampling depths (0-30 cm) used by Farmer *et al.* (1999b). Samples 19 and 24, which also have a history associated

with COPR disposal, had soil pHs at the upper end of the observed range (≥ pH 6.2, 90th percentile).

Table 5.2 The TOC and pH of the 27 Glasgow soil samples.

Sample ID	TOC (%, w/w*)	Soil pH
1	10.7 ± 0.1	4.2
2	9.6 ± 0.2	4.8
3	21.3 ± 0.1	5.7
4	11.8 ± 0.1	5.6
5	14.5 ± 0.4	5.6
6	16.6 ± 0.2	5.1
7	18.0 ± 0.6	4.8
8	15.2 ± 0.1	3.8
9	13.4 ± 0.2	6.1
10	13.3 ± 0.5	5.6
11	30.5 ± 0.04	4.7
12	16.6 ± 0.7	5.8
13	17.9 ± 2.5	4.4
14	8.1 ± 0.2	4.7
15	18.1 ± 0.2	5.3
16	14.6 ± 0.3	4.4
17	17.7 ± 0.4	4.7
18	29.6 ± 0.5	4.3
19	18.2 ± 0.05	6.2
20	16.7 ± 0.9	7.7
21	22.9 ± 1.6	6.0
22	8.0 ± 1.4	6.3
23	11.9 ± 0.3	6.1
24	12.7 ± 0.4	6.2
25	16.5 ± 0.03	4.9
26	7.7 ± 0.1	5.4
27	14.7 ± 0.1	5.3

mean ± SD. n = 2
*dry weight

5.3 Mineralogical Composition

The major and minor minerals identified in the Glasgow soils are listed in Table 5.3. Examples of XRD spectra, interpreted using DIFFRAC^{plus} EVA software, are shown in Figure 5.9.

ISC5) and therefore its contribution to overall soil Cr concentration is significant. Chromium associated with ISC5 contributes, on average, 20% (range 0.5 – 48%) of the overall soil Cr concentration (Figure 5.16). Conversely, the silicate constituent, ISC10, has no associated Cr.

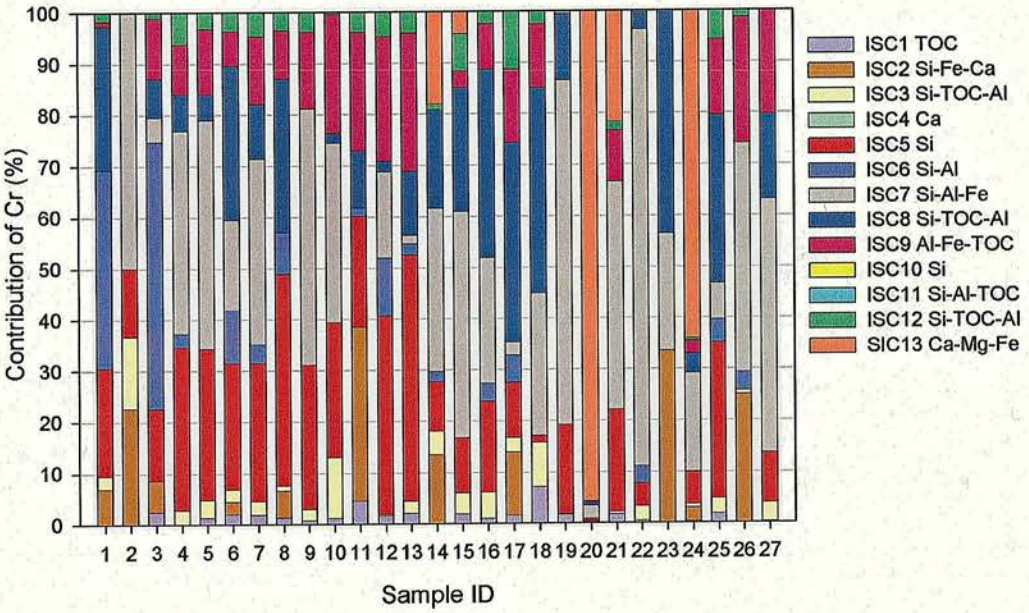

Figure 5.16 The contribution that each ISC makes to the overall soil Cr concentration Glasgow in the soil samples..

The natural compost/humus constituent, ISC8, has a Cr content of approximately 530 mg/kg, of which 100 mg/kg is Cr(VI). This represents 7% of the total Cr found in the soils and 5% of the Cr(VI). ISC8 is present in all but four soils (2, 9, 21 and 26), constituting 29% on average of each soil. This makes it the most abundant ISC in the collected soils, which further means that it contributes, on average, 18% (range 1 - 43%) of the Cr found in a given soil and 30% (range 0.3 - 79%) of the Cr(VI). The similar constituent, ISC3, contains a lot less Cr, 98 mg/kg Cr and 16 mg/kg Cr(VI). This fact, despite it being the second most abundant ISC, constituting on average 18% of analysed soils, means that its contribution to the overall soil Cr concentration is minimal. ISC3 contributes, on average, only 3% (range 0.03 - 14%) of Cr to the total soil concentration and 5% (range 0.01 – 27%) of Cr(VI). Similar observations are made for ISC12, whilst ISC11 has no associated Cr.

ISC9, the tentatively named Fe oxide constituent, is associated with approximately 420 mg/kg Cr, of which 79 mg/kg is Cr(VI). This ISC is found in all but five soils and, given that it constitutes, on average, 15% of those soils, its contribution to the overall soil Cr concentration is important. In the 22 soils where it is present ISC9 contributes, on average, 13% (range 0.3 – 27%) of soil Cr and 22% (range 0.2 – 50%) of soil Cr(VI).

The organic constituent, ISC1, plays a minor role in contributing to the overall soil Cr concentration. It has a low associated Cr concentration of only 56 mg/kg, none of which is Cr(VI). The lack of any Cr(VI) is probably due to the reducing nature of soil organic matter, which converts Cr(VI) to Cr(III). This low Cr content, combined with a low abundance (making-up 8% of the 23 soils in which it is present), means that ISC1 contributes, on average, only 2% (range 0.1 – 7%) of Cr to the overall soil concentration.

5.4.2.3 Lead Distribution Among the Intrinsic Soil Constituents

The distribution of Pb among the ISCs identified is a lot simpler than that of Cr. As Figure 5.17 shows, the vast majority of Pb (78%) is associated with ISC11. This ISC was given the tentative name 'natural compost/humus' and is 13% organic matter (TOC), which is known to sorb Pb species in the environment (Covelo *et al.*, 2007). While this constituent is not the most abundant within the samples, on average making up only 4% of any given soil, the high concentration of Pb makes it the most important ISC in determining the final soil Pb concentration (Figure 5.18). On average, it contributes 75% (range 33 – 99%) of the Pb found in an individual soil sample.

Other than ISC11, only the two calcite constituents that have any major effect on the final soil Pb concentration. ISC2 and ISC4 are associated with 1280 and 1780 mg/kg of Pb, respectively, although neither has a high abundance (on average ISC2 makes up 4% of a soil and ISC4 1%) within the soils. Therefore, ISC2 contributes, on average, 24% (range 2 – 65%) of the overall soil Pb concentration, while ISC4 contributes 18% (range 5 – 50%).

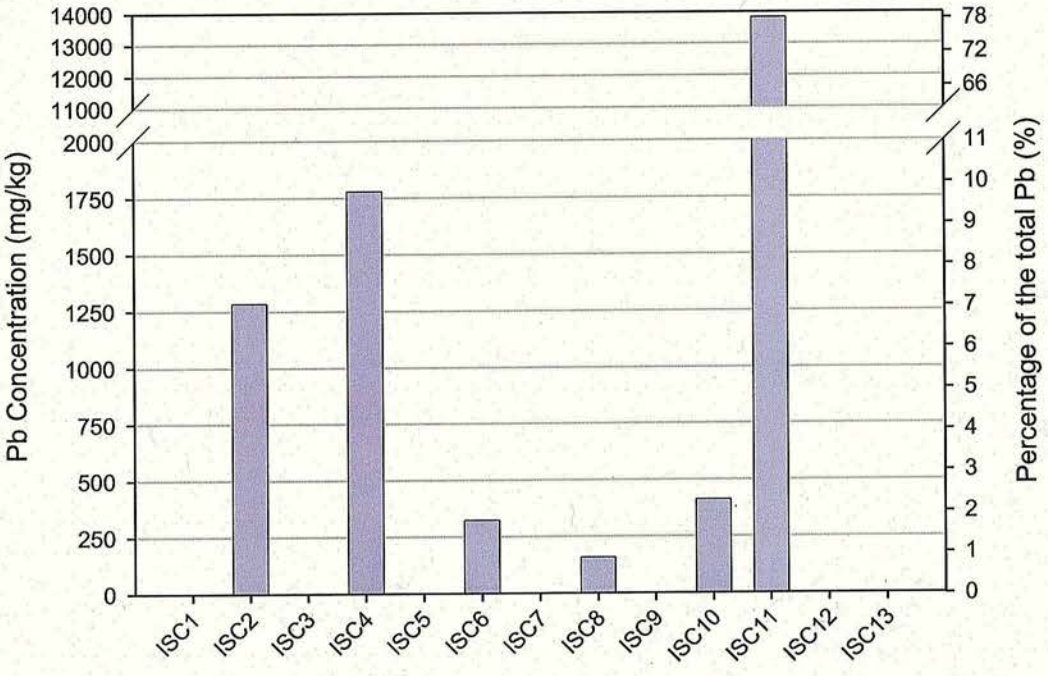

Figure 5.17 The distribution of Pb among the 13 ISCs identified in the Glasgow soil samples.

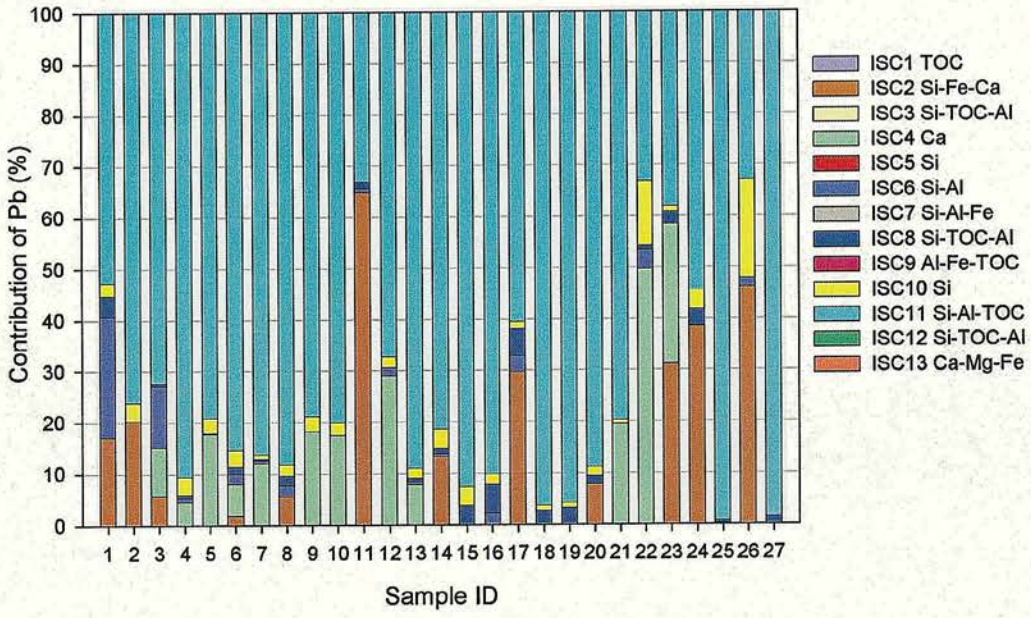

Figure 5.18 The contribution that each ISC makes to the overall soil Pb concentration in the Glasgow soil samples.

5.4.2.4 Arsenic Distribution Among the Intrinsic Soil Constituents

The mixture resolution algorithm identified eight ISCs that contain As. Of these, ISC6, a clay constituent, contained the most As, its concentration of 245 mg/kg, amounting to 37% of all the As found in the collected samples (Figure 5.19). This ISC is found in 15 of the soil samples, generally constituting only a small fraction of each (on average, 2% of a soil). However, in Samples 1 and 3, this portion increases to 9 and 16%, respectively. Thus, ISC6 on average contributes 37% of the As found in those soils in which it is present, but in the case of Soils 1 and 3 this increases to 88 and 86%, respectively (Figure 5.20). The other clay constituent, ISC7, has no associated As.

All of the identified carbonate constituents contain As. ISC4 contains the most at 85 mg/kg, followed by ISC13 and ISC2, which each contain 28 mg/kg. As remarked previously, ISC4 is the least abundant constituent of the soils, contributing only 1%, on average, of any particular soil. Despite this, it is an important As-containing constituent, on average contributing 28% (range 4 – 60%) of As found in the soils where it is present. It should be highlighted that just because an ISC contributes a large proportion of As to a given soil does not mean it provides a large amount of As, as generally the As soil concentration is low (62% of soils having <20 mg/kg of As, Figure 5.1). ISC2 is present in 12 and ISC13 in five out of the 27 soil samples, each constituent making up on average 4% and 5% of a given soil, respectively. Since they each contain 28 mg/kg of As, ISC2 and ISC13 provide, on average, 12 and 19%, respectively, of the As found in any given soil.

The organic and compost constituents ISC1 and ISC3 both also act as sources of As within the Glasgow soils. ISC1 is associated with ~89 mg/kg As and has an average soil abundance of 8%, while ISC3 is associated with 49 mg/kg of As and has an average soil abundance of 18%. When they are present in a soil ISC1 and ISC3 account for, on average, 22% and 15%, respectively, of the As found.

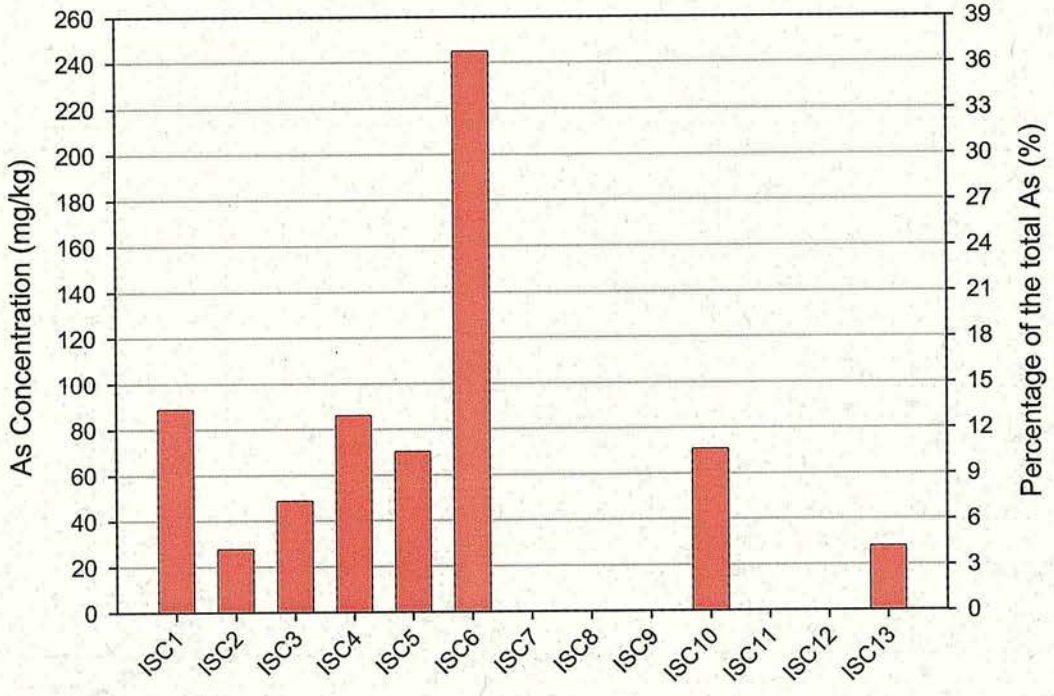

Figure 5.19 The distribution of As among the 13 ISCs identified in the Glasgow soil samples.

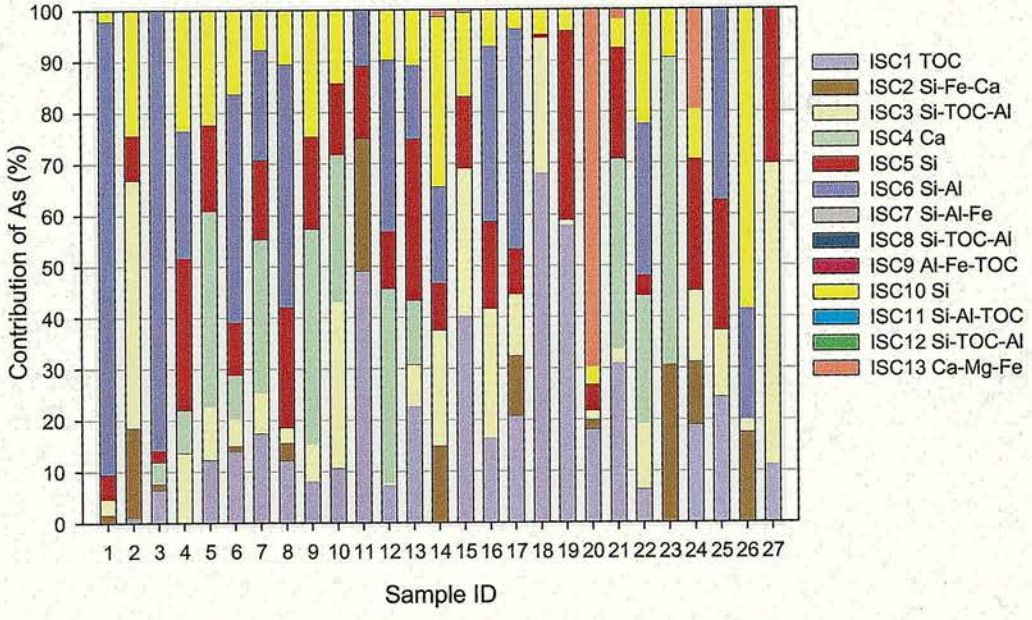

Figure 5.20 The contribution that each ISC makes to the overall soil As concentration in the Glasgow soil samples..

Of the remaining constituents only the Si dominated constituents have any associated As. Both ISC5 and ISC10 are associated with As concentrations of ~70 mg/kg, which represents 11% of all the As found in the soils (Figure 5.19). They also make a similar contribution to the overall soil As content amounting, on average, to 3 mg/kg of As in any given soil, which accounts for between 14 and 16% of the final concentration.

5.5 Summary

- In total nine soils had a Cr concentration above the SGV for residential land with plant uptake (130 mg/kg) and four above that without plant uptake (200 mg/kg). The highest recorded concentrations of 3680 ± 23 mg/kg total Cr and 1485 ± 24 mg/kg Cr(VI) were found in Sample 20, collected in Rutherglen. The concentrations of Cr and Cr(VI) in this sample were significantly greater than those observed in the remaining 26 soils. The second highest concentration was observed in Sample 24 from Muirend (658 ± 23 mg/kg total Cr and 171 ± 5 mg/kg Cr(VI)). Generally, with the exception of these two samples, the Cr(VI) concentration in the soils was <20 mg/kg.

- Total Cr concentrations appeared to correlate with the Ca soil content. This link between Cr and Ca, at least in the high Cr samples, was explained by the identification of a carbonate intrinsic soil constituent (ISC) containing a large amount of Cr. ISC13, found in only 5 soils, formed a major portion (23%) of Sample 20, contributing 3460 mg/kg of Cr. It makes up a smaller proportion (2%) of Sample 24, where the major contribution of Cr came from a clay constituent (ISC7). These two constituents, carbonate ISC13 and clay ISC7, thus comprised the major sources of Cr within the soil samples.

- Of the 27 samples, 17 had concentrations of Pb above the SGV for residential land (450 mg/kg). The soil with the highest concentration, 2157 ± 18 mg/kg, was Sample 25, which was collected from a residential area in Rutherglen. The next highest sample (Sample 12), with 1318 ± 11 mg/kg, came from an area of urban open space in Paisley.

- Unlike the situation with Cr, the occurrence of Pb in the soils appeared to be linked to one ISC in particular. ISC11, a natural compost/humus constituent present in all soils, was found to be associated with 13820 mg/kg of Pb. When

the amount of Pb in each soil sample was accumulatively summed, ISC11 accounted for 78% of the Pb in the soils.

- The majority of soil samples (75%) had As concentrations <25 mg/kg. Ten samples had concentrations above the SGV of 20 mg/kg, with the highest measured concentration being 135 ± 6 mg/kg (Sample 3). This sample came from a grassed area in front of a library in Scotstoun. The higher concentrations tended to be found in the northwest of Glasgow.

- Arsenic was found associated with several ISCs, being more equally distributed than either Cr or Pb. The most important was ISC6, a clay constituent, associated with 245 mg/kg of As, which accounted for 37% of all the As found in the soils (summed As content of each soil). Arsenic was also found in all three calcite/carbonate constituents, with ISC4 (85 mg/kg) and the organic constituent ISC1 (89 mg/kg) associated with the greatest concentrations.

CHAPTER 6 SOLID PHASE DISTRIBUTION OF CHROMIUM, LEAD AND ARSENIC

6.1 CISED Mixture Resolution

To determine the solid phase distribution of the Cr, Pb and As present in the Glasgow soils the CISED extraction scheme was employed (Section 4.5.1.4). The CISED method uses a mixture resolution algorithm to determine the acid-extractable soil components in each soil and the physico-chemical distribution of the chosen analytes among the identified components. As a result, in addition to identifying the sinks/reservoirs of PHEs within soils, the CISED methodology gives an insight into the mechanisms and potential interactions occurring within the reactive phases of the test soils.

Practical details of the extraction method and the multi-element analysis of each extraction fluid are described in Sections 4.5.2 and 4.5.2.1. The original data for each acid extraction of the 27 Glasgow soils are listed in Appendix 3. Prior to using the mixture resolution programme several operations were performed on the data. If >75% of the data was below the detection limit, the element was removed from the matrix. Thus, Se was removed from the matrix for all Samples, except 3, 8, 9, 17, 20, 24, 25 and 26, Mo was removed from all Samples except 3, 8, 9, 17, 24 and 25 and Na was removed for Sample 2. If <75% of data was below detection limits, the element was left in the matrix. The mixture resolution programme required matrices containing only positive real numbers, thus any individual extract that was less than the detection limit for an element was assigned a nominal concentration equal to half the detection limit (Clark, 1998). The leachate concentration matrix for each sample then served as an individual input into the mixture resolution programme.

The mixture resolution programme produces data in several output forms. A table showing the amount of each component extracted at each stage is obtained, which can be used to produce a series of profiles, or 'extractograms', for each sample. An extractogram consists of a simple plot of the total extracted solids vs extraction solution (numbers 1-14, i.e. deionised water to 5.0 M aqua regia, see Section 4.5.2). An example of a series of extractograms for a sample soil (Sample 24) is shown in Figure 6.1.

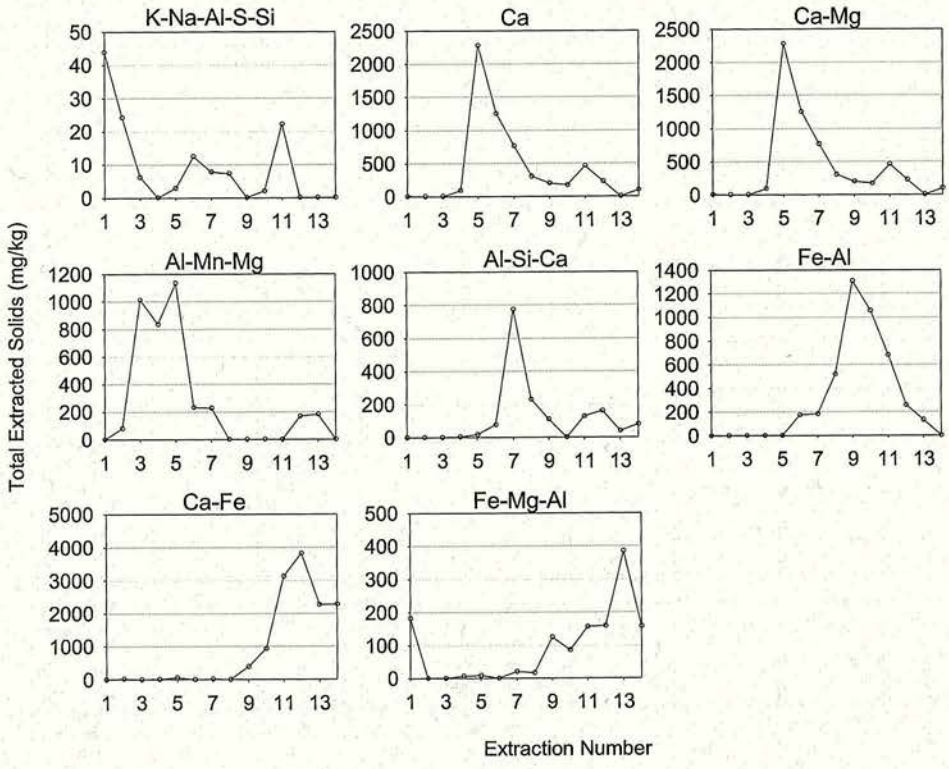

Figure 6.1 Example CISED extractograms for Sample 24 extracted with increasing concentrations of aqua regia.

In addition, the elemental composition of each of the extracted components is obtained from the mixture resolution programme. From this information the distribution of the extracted elements among the identified components can be gained. This gives clues as to the nature of the identified components. Initially each component is given a name based on those elements which compose >10% of it, e.g. the Ca-Mg component shown in Figure 6.1 is 85% Ca and 11% Mg. This is the same naming procedure used to identify the ISCs in Chapter 5. From these data the solid phase distribution of Cr, Pb and As within each soil is gained. The solid phase distribution of Cr, Pb and As within Sample 24 (Figure 6.2) shows that the largest Cr-containing component is different from the largest Pb- and As-containing components, most of the Cr occurring in an Fe-Al component.

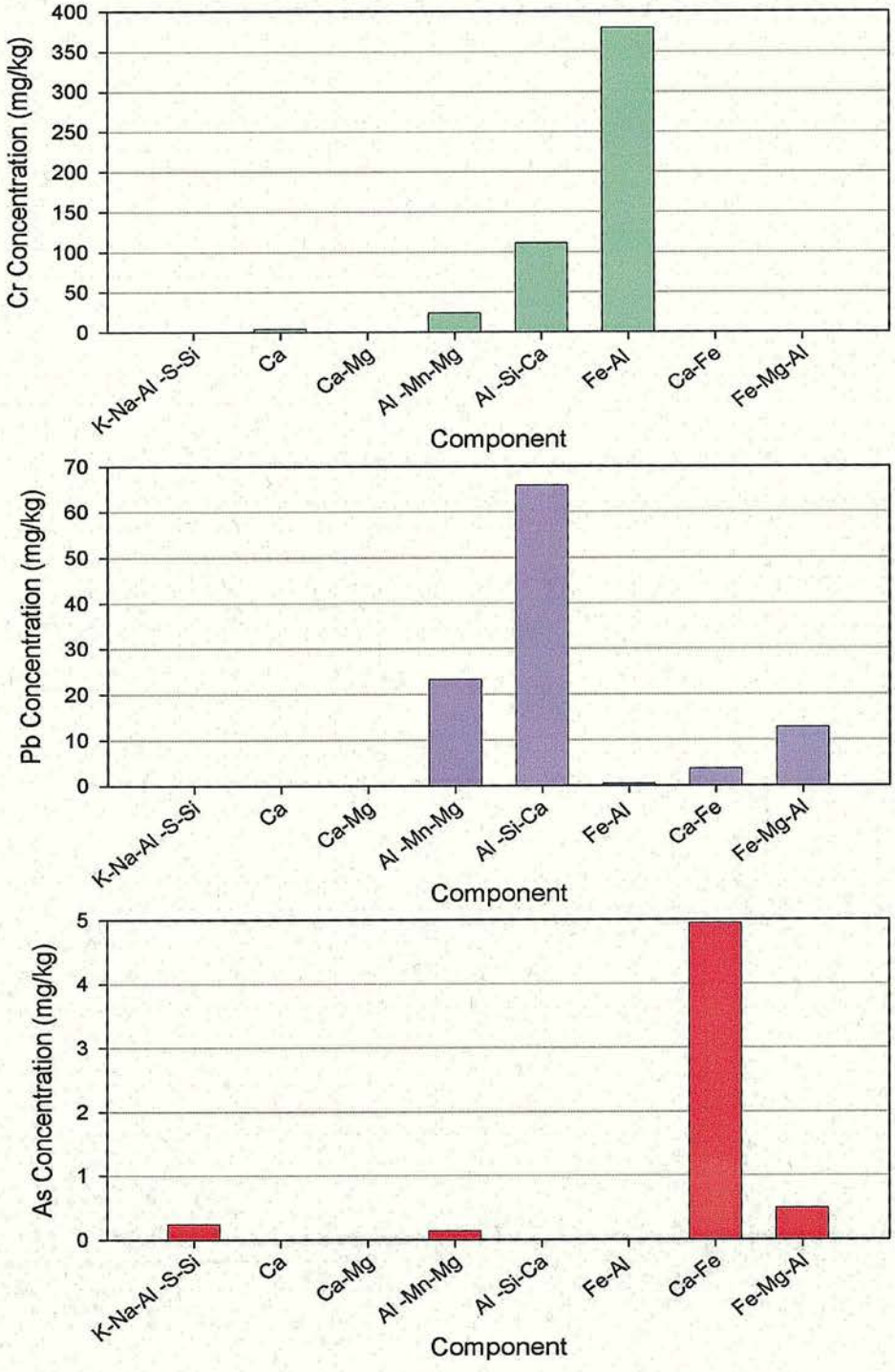

Figure 6.2 Solid phase distribution of Cr, Pb and As within soil Sample 24.

6.2 Cluster Analysis

One of the problems of using the CISED extraction methodology is that it identifies the extractable components specific to an individual soil, thereby making direct

comparison of the solid phase distribution between samples more difficult. To categorise the components into a common set of physico-chemical groups (clusters), a data matrix containing all the components identified in every sample was constructed. Each component was described by its major element composition and the amount of that component leached in each of the 14 extracts. This was subjected to cluster analysis, as described in Section 4.14.4. Thus, information about the solid phase distribution within the 27 Glasgow soils was treated as a whole instead of as individual extraction components for each soil.

Thirteen clusters of components were identified in the 27 Glasgow soil samples (Figure 4.6). These have been given tentative names based on their elemental composition (i.e. the average elemental composition for all the components that make up a cluster), extraction profile and XRD-identified mineral phases (Table 6.1).

Table 6.1 Tentative geochemical assignment of clusters identified in the Glasgow soils.

Cluster Number	Major Elements (>10%)	Geochemical Assignment
C1	Ca-Al	Ca Carbonate 1
C2	Ca	Ca Carbonate 2
C3	K-S-Na	Exchangeable 1
C4	S-Na-Ca	Organic 1
C5	K-Na-S	Exchangeable 2
C6	S-Ca-Si	Organic 2
C7	Al-Fe-Si-Ca	Clay 1
C8	Al-Fe-Si	Clay 2
C9	Al-Mn-Ca	Mn Oxide
C10	Fe-Ca	Fe Oxide
C11	Mg-Ca	Bound Carbonate
C12	Fe-Al	Fe-Al oxyhydroxides 1
C13	Fe-Al	Fe-Al oxyhydroxides 2

Calcium-dominated clusters (C1, C2 and C11)

Table 6.1 shows three geochemically distinct clusters dominated by Ca, which were tentatively identified as Ca carbonates. Table 6.2 shows that these clusters, C1, C2 and C11, were 68%, 81% and 27% Ca, respectively. Whilst Cluster C2 is dominated by only Ca, C1 and C11 also contain 12% Al and 47% Mg, respectively.

Table 6.2 Average major element composition of each identified cluster (expressed as % of the total extracted solids)

Cluster Name		Al	Ca	Fe	K	Mg	Mn	Na	P	S	Si
Ca Carbonate 1	C1	12	68	3	0	1	1	0	2	0	2
Ca Carbonate 2	C2	2	81	1	4	7	1	0	0	0	1
Exchangeable 1	C3	2	3	1	48	4	0	16	4	17	3
Organic 1	C4	1	16	1	8	4	0	21	2	36	3
Exchangeable 2	C5	1	7	0	29	4	0	25	2	23	8
Organic 2	C6	0	17	3	10	3	0	9	2	39	11
Clay 1	C7	29	13	24	1	4	1	1	2	1	20
Clay 2	C8	38	7	19	0	1	2	0	8	0	10
Mn Oxide	C9	27	17	6	1	3	20	0	6	1	4
Fe Oxide	C10	6	10	56	1	2	1	0	8	8	4
Bound Carbonate	C11	7	39	2	1	47	0	0	0	0	4
Fe-Al oxyhydroxides 1	C12	18	0	69	0	5	1	0	2	2	1
Fe-Al oxyhydroxides 2	C13	19	2	61	1	9	0	0	1	1	1

Examination of the extractograms (Figure 6.3) (for clusters C1 and C2) shows that the constituent components tend to be extracted early in the procedure, where dilute acids are used. The amount of cluster C1 extracted starts to increase at stage 4 (the second extraction with 0.01 M aqua regia) and peaks at stage 5 (the first extraction with 0.05 M aqua regia). The extraction of C2 peaks at stage 3, which is the first acid extraction stage (0.01 M aqua regia). Both these clusters are present in the majority of soils, C1 being found in all samples except 1, 8, 13 and 20, whilst C2 is found in all but 19 and 20. The dominance of Ca in these clusters, which are themselves easily extracted with dilute acids, leads to the conclusion that each is probably a cluster of carbonate (calcium carbonate) components.

In contrast to clusters C1 and C2, cluster C11 tends to be extracted late in the CISED procedure (Figure 6.3) where more concentrated acids are used. The amount of C11 extracted begins to increase at stage 9, peaking at stage 10, when 0.5 M aqua regia is used. This apparent stability under acid conditions would not be expected in a carbonate-based component. Cluster C11 contains components from Sample 20 only, which was demonstrated by the ISC assessment to contain a large amount of Ca carbonate (Section 5.4.2.1). This ISC (ISC13), dominated by Ca, Mg, was found in five soils, although in four of these it made up <2% of the total soil. However, in Sample 20, ISC13 accounted for 23% of the total mass of the soil. Therefore, a large

part of Soil 20 was formed from a different Ca carbonate constituent than the other soil samples, so it is not unexpected that in the CISED test a different Ca carbonate physico-chemical component is also indicated. In addition, it has been noted in previous CISED studies that physico-chemical components can be bound, or encapsulated, by another component, e.g. a carbonate component encased by a Fe oxide component would result in the former not being extracted until after the latter was dissolved, which would only occur at greater acid strengths (Cave, 2006). Thus it seems that C11 is a cluster of Ca carbonate components that are closely associated with another, more acid-stable, cluster. The other cluster could possibly be C10, as it is also present in Soil 20 and begins to be extracted at stage 9, similar to C11.

Exchangeable Clusters (C3 and C5)

Clusters C3 and C5 were each dominated by the presence of K (48 and 29%, respectively), Na (16 and 25%, respectively) and S (17 and 23%, respectively) (Table 6.2). Figure 6.3 shows there is not a discrete window of extraction for these clusters. The majority of C3 was extracted early in the procedure, by the de-ionised water and 0.01 M aqua regia (stages 1-4). Cluster C5 has a much broader extraction profile, with a large amount extracted by de-ionised water but peaking at stage 6 (0.05 M aqua regia). The relative ease of extraction and the predominance of K and Na in these clusters, suggests that they contain exchangeable soil components (Rowell, 1994; Wragg, 2005). These clusters also make a very small contribution (on average <0.5%) to the total extracted solids (Figure 6.4), as would be expected of an exchangeable component in any given soil.

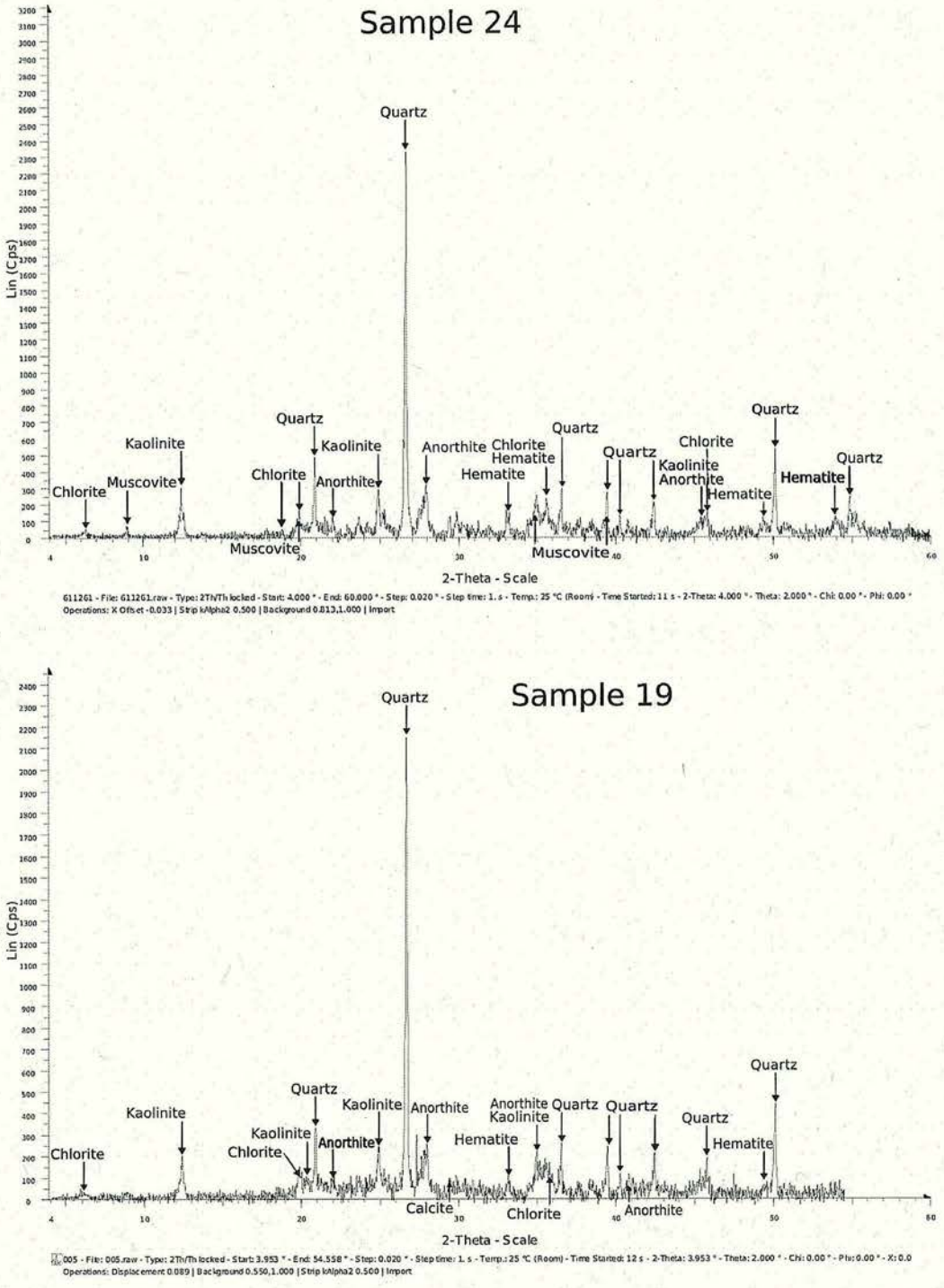

Figure 5.9 XRD spectra for Glasgow soil Samples 19 and 24.

All soils contained quartz as a major constituent. In addition anorthite, kaolinite and hematite were found in all soils, but in much lower amounts. Anorthite ($CaAl_2Si_2O_8$) is a type of feldspar. Kaolinite ($Al_2Si_2O_5(OH)_4$) is a clay mineral, while hematite (Fe_2O_3) is a common form of iron oxide found in soils. Traces of calcite ($CaCO_3$)

were observed in about half of the soil samples analysed. It is likely that calcite was lost during the process of isolating the fine material (Section 4.11.1). During initial investigation of mineral composition of the bulk material, analysis showed that calcite was present in the samples processed (1, 4, 5, 9, 11, 14, 15, 16, 18, 19, 20, 22, 23, 26, 27). It is therefore likely that all the soils contain calcite but the method employed is not ideally suited for its identification.

Table 5.3 Major and minor minerals identified in the selected Glasgow soils

Sample ID	Major	Minor
1	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite
2	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite
3	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Mullite
4	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite, Muscovite
5	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite, Muscovite
6	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite
7	Quartz	Anorthite, Kaolinite, Hematite, Muscovite, Goethite
8	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite
9	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite, Muscovite
10	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Greenalite
11	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Greenalite
12	Quartz	Anorthite, Kaolinite, Dickite, Calcite, Hematite, Goethite
13	Quartz	Anorthite, Kaolinite, Dickite, Hematite, Goethite, Greenalite
14	Quartz	Anorthite, Kaolinite, Hematite, Chlorite
15	Quartz	Anorthite, Kaolinite, Hematite, Chlorite
16	Quartz	Anorthite, Kaolinite, Hematite, Chlorite, Goethite
17	Quartz	Anorthite, Kaolinite, Dickite, Hematite, Chlorite, Goethite
18	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite, Goethite
19	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite
20	Quartz	Anorthite, Kaolinite, Dickite, Calcite, Hematite, Chlorite, Muscovite, Goethite, Greenalite
21	Quartz	Anorthite, Kaolinite, Hematite, Chlorite, Greenalite
22	Quartz	Anorthite, Kaolinite, Hematite, Chlorite, Greenalite
23	Quartz	Anorthite, Kaolinite, Hematite, Chlorite, Goethite, Greenalite
24	Quartz	Anorthite, Kaolinite, Calcite, Hematite, Chlorite, Muscovite
25	Quartz	Anorthite, Kaolinite, Hematite, Chlorite, Muscovite
26	Quartz	Anorthite, Kaolinite, Hematite, Chlorite, Muscovite
27	Quartz	Anorthite, Kaolinite, Hematite, Chlorite, Muscovite

Dickite ($Al_2Si_2O_5(OH)_4$), a clay mineral with a similar structure to kaolinite, was identified in Samples 12, 13, 17 and 20. Another clay mineral, mullite ($Al_6Si_2O_{13}$), was identified in Sample 3. This is a rare clay mineral produced artificially during various smelting and firing processes and is used as a refractory material, e.g. furnace lining. Muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$) was found in Samples 4, 5, 7, 9, 20, 23,

24, 25, 26 and 27. It is a common form of mica (closely related to clays) used as a fireproofing and insulating material. Samples 7, 12, 13, 16, 17, 18 and 20 were found to contain goethite (FeO(OH)), an iron-bearing oxide mineral commonly present in soil. The iron silicate greenalite ($Fe_{2-3}Si_2O_5(OH)_4$) was identified in Samples 10, 11, 13, 20, 21 and 23.

Hillier *et al.* (2003) reported the characteristic minerals in COPR from site in Glasgow. These were chromite, brownmillerite, periclase, larnite, brucite, calcite, aragonite, ettringite, hydrocalumite and hydrogarnet. In that study a sample of COPR was collected from Rutherglen Glencairn FC (close to the site of Sample 20) and all of the characteristic minerals were identified, except larnite. The reason that none of these minerals were detected in Sample 20 during the present study could be that Hillier *et al.* (2003) collected the actual COPR material (from terracing constructed out of COPR), while in this study surface soil was collected. As such, any characteristic COPR minerals present are likely to be at far lower concentrations and thus more difficult to detect.

5.4 Modelling Soil Chromium Concentrations

Two methods were used to identify any relationships between the soil concentrations of Cr and the other elements present. The first method was a Pearson's product moment correlation (Miller and Miller, 2000), which identifies any relationships between two variables. The second used a multivariate statistical approach using a mixture resolution algorithm, similar to that used in the CISED method (Section 4.5.2.1), to determine the number of intrinsic soil constituents (ISCs) present in the soils (Section 4.14.3) and the distribution of Cr among them.

5.4.1 Pearson's Product-Moment Correlations

A Pearson's product-moment correlation coefficient (Section 4.14.1), r, was calculated for the relationship between either Cr or Cr(VI) and a number of other quantified soil parameters (Table 5.4). A significant correlation was deemed to be one with a p value (the probability that a variant would assume a value equal to the observed value by chance alone) of less than 0.1.

A strong and significant correlation was observed between both the total Cr and Cr(VI) concentrations and that of Ca, r being 0.9151 and 0.9122 respectively.

However, when the data are plotted (Figure 5.10) it becomes clear that Sample 20 contains considerably more Cr, Cr(VI) and Ca than any other sample. This has the effect of skewing the correlation and, if Sample 20 is removed from the data set, r is only 0.1906 and 0.0669 (p being 0.3525 and 0.7404) for Cr and Cr(VI), respectively. Therefore there appears to be little correlation between Cr/Cr(VI) and Ca concentration.

Table 5.4 Pearson coefficients for the correlation of total Cr and Cr(VI) with other soil properties.

Soil	Total Cr		Cr(VI)	
Property	Correlation	p value	Correlation	p value
Al	-0.1559	0.43741	-0.1754	0.38152
As	0.0837	0.68160	0.0621	0.76271
Ba	-0.0752	0.70962	-0.0775	0.70202
Ca	0.9151	0.00000	0.9122	0.00000
Cr	N/A	N/A	0.9974	0.00000
Cr(VI)	0.9974	0.00000	N/A	N/A
Cu	-0.1055	0.60165	-0.1190	0.55602
Fe	0.1382	0.49229	0.1185	0.55584
K	-0.2881	0.14490	-0.2739	0.16694
Mg	0.9596	0.00000	0.9609	0.00000
Mn	0.2159	0.28001	0.1777	0.37623
Na	-0.1008	0.61680	-0.1113	0.58065
Ni	0.4425	0.02103	0.4146	0.03179
P	-0.3737	0.05490	-0.3613	0.06411
Pb	-0.0268	0.45831	-0.0205	0.48682
S	0.0735	0.71498	0.0401	0.84200
Si	-0.5781	0.00159	-0.5635	0.00221
V	0.1264	0.53144	0.0982	0.62732
Zn	-0.0281	0.88951	-0.0530	0.79323
TOC	0.0245	0.90317	0.0195	0.92296
pH	0.6057	0.00082	0.5796	0.00154

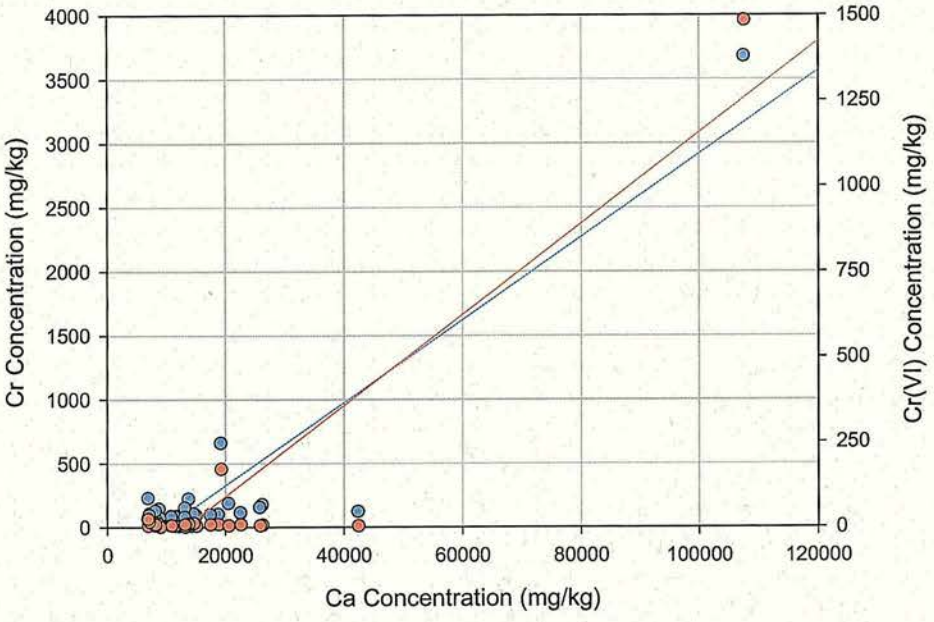

Figure 5.10 Correlation between total Cr/Cr(VI) and Ca in Glasgow soil samples.
Blue = Total Cr (r = 0.9151), Red = Cr(VI) (r = 0.9122).

The correlations between total Cr and Cr(VI) and soil pH are also statistically significant, although once again the relationships are more complex. They are skewed by the inclusion of Samples 20 and 24 (Figure 5.11). When they are removed a different, but still significant, relationship is observed, the higher pH occurring in soils with higher Cr concentrations. The relationship between pH and Cr(VI) is not significant ($p = 0.234$) when Samples 20 and 24 are excluded.

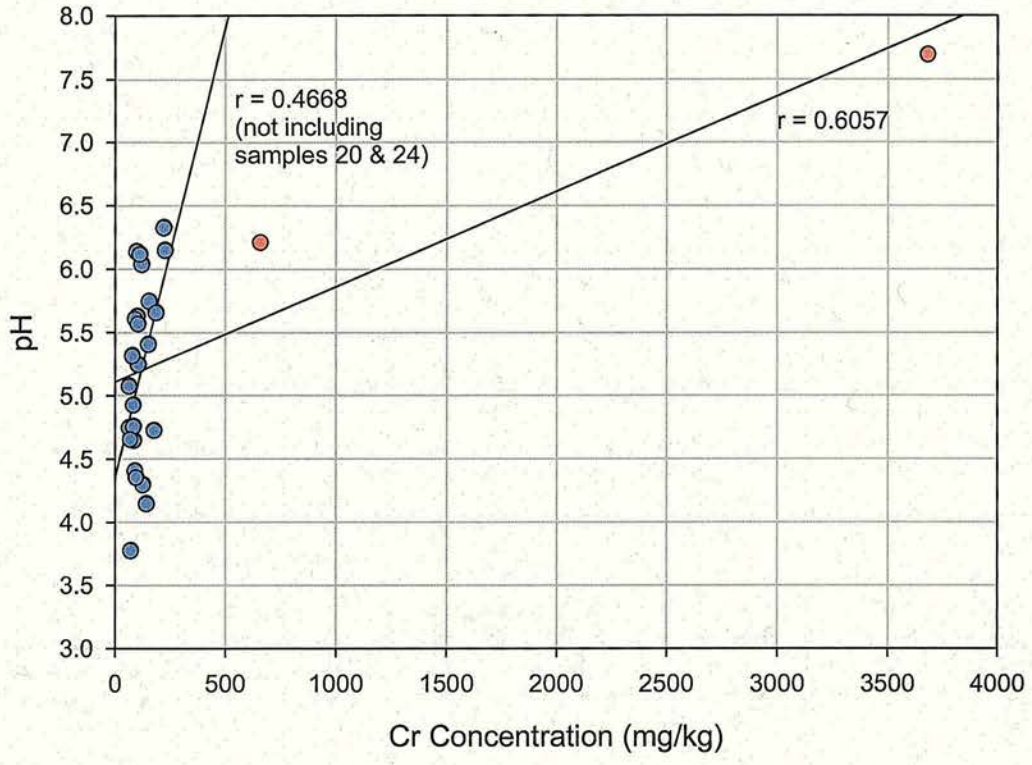

Figure 5.11 Relationship between pH and Cr concentration for the 27 Glasgow soil samples. Red points indicate Samples 20 & 24 (Sample 20 being the higher Cr content).

It is appears that the data set is not normally distributed and therefore the application of the Spearman Rank correlation might be more appropriate then the Pearson's Product Moment. Table 5.5 shows the Spearman Rank correlation coefficients and their significance. Interestingly, while Ca still has a strong correlation with total Cr, it is not deemed to correlate with Cr(VI). This observation is repeated for several other elements/parameters, with Mg, Fe and pH all correlating strongly with total Cr, but not with Cr(VI). The only element found to relate to both total Cr and Cr(VI) is Mn, a relationship that was also identified by the Pearson's test. This indicates that, although Samples 20 and 24 both have very high Ca and Cr(VI), in general the Cr(VI) concentration of a soil is not related to its Ca content. Thus it appears that the Mn content (and possibly pH as well) is an important parameter linked to the Cr content of these Glasgow soils, although Ca and Mg may also be important in certain circumstances (i.e sites with a known history of COPR disposal).

Table 5.5 Spearman Rank coefficients for the correlation of total Cr and Cr(VI) with other soil properties.

Soil	Total Cr		Cr(VI)	
Property	Correlation	*p* value	Correlation	*p* value
Al	0.2510	0.2067	-0.2880	0.1451
As	0.2876	0.1457	-0.3374	0.0852
Ba	0.0391	0.8466	-0.4147	0.0315
Ca	0.4342	0.0236	-0.0412	0.8381
Cr	N/A	N/A	0.5009	0.0078
Cr(VI)	0.5009	0.0078	N/A	N/A
Cu	0.2519	0.2050	-0.3894	0.0447
Fe	0.4485	0.0190	-0.1176	0.5592
K	-0.2483	0.2117	-0.0247	0.9025
Mg	0.3590	0.0659	0.0788	0.6961
Mn	0.6571	0.0002	0.3395	0.0832
Na	-0.0171	0.9325	-0.2180	0.2746
Ni	0.5504	0.0029	-0.1972	0.3243
P	-0.2976	0.1317	-0.1634	0.4153
Pb	-0.1969	0.3249	-0.5308	0.0044
S	0.4054	0.0359	-0.1212	0.5469
Si	-0.4125	0.0325	0.1316	0.5128
V	0.3072	0.1190	-0.3525	0.0713
Zn	0.4296	0.0253	-0.1770	0.3771
TOC	0.0721	0.7210	-0.0687	0.7334
pH	0.5761	0.0017	0.3219	0.1016

5.4.2 Constituent Resolution: Multivariate Statistical Approach

A multivariate statistical approach, using predictive modelling, was used to identify the intrinsic soil constituents (ISCs) that make up the Glasgow soils.

5.4.2.1 Identification of Intrinsic Soil Constituents

Thirteen ISCs were identified (see Section 4.14.3 for method) as making up the 27 Glasgow soils. Figure 5.12 shows the output from the mixture resolution algorithm used to resolve the ISCs. The amount of each ISC in the soils is shown as well as the errors (difference between modelled and measured data) associated with the resolution procedure. These ISCs were tentatively named according to their chemical composition, using those elements that were present in a constituent at >10%. The adoption of 10% as the 'cut-off' for the elemental composition was based on that previously used by Cave *et al.* (2004), when employing the same algorithm in the CISED methodology. Using this information, along with the XRD and sample meta-data, the constituents were given tentative geochemical names/classification (Table

5.6). Several of the constituents have been given the same geochemical name, e.g. there are two clay constituents. This means that in the soil samples there are two geochemically distinct forms of clay present, due to their association with other elements within the soil. Figure 5.13 shows how the identified ISCs combine to make up the 27 soils.

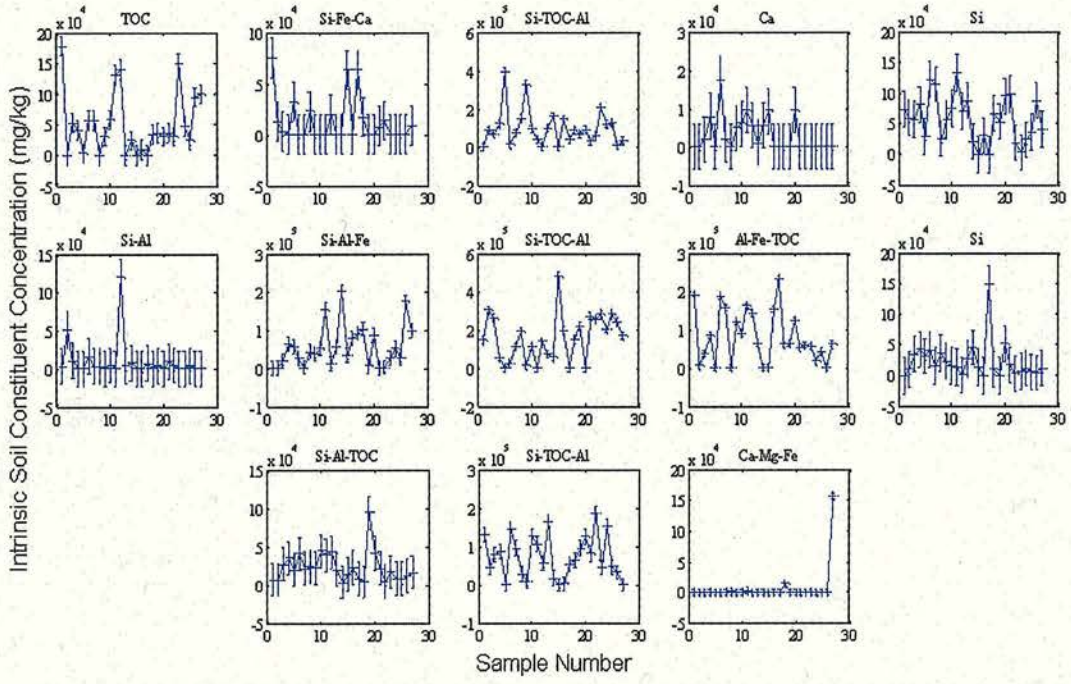

Figure 5.12 The concentrations (and errors) of each ISC identified in the Glasgow soils.

Table 5.6 Assignment of Geochemical names to the 13 identified ISCs.

Constituent Number	Composition Name	Geochemical Assignment
ISC1	TOC	Organic matter
ISC2	Si-Fe-Ca	Iron rich Calcite with Si
ISC3	Si-TOC-Al	Natural Compost/Humus Constituents
ISC4	Ca	Calcite
ISC5	Si	Quartz
ISC6	Si-Al	Clay
ISC7	Si-Al-Fe	Clay with associated Fe
ISC8	Si-TOC-Al	Natural Compost/Humus Constituents
ISC9	Al-Fe-TOC	Al, Fe, TOC association constituent
ISC10	Si	Quartz
ISC11	Si-Al-TOC	Natural Compost/Humus Constituents
ISC12	Si-TOC-Al	Natural Compost/Humus Constituents
ISC13	Ca-Mg-Fe	Calcite with associated Fe

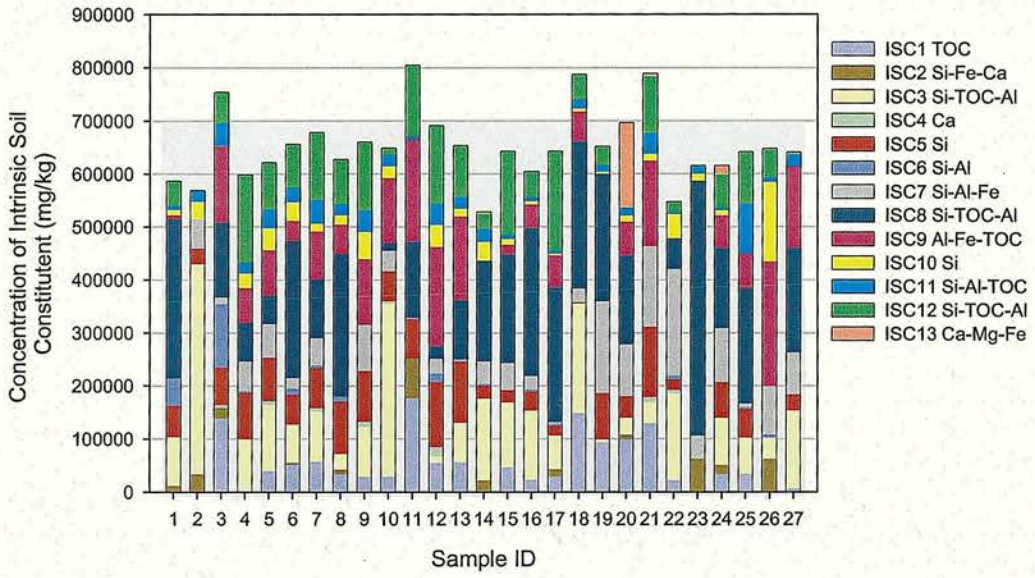

Figure 5.13 Concentration of ISC in each of the 27 Glasgow soil samples.

Clay Constituents (ISC6 and ISC7)

Two constituents, ISC6 and ISC7, were tentatively categorised as clays (Table 5.6) This is due to the dominance of Al and Si (around 25 and 55%, respectively) in each constituent, with smaller contributions from K and Fe, which are typical elements associated with clays (Krauskopf, 1979). Indeed, ISC7 contains Fe at greater than 10%. Constituent ISC6 was present in Soils 1, 3, 4, 6, 7, 8, 11, 12, 13, 14, 16, 17, 22, 25 and 26 whilst ISC7 was present in all soils except 1, 8 and 11. Thus all soils have at least one associated clay constituent. This fits with the XRD data (Section 5.3), which showed at least one clay mineral phase in all soils.

Calcite Constituents (ISC2, ISC4 and ISC13)

Constituents ISC4 and ISC13 were both dominated by Ca, at 77% and 64%, respectively. As such, they been tentatively named as calcite constituents. As discussed in Section 5.3, XRD analysis of the whole soil showed calcite to be a major component of all soils. Constituent ISC4 was present in Soils 3, 4, 6, 7, 9, 10, 12, 13, 21, 22 and 23, whilst ISC13 was present only in Soils 14, 15, 20 and 21. It should be pointed out that the error bars associated with ISC4 were relatively large and therefore it may be present in low concentrations in other soils without detection. Constituent ISC13 is also rich in Mg (~25%).

Constituent ISC2 was dominated by the presence of Si (54%), Fe (21%) and Ca (10%). It had a similar composition to a constituent observed in soil samples from Wellingborough, UK, by Wragg (2005), who identified it as a mixture of Fe-rich calcite and silica. The presence of small amounts of Mg (7%) in the constituent suggests that it may be derived from calcites. This constituent is found in 12 of the 27 soils, although its identification is more uncertain due to the sizeable error (difference between modelled and measured data) encountered during its resolution.

Silicon Dominated Constituents (ISC5 and ISC10)

Two constituents with a composition dominated by Si (~81%) were identified. Constituent ISC5 was present in all soils except 23 and 26, while ISC10 was present in all but 11, 25 and 27. Thus one or both of these constituents were present in all soil samples. XRD analysis identified quartz as a major component in all of the soil samples (Table 5.3). As ISC5 consisted almost entirely of Si, with no other element comprising greater than 5% of the total mass, it was given a tentative geochemical names of quartz. In contrast, ISC10 comprised 6.9% Al and 9.9% Na and was given a tentative geochemical name of silicate with associated Al and Na. Constituent ISC5 was generally found in soils in greater amounts than ISC10.

Natural Compost/Humus Constituents (ISC3, ISC8, ISC11 and ISC12)

The four soil constituents, ISC3, ISC8, ISC11 and ISC12, were tentatively named natural compost/humus. TOC (~20%) and Si (50-60%) dominate these constituents. ISC3, ISC8, ISC11 and ISC12 were distinguished from other TOC-dominated soil constituents by their association with Si, with neither ISC1 nor ISC9 containing any Si. Wragg (2005) identified similar constituents in test soils from Wellingborough, UK, where it was believed that the organic matter associated with the natural compost/humus constituents was present as coatings on silicate materials. Al (10-15%) also makes up a small part of these constituents. Constituent ISC11 is present in all soils, while the other three constituents are present in the vast majority of soils collected.

Additional Constituents (ISC1 and ISC9)

Constituent ISC1 was dominated by TOC, comprising 93% of the total mass. It therefore seems likely that this is an organic matter constituent. ISC1 was present in all soils except 1, 4, 14, 23 and 26.

Constituent ISC9 was dominated by the presence of Al, Fe and TOC and has proven difficult to name. It is present in all soils except 2, 14, 19, 22 and 23. At ~28% Fe it contains the largest amount of Fe of all the identified constituents and therefore could be an Fe oxide phase with associated Al and TOC. This would fit with the XRD data (Table 5.3), which shows several Fe oxide mineral phases in the soil samples.

Constituent pH Stability

As discussed in Chapter 1, COPR is a high-pH waste material and can have the effect of raising the pH of the surrounding soil. It is therefore important to determine if any constituents are present only in high-pH soils, as these could perhaps reflect the presence of COPR. Table 5.7 shows the Pearson correlation coefficients for the relationship between the concentration of each ISC in a given soil and the soil pH. Three ISCs are identified as having a statistically significant correlation with soil pH (ISC13, ISC4 and ISC7). Each of these ISCs shows a positive correlation with soil pH. ISC13 and ISC4, both identified as calcite (Table 5.6), exert a greater effect on soil pH than ISC7, i.e. an increase in their concentration results in a greater pH. Indeed ISC13 constitutes 23% of Sample 20, which has the highest soil pH (7.7)

Table 5.7 Pearson coefficients and *t* significant values for the correlation between pH and ISC abundance in the Glasgow soil samples.

Constituent name	Correlation	*t* value
ISC1	0.0918	0.4610
ISC2	0.0395	0.1976
ISC3	-0.1872	0.9529
ISC4	0.4737	2.690
ISC5	0.1360	0.6863
ISC6	0.1913	0.9748
ISC7	0.6118	3.867
ISC8	-0.2434	1.2550
ISC9	0.2020	1.0314
ISC10	0.0907	0.4556
ISC11	-0.0074	0.0372
ISC12	-0.0389	0.1948
ISC13	0.8674	8.716
		$t_{crit} = 2.18$

5.4.2.2 Distribution of Chromium Among the Intrinsic Soil Constituents

As the mixture resolution procedure produces information on the distribution of each input element among the identified ISCs, the source of Cr within the soil can, in principle, be obtained. As Figure 5.14 shows, ISC13 is associated with the majority of Cr, containing ~3870 mg/kg of Cr. This represents 50% of all the Cr measured in the samples, i.e. the sum of total Cr in each sample. ISC13 is a calcite constituent that is found in five soils (14, 15, 20, 21 - collected from the area in and around Rutherglen - and 24 - collected from Muriend). Soils 14, 15 and 21 contain relatively little of this constituent (<1%), but Soils 20 and 24 contain larger amounts. Indeed ISC13 makes up almost a quarter (23%) of Soil 20 (Figure 5.13). This ISC also contains the largest concentration (~1600 mg/kg) of Cr(VI) (Figure 5.15). This represents 80% of all the Cr(VI) found in the collected soils (i.e. the concentration of Cr(VI) in every soil summed). As has been stated previously, both Samples 20 and 24 were collected from sites with a known history of COPR disposal. Considering that many of the minerals known to be present in COPR are Ca and Mg based (e.g. Brownmillerite - $Ca_2(Fe,Al)_2O_5$, Periclase – MgO, Larnite - Ca_2SiO_4, Brucite - $Mg(OH)_2$, Calcite - $CaCO_3$, Aragonite - $CaCO_3$, Hydrocalumite - $Ca_2(Al,Fe)(OH)_6(OH)$, Hydrogarnet - $Ca_3(Al,Fe)_2(H_4O_4)_3$ and Ettringite - $Ca_6Al_2(SO_4)_3(OH)_{12}$) (Hillier *et al.*, 2003) and given the high Cr(VI) content, it seems that ISC13 is derived from COPR waste material. As such, it seems more appropriate to identify ISC13 as a carbonate

constituent, opposed to calcite. This would also explain the strong positive relationship between the presence of ISC13 and soil pH, discussed earlier. In addition, this constituent, which is present in only a limited number of samples, explains the relationship between Cr and Ca identified by the Pearson's correlation (Section 5.4.1).

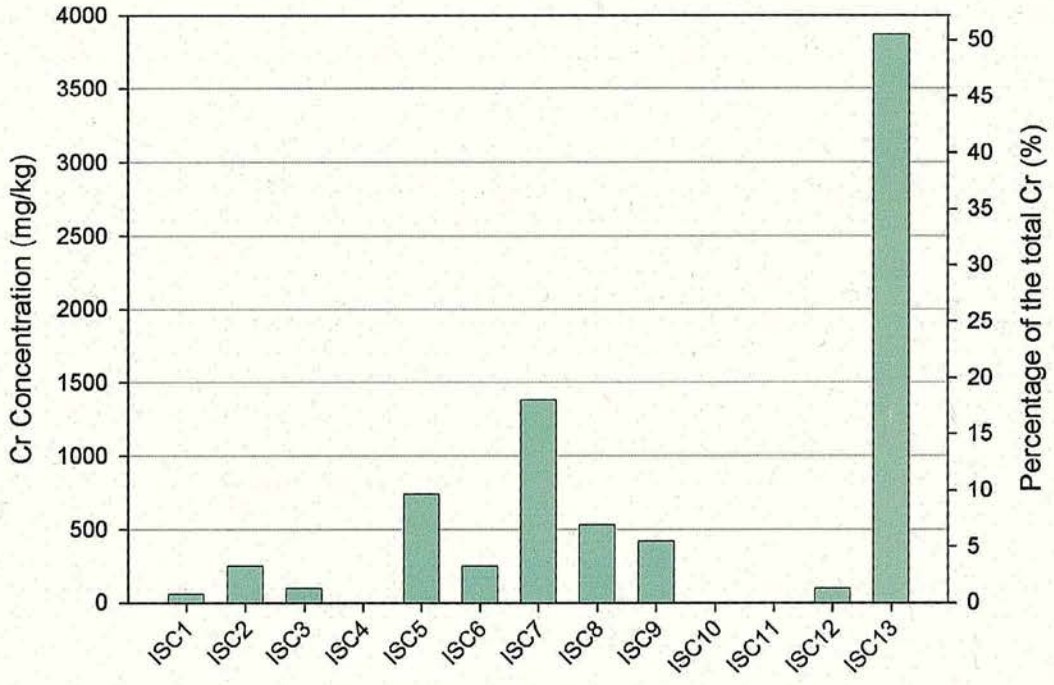

Figure 5.14 The distribution of Cr among the 13 ISCs identified in the Glasgow soil samples.

Two more calcite constituents were identified, ISC2 and ISC4. ISC2 is associated with ~250 mg/kg Cr of which <1 mg/kg is Cr(VI). This constituent has a low abundance within the soil, constituting on average only 4% of any soil. Despite this low abundance, ISC2 makes an important contribution to the overall soil Cr concentration, providing, on average, 14% (range 0.2 – 34%) of the total Cr (Figure 5.16). ISC4, on the other hand, has no associated Cr.

ISC7 has the second highest Cr concentration. This ISC is a clay constituent that is present in all soil samples, except 1, 8 and 11. The amount of ISC7 within a given soil varies from 0.3 to 37% with the average being around 10%. As Cr is well known to have an affinity for clay minerals (Bartlett and Kimble, 1976; James and Bartlett, 1983; Rai and Eary, 1989; Jardine *et al.*, 1999; Kimbrough *et al.*, 1999), a Cr and Cr(VI) content of ~1380 and 130 mg/kg, respectively, is not unexpected in this

constituent. This represents 18% of all the Cr found in the soils. ISC7 represents an important source of Cr. When it is present, except where ISC13 is dominant, ISC7 provides 33% (on average) of the final Cr concentration in a given soil (Figure 5.16).

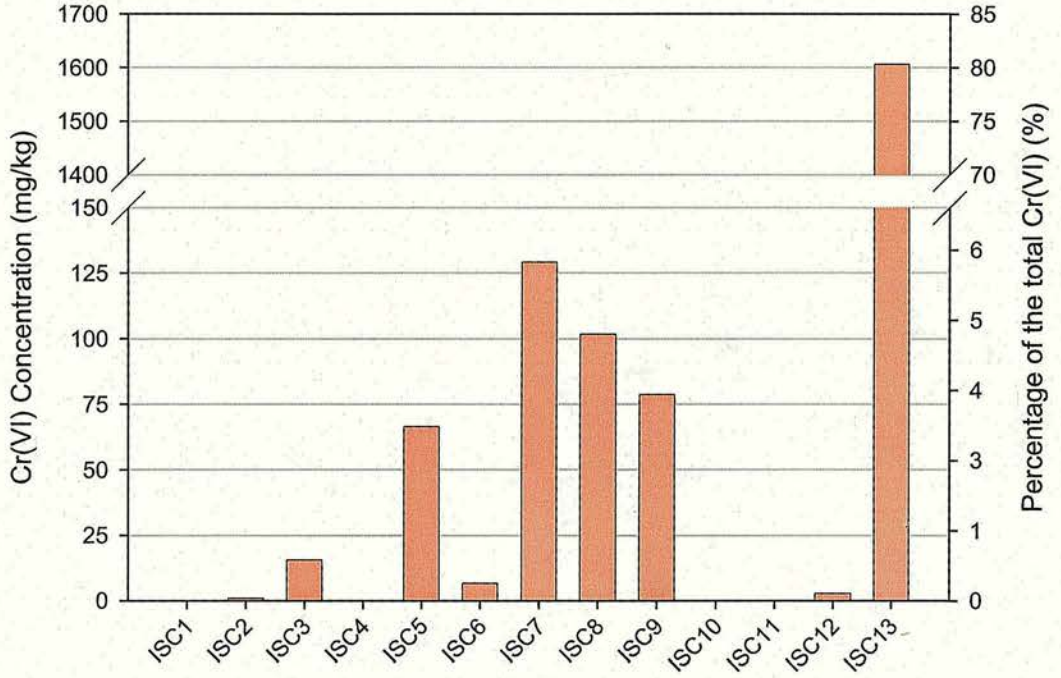

Figure 5.15 The distribution of Cr(VI) among the 13 ISCs identified in the Glasgow soil samples

Interestingly, ISC7 also contains the largest amount of Mn (11,700 mg/kg) of all the identified ISCs, accounting for 58% of all the Mn found (summed concentrations) in the collected soils. Thus soils containing large amounts of ISC7 also have large amounts of both Cr and Mn, explaining the relationship identified in Section 5.4.1.

The other clay constituent, ISC6, in contrast to ISC7, has very little associated Cr, with a concentration of ~250 and 6.6 mg/kg for Cr and Cr(VI), respectively. This represents only 3% of the total Cr found in the soils and only 0.3% of Cr(VI).

The quartz constituent, ISC5, is associated with ~740 mg/kg Cr, of which 66 mg/kg is Cr(VI). This represents 10% of the total Cr found in the collected soils and 3.3% of the Cr(VI). While these concentrations are much lower than those observed in ISC7 and ISC13, quartz represents an important constituent of each soil (on average 9% of

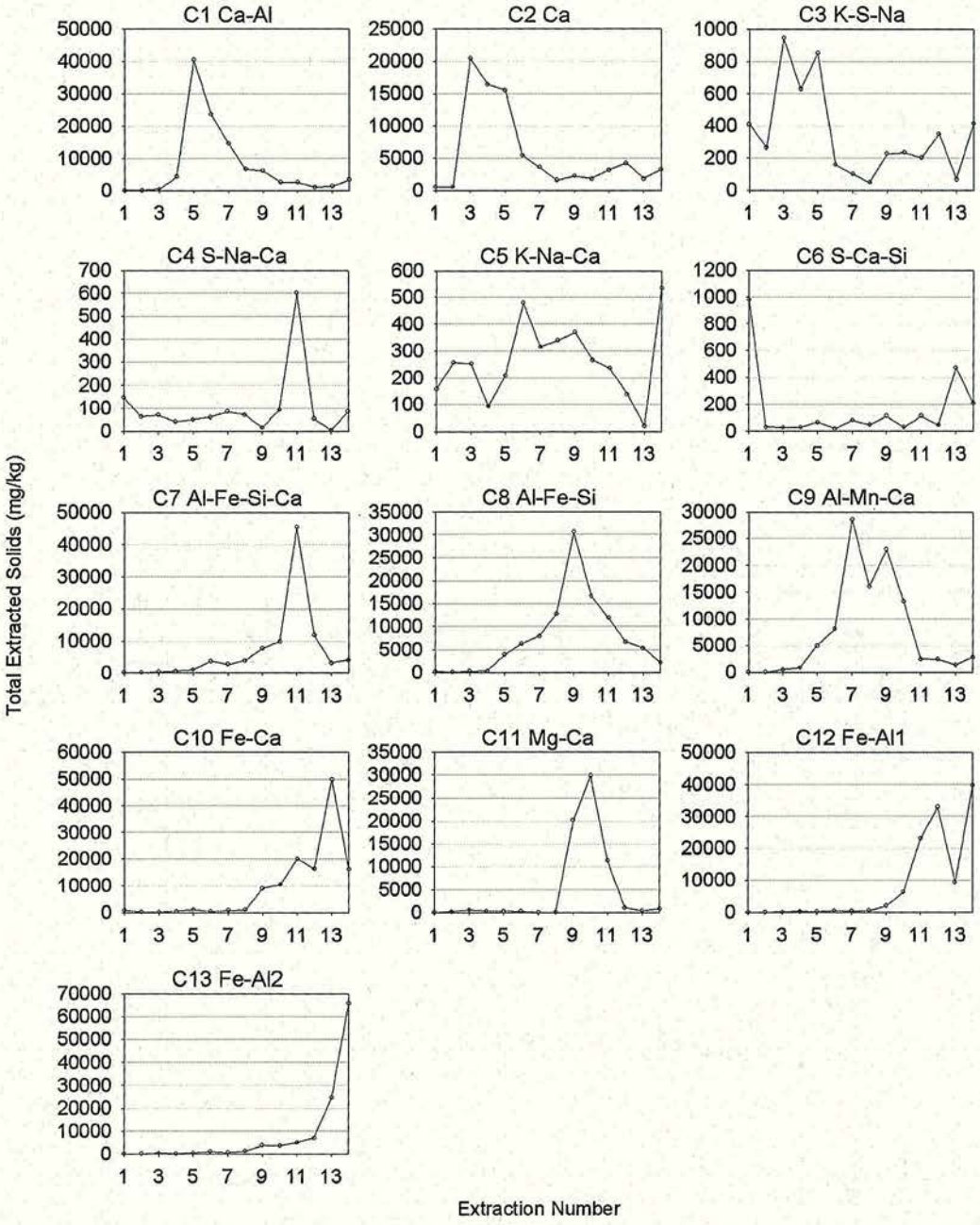

Figure 6.3 Extractograms for the 13 identified clusters of components found in the 27 Glasgow soils.

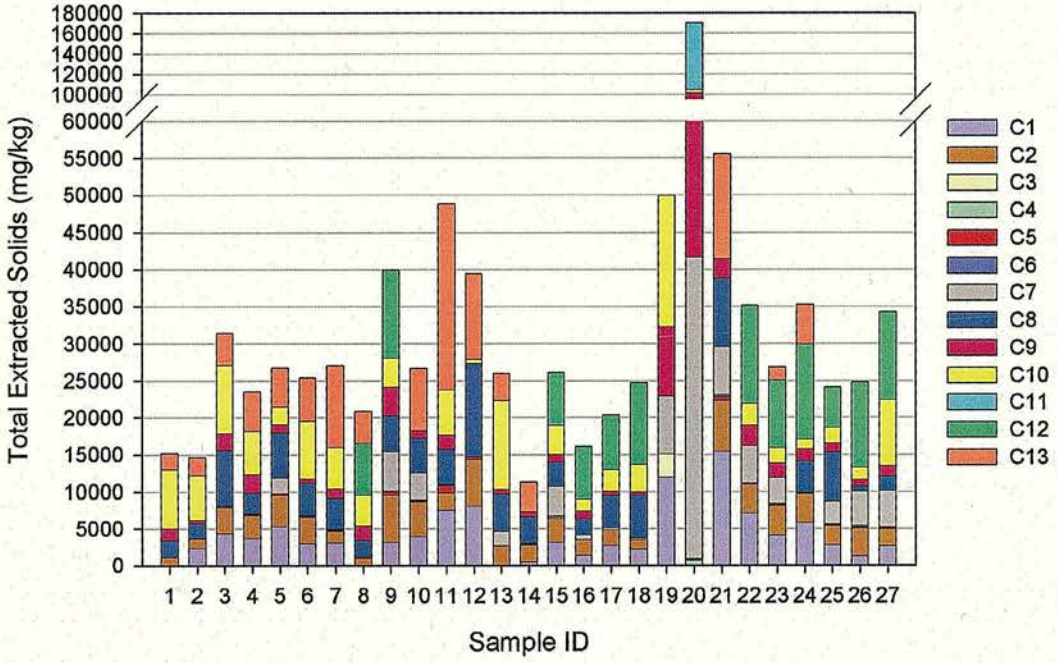

Figure 6.4 Distribution of the 13 component clusters among the 27 Glasgow soil samples.

Organic Clusters (C4 and C6)

Clusters C4 and C6 were characterised by the predominance of S, 36 and 39%, respectively (Table 6.2). In addition to S, C4 also contained Na (21%) whilst C6 contained Ca (17%) and Si (11%). Both these clusters appeared in the first three extracts of the CISED procedure before tailing off, followed by increasing amounts extracted in the final stages (Figure 6.3). This profile shape probably indicates the presence of a humic acid type of material, as it is initially dissolved in deionised water but becomes insoluble when the extract becomes acidic. With increasing acid strengths, however, humic acid is oxidized and broken down, releasing its inorganic content into solution (Cave *et al.*, 2004). As with the exchangeable clusters, both organic clusters contributed a very small fraction of the total extracted solids (<0.30%) (Figure 6.4).

Clay Clusters (C7 and C8)

Clusters C7 and C8 were characterised by the dominance of Al (29 and 38%, respectively), Fe (24 and 19%, respectively) and Si (20 and 10%, respectively). Both clusters were extracted late in the procedure, requiring higher acid strength, C7 peaking at stage 11 (1.0 M aqua regia) and C8 at stage 9 (0.5 M aqua regia). Cluster

C7 is made up of components from 13 soils (Samples 5, 9, 10, 13, 15, 19-23, 25, 26 and 27) and C8 from 23 soils (all but Samples 19, 20, 22 and 23). Thus, all the soils have a component in cluster C7 or C8, if not both (Figure 6.4). As discussed in Chapter 5, clay minerals were identified in all soils by XRD analysis. The predominance of Fe and Al, and the high acid strength required to extract the components of these clusters, suggest that they are derived from clay-like materials (Rowell, 1994; Wragg, 2005). These clay clusters contribute 7% and 14%, respectively, of the total extracted solids from the collected soils.

Manganese Oxide Cluster (C9)

Table 6.2 shows that the cluster tentatively named Mn oxide (C9) was made up predominantly from Al (27%), Mn (20%) and Ca (17%). The extractogram for this cluster shows a peak at stage 7, which is the point in the CISED method where the first addition of H_2O_2 is made. It is known that Mn oxides are readily dissolved by H_2O_2 (Manning and Goldberg, 1996). Given this, and that Mn is one of the dominant elements, it appears that this cluster was probably derived as an Mn oxide material. Cluster C9 is present in all but Sample 12 and, on average, contributes 7% of the total extracted solids.

Iron Dominated Clusters (C10, C12 and C13)

Clusters C10, C12 and C13 were characterised by the dominance of Fe (56, 69 and 61%, respectively) and their extraction late in the scheme. Clusters C12 and C13 also show a high concentration of Al (18 and 19%, respectively), whilst a smaller proportion of C10 is Ca (10%). The dominance of Fe and the extraction under highly acidic conditions (extraction of all three clusters begins at the addition of 0.5 M aqua regia, peaking after the addition of the 1 M aqua regia), leads to the conclusion that these clusters are Fe oxide minerals. The extraction of clusters C10 and C12 begins at stage 9, peaking at stages 13 and 12, respectively, whilst C13 remains poorly extracted until stage 14. This difference in the extractograms may be due to differences in the physical or chemical structure of the cluster components, e.g. C10 and C12 being made up of finer grained material, which is more readily dissolved by the acid. This observation has also been made by Wragg (2005).

6.3 Chromium Distribution

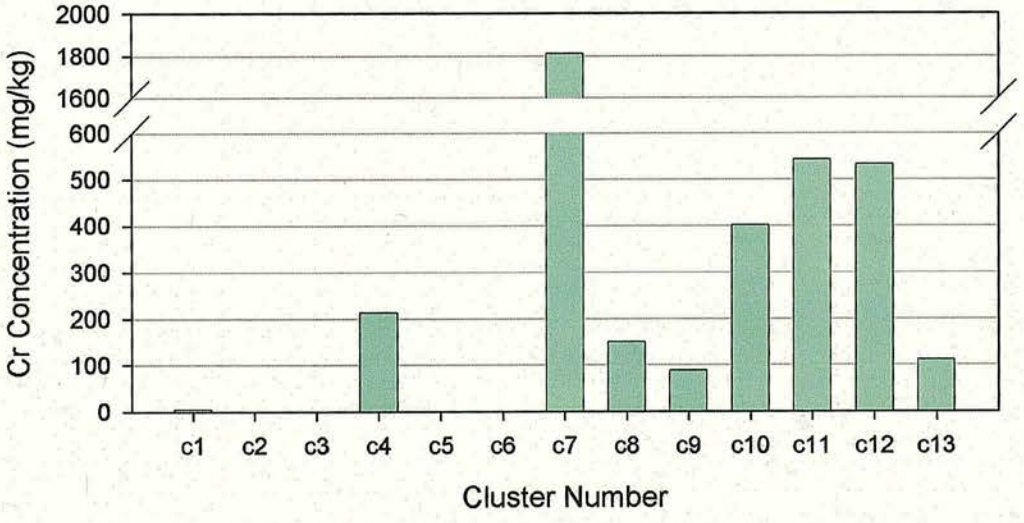

Figure 6.5 The distribution of Cr among the 13 clusters of identified soil components for the 27 soils.

As with the ISC analysis, the mixture resolution process gives information about the elemental distribution among the different clustered components. Figure 6.5 shows the distribution of Cr among the 13 clusters. Cluster C7, made up of clay components, has the most Cr associated with it, containing ~1810 mg/kg. This is by far the largest Cr-bearing cluster, accounting for 47% of all the extractable Cr in the soils. The next most important Cr-bearing cluster is C11 (bound Ca carbonate) with 542 mg/kg Cr. Cluster C12 contains a similar Cr concentration to C11, the highest Cr content of the Fe-dominated clusters. When combined, the Fe-dominated clusters account for 1045 mg/kg of the Cr extracted from the soils. In fact, in the majority of samples (25 out of 27) the highest Cr-containing cluster is one of the three Fe oxide clusters. Samples 19 and 20 have more Cr in cluster C7 (~1720 mg/kg in the case of Sample 20). Of the three remaining Cr-containing clusters, the organic cluster C4, contains the most Cr (212 mg/kg).

Clusters C1 to C6 can be grouped together as readily soluble components. This broad grouping can be made because the extraction peak (or larger proportion of the cluster being extracted) is associated with either deionised water or the dilute acids. Clusters C7 to C13, on the other hand, can be classed as poorly soluble due to the strongly acidic conditions (>0.1 M aqua regia) required to extract them. Using these broad

groupings some 220 mg/kg of Cr, in the 27 soil samples, is present in readily soluble soil phases, whilst 3635 mg/kg of Cr is in poorly soluble phases. Of the 220 mg/kg that is in the readily soluble clusters, the majority can be accounted for by one component from one sample. As mentioned above, C4 contains 212 mg/kg of Cr, the source of which is a S-Cr-Na physico-chemical component in Soil 20. If this component is ignored, only 7.6 mg/kg of Cr is present in readily soluble clusters for all 27 soils. Therefore, it appears that, with the exception of one sample, virtually all the acid extractable Cr in the collected soil samples is in poorly soluble clusters.

Due to the use of highly acidic reagents in the extraction procedure, no information on speciation is gained from the CISED extraction. It is possible, however, to see if there are any links between the solid phase distribution of Cr within a given soil and its Cr(VI) concentration. Thus, it can be assessed whether the presence of Cr in a particular physico-chemical phase tends to be associated with a greater proportion total Cr being in the form of Cr(VI). A stepwise multiple linear regression method was used, in which a data matrix of the Cr concentration in each cluster for each sample was used as the explanatory variables and Cr(VI) as the response variable. Details of how the regression was performed are given in Section 4.14.5. Eight clusters (C4, C7, C8, C9, C10, C11, C12 and C13) were identified as being statistically significant in modelling the Cr(VI) concentration. The model-produced Cr(VI) concentrations (Equation 6.1) correlate well with the true Cr(VI) soil concentrations (Figure 6.6), with an r^2 of 0.9999. As two soils contain much more Cr(VI) than the others, this makes the model essentially a two point graph which explains the very good fit. Inspection of the <25 mg/kg section of the graph (Figure 6.6) confirms that the model does not fit as well as might be expected. If Samples 20 and 24 are excluded from the calculation of r^2 then its value reduces to 0.6712. Despite this, Equation 6.1 appears to be the best estimation of Cr(VI) distribution, since, producing an entirely new model, excluding Samples 20 and 24, does not significantly improve the correlation between modelled and true data for the <25 mg/kg samples (Figure 6.7).

$$[Cr(VI)] = 0.95C4 + 0.41C7 + C8 + 0.56C9 + 0.01C10 + C11 + 0.13C12 + 0.28C13 + 0.13$$

Equation 6.1 The model for predicting the Cr(VI) concentration in a soil sample. RMSE = 2.70 mg/kg. [Cr(VI)] = the Cr(VI) concentration; C4, C7, C8, etc = the amount of total Cr associated with that cluster in the test soil.

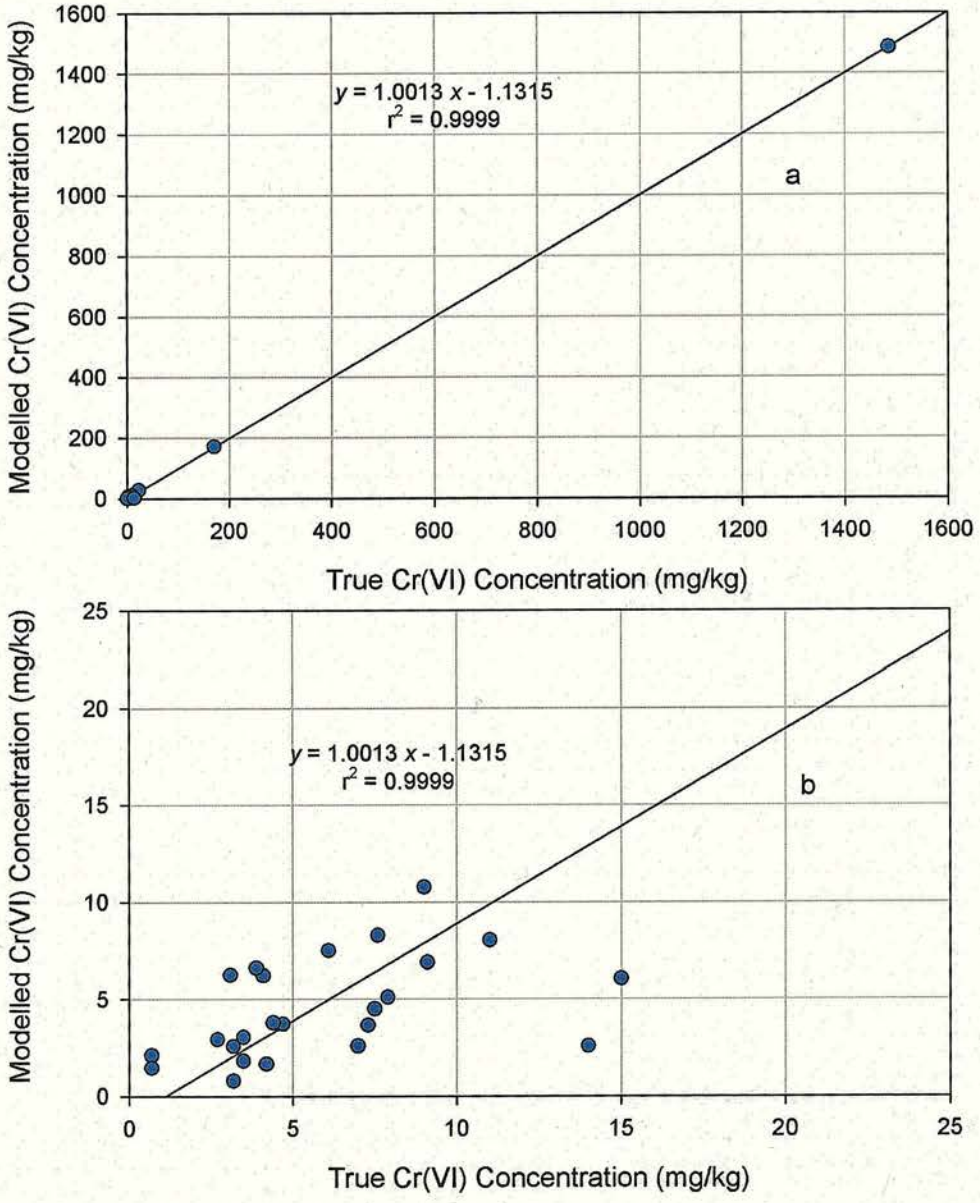

Figure 6.6 Soil Cr(VI) concentration modelled with Cr solid phase distribution data. a = all data, b = enlargement of the <25 mg/kg section of graph a.

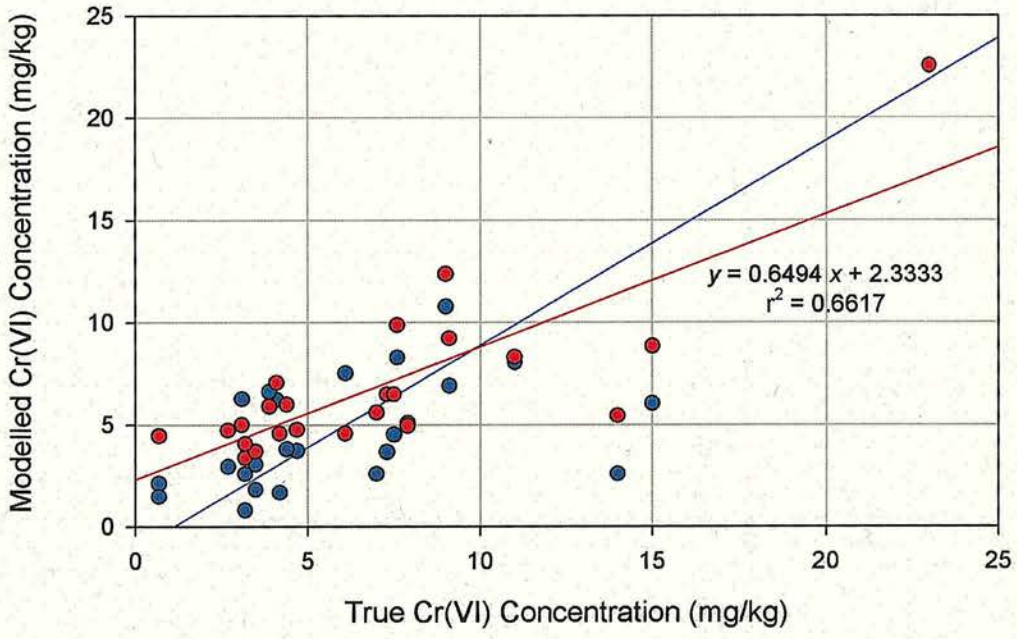

Figure 6.7 Soil Cr(VI) concentration modelled with Cr solid phase distribution data. RMSE = 2.9 mg/kg. ● = model excluding Samples 20 and 24 (equation describes this model), ● = model including all samples.

In this model, 100% of the Cr associated with clusters C8 and C11 and 95% of that associated with C4, appears to be Cr(VI). Cluster C11 is a Ca carbonate phase that is found only in Sample 20 and is probably related to ISC13 (both C11 and ISC13 are dominated by Ca and Mg), which was found to dominate this soil. Given this link between C11, Cr(VI) and ISC13, the Ca components that make up this cluster could be COPR-derived minerals (Hillier *et al.*, 2003). Cluster C8 is composed of clay components from 23 soils (those being all but 19, 20, 22 and 23). The Cr content of this cluster is <5 mg/kg (average 1.5 mg/kg) for 22 of the soil samples, with only Sample 24 containing greater amounts of Cr (111 mg/kg). Thus, despite the model showing that 100% of Cr contained within these clusters is Cr(VI), this represents (with the exception of one sample) only 1.5 mg/kg Cr(VI) per sample. C4 was identified as a cluster of organic components and it is unexpected that its presence should correspond to an increase in Cr(VI). The model suggests that 95% of Cr associated with this cluster is Cr(VI), when soil organic matter is known to readily reduce Cr(VI) to Cr(III). Cluster C4 is found only in significant quantities in Sample 20 (small amounts are present in Sample 16, contributing 0.08 mg/kg of Cr) in which it contains 212 mg/kg of Cr, of which 201 mg/kg is Cr(VI). Since C4 is effectively

found only in one sample, that with the highest Cr(VI) content, its inclusion within the model may represent an error within the model itself and not a trend with the data set. This would explain why an organic cluster appears to contain so much Cr(VI) despite being a known reducing agent.

Although the model suggests virtually all the Cr in clusters C11, C8 and C4 is Cr(VI), it appears that C7 makes a far larger contribution of Cr(VI) to the samples. About 41% of the Cr contained in the clay cluster C7 is Cr(VI), but given that C7 contains in total (sum of each sample) 1811 mg/kg of Cr, this relates to ~750 mg/kg of Cr(VI). Most of this (711 mg/kg) is present in Sample 20. The average Cr(VI) concentration in this cluster is low (3.2 mg/kg) if the contribution of Sample 20 is excluded from calculation. Of the remaining terms in the model, 56% of the Cr associated with the Mn oxide cluster C9 is Cr(VI), with corresponding values for the Fe-dominated cluster C10, C12 and C13 of 1, 13 and 28% respectively.

As with total Cr, the majority of soils (16 out of 27) have more Cr(VI) in one of the Fe oxide clusters than in any other cluster. Of the remaining Samples, 15, 19 and 20 have more Cr(VI) in cluster C7 and Samples 3, 4, 12, 13, 14, 18, 24 and 25 have more Cr(VI) in C8 than in any other cluster.

6.4 Lead Distribution

The distribution of Pb among the identified clusters is shown in Figure 6.8. Cluster C8 is the highest Pb-containing cluster, with 9860 mg/kg of associated Pb. This cluster is composed of clay components that are found in 23 of the 27 collected soils, making this cluster the most common of the two clay clusters. In addition, C8 represents the largest Pb-containing cluster in 20 of the 27 samples. The other clay cluster, C7, has a lower Pb content of 895 mg/kg. Cluster C9 also contains a large amount of Pb. This Mn oxide cluster, which contains ~3680 mg/kg of Pb, is the largest Pb-containing cluster in Samples 3, 4, 16 and 22. Considering the ease of extraction, it is interesting that Cluster C1 (the dominant Pb-containing cluster in Sample 19) contains almost 1200 mg/kg of Pb. This cluster is made up of Ca carbonate components and thus is extracted early in the CISED procedure by the most dilute acidic extractants (Figure 6.3). Therefore, the Pb in this cluster would be expected to have a high mobility in the environment, compared with that in clusters C8 and C9 and is also expected to have greater bioaccessibility. This is a very common cluster, with components present in all

but four soils, those being 1, 8, 13 and 20. The other Ca carbonate clusters, C2 and C11, contain little Pb, 42 and 116 mg/kg, respectively. Of the Fe-dominated clusters, C13 contains the most Pb with 841 mg/kg. This cluster is present in 13 soils, making up on average 24% of a soil, and as such, often makes a significant contribution to the soil Pb concentration. The other Fe oxide clusters C10 and C12 contain 485 and 72 mg/kg of Pb, respectively. Given the relationship between Pb and the humus ISC11 (Section 5.4.2.3), it is interesting that no Pb was found associated with organic physico-chemical phases. This suggests that although Pb tends to be found in soils with a high organic matter, the two are not physically bound/associated.

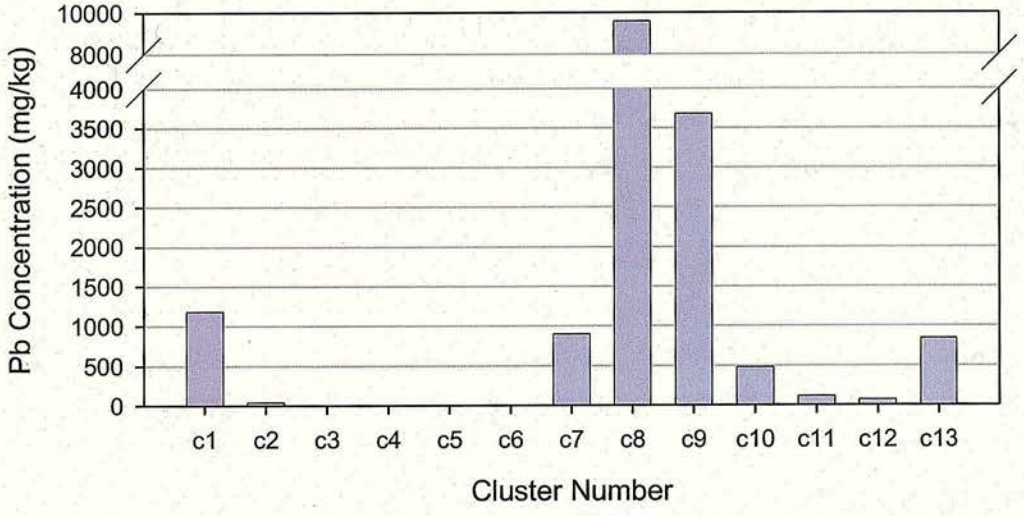

Figure 6.8 The distribution of Pb among the 13 clusters of identified soil components.

Grouping the clusters together into readily and poorly soluble clusters, as in Section 6.3, it is evident that a large amount of Pb is in readily soluble clusters. Clusters C1 to C6 contain 1242 mg/kg of Pb, whilst C7 to C13 contain 15667 mg/kg. Most of the readily soluble Pb is accounted for by cluster C1, which contains 1182 mg/kg (Figure 6.8). As discussed above, this cluster is very common in the soils and behaves as a readily available source of Pb in the majority of samples.

6.5 Arsenic Distribution

The distribution of As among the 13 clusters identified is shown in Figure 6.9. Cluster C10 is the largest As-containing cluster, with 271 mg/kg and is the dominant As cluster in 22 out of the 27 samples. This is an Fe-dominated cluster, which is a similar

observation to that reported by Wragg (2005), who found that the As concentration in soils from Wellingborough was closely linked to that of Fe. Cluster C10 is present in all samples, except for 10 and 21. The other Fe-dominated clusters contain little As, with C12 and C13 containing 17 and 27 mg/kg As, respectively. Despite this, cluster C13 is the largest As-containing phase in Sample 11. The organic cluster C6, containing 52 mg/kg of As, is the second largest As-containing cluster. Cluster C6 is not overly abundant, although it is the largest As-containing cluster in Samples 10 and 21. The clay clusters C7 and C8 (which is the largest As-containing cluster in Sample 25) contain 27 and 47 mg/kg As, respectively. The remaining clusters all contain <13 mg/kg of As, although it is of note that C4 is the largest As-containing phase in Sample 16.

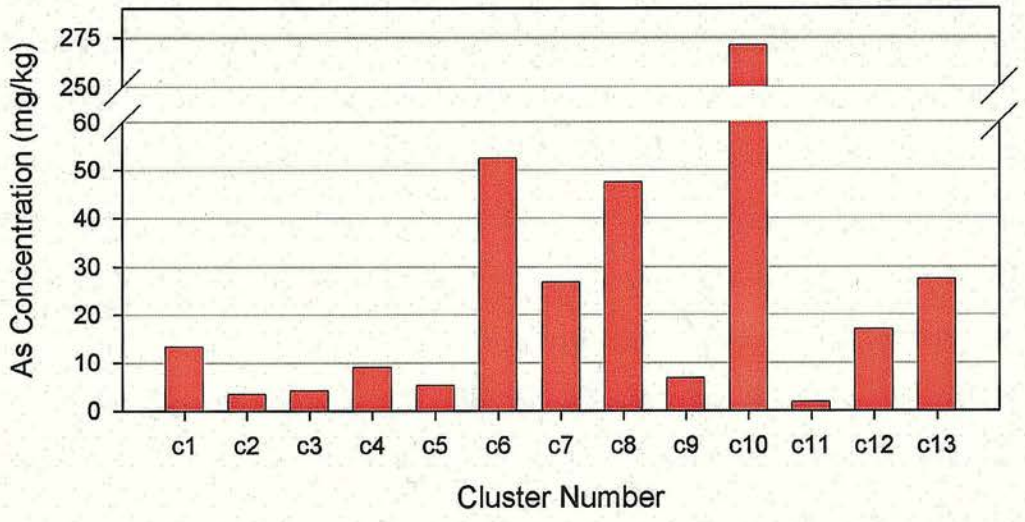

Figure 6.9 The distribution of As among the 13 clusters of identified soil components.

Grouping the clusters together into readily and poorly soluble clusters, as in Section 6.3 and 6.4, it is evident that a significant proportion of As is in readily soluble clusters. Clusters C1 to C6 contain 88 mg/kg of As, whilst C7 to C13 contain 398 mg/kg. As Figure 6.9 shows, the majority of the readily soluble As is present in cluster C6, which contains 52 mg/kg.

6.6 Summary

- In total 13 different acid extractable physico-chemical clusters were identified in the 27 samples. These included three Ca carbonate clusters, two

exchangeable, two organic, two clay, one Mn oxide and three Fe-dominated clusters.

- In the majority (25 out of 27) of soils, Cr was more concentrated in one of the three Fe-dominated clusters. This means that in most of the soils Cr was present in a poorly soluble form, therefore having a low environmental mobility and potentially a low bioaccessibility.

- In two samples (19 and 20), however, Cr was far more concentrated in the clay cluster C7. This cluster contained more Cr than any other, with 1810 mg/kg, which represents 47% of all the extractable Cr in the soils. Most of this 1810 mg/kg came from Sample 20, which had 1720 mg/kg of Cr associated with C7. Looking at the soils as a whole, it was evident that 220 mg/kg of Cr was present in readily soluble clusters (1-6), whilst 3635 mg/kg was in poorly soluble clusters (7-13).

- Modelling Cr(VI) concentrations suggested that 100% of the Cr in clusters C11 (bound carbonate)and C8 (clay), and the majority in cluster C4 (organic), was Cr(VI). As with the distribution of total Cr, cluster C7 made a major contribution to that of Cr(VI). The model indicated that 41% of the Cr associated with C7 was Cr(VI).

- The dominant Pb-containing cluster in most (20 out of 27) samples was a clay cluster. Cluster C8 was associated with the highest amount of Pb at 9860 mg/kg. The Mn oxide cluster C9 contained the second highest Pb concentration at 3680 mg/kg and was the dominant cluster in Samples 3, 4, 16 and 22. An interesting result is that the Ca carbonate cluster C1 was associated with ~1200 mg/kg of Pb, suggesting a large amount of Pb was in an easily soluble form.

- The majority (22 out of 27) of samples show As was associated with Fe-dominated phases. The Fe-dominated cluster C10 was the most important, containing 271 mg/kg, i.e. more As than in any other cluster. The largest As-containing cluster, which was not dominated by Fe, was organic cluster C6

with an associated 52 mg/kg. C6 was the dominant As-containing cluster in Samples 10 and 21.

CHAPTER 7 CHROMIUM, LEAD AND ARSENIC BIOACCESSIBILITY

7.1 Oral Bioaccessibility

7.1.1 Stomach vs Stomach+Intestine Extracts

The bioaccessibility of Cr, Pb and As was determined in the 27 Glasgow soil samples using the UBM, as described in Section 4.3.2. This method produces two bioaccessibility values per sample, one representing the fraction of the chosen analyte in solution following the stomach stage and the other encompassing both the stomach and intestine (stomach+intestine) stages. With the aim of obtaining a conservative estimate of an analyte's oral bioaccessibility, the larger of the two was taken as the bioaccessibility value.

Table 7.1 Bioaccessibility of Cr, Pb and As in the Glasgow soil samples.

Sample ID	Cr (mg/kg)		Pb (mg/kg)		As (mg/kg)	
	Stomach	Stomach+ Intestine	Stomach	Stomach+ Intestine	Stomach	Stomach+ Intestine
1	12 ± 1	9.2 ± 0.2	150 ± 4	67 ± 0	9.2 ± 4.5	10 ± 2
2	< 3	< 5	223 ± 19	108 ± 1	< 6	< 5
3	7.0 ± 1.0	5.4 ± 1.1	500 ± 44	275 ± 0	21 ± 3	25 ± 2
4	8.3 ± 1.0	5.7 ± 0.9	307 ± 24	149 ± 6	< 6	< 5
5	3.0 ± 0.7	< 5	376 ± 31	164 ± 4	< 6	< 5
6	< 3	< 5	469 ± 0	208 ± 3	< 6	< 5
7	< 3	< 5	743 ± 20	410 ± 12	< 6	< 5
8	< 3	< 5	270 ± 11	144 ± 2	< 6	5.9 ± 4.3
9	3.9 ± 0.7	< 5	405 ± 37	199 ± 2	9.7 ± 2.4	9.0 ± 1.5
10	< 3	< 5	281 ± 30	59 ± 0	< 6	< 5
11	< 3	< 5	159 ± 12	78 ± 0	< 6	< 5
12	5.3 ± 1.9	< 5	754 ± 61	109 ± 4	15 ± 2	23 ± 0
13	< 3	< 5	251 ± 11	122 ± 1	< 6	5.5 ± 4.6
14	< 3	< 5	512 ± 22	279 ± 0	< 6	< 5
15	4.0 ± 0.3	< 5	76 ± 8	41 ± 1	< 6	< 5
16	4.4 ± 0.3	< 5	77 ± 3	38 ± 0	< 6	< 5
17	< 3	< 5	72 ± 2	35 ± 2	< 6	< 5
18	4.7 ± 0.7	< 5	204 ± 10	99 ± 2	< 6	< 5
19	19 ± 1	8.7 ± 0.1	123 ± 11	44 ± 2	< 6	< 5
20	1156 ± 32	52 ± 1	228 ± 4	6.0 ± 2.3	< 6	< 5
21	8.5 ± 2.5	< 5	609 ± 72	224 ± 2	8.0 ± 3.7	11 ± 0
22	9.0 ± 0.6	5.5 ± 0.2	129 ± 5	62 ± 4	< 6	< 5
23	3.1 ± 0.6	< 5	528 ± 69	318 ± 2	< 6	6.4 ± 0.4
24	116 ± 2	83 ± 0	46 ± 3	23 ± 2	< 6	< 5
25	< 3	< 5	1575 ± 241	623 ± 4	< 6	< 5
26	< 3	< 5	123 ± 20	45 ± 2	8.6 ± 2.9	10 ± 2
27	< 3	< 5	365 ± 18	96 ± 5	< 6	< 5

mean ± SD. n = 2

In the case of Cr (Table 7.1 & Figure 7.1) the stomach produces a larger soluble value than the stomach+intestine. In Sample 20 the difference between the stomach and stomach+intestine values is very large, dropping from 1156 ± 32 to 52 ± 1 mg/kg. The remaining samples show a less extreme difference between the two measurements. It has not previously been reported that the stomach stage of a PBET procedure will produce greater amounts of bioaccessible Cr, although this has been assumed to be the case as previous studies have only incorporated a stomach stage and not an intestine stage (Skowronski *et al.*, 2001; Stewart *et al.*, 2003a; Stewart *et al.*, 2003b; Fendorf *et al.*, 2004). This reduction in Cr solubility between the stomach and intestine stages of the UBM is likely to be a result of both speciation and pH. As will be discussed later in this chapter, the stomach stage of the UBM results in the reduction of any Cr(VI) present to Cr(III), a species with solubility sensitive to pH change (Figure 4.1). Under acid conditions any Cr(III) present will tend to be soluble, while neutral to basic conditions will result in precipitation (e.g. as $Cr(OH)_3$) out of solution (Kimbrough *et al.*, 1999). Given that changing from stomach to intestine conditions in the UBM involves a pH increase from 1.2 to 6.3, it seems likely that precipitation of Cr is occurring.

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 26 M	1	39.5	1.1	0.4	1.4	20.4	0.0	0.0	0.2	1.2	Dil	1.5	0.0	3.3	5.0	0.0	0.2	0.2	26.0	2.3	9.4	0.0	21.8	0.5	0.8	0.7
Sample 26 M	5	38.6	1.1	0.4	1.4	21.0	0.0	0.0	0.2	1.3	238.1	1.6	0.0	3.5	5.1	0.1	-0.5	0.3	25.9	2.4	10.3	0.0	22.7	0.4	0.8	0.7
Sample 26 N	1	Dil	0.6	Dil	3.9	68.5	0.0	0.2	0.4	2.5	Dil	4.5	0.1	16.4	23.9	0.1	1.5	0.7	33.3	5.2	11.4	0.0	17.2	1.7	2.0	2.7
Sample 26 N	10	140.2	0.7	1.1	3.8	70.6	0.0	0.1	0.4	2.5	688.2	4.8	0.2	17.7	24.8	0.1	-0.6	0.7	34.5	5.5	12.8	0.0	18.1	1.7	2.0	2.9
Sample 27 A	5	0.2	0.2	0.0	0.0	9.1	0.0	0.0	0.0	0.0	0.7	1.1	0.0	0.9	0.2	-0.1	3.0	0.0	1.0	0.0	4.5	0.1	1.2	0.0	0.0	0.0
Sample 27 B	1	0.1	0.0	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.1	0.8	0.0	0.3	0.1	0.0	1.3	0.0	0.4	0.0	1.0	0.0	0.8	0.0	0.0	0.0
Sample 27 C	1	0.2	0.0	0.0	0.6	157.3	0.0	0.0	0.0	0.0	0.0	5.0	0.0	13.2	3.7	0.0	1.5	0.0	0.1	0.1	0.4	0.0	1.1	0.7	0.0	0.0
Sample 27 D	1	0.6	0.0	0.0	1.4	134.6	0.0	0.0	0.0	0.0	0.1	3.9	0.0	9.1	4.7	0.0	0.3	0.0	0.2	0.8	0.4	0.0	2.0	0.7	0.0	0.1
Sample 27 E	1	10.5	0.0	0.0	6.6	263.2	0.0	0.1	0.0	0.2	1.4	5.3	0.0	12.5	11.9	0.0	0.2	0.1	0.9	10.3	0.4	0.0	3.8	1.4	0.0	0.4
Sample 27 F	1	29.6	0.0	0.0	6.5	160.6	0.0	0.1	0.0	0.3	3.2	4.4	0.0	7.6	12.2	0.0	0.3	0.1	1.2	15.0	0.5	0.0	7.7	0.9	0.0	0.5
Sample 27 G	1	62.0	0.0	0.0	6.9	116.4	0.0	1.3	0.0	0.6	19.6	3.7	0.0	4.8	Dil	0.0	0.2	0.3	2.2	Dil	1.0	0.1	9.1	0.7	0.1	0.7
Sample 27 G	2	57.2	0.0	0.1	6.1	108.8	0.0	1.2	0.0	0.5	18.5	3.4	0.0	4.6	99.9	0.0	0.5	0.2	2.1	27.6	0.9	0.1	8.5	0.6	0.1	0.6
Sample 27 G	5	64.8	0.0	0.0	7.1	126.4	0.0	1.5	0.0	0.6	21.7	4.2	0.0	5.3	114.4	0.0	-0.6	0.3	2.3	31.8	1.5	0.1	11.6		0.1	0.7
Sample 27 H	1	52.3	0.0	0.0	2.5	40.9	0.0	0.4	0.0	0.5	26.4	2.1	0.0	2.6	29.9	0.0	0.3	0.1	2.4	19.9	0.9	0.0	9.7	0.3	0.1	0.3
Sample 27 I	1	Dil	0.0	0.2	1.3	31.8	0.0	0.1	0.1	0.7	Dil	2.0	0.0	4.2	9.6	0.0	-0.3	0.1	11.6	Dil	3.0	0.0	16.5	0.3	0.3	0.4
Sample 27 I	5	99.8	0.0	0.3	1.2	30.8	0.0	0.1	0.1	0.7	156.2	1.9	0.0	4.1	9.3	0.0	-0.5	0.1	10.7	23.9	3.0	0.0	15.8	0.2	0.2	0.3
Sample 27 J	1	83.2	0.0	0.3	0.5	22.6	0.0	0.1	0.1	0.4	Dil	1.4	0.0	6.7	5.2	0.0	-0.2	0.1	10.5	8.8	2.8	0.0	22.3	0.2	0.3	0.4
Sample 27 J	5	74.0	0.0	0.4	0.4	21.8	0.0	0.1	0.1	0.4	231.5	1.3	0.0	6.5	4.9	0.0	-0.1	0.1	9.5	8.2	2.8	0.0	21.6	0.2	0.2	0.4
Sample 27 K	1	Dil	0.1	Dil	0.7	25.9	0.0	0.2	0.6	0.4	Dil	2.2	0.0	27.1	13.7	0.0	-0.2	0.2	19.2	7.8	11.8	0.0	Dil	0.2	0.9	1.2
Sample 27 K	10	167.4	0.1	1.0	0.6	25.0	0.0	0.1	0.5	0.4	682.5	2.0	0.0	26.2	12.9	0.0	-1.1	0.2	17.6	7.5	11.8	0.0	34.9	0.1	0.8	1.2
Sample 27 L	1	Dil	0.0	Dil	0.6	12.2	0.0	0.2	0.7	0.3	Dil	1.9	0.1	23.6	21.2	0.0	-0.4	0.2	15.2	3.7	11.6	0.0	20.7	0.1	1.0	1.2
Sample 27 L	10	149.0	0.0	1.3	0.5	11.9	0.0	0.1	0.6	0.2	896.3	1.8	0.1	23.3	20.1	0.0	-2.1	0.2	14.3	3.6	12.1	0.0	20.1	0.0	0.9	1.2
Sample 27 M	1	69.4	0.3	Dil	0.2	2.5	0.0	0.1	0.5	0.2	Dil	2.2	0.0	6.0	9.0	0.0	-0.3	0.1	40.9	1.6	21.0	0.0	20.5	0.0	0.6	0.6
Sample 27 M	10	64.3	0.3	1.1	0.2	2.5	0.0	0.1	0.5	0.2	732.5	2.2	0.0	6.2	8.9	0.0	-2.1	0.1	42.2	1.6	22.4	-0.1	20.6	0.0	0.5	0.6
Sample 27 N	1	Dil	0.1	Dil	0.5	5.1	0.0	0.1	1.0	0.2	Dil	3.0	0.1	23.6	10.5	0.0	-0.3	0.3	22.3	0.8	10.0	0.0	13.1	0.0	0.7	1.5
Sample 27 N	10	176.8	0.1	1.7	0.5	5.2	0.0	0.1	0.9	0.2	Dil	3.1	0.1	24.5	10.5	0.0	-2.1	0.3	21.7	0.9	10.9	-0.1	13.1	0.0	0.7	1.5
Sample 27 N	20	186.5	0.1	1.8	0.5	5.3	0.0	0.1	1.0	0.2	1180	3.2	0.1	25.0	11.2	0.0	-6.2	0.3	23.0	0.9	13.2	0.0	15.4		0.7	1.6

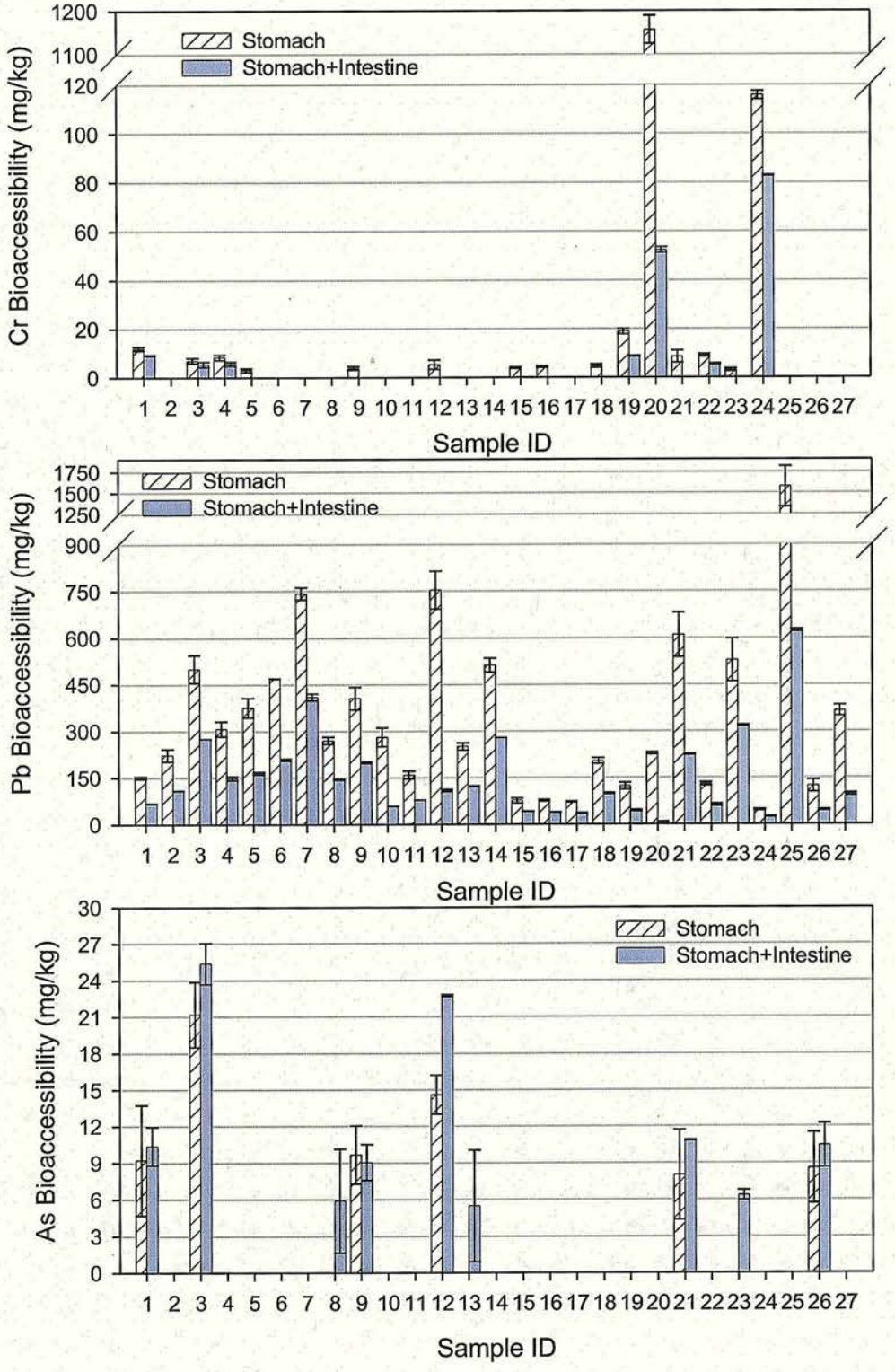

Figure 7.1 Cr, Pb and As bioaccessibility in the Glasgow soil samples as measured in the two extracts of the UBM method.

As with Cr, Pb was present in higher concentrations in the stomach extract compared to the stomach+intestine extract (Table 7.1 & Figure 7.1). This observation is the same as that reported in previous studies (Ruby *et al.*, 1996; Hamel *et al.*, 1999). Arsenic on the other hand, tends to be slightly more soluble when an intestine stage is incorporated, which is consistent with other studies (Rodriguez *et al.*, 1999; Palumbo-Roe *et al.*, 2005; Wragg *et al.*, 2007). Therefore, when the bioaccessibility of Cr or Pb is discussed in this thesis it will refer to the solubility in the stomach extract, whereas bioaccessibility of As will refer to the solubility in the stomach+intestine extract.

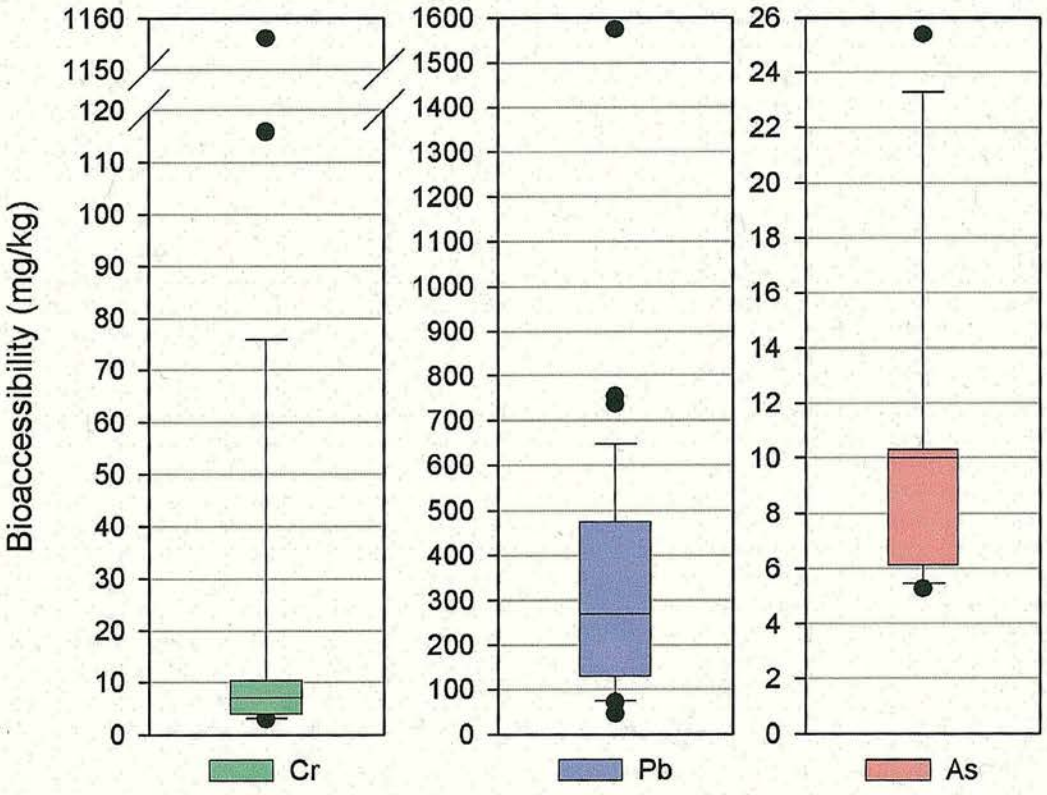

Figure 7.2 Box and Whisker plots showing the range of Cr, Pb and As bioaccessibility for the 27 Glasgow soils
(calculated percentile values do not include samples below detection limits).

7.1.2 Chromium Bioaccessibility in Glasgow Soil Samples

Generally, the bioaccessibility of Cr in the 27 Glasgow soils lay within a narrow range of values (Figure 7.2), with 75% of samples between 3.0 and 10 mg/kg. The most significant samples outwith this range were Samples 20 and 24, which had a bioaccessibility of 1156 ± 32 and 116 ± 2 mg/kg, respectively. The amount of bioaccessible Cr in Sample 20 was almost 6 times the SGV for residential land (200

mg/kg). The amount of bioaccessible Cr in Sample 24 does not exceed the SGV of residential land either with or without plant uptake (130 and 200 mg/kg, respectively), but still represents a relatively large bioaccessible component. As Figure 7.3 shows, the bioaccessible Cr was generally significantly lower than the total Cr concentration, averaging 8% of the latter. In contrast, the bioaccessible Cr and Cr(VI) concentrations in the soils were similar. On average, the bioaccessibility was 93% (median 73%) of the Cr(VI) concentration, though in three samples the bioaccessible fraction was greater than that of Cr(VI). In 12 of the 27 soils the bioaccessible Cr fraction was below the method detection limit.

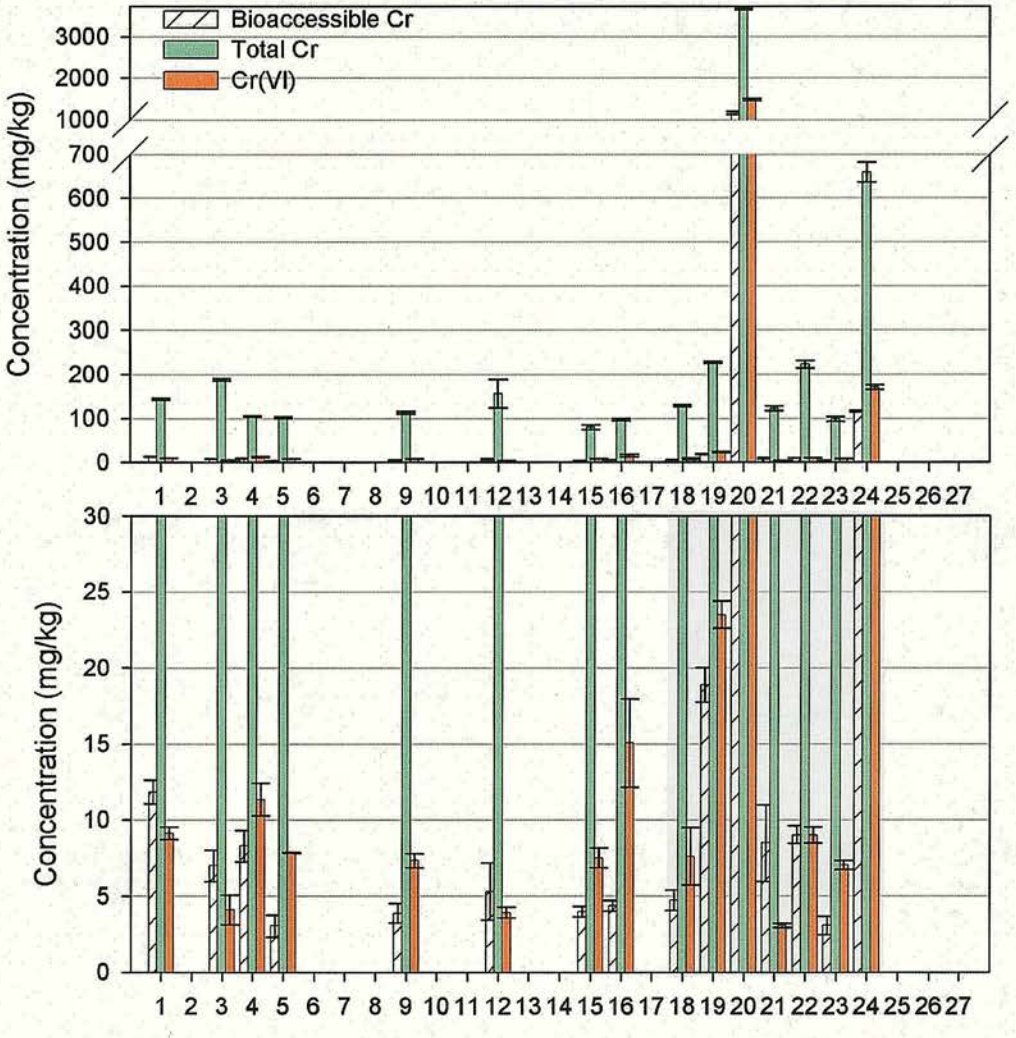

Figure 7.3 Comparison of bioaccessible Cr, total Cr and Cr(VI) in those Glasgow soils with detectable bioaccessible Cr.

Figure 7.4 shows the spatial distribution of bioaccessible Cr values across Glasgow. As with the distribution of Cr(VI), the soils with a greater Cr bioaccessibility were mainly located in the southeast. Samples 20 and 24 were easily identifiable as those with the largest bioaccessible Cr content. The next highest Cr bioaccessibility value was for Sample 19, which at only 19 mg/kg is notably lower than the values for Samples 20 and 24.

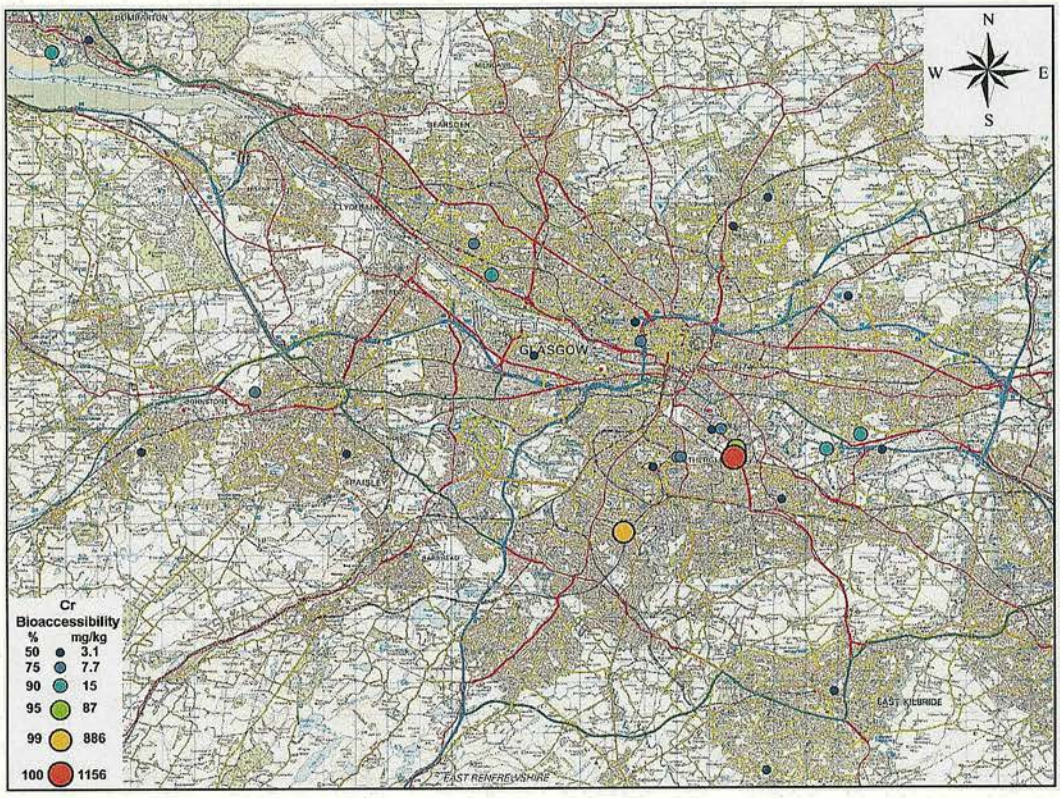

Figure 7.4 Geographical distribution of the soil Cr bioaccessibility values across Glasgow (percentile values calculated with all samples included).

7.1.3 Lead Bioaccessibility in Glasgow Soil Samples

All 27 soil samples had a bioaccessible Pb content above detection limits. Fifteen of these had a Pb bioaccessibility between 140 and 484 mg/kg (Figure 7.1), with eight >450 mg/kg (the Pb SGV (DEFRA, 2002c)). Sample 25, which contained the largest Pb concentration, had the highest bioaccessible fraction of 1575 ± 241 mg/kg (Table 7.1). As with Cr, the Pb bioaccessibility was, generally, considerably lower than the total Pb concentration (Figure 7.5), averaging 50% of the latter. In the case of Sample 25, 73% of the soil Pb content was bioaccessible. As with the total soil Pb

concentration (Figure 5.5), no spatial clusters of high bioaccessible Pb values were identified across Glasgow (Figure 7.6) unlike that of bioaccessible Cr (Figure 7.4).

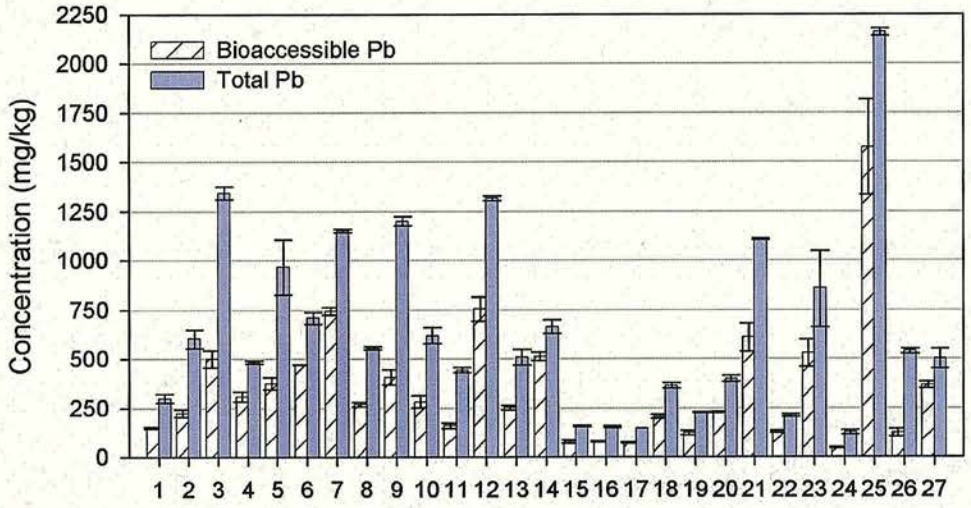

Figure 7.5 Comparison between bioaccessible and total Pb in the Glasgow soil samples.

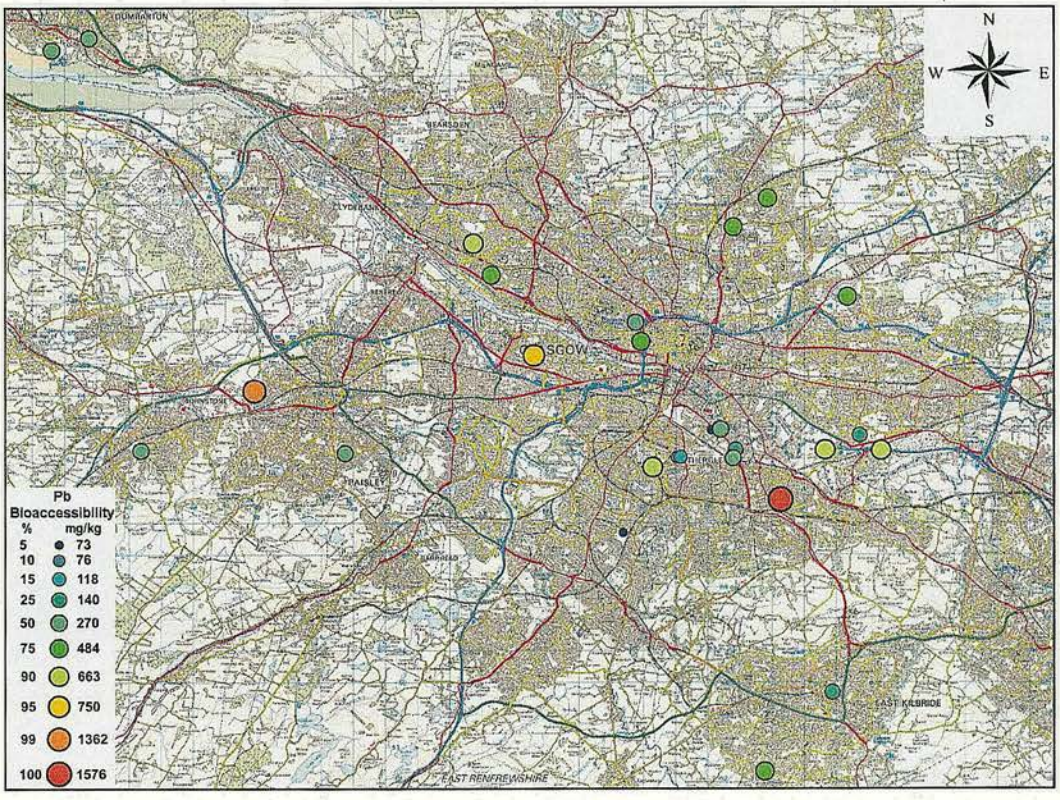

Figure 7.6 Geographical distribution of the soil Pb bioaccessibility values across Glasgow (percentile values calculated with all samples).

The $^{206}Pb/^{207}Pb$ isotope ratio of bioaccessible Pb differed little from that of the whole soil (Table 7.2), although a paired *t* test (paired *t* test, $t = 3.879$, $t_{crit} = 2.056$, $p = 0.0006$) did show that the data sets were distinguishable statistically, the $^{206}Pb/^{207}Pb$ ratio being very slightly lower (with the exception of Sample 2) in 24 of the 27 samples. There seemed to be no link between the soil Pb isotope ratio and Pb bioaccessibility. Initial investigations using the Pearsons Product Moment Coefficient appeared to indicate a significant correlation (r = 0.5269), with *p* being calculated as 0.0046. However, as Figure 7.7 shows, the data set includes one outlier (Sample 25) with both a significantly higher Pb bioaccessibility and a lower $^{206}Pb/^{207}Pb$ ratio in the soil, i.e. the data set is not normally distributed. Repeating using the Spearman Rank Correlation reveals that no correlation exists, *p* being calculated as 0.7749 and 0.7225, respectively. Since the Pb isotope ratio of a sample varies based on the Pb source (e.g. different anthropogenic sources, Section 5.1.2), this suggests that the anthropogenic origin of the Pb contamination has little bearing on its bioaccessibility, i.e. Pb originating from the combustion of petrol is no more bioaccessible than that from the combustion of coal and vice versa.

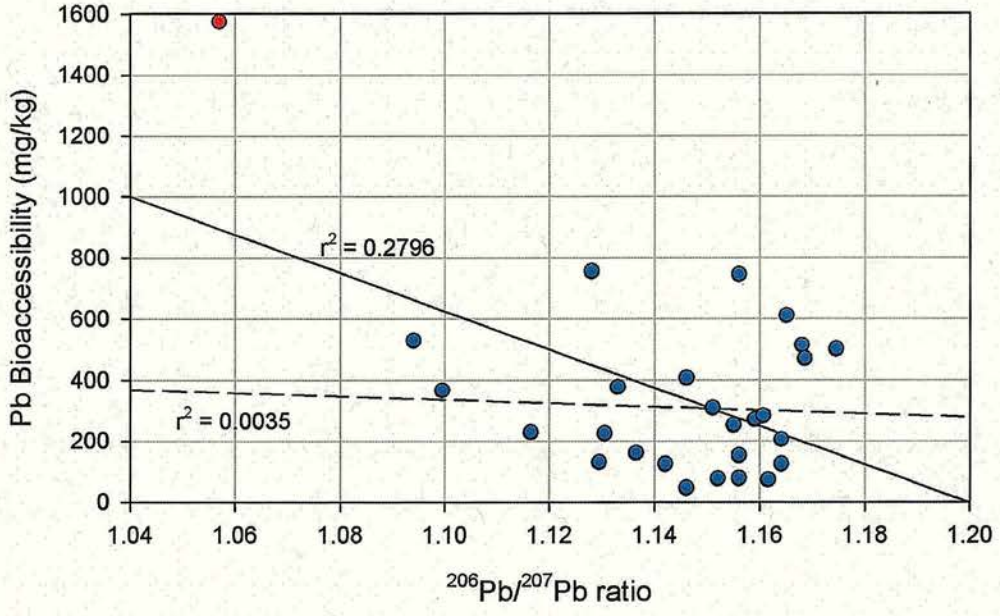

Figure 7.7 The relationship between soil Pb isotope ratio and Pb bioaccessibility. Dashed line shows correlation excluding Sample 25 (the red data point).

Table 7.2 $^{206}Pb/^{207}Pb$ ratio in original whole soil and the bioaccessible fraction.

Sample ID	Soil Pb	Bioaccessible Pb
1	1.156 ± 0.0012	1.153 ± 0.0014
2	1.131 ± 0.0014	1.100 ± 0.0011
3	1.175 ± 0.0008	1.170 ± 0.0011
4	1.151 ± 0.0014	1.150 ± 0.0019
5	1.133 ± 0.0012	1.130 ± 0.0014
6	1.169 ± 0.0008	1.168 ± 0.0016
7	1.156 ± 0.0010	1.154 ± 0.0016
8	1.159 ± 0.0010	1.153 ± 0.0015
9	1.146 ± 0.0008	1.142 ± 0.0015
10	1.161 ± 0.0008	1.160 ± 0.0019
11	1.137 ± 0.0014	1.128 ± 0.0011
12	1.128 ± 0.0007	1.119 ± 0.0017
13	1.155 ± 0.0022	1.154 ± 0.0014
14	1.168 ± 0.0017	1.166 ± 0.0020
15	1.152 ± 0.0017	1.147 ± 0.0016
16	1.156 ± 0.0016	1.151 ± 0.0015
17	1.162 ± 0.0010	1.158 ± 0.0015
18	1.164 ± 0.0019	1.162 ± 0.0014
19	1.142 ± 0.0011	1.138 ± 0.0015
20	1.117 ± 0.0011	1.117 ± 0.0010
21	1.165 ± 0.0008	1.163 ± 0.0009
22	1.130 ± 0.0011	1.123 ± 0.0011
23	1.094 ± 0.0015	1.098 ± 0.0011
24	1.146 ± 0.0014	1.146 ± 0.0013
25	1.057 ± 0.0016	1.054 ± 0.0015
26	1.164 ± 0.0005	1.155 ± 0.0011
27	1.100 ± 0.0015	1.094 ± 0.0013

7.1.4 Arsenic Bioaccessibility in Glasgow Soil Samples

Only nine out of the 27 soil samples had a bioaccessible As content above detection limits (Table 7.1), with only two above the 20 mg/kg SGV (DEFRA, 2002f), these being Sample 3 (the soil with the highest total As concentration) and Sample 12 (the third highest). Apart from these two samples, the bioaccessibility of As was generally low, with 90% of samples below 11 mg/kg (Figure 7.2). As with Cr and Pb, the bioaccessible As was significantly less than the total As concentration, averaging 36% (median 41%) of the total (Figure 7.8). In the case of Sample 3, 19% of the total As was bioaccessible. The two samples with the largest bioaccessible As content were in the north and west of Glasgow, while the remaining seven soils with detectable bioaccessible contents were distributed across the city (Figure 7.9).

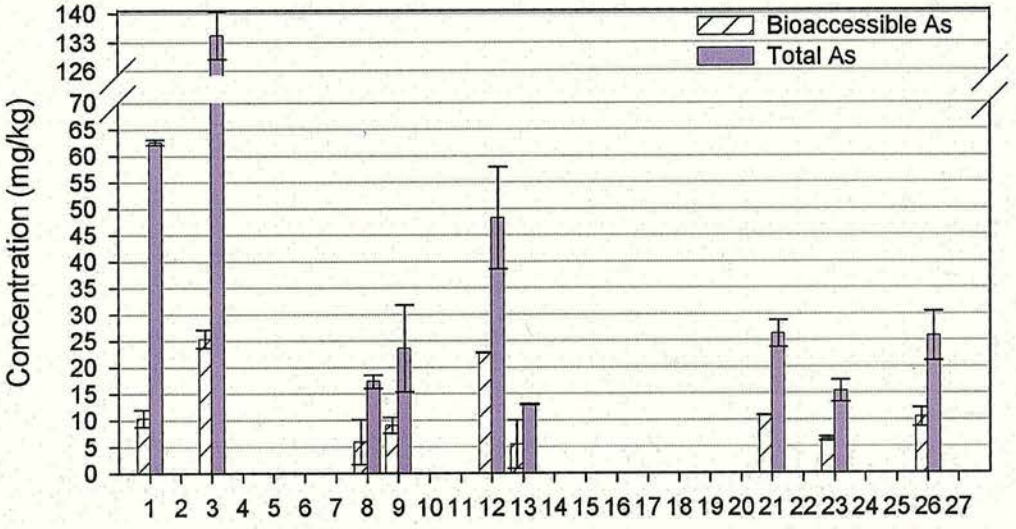

Figure 7.8 Comparison of bioaccessible and total As in the Glasgow soil samples.

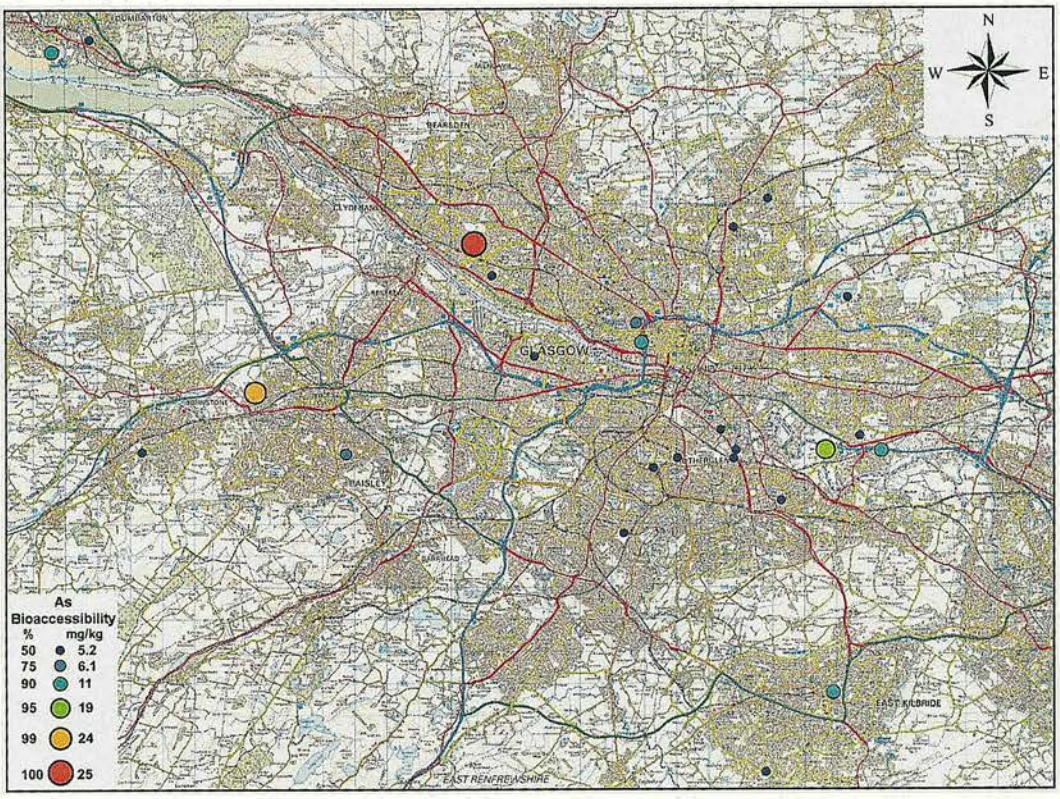

Figure 7.9 Geographical distribution of the soil As bioaccessibility values across Glasgow (percentile values calculated with all samples).

7.1.5 Chromium(VI) Bioaccessibility in Glasgow Soil Samples

7.1.5.1 Colorimetric Determination of Chromium(VI) with Diphenylcarbazide

Of the two commonly found species of Cr in the environment, Cr(VI) is by far the most toxic and as such is of great interest during risk assessment (DEFRA, 2002a). It was therefore important to determine the bioaccessibility of Cr(VI) in the Glasgow soils, in particular Samples 20 and 24, which contained high concentrations of this species. It was decided to employ the same colorimetric procedure used to measure the Cr(VI) concentration in the whole soil. The first stage was to determine whether the more complex matrix of the UBM biofluids would have an effect on the reaction between DPC and Cr(VI) in solution. To do this, two reagent blanks were prepared, one containing saliva and gastric solution as for the stomach stage and the other containing saliva, gastric, duodenal and bile solutions as for the stomach+intestine stages. Both of these reagent blanks were spiked with enough Cr(VI) standard to produce a solution of concentration 1 mg/l. They were then placed in a water bath (as for the UBM) and mixed for 2 and 6 hours, respectively, with aliquot sub-samples collected at regular intervals. As soon as the aliquots were collected the DPC reagent was added to complex Cr(VI), preventing any further reaction between it and the UBM matrix.

As Figure 7.10 shows, both the stomach and stomach+intestine stages of the UBM contain a species that absorbs at the same wavelength (540 nm) as the Cr(VI)-DPC complex. While it is still possible to measure Cr(VI) in this matrix, the detection limits are likely to be higher than those encountered following alkaline digestion of a soil sample. In the stomach stage the 1 mg/l Cr(VI) solution starts with an absorbance of 0.113, which over the next hour drops to 0.085 (a decrease of ~25%). Although this is the time when the stomach stage comes to an end in the UBM, the Cr(VI) content continues to fall if the residence time in the stomach is extended. In the stomach+intestine stage the 1 mg/l Cr(VI) solution starts with an absorbance of 0.164 and remains roughly constant for the next 3 hours. The absorbance appears to rise in the 4 and 5 hour aliquots, before dropping back to 0.181 after 6 hours. The apparent increase in Cr(VI) content at 4 and 5 hours is likely to be due to an experimental/human error as, with the exception of these two points, the other seven data points remain roughly constant. Given that a decrease in Cr(VI) absorbance is

observed in the stomach stage, but not the stomach+intestine stage (which also contains saliva and gastric solution as in the stomach stage), the decrease in the former is likely to be due to the lower pH of the stomach. If the decrease was due to a reaction with one of the reagents in the stomach stage, the same reaction would be expected to take place in the stomach+intestine, as it also contains the stomach reagents. In acidic conditions Cr(VI) is thermodynamically unstable (James and Bartlett, 1983; Rai and Eary, 1989; Saleh *et al.*, 1989; Kotás and Stasicka, 2000) and is reduced to Cr(III) (Figure 4.2). The reduction does not seem to be occurring at a fast enough rate to remove all of the Cr(VI) from solution within the 1-hour stomach residence time used by the UBM, suggesting that the colorimetric approach maybe fit for purpose. When the soil samples were processed, however, none had a bioaccessible Cr(VI) concentration above the detection limits. It is likely that the low pH of the stomach stage, combined with the contribution of soil organic matter originating from the samples, was able to reduce the Cr(VI) present rapidly to Cr(III).

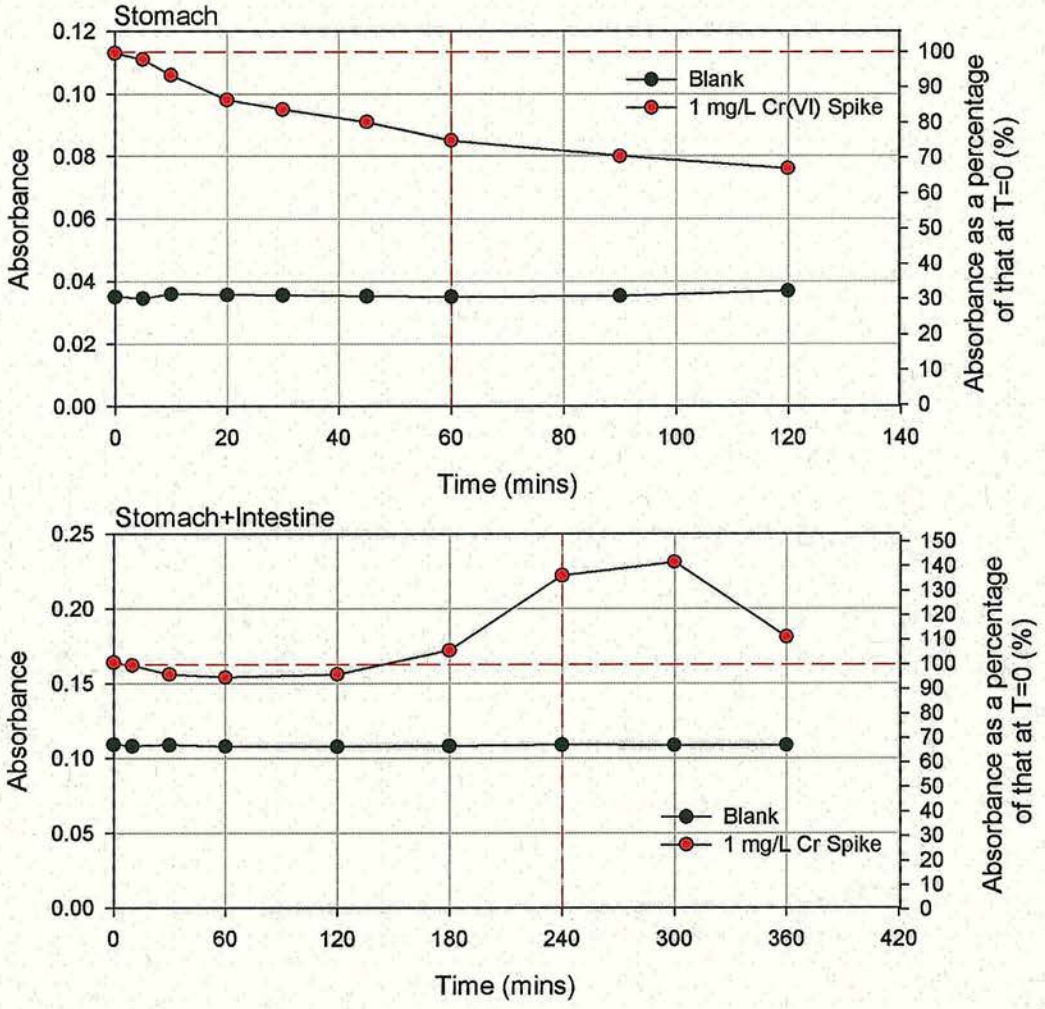

Figure 7.10 The effect the PBET reagents have on a Cr(VI) spike over time.
Vertical red line indicates UBM extraction time. Horizontal red line indicates absorbance at 0 mins.

To assess whether Cr(VI) is extracted by the UBM, a mass balance experiment was performed. Since the alkaline digest (Section 4.2.2) requires 2.5 g of soil, a scaled up version of the UBM was used to extract Samples 20 and 24. The post-UBM residual soil was collected and the Cr(VI) content determined. The results are shown in Table 7.3. If it is assumed that any bioaccessible Cr results from the extraction of Cr(VI), then overall recoveries of 95 and 93% were obtained for Sample 20 and 24, respectively. This mass balance suggests that Cr(VI) within these samples is largely being extracted by the UBM, before being reduced to Cr(III) in solution. The

reduction does not appear to occur prior to extraction, since significant measurable Cr(VI) was found within the post-UBM soil residue.

Table 7.3 Cr(VI) mass balance during the UBM extraction.
Recovery calculation assumes bioaccessible Cr is Cr(VI)

	Cr(VI) Pre-UBM (mg/kg)	UBM Cr Bioaccessibility (mg/kg)	Cr(VI) Post-UBM (mg/kg)	Cr(VI) Bioaccessibility (mg/kg)	Cr(VI) Recovery (%)
Sample 20	1485 ± 24	1203 ± 49	209 ± 8	1412 ± 24	95
Sample 24	171 ± 5	112 ± 6	47 ± 13	159 ± 7	93

7.1.5.2 Gel Electrophoresis

If soil organic matter is involved in the reduction of Cr(VI) to Cr(III) within the stomach stage of the UBM, it would be expected that Cr(III)-organic complexes will be present in solution. These could also be present as a result of organically bound Cr(III) in the soil being leached during the extraction. Four selected soils were analysed using gel electrophoresis to investigate the nature of the organic Cr species present. These soils, Samples 1, 19, 20 and 24, were chosen on the basis that they contained the greatest amounts of bioaccessible Cr out of the 27 samples. Each sample was taken through the UBM procedure as normal, except that, following centrifugation, the whole stomach supernatant was collected. This was stored at 4°C until analysis.

The UBM extracts were initially ultrafiltered (Section 4.10) to separate the colloidal material from dissolved species. After the 30 minute gel electrophoretic fractionation, several bands could be identified for Sample 1 following the stomach stage of the UBM. The colloid sub-sample showed a sharp brown-coloured fluorescent band was present in F1, whilst a thicker fluorescent band was in F2. In addition, some strongly fluorescing material remained in the sample well. A similar pattern was observed in the dissolved sub-sample, but fainter than that in the colloids. Chromium was found to be present only in the colloid fraction F2, with none detected in the dissolved sub-sample (Figure 7.11). This would indicate that the Cr in this sample, at the point of stomach emptying, is bound to a large, charged species. It is likely to be large since it is present only in the colloid sub-sample and not in the dissolved fraction phase. The fact that the Cr corresponds to a fluorescing band suggests that the Cr is bound to a

soil humic species (Farmer *et al.*, 2002). It is clear that there are no free Cr species, as these, being small, would move rapidly across the gel during fractionation to F8.

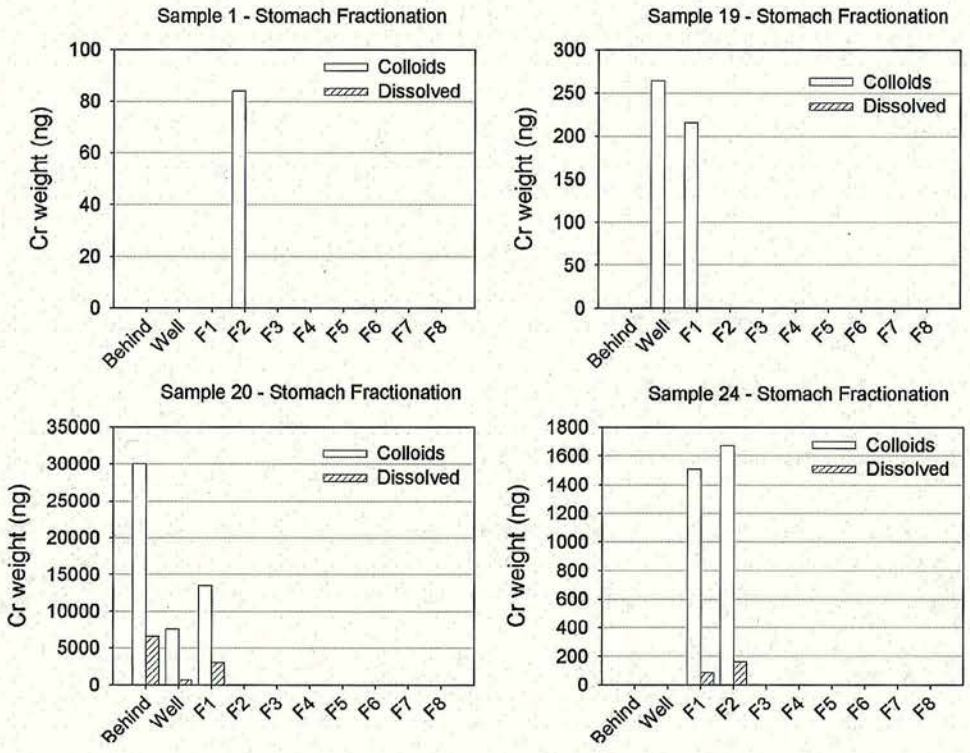

Figure 7.11 The weight of Cr in each gel electrophoretic fraction (0.5 cm width) obtained from tangential-flow ultrafiltered UBM extracts.
Size fractions: 3kD – 0.2μm (colloid) and <3kD (dissolved)

Sample 19, at the stage of stomach emptying, showed a similar pattern to that observed in Sample 1. The only difference was that the material remaining in the well was brown in colour. Once again the dissolved sub-sample showed a similar pattern to the colloidal, only fainter. The colloid sub-sample showed a large portion of the Cr remaining in the well, with only a small fraction migrating to F1 (Figure 7.11). High concentrations of Cr remaining in the well indicate that Cr is present in a complex/form, that is either very large or has no overall charge. The Cr present in F1, corresponding to a slightly brown and fluorescent band, indicates humic-bound Cr. There was no Cr in the dissolved sub-sample.

Sample 20 presents a very different set of bands than Samples 1 and 19. In the colloidal sub-sample a sharp brown band is observed behind the well, while another sharp brown and fluorescent band is observed in F1. Brown material remains in the

well, while there is no fluorescent band observed in F2. The dissolved sub-sample shows the same pattern but much fainter. In the colloids, most of the Cr (30,090 ng) is present in the fraction behind the well, while approximately half as much (13,560 ng) progresses to F1 and a relatively small portion of Cr (7635 ng) remains in the well (Figure 7.11). The Cr present in F1, as with the other samples, is likely to be humic-bound Cr, given that it corresponds to a brown and fluorescent band. The Cr presence behind the well suggests that it is present in a positively charged complex, as it is migrating towards the cathode. It is expected that most organic complexes are negatively charged and thus progress towards the anode. The gel electrophoresis procedure normally involves the test solutions being pH adjusted to 8.5 prior to fractionation. This step was not performed as it may have affected the Cr speciation in the low pH stomach samples. It is possible that in the acidic conditions of the stomach a portion of the soil humic matter could become neutral or positively charged, due to acceptance of H^+ ions, and migrate towards the cathode. Why this appears to occur in only one out of the four fractionated samples is unclear, though it is likely to be due to a difference in the geochemistry of Sample 20 as a result of the significant contamination existing at the site.

Sample 24 showed a similar colloidal pattern to that observed in Samples 1 and 19, i.e. a clearly defined brown, fluorescent band in F1 and a slightly broader fluorescent band in F2. The pattern in the dissolved sub-sample was the same (but fainter) as that of the colloids. In the colloids all of the Cr migrated away from the injection well (Figure 7.11), with most residing in F2 (~1670 ng) and marginally less in F1 (~1500 ng). This distribution is mirrored in the dissolved sub-sample, with most Cr advancing to F2 (~160 ng) and a smaller amount reaching F1 (~90 ng). The colloidal Cr, as with Samples 1 and 19, is likely to be bound with relatively large humic substances, whilst that in the dissolved phase is bound to a smaller, less charged organic species.

The gel electrophoretic fractionation, following the stomach stage of the UBM, has shown that the majority of extracted Cr is associated with humic substances. In Samples 1, 19 and 24 the Cr is most likely to be Cr(III)-humic complexes, although it is less certain with respect to Sample 20 because of its more complex fractionation pattern.

shows a large peak at 2.6 minutes, followed by a smaller peak at 3.7 minutes. These peaks are smaller than that observed for mucin, which had a broad peak with a similar retention time, making differentiation of the two difficult. Other minor peaks were observed at 5.1, 9.9, 13.9 and 17.5 minutes, reflecting the heterogeneous nature of humic substances, in that there are several different humic species present.

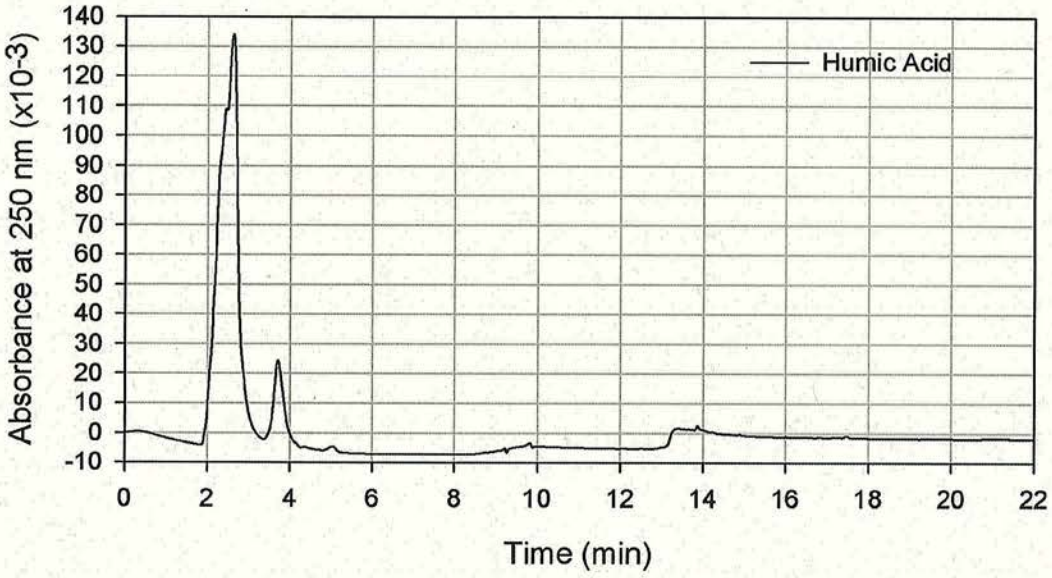

Figure 7.13 Chromatogram for the elution of the commercial humic acid reagent.

Sample 1 (Figure 7.14) shows a large peak in absorbance (0.502 abs) at 2.4 minutes, followed by a smaller peak (0.027 abs) at 3.8 minutes. It appears that the large 2.4 minute peak may be two unresolved species, given that a secondary peak rises briefly at 2.5 minutes. There are further minor peaks at 9.8 and 13.8 minutes. These four peaks form a similar elution pattern to that of the commercial humic acid (Figure 7.13), with similar retention times. There is no peak at 5.1 minutes, as seen for the commercial humic acid, but the chromatograms would not necessarily be exactly identical due to the variable nature of humic substances. There is no sign of a mucin peak, which, as shown previously had a broad peak at 3.9 minutes (abs 0.792) that was eluted between 2.2 and 7.5 minutes. This is strange as all samples contain mucin as it is a reagent in both the saliva and gastric bio-fluids. This may be a consequence of mucin (a protein) becoming denatured, or changed (i.e. binding to another species) in some way during the UBM extraction, thus affecting how/when it is eluted during analysis. The ICP-MS trace shows an ion count peak in *m/z* 52 at ~2.4 minutes (^{52}Cr being the principal Cr isotope, see Figure 7.14). The use of a collision cell removed

7.1.5.3 HPLC-ICP-MS

In addition to the gel electrophoretric fractionation, the samples were also analysed using a coupled HPLC-ICP-MS technique. The HPLC conditions were selected to resolve humic substances, as described in Section 4.9.3. Initially the nine individual organic reagents that make up the UBM bio-fluids were run through the HPLC system (at the concentration and pH stipulated by the stomach stage of the UBM) to determine their retention times/patterns (Figure 7.12). Eight out of the nine organic reagents produced only a minor response in the HPLC photo diode array (PDA). In fact the chromatograms produced for urea, bovine serum albumin, glucose, glucuronic acid, glucosamine hydrochloride, amylase, pepsin and uric acid could largely be attributed to instrumental noise given the very similar patterns produced. The only organic reagent that produced a response was mucin, with a large peak at 3.9 minutes.

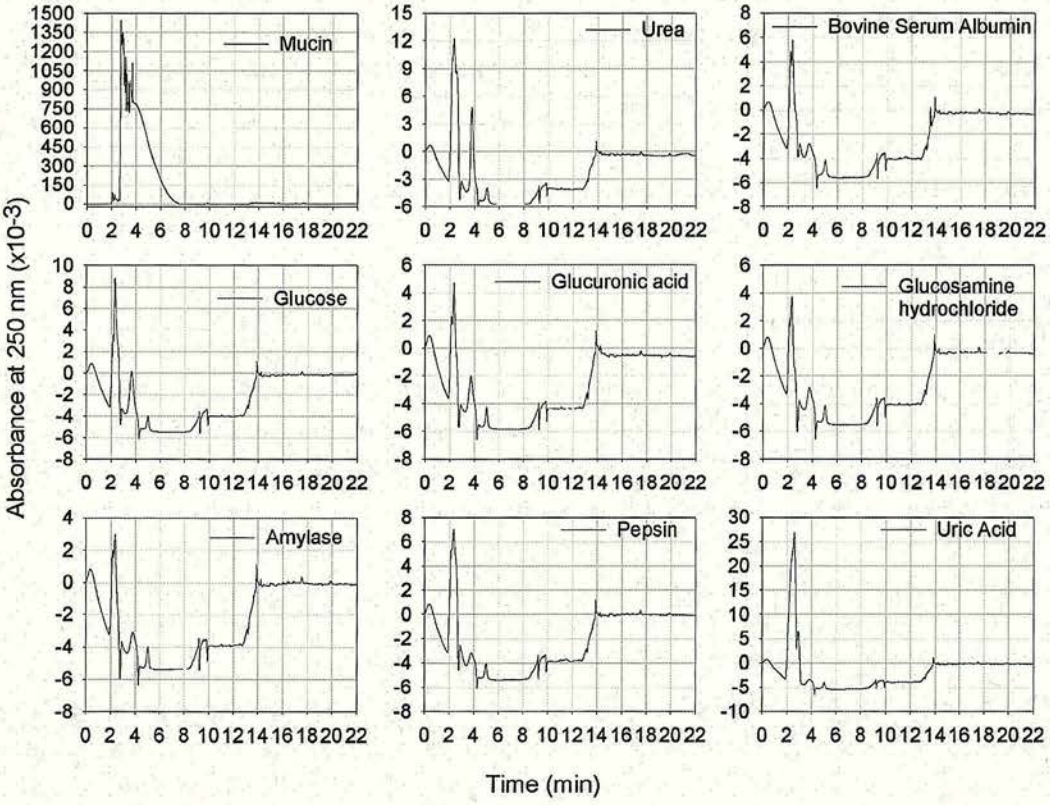

Figure 7.12 Chromatograms for the elution of the nine organic reagents used in the UBM bio-fluids.

A commercial humic acid (Fisher, UK) reagent was obtained with the aim of establishing a humic elution pattern. Assuming a TOC of 30% (the highest observed in the soils), 0.2 g of humic acid was dissolved in 22.5 ml of DI water, before adjustment of the pH to 1.2 – 1.7 with HCl. The resultant chromatogram (Figure 7.13)

the possibility of $^{40}Ar^{12}C^{+}$ contribution), which is consistent with the first (and largest) humic acid peak. Indeed, peaks in the PDA and the ICP-MS mirror each other well, rising from and peaking at the same point. The ICP-MS peak shows more tailing than that from the PDA. This suggests that the bioaccessible Cr in Sample 1 is bound to soil humic matter. The other peaks associated with humic acid do not have a corresponding peak in the *m/z* 52 trace, indicating that only one form of soil humic acid is responsible for binding Cr.

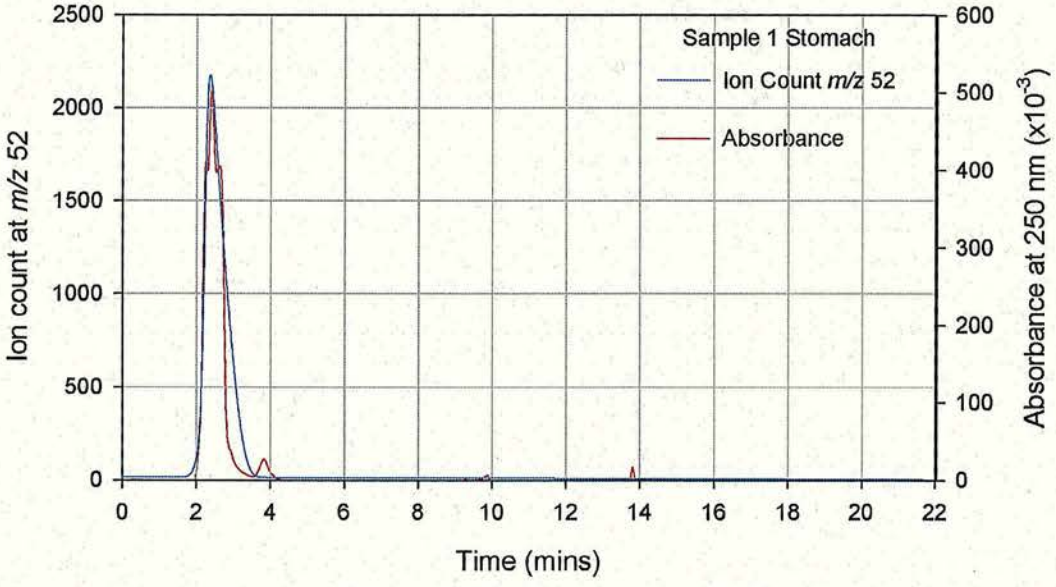

Figure 7.14 HPLC and ICP-MS chromatograms for Sample 1.

Similar observations were made for the other three samples (Figure 7.15), with the Cr peak eluting at the same time as the largest humic acid peak. The nature of the humic matter appears to vary between samples, as the ratios between PDA peaks at 2.4 and 2.5 minutes are different for each sample. This, once again, highlights the heterogeneity of soil humic substances. It is interesting that Sample 20, which produced a very different gel electrophoresis fractionation pattern from the other samples, produces a trace similar to the other samples. In fact the only difference exhibited by Sample 20 is the absence of a humic acid peak at ~3.8 minutes.

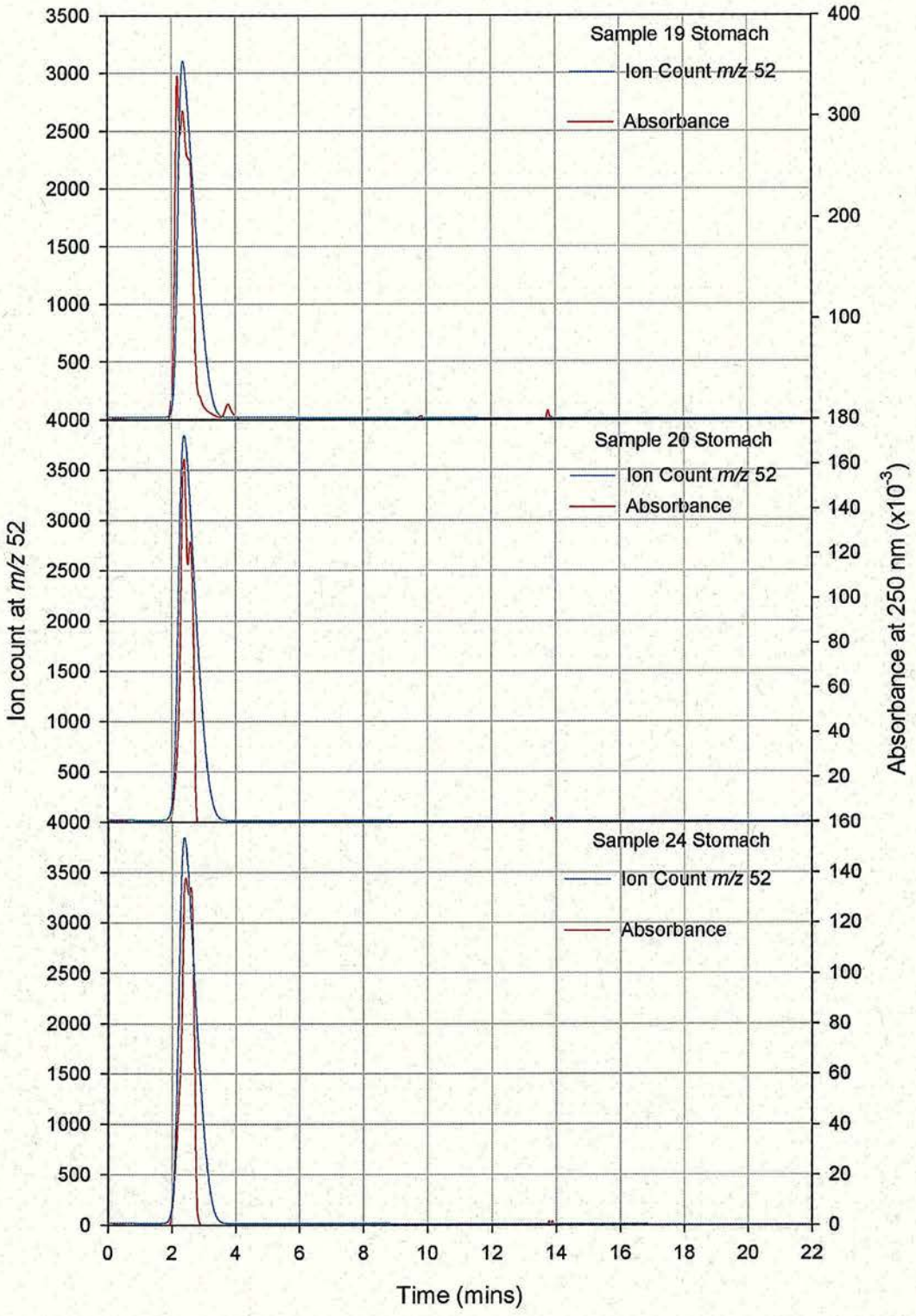

Figure 7.15 HPLC and ICP-MS chromatograms for Glasgow soil Samples 19, 20 and 24.

The HPLC-ICP-MS procedure was used to determine the Cr speciation quantitatively. Given that there was only one peak, therefore one Cr-containing species, was resolved by the HPLC-ICP-MS procedure for all four samples, quantitative speciation analysis

has become unnecessary. It was possible, however, to compare Cr bioaccessibility measured by the ICP-OES and HPLC-ICP-MS. It is shown (Table 7.4) in Samples 1 and 19 that the bioaccessible Cr is lower if determined by HPLC-ICP-MS compared with ICP-OES. The difference is slight, only 1.3 and 5 mg/kg out with the confidence limits associated with the ICP-OES determination, respectively. At the same time Samples 20 and 24 show a larger bioaccessibility when analysed by HPLC-ICP-MS, with recoveries of 114 and 118% relative to the ICP-OES data, respectively. These differences are most likely due to analytical problems encountered during the scaling up of the UBM to provide enough extract for both the HPLC-ICP-MS and gel electrophoretic methods. Due to time constraints the extraction could not be repeated during this section of work. This is also the reason why samples were analysed only once and not in duplicate.

Table 7.4 Recovery of bioaccessible Cr when the UBM solutions were analysed by HPLC-ICP-MS

Sample ID	Cr Bioaccessibility ICP-OES (mg/kg)	Cr Bioaccessibility HPLC-ICP-MS (mg/kg)	Recovery (%)
1	12 ± 1	9.7*	81
19	19 ± 1	13*	68
20	116 ± 2	132*	114
24	1156 ± 32	1369*	118

* n = 1

7.2 Solid Phase Source of Bioaccessible Fraction

To identify the physico-chemical sources of bioaccessible Cr, Pb and As in the Glasgow soils the CISED procedure was applied to the residual material collected from the UBM. The resolved components were included in the cluster analysis described in Section 6.2, thereby allowing a direct comparison between the solid phase distribution before and after the UBM. This allowed the physico-chemical phases from which bioaccessible Cr, Pb and As was lost to be identified. This procedure was applied to only certain samples, these being Samples 3, 19, 20, 24, 25 and 26, selected on the basis of their containing a large proportion of bioaccessible Cr, Pb or As.

7.2.1 Chromium

Before discussing these data, it should be noted that a sizeable experimental error was observed during the CISED extraction process. This is highlighted by a larger

apparent bioaccessibility obtained (calculated via a mass balance of CISED extractable Cr before and after the UBM, see Table 7.5) than the measured values in Table 7.1. This probably arises from problems encountered during application of the CISED procedure to the UBM residues. The residues contained more fine-grained or organic material, which blocked the centrifuge tube filter, resulting in the acid being in contact with the sample material for longer periods of time than would otherwise occur. Normally in the CISED method the acid is in contact with the soil for no more than 10 minutes, but, when processing the UBM residue, it could take several hours to go through the filter. This in turn could result in more material being leached, thus making it appear that a smaller proportion is bioaccessible.

Table 7.5 Comparison of UBM-measured Cr bioaccessibility and change in acid-extractable Cr before and after UBM.

Sample ID	Acid Extractable Cr pre-UBM (mg/kg)	Acid Extractable Cr post-UBM (mg/kg)	Difference (mg/kg)	UBM bioaccessibility (mg/kg)
3	36	24	12	7.0 ± 1.0
19	118	62	56	19 ± 1
20	2701	780	1921	1156 ± 32
24	517	260	257	116 ± 2
25	14	7.6	5.9	< 3
26	7.4	43	(-35)	< 3

n = 1

Figure 7.16 shows the change in Cr solid phase distribution as a result of the UBM scheme. It shows that all of the Cr in clusters C4, C7 and C11 was lost and, therefore, bioaccessible. Cluster C4 is made up of organic components, while clusters C7 and C11 consist of clay and bound-carbonate components. Cluster C7, as discussed in Chapter 6, was identified as the largest Cr-containing cluster, and it is therefore significant that all of its associated Cr (1788 mg/kg) was lost during the UBM. The other clay cluster, C8, was only partially dissolved by the UBM, with the loss of 32 (out of 117) mg/kg of Cr. The fact that organic cluster C4 appeared to be completely dissolved by the UBM supports the results of the speciation analysis (Section 7.1.5.2 and 7.1.5.3) that soil organic material (humic), capable of reducing Cr(VI), is also extracted by the UBM.

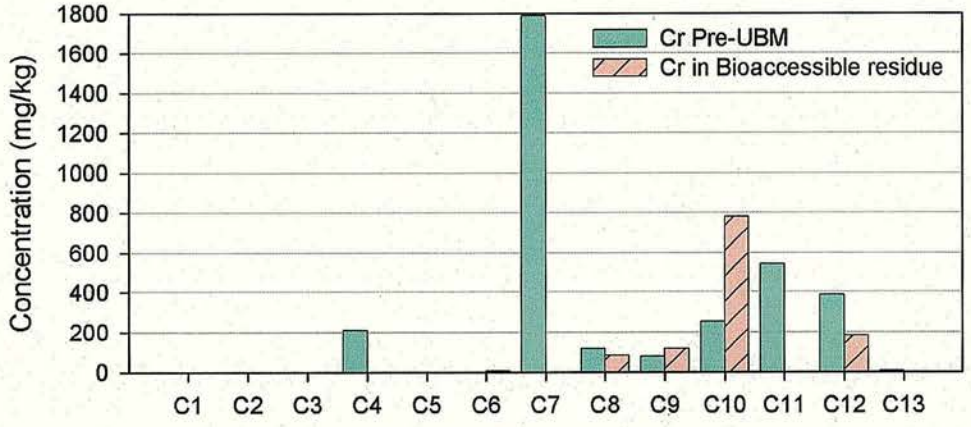

Figure 7.16 The change in solid phase distribution of Cr before and after UBM for selected soil samples.

All of the Cr in clusters C1 and C3 was also lost, but this constitutes only a small amount of Cr (3.5 and 0.7 mg/kg, respectively). It is not unexpected that the carbonate (C1) and exchangeable (C3) phases would be easily dissolved and bioaccessible in the acidic stomach.

Cluster C10 appeared to gain Cr during the UBM, rising from 255 to 779 mg/kg. This phenomenon mainly arises from two soils, Samples 20 and 24, which apparently contain 344 and 175 mg/kg more Cr in C10 after the UBM than before (Figure 7.17), possibly resulting from re-absorption of Cr by the Fe oxide phase during the extraction. In the case of Sample 20, for which the Cr content also increased in clusters C8, C9 and C12 (by 83, 11 and 115 mg/kg, respectively), the overall concentration of Cr gained is 553 mg/kg, which is approximately equal to that lost from C11 (543 mg/kg). Sample 24 lost 468 mg/kg of Cr during the UBM, of which 211 mg/kg was reabsorbed into clusters C6, C9 and C10. This leaves 257 mg/kg of bioaccessible Cr, notably more than the bioaccessibility measured in UBM (Table 7.1).

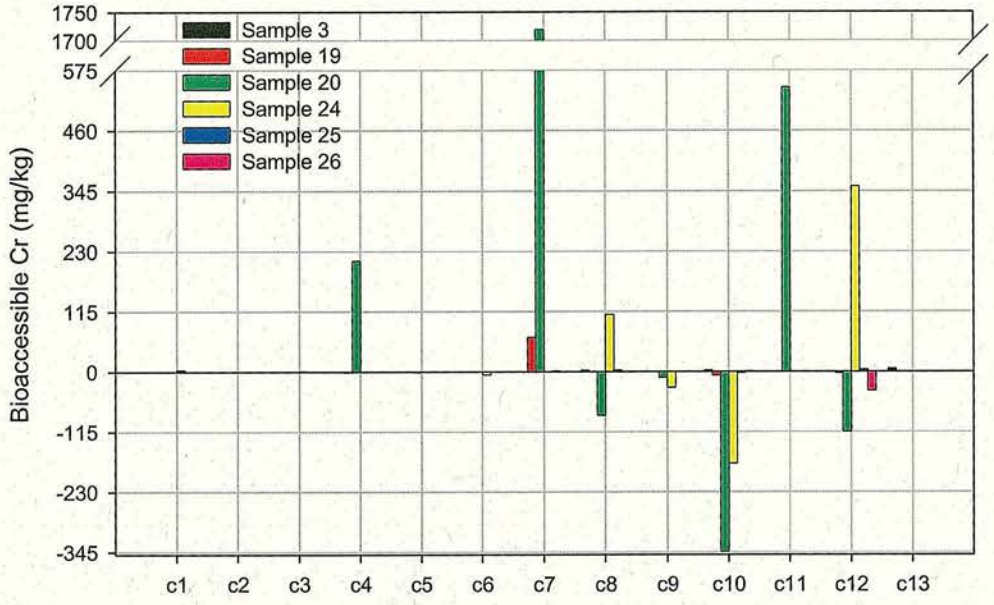

Figure 7.17 Solid phase distribution of bioaccessible Cr in the six selected soils, as measured with the CISED procedure.

It is expected that any Cr(VI) present in the soil will be bioaccessible, due to its well documented environmental mobility (Bartlett and Kimble, 1976; Kimbrough *et al.*, 1999; Kotás and Stasicka, 2000; Rowbotham *et al.*, 2000; DEFRA, 2002b; Geelhoed *et al.*, 2002). While the Cr in C4 and C11 appeared to be both entirely Cr(VI) and entirely bioaccessible (Section 6.3 & Figure 7.16), a relationship between Cr(VI) and bioaccessible Cr is not so clear (Figure 7.18). Both C8 and C9 show considerably less bioaccessible Cr than Cr(VI) content, which could be due to re-absorption, as previously discussed, as this would make the bioaccessible content appear lower. For example, in C8 (excluding Sample 20 due to its re-absorption of 83 mg/kg Cr), the Cr(VI) and bioaccessible Cr contents are approximately equal (117 and 115 mg/kg, respectively), suggesting that all of the Cr(VI) is bioaccessible.

Figure 7.18 Comparison of the solid phase distribution of total Cr, Cr(VI) and bioaccessible Cr in the six selected soils.

7.2.2 Lead

As Figure 7.19 shows, all of the Pb in clusters C1, C11 and C13 was lost during the UBM, showing they that contained bioaccessible Pb. Both C1 and C11 are clusters of carbonate components and, as such, would be expected to be unstable in the acidic conditions of the stomach. The complete dissolution of Pb from C11 is similar to that observed with Cr and is perhaps indicative of the complete dissolution of the C11 components during the UBM. Cluster C13, however, is composed of Fe-dominated components, which are expected to have a greater acid stability. It is therefore rather surprising that all of this Pb is bioaccessible. It is possible that Pb is being desorbed without the associated components being dissolved.

Clusters C7, C8 and C9 lost the majority of their Pb, with a portion remaining inaccessible. In the clay clusters, C8 (the largest Pb-containing cluster) and C7, ~85% of the associated Pb is bioaccessible, i.e. 1320 and 375 mg/kg of bioaccessible Pb, respectively. Meanwhile, the Mn oxide cluster C9 lost 811 mg/kg (~70% of the associated Pb) during the UBM. These observations are very different from those for Cr, as all of the Cr associated with C7 was bioaccessible. This indicates that the entire cluster is not dissolved during the UBM, in contrast to the exchangeable and carbonate clusters.

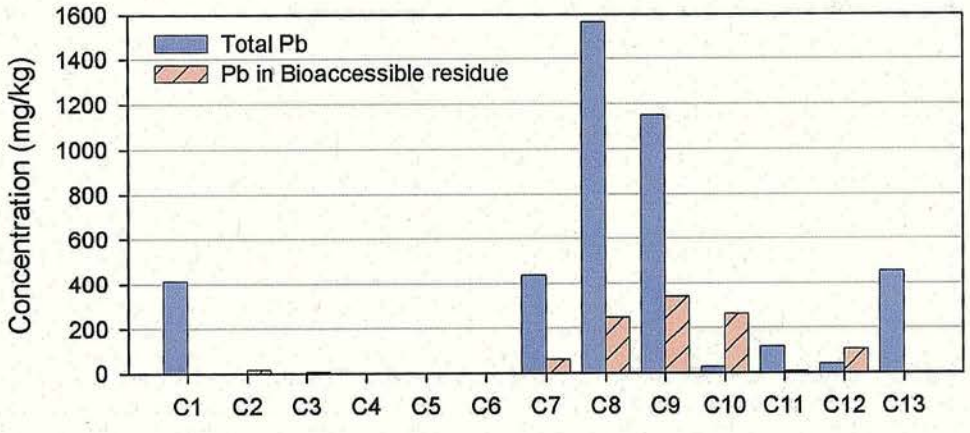

Figure 7.19 The change in Pb solid phase distribution before and after UBM for selected samples.

As with Cr, the Pb content of cluster C10 increased during the UBM. It increases by 235 mg/kg, although this is mainly due to two Samples, 3 and 26, which probably re-absorbs 144 and 68 mg/kg, respectively. C12 also shows an increase, from 37 mg/kg to 105 mg/kg.

7.2.3 Arsenic

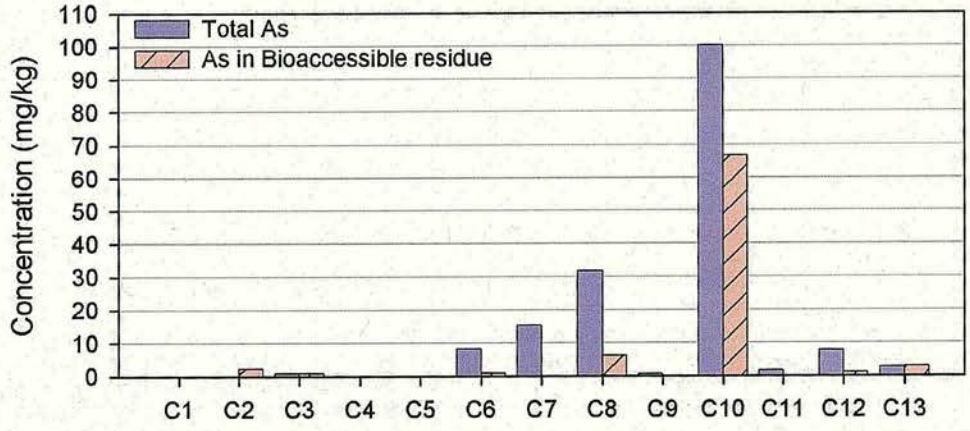

Figure 7.20 The change in As solid phase distribution before and after UBM for selected samples.

As Figure 7.20 shows, all of the As in clusters C7, C9 and C11 was lost during the UBM and is therefore deemed bioaccessible. As previously discussed, C11 consists of carbonate clusters and, as such, is expected to dissolve during the acidic stomach stage. The clay cluster C7 lost all the As present (15 mg/kg) in addition to all of the

Cr, unlike Pb, of which a small portion remained inaccessible. Arsenic was the only element of the three that was entirely bioaccessible in the Mn oxide cluster C9.

Unlike Pb, the As associated with the Fe-dominated cluster C13 was inaccessible. The As associated with C3 also appeared inaccessible, despite this cluster consisting of exchangeable components. It is likely that this observation is simply an artefact (or error) of the resolution algorithm, as the concentrations involved are very small, i.e. the As content of C3 is only 0.9 mg/kg both before and after the UBM. Most of the As in C6 (organic), C8 (clay) and C12 (Fe dominated) was bioaccessible, with the loss of 7.4, 26 and 6.9 mg/kg, respectively, during the UBM. In the largest As-containing cluster, C10 (Fe-dominated), the majority of As was in an inaccessible form, with only 34 (of 100) mg/kg being lost. In contrast, C10 absorbed more Cr and Pb during the UBM.

7.3 Chomium Inhalation Bioaccessibility

As Cr(VI) is a known lung carcinogen, the inhalation bioaccessibility of Cr was determined in three selected soil samples. These soils, Samples 20, 22 and 24, were selected based on their high oral bioaccessibility, Cr(VI) content and the geographical location (close to a major future road building programme, which could cause significant land disturbance). Sample 19 was not selected despite having the third highest oral bioaccessibility because of the difficulty in collecting a large sample mass (required to isolate enough <10 μm soil fraction) as a result of the gravelly nature of the soil. The total concentration of Cr in the <10 μm and inhalation bioaccessibility after 24 and 672 hours is shown in Table 7.6.

The extraction profile for Sample 20 (Figure 7.21) shows a rapid initial increase in the amount of Cr leached. After 24 hours a total of 296 ± 32 mg/kg of Cr was removed from the soil, which continued to increase slowly over the next 27 days, to a final concentration of 330 ± 36 mg/kg. Any material that remains undissolved in the lung will eventually be removed, carried back up the trachea by the cilia into the mouth, where it will be either expelled from the body (e.g. coughing/sneezing or spitting) or swallowed (Wragner, 1980). This means that any material that is not bioaccessible in the lung is likely to be exposed to the much more extreme conditions of the gastro-intestinal environment. For this reason the residual material from the lung simulation (after 672 hr) was taken though the UBM as well. In the case of Sample 20, no

detectable Cr (<3 mg/kg) was extracted by the UBM from the residual <10 μm soil. This shows that, following the lung simulation, the remaining Cr (~1730 mg/kg) is present in particularly acid-stable forms that are unaffected by the UBM.

Table 7.6 Cr Inhalation bioaccessibility in three selected soil samples

Sample ID	Total Cr in <10μm fraction (mg/kg)	Cr bioaccessibility after 24hr (mg/kg)	Cr bioaccessibility after 672hr (mg/kg)	Cr(VI) bioaccessibility after 24hr (mg/kg)
20	2062 ± 170	296 ± 32	330 ± 36	18 ± 4
22	310*	21 ± 7	39 ± 10	N/A
24	297 ± 3	23 ± 10	41 ± 12	13 ± 3

*run without duplicate due to lack of sample

Samples 22 and 24 also show rapid increases in the first 24 hours, but then a further gradual increase relative to Sample 20, approximately doubling in bioaccessibility over the next 27 days (Figure 7.21). It is possible that the bioaccessible Cr listed for Samples 22 and 24 in Table 7.6 is misleading, because Cr was above the detection limit in only one extract for each of these two samples. This means that the majority of the bioaccessible Cr reported in Table 7.6 results from the cumulative addition of the 3.0 ± 3.0 mg/kg value assigned to below detection limit extracts, as outlined above. Therefore, the 39 ± 10 and 41 ± 12 mg/kg bioaccessible fractions assigned to Samples 22 and 24 should be considered more a maximum possible bioaccessibility. Following the lung simulation, both sample residues were processed with the UBM, where a further 11 (no duplicate analysed) and 53 ± 2 mg/kg of Cr was extracted for Samples 22 and 24, respectively. This gives an overall Cr bioaccessibility (via inhalation and ingestion) for the inhaled dust of 50 ± 10 and 94 ± 12 mg/kg for Samples 22 and 24, respectively.

The Cr(VI) bioaccessibility was measured using the DPC colorimetric method (Section 4.6). This showed that, of the 296 ± 32 mg/kg of bioaccessible Cr in Sample 20, 18 ± 4 mg/kg was in the form of Cr(VI). In the case of Sample 24, approximately a half, 13 ± 3 mg/kg, of bioaccessible Cr was Cr(VI). While the Cr(VI) bioaccessibility is much less than the total Cr bioaccessibility, Cr(VI) is a known lung carcinogen (ATSDR, 2000; DEFRA, 2002a). Thus the fact that dust from these sample sites is able to deposit Cr(VI) into the lung environment is an important result.

The bioaccessible Cr(VI) content of Sample 22 was not measured due to time constraints.

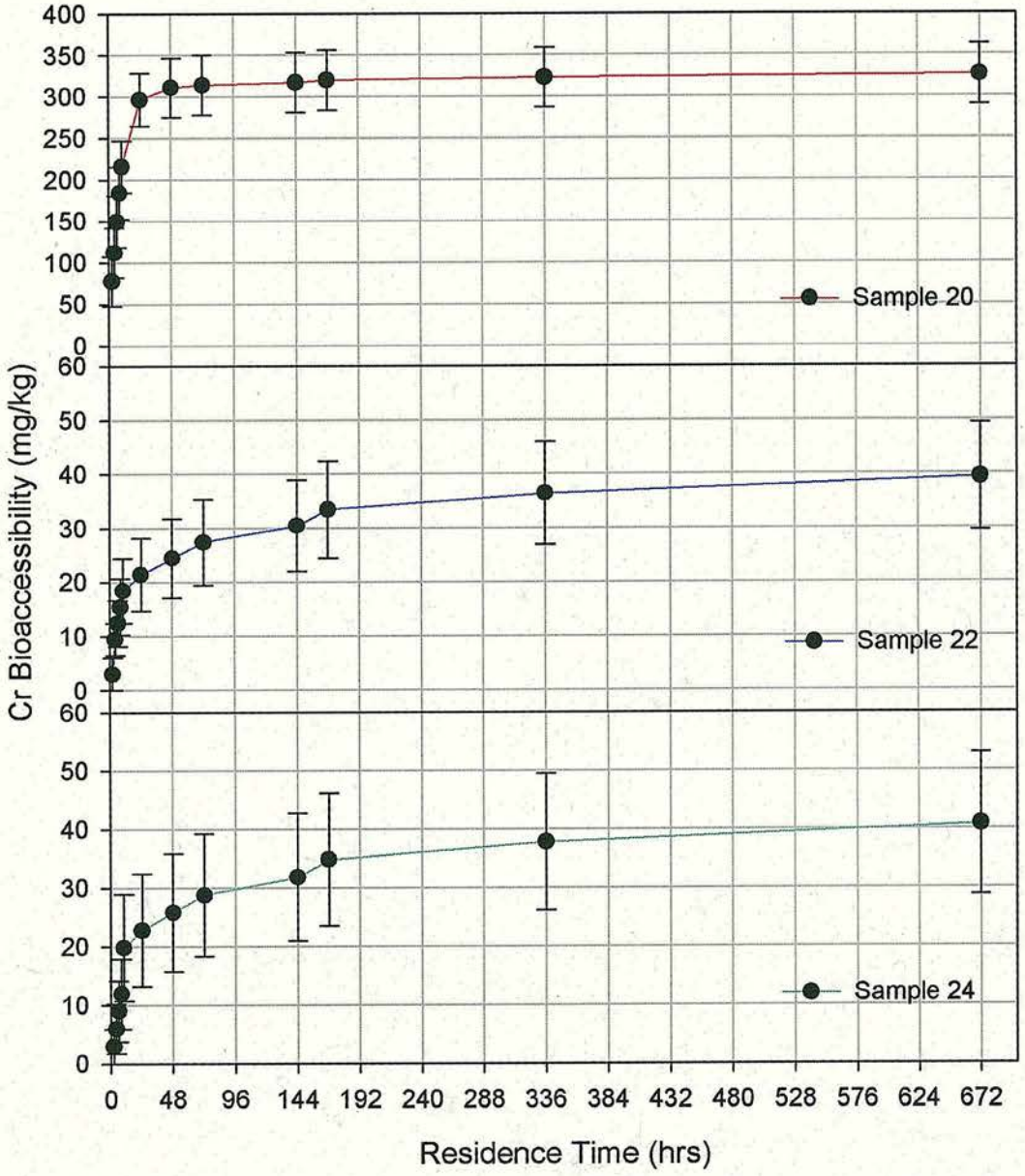

Figure 7.21 Cr extraction profiles in the lung simulation for the three selected Glasgow soil samples

As with the UBM extracts, the Cr speciation in the lung simulation was further investigated using a gel electrophoresis technique. Due to time constraints this was performed only on the Sample 20 extracts. Two time extracts were fractionated, those at 2 and 24 hours, since after 24 hours almost all the bioaccessible Cr was extracted. In the colloidal sub-sample (3 kD – 0.2 μm) fluorescent bands were observed in F3 and F4, whereas in the dissolved phase (<3 kD) a sharp fluorescent band was present

in F1. The 2 and 24 hour extracts showed exactly the same fluorescent bands. All the Cr in the colloids migrated from the gel well towards the anode (Figure 7.22) and was present in fractions F1 to F8. The Cr content of the 2-hour extract peaked in F3 before declining again. The same trend was observed for the 24-hour colloidal extract, except that the Cr contents in F3 and F4 were much larger (108 and 72 ng compared with 87 and 45 for the 2 hour extract). The Cr content in the other bands remained roughly the same. In the 2-hour dissolved sub-sample the Cr content peaks in F2, while in the 24-hour sample dissolved Cr is highest in F1. The range of Cr masses observed in the dissolved sub-sample differs little between the 2-hour (21 – 66 ng Cr) and 24-hour (12 – 66 ng Cr) extracts.

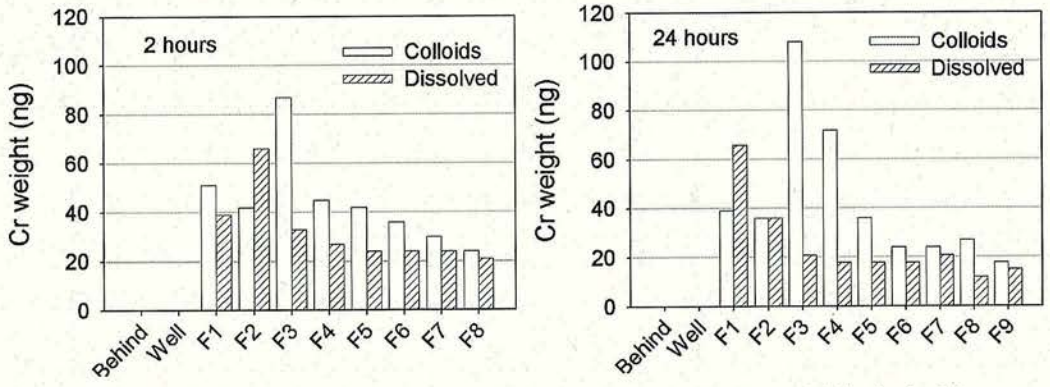

Figure 7.22 The weight of Cr in each gel electrophoretic fraction (0.5 cm width) obtained from tangential-flow ultrafiltered lung extract for Sample 20, 2 hours and 24 hours.
Size fractions: 3kD – 0.2μm (colloid) and <3kD (dissolved)

The colloidal bands in F3 and F4 are likely to be humic substances leached from the soil, as they are not present if a reagent blank is fractionated. In contrast, as the F1 band observed in the dissolved sub-sample is also present in the reagent blanks, it is an organic component of the simulated lung fluid. Therefore, it can be concluded that the majority of Cr in the colloidal sub-samples, at both 2 and 24 hours, is present as a Cr(III)-humic complex. In contrast, the Cr in the dissolved sub-sample is mostly present in a Cr(III)-organic complex, where the organic species originates from the simulated lung fluid and not the soil. The fact that Cr is observed in the dissolved sub-sample, migration into fraction F8/F9 could signify the presence of an unbound Cr species. This could be a chromate, which, having remained unbound to an organic species, has not been reduced to Cr(III).

7.4 Summary

- The oral bioaccessibility of Cr, Pb and As was generally much less than the total concentration, averaging 5, 52 and 27 % of the total, respectively. The Cr bioaccessibility compares well with the soil Cr(VI) concentration.

- The major soil physico-chemical phases responsible for the oral bioaccessible Cr were identified as organic, clay and a specific carbonate phase found only in Sample 20. The major sources of Pb were identified as carbonates, clays, Mn oxide and Fe oxide phases, whereas, for As, soil, organics, clays and Fe oxide phases were important.

- Chromium(VI) was reduced in the UBM stomach simulation, through a combination of low pH and soluble organic matter, to Cr(III). Evidence of soluble Cr(III)-humic complexes was found in the stomach stage of the UBM.

- Dust collected from three sites was found to have Cr in a form that was bioaccessible in the lung simulation. The majority of the inhalation bioaccessible Cr was in the form of Cr(III)-humic and Cr(III)-organic complexes, but a minor component was present as Cr(VI).

CHAPTER 8 DISCUSSION AND HUMAN HEALTH RISK ASSESSMENT

To better understand and interpret the Cr, Pb and As bioaccessibility data reported in Chapter 7, it is important (Cave *et al.*, 2002) to relate it to the total concentrations and solid phase distribution of Cr, Pb and As presented in Chapters 5 and 6, respectively. This was achieved using a multiple linear regression approach to model the bioaccessibility.

8.1 Bioaccessible Chromium Relationships

8.1.1 Multiple Linear Regression of Chromium Bioaccessibility with Intrinsic Soil Constituent Chromium Distribution

In Chapter 5, a predictive modelling approach based on the CISED algorithm (Cave *et al.*, 2004) was used to determine the intrinsic soil constituents (ISC) of the Glasgow soils. Thirteen ISCs were identified, along with the concentration of Cr associated with each. A stepwise multiple linear regression method was used to determine whether the Cr associated with each of these ISCs could be used to model Cr bioaccessibility. In the approach used (Section 4.14.5) the Cr content of each ISC was used as possible predictor values.

The model produced by the multiple linear regression analysis is shown in Figure 8.1. Five of the 13 identified ISCs were found to be significant in predicting the Cr bioaccessibility, these being ISC3, ISC6, ISC7, ISC8 and ISC13. These ISCs were identified in Section 5.4.2.1 as natural humus, clay, clay, natural humus and carbonate soil constituents, respectively. The model (Equation 8.1) places a large emphasis on ISC13, with approximately a third of the Cr associated with this constituent being deemed bioaccessible. As was discussed in Chapter 5, ISC13 is a carbonate constituent found in five of the 27 collected soil samples and made up a large amount of Sample 20. It was proposed in Section 5.4.2.2 that ISC13 was derived from COPR waste material. Thus it appears that Cr originating from COPR waste disposal is in a highly bioaccessible form. Indeed, in total (sum of all soils) ISC13 accounts for 1279 mg/kg of bioaccessible Cr. The model also shows that ~13% of Cr associated with ISC8 is bioaccessible, which relates to ~40 mg/kg of Cr. This makes the natural humus constituent the second largest source of bioaccessible Cr, after ISC13. ISC8

was found to be present in all samples that had a detectable Cr bioaccessibility. The other humus constituent included in the model, ISC3, accounts for very little bioaccessible Cr in comparison to ISC8, with only 1% of its associated Cr appearing to be bioaccessible. Both clay constituents, ISC6 and ISC7, were also identified as significant predictors of Cr bioaccessibility. In Chapter 5, ISC7 was recognised as an important source of Cr in the majority of the Glasgow soils, being much more common than ISC13. Therefore, despite only 3% of the associated Cr appearing bioaccessible, ISC7 accounts for ~33 mg/kg of bioaccessible Cr in total (sum of all samples). In comparison, ISC6 has less associated Cr (Section 5.4.2.2), of which ~6% is bioaccessible.

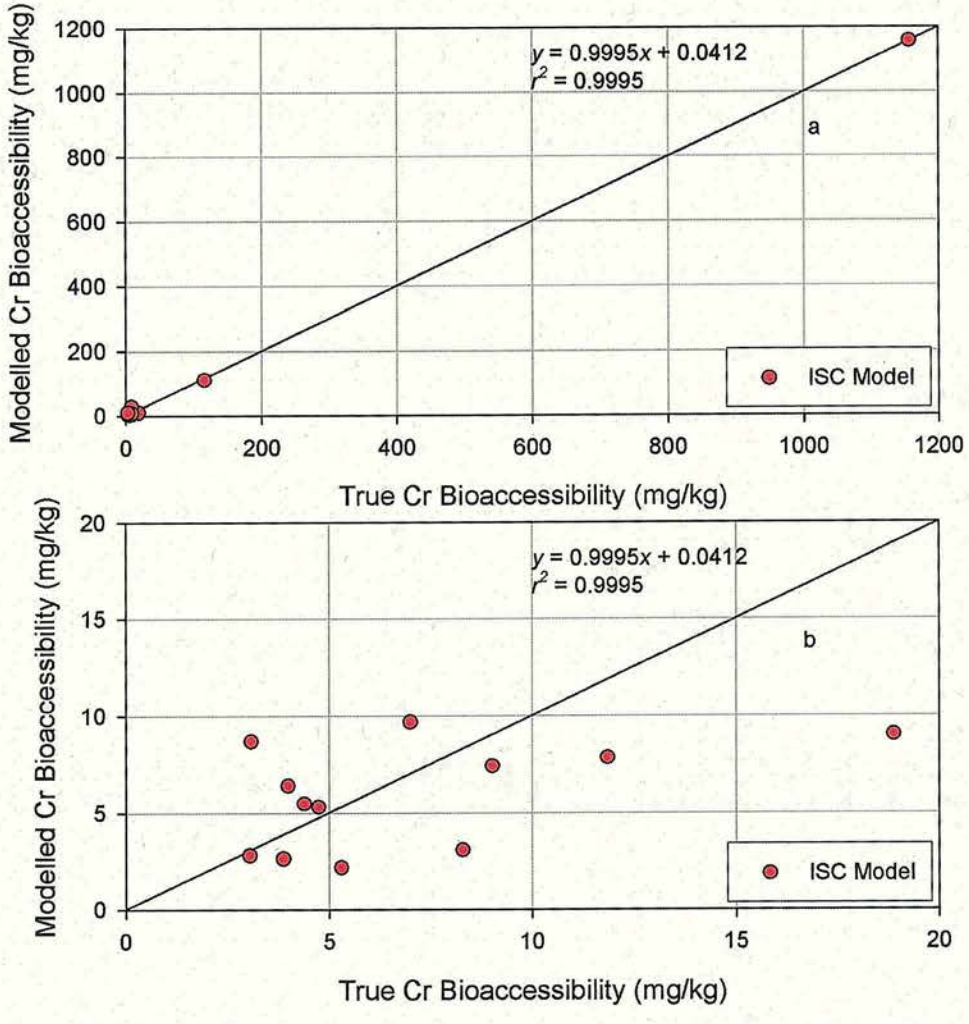

Figure 8.1 Soil Cr Bioaccessibility modelled with the Cr associated with identified ISCs. Graph b is an enlargement of <20 mg/kg section of graph a. RMSE = 6.2 mg/kg

$$Cr_{Bio} = 0.0117ISC3 + 0.0574ISC6 + 0.0325ISC7 + 0.1278ISC8 + 0.3325ISC13 + 0.0023$$

Equation 8.1 Model predicting the bioaccessibility of Cr in the Glasgow soils using the Cr distribution among the identified ISCs.

It can be seen that, for soils with a measured bioaccessible Cr content <20 mg/kg, the model does not fit the 'true' data very well (Figure 8.1). This is highlighted by a root mean square error (RMSE) of 6.2 mg/kg, which makes a considerable difference to samples with a low bioaccessibility. The model outlined in Equation 8.1 only provides a first order estimate of the likely sources of bioaccessible Cr in the Glasgow soils. The relatively large RMSE, and the difficulty fitting the model to all soils, is likely to be an indication that other mechanisms are involved in determining Cr bioaccessibility. To ascertain whether this is the case, an interaction stepwise multiple linear regression was performed, thus determining if a combination of certain constituents exerted a greater influence over Cr bioaccessibility than a single constituent. The interaction effects were generated by multiplying the Cr content of two existing ISCs together (i.e. the Cr content of ISC2 and ISC3 in Sample 1 is 9.3 and 3.4 mg/kg, respectively, yielding an interaction effect of 9.3 x 3.4 = 32). This was continued until all constituents had been cross-multiplied to form a new set of predictor values for use in the multiple linear regression programme (Wragg, 2005). The resulting model is shown in Figure 8.2 and Table 8.1.

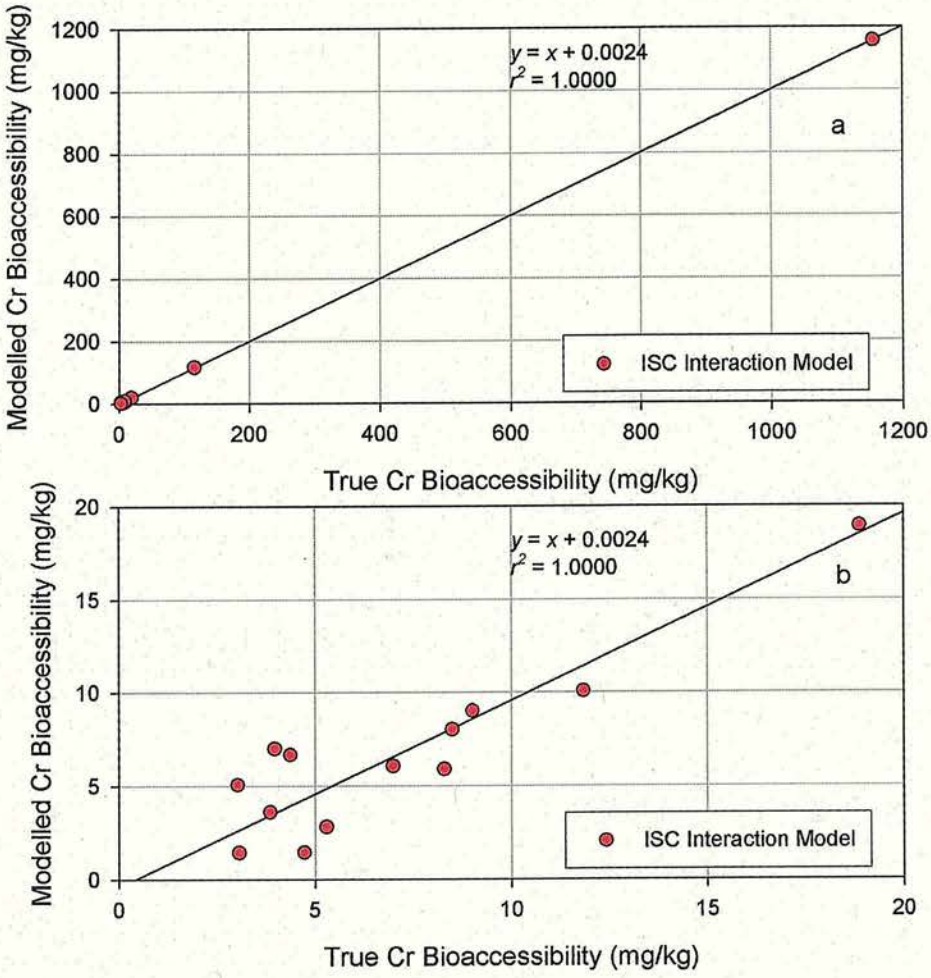

Figure 8.2 Soil Cr Bioaccessibility modelled with the Cr associated with identified ISCs, including interactions between ISCs.

Graph b is an enlargement of the <20 mg/kg section of graph a. RMSE = 1.7 mg/kg.

Table 8.1 Coefficients and intercept for the interaction ISC model of Cr bioaccessibility

ISC name	ISC assignment	Original / Interaction predictor	Model coefficient
ISC7	Clay (Fe)	Original	0.0374
ISC3 vs ISC13	Humus vs Carbonate (Fe)	Interaction	0.0170
ISC5 vs ISC8	Quartz vs Humus	Interaction	0.0090
ISC7 vs ISC13	Clay (Fe) vs Carbonate (Fe)	Interaction	0.0001
ISC8 vs ISC13	Humus vs Carbonate (Fe)	Interaction	0.0146
Model Intercept =	1.0793		

Only one predictor term from Equation 8.1 features in the new model (Table 8.1), that being ISC7. This means that a better predictive model is produced when the

interactions of ISC3, ISC6, ISC8 and ISC13 are considered, as opposed to the individual constituents. There are four significant interaction constituents identified by the model, three of which involve ISC13. The result is a predictive model that fits the true bioaccessibility data much better than Equation 8.1. When interaction constituents are included, the RMSE is reduced to 1.7 mg/kg, which is highlighted by the improved fit for samples with a Cr bioaccessibility < 20 mg/kg (Figure 8.2).

The interaction model suggests that ISC13 interacts with several other soil constituents. The most important of these is ISC8, which accounts for ~1146 mg/kg of bioaccessible Cr (sum of all samples). ISC13 also interacts with ISC3 and ISC7 to contribute in total ~89 and 51 mg/kg of bioaccessible Cr, respectively. It is believed that the mechanism by which these soil constituents interact to release the Cr associated with ISC13 is the same. ISC3, ISC7 and ISC8 all contain P in various amounts (5021, 34718 and 2522 mg/kg, respectively) whereas ISC13 contains none. It is believed that HPO_4^{2-} from these ISCs releases Cr from ISC13 via an ion exchange mechanism with CrO_4^{2-}. The ability of HPO_4^{2-} to exchange with soil CrO_4^{2-} has been previously observed (James and Bartlett, 1983) and is used in routine methods to measure exchangeable Cr. The mechanism of HPO_4^{2-} to enhance bioaccessibility though ISC interaction has also been observed for As (Wragg, 2005). The mechanism is also likely to explain the interaction between ISC5 and ISC8. ISC5 was identified (Section 5.4.2.2) as a quartz constituent with a small, but important, Cr and Cr(VI) content. This ISC was not included in the first model, but the interaction between it and phosphate-containing ISC8 results in a significant interactive constituent, accounting for a total of 51 mg/kg for bioaccessible Cr.

The RMSE obtained for the interaction model, 1.7 mg/kg (Figure 8.2), indicates that the uncertainty associated with this model is smaller than that associated with the simple model (6.2 mg/kg, Figure 8.1). The inclusion of the possible interactions that may be occurring between the identified ISCs has indicated the potential sources of bioaccessible Cr in the Glasgow soils. The slope of the regression line is 1, as is the r^2 value, although the low bioaccessibility samples do not fit the model perfectly. Despite this, the interaction model does appear to be a good predictor of the sources of bioaccessible Cr in the Glasgow soils. To check the robustness of the model a

cross-validation method was used. The method employed was described by Brereton (2003) and involved the following stages:

- Remove the predictor, interaction predictor and measured Cr bioaccessibility data for an individual sample from the interaction model and re-apply the multiple linear regression. Obtain the coefficients for the predictors and interaction predictors included and the intercept for the cross-validation interaction model.

- Replace the removed sample data into the cross-validation interaction multiple linear regression dataset and remove the interaction predictor and measured bioaccessible Cr data for the next soil.

- Re-apply multiple linear regression as before and obtain the coefficients for the predictors and interaction predictors included and the intercept as for the previous sample.

- Repeat the steps above until all of the samples have been individually excluded from the cross-validation interaction multiple linear regression.

- At each stage of the cross-validation, use the generated coefficients and intercept to predict the Cr bioaccessibility of the excluded sample.

- Plot the Cr bioaccessibility of the samples against the cross-validation predicted Cr values on the same plot as the original interaction model. This will give an indication of the robustness of the model. If the two data sets are plotted over one another with no major differences the original model is deemed to be robust.

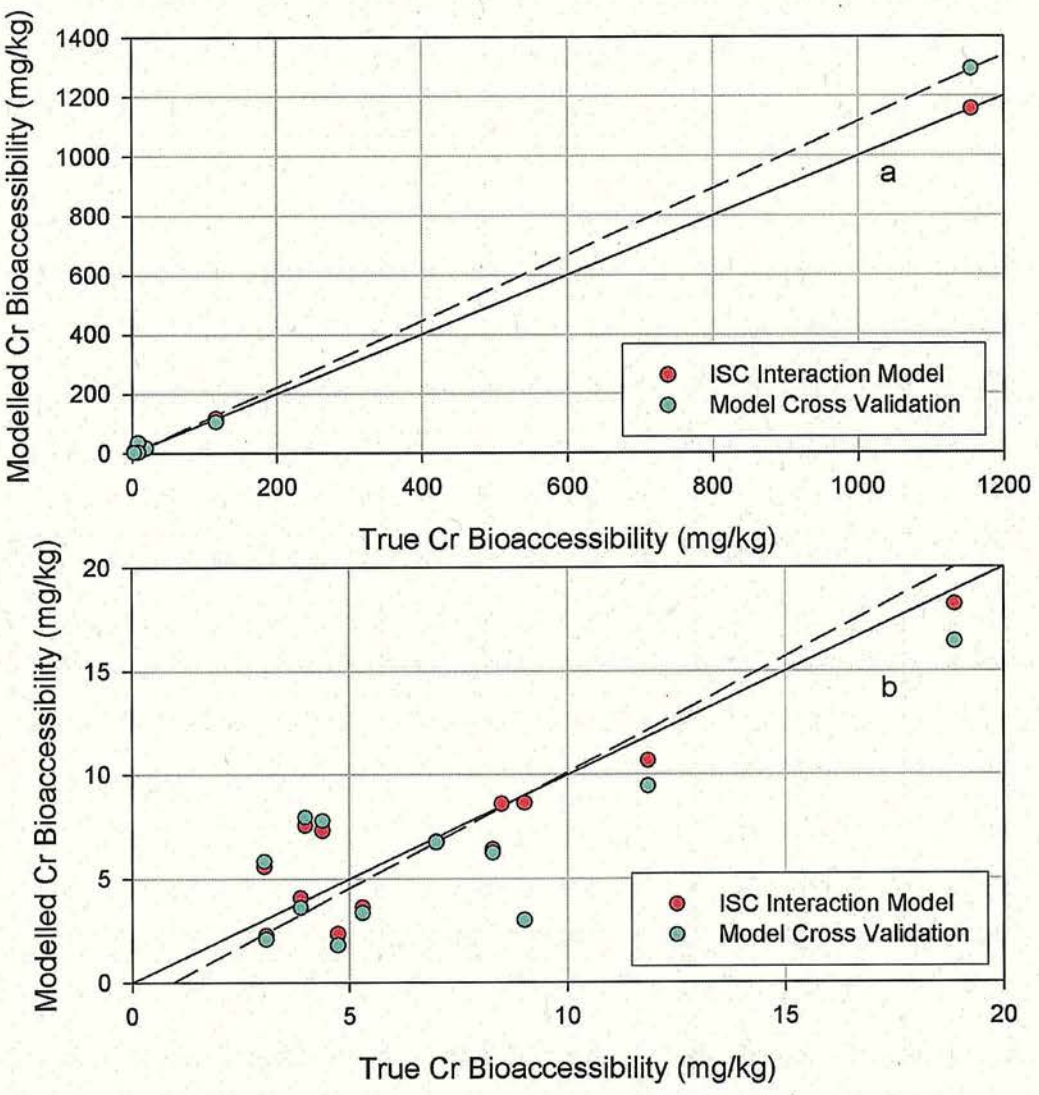

Figure 8.3 True vs modelled bioaccessible Cr for ISC interaction and cross-validation model. Graph b is an enlargement of the <20 mg/kg section of graph a.

Figure 8.3 shows that, generally, there are only small differences between the interaction and cross-validation models. The major exception to this observation is Sample 20, where the interaction model predicts a Cr bioaccessibility of 1156 mg/kg compared with the cross-validation value of 1290 mg/kg (true Cr bioaccessibility 1156 ± 32 mg/kg). The difference observed between the two models for Sample 20 is not unexpected. It is clear, from the results presented in Chapters 5, 6 and 7, that Sample 20 has a very different geochemistry to that of the other 26 samples studied in this work. There is also a problem with the cross-validation prediction of Sample 21 Cr bioaccessibility, which is 35 mg/kg compared with the interaction model

prediction of 8.6 mg/kg (true bioaccessibility 8.5 ± 2.5 mg/kg). There is very little difference between the interaction model and the cross-validation for the remaining 15 samples. The fact that there is a difference between the models for the outlying Sample 20 means that the regression lines also differ, despite the similarity between the two data sets (Table 8.2). The similarity shown in Table 8.2 indicates that the original interaction model was a reasonable prediction of which Cr-bearing ISCs act as a source of bioaccessible Cr.

Table 8.2 Cr bioaccessibility in each sample as predicted by the interaction and cross-validation models

Sample ID	True Cr bioaccessibility (mg/kg)	Interaction modelled Cr bioaccessibility (mg/kg)	Cross-validation Cr bioaccessibility (mg/kg)
1	12 ± 1.0	11	9.4
3	7.0 ± 1.0	6.8	6.7
4	8.3 ± 1.0	6.4	6.2
5	3.0 ± 0.7	5.6	5.8
9	3.9 ± 0.7	4.1	3.6
12	5.3 ± 1.9	3.6	3.4
15	4.0 ± 0.3	7.6	8.0
16	4.4 ± 0.3	7.3	7.8
18	4.7 ± 0.7	2.3	1.8
19	19 ± 1	18	16
20	1156 ± 32	1156	1290
21	8.5 ± 2.5	8.6	35
22	9.0 ± 0.6	8.6	3.0
23	3.1 ± 0.6	2.3	2.1
24	116 ± 2	116	105

8.1.2 Multiple Linear Regression of Chromium Bioaccessibility with Intrinsic Soil Constituent Chromium(VI) Distribution

In addition to information on total Cr, the distribution of Cr(VI) among the identified ISCs was given in Chapter 5. This allows modelling of Cr bioaccessibility using a species the presence of which likely arises from anthropogenic sources, thus possibly providing a better predictor species. The Cr(VI) interaction model (Figure 8.4) has a similar RMSE to that when total Cr is used. In fact the outcomes of the two models are very similar, with all but one of the same ISCs and ISC interactions being deemed significant in predicting Cr bioaccessibility (Table 8.3). The interaction between the Cr(VI) content of ISC7 and ISC13 was not significant in predicting Cr bioaccessibility.

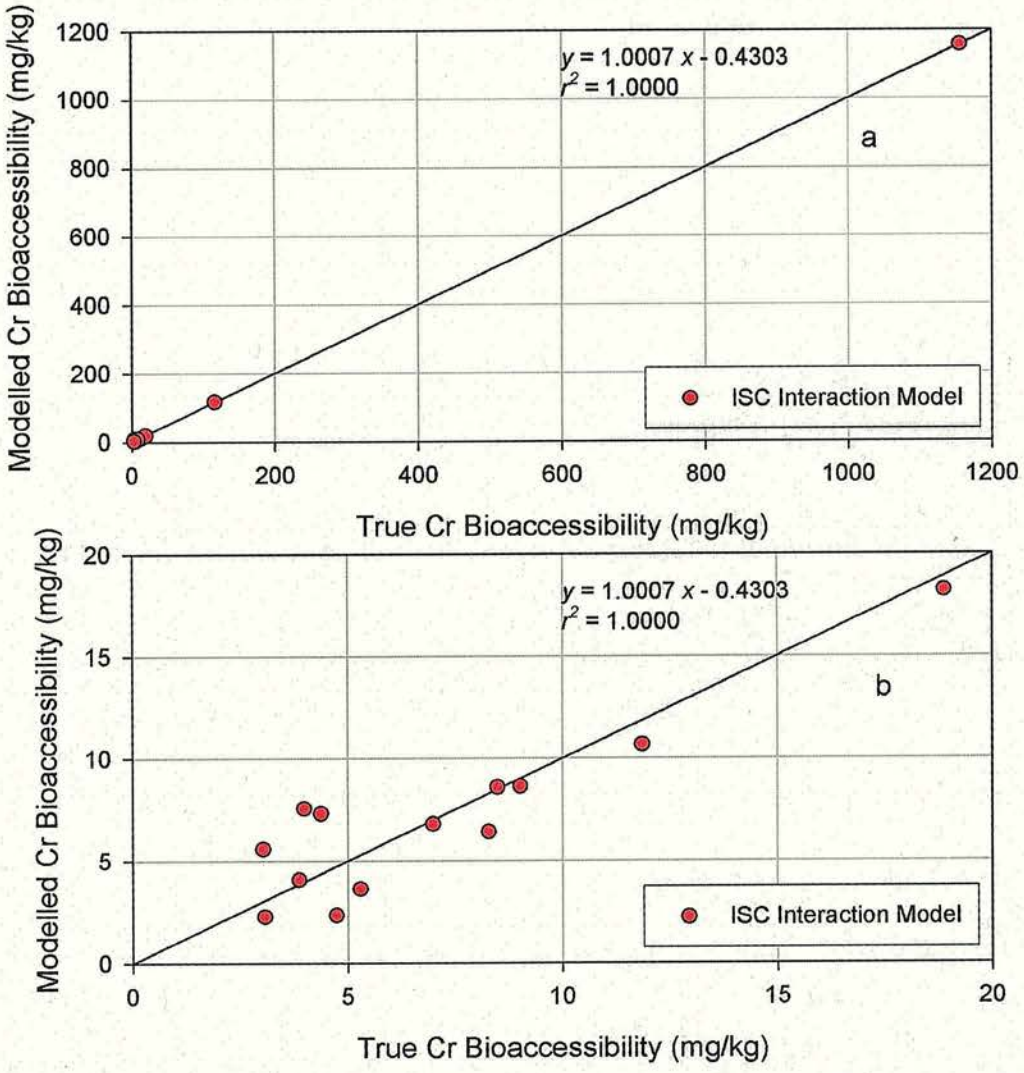

Figure 8.4 Soil Cr Bioaccessibility modelled with the Cr(VI) associated with identified ISCs, including interactions between ISCs.

Graph b is an enlargement of the <20 mg/kg section of graph a. RMSE = 1.8 mg/kg.

Table 8.3 Coefficients and the intercept for the Cr(VI) interaction ISC model of Cr bioaccessibility

ISC name	ISC assignment	Original / Interaction predictor	Model coefficient
ISC7	Clay (Fe)	Original	0.4841
ISC3 vs ISC13	Humus vs Carbonate (Fe)	Interaction	0.2644
ISC5 vs ISC8	Quartz vs Humus	Interaction	0.5616
ISC8 vs ISC13	Humus vs Carbonate (Fe)	Interaction	0.1856
Model Intercept =	0.0000		

The Cr(VI) interaction model seems to be a slightly more robust model of Cr bioaccessibility compared with the total Cr interaction model. Table 8.4 shows that the cross-validation model still has problems estimating the Cr bioaccessibility of Samples 20, 21 and 24, but the predicted bioaccessibility of the remaining 12 samples is closer to the true measured values than that for total Cr (Figure 8.5). This demonstrates that the bioaccessibility of Cr in the Glasgow soils more closely relates to the Cr(VI) soil concentration than to the total Cr. This would be anticipated given that any Cr(VI) present will have originated from an anthropogenic source.

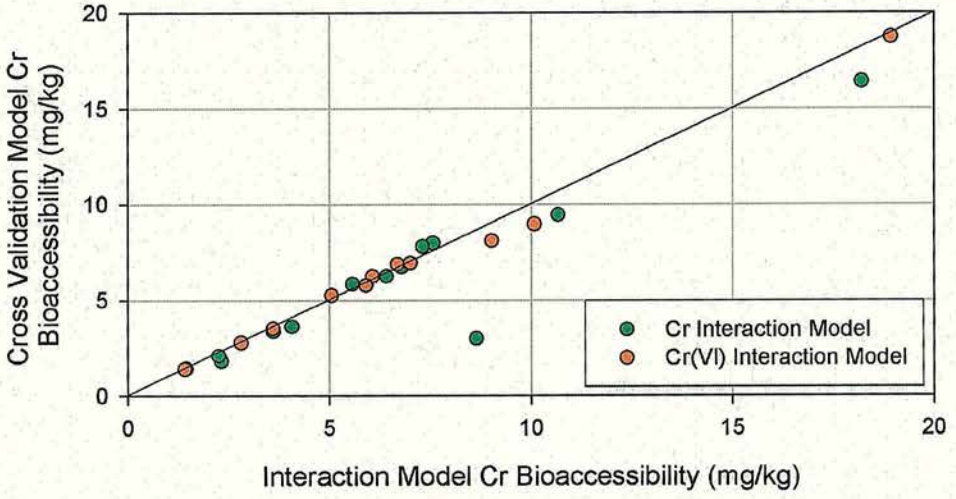

Figure 8.5 Comparison between the cross-validation of the Cr and Cr(VI) ISC interaction models for samples with a low bioaccessibility.
Line shows equivalence.

Table 8.4 Cr bioaccessibility in each sample as predicted by the Cr(VI) interaction and cross-validation models

Sample ID	True Cr bioaccessibility (mg/kg)	Interaction modelled Cr bioaccessibility (mg/kg)	Cross-validation Cr bioaccessibility (mg/kg)
1	12 ± 1.0	10	8.9
3	7.0 ± 1.0	6.1	6.2
4	8.3 ± 1.0	5.9	5.8
5	3.0 ± 0.7	5.1	5.2
9	3.9 ± 0.7	3.6	3.5
12	5.3 ± 1.9	2.8	2.8
15	4.0 ± 0.3	7.0	6.9
16	4.4 ± 0.3	6.7	6.9
18	4.7 ± 0.7	1.5	1.4
19	19 ± 1	19	19
20	1156 ± 32	1156	1290
21	8.5 ± 2.5	8.0	33
22	9.0 ± 0.6	9.0	8.1
23	3.1 ± 0.6	1.4	1.4
24	116 ± 2	116	105

8.1.3 Multiple Linear Regression of Chromium Bioaccessibility with Chromium Solid Phase Distribution

As with the identified ISC, the Cr distribution among the clustered physico-chemical components identified with the CISED procedure was used to model the Cr bioaccessibility. In this way it is possible to identify any connection between the solid phase distribution of Cr and its bioaccessibility. The model resulting from the multiple linear regression analysis is shown in Figure 8.6 and Equation 8.2. Six significant clusters of physico-chemical components were identified, those being clay clusters C7 and C8, Mn oxide cluster C9, bound carbonate cluster C11 and Fe oxide clusters C12 and C13.

The model suggests that all of the Cr associated with clusters C9 and C11 is bioaccessible. Cluster C11 contains components from Sample 20 only, accounting for 542 mg/kg of the 1156 mg/kg bioaccessible Cr. Interestingly, modelling for the soil Cr(VI) content with Cr solid phase distribution (Section 6.3) suggested that 100% of the Cr in this cluster was Cr(VI) as well. This shows that cluster C11 is very important in determining the high bioaccessibility observed in Sample 20. Cluster C9 is present in all but one of the samples (Sample 12) with a detectable Cr bioaccessibility. Components that make up C9 generally have a low Cr content (<3

mg/kg), with the exception of Samples 20 and 24 where 55 and 23 mg/kg of Cr are present, respectively. Given that both of these samples come from sites with a documented history of COPR waste disposal, the existence of Cr associated with Mn oxide soil components could be an indicator of anthropogenic Cr. As COPR does not contain any Mn mineralogy, this suggests that natural Mn phases with the soil are absorbing Cr released from the deposited waste.

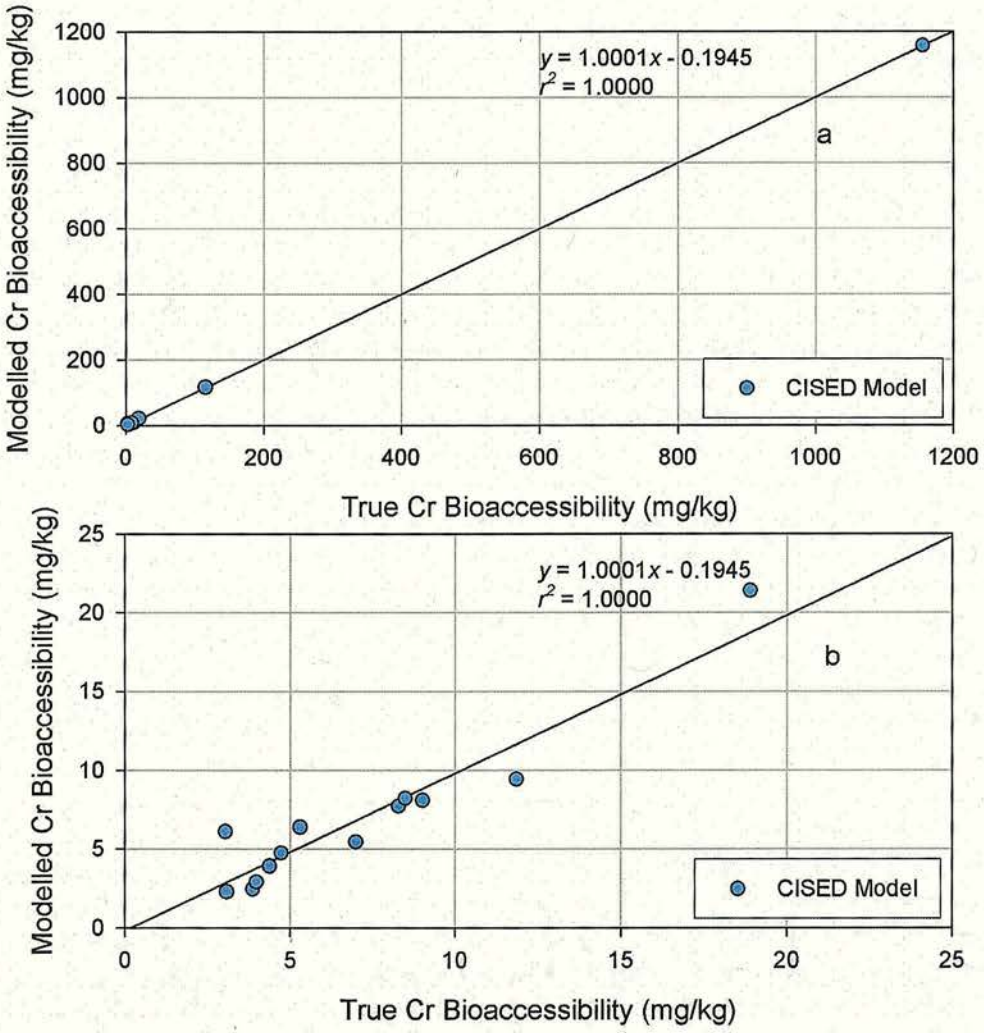

Figure 8.6 Soil Cr Bioaccessibility modelled with solid phase distribution of Cr within the Glasgow soils.

Graph b is an enlargement of the <25 mg/kg section of graph a. RMSE = 1.4 mg/kg

$$Cr_{Bio} = 0.3247C7 + 0.5047C8 + C9 + C11 + 0.0979C12 + 0.4912C13 - 0.0894$$

Equation 8.2 Model predicting the bioaccessibility of Cr in the Glasgow soils using the solid phase distribution of Cr.

The model also shows that 32 and 50% of the Cr associated with clay clusters C7 and C8 is bioaccessible, respectively. Section 6.3 showed that C7 contains more Cr than any other cluster. This is mainly due to Sample 20, where ~1720 mg/kg of Cr is associated with C7. Indeed 558 of the 1156 mg/kg of bioaccessible Cr found in Sample 20 are associated with this clay cluster. Cluster C7 also provides most of the bioaccessible Cr observed in Sample 19. For the remaining samples, very little (<4mg/kg) bioaccessible Cr comes from C7. Clay C8 accounts for 56 mg/kg of the bioaccessible Cr observed in Sample 24, but as it generally contains little Cr (Section 6.3), does not have a big impact in any other sample. The remaining bioaccessible Cr detected in Sample 24 is extracted from Fe oxide cluster C12, where ~10% of associated Cr is bioaccessible. The other Fe oxide cluster C13 is an important source of Cr in samples with a low Cr bioaccessibility. Approximately 55% of the bioaccessible Cr measured in Samples 1, 3 and 4 and ~80% in Samples 5, 12 and 21 comes from C13. In these samples C13 is either the largest, or second largest, Cr-containing cluster, which differentiates them from Samples 19, 20 and 24 (i.e. the samples with a high Cr bioaccessibility).

The CISED model was also validated using a cross-validation procedure, with the results shown in Figure 8.7. There was a very large discrepancy (~700 mg/kg) between the predicted Cr bioaccessibility in Sample 20 for the two models. Apart from this, the two models are very similar, with a RMSE of 3.8 mg/kg (excluding Sample 20). This highlights the differences in geochemistry between Sample 20 and the other Glasgow soils, in that accurate predictions cannot be made about Sample 20 based on what is observed in other samples. This is different from what is found with Sample 24, the second largest Cr (as well as Cr(VI) and bioaccessible Cr) containing sample, where accurate (± 12 mg/kg) predictions can be made. However, with the exception of this one outlying data point, the cross-validation seems to agree with the interaction model, showing that it is a reasonable prediction of Cr bioaccessibility in the Glasgow soils.

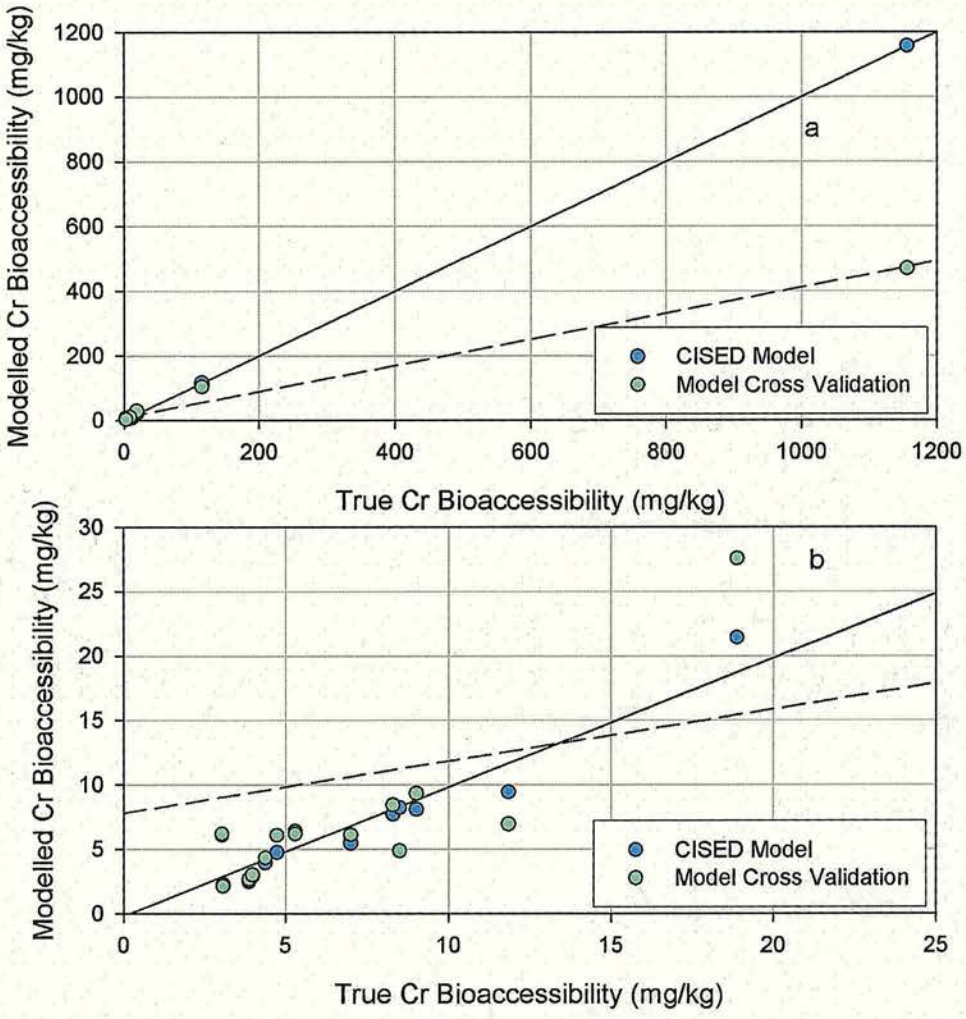

Figure 8.7 True vs modelled bioaccessible Cr for CISED and cross-validation model. Graph b is an enlargement of the <25 mg/kg section of graph a.

8.2 Bioaccessible Lead Relationships

8.2.1 Multiple Linear Regression of Lead Bioaccessibility with Intrinsic Soil Constituent Lead Distribution

Taking the same approach as in Section 8.1.1, Pb bioaccessibility was modelled using the Pb associated with each identified ISC (Figure 8.8). The initial model, which did not take into account any interactions between ISCs, identified four ISCs that were significant in predicting Pb bioaccessibility (Equation 8.3).

$$Pb_{bio} = 0.5705ISC2 + 0.1955ISC4 + C8 + 0.7233ISC11 - 62.33$$

Equation 8.3 Model predicting the bioaccessibility of Pb in the Glasgow soils using the Pb distribution among the identified ISCs.

The most important ISC identified was ISC11, a natural humus constituent that contains more Pb than any other resolved ISC (Section 5.4.2.3). The multiple linear regression suggests that ~70% of the Pb associated with this ISC is bioaccessible, accounting for an average of ~370 mg/kg of bioaccessible Pb per sample. In addition, another humus ISC was identified as a significant predictor, showing the importance of soil organic matter as a source of bioaccessible Pb.

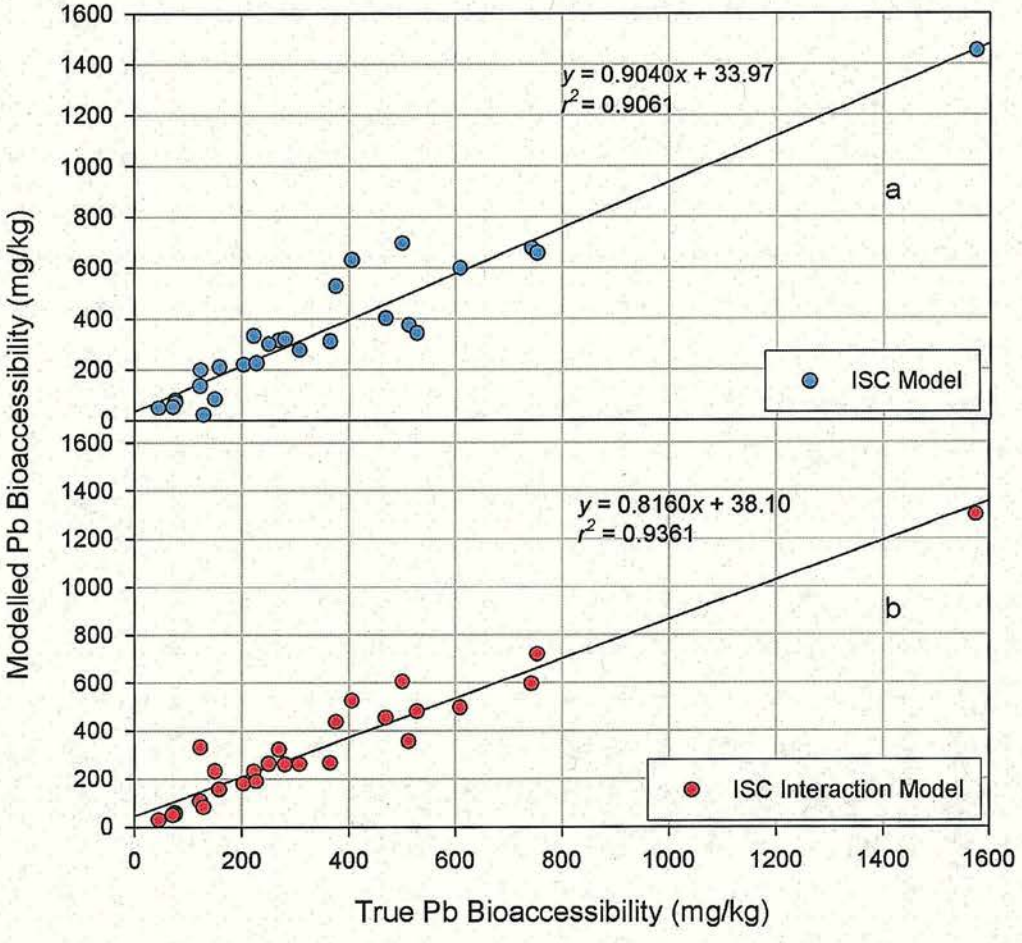

Figure 8.8 Soil Pb Bioaccessibility modelled with (a) the Pb associated with identified ISCs and (b) a second model including interactions between ISCs.

This ISC model had an RMSE of 95 mg/kg and an r^2 of 0.9061, showing that the predicted Pb bioaccessibility did not fit the true data well. To see if these modelling errors are due to interactions between ISCs, an ISC interaction model was produced (Figure 8.8 and Table 8.5). Constituent ISC11 remains a significant predictor of Pb bioaccessibility, accounting for ~84% of bioaccessible Pb for all samples. The interaction between ISC6 and ISC10 (clay and silicate constituents, respectively) is also important, accounting for ~1000 mg/kg of bioaccessible Pb in total. These two ISCs, while not significant as individual variables in the previous model, appeared to be important in the 13 soils where they exist together. It is unclear why the combination of these two ISCs appears to enhance the bioaccessibility of their associated Pb. A similar observation is made for the interaction between ISC2 and ISC8, both of which were identified as individual predictors in the previous model. However their influence appears to be greater when they exist in a soil together.

Table 8.5 Coefficients and intercept for the Pb interaction ISC model of Pb bioaccessibility

ISC name	ISC assignment	Original / Interaction predictor	Model coefficient
ISC11	Humus	Original	0.6545
ISC2 vs ISC8	Fe rich calcite vs Humus	Interaction	0.0828
ISC6 vs ISC10	Clay vs Silicate	Interaction	0.3361
Model Intercept =	-64.53		

The interaction model produces an improved RMSE, compared with that of the simple model (77 vs. 95 mg/kg), and the corresponding cross-validation confirms its suitability (Figure 8.9). There is still a large negative intercept of –65 mg/kg (Table 8.5), which suggests that there are other mechanisms controlling Pb bioaccessibility that have not been accounted for. The correlation between the interaction model and true bioaccessibility (Figure 8.8) shows a slope of 0.816, compared with 0.904 in the simple model. This indicates that in samples where a high Pb bioaccessibility is observed, the interaction model does not fit the data as well as the simple model, the correlation being further removed from equivalence. This is highlighted by the fact that the predicted Pb bioaccessibility in Sample 25 (for which the true bioaccessibility is 1575 mg/kg) was 1453 and 1299 mg/kg for the simple and interaction models, respectively.

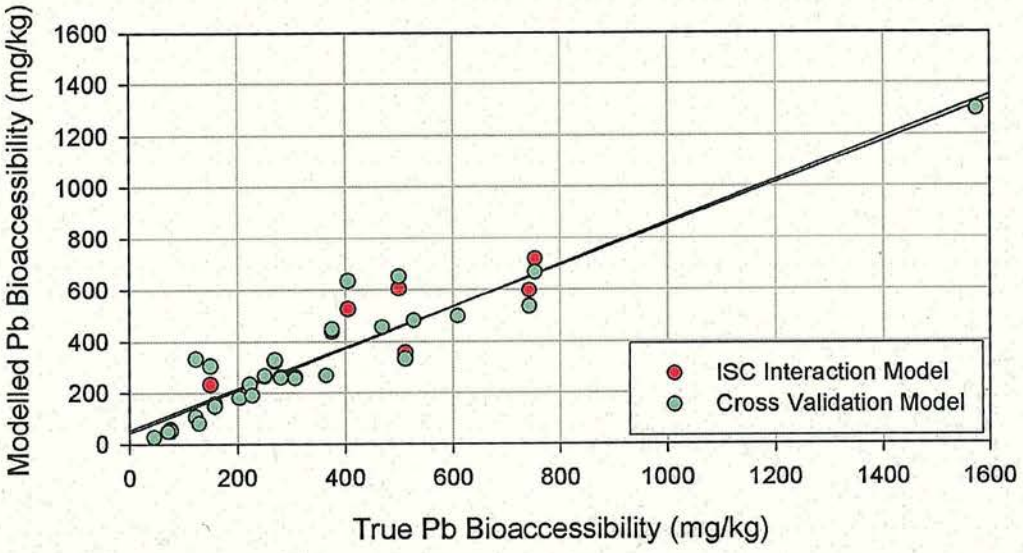

Figure 8.9 True vs modelled bioaccessible Pb for ISC and cross-validation model.

8.2.2 Multiple Linear Regression of Lead Bioaccessibility with Lead Solid Phase Distribution

As for Cr (Section 8.1.3), the bioaccessibility of Pb was also modelled using the distribution of Pb among the clustered physico-chemical components, identified by the CISED extraction. In total only four clusters were found to be important when predicting Pb bioaccessibility, these being C1 (Ca carbonate), C7, C8 (both clays) and C9 (Mn oxide). The majority of Pb contained in the clusters appears to be bioaccessible, with the lowest bioaccessible fraction being ~65% (Equation 8.4).

$$Pb_{bio} = 0.8888C1 + 0.7595C7 + 0.6558C8 + 0.7929C9 - 51.02$$

Equation 8.4 Model predicting the bioaccessibility of Pb in the Glasgow soils using the solid phase distribution of Pb.

Carbonate cluster C1 has the largest fraction for bioaccessible Pb, with just under 90% being leached during the UBM extraction. This observation is in line with what would be expected, that carbonates are soluble under acidic conditions. The Pb content of clay cluster C8 is the most important variable in predicting Pb bioaccessibility. While only 66% of associated Pb is bioaccessible, this equates to a large amount due to the large Pb content of C8 (Chapter 6). On average, C8 accounts for 59% of the bioaccessible Pb in a given sample.

The model produced correlates well with the true Pb bioaccessibility, as shown in Figure 8.10. The RMSE seems high at 91 mg/kg, but given that the Pb bioaccessibility is generally high (65% of samples >206 mg/kg), the size of this error can be justified. In fact the median error between the true and modelled data is only 14% of the modelled bioaccessibility. Figure 8.10 shows that the relationship between the modelled and true Pb bioaccessibility deviates only slightly from equivalence, the r^2 coefficient being ~0.91. This means that the model-predicted data are generally (17 out of 27 samples) lower than the true values.

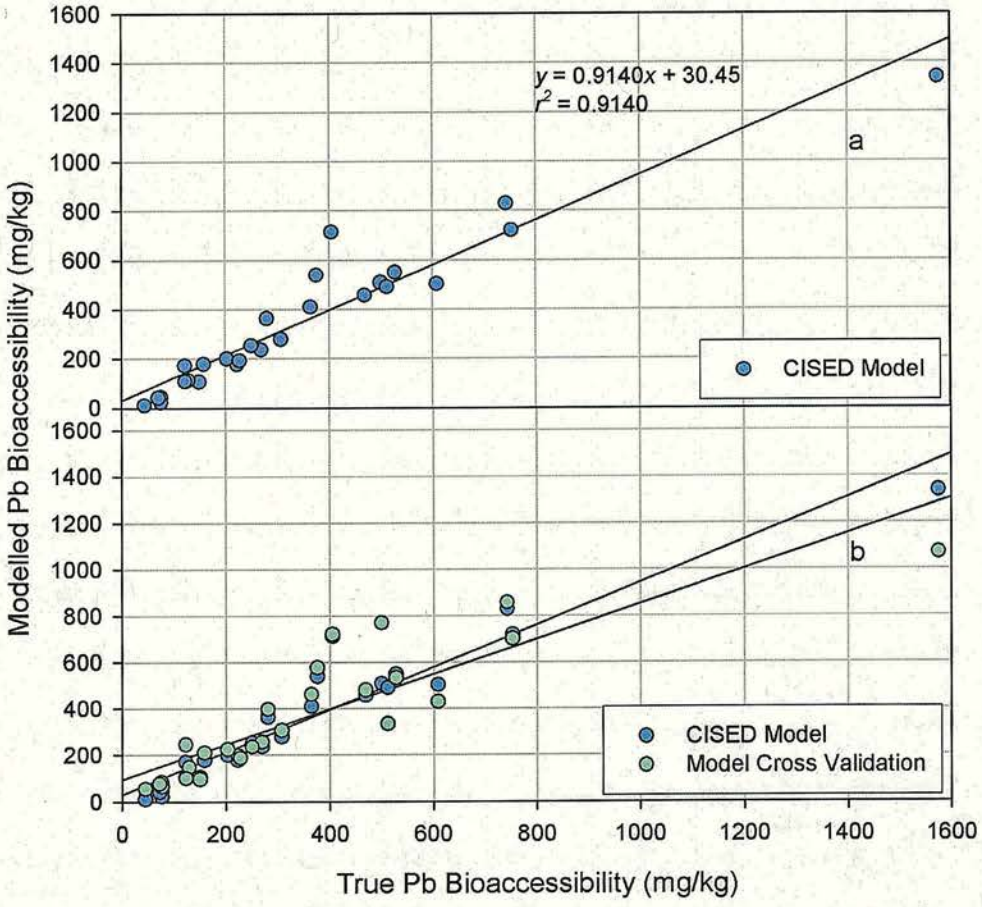

Figure 8.10 Soil Pb Bioaccessibility modelled with solid phase distribution of Pb (a) within the Glasgow soils (RMSE = 91 mg/kg). The cross-validation model is also shown (b).

The model (Equation 8.4) was cross-validated as with the Cr model. The cross-validated data were largely comparable with those of the original model (Figure 8.10), with the exception of four samples where predicted Pb bioaccessibility varied

significantly. The most obvious example of this is Sample 25 where the original model predicted a bioaccessibility of 1338 mg/kg and the cross-validated model predicted only 1070 mg/kg.

8.3 Bioaccessible Arsenic Relationships

8.3.1 Multiple Linear Regression of Arsenic Bioaccessibility with Intrinsic Soil Constituent Arsenic Distribution

Taking the same approach as for Cr and Pb, the As bioaccessibility was modelled using the As associated with each resolved ISC (Figure 8.11). The initial model, which did not take into account any interaction effects, identified four ISCs that were significant in predicting As bioaccessibility (Equation 8.5), the most important of which was ISC6.

$$As_{bio} = 0.5676ISC4 + ISC5 + 0.1524ISC6 + 0.5405ISC10 + 0.4952$$

Equation 8.5 Model predicting the bioaccessibility of As in the Glasgow soils using the As distribution among the identified ISCs.

This clay constituent, present in five of the six samples with a detectable As bioaccessibility, was shown to contain more As than any other ISC (Section 5.4.2.4). The multiple linear regression suggests that only ~15% of the As associated with this ISC is bioaccessible, accounting for an average of ~6.1 mg/kg of bioaccessible As per sample. The importance of this ISC mainly arises from the large amount of As in Sample 3, both the largest As concentration and largest bioaccessible fraction of As in the collected samples. ISC5 is also significant in predicting the bioaccessibility. This is interesting because ISC5 is a quartz constituent, which would be expected to be stable under the acidic conditions of the UBM and thus have a low bioaccessibility. However, 100% of associated As appears to be bioaccessible. In addition, the other identified silicate constituent, ISC10, also has a sizeable bioaccessible As fraction (~54%).

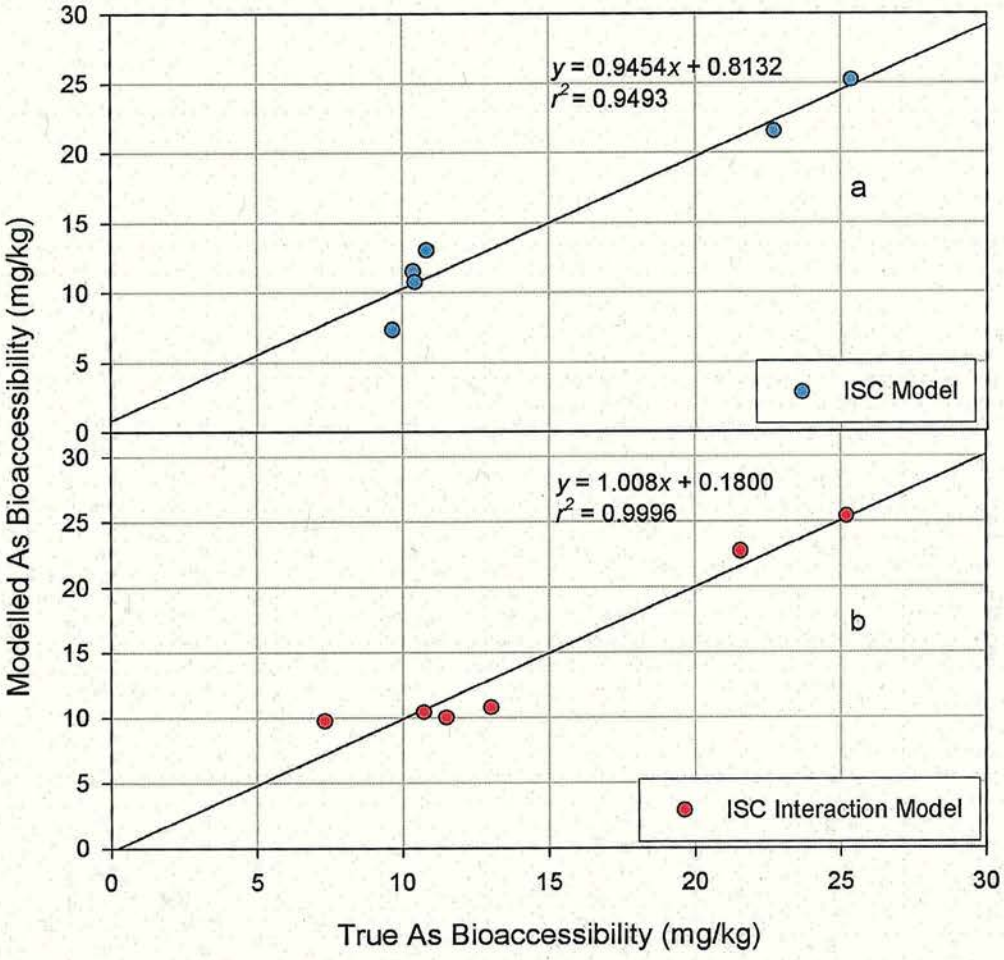

Figure 8.11 Soil As Bioaccessibility modelled with the As associated with identified ISCs (a). Second model includes interactions between ISCs (b).

To rationalise the apparent solubility of the silicate constituents, an interaction model was also produced (Figure 8.11). None of the original predictors were deemed significant and were replaced by three interaction predictors (Table 8.6). Although constituent ISC6 is still important, the interaction between it and calcite constituent ISC4 was more significant, i.e. more As is bioaccessible from both constituents when they are present together. The two constituents are only present together in two samples out of the six that have a detectable As bioaccessibility. Constituent C4 has a similar interaction with silicate ISC10, which coexists in three of the six samples. Quartz constituent ISC5 is not present in the interaction model, which suggests that the interpretation of the simple model that the quartz-bound As was largely bioaccessible does not hold true. In the new model the As bound to ISC5 remains

inaccessible to the stomach and intestine fluids, while ISC10 As only becomes bioaccessible via an interaction with another soil constituent.

Table 8.6 Coefficients and intercept for the As interaction ISC model of As bioaccessibility

ISC name	ISC assignment	Original / Interaction predictor	Model coefficient
ISC2 vs ISC3	Calcite vs Humus	Interaction	0.1971
ISC4 vs ISC6	Calcite vs Clay	Interaction	0.0221
ISC4 vs ISC10	Calcite vs Silcate	Interaction	0.0718
Model Intercept =	9.659		

Relative to the simple model, the interaction model better matches the true bioaccessibility. The RMSE reduces from 1.5 to 0.2 mg/kg when the interactions between constituents are considered and there is also an improvement in the r^2 (Figure 8.11). It should be pointed out that the model intercept increased from 0.4952 to 9.659 mg/kg when the interactions were considered. This increase, to what is a large concentration relative to the range of As bioaccessibilities observed, shows that there is a factor controlling As bioaccessibility which is not accounted for by the interaction model. Cross-validation of the interaction model shows (Figure 8.12) a good agreement for all but one sample. The interaction model predicted the As bioaccessibility in Sample 21 at 10 mg/kg, whereas the cross-validation estimated it at 32 mg/kg. This is a major difference and, given that only six samples had a detectable As bioaccessibility, it has a sizeable effect on the correlation with the true data. This result possibly arises from the heterogeneous nature of the samples (all being from different locations) and the inclusion of a small number in the As models. Such a small data set will result in a less robust model.

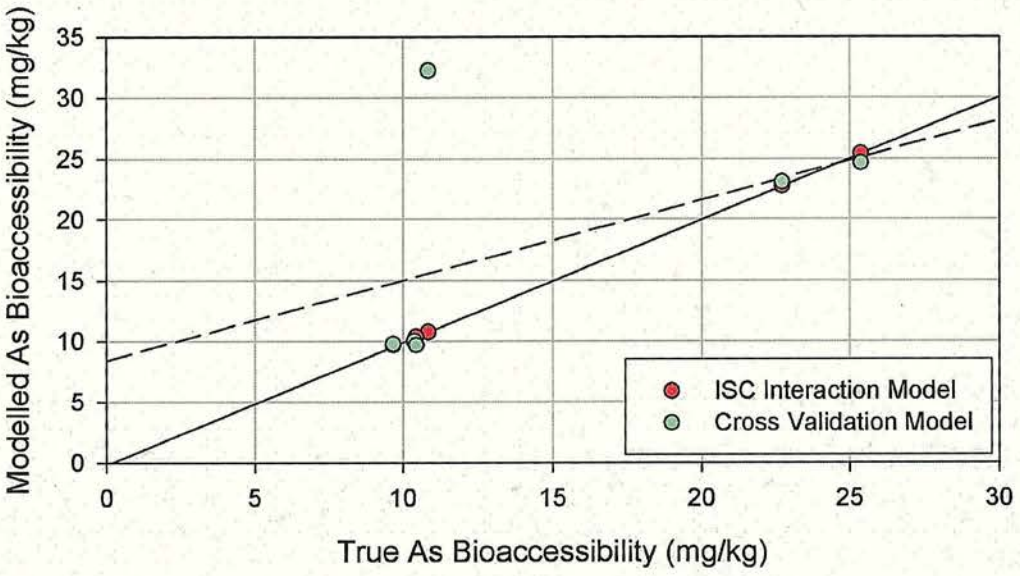

Figure 8.12 True vs modelled bioaccessible As for ISC interaction and cross-validation models.

8.3.2 Multiple Linear Regression of Arsenic Bioaccessibility with Arsenic Solid Phase Distribution

As for Cr and Pb, the bioaccessibility of As was also modelled using the distribution of As among the clustered physico-chemical components, identified by the CISED extraction. Two clusters were found to be important when predicting As bioaccessibility (Equation 8.6), these being carbonate cluster C1 and clay cluster C8.

$$As_{bio} = 0.9464C1 + 0.5557C8 + 9.105$$

Equation 8.6 Model predicting the bioaccessibility of As in the Glasgow soils using the solid phase distribution of As.

Nearly all (~95%) of the As associated with C1 is bioaccessible, while approximately 56% of C8 is leached during the UBM. Despite this, C8 accounts for more bioaccessible As than does C1, containing in total 23 mg/kg compared with 11 mg/kg of bioaccessible As. Unlike with Pb, the cluster with the largest As content (Fe oxide C10) does not seem to have an effect on As bioaccessibility. The observation that Fe oxide-bound As is not bioaccessible was also made by Wragg (2005).

The model produced correlates well with the true As bioaccessibility (Figure 8.13) with a RMSE of 1.0 mg/kg. When the model was cross-validated (Figure 8.13), however, only three out of the six data points could be accurately reproduced. The

model cannot therefore be considered robust for predicting As bioaccessibility. This problem probably results from the small number of samples used, as trends are harder to identify in small groups.

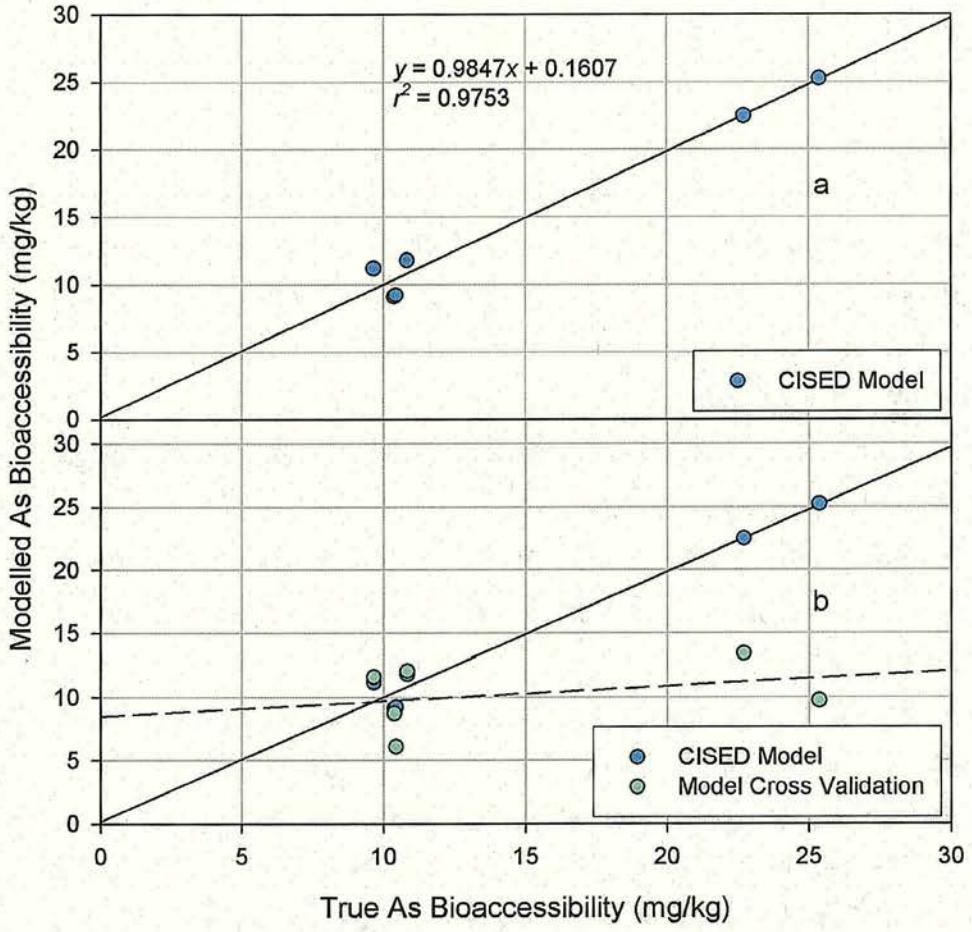

Figure 8.13 Soil As Bioaccessibility modelled with solid phase distribution of As (a) within the Glasgow soils (RMSE = 1.0 mg/kg). The cross-validation model is also shown (b).

8.4 Human Health Risk Assessment

Generic risk assessments, for example via the SGVs used in this thesis, generally assume 100% bioavailability of a contaminant. The SGVs are supposed to act as 'green lines', below which there is little or no possibility of harm to human health (DEFRA, 2002e; Nathanail and Smith, 2007). Site-specific assessment criteria (SSAC) incorporating information on site soil conditions and other parameters, such as receptor activity, can demonstrate that a much higher soil contaminant concentration can pose similarly low risk to human health. Current UK policy and

practice allows, and in some places encourages, the site-specific estimates of oral bioavailability (such as bioaccessibility) to be used in these quantitative risk assessments.

8.4.1 Conceptual Site Models

Conceptual site models depict the spatial relationship between sources of contamination, receptors that may be affected by such contamination and pathways permitting contaminants to reach receptors. In the work described in this thesis, the source is both anthropogenic and natural Cr, Pb and As in surface soils. These could be present in the soil as a result of the underlying geological material (Chapter 3), from the disposal of industrial waste (Cr) or from atmospheric deposition (Pb and As).

The pathway connecting the contamination source and the receptor is a key part of the conceptual model, taking into account how the receptor interacts with the test site. The CLEA guidelines contain only a limited number of generic land uses, these being residential, allotments and industrial/commercial (Table 8.7). There are no generic guidelines for land used as a recreational/city park. This is due to the complication that there is no standard use of recreational land, unlike an allotment, which makes it very difficult to decide on an acceptable model. Examples of questions that are difficult to answer include "who visits the site?", "how long is the average visit?", "is there seasonal variation?" and whether or not the answers to these questions vary between the wide range of recreational land available (e.g. city park, school playing field or a golf course). In this project a large proportion of samples come from recreational/city parks and urban open space (grassed spaces in residential areas that are not gardens). How the local population uses these sites is unknown as no detailed survey could be performed, and a certain number of assumptions therefore need to be made to allow a risk assessment to be performed. The sites labelled urban open spaces can be considered residential land, the definition of which incorporates an area of community open space close to the home (Table 8.7). For simplicity it also seems appropriate to use the residential land without plant uptake category for samples from city parks and recreational land. These sites could also be considered community open spaces, given that they are generally surrounded by residential properties. The only problem with this is that the period of time spent at a park is going to be much smaller than that at home. Thus a risk assessment of a park using the parameters set out for

residential land is likely to be a conservative estimation of the risks posed, but given the circumstances this appears to be the closest-fit scenario. The default receptor in the residential site model, both with and without plant uptake, is a female child in the first 6 years of life (DEFRA, 2002e).

Table 8.7 Descriptions of different land-uses covered by the CLEA model (DEFRA, 2002b)

Residential without plant uptake	This land-use takes into account several different house designs including buildings based on suspended floors and ground-bearing slabs. It assumes that residents have private gardens and/or access to community open spaces close to the home. Exposure has been estimated with and without a contribution from eating home grown vegetables, which represents the key difference in potential exposure to contamination between those living in a house with a garden and those living where no private area is available.
Allotments/ Residential with plant uptake	Provision of open space, commonly made by the local authority, for local people to grow fruit and vegetables for their own consumption. Typically, each plot is about one-fortieth of a hectare with several plots to a site. Although some allotments holders may choose to keep animals, including rabbits, hens and ducks, potential exposure to contaminated meat and eggs has not been considered.
Commercial/ Industrial	This land-use assumes that work takes place in a permanent single-storey building, factory, or warehouse where employees spend most of there time indoors involved in office-based or relatively light physical work. This land-use is not designed to consider those sites involving 100% hard cover (such as car parks) where the risks to the site-user are from ingestion or skin contact because of the implausibility of such exposures arising while the constructed surface remains intact.

8.4.2 Chromium Risk Assessment

When deriving generic SGVs of Cr-contaminated soil, a 100% bioavailability is assumed, thus taking a worst-case scenario approach. This project has shown that the bioaccessibility, and therefore the resultant bioavailability, at the Glasgow sites is considerably less than 100% (Chapter 7). For this risk assessment, in the case where no bioaccessible Cr was detected for a sample, a nominal bioaccessibility equal to half the method detection limit (3 mg/kg) is assigned, thereby allowing the generation of SSAC for all sites. The bioaccessibility of Cr in the Glasgow soils was shown to range from 1% to 31% of the total Cr, with an average of just 5%. The Scottish & Northern Ireland Forum For Environmental Research (SNIFFER) model (SNIFFER, 2003) was used to assess the risks posed by Cr at each site, as it allows the inclusion of bioaccessibility in generating SSAC. This model involves several different stages and

cannot be explained fully here. Details on the SNIFFER algorithms used to derive the SSAC are given in SNIFFER (2003).

- One sample out of the 27 satisfies the parameters for residential land with plant uptake, that being Sample 7. This sample comes from a back garden in the Govan area of the city, which could potentially be used to grow vegetables. This sample has a Cr content below the 130 mg/kg SGV, at 84 ± 2 mg/kg with no detectable bioaccessible Cr (Table 7.1). Therefore an assumed bioaccessibility of 1.5 mg/kg is incorporated into the risk assessment, giving a bioaccessible fraction of 2%. Default plant uptake and consumption rates (SNIFFER, 2003) are assumed, giving a SSAC of 230 mg/kg. This is greater than the Cr content of Sample 7, showing that this site poses no risk to human health.

Four of the remaining 26 samples have a Cr concentration above the residential land without plant uptake SGV (200 mg/kg). If the bioaccessibility of Cr in each sample is incorporated into site-specific risk assessment this number is reduced to just a single sample (Table 8.8). Sample 20 is the only soil sample that had a Cr content greater than the SSAC. With 31% of Cr in a bioaccessible form, the SSAC for this site was calculated to be 850 mg/kg, while Sample 20 had a greater Cr concentration of 3680 ± 23 mg/kg. This site appears, therefore, to pose an unacceptable risk to human health, although questions still arise over the pathway of exposure used in this model. As has been discussed, the conceptual model used in this risk assessment is that of residential land, where the main pathway of exposure is assumed to take place 365 days a year. It is unlikely that the critical receptor for this model (female child in the first six years of life) is going to visit this site that often, it being a small patch of ground adjacent to a football club (although there is evidence that people visit). Thus the true SSAC could be higher. The present assumption, however, is the best that can be made without more information about the site use.

Sample 24 from the Braidholm Sports Field, while having a large total Cr concentration of 658 ± 23 mg/kg, did not exceed the SSAC. This is because of the lower bioaccessibility of Cr in the sample, 18% being leached by the UBM. This gives a SSAC of 1510 mg/kg, more than double the total Cr content. As with Sample 20, the SSAC could be refined, taking into account the true exposure times, but this would only result in an even higher SSAC. Thus, the use of bioaccessibility data has

revealed that the Cr content of Sample 24 poses no risk to the health of the local population.

Table 8.8 The fraction of Cr that is bioaccessible in each Glasgow soil sample and the resulting site specific assessment criteria (SSAC) generated by the SNIFFER model for residential land without plant uptake.

Sample ID	Total Cr (mg/kg)	Bioaccessible Cr (mg/kg)	Bioaccessible Fraction	SSAC (mg/kg)
1	144 ± 2	12 ± 1	0.083	3200
2	65 ± 3	< 3	0.023	11500
3	188 ± 2	7.0 ± 1.0	0.037	7160
4	105 ± 1	8.3 ± 1.0	0.079	3370
5	102 ± 2	3.0 ± 0.7	0.029	9060
6	65 ± 4	< 3	0.023	11500
7	84 ± 2	< 3	0.018	230*
8	72 ± 3	< 3	0.021	12800
9	113 ± 3	3.9 ± 0.7	0.035	7720
10	92 ± 0	< 3	0.016	16300
11	178 ± 9	< 3	0.008	31600
12	156 ± 32	5.3 ± 1.9	0.034	7840
13	91 ± 6	< 3	0.016	16200
14	86 ± 1	< 3	0.017	15300
15	79 ± 6	4.0 ± 0.3	0.051	5260
16	97 ± 3	4.4 ± 0.3	0.045	5870
17	70 ± 2	< 3	0.021	12400
18	128 ± 2	4.7 ± 0.7	0.037	7260
19	229 ± 2	19 ± 1	0.083	3210
20	3680 ± 23	1156 ± 32	0.314	850
21	122 ± 6	8.5 ± 2.5	0.070	3820
22	223 ± 8	9.0 ± 0.6	0.040	6600
23	98 ± 5	3.1 ± 0.6	0.032	8420
24	658 ± 23	116 ± 2	0.176	1510
25	83 ± 0	< 3	0.018	14700
26	152 ± 1	< 3	0.010	27000
27	106 ± 1	< 3	0.014	18830

*Residential land with plant uptake

The risk assessment carried out above uses a tolerable daily intake (or health criteria value, HCV) of 2.6 μg/kg-bw per day (DEFRA, 2002b). This value assumes that 100% of the Cr present is Cr(VI), as this has a greater toxicity than Cr(III) due to its ability to penetrate cell membranes. The SSAC generated in Table 8.8 are therefore for Cr(VI) and not total Cr, but obviously if the total Cr content of a sample is below the SSAC then the Cr(VI) content must be as well. As such the only sample that requires further consideration is Sample 20, which has a total Cr content above the

SSAC. Table 8.8 shows that the Cr(VI) content of Sample 20 is also above the SSAC. It should be remembered that the speciation study carried out (Section 7.1.5) revealed that in the UBM procedure all of the available Cr(VI) was reduced to Cr(III) before entering the intestines, where absorption into the circulatory system would take place. This reduction is used by many as evidence that oral exposure to Cr(VI) does not pose a risk to human health (Kerger *et al.*, 1996; Pellerin and Booker, 2000). It has been shown, however, that Cr(III)-organic complexes have a higher rate of uptake into the systemic system than that of inorganic Cr(III) (Amatya *et al.*, 2005). In addition, as the believed lack of toxicity of Cr(III) is currently being called into question (Pellerin and Booker, 2000; Qi *et al.*, 2000), the health risk posed by the possible ingestion of Cr(III) should not be discounted. The possibility of Cr(III) toxicity should not affect any of the samples for which risk to human health has already been discounted, however due to the fact (ATSDR, 2000; Pellerin and Booker, 2000; Febel *et al.*, 2001; DEFRA, 2002a; Amatya *et al.*, 2005) that Cr(VI) has a much greater rate of absorption than any Cr(III) complex. Therefore, if the Cr content is below the SSAC, which assumes 100% Cr(VI), any bioaccessible Cr(III) is unlikely to pose a health threat. For Sample 20, however, this means that there is still a potential risk due to the 1485 ± 24 mg/kg of humic-bound bioaccessible Cr(III) (Sections 7.1.5.2 and 7.1.5.3).

8.4.2.1 Inhalation Risk Assessment

Chromium(VI), a known human carcinogen, was found to be lung fluid bioaccessible in Samples 20 and 24. This branch of bioaccessibility research is very much in its infancy and there are no risk assessment models available that take into account lung fluid bioaccessibility. As such, it is unclear at this time how this information can be incorporated into human health risk assessment. Risk assessment models such as SNIFFER or CLEA use data from the bulk soil (e.g. total concentration), which creates problems when looking at inhalation exposure. Taking Sample 20 as an example, 18 mg/kg of Cr(VI) was found to be bioaccessible (Table 7.6) in 3 g of <10 μm particles that was isolated from 0.91 kg of soil. Since only the <10 μm particles can reach the lungs, this means that 0.06 mg/kg of Cr(VI) in the bulk soil is accessible via inhalation. Does this constitute a risk? It is clearly far below the Cr SGV, but that assumes exposure via oral ingestion and not inhalation.

DEFRA (2002b) does provide an Index Dose for inhaled Cr(VI), which represents a dose that poses a minimal health risk. The dose, 0.001 μg/kg bw/day, assumes a 70 kg adult inhaling 20 m^3 of air a day. To exceed this dose 3.9 mg of <10 μm Sample 20 material would need to be inhaled, which corresponds to 0.2 mg of <10 μm dust being dispersed per m^3 of air. For Sample 24 to exceed this dose 5.4 mg of <10 μm material would need to be inhaled, relating to 0.3 mg of <10 μm dust being dispersed per m^3 of air. Recently DEFRA (2008) have proposed a Cr(VI) Air Quality Standard of 0.2 ng/m^3, in PM_{10}. This standard does not take account of inhalation bioaccessibility. To obtain a bioaccessible Cr(VI) equal to 0.2 ng/m^3 0.011 and 0.015 mg of <10 μm dust from Sample 20 and Sample 24, respectively, will need to be dispersed per m^3. Whether it is likely that this much <10 μm dust will be dispersed at either site is unknown. The generation of airborne dust will depend on numerous factors, including climate conditions, vegetation cover and ground disturbance.

8.4.3 Lead Risk Assessment

Risk assessment for land contaminated with Pb is very different from that of Cr or As, there being considerably more data and knowledge available concerning human exposure to Pb than there is for any other contaminant. This knowledge allows generic risk assessments to be based on uptake as opposed to intake (DEFRA, 2002c). As both the SNIFFER and CLEA models use intake values, a different approach is needed to assess the health risks arising from Pb contamination. In deriving generic SGV for Pb, DEFRA (2002c) uses a model (Equation 8.7) developed by the Society for Environmental Geochemistry and Health (SEGH).

$$S = \left(\frac{\frac{T}{G^n} - B}{\delta} \right) \times 1000$$

Equation 8.7 SEGH model for generating generic SGV for lead in UK soils, where:
S is the soil or dust guideline (μg/g or mg/kg). T is the blood lead target concentration (μg/dL).
G is the geometric standard deviation of the blood lead distribution.
B is the background or baseline blood lead concentration in the population from sources other than soil and dust (μg/dL).
T is the blood lead target concentration (μg/dL).
n is the number of standard deviations corresponding to the degree of protection required for the population at risk.
δ is the slope or response of the blood lead versus soil and dust lead relationship in children (μg/dL blood increase per 1000 μg/g increment of soil or dust lead)

This model requires the measurement, or estimate, of the relationship between soil Pb concentration and the blood Pb concentration of children living at the site. This relationship varies from site to site, as it is dependent on numerous factors, including bioavailability and the rates of exposure. In addition, δ is based only on empirical studies of environmental Pb exposure and blood Pb concentrations in children; as such it is not appropriate for adults. For this reason a different model is used to generate the SGV of commercial/industrial land use.

One problem with the SEGH model is that, unless an investigation involves the collection and analysis of child blood lead concentration, it cannot be used for a site-specific risk assessment. However, the adult exposure model used to derive generic SGV for commercial/industrial land use (DEFRA, 2002c) does have this ability (Equation 8.8). The Absorption Factor (AF) term in the generic model makes two assumptions. Firstly that 60% of the total Pb in a soil sample is bioaccessible in the gastrointestinal environment and, secondly, that 20% of this is absorbed into the systemic circulatory system. This means that 12% (0.60 x 0.20) of soil Pb is absorbed. By replacing the assumed 60% bioaccessibility by the measured bioaccessibility at each site from the present project a more accurate risk assessment can be made.

$$S = \left(\frac{T}{G^n} - B\right) \times \left(\frac{AT}{BKSF \times IR \times AF \times EF \times ED}\right)$$

Equation 8.8 Model used generating generic Pb SGV for in adults, where:
S is the soil or dust guideline (μg/g or mg/kg)
T is the blood lead target concentration among mothers exposed to the specified site soil lead concentrations (μg/dL)
G is the geometric standard deviation of the blood lead distribution among adults having exposures similar to on-site lead concentrations but having a non-uniform response to site lead and non-uniform off-site lead exposures
B is the background or baseline blood lead concentration in women of childbearing age in the absence of exposures to the site that is being assessed (μg/dL)
n is the number of standard deviations corresponding to the degree of protection required for the population at risk
AT is the averaging time in days
BKSF is the biokinetic slope factor relating (quasi-steady-state) increase in typical blood lead concentration to average daily lead uptake (μg/dL blood lead increase per μg/day lead uptake)
IR is the daily adult soil ingestion rate including outdoor soil and indoor soil-derived dust (g/day)
AF is the absolute gastrointestinal absorption factor for ingested lead in soil and lead in dust derived from soil (dimensionless)
EF is the exposure frequency for contact with contaminated soils and/or dust (day/yr)
ED is the exposure duration (yr)

For this model to be used for the assessment of risks to a female child in the first 6 years of life on residential land, a number of the default values need to be changed from those set out in DEFRA (2002c). The Average Time (AT) was reduced from 15695 days to 2190 (DEFRA, 2002d), Exposure Frequency (EF) was increased from 230 days/year to 365 days/year and the Exposure Duration (ED) was set at 6 years. The Biokinetic Slope Factor (BKSF) is left the same at 0.4 μg/dL per μg/day as this value is also suitable for children (von Braun *et al.*, 2002). The Ingestion Rate (IR) was estimated using the default assumptions for the SNIFFER model (SNIFFER, 2003). SNIFFER uses a default Soil Equivalent Intake (SEI) of 9.85319×10^{-6} kg/kg-bw per day and assumes a Time Average Body Weight (TABW) for a female child in the first six years of life as 11.15 kg. Thus, the SNIFFER model assumed an IR of 0.11 g/day. The values of T, G, n and B are those used by the SEGH model (DEFRA, 2002c). Taking an assumed bioaccessibility of 60%, Equation 8.8 gives a guideline value of 438 mg/kg. This is sufficiently close to the SGV calculated with Equation 8.7 (450 mg/kg) to show that, given the correct parameters, Equation 8.8 produces similar data to Equation 8.7 and therefore it is suitable for SSAC in this situation.

As stated above, the risk assessment model assumes a default Pb bioaccessibility of 60%. The measured Pb bioaccessibility in the 27 Glasgow soils ranged from 23 to 77%, with an average of 50% bioaccessibility (Table 8.9). This shows that while an assumed Pb bioaccessibility of 60% is a suitable conservative figure for the average site in Glasgow, for many it is not accurate enough. Using Equation 8.8 and the true Pb bioaccessible fraction, SSAC was calculated for each site (Table 8.9). The SSAC is the concentration of total Pb above which there may be an unacceptable risk to human health. At 14 of the 27 sites the Pb concentration is greater than the SSAC (Table 8.9). The importance of generating SSAC using the true Pb bioaccessibility is demonstrated by the fact that Sample 2, with a Pb content of 602 ± 47 mg/kg, is no longer considered a health risk. This is also the case for Samples 13 and 26, with all three containing large amounts of inaccessible Pb. Sample 11, with a Pb content very close to the generic SGV (where the uncertainty of the measurement places it above the 450 mg/kg SGV), was demonstrated to pose no health risks. With only 36% of Pb bioaccessible, the SSAC for Sample 11 is raised to 730 mg/kg.

It can be seen that Sample 25, which has the greatest Pb content, is unsurprisingly above the SSAC. The SSAC for this site was revised to 360 mg/kg as a result of the large fraction of Pb that was bioaccessible. It can be concluded therefore that Sample 25 poses a potential risk to human health and requires further site investigation. The sample was collected from a grassed area of residential Rutherglen.

Table 8.9 The fraction of Pb that is bioaccessible in each Glasgow soil sample and the resulting site-specific assessment criteria (SSAC).

Sample ID	Total Pb (mg/kg)	Bioaccessible Pb (mg/kg)	Bioaccessible Fraction	SSAC (mg/kg)
1	298 ± 21	150 ± 4	0.50	520
2	602 ± 47	223 ± 19	0.37	710
3	1344 ± 32	500 ± 44	0.37	710
4	482 ± 8	307 ± 24	0.64	410
5	965 ± 140	376 ± 31	0.39	670
6	709 ± 30	469 ± 0	0.66	400
7	1152 ± 9	743 ± 20	0.64	410
8	555 ± 7	270 ± 11	0.49	540
9	1200 ± 23	405 ± 37	0.34	780
10	618 ± 41	281 ± 30	0.45	580
11	441 ± 13	159 ± 12	0.36	730
12	1318 ± 11	754 ± 61	0.57	460
13	508 ± 41	251 ± 11	0.49	530
14	663 ± 34	512 ± 22	0.77	340
15	157 ± 2	76 ± 8	0.48	540
16	152 ± 4	77 ± 3	0.51	520
17	147 ± 0	72 ± 2	0.49	540
18	363 ± 13	204 ± 10	0.56	470
19	227 ± 3	123 ± 11	0.54	490
20	399 ± 16	228 ± 4	0.57	460
21	1107 ± 4	609 ± 72	0.55	480
22	210 ± 8	129 ± 5	0.61	430
23	856 ± 194	528 ± 69	0.62	430
24	126 ± 11	46 ± 3	0.37	720
25	2157 ± 18	1575 ± 241	0.73	360
26	539 ± 14	123 ± 20	0.23	1150
27	500 ± 50	365 ± 18	0.73	360

Samples 3, 7, 9, 12 and 21 all had a Pb content of >1000 mg/kg, which is above the SSAC at each site. Sample 7 is of interest because it is the only sample that comes from a residential backgarden, which would have the potential to be used as an allotment. In deriving the generic SGV (Equation 8.7), the actual rate of soil ingestion is not considered as it, along with other parameters such as bioavailability, are encompassed in δ. As such, the generic SGVs calculated for residential land without

plant uptake and allotments are the same. The model used to perform the SSAC (Equation 8.8) does require the input of an ingestion rate and can produce a specific SSAC for sites with plant uptake. DEFRA (2002d) provides soil to plant concentration factors (CF) for Pb, thus allowing the exposure rate from eating an assumed amount of home grown vegetables to be calculated using the SNIFFER model (SNIFFER, 2003). This gives a SEI of 3.71×10^{-6} kg/kg-bw per day, with an additional 1.13×10^{-6} kg/kg-bw per day of soil attached to the vegetables. Overall, therefore, the new SEI is 1.47×10^{-5} kg/kg-bw per day, giving an IR of 0.164 g/day. Thus, for Sample 7, for which 64% of the total Pb is bioaccessible, a SSAC for residential land with plant uptake of 270 mg/kg is generated, which is lower than that without plant uptake (410 mg/kg). This additional step, however, does appear unnecessary as Sample 7 has a Pb concentration in excess of the SSAC without plant uptake and thus it was always going to be above any SSAC tailored to sites with plant uptake.

8.4.4 Arsenic Risk Assessment

There are nine of the 27 samples that have a total concentration above the As SGV, which is 20 mg/kg for all land uses (DEFRA, 2002f). As with Cr, the model used to derive the generic SGV assumes 100% bioavailability of As in the soil, which has been shown to not be the case for the Glasgow samples (Table 8.10). Using the SNIFFER model a site-specific risk assessment was performed incorporating the measured As bioaccessibility. Bioaccessible As was detected in only nine samples out of the 27 analysed. The reason for so few samples with a detectable bioaccessible As content is likely to be due to the relatively large method detection limit of 5 mg/kg. This means that these samples could have a bioaccessible As portion, which, given the low SGV, could be significant, but that cannot be discerned from instrumental noise. As such a nominal value equal to half the detection limit (2.5 mg/kg) is assigned to such samples, thus allowing a bioaccessible fraction to be obtained for the SSAC calculation. The calculated SSAC of each sample can be seen in Table 8.10.

Despite there being nine samples with an As content in excess of the generic SGV, only two samples exceed the SSAC, Samples 3 and 12. Sample 3 contained more As than any other sample at 135 ± 6 mg/kg, of which 19% was bioaccessible. This gives a SSAC of 70 mg/kg. Thus it can be seen that this site, an open space at a library in

Knightswood, poses a risk to human health. Sample 12 contained less As than Sample 3, although 48% of it was in a bioaccessible form. This resulted in a SSAC of 27 mg/kg, which is exceeded by the As content of the sample, 48 ± 10 mg/kg. Thus this site, a city park in Paisley, also has the potential to pose a risk to humans.

Table 8.10 The fraction of As that is bioaccessible in each Glasgow soil sample and the resulting site-specific assessment criteria (SSAC) for residential land without plant uptake.

Sample ID	Total As (mg/kg)	Bioaccessible As (mg/kg)	Bioaccessible Fraction	SSAC (mg/kg)
1	63 ± 1	10 ± 2	0.16	81
2	15 ± 5	< 5	0.17	77
3	135 ± 6	25 ± 2	0.19	70
4	14 ± 5	< 5	0.18	72
5	14 ± 1	< 5	0.18	72
6	25 ± 1	< 5	0.10	130
7	23 ± 4	< 5	0.11	25*
8	17 ± 1	5.9 ± 4.3	0.35	37
9	24 ± 8	9.0 ± 1.5	0.38	34
10	13 ± 1	< 5	0.19	67
11	23 ± 2	< 5	0.11	120
12	48 ± 10	23 ± 0	0.48	27
13	13 ± 0	5.5 ± 4.6	0.42	30
14	8.1 ± 6.0	< 5	0.31	42
15	2.0 ± 2.9	< 5	1.25	10
16	4.9 ± 1.0	< 5	0.51	25
17	6.5 ± 0.5	< 5	0.38	34
18	15 ± 0	< 5	0.17	77
19	2.1 ± 0.2	< 5	1.19	11
20	33 ± 2	< 5	0.08	170
21	26 ± 3	11 ± 0	0.42	30
22	18 ± 1	< 5	0.14	93
23	15 ± 2	6.4 ± 0.4	0.43	30
24	<0.1	< 5	N/A	0.3
25	7.1 ± 1.2	< 5	0.35	37
26	26 ± 5	10 ± 2	0.38	34
27	0.4 ± 1.9	< 5	6.25	2

*Residential land with plant uptake

8.4.5 Contaminant Mixtures

An issue arising from this project relates to mixtures of contaminants, as there may be concern about the possible effects of exposure to combinations of contaminants, even when the SSAC is not exceeded. The SSAC values calculated above are based on recommended tolerable daily intakes derived from studies in which large doses of single chemicals are administered to experimental animals. The reality, however, is

that most of the pollution sources to which the public is exposed produce a wide range of individual contaminants. Knowledge about the toxicity of any particular group of contaminants in combination is rarely available, due to the practical difficulties of testing mixtures of contaminants. This is a consequence of the huge numbers of possible contaminant mixtures encountered compared with individual chemicals. In practice, concern over combinations of contaminants should only be an issue when the two share the same toxicological pathway leading to identical effects on the same target organ.

There are two samples that both contain more than one analysed PHE above the associated SSAC. These are Samples 3 and 12, which both have excess Pb and As. In addition, Sample 21 has an excess of Pb and an As content only just below the SSAC. As both Pb and As do appear to produce similar toxicological effects (DEFRA, 2002g, 2002h), a combined effect cannot be ruled out, although combined toxicity is a very complex matter and is outside the brief of this thesis.

CHAPTER 9 SUMMARY AND CONCLUSIONS

9.1 Summary

9.1.1 Quantifying Chromium Bioaccessibility with the UBM

One of the main objectives of this project was to assess the use of and, if necessary, refine, the UBM for quantifying Cr bioaccessibility. As was discussed in Chapters 1 and 2, to date there has been limited published research on Cr bioaccessibility in soils. That which has been published has not assessed the impact of an intestine stage on Cr solubility or made an attempt to validate methods against other models (either *in vivo* or *in vitro*).

9.1.1.1 Validation

Ideally, any PBET developed should be validated either against human or animal models, to ensure that the data produced are a satisfactory estimation of bioavailability. *In vivo* experiments can be both time consuming and expensive, however, and so were not practical in this project. The UBM was therefore compared with another *in vitro* model, the TIM method developed by TNO Nutrition in Zeist, Netherlands. The method is a dynamic model that represents a close analogue of the human gastrointestinal tract (Section 2.1.10). It has been suggested that it could be used to validate batch *in vitro* methods. Since the TIM method always incorporates an intestinal stage, the data were compared with the stomach+intestine data from the UBM. For the analysed sample the TIM method gave a Cr bioaccessibility of 41 ± 2 mg/kg, while the UBM gave 52 ± 1 mg/kg. Whilst not completely validating the UBM method for Cr, since the comparison is based on a single sample (in duplicate), it does give some confidence in the accuracy of the data produced.

9.1.1.2 Refinement of the UBM

It was demonstrated in Chapter 7 that the addition of the intestine stage to the UBM resulted in a sometimes large decrease in Cr solubility. This was emphasised by Sample 20, for which the Cr bioaccessibility decreased from 1156 ± 32 to 52 ± 1 mg/kg when an intestine stage was incorporated into the method. The difference between stomach and stomach+intestine bioaccessibility, however, was generally not as pronounced as for Sample 20 (Table 7.1), with stomach+intestine bioaccessibility being on average 57% (median 62%) of the stomach bioaccessibility. This decrease in

Cr solubility between the stomach and intestine stages of the UBM is thought to be the result of both Cr speciation and pH. The low pH of the stomach stage ensures that all the Cr present is in the form of Cr(III) (Figure 4.1). Whilst Cr(III) will remain soluble under the acid conditions of the stomach (pH 1.2), it will precipitate out of solution as $Cr(OH)_3$ under the more basic conditions of the intestine (pH 6.3).

In the area of human health risk assessment, bioaccessibility data are used to estimate human bioavailability of an identified contaminant. It is normally preferable if this estimation is conservative. It can therefore be concluded that, when determining Cr bioaccessibility for human health risk assessment, the UBM should be used without the intestine stage, thus producing a higher, more conservative, bioaccessibility value.

The toxicology of Cr is very dependent on its speciation, with Cr(VI) deemed much more hazardous than Cr(III) (Section 1.4). This difference is mainly due to the ability of Cr(VI) to pass through biological barriers readily, unlike Cr(III). The ability to differentiate between Cr species in the UBM, to assess if any Cr(VI) is bioaccessible, is therefore very important. In this study the combination of low stomach pH and the simultaneous extraction of organic matter resulted in the reduction of any bioaccessible Cr(VI) to Cr(III). A combination of HPLC-ICP-MS and gel electrophoresis showed that all of the bioaccessible Cr in solution was complexed to soil humic matter (Section 7.1.5). It was, however, demonstrated in initial method development that the pH of the stomach was not capable of complete reduction of soluble Cr(VI) during the time of the UBM (Section 7.1.5.1). This suggests that the lack of bioaccessible Cr(VI) in this project was due to the specific geochemistry (high organic content) of the analysed samples, and not the method itself, i.e. there is no bioaccessible Cr(VI) in the sample. A Cr(VI) contaminated soil with a low organic content, however, would be expected to have bioaccessible Cr(VI), which could be measured by the UBM with DPC analysis.

9.1.2 Chromium Bioaccessibility in Glasgow Urban Soils

In this project 27 surface soil samples were obtained from across Glasgow and its environs. Of these samples, nine had a total Cr concentration (Table 5.1) that exceeded the soil guideline value (SGV) for residential land with plant uptake (130 mg/kg), four of which exceeded the SGV of residential land without plant uptake (200 mg/kg). An exceedance of an SGV indicates that there may be an unacceptable risk to

human health and further investigation is required. These four samples all came from roughly the same location, a 23 km^2 area around Rutherglen, in SE Glasgow. This part of Glasgow was the site of a former major chromite ore processing and Cr chemical factory, the waste from which is known to have been used as landfiller in the surrounding area (Section 1.1.2).

The Cr(VI) content of each sample was also determined (Table 5.1) and was found to be generally very low compared with total Cr. On average the Cr(VI) concentration was 8% (median 5%) of the total Cr. Two samples were identified as having both a greater total Cr and Cr(VI) concentration than the other 25 samples. Sample 20 had a Cr content of 3680 ± 23 mg/kg, of which 1485 ± 24 mg/kg was Cr(VI), while Sample 24 had a Cr content of 658 ± 23 mg/kg, of which 171 ± 5 mg/kg was Cr(VI). Both of these samples came from sites with a known history of COPR landfilling. These were also the only two samples with a Cr(VI) content above either of the residential SGVs. The next highest sample, Sample 19, had a total Cr content of 229 ± 8 mg/kg, of which only 23 ± 1 mg/kg was Cr(VI).

The bioaccessibility of Cr was determined in each sample using the UBM (Table 7.1). As with Cr(VI), the Cr bioaccessibility was much lower than the total Cr content. On average the Cr bioaccessibility was 5% (median 3%) of the total Cr concentration. At 1156 ± 32 mg/kg, Sample 20 contained the most bioaccessible Cr, whilst Sample 24 contained the second highest at 116 ± 2 mg/kg. Once again these two samples were very different from the other 25 samples, with the third highest Cr bioaccessibility being just 19 ± 1 mg/kg.

The solid phase distribution of Cr within each sample was determined using the CISED extraction scheme (Section 6.3). Very little Cr was identified in easily extracted physico-chemical phases, e.g. exchangeable or carbonate phases. Using a combination of cluster analysis and multiple linear regression, information on Cr solid phase distribution was used to model Cr bioaccessibility. The CISED showed that both Samples 20 and 24 have a large amount of Cr in clay physico-chemical phases, 1719 and 111 mg/kg respectively, compared with other samples, for which the average is 8.7 mg/kg. The multiple linear regression (Section 8.1.3) approach suggested that a large amount of Cr is extracted from these clay phases during the UBM, explaining why Samples 20 and 24 have a much greater bioaccessibility than

the other samples. The model produced also suggested that Mn oxide bound Cr, which once again was only identified in significant amounts in Samples 20 and 24, was extracted by the UBM.

The CISED also identified a carbonate phase (C11) that was unique to Sample 20. This phase was believed to be related to a Ca Mg carbonate intrinsic soil constituent (ISC13) that makes up a quarter (23%) of Sample 20. Given the well documented history of COPR disposal at this site and known mineralogy for COPR (Hillier *et al.*, 2003), it is believed that this carbonate phase was derived from the COPR waste. The model suggested that all of the Cr contained within this phase was bioaccessible, accounting for almost half (47%) of the bioaccessible Cr in Sample 20.

In the remaining 25 samples, Cr tended to be distributed between several Fe oxide phases, being relatively hard to extract. These Fe oxide phases account for an average 16% (39 mg/kg) of the total Cr in a sample. To put this into context, for these 25 samples, on average only 20% of total Cr was extracted by the CISED, whereas for Samples 20 and 24 the CISED extracted 73% and 79% of total Cr, respectively. This indicates that 80% of Cr was not acid (HCl/HNO_3) extractable, probably associated with naturally occurring silicate minerals. This suggests the majority of Cr was derived from non-anthropogenic sources and does not pose a risk to human health.

To assess the risk posed to human health by Samples 20 and 24, both of which showed a high Cr(VI) and Cr bioaccessibility, the SNIFFER risk assessment model was used. This mathematical model takes into account contaminant bioaccessibility, among other parameters, to produce site-specific assessment criteria (SSAC). This approach revealed that Sample 24, with only 18% of Cr in a bioaccessible form, did not pose a risk to human health. Indeed the only sample that had a Cr content in excess of its SSAC was Sample 20 (Table 8.8).

The inhalation bioaccessibility of Cr was determined in selected samples using the method previously reported by Wragg and Klinck (2007). This demonstrated that Cr(VI), a known lung carcinogen, was bioaccessible in Samples 20 and 24 (Table 7.3). There are no known studies that have examined the bioaccessibility of inhaled Cr(VI) from general environmental exposure, including soils, and the implications of these findings for human health risk require further examination (Section 8.4.2.1).

9.1.3 Lead Bioaccessibility in Glasgow Urban Soils

The concentration of total Pb ranged from 126 to 2157 mg/kg in the 27 samples. Seventeen of these samples had a concentration (Section 5.1) above the SGV for residential land (450 mg/kg), eight of which exceeded the SGV for industrial land (750 mg/kg). There is no apparent geographical clustering of high concentrations, as was observed with Cr. The $^{206}Pb/^{207}Pb$ ratio was also assessed in each sample and ranged from 1.057 to 1.175 (Table 7.1 & Figure 5.6), consistent with mixtures of Pb deposited in the past from a variety of industrial, domestic and vehicular sources. Sample 25, identified as having both the highest Pb concentration (2157 ± 18 mg/kg) and the lowest isotope ratio (1.056 ± 0.001), was collected from a residential area of Rutherglen.

The bioaccessibility of Pb was determined in each sample using the UBM (Table 7.1). The bioaccessibility tended to be notably lower than the total Pb concentration (Figure 7.5). On average the Pb bioaccessibility was 52% (median 51%) of the total Pb concentration. Eight samples had a bioaccessibility greater than the SGV for residential land (Samples 3, 6, 7, 12, 14, 21, 23 & 25), two of which also exceeded that for industrial land (Samples 12 & 25). Sample 25 once again had the highest Pb bioaccessibility at 1575 ± 24 mg/kg, which is 73% of the total Pb content. Sample 12 was the second highest at 754 ± 61 mg/kg.

The solid phase distribution of Pb was also determined using the CISED extraction scheme (Section 6.4). In the majority of samples (20 out of 27) Pb was associated with a clay cluster (C8), accounting for an average 53% (median 62%) of a samples Pb concentration. The other identified major Pb-containing cluster was a Mn oxide (C9), which accounted for an average of 24% (median 21%) of total concentrations. Sample 25 had a large amount of Pb in each of these clusters, with 1253 and 510 mg/kg associated with C8 and C9, respectively. Interestingly, a considerable amount of Pb was identified in an easily extractable carbonate phase (Figure 6.8). As with Cr, the Pb solid phase distribution was used to model Pb bioaccessibility. This model suggested that a large amount of the Pb associated with clusters C8 and C9 was extracted during the UBM, explaining why Sample 25 had such a high Pb bioaccessibility. This was a similar observation to that of Cr bioaccessibility, where

clay and Mn oxide clusters appeared to be important in determining the bioaccessibility.

Unlike the situation with Cr, the 19 samples that had a Pb bioaccessibility below the SGV for residential land did not appear to have a greater proportion of Pb associated with Fe oxide phases. Instead, it appeared that they simply have less Pb associated with clay and Mn oxide clusters, which were identified as being important in controlling bioaccessibility. These samples also appeared to contain slightly more Pb that was not extracted by the CISED.

To assess the risk posed by the 17 sites with a Pb concentration above the SGV, an adapted adult exposure model was used. This mathematical model took the Pb bioaccessibility into account to produce a SSAC. Taking this approach it was revealed that 15 samples had a Pb concentration above the SSAC (Table 8.9). Samples 2 and 13 both had a Pb concentration above the 450 mg/kg SGV, but did not exceed their respective SSAC. As expected Sample 25 exceeded its SSAC, revealing that the Pb concentration posed a potential risk to human health.

The $^{206}Pb/^{207}Pb$ ratio of the bioaccessible Pb differed little from that of the whole soil. In addition there seems to be no correlation between the soil Pb isotope ratio and Pb bioaccessibility. This indicates that the specific anthropogenic origin of the Pb contamination has little bearing on its bioaccessibility, i.e. Pb originating from the combustion of petrol is no more bioaccessible than that from the combustion of coal and vice versa.

9.1.4 Arsenic Bioaccessibility in Glasgow Urban Soils

The concentration of total As ranged from <0.1 to 135 mg/kg in the 27 samples. Ten of these samples had a concentration (Section 5.1.3) above the SGV for residential land (20 mg/kg). The highest concentrations tended to occur in the NW of the city. The highest concentration found was 135 ± 6 mg/kg in Sample 3, which was collected from Knightswood.

The bioaccessibility of As was determined in each sample using the UBM (Table 7.1). The bioaccessibility tended to be considerably lower than the total As concentration (Figure 7.8). On average the As bioaccessibility was 27% (median 19%) of the total As concentration. Two samples had a bioaccessibility greater than the SGV for

residential land (Samples 3 and 12). Sample 3 had the highest As bioaccessibility at 25 ± 2 mg/kg, which was just 19% of the total As content. Sample 12 was the second highest at 23 ± 0 mg/kg.

The solid phase distribution of As was also determined using the CISED extraction scheme (Section 6.5). The Fe oxide cluster C10 was identified as the dominant As-containing cluster in all but five samples. In one of these five samples, the major As-containing cluster was a different Fe-dominated cluster other than C10. Notable amounts of As were also associated with soil organic and clay clusters. Interestingly, Sample 12, which had the second highest bioaccessibility, was the only sample with a noticeable As content associated with a carbonate phase. These phases would be expected to have a low acid stability and thus the As held within them bioaccessible.

As with both Cr and Pb, the solid phase distribution was used to model As bioaccessibility. This model suggested that a large amount of the As associated with clusters C1 and C8 were extracted during the UBM. Cluster C10 was not found to be significant in modelling As-bioaccessibility. Since this is the dominant As-containing cluster, it can be seen why the bioaccessibility is considerably less than the total concentration.

To assess the risk posed to human health by Samples 1, 3, 6, 7, 9, 11, 20, 21 and 26, which all showed a As concentration above the SGV, the SNIFFER risk assessment model was used. Taking this approach revealed that only Samples 3 and 12 posed a risk to human health. These were the only samples where the As concentration exceeded the SSAC, although Samples 7, 9, 21 and 26 had a concentration just below the SSAC.

9.2 Conclusions

The main outcomes of this study are:

- Confirmation that the stomach stage of a batch PBET procedure produces a higher Cr bioaccessibility than a stomach+intestine stage. It can be recommended that future use of the UBM for Cr human health risk assessment, where a precautionary approach is preferable, should incorporate only the stomach stage.

- The TIM method, an *in vitro* procedure recommended to validate PBETs without using *in vivo* models, appeared to accurately reproduce the limited Cr bioaccessibility data available from the UBM. The UBM can, therefore, be considered suitable for assessing Cr oral bioaccessibility in soils.

- It was demonstrated (Section 7.1.5.1) that it is possible to measure Cr(VI) in the complex matrix of the UBM biofluids using standard analytical methods (DPC colorimetric analysis). The low pH of the stomach was shown to have little effect on a Cr(VI) spike for the duration of the UBM. However, during the analysis of the actual soil samples, no bioaccessible Cr(VI) was detected. It was concluded that soil properties (organic content), in combination with the low pH, resulted in the reduction of bioaccessible Cr(VI) in the stomach phase of the UBM. The UBM with DPC analysis is believed capable of accessing Cr(VI) bioaccessibility, although Cr(VI) is only likely to be bioaccessible in soils without sufficient soluble reducing agents, such as humic matter.

- The bioaccessibility of Cr in the studied Glasgow urban soils was significantly less than the total Cr concentration. This suggests that the use of total Cr concentrations in human health risk assessment will provide an overly conservative assessment. Similar observations were also made for both Pb and As.

- Chromium(VI) was bioaccessible via inhalation of dust from sites with a history of COPR disposal.

- The anthropogenic origin of the Pb had little bearing on its bioaccessibility, i.e. Pb originating from the combustion of petrol was no more bioaccessible than that from the combustion of coal and vice versa.

- Iron oxides were identified as the main sources of total Cr present in the Glasgow soils. However, this study has shown that the Fe oxides were only minor sources of the bioaccessible Cr, with clay and carbonate phases representing the major sources.

- Unique physico-chemical phases and a unique intrinsic soil constituent were identified at sites with a history of COPR disposal. These contained considerably more Cr than any other soil constituents.

- The Cr bioaccessibility was greater in samples from sites with a documented history of COPR disposal. These samples had a much greater Cr content present in an acid-extractable form than other samples. These samples had a greater proportion of Cr associated with clay and carbonate phases, in contrast to the dominance of Fe phases in the other samples. The lack of acid extractable Cr in the non-COPR samples suggests that, in general, Cr in Glasgow is held in the form of naturally derived mineral phases.

- Relatively small fractions of Cr and As were found to be bioaccessible compared to Pb, indicating that Pb poses a greater treat to human health in the Glasgow soils. However, Cr(VI) was found to be bioaccessible via inhalation in a soil from Rutherglen, which has potential implications for the future redevelopment/regeneration of the area.

9.3 Future work

This study has demonstrated that the UBM is capable of accurately determining Cr oral bioaccessibility. Given this success, further validation with animal models should be completed to give greater reliability in the ability of the UBM to estimate Cr bioavailability. In addition the ability of the UBM, with DPC analysis, to determine Cr(VI) bioaccessibility in low organic soils/material should be assessed. Given the known carcinogenic risk from inhaled Cr(VI), further development and refinement of the Respiratory Uptake Test should be undertaken.

The methods used in this study could also be used to assess the success of future remediation of the Cr-contaminated sites in Glasgow and elsewhere. Application of the CISED methodology with the UBM could provide information of any change in the Cr geochemistry and bioaccessibility after chemical remediation of a site.

CHAPTER 10 BIBILOGRAPHY

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Appendix 1

Pb Isotope Ratios

		206Pb/207Pb Total Digest	206Pb/207Pb Bioaccessible Fraction
Sample 1	dup 1	1.156 ± 0.0015	1.153 ± 0.0022
Sample 1	dup 2	1.156 ± 0.0018	1.152 ± 0.0016
Sample 2	dup 1	1.131 ± 0.0021	1.100 ± 0.0015
Sample 2	dup 2	1.130 ± 0.0019	1.100 ± 0.0016
Sample 3	dup 1	1.174 ± 0.0013	1.170 ± 0.0016
Sample 3	dup 2	1.175 ± 0.0010	1.170 ± 0.0014
Sample 4	dup 1	1.151 ± 0.0021	1.150 ± 0.0028
Sample 4	dup 2	1.151 ± 0.0019	1.150 ± 0.0027
Sample 5	dup 1	1.134 ± 0.0021	1.130 ± 0.0018
Sample 5	dup 2	1.132 ± 0.0011	1.130 ± 0.0022
Sample 6	dup 1	1.168 ± 0.0010	1.169 ± 0.0022
Sample 6	dup 2	1.169 ± 0.0013	1.167 ± 0.0024
Sample 7	dup 1	1.157 ± 0.0016	1.154 ± 0.0024
Sample 7	dup 2	1.155 ± 0.0011	1.154 ± 0.0022
Sample 8	dup 1	1.159 ± 0.0013	1.153 ± 0.0021
Sample 8	dup 2	1.159 ± 0.0014	1.153 ± 0.0021
Sample 9	dup 1	1.147 ± 0.0008	1.143 ± 0.0022
Sample 9	dup 2	1.145 ± 0.0013	1.141 ± 0.0021
Sample 10	dup 1	1.160 ± 0.0009	1.159 ± 0.0026
Sample 10	dup 2	1.161 ± 0.0013	1.160 ± 0.0029
Sample 11	dup 1	1.136 ± 0.0023	1.128 ± 0.0015
Sample 11	dup 2	1.137 ± 0.0016	1.128 ± 0.0016
Sample 12	dup 1	1.123 ± 0.0010	1.116 ± 0.0024
Sample 12	dup 2	1.133 ± 0.0011	1.122 ± 0.0023
Sample 13	dup 1	1.157 ± 0.0040	1.153 ± 0.0017
Sample 13	dup 2	1.153 ± 0.0016	1.154 ± 0.0021
Sample 14	dup 1	1.168 ± 0.0029	1.166 ± 0.0028
Sample 14	dup 1	1.156 ± 0.0024	1.151 ± 0.0016
Sample 14	dup 2	1.168 ± 0.0019	1.166 ± 0.0028
Sample 14	dup 2	1.156 ± 0.0022	1.150 ± 0.0025
Sample 15	dup 1	1.151 ± 0.0014	1.147 ± 0.0021
Sample 15	dup 2	1.153 ± 0.0030	1.147 ± 0.0025
Sample 17	dup 1	1.161 ± 0.0015	1.158 ± 0.0015
Sample 17	dup 2	1.162 ± 0.0012	1.157 ± 0.0025
Sample 18	dup 1	1.162 ± 0.0031	1.163 ± 0.0023
Sample 18	dup 2	1.166 ± 0.0021	1.161 ± 0.0017
Sample 19	dup 1	1.141 ± 0.0016	1.138 ± 0.0018
Sample 19	dup 2	1.143 ± 0.0016	1.137 ± 0.0024
Sample 20	dup 1	1.116 ± 0.0012	1.117 ± 0.0011
Sample 20	dup 2	1.117 ± 0.0019	1.117 ± 0.0017
Sample 21	dup 1	1.165 ± 0.0010	1.163 ± 0.0010
Sample 21	dup 2	1.165 ± 0.0012	1.163 ± 0.0016
Sample 22	dup 1	1.129 ± 0.0017	1.123 ± 0.0018
Sample 22	dup 2	1.130 ± 0.0014	1.123 ± 0.0012
Sample 23	dup 1	1.089 ± 0.0023	1.098 ± 0.0015
Sample 23	dup 2	1.099 ± 0.0019	1.097 ± 0.0015
Sample 24	dup 1	1.140 ± 0.0020	1.146 ± 0.0018
Sample 24	dup 2	1.152 ± 0.0019	1.146 ± 0.0018
Sample 25	dup 1	1.057 ± 0.0030	1.054 ± 0.0022
Sample 25	dup 2	1.057 ± 0.0012	1.053 ± 0.0019
Sample 26	dup 1	1.164 ± 0.0020	1.154 ± 0.0019
Sample 26	dup 2	1.164 ± 0.0020	1.156 ± 0.0012
Sample 27	dup 1	1.102 ± 0.0027	1.094 ± 0.0016
Sample 27	dup 2	1.097 ± 0.0015	1.094 ± 0.0021

Appendix 2

Total Elemental Concentrations

	Al*	As	Ba*	Ca*	Cr	Cr(VI)	Cu	Fe*	K*	Mg	Mn	Na	Ni	P*	Pb	S	Si*	V*	Zn	TOC	pH
Sample 1	78363	63	463	8734	144	9.1	125	42073	12361	3790	239	4663	53	1920	298	1004	331415	153	176	107335	4.15
Sample 2	78289	15	747	6891	65	3.2	53	36187	23691	10822	490	5064	35	1397	602	547	323205	106	184	95594	4.75
Sample 3	132495	135	669	20497	188	4.1	505	65339	9656	3617	555	2362	327	1920	1344	2546	281054	708	1217	212597	5.66
Sample 4	88586	14	871	14616	105	11	98	47609	12530	3754	665	4334	70	3535	482	813	318126	157	351	118417	5.57
Sample 5	94249	14	1219	18797	102	7.9	496	50973	12784	4033	793	5222	136	2313	965	898	309070	212	916	145492	5.63
Sample 6	86747	25	674	14190	65	3.5	291	44876	11093	3115	449	5727	100	2357	709	1079	323586	204	493	165723	5.08
Sample 7	103516	23	960	11427	84	3.5	345	62045	12615	3474	666	4224	87	3099	1152	1199	303145	237	978	179648	4.76
Sample 8	88365	17	599	8947	72	0.7	147	44386	11178	3648	278	4553	65	2357	555	1405	326717	228	169	151812	3.78
Sample 9	102413	24	1361	22553	113	7.3	551	65199	13545	3327	987	6931	149	2837	1200	1102	288798	269	1125	134030	6.12
Sample 10	130877	13	948	15041	92	3.2	297	55948	19210	5756	553	3641	98	1440	618	840	285371	196	645	133028	5.61
Sample 11	125140	23	725	26237	178	6.1	231	89305	8303	4949	577	1983	138	2793	441	2359	260825	942	607	304536	4.73
Sample 12	125140	48	1605	25812	156	3.9	1037	64007	10501	3977	718	4857	246	3011	1318	1530	277626	407	1430	166183	5.75
Sample 13	115064	13	997	12135	91	2.7	170	62536	10248	3071	470	2503	124	2313	508	1288	296543	358	431	178659	4.41
Sample 14	75200	8.1	453	10718	86	4.7	51	36747	13968	5908	518	5852	44	1615	663	502	334377	128	189	80792	4.65
Sample 15	91234	2.0	476	13128	79	7.5	94	43124	12361	1608	643	2666	56	3884	157	785	321766	147	194	181371	5.32
Sample 16	99251	4.9	419	7104	97	15	50	48380	11262	1066	504	2506	38	2008	152	705	321131	153	198	145831	4.36
Sample 17	102487	6.5	375	8096	70	4.2	61	53986	9656	1036	337	2496	35	4190	147	790	309789	292	165	177341	4.66
Sample 18	113225	15	538	8096	128	7.6	225	58191	13714	2767	553	2692	95	2400	363	1179	302256	247	483	295629	4.30
Sample 19	92043	2.1	403	6891	229	23	132	44526	10501	5769	1689	3581	63	1920	227	1777	329299	142	466	182386	6.15
Sample 20	83732	33	637	107448	3680	1485	149	68772	7711	43405	1071	3006	292	786	399	1230	213553	379	506	166925	7.69
Sample 21	121904	26	1272	42395	122	3.1	499	89725	12953	8673	1505	4995	165	2706	1107	2207	252064	321	1595	229123	6.04
Sample 22	88733	18	756	13765	223	9.0	289	42353	11939	3467	1618	5897	111	1353	210	525	326590	128	1137	79627	6.33
Sample 23	60785	15	360	17450	98	7.0	809	63096	8895	2969	723	5031	48	1222	856	814	328495	178	732	119202	6.14
Sample 24	100869	0.1	437	19222	658	171	52	60784	13376	8002	1105	3349	81	2226	126	1307	294427	218	240	126721	6.21
Sample 25	103958	7.1	575	10860	83	4.4	96	45016	12023	847	432	1871	55	2793	2157	845	317322	160	255	164583	4.93
Sample 26	157869	26	631	13128	152	0.7	349	105142	10839	1752	1295	16517	287	1571	539	753	249525	558	506	76509	5.41
Sample 27	147278	0.4	393	7175	106	14	17	85731	12108	2833	1179	1949	47	1440	500	653	268019	158	134	146992	5.25

Determined using a combination of ICP-OES and XRF. All concetration are in mg/kg. * denotes XRF analysis.

Appendix 3

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 1 A	5	0.6	0.2	0.0	0.0	1.4	0.0	0.0	0.0	0.0	1.9	3.1	0.0	0.6	0.0	-0.1	2.3	0.0	0.7	0.0	4.4	0.1	3.3	0.0	0.0	0.0
Sample 1 B	1	0.2	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.1	1.3	0.0	0.1	0.0	0.0	0.6	0.0	0.2	0.0	0.9	0.0	0.2	0.0	0.0	0.0
Sample 1 C	1	5.1	0.0	0.0	3.2	64.4	0.0	0.0	0.0	0.8	1.2	9.2	0.0	11.0	1.2	0.0	0.9	0.1	0.3	0.9	0.3	0.0	0.8	0.5	0.0	1.9
Sample 1 D	1	8.4	0.0	0.0	2.0	25.9	0.0	0.0	0.0	0.7	1.3	3.7	0.0	3.4	0.6	0.0	0.4	0.0	0.4	1.0	0.2	0.0	1.9	0.2	0.0	0.8
Sample 1 E	1	24.4	0.0	0.0	2.0	21.7	0.0	0.0	0.1	1.4	8.0	2.0	0.0	1.6	0.4	0.0	0.4	0.0	3.0	5.5	0.4	0.0	3.2	0.2	0.0	0.7
Sample 1 F	1	26.9	0.0	0.0	1.2	23.4	0.0	0.0	0.1	0.9	5.7	1.3	0.0	1.1	0.6	0.0	0.6	0.0	3.9	4.0	0.4	0.0	5.5	0.1	0.0	0.6
Sample 1 G	1	28.8	0.1	0.0	0.9	27.4	0.0	0.2	0.2	1.0	15.9	1.0	0.0	0.7	3.3	0.0	0.5	0.0	10.1	5.6	0.7	0.0	5.2	0.1	0.1	0.5
Sample 1 H	1	30.4	0.1	0.0	0.8	33.0	0.0	0.1	0.2	0.9	17.2	0.8	0.0	0.9	1.8	0.0	0.8	0.0	12.1	4.1	0.9	0.0	6.8	0.1	0.1	0.5
Sample 1 I	1	71.2	0.5	0.2	1.3	53.1	0.0	0.1	1.0	2.1	91.0	1.4	0.0	2.3	3.0	0.0	0.9	0.1	32.7	8.8	3.8	0.0	14.7	0.3	0.2	1.2
Sample 1 J	1	49.9	0.7	0.2	1.0	25.5	0.0	0.1	1.2	1.6	Dil	1.0	0.0	2.7	2.2	0.0	0.5	0.0	22.5	4.9	3.1	0.0	13.4	0.1	0.2	0.9
Sample 1 K	1	40.3	1.2	0.2	0.9	14.0	0.0	0.0	1.6	1.4	Dil	1.1	0.0	3.4	1.5	0.0	0.4	0.1	22.1	4.1	4.6	0.0	13.1	0.1	0.3	0.9
Sample 1 K	5	42.8	1.3	0.3	0.9	15.7	0.0	0.0	1.8	1.6	146.2	1.2	0.0	3.8	1.7	0.1	0.0	0.1	24.2	4.6	5.5	0.0	15.8		0.3	1.0
Sample 1 L	1	30.9	1.1	0.2	0.7	8.3	0.0	0.0	1.5	1.1	Dil	1.0	0.0	4.2	1.0	0.0	0.5	0.0	14.6	3.0	3.8	0.0	11.6	0.1	0.3	0.9
Sample 1 L	5	33.2	1.3	0.3	0.8	9.5	0.0	0.0	1.7	1.2	152.1	1.1	0.0	4.6	1.1	0.0	-0.6	0.0	16.1	3.3	4.8	0.0	14.0		0.3	1.0
Sample 1 M	1	59.4	4.3	0.8	0.7	7.6	0.0	0.0	4.4	2.0	Dil	1.8	0.0	10.8	1.3	0.0	0.2	0.1	36.3	5.0	17.8	0.0	18.2	0.0	0.8	2.8
Sample 1 M	10	61.6	4.6	0.9	0.8	8.2	0.0	0.0	4.8	2.2	560.0	1.9	0.0	11.6	1.4	0.0	-2.4	0.1	39.1	5.5	19.7	0.0	19.8		0.9	3.2
Sample 1 N	1	Dil	1.1	0.6	1.2	16.4	0.0	0.1	3.5	2.1	Dil	2.9	0.1	40.0	1.6	0.0	1.9	0.3	15.2	3.8	17.5	0.0	11.8	0.2	0.5	3.9
Sample 1 N	10	99.1	1.2	0.7	1.2	17.2	0.0	0.1	3.8	2.2	425.7	3.0	0.1	41.5	1.8	0.0	-0.5	0.3	16.7	4.1	19.4	0.0	13.3		0.5	4.3
Sample 2 A	5	0.4	0.2	0.0	0.1	4.9	0.0	0.0	0.0	0.1	0.5	2.2	0.0	1.5	0.1	-0.1	2.4	0.0	1.0	0.1	3.7	0.1	3.3	0.0	0.0	0.0
Sample 2 B	1	0.2	0.0	0.0	0.0	1.6	0.0	0.0	0.0	0.0	0.1	0.3	0.0	0.5	0.0	0.0	0.9	0.0	0.3	0.0	0.6	0.0	0.3	0.0	0.0	0.0
Sample 2 C	1	0.8	0.0	0.0	4.2	124.5	0.0	0.0	0.0	0.0	0.1	8.2	0.0	28.7	3.1	0.0	0.8	0.0	0.4	0.0	0.2	0.0	0.6	0.8	0.0	0.7
Sample 2 D	1	1.2	0.0	0.0	5.6	102.6	0.0	0.0	0.0	0.1	0.3	5.9	0.0	17.8	2.8	0.0	0.1	0.1	0.8	0.3	0.2	0.0	0.9	0.7	0.0	0.9
Sample 2 E	1	15.9	0.0	0.0	Dil	172.8	0.0	0.0	0.0	1.0	2.8	6.2	0.0	17.8	5.1	0.0	0.1	0.2	5.0	6.3	0.3	0.0	1.8	1.3	0.0	2.1
Sample 2 E	5	17.2	0.0	0.0	20.7	185.9	0.0	0.0	0.0	1.1	3.0	6.6	0.0	19.5	5.8	0.0	-0.3	0.2	5.3	7.0	0.9	0.0	2.1		0.0	2.3
Sample 2 F	1	23.9	0.0	0.0	Dil	82.3	0.0	0.0	0.0	0.8	2.4	3.8	0.0	5.7	3.7	0.0	0.0	0.1	5.1	6.4	0.3	0.0	3.1	0.6	0.1	1.3
Sample 2 G	1	41.2	0.0	0.0	6.3	32.9	0.0	0.4	0.0	1.3	12.9	2.4	0.0	1.5	28.4	0.0	-0.2	0.1	8.8	15.7	0.7	0.0	3.0	0.2	0.2	0.8
Sample 2 G	2	42.0	0.0	0.0	6.5	34.7	0.0	0.4	0.0	1.4	13.0	2.4	0.0	1.5	29.7	0.0	0.1	0.1	9.1	16.6	0.9	0.0	3.4		0.2	0.9
Sample 2 H	1	35.1	0.0	0.0	3.1	22.1	0.0	0.1	0.0	0.9	15.2	1.6	0.0	1.5	8.8	0.0	-0.2	0.1	8.4	10.6	1.0	0.0	3.9	0.1	0.2	0.7
Sample 2 I	1	89.3	0.1	0.2	3.1	32.4	0.0	0.1	0.1	1.5	Dil	2.1	0.0	4.5	6.1	0.0	-0.1	0.1	20.6	17.5	3.9	0.0	10.0	0.3	0.3	1.3
Sample 2 I	2	89.7	0.1	0.2	3.2	34.3	0.0	0.1	0.1	1.6	111.7	2.2	0.0	4.8	6.4	0.0	-0.2	0.1	21.4	18.4	4.3	0.0	11.1		0.3	1.3
Sample 2 J	1	49.3	0.1	0.2	1.5	16.4	0.0	0.0	0.1	0.8	Dil	1.5	0.0	4.3	4.2	0.0	-0.2	0.0	14.8	6.5	2.6	0.0	9.1	0.1	0.3	1.0
Sample 2 K	1	43.0	0.1	0.2	1.2	9.3	0.0	0.0	0.1	0.6	Dil	1.7	0.0	5.2	4.6	0.0	-0.4	0.0	15.1	4.3	3.6	0.0	10.0	0.1	0.4	1.0
Sample 2 K	2	45.7	0.1	0.2	1.2	10.3	0.0	0.0	0.1	0.7	161.0	1.8	0.0	5.8	5.1	0.0	-0.6	0.0	16.6	4.8	4.1	0.0	11.7		0.4	1.1
Sample 2 L	1	31.3	0.1	0.2	1.0	5.2	0.0	0.0	0.1	0.4	Dil	1.4	0.0	5.8	5.1	0.0	-0.3	0.0	10.4	2.8	2.4	0.0	10.5	0.0	0.4	1.0
Sample 2 L	2	32.0	0.1	0.2	1.0	5.5	0.0	0.0	0.1	0.4	129.4	1.5	0.0	6.2	5.5	0.0	-0.5	0.0	10.9	3.0	2.9	0.0	11.7		0.4	1.1
Sample 2 M	1	52.3	0.4	0.5	1.0	3.9	0.0	0.0	0.2	0.7	Dil	2.9	0.0	10.3	8.9	0.0	-0.2	0.1	33.9	3.8	11.8	0.0	15.9	0.0	0.8	2.2
Sample 2 M	5	53.8	0.4	0.5	1.1	4.4	0.0	0.0	0.2	0.8	283.7	3.2	0.0	11.3	9.9	0.0	-1.2	0.1	37.1	4.3	13.2	0.0	18.7		0.9	2.4
Sample 2 N	1	Dil	0.1	0.4	2.0	5.4	0.0	0.1	0.3	0.6	Dil	4.0	0.1	50.7	3.1	0.0	0.2	0.3	12.8	3.7	8.3	0.0	11.3	0.1	0.5	3.6
Sample 2 N	5	130.3	0.2	0.4	2.3	6.4	0.0	0.1	0.4	0.7	254.9	4.9	0.1	58.6	3.6	0.0	-0.8	0.3	15.3	4.4	10.1	0.0	14.3		0.6	4.2

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 3 A	5	0.3	0.4	0.0	0.0	3.7	0.0	0.0	0.0	0.1	0.4	2.1	0.0	0.6	0.0	0.0	2.7	0.0	0.9	0.1	6.1	0.3	2.6	0.0	0.0	0.1
Sample 3 B	1	0.1	0.0	0.0	0.0	4.0	0.0	0.0	0.0	0.0	0.1	1.7	0.0	0.6	0.0	0.0	0.9	0.0	0.3	0.0	1.1	0.0	0.6	0.0	0.0	0.0
Sample 3 C	1	0.2	0.0	0.0	0.6	155.6	0.0	0.0	0.0	0.0	0.0	6.4	0.0	16.7	0.4	0.0	1.1	0.0	0.1	0.0	0.4	0.0	2.5	1.0	0.0	1.0
Sample 3 D	1	0.3	0.0	0.0	0.7	174.8	0.0	0.0	0.0	0.0	0.0	4.5	0.0	11.5	0.6	0.0	0.5	0.1	0.0	0.0	0.3	0.0	2.9	1.2	0.0	1.7
Sample 3 E	1	66.2	0.0	0.2	Dil	478.6	0.2	0.1	0.0	4.5	1.9	5.9	0.0	12.1	2.7	0.0	2.8	0.9	1.9	8.4	0.4	0.0	14.9	4.1	0.4	19.0
Sample 3 E	2	28.1	0.1	0.1	7.0	556.7	0.2	0.0	0.1	1.9	3.1	2.9	0.0	19.7	5.3	0.0	1.0	0.4	3.0	3.3	1.6	0.0	16.9	1.3	0.4	7.7
Sample 3 F	1	70.9	0.1	0.1	6.4	168.7	0.1	0.2	0.1	7.0	4.8	3.7	0.0	11.8	3.0	0.0	2.0	0.8	2.6	17.6	0.5	0.0	22.5	1.6	0.8	12.6
Sample 3 F	2	70.3	0.1	0.1	6.5	180.4	0.1	0.2	0.1	7.3	5.2	4.1	0.0	12.8	3.3	0.0	1.2	0.9	2.8	18.7	0.7	0.0	23.7		0.8	13.7
Sample 3 G	1	Dil	0.2	0.2	5.0	104.4	0.1	0.9	0.1	10.4	20.6	2.2	0.0	10.5	21.6	0.0	2.1	0.9	7.5	Dil	1.0	0.0	Dil	1.0	2.7	12.2
Sample 3 G	10	103.1	0.2	0.2	5.1	104.5	0.1	1.0	0.1	10.5	22.4	2.1	0.0	10.8	23.2	0.0	0.7	0.9	8.1	42.5	2.2	0.1	28.4		2.8	12.9
Sample 3 H	1	94.8	0.3	0.2	2.5	55.4	0.0	0.5	0.2	6.8	22.8	1.5	0.0	9.4	9.8	0.0	1.4	0.6	6.2	Dil	1.1	0.0	Dil	0.6	2.0	8.2
Sample 3 H	5	91.2	0.3	0.2	2.7	59.7	0.0	0.5	0.2	7.3	24.7	1.6	0.0	10.0	11.1	0.0	0.1	0.7	6.6	30.5	1.8	0.0	31.7		2.1	8.9
Sample 3 I	1	Dil	1.1	0.4	2.0	45.6	0.0	0.3	0.4	7.9	Dil	1.5	0.0	9.6	6.7	0.1	1.1	0.6	14.8	Dil	3.8	0.0	Dil	0.5	2.1	7.7
Sample 3 I	5	128.8	1.1	0.4	2.2	49.6	0.0	0.4	0.5	8.1	118.7	1.6	0.0	10.4	7.5	0.1	-1.4	0.6	15.7	35.8	4.5	0.0	53.2		2.2	8.5
Sample 3 J	1	Dil	1.6	0.5	1.5	35.8	0.0	0.2	0.6	5.0	Dil	1.3	0.0	9.6	5.2	0.1	-0.1	0.5	14.2	18.0	4.1	0.0	Dil	0.4	2.7	6.9
Sample 3 J	10	157.2	1.6	0.5	1.6	36.5	0.0	0.2	0.6	5.0	146.7	1.2	0.0	9.7	5.6	0.1	-2.1	0.6	15.1	18.0	5.4	0.0	71.4		2.7	7.2
Sample 3 K	1	Dil	2.5	0.6	1.3	35.8	0.0	0.1	0.7	4.0	Dil	1.3	0.0	8.8	4.1	0.1	1.0	0.5	16.0	12.7	6.8	0.0	Dil	0.4	3.0	5.1
Sample 3 K	10	132.7	2.6	0.6	1.4	37.0	0.0	0.1	0.7	4.0	213.4	1.2	0.0	9.1	4.5	0.1	-1.6	0.5	16.8	13.0	8.2	0.1	68.6		3.1	5.5
Sample 3 L	1	98.5	1.9	0.5	1.1	33.9	0.0	0.1	0.6	2.6	Dil	1.1	0.0	8.5	3.4	0.1	0.6	0.4	10.9	7.7	5.9	0.0	Dil	0.3	2.4	4.0
Sample 3 L	10	93.1	2.0	0.5	1.1	33.9	0.0	0.1	0.6	2.5	183.2	1.1	0.0	8.6	3.6	0.1	-0.6	0.4	10.8	7.8	6.9	0.0	51.6		2.5	4.2
Sample 3 M	1	Dil	6.0	Dil	2.3	74.6	0.0	0.2	2.6	6.4	Dil	3.5	0.0	24.2	7.7	0.2	1.5	1.4	28.9	Dil	27.0	0.2	Dil	0.9	6.2	9.7
Sample 3 M	10	155.5	6.1	1.4	2.4	73.5	0.0	0.1	2.6	5.9	670.7	3.7	0.0	24.8	8.2	0.2	-2.3	1.4	26.5	20.8	27.1	0.2	66.2		6.4	10.6
Sample 3 N	1	Dil	3.0	Dil	4.3	79.2	0.0	0.2	1.8	6.1	Dil	8.6	0.1	40.6	4.9	0.3	2.2	1.3	15.6	19.3	32.3	0.1	Dil	2.4	5.2	9.2
Sample 3 N	10	160.3	3.0	1.1	4.1	75.4	0.0	0.2	1.7	5.5	449.6	8.8	0.1	40.0	5.0	0.3	-0.9	1.4	15.6	19.0	32.1	0.1	41.0		5.2	9.7
Sample 4 A	5	0.2	0.4	0.0	0.0	3.2	0.0	0.0	0.0	0.0	0.2	1.2	0.0	0.3	0.0	0.0	4.0	0.0	1.0	0.0	4.4	0.3	2.7	0.0	0.0	0.0
Sample 4 B	1	0.1	0.0	0.0	0.0	3.2	0.0	0.0	0.0	0.0	0.1	1.1	0.0	0.3	0.0	0.0	0.9	0.0	0.9	0.0	0.5	0.0	0.5	0.0	0.0	0.0
Sample 4 C	1	0.4	0.0	0.0	1.5	168.6	0.0	0.0	0.0	0.0	0.1	5.2	0.0	11.1	0.8	0.0	1.1	0.0	1.4	0.0	0.3	0.0	1.9	0.8	0.0	0.4
Sample 4 D	1	1.3	0.0	0.0	3.1	169.5	0.0	0.0	0.0	0.0	0.1	3.8	0.0	6.6	1.1	0.0	0.7	0.0	3.1	0.1	0.2	0.0	2.5	0.9	0.0	1.1
Sample 4 E	1	38.1	0.0	0.1	Dil	351.4	0.0	0.0	0.0	1.2	2.3	4.6	0.0	7.1	3.1	0.0	2.0	0.3	26.0	5.4	0.4	0.0	9.1	2.2	0.1	4.7
Sample 4 E	2	39.1	0.0	0.1	17.5	356.1	0.0	0.1	0.0	1.2	2.5	5.0	0.0	7.7	3.5	0.0	1.6	0.3	26.8	5.9	0.6	0.0	10.6		0.1	5.1
Sample 4 F	1	48.5	0.0	0.1	Dil	170.3	0.0	0.1	0.1	1.3	3.1	2.8	0.0	5.0	3.7	0.0	2.9	0.2	24.9	7.5	0.4	0.0	18.3	1.1	0.1	3.0
Sample 4 G	1	76.2	0.1	0.1	9.0	109.9	0.0	0.5	0.1	2.5	15.3	2.2	0.0	3.6	26.5	0.0	2.9	0.3	38.6	Dil	0.8	0.0	17.3	0.6	0.5	2.6
Sample 4 G	5	75.9	0.1	0.1	9.0	117.2	0.0	0.6	0.1	2.7	16.4	2.4	0.0	3.9	28.7	0.0	1.9	0.4	40.7	22.4	1.4	0.1	19.3		0.6	2.9
Sample 4 H	1	67.7	0.1	0.1	4.1	55.3	0.0	0.2	0.1	1.7	17.9	1.4	0.0	3.4	13.3	0.0	2.6	0.2	29.9	14.9	0.9	0.0	18.4	0.3	0.4	1.7
Sample 4 H	2	67.9	0.1	0.0	4.4	59.4	0.0	0.3	0.2	1.8	19.1	1.5	0.0	3.6	14.4	0.0	2.3	0.2	31.2	15.9	1.1	0.0	20.5		0.5	1.8
Sample 4 I	1	Dil	0.2	0.2	4.3	62.8	0.0	0.2	0.5	2.8	Dil	1.9	0.0	7.2	14.5	0.0	3.8	0.3	56.1	Dil	3.2	0.0	Dil	0.4	0.6	2.5
Sample 4 I	5	116.6	0.2	0.2	4.6	67.6	0.0	0.3	0.6	3.0	118.6	2.0	0.0	7.8	15.6	0.0	3.1	0.3	57.8	28.2	3.9	0.0	39.2		0.6	2.7
Sample 4 J	1	93.6	0.2	0.2	2.6	32.8	0.0	0.1	0.8	1.6	Dil	1.4	0.0	8.2	9.1	0.0	2.1	0.3	40.1	10.9	2.7	0.0	Dil	0.2	0.5	1.8
Sample 4 J	5	90.4	0.2	0.2	2.8	35.5	0.0	0.1	0.8	1.6	126.9	1.5	0.0	8.8	10.1	0.0	2.2	0.3	41.8	11.7	3.4	0.0	37.4		0.6	2.0

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 4 K	1	68.8	0.3	0.3	2.3	20.9	0.0	0.1	1.0	1.2	Dil	1.4	0.0	9.1	5.3	0.0	1.7	0.2	35.8	6.6	4.0	0.0	Dil	0.1	0.6	1.4
Sample 4 K	5	67.5	0.3	0.3	2.5	22.6	0.0	0.1	1.1	1.2	173.0	1.6	0.0	9.5	5.8	0.0	1.1	0.2	37.0	7.1	4.7	0.0	32.6		0.6	1.6
Sample 4 L	1	50.8	0.2	0.3	1.8	14.4	0.0	0.0	1.0	0.7	Dil	1.1	0.0	9.7	3.4	0.0	1.2	0.2	21.5	3.4	3.2	0.0	Dil	0.1	0.5	1.2
Sample 4 L	5	52.5	0.2	0.3	2.0	16.0	0.0	0.0	1.1	0.7	161.2	1.3	0.0	10.5	3.8	0.1	0.8	0.2	23.1	3.8	3.9	0.0	26.7		0.5	1.4
Sample 4 M	1	77.5	0.8	0.7	1.6	17.1	0.0	0.0	2.2	1.1	Dil	2.0	0.0	17.7	5.6	0.0	0.6	0.4	47.8	5.1	11.3	0.0	Dil	0.1	1.1	2.5
Sample 4 M	10	72.6	0.8	0.7	1.6	16.7	0.0	0.0	2.1	1.1	448.7	2.0	0.0	17.6	5.7	0.0	-1.3	0.4	44.4	5.1	11.9	0.0	30.8		1.1	2.6
Sample 4 N	1	Dil	0.4	1.0	1.8	22.9	0.0	0.1	2.1	1.2	Dil	3.3	0.1	50.9	7.5	0.0	1.3	0.8	25.9	4.7	11.3	0.0	14.8	0.2	1.2	4.8
Sample 4 N	10	133.9	0.3	1.1	1.8	22.5	0.0	0.1	2.0	1.1	676.2	3.4	0.1	50.1	7.8	0.0	-1.3	0.8	25.8	4.8	12.1	0.0	15.3		1.1	5.1
Sample 5 A	5	0.2	0.3	-0.1	0.0	5.1	0.0	0.0	0.0	0.1	0.4	1.2	0.0	0.7	0.0	-0.1	2.7	0.0	0.6	0.1	4.2	0.2	2.4	0.0	0.0	0.0
Sample 5 B	1	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.4	0.0	0.0	1.2	0.0	0.3	0.0	0.7	0.0	0.5	0.0	0.0	0.0
Sample 5 C	1	0.3	0.0	0.0	1.4	163.4	0.0	0.0	0.0	0.0	0.0	4.2	0.0	13.8	1.0	0.0	2.0	0.0	2.7	0.0	0.9	0.0	2.3	1.1	0.0	0.4
Sample 5 D	1	0.7	0.0	0.0	2.2	175.5	0.0	0.0	0.0	0.0	0.1	3.7	0.0	9.8	1.3	0.0	1.0	0.0	3.3	0.0	0.5	0.0	2.2	1.3	0.0	1.1
Sample 5 E	1	28.9	0.1	0.1	Dil	Dil	0.1	0.1	0.0	2.0	1.2	7.0	0.0	13.6	5.3	0.0	2.9	0.3	18.6	4.8	1.1	0.0	10.0	5.0	0.3	10.8
Sample 5 E	5	32.3	0.1	0.2	21.3	570.9	0.1	0.1	0.0	2.4	1.4	7.4	0.0	15.7	6.2	0.0	1.3	0.4	21.1	5.5	1.8	0.0	12.2		0.3	12.4
Sample 5 F	1	33.3	0.1	0.1	Dil	236.0	0.0	0.1	0.0	2.8	1.7	5.2	0.0	7.7	4.3	0.0	3.2	0.3	13.3	7.1	0.8	0.0	15.6	2.4	0.3	8.4
Sample 5 F	2	34.8	0.1	0.1	13.1	247.2	0.0	0.1	0.0	3.0	1.7	5.4	0.0	8.3	4.7	0.0	2.6	0.3	14.1	7.7	1.1	0.0	17.3		0.3	9.0
Sample 5 G	1	83.9	0.1	0.1	Dil	196.9	0.1	0.6	0.1	8.1	11.3	4.3	0.0	6.5	41.3	0.0	3.3	0.5	31.1	Dil	1.3	0.0	18.8	2.0	1.5	10.2
Sample 5 G	5	87.7	0.2	0.1	15.8	219.9	0.1	0.6	0.1	9.1	12.5	4.7	0.0	7.4	48.8	0.0	2.7	0.6	35.0	32.8	2.0	0.1	22.7		1.7	11.7
Sample 5 H	1	64.1	0.1	0.1	6.6	90.2	0.0	0.2	0.1	6.3	13.9	2.8	0.0	6.7	12.9	0.0	3.0	0.3	21.2	Dil	1.2	0.0	20.8	0.8	0.7	6.8
Sample 5 H	5	67.4	0.1	0.1	7.1	99.0	0.0	0.2	0.1	7.2	14.9	3.0	0.0	7.5	14.8	0.0	2.4	0.3	23.4	24.0	1.9	0.0	24.8		0.8	7.5
Sample 5 I	1	Dil	0.2	0.3	7.5	93.8	0.0	0.2	0.2	13.3	Dil	3.8	0.0	14.8	9.7	0.0	4.7	0.4	35.6	Dil	3.4	0.0	Dil	1.0	0.7	10.4
Sample 5 I	10	126.1	0.2	0.3	7.9	97.4	0.0	0.2	0.2	14.4	117.6	3.7	0.0	15.6	10.8	0.0	3.5	0.5	40.2	50.2	4.8	0.0	44.0		0.7	11.2
Sample 5 J	1	80.7	0.1	0.3	4.7	35.7	0.0	0.1	0.2	7.2	Dil	2.3	0.0	12.6	4.6	0.0	2.5	0.3	18.1	17.7	2.8	0.0	Dil	0.5	0.4	6.4
Sample 5 J	5	85.5	0.2	0.3	5.3	41.8	0.0	0.1	0.2	8.2	104.3	2.6	0.0	14.5	5.5	0.0	2.2	0.3	20.8	20.4	3.8	0.0	40.2		0.5	7.3
Sample 5 K	1	65.6	0.2	0.3	4.6	22.7	0.0	0.1	0.2	6.4	Dil	2.2	0.0	12.4	3.1	0.0	1.8	0.3	15.8	12.1	3.9	0.0	Dil	0.4	0.5	5.3
Sample 5 K	5	69.6	0.2	0.3	5.2	26.5	0.0	0.1	0.2	7.2	138.6	2.4	0.0	14.1	3.6	0.0	1.4	0.3	17.8	13.9	5.0	0.0	37.1		0.5	6.0
Sample 5 L	1	50.9	0.1	0.3	4.1	16.2	0.0	0.1	0.2	4.0	Dil	1.9	0.0	12.5	2.7	0.0	1.7	0.2	10.0	6.0	3.1	0.0	Dil	0.3	0.4	4.7
Sample 5 L	2	51.9	0.2	0.3	4.3	17.2	0.0	0.1	0.2	4.2	110.9	1.9	0.0	13.2	2.8	0.0	1.4	0.2	10.4	6.4	3.4	0.0	28.0		0.4	5.0
Sample 5 M	1	78.5	0.5	0.6	3.5	15.4	0.0	0.1	0.8	7.2	Dil	2.8	0.1	20.7	6.2	0.0	1.3	0.5	25.9	8.4	9.7	0.0	Dil	0.3	1.1	7.5
Sample 5 M	10	77.0	0.5	0.6	3.6	15.8	0.0	0.1	0.8	7.3	293.3	2.9	0.1	21.3	6.7	0.0	0.1	0.5	26.7	8.9	11.2	0.1	28.9		1.1	8.0
Sample 5 N	1	Dil	0.3	1.0	5.4	37.6	0.0	0.3	1.5	5.4	Dil	6.2	0.3	77.6	9.1	0.1	4.0	1.4	14.7	11.5	9.7	0.0	17.1	0.8	1.4	17.0
Sample 5 N	10	203.0	0.4	1.1	5.6	39.4	0.0	0.3	1.6	5.7	510.7	6.5	0.2	79.6	10.0	0.1	2.0	1.5	16.0	12.3	11.4	0.0	18.1		1.4	18.7
Sample 6 A	5	0.2	0.3	-0.1	0.0	3.6	0.0	0.0	0.0	0.1	0.4	1.2	0.0	0.6	0.0	-0.1	2.0	0.0	0.6	0.0	4.8	0.3	1.4	0.0	0.0	0.0
Sample 6 B	1	0.1	0.0	0.0	0.0	2.9	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.4	0.0	0.0	0.7	0.0	0.2	0.0	0.8	0.0	0.5	0.0	0.0	0.0
Sample 6 C	1	0.4	0.0	0.0	1.0	154.3	0.0	0.0	0.0	0.0	0.0	4.7	0.0	16.0	1.2	0.0	1.1	0.0	0.8	0.0	0.5	0.0	1.6	0.8	0.0	0.8
Sample 6 D	1	0.7	0.0	0.0	1.5	173.4	0.0	0.0	0.0	0.0	0.1	3.6	0.0	11.2	1.5	0.0	0.2	0.0	1.0	0.0	0.3	0.0	1.7	1.0	0.0	1.8
Sample 6 E	1	38.5	0.0	0.1	Dil	408.9	0.1	0.1	0.0	3.3	2.6	4.4	0.0	9.3	5.4	0.0	1.9	0.5	9.9	8.3	0.4	0.0	5.8	3.3	0.2	13.6
Sample 6 E	2	41.6	0.0	0.1	17.4	434.6	0.1	0.1	0.0	3.7	2.8	4.6	0.0	10.4	6.0	0.0	0.4	0.6	10.6	9.2	0.7	0.0	6.8		0.2	15.2
Sample 6 F	1	49.7	0.0	0.0	7.9	133.6	0.0	0.1	0.0	4.1	4.0	2.5	0.0	3.4	4.3	0.0	1.4	0.3	9.5	12.4	0.4	0.0	9.2	1.2	0.2	7.0

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 6 F	2	50.5	0.0	0.0	8.2	140.9	0.0	0.1	0.0	4.4	4.2	2.5	0.0	3.6	4.5	0.0	0.8	0.4	9.8	13.0	0.7	0.0	10.3		0.2	7.4
Sample 6 G	1	64.6	0.1	0.1	5.3	67.7	0.0	0.6	0.0	6.8	20.9	1.4	0.0	2.2	25.4	0.0	0.8	0.3	16.0	Dil	0.8	0.0	9.2	0.6	0.8	4.4
Sample 6 G	10	67.7	0.1	0.1	5.6	71.0	0.0	0.7	0.0	7.3	23.1	1.4	0.0	2.3	27.8	0.0	-0.3	0.3	17.8	29.4	2.3	0.0	10.3		0.8	4.8
Sample 6 H	1	54.9	0.0	0.1	2.7	40.6	0.0	0.1	0.0	4.9	25.7	1.1	0.0	2.8	5.2	0.0	0.7	0.2	12.4	Dil	1.0	0.0	11.6	0.3	0.6	3.4
Sample 6 H	10	58.5	0.1	0.1	3.0	43.5	0.0	0.2	0.0	5.4	28.5	1.0	0.0	2.9	6.0	0.0	-0.6	0.2	14.0	21.5	2.4	0.0	13.1		0.6	3.7
Sample 6 I	1	Dil	0.2	0.3	2.9	50.2	0.0	0.1	0.1	8.5	Dil	1.6	0.0	7.3	3.1	0.0	0.5	0.2	31.0	Dil	4.1	0.0	Dil	0.5	0.9	5.5
Sample 6 I	10	109.2	0.2	0.4	3.1	51.6	0.0	0.1	0.1	8.9	195.3	1.5	0.0	7.5	3.4	0.1	-1.8	0.3	33.9	37.0	5.4	0.1	29.7		0.9	5.8
Sample 6 J	1	81.9	0.2	0.4	1.5	21.5	0.0	0.0	0.1	4.4	Dil	1.0	0.0	7.6	2.3	0.0	0.4	0.2	21.6	14.1	3.8	0.0	Dil	0.2	0.9	3.8
Sample 6 J	10	81.5	0.2	0.4	1.6	22.4	0.0	0.1	0.1	4.7	213.6	1.0	0.0	7.9	2.5	0.0	-0.3	0.2	23.8	14.6	5.2	0.0	29.6		0.9	4.0
Sample 6 K	1	71.8	0.4	0.5	1.3	13.7	0.0	0.0	0.2	3.3	Dil	1.0	0.0	9.3	2.6	0.0	0.3	0.1	24.5	9.4	6.0	0.0	Dil	0.2	1.1	3.4
Sample 6 K	10	71.9	0.4	0.6	1.3	14.2	0.0	0.0	0.2	3.7	305.1	1.0	0.0	9.6	2.8	0.0	-3.0	0.1	26.6	9.7	7.3	0.0	31.3		1.1	3.6
Sample 6 L	1	61.6	0.3	0.4	1.1	9.4	0.0	0.0	0.1	2.1	Dil	0.9	0.0	10.7	3.0	0.0	0.2	0.1	15.7	5.2	4.8	0.0	Dil	0.1	0.9	3.1
Sample 6 L	10	62.3	0.3	0.5	1.1	9.8	0.0	0.0	0.1	2.3	258.2	0.9	0.0	11.0	3.2	0.0	-2.5	0.1	17.1	5.4	6.1	0.1	28.9		0.9	3.2
Sample 6 M	1	93.9	0.9	0.8	1.0	8.3	0.0	0.0	0.3	3.2	Dil	1.4	0.0	17.7	6.4	0.1	0.3	0.3	33.0	6.2	15.4	0.0	Dil	0.1	1.8	4.7
Sample 6 M	20	92.7	0.9	0.9	1.0	8.7	0.0	0.0	0.3	3.3	508.0	1.3	0.0	18.7	6.9	0.1	-3.2	0.3	33.4	6.5	18.2	0.0	36.4		1.7	5.2
Sample 6 N	1	Dil	0.3	0.8	1.9	20.7	0.0	0.2	0.5	2.5	Dil	2.8	0.1	51.3	4.7	0.1	1.8	0.6	15.2	5.2	14.2	0.0	15.4	0.4	1.4	9.0
Sample 6 N	20	177.7	0.4	0.8	1.9	21.3	0.0	0.2	0.5	2.5	485.8	2.6	0.1	52.2	5.1	0.1	-4.0	0.6	15.9	5.4	16.8	0.1	16.7		1.3	9.8
Sample 7 A	5	0.3	0.5	-0.1	0.0	2.0	0.0	0.0	0.0	0.1	0.2	3.2	0.0	0.3	0.0	-0.1	0.6	0.0	0.9	0.1	4.8	0.4	1.8	0.0	0.0	0.1
Sample 7 B	1	0.3	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.1	3.1	0.0	0.3	0.0	0.0	0.7	0.0	0.5	0.0	0.7	0.0	0.3	0.0	0.0	0.1
Sample 7 C	1	1.4	0.0	0.0	3.1	152.6	0.0	0.0	0.0	0.1	0.1	13.2	0.0	14.0	1.9	0.0	0.9	0.1	0.2	0.0	0.3	0.0	0.7	1.2	0.0	8.3
Sample 7 D	1	9.1	0.0	0.0	7.2	136.1	0.0	0.0	0.0	0.7	0.5	7.7	0.0	6.1	1.9	0.0	0.5	0.2	0.5	0.9	0.2	0.0	1.8	1.3	0.0	14.5
Sample 7 E	1	57.4	0.0	0.1	Dil	142.4	0.1	0.1	0.0	7.3	4.8	5.9	0.0	3.8	2.6	0.0	2.8	0.4	5.6	Dil	0.4	0.0	4.3	1.8	0.1	20.0
Sample 7 E	5	59.2	0.0	0.1	16.5	152.6	0.1	0.1	0.0	8.1	5.1	6.2	0.0	4.2	2.9	0.0	0.6	0.4	5.9	31.5	1.0	0.0	5.1		0.1	21.5
Sample 7 F	1	60.5	0.0	0.0	7.7	66.7	0.0	0.1	0.0	5.4	4.7	3.2	0.0	2.1	2.7	0.0	2.6	0.2	7.0	Dil	0.4	0.0	8.6	0.8	0.1	9.9
Sample 7 F	5	59.5	0.1	0.0	7.6	69.1	0.0	0.1	0.0	5.6	4.7	3.3	0.0	2.1	2.9	0.0	1.4	0.2	7.2	28.8	1.0	0.0	9.7		0.1	10.2
Sample 7 G	1	64.3	0.1	0.1	5.3	45.3	0.0	0.7	0.0	6.6	19.3	2.0	0.0	1.4	30.0	0.0	1.8	0.2	14.1	Dil	1.0	0.0	9.1	0.5	0.5	6.7
Sample 7 G	10	64.7	0.1	0.1	5.4	45.9	0.0	0.6	0.0	6.8	19.8	1.8	0.0	1.4	31.4	0.0	1.7	0.2	15.2	48.0	2.3	0.1	10.2		0.5	7.0
Sample 7 H	1	61.3	0.1	0.0	3.7	35.0	0.0	0.2	0.1	4.6	20.3	1.4	0.0	1.7	15.1	0.0	1.9	0.1	13.3	Dil	1.2	0.0	11.6	0.3	0.4	5.5
Sample 7 H	5	61.1	0.1	0.0	3.8	37.2	0.0	0.3	0.1	4.9	20.8	1.5	0.0	1.8	15.7	0.0	1.4	0.1	13.9	32.0	1.8	0.0	13.1		0.5	5.7
Sample 7 I	1	Dil	0.3	0.2	5.0	47.0	0.0	0.2	0.2	8.0	Dil	2.2	0.0	4.0	15.4	0.0	3.3	0.2	35.3	Dil	5.0	0.0	Dil	0.5	0.7	9.0
Sample 7 I	10	114.9	0.2	0.3	4.9	46.3	0.0	0.2	0.2	7.8	129.4	2.0	0.0	4.0	15.9	0.1	1.1	0.2	36.6	50.0	6.0	0.1	28.0		0.7	9.0
Sample 7 J	1	92.4	0.3	0.2	2.8	25.1	0.0	0.1	0.2	4.1	Dil	1.5	0.0	4.0	6.4	0.0	2.1	0.1	26.5	Dil	3.9	0.0	Dil	0.3	0.7	5.9
Sample 7 J	5	88.5	0.3	0.2	2.9	26.8	0.0	0.1	0.3	4.4	113.0	1.5	0.0	4.2	6.9	0.0	1.1	0.2	27.3	22.9	4.5	0.0	29.6		0.7	6.2
Sample 7 K	1	73.4	0.4	0.3	2.3	18.7	0.0	0.0	0.3	3.4	Dil	1.5	0.0	4.5	3.8	0.0	1.4	0.1	29.5	14.6	5.8	0.0	Dil	0.2	0.8	4.7
Sample 7 K	5	71.3	0.4	0.3	2.4	20.1	0.0	0.0	0.3	3.7	172.8	1.6	0.0	4.7	4.1	0.1	0.3	0.1	30.2	15.2	6.4	0.0	29.8		0.8	4.8
Sample 7 L	1	55.7	0.3	0.3	1.8	15.1	0.0	0.0	0.3	2.3	Dil	1.3	0.0	4.8	2.7	0.0	0.8	0.1	20.1	8.4	4.6	0.0	23.0	0.2	0.7	3.7
Sample 7 L	5	55.7	0.4	0.3	1.9	16.1	0.0	0.0	0.3	2.6	167.8	1.3	0.0	5.1	2.9	0.0	0.5	0.1	20.4	8.9	5.4	0.0	25.9		0.8	3.9
Sample 7 M	1	Dil	1.6	Dil	2.1	32.2	0.0	0.0	1.2	4.8	Dil	2.7	0.0	14.8	7.2	0.1	1.7	0.5	58.9	15.6	21.4	0.0	Dil	0.2	2.7	9.6
Sample 7 M	10	116.7	1.6	1.4	2.1	32.6	0.0	0.0	1.2	4.8	900.3	2.6	0.0	15.2	7.7	0.1	-1.1	0.5	65.6	16.1	22.5	0.0	46.8		2.7	10.2

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 7 N	1	Dil	0.7	Dil	2.8	28.9	0.0	0.0	1.1	3.8	Dil	4.7	0.1	31.6	7.1	0.1	2.4	0.7	28.9	10.1	19.9	0.0	Dil	0.4	1.9	14.2
Sample 7 N	10	136.5	0.7	1.5	2.8	29.6	0.0	0.0	1.1	3.8	984.0	4.8	0.1	32.8	7.6	0.1	-0.7	0.7	31.2	10.6	21.3	0.0	30.3		1.9	15.3
Sample 8 A	5	1.1	0.1	0.1	0.1	2.8	0.0	0.0	0.0	0.1	1.2	1.5	0.0	0.9	0.1	-0.1	1.2	0.0	0.6	0.1	4.8	0.1	1.2	0.0	0.0	0.0
Sample 8 B	1	0.6	0.0	0.0	0.1	1.3	0.0	0.0	0.0	0.0	0.2	0.9	0.0	0.4	0.0	0.0	0.9	0.0	0.2	0.0	1.5	0.0	0.2	0.0	0.0	0.0
Sample 8 C	1	32.1	0.0	0.0	5.3	39.8	0.0	0.0	0.0	1.0	3.4	4.3	0.0	4.8	0.7	0.0	0.9	0.1	0.2	3.7	0.4	0.0	0.4	0.4	0.0	0.9
Sample 8 D	1	35.3	0.0	0.0	2.6	11.2	0.0	0.0	0.0	1.1	3.8	2.2	0.0	1.0	0.3	0.0	0.9	0.0	0.3	4.9	0.4	0.0	1.3	0.1	0.0	0.3
Sample 8 E	1	52.7	0.0	0.1	2.1	11.2	0.0	0.0	0.0	2.0	20.9	1.5	0.0	0.4	0.2	0.0	1.4	0.0	1.9	16.2	0.8	0.0	2.9	0.2	0.1	0.2
Sample 8 F	1	57.1	0.0	0.0	1.8	22.2	0.0	0.0	0.0	1.5	17.1	0.9	0.0	0.5	0.4	0.0	2.4	0.0	3.2	10.0	1.0	0.0	5.5	0.2	0.1	0.2
Sample 8 G	1	53.5	0.0	0.1	2.0	36.2	0.0	0.1	0.0	1.5	39.4	0.7	0.0	0.6	2.2	0.0	2.4	0.0	10.4	9.7	1.9	0.0	6.6	0.2	0.4	0.2
Sample 8 H	1	51.4	0.0	0.1	1.7	34.4	0.0	0.0	0.1	1.4	41.1	0.5	0.0	0.9	1.2	0.0	1.7	0.0	12.2	7.3	2.5	0.0	6.5	0.2	0.5	0.2
Sample 8 I	1	98.2	0.3	0.3	2.4	39.4	0.0	0.1	0.2	3.2	Dil	0.8	0.0	2.7	2.1	0.0	1.3	0.0	38.2	13.3	10.0	0.0	12.5	0.2	1.0	0.3
Sample 8 I	5	90.8	0.3	0.3	2.5	40.5	0.0	0.0	0.2	3.3	197.3	0.8	0.0	2.9	2.2	0.0	0.3	0.0	38.2	13.9	11.2	0.0	14.9		1.1	0.3
Sample 8 J	1	82.2	0.3	0.3	2.2	14.1	0.0	0.1	0.2	2.2	Dil	0.7	0.0	6.9	2.0	0.0	1.0	0.0	21.4	8.5	8.4	0.0	16.1	0.1	1.3	0.3
Sample 8 J	5	76.6	0.3	0.4	2.2	14.6	0.0	0.0	0.3	2.3	208.3	0.7	0.0	7.2	2.0	0.0	0.3	0.0	21.1	8.9	9.6	0.1	19.4		1.4	0.4
Sample 8 K	1	Dil	0.6	0.7	3.1	17.0	0.0	0.1	0.6	2.9	Dil	1.7	0.0	35.8	3.5	0.1	1.5	0.1	29.2	14.4	19.8	0.0	23.8	0.2	3.0	1.0
Sample 8 K	10	143.9	0.6	0.8	3.2	18.5	0.0	0.0	0.6	3.0	473.5	1.8	0.0	37.9	3.9	0.1	-1.7	0.1	28.7	15.4	22.2	0.0	29.7		3.1	1.1
Sample 8 L	1	Dil	0.4	0.8	1.9	13.3	0.0	0.0	0.5	2.0	Dil	1.5	0.1	37.2	3.5	0.0	0.0	0.2	22.0	8.5	16.8	0.0	13.5	0.2	2.6	1.3
Sample 8 L	10	114.1	0.4	0.8	2.1	14.7	0.0	0.0	0.6	2.1	521.0	1.7	0.1	40.2	3.9	0.0	-3.3	0.2	22.3	9.5	19.5	0.1	17.1		3.0	1.4
Sample 8 M	1	29.2	1.1	0.5	1.0	3.1	0.0	0.0	0.3	1.3	Dil	0.8	0.0	6.9	1.7	0.1	-0.2	0.1	29.5	3.0	20.3	0.1	11.0	0.0	1.1	0.5
Sample 8 M	10	31.9	1.3	0.6	1.1	3.7	0.0	0.0	0.4	1.4	351.1	1.1	0.0	7.9	2.0	0.1	-2.9	0.1	45.5	3.5	24.9	0.1	14.6		1.2	0.7
Sample 8 N	1	92.5	0.4	0.6	1.4	9.7	0.0	0.1	0.5	1.5	Dil	2.8	0.1	31.8	3.9	0.1	0.1	0.3	14.7	3.3	15.3	0.0	7.1	0.2	1.1	1.5
Sample 8 N	10	98.3	0.5	0.7	1.6	11.8	0.0	0.1	0.6	1.7	456.8	3.8	0.1	37.8	4.7	0.1	-2.7	0.4	20.0	4.1	19.3	0.1	9.8		1.3	1.8
Sample 9 A	5	0.1	0.1	0.0	0.0	8.0	0.0	0.0	0.0	0.1	0.6	2.0	0.0	0.6	0.0	-0.1	2.9	0.0	0.8	0.0	3.9	0.1	1.4	0.0	0.0	0.0
Sample 9 B	1	0.0	0.0	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.0	1.3	0.0	0.2	0.0	0.0	1.7	0.0	0.5	0.0	0.7	0.0	0.9	0.0	0.0	0.0
Sample 9 C	1	0.0	0.0	0.0	1.3	189.6	0.0	0.0	0.0	0.0	0.0	7.5	0.0	10.5	0.3	0.0	2.0	0.0	2.4	0.0	0.8	0.0	3.5	1.0	0.0	0.1
Sample 9 D	1	0.5	0.1	0.1	1.9	205.8	0.0	0.0	0.0	0.0	0.0	6.3	0.0	8.7	0.7	0.0	1.0	0.0	4.0	0.0	0.8	0.0	5.4	1.2	0.0	0.6
Sample 9 E	1	29.3	0.2	0.2	Dil	Dil	0.1	0.1	0.0	1.4	0.6	11.3	0.0	14.9	4.3	0.0	2.5	0.3	18.4	4.1	0.9	0.0	15.9	5.0	0.2	8.1
Sample 9 E	5	30.3	0.2	0.2	20.9	645.7	0.1	0.1	0.0	1.5	0.7	11.7	0.0	16.0	4.6	0.0	1.2	0.3	18.5	4.5	1.4	0.0	19.6		0.2	8.9
Sample 9 F	1	43.5	0.1	0.1	Dil	405.5	0.1	0.1	0.0	2.9	1.2	9.9	0.0	11.8	6.6	0.0	4.7	0.3	18.0	8.2	0.9	0.0	Dil	3.3	0.3	10.0
Sample 9 F	5	42.8	0.2	0.1	18.4	384.2	0.1	0.1	0.0	3.0	1.2	10.1	0.0	12.3	6.9	0.0	4.1	0.3	17.7	8.7	1.3	0.0	37.8		0.3	10.6
Sample 9 G	1	Dil	0.2	0.2	Dil	238.9	0.1	0.6	0.1	9.7	7.5	7.3	0.0	10.7	33.7	0.0	6.0	0.6	36.4	Dil	1.2	0.0	Dil	2.1	1.6	12.7
Sample 9 G	5	110.4	0.2	0.2	19.9	245.4	0.1	0.7	0.1	10.3	8.0	7.8	0.0	11.5	37.2	0.0	4.5	0.6	37.0	36.0	1.6	0.0	50.1		1.7	13.9
Sample 9 H	1	Dil	0.2	0.1	Dil	120.8	0.0	0.2	0.1	9.6	9.1	4.9	0.0	10.2	14.1	0.0	5.3	0.4	30.1	Dil	1.3	0.0	Dil	1.0	0.9	9.2
Sample 9 H	5	104.9	0.2	0.1	10.2	126.5	0.0	0.3	0.1	10.1	9.8	5.4	0.0	10.9	15.4	0.0	5.1	0.4	30.6	31.0	1.8	0.0	51.1		1.0	10.0
Sample 9 I	1	Dil	0.3	0.3	Dil	118.2	0.0	0.2	0.2	21.2	93.7	5.7	0.0	15.0	11.7	0.0	5.2	0.5	51.5	Dil	3.4	0.0	Dil	1.1	0.9	10.2
Sample 9 I	5	167.5	0.4	0.4	10.0	123.5	0.0	0.2	0.2	22.6	92.5	6.4	0.0	16.5	12.8	0.1	4.4	0.5	54.3	68.7	4.2	0.1	74.6		0.9	11.2
Sample 9 J	1	Dil	0.2	0.3	5.9	59.2	0.0	0.2	0.2	10.3	Dil	4.3	0.0	20.3	8.9	0.0	5.2	0.4	29.3	Dil	3.4	0.0	Dil	0.7	0.6	9.4
Sample 9 J	5	149.7	0.3	0.3	5.8	62.2	0.0	0.2	0.2	11.3	95.7	4.7	0.0	21.5	9.7	0.0	4.7	0.5	29.6	26.0	4.2	0.0	74.1		0.6	10.0
Sample 9 K	1	Dil	0.3	0.6	9.6	105.1	0.0	0.3	0.6	10.5	Dil	8.5	0.2	74.1	14.9	0.0	10.6	1.1	32.6	Dil	9.4	0.0	Dil	1.8	1.8	20.4

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 9 K	10	265.4	0.3	0.7	9.6	112.6	0.0	0.4	0.7	11.2	296.5	9.4	0.2	79.2	16.6	0.0	5.4	1.3	32.4	26.1	11.6	0.0	101.3		1.9	22.6
Sample 9 L	1	Dil	0.2	0.8	8.2	91.3	0.0	0.3	0.9	7.3	Dil	7.4	0.2	78.8	13.2	0.0	6.0	1.3	25.0	16.1	10.3	0.0	Dil	2.0	2.3	15.6
Sample 9 L	10	276.9	0.3	0.9	8.2	99.4	0.0	0.4	1.0	7.9	420.9	8.1	0.2	84.7	14.8	0.0	1.8	1.5	25.7	18.0	12.5	0.0	58.1		2.5	17.5
Sample 9 M	1	52.4	0.7	0.6	2.6	13.3	0.0	0.0	0.5	6.2	Dil	3.0	0.0	11.7	4.1	0.0	0.6	0.4	31.6	7.2	15.4	0.0	17.7	0.3	0.8	2.9
Sample 9 M	10	56.9	0.8	0.8	2.9	15.6	0.0	0.0	0.6	7.4	371.6	4.0	0.0	13.7	4.8	0.0	-1.4	0.5	45.1	8.7	19.3	0.1	22.8		0.9	3.5
Sample 9 N	1	Dil	0.6	Dil	4.6	37.3	0.0	0.3	1.5	5.0	Dil	8.2	0.2	62.8	16.7	0.1	3.0	1.3	22.2	12.5	14.7	0.0	11.4	0.8	1.6	11.2
Sample 9 N	10	201.3	0.7	1.7	5.0	43.7	0.0	0.3	1.7	5.5	870.0	10.3	0.2	72.5	19.6	0.1	-0.4	1.6	26.7	14.8	18.4	0.0	15.5		1.8	13.4
Sample 10 A	5	0.2	0.3	-0.1	0.0	2.7	0.0	0.0	0.0	0.0	0.3	0.8	0.0	0.4	0.0	-0.1	1.8	0.0	0.5	0.0	4.4	0.3	1.6	0.0	0.0	0.0
Sample 10 B	1	0.1	0.0	0.0	0.0	2.4	0.0	0.0	0.0	0.0	0.1	0.9	0.0	0.3	0.0	0.0	0.5	0.0	0.1	0.0	0.7	0.0	0.9	0.0	0.0	0.0
Sample 10 C	1	0.0	0.0	0.0	0.8	161.3	0.0	0.0	0.0	0.0	0.0	5.5	0.0	17.6	0.6	0.0	1.3	0.0	1.7	0.0	0.4	0.0	2.6	1.0	0.0	0.2
Sample 10 D	1	0.8	0.0	0.0	1.8	181.0	0.0	0.0	0.0	0.0	0.1	5.7	0.0	14.6	1.4	0.0	0.8	0.0	6.6	0.0	0.5	0.0	4.3	1.2	0.0	1.1
Sample 10 E	1	18.4	0.1	0.1	Dil	Dil	0.1	0.1	0.0	1.5	1.8	11.2	0.0	24.3	8.2	0.0	2.4	0.4	31.1	3.8	0.9	0.0	13.2	3.9	0.3	8.7
Sample 10 E	2	18.6	0.1	0.1	15.0	515.4	0.1	0.1	0.0	1.6	1.7	10.5	0.0	25.4	8.3	0.0	2.1	0.4	31.3	4.0	1.1	0.0	14.2		0.3	9.0
Sample 10 F	1	33.8	0.1	0.1	Dil	241.4	0.0	0.2	0.0	2.6	3.9	7.8	0.0	11.5	8.1	0.0	2.7	0.4	27.3	7.1	0.6	0.0	17.3	1.8	0.4	8.1
Sample 10 F	2	32.7	0.1	0.1	11.7	234.9	0.0	0.2	0.0	2.7	3.7	7.3	0.0	11.6	8.0	0.0	2.3	0.4	26.8	7.1	0.8	0.0	18.1		0.4	8.1
Sample 10 G	1	63.9	0.1	0.1	Dil	174.2	0.0	0.6	0.0	4.9	14.1	6.7	0.0	9.1	33.0	0.0	2.4	0.5	29.7	19.8	1.0	0.0	17.9	1.3	1.0	7.9
Sample 10 G	5	62.4	0.1	0.1	11.9	178.0	0.0	0.6	0.0	5.2	14.2	6.8	0.0	9.4	34.1	0.0	0.9	0.6	30.4	20.4	1.5	0.1	19.7		1.0	8.2
Sample 10 H	1	42.9	0.1	0.1	5.2	60.7	0.0	0.1	0.0	3.8	17.3	4.1	0.0	7.2	5.9	0.0	1.5	0.2	17.2	14.0	0.8	0.0	15.6	0.4	0.4	4.5
Sample 10 H	2	41.1	0.1	0.0	5.0	60.3	0.0	0.1	0.0	3.9	16.4	4.1	0.0	7.3	5.9	0.0	1.2	0.2	17.3	14.0	1.0	0.0	16.9		0.4	4.5
Sample 10 I	1	Dil	0.2	0.3	5.6	61.4	0.0	0.1	0.1	8.9	Dil	6.3	0.1	21.5	3.4	0.0	1.6	0.4	27.7	Dil	2.8	0.0	Dil	0.5	0.5	8.2
Sample 10 I	5	116.7	0.2	0.3	5.8	66.0	0.0	0.1	0.1	9.6	132.4	6.7	0.1	23.1	3.8	0.0	2.2	0.4	29.6	36.3	3.5	0.0	48.7		0.5	8.8
Sample 10 J	1	63.1	0.1	0.2	3.1	21.2	0.0	0.1	0.1	5.0	Dil	5.4	0.0	17.9	2.1	0.0	1.1	0.2	12.9	13.0	2.2	0.0	Dil	0.2	0.4	5.2
Sample 10 J	5	64.2	0.2	0.2	3.3	23.2	0.0	0.1	0.1	5.5	113.3	5.7	0.0	19.2	2.3	0.0	0.0	0.2	13.7	14.0	3.0	0.0	39.8		0.4	5.6
Sample 10 K	1	68.6	0.2	0.3	3.4	12.3	0.0	0.1	0.1	5.2	Dil	8.0	0.1	21.7	2.0	0.0	0.7	0.2	10.1	9.9	3.1	0.0	Dil	0.2	0.4	5.2
Sample 10 K	5	70.6	0.2	0.3	3.7	13.9	0.0	0.1	0.1	5.7	164.9	8.8	0.1	24.0	2.2	0.0	0.1	0.3	11.1	11.0	4.0	0.0	45.5		0.5	5.7
Sample 10 L	1	48.8	0.1	0.2	2.8	7.5	0.0	0.1	0.1	3.1	Dil	7.4	0.1	21.0	1.6	0.0	0.1	0.2	5.6	4.4	2.4	0.0	Dil	0.2	0.3	4.3
Sample 10 L	5	48.5	0.1	0.2	2.9	8.0	0.0	0.1	0.1	3.3	121.2	7.8	0.1	21.9	1.7	0.0	0.2	0.2	5.7	4.7	3.1	0.0	38.5		0.3	4.5
Sample 10 M	1	82.6	0.5	0.5	2.4	7.0	0.0	0.1	0.2	5.8	Dil	13.6	0.1	36.4	2.8	0.0	0.6	0.4	11.3	6.0	8.5	0.0	Dil	0.2	0.8	7.1
Sample 10 M	10	84.6	0.5	0.6	2.5	7.6	0.0	0.1	0.3	6.1	308.9	14.5	0.1	38.7	3.1	0.0	-0.3	0.4	12.8	6.5	10.2	0.1	46.4		0.8	7.9
Sample 10 N	1	Dil	0.3	Dil	3.4	20.3	0.0	0.4	0.6	4.7	Dil	16.5	Dil	110.2	7.8	0.0	1.2	1.1	10.2	8.3	16.0	0.0	Dil	0.6	1.1	16.8
Sample 10 N	2	Dil	0.3	1.2	3.4	20.8	0.0	0.4	0.6	4.7	Dil	16.2	0.3	109.9	8.0	0.0	1.6	1.2	10.3	8.6	16.2	0.0	26.6		1.1	17.4
Sample 10 N	10	230.4	0.3	1.3	3.4	20.5	0.0	0.3	0.6	4.6	741.3	16.2	0.4	107.2	8.2	0.0	-1.6	1.2	10.8	8.6	16.9	0.0	26.1		1.1	17.9
Sample 11 A	5	0.4	0.3	0.0	0.0	5.4	0.0	0.0	0.0	0.1	0.2	3.6	0.0	1.0	0.0	-0.1	5.5	0.0	1.1	0.0	6.7	0.3	0.7	0.0	0.0	0.0
Sample 11 B	1	0.5	0.0	0.0	0.0	4.0	0.0	0.0	0.0	0.0	0.2	2.8	0.0	0.7	0.0	0.0	3.3	0.0	0.6	0.0	1.5	0.0	0.6	0.0	0.0	0.0
Sample 11 C	1	0.4	0.0	0.0	0.5	139.0	0.0	0.0	0.0	0.0	0.1	12.3	0.0	21.9	0.7	0.0	3.9	0.0	0.1	0.0	0.5	0.0	1.0	0.6	0.0	0.4
Sample 11 D	1	0.9	0.0	0.0	0.6	168.5	0.0	0.0	0.0	0.0	0.1	8.0	0.0	17.5	1.1	0.0	1.3	0.1	0.1	0.0	0.5	0.0	1.9	0.8	0.0	0.8
Sample 11 E	1	48.2	0.0	0.1	8.2	494.9	0.1	0.1	0.0	1.8	5.0	8.5	0.0	16.9	4.1	0.0	1.9	0.8	3.2	1.2	0.6	0.0	6.4	3.5	0.2	8.1
Sample 11 F	1	78.5	0.0	0.1	7.0	205.5	0.0	0.2	0.0	2.9	8.0	4.9	0.0	5.8	3.9	0.0	3.8	0.7	6.9	2.5	0.6	0.0	16.6	2.2	0.4	5.3
Sample 11 G	1	Dil	0.0	0.1	5.7	103.5	0.0	0.7	0.0	5.2	26.3	2.6	0.0	3.6	19.1	0.0	3.5	0.6	15.6	10.1	1.3	0.0	20.4	1.2	1.4	3.5

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 11 G	2	111.0	0.0	0.1	5.7	103.3	0.0	0.7	0.0	4.9	26.1	2.6	0.0	3.7	19.3	0.0	3.0	0.6	15.2	10.2	1.4	0.0	19.4		1.4	3.6
Sample 11 H	1	Dil	0.0	0.1	3.4	58.7	0.0	0.3	0.1	3.9	30.6	1.8	0.0	4.2	6.9	0.0	3.7	0.4	12.9	9.1	1.7	0.0	Dil	0.7	1.2	2.3
Sample 11 I	1	Dil	0.2	0.5	4.9	63.3	0.0	0.4	0.2	6.8	Dil	2.7	0.0	11.3	8.5	0.1	5.9	0.5	32.9	Dil	8.4	0.0	Dil	1.0	2.0	3.5
Sample 11 I	10	211.3	0.2	0.6	4.9	62.4	0.0	0.4	0.2	6.6	231.6	2.6	0.0	11.3	8.9	0.1	4.5	0.6	33.6	20.8	9.7	0.0	60.0		2.0	3.7
Sample 11 J	1	Dil	0.2	0.4	3.2	30.1	0.0	0.3	0.2	3.7	Dil	1.8	0.0	15.3	6.4	0.0	3.4	0.4	20.1	8.7	6.9	0.0	Dil	0.6	2.0	2.4
Sample 11 J	10	152.4	0.2	0.5	3.1	29.4	0.0	0.2	0.2	3.5	196.1	1.7	0.0	14.8	6.5	0.1	1.7	0.4	20.0	8.6	8.0	0.0	52.6		1.9	2.4
Sample 11 K	1	Dil	0.3	0.6	3.0	24.8	0.0	0.2	0.3	2.9	Dil	1.8	0.0	24.4	6.6	0.1	3.0	0.3	22.6	6.1	11.5	0.0	Dil	0.5	2.7	2.1
Sample 11 K	10	130.9	0.3	0.6	2.9	24.0	0.0	0.2	0.3	2.6	296.7	1.6	0.0	23.5	6.5	0.1	1.1	0.3	21.1	6.0	12.1	0.0	50.4		2.5	2.2
Sample 11 L	1	94.6	0.3	0.5	2.4	22.4	0.0	0.1	0.3	1.7	Dil	1.4	0.0	28.6	5.2	0.0	1.9	0.3	14.2	3.2	8.7	0.0	Dil	0.4	2.4	1.7
Sample 11 L	10	91.7	0.2	0.5	2.4	22.4	0.0	0.1	0.3	1.6	280.6	1.3	0.0	28.2	5.3	0.1	0.5	0.3	13.5	3.3	9.8	0.0	40.3		2.4	1.8
Sample 11 M	1	Dil	1.7	3.0	5.4	59.9	0.0	0.1	2.1	4.2	Dil	4.0	0.1	176.2	12.2	0.3	2.5	1.5	52.8	7.4	51.3	0.0	Dil	1.0	Dil	7.0
Sample 11 M	20	421.9	2.2	4.8	8.0	92.1	0.0	0.2	3.2	5.8	Dil	5.4	0.2	273.4	19.7	0.5	-2.9	2.5	74.9	11.5	71.7	0.0	107.0		16.2	11.4
Sample 11 M	50	309.4	1.6	2.5	6.2	75.7	0.0	0.1	2.4	4.6	2175	5.0	0.2	215.2	15.2	-0.6	-14.3	1.9	72.3	9.2	69.1	0.0	74.5		11.8	1114
Sample 11 N	1	Dil	0.7	2.1	6.7	87.0	0.0	0.3	2.1	2.7	Dil	8.9	0.3	216.8	7.0	0.2	5.6	1.6	26.9	4.2	59.4	0.0	Dil	2.3	9.1	7.4
Sample 11 N	20	422.9	0.9	3.1	9.1	118.7	0.0	0.4	2.9	3.4	1832	10.9	0.3	300.4	10.2	0.3	-0.7	2.4	36.9	6.0	75.9	0.0	54.6		12.4	11.3
Sample 12 A	5	0.1	0.4	-0.1	0.0	3.5	0.0	0.0	0.0	0.1	0.0	0.8	0.0	0.3	0.0	0.0	2.5	0.0	0.5	0.0	4.6	0.4	0.6	0.0	0.0	0.0
Sample 12 B	1	0.0	0.0	0.0	0.0	4.1	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.3	0.0	0.0	1.1	0.0	0.2	0.0	0.8	0.0	0.8	0.0	0.0	0.0
Sample 12 C	1	0.0	0.0	0.0	1.1	168.6	0.0	0.0	0.0	0.0	0.0	4.2	0.0	11.1	0.3	0.0	2.2	0.0	0.5	0.0	0.7	0.0	3.7	1.4	0.0	0.5
Sample 12 D	1	0.1	0.1	0.0	1.3	184.0	0.0	0.0	0.0	0.0	0.0	3.8	0.0	8.9	0.5	0.0	1.1	0.0	1.5	0.0	0.6	0.0	3.7	1.7	0.0	1.0
Sample 12 E	1	43.0	0.7	0.3	Dil	Dil	0.2	0.1	0.0	3.9	0.7	9.8	0.1	16.0	4.1	0.0	4.5	0.5	17.0	2.8	1.4	0.0	21.9	9.7	0.2	20.6
Sample 12 E	5	46.8	0.8	0.3	25.5	758.1	0.2	0.1	0.0	4.5	0.8	10.1	0.1	18.4	4.7	0.0	2.5	0.6	19.2	3.3	2.1	0.1	26.3		0.3	23.7
Sample 12 F	1	56.6	0.5	0.2	Dil	372.2	0.1	0.1	0.0	10.2	2.0	8.1	0.1	11.5	4.4	0.0	4.9	0.5	18.5	10.9	1.1	0.0	Dil	5.9	0.5	18.0
Sample 12 F	5	61.9	0.6	0.2	23.7	404.5	0.1	0.1	0.0	11.4	2.2	8.7	0.1	13.2	5.1	0.0	3.2	0.6	21.0	12.5	1.7	0.0	34.4		0.5	20.8
Sample 12 G	1	Dil	1.0	0.3	Dil	291.0	0.1	0.8	0.1	23.9	11.2	6.0	0.1	12.7	35.4	0.0	6.0	1.0	54.3	Dil	1.7	0.0	Dil	4.7	2.8	23.5
Sample 12 G	5	148.4	1.1	0.3	25.3	320.0	0.2	1.0	0.1	27.0	12.5	6.6	0.1	14.7	42.0	0.0	4.3	1.1	61.2	44.1	2.4	0.1	47.4		3.2	27.1
Sample 12 H	1	Dil	0.5	0.3	Dil	149.8	0.1	0.4	0.1	17.9	14.0	4.2	0.1	15.9	12.9	0.0	5.2	0.7	40.3	Dil	1.5	0.0	Dil	2.2	1.6	16.3
Sample 12 H	5	114.9	0.6	0.3	12.2	164.5	0.1	0.4	0.1	19.9	14.7	4.5	0.1	17.8	14.4	0.0	3.9	0.7	44.5	35.4	2.2	0.0	51.7		1.8	18.3
Sample 12 I	1	Dil	0.7	0.7	Dil	169.1	0.0	0.3	0.2	30.5	Dil	5.9	0.1	32.9	9.2	0.1	7.5	1.0	65.2	Dil	4.0	0.0	Dil	2.6	1.7	21.5
Sample 12 I	10	188.3	0.8	0.7	12.5	172.8	0.0	0.3	0.2	31.6	124.1	5.6	0.1	34.5	10.1	0.1	6.3	1.1	73.3	66.2	5.4	0.0	84.1		1.8	23.3
Sample 12 J	1	Dil	0.5	0.6	6.8	70.3	0.0	0.2	0.2	15.3	Dil	3.9	0.1	28.1	5.1	0.1	4.8	0.9	30.7	Dil	3.4	0.0	Dil	1.4	1.3	14.1
Sample 12 J	10	146.6	0.5	0.6	6.8	70.9	0.0	0.2	0.2	15.5	109.0	3.7	0.1	28.7	5.4	0.1	1.8	1.0	33.6	24.5	4.8	0.1	72.7		1.3	14.9
Sample 12 K	1	Dil	0.5	0.6	5.6	41.4	0.0	0.2	0.2	11.6	Dil	3.4	0.1	25.1	3.5	0.1	4.0	0.9	22.0	14.5	4.5	0.0	Dil	1.1	1.2	10.2
Sample 12 K	10	121.1	0.5	0.7	5.9	43.2	0.0	0.2	0.2	12.3	149.5	3.3	0.1	26.2	3.9	0.1	2.1	1.0	24.5	15.3	5.9	0.0	66.7		1.3	10.9
Sample 12 L	1	Dil	0.4	0.6	4.8	29.3	0.0	0.2	0.2	8.1	Dil	3.0	0.1	24.8	3.0	0.1	2.7	1.0	14.1	8.0	4.2	0.0	Dil	0.9	1.1	8.6
Sample 12 L	10	116.0	0.4	0.8	5.6	33.8	0.0	0.2	0.2	9.3	151.7	3.2	0.1	28.2	3.7	0.1	2.9	1.1	17.3	9.3	5.9	0.1	63.9		1.3	10.0
Sample 12 M	1	Dil	1.1	Dil	4.2	27.0	0.0	0.3	0.6	12.3	Dil	3.9	0.1	35.9	4.8	0.1	2.1	1.9	27.2	10.8	11.8	0.0	Dil	0.8	2.4	12.3
Sample 12 M	10	154.6	1.2	1.3	4.8	30.6	0.0	0.3	0.7	13.7	393.2	4.4	0.2	40.3	5.6	0.1	1.1	2.1	30.7	12.4	14.5	0.0	59.9		2.7	14.4
Sample 12 N	1	Dil	0.8	Dil	6.9	61.8	0.0	0.7	1.1	11.9	Dil	11.1	Dil	123.5	10.2	0.2	7.0	4.4	20.8	16.2	16.7	0.0	Dil	2.4	3.9	22.3
Sample 12 N	2	Dil	0.8	Dil	7.3	66.4	0.0	0.8	1.2	12.9	Dil	11.8	0.6	135.4	11.0	0.2	6.2	4.8	22.7	17.8	18.2	0.0	26.4		4.2	24.6

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 12 N	10	363.7	0.9	2.3	7.5	67.3	0.0	0.8	1.2	13.0	788.8	11.6	0.5	134.1	11.8	0.2	5.7	5.0	24.2	18.3	19.3	0.1	29.6		4.3	26.0
Sample 13 A	5	0.6	0.3	0.0	0.1	2.6	0.0	0.0	0.0	0.1	0.5	1.5	0.0	0.6	0.1	-0.1	2.2	0.0	0.9	0.1	4.4	0.2	3.4	0.0	0.0	0.1
Sample 13 B	1	0.4	0.0	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.1	1.0	0.0	0.3	0.0	0.0	0.7	0.0	0.3	0.0	0.9	0.0	0.3	0.0	0.0	0.0
Sample 13 C	1	11.7	0.0	0.0	7.6	110.2	0.0	0.0	0.0	0.1	0.3	4.9	0.0	10.1	2.3	0.0	1.2	0.2	0.2	0.1	0.2	0.0	0.8	1.1	0.0	2.9
Sample 13 D	1	23.0	0.0	0.0	6.8	49.7	0.0	0.0	0.0	0.5	0.7	2.7	0.0	2.6	1.0	0.0	0.3	0.1	0.3	0.6	0.2	0.0	1.6	0.6	0.0	1.9
Sample 13 E	1	56.1	0.0	0.0	8.8	41.5	0.0	0.0	0.0	1.7	6.0	1.6	0.0	1.3	0.9	0.0	0.2	0.2	2.4	6.6	0.3	0.0	3.3	0.5	0.1	2.0
Sample 13 F	1	61.1	0.0	0.0	6.4	37.2	0.0	0.0	0.0	1.2	4.8	1.1	0.0	1.2	1.2	0.0	0.6	0.1	2.6	5.9	0.4	0.0	6.1	0.4	0.1	1.8
Sample 13 G	1	61.6	0.0	0.1	6.3	33.1	0.0	0.5	0.0	1.6	14.9	0.8	0.0	1.0	13.6	0.0	0.6	0.1	5.8	11.3	0.8	0.0	6.4	0.3	0.4	1.7
Sample 13 G	2	62.7	0.0	0.1	6.5	34.9	0.0	0.5	0.0	1.7	15.5	0.8	0.0	1.0	14.3	0.0	0.4	0.1	6.0	11.8	1.1	0.0	7.5		0.5	1.8
Sample 13 H	1	66.3	0.0	0.1	5.7	29.8	0.0	0.3	0.0	1.4	15.1	0.7	0.0	1.3	8.9	0.0	0.6	0.1	5.2	9.1	1.0	0.0	8.4	0.3	0.5	1.8
Sample 13 I	1	Dil	0.1	0.2	9.9	50.5	0.0	0.4	0.1	4.2	Dil	1.2	0.0	3.4	15.0	0.0	1.1	0.3	17.4	Dil	4.9	0.0	22.7	0.6	1.0	3.8
Sample 13 I	5	164.5	0.1	0.2	10.8	57.2	0.0	0.4	0.1	4.7	104.1	1.4	0.0	3.8	16.8	0.0	0.4	0.3	20.4	25.0	6.0	0.1	26.8		1.1	4.2
Sample 13 J	1	Dil	0.1	0.2	7.4	30.4	0.0	0.2	0.2	2.9	Dil	0.8	0.0	4.1	10.4	0.0	0.7	0.2	14.6	14.5	4.7	0.0	Dil	0.4	1.1	3.2
Sample 13 J	5	142.7	0.1	0.2	7.6	32.8	0.0	0.2	0.2	3.0	112.9	0.9	0.0	4.4	11.3	0.0	-0.1	0.2	14.7	15.4	5.5	0.0	30.1		1.2	3.4
Sample 13 K	1	Dil	0.2	0.4	5.9	20.4	0.0	0.1	0.2	2.3	Dil	0.8	0.0	5.6	7.2	0.0	0.3	0.2	19.3	11.6	7.7	0.0	Dil	0.3	1.6	2.7
Sample 13 K	5	122.5	0.3	0.4	6.5	23.9	0.0	0.1	0.2	2.7	211.9	0.9	0.0	6.4	8.4	0.1	-0.3	0.2	21.7	13.3	9.2	0.0	32.5		1.8	3.1
Sample 13 L	1	89.6	0.2	0.4	4.2	15.3	0.0	0.1	0.2	1.5	Dil	0.6	0.0	7.3	5.3	0.0	0.2	0.2	12.9	7.2	6.1	0.0	22.3	0.2	1.6	2.2
Sample 13 L	5	90.5	0.3	0.4	4.6	17.2	0.0	0.1	0.2	1.7	213.5	0.7	0.0	8.1	6.1	0.0	-0.2	0.2	13.9	8.2	7.3	0.0	26.6		1.7	2.4
Sample 13 M	1	Dil	1.1	1.0	3.4	16.3	0.0	0.1	0.6	2.1	Dil	1.6	0.1	34.6	7.4	0.1	0.7	0.5	39.8	7.0	32.3	0.1	Dil	0.2	3.7	5.6
Sample 13 M	10	245.8	1.4	1.8	6.3	32.3	0.0	0.2	1.1	3.5	Dil	2.2	0.1	64.5	14.6	0.2	-2.2	0.9	51.5	11.9	37.7	0.0	51.2		6.1	8.8
Sample 13 M	20	249.4	1.4	1.2	6.3	34.9	0.0	0.2	1.2	3.7	1158	2.4	0.1	68.6	14.8	-0.2	-6.8	0.9	67.0	12.4	41.9	0.0	46.2		6.2	Dil
Sample 13 N	1	Dil	0.4	Dil	6.8	55.6	0.0	0.3	0.9	2.0	Dil	5.8	0.3	107.9	6.1	0.1	2.6	1.2	21.2	5.4	23.8	0.0	Dil	0.7	3.0	9.2
Sample 13 N	10	281.5	0.5	1.5	7.3	58.8	0.0	0.3	1.0	2.1	889.3	6.0	0.3	115.6	7.0	0.1	-1.9	1.3	24.7	5.9	26.4	0.0	30.3		3.1	10.3
Sample 14 A	5	0.4	0.2	0.0	0.0	4.7	0.0	0.0	0.0	0.0	0.8	2.1	0.0	0.8	0.1	-0.1	2.1	0.0	0.8	0.1	3.3	0.1	4.0	0.0	0.0	0.0
Sample 14 B	1	0.1	0.0	0.0	0.0	1.6	0.0	0.0	0.0	0.0	0.1	0.9	0.0	0.2	0.0	0.0	0.4	0.0	0.2	0.0	0.5	0.0	0.2	0.0	0.0	0.0
Sample 14 C	1	2.1	0.0	0.0	3.4	150.0	0.0	0.0	0.0	0.0	0.1	5.8	0.0	12.1	4.4	0.0	0.6	0.1	0.3	0.6	0.2	0.0	0.8	0.7	0.0	1.4
Sample 14 D	1	6.4	0.0	0.0	4.2	85.5	0.0	0.0	0.0	0.1	0.3	3.0	0.0	4.0	3.0	0.0	0.4	0.1	0.4	2.6	0.2	0.0	2.3	0.4	0.0	1.4
Sample 14 E	1	32.6	0.0	0.0	5.2	53.3	0.0	0.0	0.0	0.9	2.9	2.0	0.0	1.8	2.6	0.0	0.7	0.1	2.2	Dil	0.2	0.0	5.1	0.3	0.1	1.2
Sample 14 E	5	35.1	0.0	0.0	5.6	59.1	0.0	0.0	0.0	1.0	3.2	2.2	0.0	2.0	3.0	0.0	0.8	0.1	2.4	26.3	0.9	0.0	6.1		0.1	1.4
Sample 14 F	1	33.1	0.0	0.0	2.2	29.8	0.0	0.0	0.0	0.5	2.0	1.3	0.0	1.4	2.8	0.0	1.2	0.1	2.4	16.6	0.2	0.0	7.7	0.2	0.1	0.8
Sample 14 F	2	33.5	0.0	0.0	2.3	31.8	0.0	0.0	0.0	0.6	2.1	1.3	0.0	1.5	3.2	0.0	1.1	0.1	2.5	17.3	0.5	0.0	9.1		0.1	0.9
Sample 14 G	1	38.9	0.0	0.0	1.4	23.8	0.0	0.4	0.0	0.8	13.4	1.0	0.0	1.1	32.0	0.0	0.9	0.1	6.0	Dil	0.7	0.0	8.4	0.1	0.3	0.8
Sample 14 G	5	39.6	0.0	0.0	1.4	25.6	0.0	0.4	0.0	0.9	13.9	1.0	0.0	1.2	32.9	0.0	-0.1	0.1	6.3	36.1	1.3	0.0	9.6		0.3	0.8
Sample 14 H	1	37.7	0.0	0.0	0.8	21.5	0.0	0.1	0.0	0.6	12.6	0.8	0.0	1.5	9.0	0.0	1.2	0.0	6.2	18.3	0.8	0.0	10.4	0.1	0.2	0.7
Sample 14 H	2	37.6	0.0	0.0	0.8	22.6	0.0	0.1	0.0	0.6	12.6	0.8	0.0	1.6	9.2	0.0	0.9	0.0	6.5	19.0	1.0	0.0	11.7		0.2	0.7
Sample 14 I	1	87.0	0.1	0.1	1.0	34.1	0.0	0.1	0.2	1.1	69.5	1.2	0.0	3.6	8.1	0.0	1.9	0.1	17.2	Dil	3.3	0.0	24.9	0.2	0.4	1.3
Sample 14 I	5	81.6	0.1	0.1	1.0	35.2	0.0	0.1	0.2	1.1	67.0	1.2	0.0	3.7	8.4	0.1	1.8	0.1	17.4	25.4	3.9	0.1	26.5		0.4	1.3
Sample 14 J	1	68.6	0.1	0.1	0.6	18.8	0.0	0.1	0.2	0.6	59.6	0.9	0.0	3.5	4.3	0.0	1.1	0.1	12.9	9.4	2.5	0.0	23.1	0.1	0.3	0.9
Sample 14 K	1	55.3	0.1	0.1	0.4	12.6	0.0	0.0	0.2	0.4	86.7	1.0	0.0	3.9	2.8	0.0	1.0	0.0	13.5	5.7	3.6	0.0	19.8	0.1	0.3	0.8

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 14 L	1	44.0	0.1	0.1	0.3	9.0	0.0	0.0	0.2	0.3	90.2	0.8	0.0	4.4	2.3	0.0	0.8	0.0	9.8	3.5	2.8	0.0	16.2	0.0	0.3	0.7
Sample 14 M	1	71.5	0.4	0.5	0.4	10.7	0.0	0.0	0.6	0.5	Dil	1.3	0.0	8.3	5.0	0.1	0.3	0.1	33.2	6.0	13.8	0.0	20.2	0.0	0.8	1.5
Sample 14 M	10	69.5	0.4	0.6	0.4	10.8	0.0	0.0	0.6	0.5	320.9	1.3	0.0	8.4	5.3	0.0	-1.3	0.1	34.7	6.1	14.8	0.0	21.5		0.7	1.6
Sample 14 N	1	Dil	0.2	0.7	1.1	16.4	0.0	0.1	0.8	0.6	Dil	2.3	0.1	34.0	6.4	0.0	0.4	0.3	15.7	6.0	10.6	0.0	11.4	0.1	0.8	3.0
Sample 14 N	10	118.3	0.2	0.7	1.1	16.3	0.0	0.1	0.8	0.6	419.9	2.2	0.1	34.0	6.7	0.0	-1.1	0.3	16.2	6.1	11.7	0.0	12.4		0.8	3.1
Sample 15 A	5	0.1	0.3	0.0	0.0	1.8	0.0	0.0	0.0	0.0	0.1	6.4	0.0	0.3	0.0	-0.1	3.1	0.0	0.7	0.0	5.4	0.2	0.3	0.0	0.0	0.0
Sample 15 B	1	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	5.1	0.0	0.2	0.0	0.0	0.8	0.0	1.0	0.0	0.7	0.0	0.3	0.0	0.0	0.0
Sample 15 C	1	0.2	0.0	0.0	0.5	156.3	0.0	0.0	0.0	0.0	0.0	25.9	0.0	17.7	0.6	0.0	1.3	0.0	1.7	0.0	0.4	0.0	1.8	0.5	0.0	0.2
Sample 15 D	1	0.8	0.0	0.1	1.0	174.2	0.0	0.0	0.0	0.0	0.1	14.1	0.0	13.4	1.2	0.0	0.5	0.0	3.0	0.0	0.4	0.0	3.6	0.6	0.0	0.6
Sample 15 E	1	30.7	0.0	0.1	8.3	424.2	0.0	0.0	0.0	0.9	1.3	13.3	0.0	14.7	4.9	0.0	1.5	0.2	12.1	0.5	0.4	0.0	8.6	1.7	0.1	4.0
Sample 15 F	1	54.5	0.0	0.1	5.4	139.6	0.0	0.1	0.1	1.3	2.5	6.2	0.0	6.8	7.1	0.0	2.4	0.2	14.1	1.0	0.5	0.0	17.9	0.7	0.1	2.8
Sample 15 G	1	89.7	0.0	0.1	3.8	55.6	0.0	0.6	0.1	2.9	18.5	3.3	0.0	5.0	53.6	0.0	2.7	0.3	23.8	4.9	1.0	0.0	19.3	0.3	0.4	2.1
Sample 15 H	1	81.2	0.0	0.1	1.8	28.4	0.0	0.2	0.1	2.0	20.6	2.0	0.0	4.0	20.8	0.0	2.6	0.1	21.6	4.4	1.3	0.0	18.6	0.2	0.4	1.2
Sample 15 I	1	Dil	0.1	0.3	1.5	28.5	0.0	0.1	0.3	2.6	Dil	2.1	0.0	5.4	12.3	0.0	2.5	0.1	50.6	7.9	4.4	0.0	Dil	0.2	0.5	1.3
Sample 15 I	5	118.5	0.1	0.3	1.6	31.8	0.0	0.1	0.3	2.8	143.6	2.3	0.0	5.9	13.8	0.0	2.2	0.1	53.8	8.9	5.2	0.0	30.6		0.5	1.4
Sample 15 J	1	Dil	0.1	0.3	0.9	24.1	0.0	0.1	0.3	1.4	Dil	1.7	0.0	7.2	9.5	0.0	3.4	0.1	43.4	3.5	4.6	0.0	Dil	0.1	0.5	1.4
Sample 15 J	10	133.6	0.1	0.3	1.0	27.1	0.0	0.1	0.4	1.5	164.2	1.9	0.0	7.8	10.8	0.0	1.4	0.1	46.7	3.9	6.1	0.0	42.4		0.5	1.5
Sample 15 K	1	Dil	0.1	0.6	1.2	56.1	0.0	0.1	0.8	1.4	Dil	3.5	0.0	33.0	13.2	0.0	10.2	0.4	52.7	2.9	14.4	0.0	Dil	0.4	1.1	3.3
Sample 15 K	10	200.5	0.1	0.5	1.3	60.1	0.0	0.1	0.9	1.4	333.8	3.8	0.1	35.0	14.2	0.0	9.1	0.4	53.4	3.2	16.1	0.0	56.0		1.1	3.6
Sample 15 L	1	Dil	0.1	0.6	0.9	28.8	0.0	0.1	0.8	1.1	Dil	3.1	0.1	36.1	7.4	0.0	1.5	0.4	39.0	1.9	14.0	0.0	21.5	0.4	1.0	2.9
Sample 15 L	10	141.0	0.1	0.6	1.0	31.3	0.0	0.1	0.9	1.1	395.4	3.4	0.1	38.1	8.0	0.0	-0.4	0.4	40.3	2.1	15.8	0.0	22.9		1.0	3.2
Sample 15 M	1	23.8	0.2	0.4	0.3	3.9	0.0	0.0	0.4	0.6	Dil	1.5	0.0	5.2	1.2	0.0	-0.1	0.1	66.6	0.6	17.1	0.1	10.7	0.0	0.3	0.7
Sample 15 M	10	26.1	0.3	0.4	0.3	4.7	0.0	0.0	0.4	0.6	267.4	1.8	0.0	5.7	1.4	0.0	-3.3	0.1	74.2	0.7	20.0	0.0	12.7		0.2	0.7
Sample 15 N	1	91.6	0.1	0.7	0.6	7.8	0.0	0.1	0.6	1.0	Dil	3.9	0.1	32.3	4.0	0.0	0.2	0.4	23.4	1.0	13.7	0.0	7.8	0.1	0.5	2.7
Sample 15 N	10	95.4	0.2	0.8	0.7	9.0	0.0	0.1	0.7	1.0	468.8	4.9	0.1	36.1	4.6	0.0	-2.8	0.5	32.0	1.2	16.5	0.0	9.6		0.5	3.1
Sample 16 A	5	0.3	0.1	0.0	0.0	3.4	0.0	0.0	0.0	0.0	0.5	1.6	0.0	0.6	0.1	-0.1	3.4	0.0	0.6	0.0	3.5	0.0	0.5	0.0	0.0	0.0
Sample 16 B	1	0.2	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.1	0.8	0.0	0.2	0.0	0.0	1.4	0.0	0.3	0.0	0.8	0.0	0.3	0.0	0.0	0.0
Sample 16 C	1	1.5	0.0	0.0	1.3	136.8	0.0	0.0	0.0	0.0	0.1	5.7	0.0	17.4	3.0	0.0	1.9	0.1	0.1	0.0	0.3	0.0	0.4	0.7	0.0	1.4
Sample 16 D	1	6.4	0.0	0.0	2.4	132.7	0.0	0.0	0.0	0.1	0.3	3.6	0.0	9.2	3.8	0.0	0.9	0.1	0.2	0.1	0.3	0.0	1.6	0.8	0.0	2.4
Sample 16 E	1	38.5	0.0	0.0	5.4	104.6	0.0	0.1	0.0	1.1	3.8	2.4	0.0	3.2	3.9	0.0	1.1	0.3	1.0	1.0	0.3	0.0	2.5	0.7	0.1	3.1
Sample 16 F	1	44.7	0.0	0.0	2.6	35.9	0.0	0.1	0.0	0.9	3.8	1.2	0.0	1.4	3.7	0.0	1.2	0.2	1.4	1.3	0.4	0.0	4.9	0.3	0.1	1.4
Sample 16 G	1	50.8	0.0	0.1	1.7	17.6	0.0	0.5	0.1	1.6	23.2	0.8	0.0	1.2	31.2	0.0	1.3	0.1	2.9	4.5	0.9	0.0	5.7	0.3	0.3	1.0
Sample 16 H	1	40.1	0.0	0.1	0.9	9.4	0.0	0.2	0.1	1.1	25.5	0.6	0.0	1.3	12.3	0.0	0.7	0.1	2.8	3.7	1.3	0.0	5.4	0.1	0.3	0.6
Sample 16 I	1	64.6	0.1	0.3	0.5	6.1	0.0	0.1	0.5	0.9	Dil	0.5	0.0	3.9	12.6	0.0	0.7	0.1	9.5	3.5	4.4	0.0	13.5	0.1	0.5	0.9
Sample 16 I	5	65.4	0.1	0.2	0.8	9.5	0.0	0.1	0.4	1.7	142.2	0.7	0.0	2.4	13.7	0.0	-0.4	0.1	10.7	7.8	5.5	0.0	10.2		0.5	0.9
Sample 16 J	1	Dil	0.1	0.6	1.0	16.1	0.0	0.1	1.5	0.9	Dil	1.4	0.0	23.6	10.8	0.0	1.3	0.2	21.8	3.3	13.8	0.0	Dil	0.1	1.6	2.5
Sample 16 J	10	69.0	0.1	0.3	0.6	7.0	0.0	0.1	0.6	0.9	167.6	0.6	0.0	4.3	14.3	0.1	-0.3	0.1	10.1	4.0	5.8	0.1	15.6		0.6	1.0

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 16 K	1	0.2	1.0	0.1	0.1	20.2	0.1	0.1	0.1	0.1	0.5	9.4	0.1	9.8	0.1	0.1	18.7	0.1	1.0	0.1	19.8	0.9	0.9	0.1	0.1	0.1
Sample 16 L	1	Dil	0.1	0.6	0.9	10.9	0.0	0.1	1.4	0.6	Dil	1.4	0.1	23.3	3.6	0.0	0.1	0.2	15.8	1.8	11.0	0.0	14.6	0.1	1.3	2.2
Sample 16 L	10	131.9	0.1	0.6	1.0	12.1	0.0	0.1	1.5	0.6	385.9	1.6	0.1	25.2	4.0	0.0	-1.4	0.3	16.4	2.0	12.7	0.0	16.3		1.3	2.4
Sample 16 M	1	24.4	0.2	0.3	0.2	1.6	0.0	0.0	0.7	0.3	Dil	0.7	0.0	3.5	0.7	0.0	-0.2	0.1	45.6	0.5	15.6	0.0	8.7	0.0	0.3	0.5
Sample 16 M	10	25.1	0.2	0.4	0.2	1.8	0.0	0.0	0.7	0.3	213.4	0.7	0.0	3.6	0.7	0.0	-0.6	0.1	45.6	0.6	17.4	0.0	9.6		0.3	0.5
Sample 16 N	1	Dil	0.1	0.7	0.7	5.3	0.0	0.1	1.2	0.5	Dil	2.1	0.1	23.6	3.2	0.0	-0.1	0.3	22.9	0.7	10.9	0.0	7.3	0.0	0.6	2.2
Sample 16 N	10	118.0	0.1	0.7	0.8	5.8	0.0	0.1	1.3	0.5	421.7	2.4	0.1	25.4	3.5	0.0	-3.6	0.3	23.9	0.8	12.9	0.0	8.5		0.6	2.4
Sample 17 A	5	0.3	0.1	0.1	0.0	3.9	0.0	0.0	0.0	0.0	0.8	8.8	0.0	0.6	0.1	-0.1	6.0	0.0	1.9	0.0	5.3	0.0	0.9	0.0	0.0	0.0
Sample 17 B	1	0.1	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	0.1	4.3	0.0	0.1	0.0	0.0	2.2	0.0	2.1	0.0	1.0	0.0	0.3	0.0	0.0	0.0
Sample 17 C	1	0.6	0.0	0.0	0.5	154.3	0.0	0.0	0.0	0.0	0.1	33.5	0.0	16.8	2.2	0.0	3.8	0.0	1.4	0.0	0.4	0.0	0.3	0.6	0.0	0.6
Sample 17 D	1	2.2	0.0	0.0	1.0	155.2	0.0	0.0	0.0	0.0	0.2	18.5	0.0	10.1	2.9	0.0	0.9	0.1	3.4	0.0	0.4	0.0	0.8	0.6	0.0	1.5
Sample 17 E	1	32.1	0.0	0.0	4.9	222.9	0.0	0.1	0.0	1.0	2.8	14.9	0.0	6.1	4.2	0.0	1.8	0.3	16.1	0.6	0.6	0.0	1.3	1.0	0.2	3.8
Sample 17 F	1	53.4	0.0	0.0	3.4	80.5	0.0	0.1	0.0	1.2	3.7	5.9	0.0	1.4	3.5	0.0	0.8	0.2	21.7	1.0	0.6	0.0	2.8	0.4	0.3	1.8
Sample 17 G	1	66.7	0.0	0.0	2.6	29.0	0.0	0.5	0.0	2.0	18.9	2.7	0.0	0.7	23.2	0.0	0.6	0.1	28.0	4.0	1.0	0.0	3.5	0.2	0.9	0.9
Sample 17 H	1	53.9	0.0	0.0	1.5	13.3	0.0	0.1	0.0	1.4	20.8	1.6	0.0	0.9	6.9	0.0	0.3	0.1	23.4	3.6	1.3	0.0	3.7	0.1	0.7	0.6
Sample 17 I	1	77.2	0.1	0.2	1.6	10.6	0.0	0.1	0.1	2.0	Dil	1.7	0.0	1.7	3.3	0.0	-0.2	0.1	51.5	7.9	4.1	0.0	6.2	0.1	1.0	0.7
Sample 17 I	2	76.2	0.1	0.2	1.6	11.0	0.0	0.1	0.1	2.1	148.1	1.8	0.0	1.7	3.5	0.0	-0.4	0.1	50.9	8.2	4.4	0.0	7.1		1.0	0.7
Sample 17 J	1	79.1	0.1	0.2	1.0	6.8	0.0	0.0	0.1	1.1	Dil	1.2	0.0	2.9	1.9	0.0	-0.1	0.1	40.8	3.7	3.6	0.0	9.8	0.1	1.0	0.8
Sample 17 J	2	75.8	0.1	0.2	1.0	6.9	0.0	0.0	0.1	1.1	136.9	1.3	0.0	3.0	2.0	0.0	-0.3	0.1	39.5	3.9	3.9	0.0	11.2		1.1	0.8
Sample 17 K	1	Dil	0.1	0.5	1.1	16.0	0.0	0.1	0.3	1.1	Dil	2.4	0.0	19.1	3.9	0.0	0.6	0.2	48.1	3.7	13.1	0.0	24.2	0.1	3.1	2.5
Sample 17 K	5	180.4	0.1	0.4	1.2	17.6	0.0	0.1	0.4	1.2	272.2	2.7	0.0	20.8	4.3	0.0	-1.5	0.2	51.0	4.2	14.6	0.0	25.7		3.3	2.7
Sample 17 L	1	Dil	0.1	0.5	0.9	9.1	0.0	0.1	0.4	0.8	Dil	2.1	0.1	19.2	3.3	0.0	-0.1	0.2	35.5	2.0	12.8	0.0	14.3	0.0	2.7	2.1
Sample 17 L	10	154.4	0.1	0.5	1.0	11.0	0.0	0.1	0.5	0.9	333.0	2.4	0.1	22.3	3.9	0.0	-2.2	0.3	40.7	2.5	15.9	0.0	17.6		3.1	2.4
Sample 17 M	1	26.4	0.2	0.4	0.2	1.4	0.0	0.0	0.2	2.1	Dil	1.3	0.0	3.0	0.7	0.0	-0.2	0.1	67.2	0.7	20.9	0.1	9.9	0.0	0.8	1.5
Sample 17 M	5	28.2	0.3	0.4	0.2	1.6	0.0	0.0	0.3	2.3	235.6	1.6	0.0	3.2	0.7	0.0	-1.3	0.1	79.7	0.8	23.5	0.0	11.4		0.9	1.7
Sample 17 N	1	Dil	0.1	0.6	0.5	3.9	0.0	0.1	0.5	0.5	Dil	2.3	0.1	17.5	2.5	0.0	-0.3	0.3	35.4	0.9	14.3	0.1	8.0	0.0	1.6	1.6
Sample 17 N	10	106.0	0.2	0.6	0.6	4.4	0.0	0.1	0.5	0.5	355.3	2.7	0.1	18.6	2.7	0.2	-4.3	0.3	37.7	0.9	16.3	0.0	9.2		1.7	1.8
Sample 18 A	5	0.1	0.3	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.1	1.9	0.0	0.1	0.0	-0.1	2.6	0.0	0.4	0.0	5.6	0.3	0.2	0.0	0.0	0.0
Sample 18 B	1	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1	1.2	0.0	0.0	0.0	0.0	0.6	0.0	0.1	0.0	1.0	0.0	0.2	0.0	0.0	0.0
Sample 18 C	1	1.8	0.0	0.0	1.9	100.4	0.0	0.0	0.0	0.2	0.1	19.3	0.0	14.6	1.2	0.0	2.0	0.1	0.0	0.1	0.2	0.0	0.4	1.0	0.0	2.3
Sample 18 D	1	18.1	0.0	0.0	3.7	94.3	0.0	0.0	0.0	0.6	0.1	8.4	0.0	7.1	1.4	0.0	0.6	0.3	0.0	0.3	0.2	0.0	1.7	1.0	0.0	4.0
Sample 18 E	1	52.3	0.0	0.0	5.5	58.5	0.0	0.0	0.0	3.6	3.5	5.0	0.0	1.8	1.0	0.0	0.7	0.3	0.9	3.3	0.3	0.0	2.7	0.7	0.0	3.1
Sample 18 F	1	78.0	0.0	0.0	3.2	36.8	0.0	0.1	0.0	3.2	4.1	2.4	0.0	0.8	1.4	0.0	1.7	0.2	2.3	4.8	0.4	0.0	6.7	0.4	0.0	2.1
Sample 18 G	1	81.7	0.0	0.1	2.0	29.3	0.0	0.9	0.1	4.2	23.9	1.5	0.0	0.7	30.7	0.0	1.2	0.2	5.9	12.2	1.0	0.0	8.0	0.3	0.3	1.6
Sample 18 G	2	84.1	0.0	0.1	2.2	31.2	0.0	1.0	0.1	4.4	24.6	1.6	0.0	0.7	31.6	0.0	0.9	0.2	6.0	12.8	1.1	0.0	8.7		0.3	1.7
Sample 18 H	1	75.0	0.0	0.1	1.4	21.6	0.0	0.3	0.1	3.2	24.6	1.1	0.0	0.8	9.1	0.0	0.9	0.1	5.8	9.7	1.5	0.0	8.8	0.2	0.4	1.4
Sample 18 I	1	Dil	0.1	0.3	1.5	21.1	0.0	0.2	0.4	5.1	Dil	1.1	0.0	1.6	6.2	0.0	0.8	0.1	19.5	16.4	5.7	0.0	16.3	0.3	0.7	2.0

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 18 I	5	110.2	0.1	0.3	1.5	22.8	0.0	0.2	0.4	5.3	149.6	1.2	0.0	1.7	6.6	0.0	0.2	0.1	19.9	17.2	6.5	0.0	17.6		0.7	2.1
Sample 18 J	1	Dil	0.1	0.4	1.3	13.9	0.0	0.1	0.6	3.3	Dil	0.9	0.0	3.9	7.7	0.0	0.7	0.1	16.6	9.1	6.5	0.0	Dil	0.2	0.9	2.5
Sample 18 J	5	134.5	0.2	0.4	1.5	16.1	0.0	0.2	0.7	3.7	221.7	1.0	0.0	4.4	8.9	0.0	-1.4	0.2	18.1	10.5	7.7	0.0	30.7		1.0	2.9
Sample 18 K	1	Dil	0.4	0.8	2.0	25.5	0.0	0.3	1.5	3.5	Dil	2.2	0.0	25.3	18.8	0.1	1.5	0.4	31.6	10.2	19.4	0.0	Dil	0.3	2.7	6.4
Sample 18 K	10	231.4	0.4	0.9	2.3	29.1	0.0	0.3	1.7	3.8	525.8	2.5	0.0	28.2	21.2	0.1	-2.3	0.4	33.9	11.6	22.5	0.1	47.2		2.9	7.2
Sample 18 L	1	Dil	0.3	0.9	1.5	22.5	0.0	0.2	1.8	2.5	Dil	2.4	0.1	36.3	12.2	0.0	0.7	0.5	27.2	6.0	18.3	0.0	Dil	0.3	2.5	5.8
Sample 18 L	10	196.0	0.3	0.9	1.6	25.0	0.0	0.2	2.0	2.7	539.0	2.6	0.1	39.2	13.3	0.1	-2.4	0.5	28.5	6.7	21.0	0.0	29.2		2.7	6.4
Sample 18 M	1	50.5	0.8	0.6	0.5	4.5	0.0	0.0	1.3	1.7	Dil	1.2	0.0	7.6	2.0	0.1	-0.2	0.3	51.9	2.0	28.0	0.1	18.8	0.0	0.9	2.3
Sample 18 M	10	53.4	0.9	0.6	0.5	5.2	0.0	0.0	1.4	1.8	364.6	1.5	0.0	8.3	2.2	0.1	-0.9	0.3	61.0	2.2	32.1	0.0	20.9		0.9	2.6
Sample 18 N	1	Dil	0.3	0.8	1.0	9.7	0.0	0.1	1.5	1.6	Dil	3.1	0.2	36.3	4.9	0.1	0.2	0.6	22.6	1.8	15.5	0.0	11.6	0.1	1.0	4.5
Sample 18 N	10	153.1	0.4	0.8	1.1	11.3	0.0	0.1	1.6	1.8	496.8	3.9	0.2	40.6	5.6	0.1	-4.3	0.7	25.0	2.0	18.5	0.0	14.0		1.1	5.1
Sample 19 A	5	0.1	0.3	0.0	0.0	4.4	0.0	0.0	0.0	0.0	0.1	4.4	0.0	0.5	0.0	-0.1	2.0	0.0	1.0	0.0	7.0	0.2	0.5	0.0	0.0	0.0
Sample 19 B	1	0.0	0.0	0.0	0.0	8.6	0.0	0.0	0.0	0.0	0.0	5.4	0.0	0.9	0.0	0.0	1.1	0.0	0.8	0.0	1.1	0.0	1.3	0.0	0.0	0.0
Sample 19 C	1	0.0	0.0	0.0	0.2	108.5	0.0	0.0	0.0	0.0	0.0	13.2	0.0	10.2	0.0	0.0	1.3	0.0	0.1	0.0	0.8	0.0	3.5	0.3	0.0	0.0
Sample 19 D	1	0.0	0.0	0.1	0.3	173.7	0.0	0.0	0.0	0.0	0.0	9.6	0.0	13.5	0.2	0.0	0.7	0.0	0.1	0.0	0.6	0.0	5.9	0.5	0.0	0.0
Sample 19 E	1	0.6	0.0	0.2	3.1	Dil	0.0	0.1	0.0	0.0	0.1	18.0	0.0	40.3	8.7	0.0	2.6	0.1	0.1	0.0	0.8	0.0	Dil	2.4	0.0	1.9
Sample 19 E	10	5.9	0.0	0.2	3.8	951.5	0.0	0.1	0.0	0.0	0.4	19.0	0.0	45.2	10.1	0.0	2.4	0.1	0.2	0.0	2.0	0.0	41.3		0.0	2.7
Sample 19 F	1	Dil	0.0	0.2	9.1	Dil	0.1	0.4	0.4	0.4	7.3	13.1	0.1	40.0	32.0	0.0	4.1	0.5	4.5	1.2	1.1	0.0	Dil	1.7	0.3	10.3
Sample 19 F	10	113.0	0.0	0.2	10.2	669.9	0.1	0.5	0.5	0.4	8.2	14.2	0.1	44.9	36.6	0.0	3.7	0.6	4.8	1.4	2.3	0.0	90.7		0.3	12.0
Sample 19 G	1	Dil	0.1	0.2	6.7	402.5	0.0	0.6	1.2	4.7	58.0	10.1	0.1	53.0	45.4	0.0	4.9	0.7	28.4	16.7	2.4	0.0	Dil	1.0	2.2	6.2
Sample 19 G	10	182.1	0.1	0.2	7.3	418.1	0.0	0.7	1.3	4.9	60.6	10.7	0.1	57.6	51.8	0.0	2.0	0.8	29.9	18.7	3.5	0.1	117.8		2.4	7.0
Sample 19 H	1	95.5	0.1	0.2	2.5	167.1	0.0	0.2	0.8	2.3	76.0	5.1	0.1	36.7	13.3	0.0	4.0	0.3	22.6	10.0	2.8	0.0	Dil	0.5	1.0	2.6
Sample 19 H	10	98.2	0.1	0.2	2.8	181.3	0.0	0.2	0.9	2.5	78.5	5.7	0.1	39.7	14.9	0.0	1.9	0.3	23.9	11.3	4.1	0.0	86.3		1.1	2.9
Sample 19 I	1	Dil	0.3	0.6	2.7	209.5	0.0	0.1	2.8	2.7	Dil	6.8	0.1	53.9	16.8	0.1	4.9	0.4	55.4	11.6	8.8	0.0	Dil	0.6	1.3	3.2
Sample 19 I	10	160.4	0.3	0.6	3.0	223.8	0.0	0.2	3.1	2.9	360.3	7.4	0.1	58.1	18.6	0.1	2.0	0.4	59.0	12.9	10.4	0.0	135.4		1.3	3.6
Sample 19 J	1	Dil	0.1	0.4	2.3	148.6	0.0	0.1	2.6	1.3	Dil	5.3	0.0	44.5	11.0	0.1	4.2	0.2	22.5	4.1	7.5	0.0	Dil	0.4	1.0	2.1
Sample 19 J	10	114.5	0.2	0.4	2.5	165.2	0.0	0.1	2.9	1.3	244.5	5.9	0.1	48.8	12.4	0.1	3.3	0.3	24.1	4.6	9.2	0.0	105.4		1.1	2.3
Sample 19 K	1	Dil	0.2	0.9	2.6	307.6	0.0	0.3	7.0	1.7	Dil	11.1	0.1	167.1	26.3	0.1	9.5	0.7	24.3	3.7	32.5	0.0	Dil	0.9	1.7	4.7
Sample 19 K	10	265.5	0.3	0.9	2.8	317.5	0.0	0.2	7.4	1.6	517.2	11.5	0.2	173.6	28.3	0.1	6.9	0.8	24.7	4.2	34.4	0.0	146.7		1.8	5.2
Sample 19 L	1	Dil	0.1	0.7	1.7	91.2	0.0	0.1	3.2	0.8	Dil	8.9	0.1	138.8	18.0	0.0	3.8	0.5	12.2	1.7	20.7	0.0	Dil	0.5	1.2	2.9
Sample 19 L	10	148.3	0.1	0.6	1.6	87.6	0.0	0.1	3.1	0.7	376.6	8.6	0.1	129.5	17.7	0.0	0.3	0.5	11.1	1.7	20.5	0.0	37.4		1.1	3.0
Sample 19 M	1	Dil	0.4	Dil	1.6	30.2	0.0	0.1	3.5	1.1	Dil	14.9	0.1	137.7	35.4	0.1	1.4	0.7	23.1	1.6	55.6	0.0	Dil	0.2	1.2	3.4
Sample 19 M	10	145.2	0.4	1.4	1.7	31.4	0.0	0.1	3.6	1.0	816.7	15.7	0.1	139.7	37.5	0.1	-0.9	0.8	23.0	1.7	57.1	0.0	22.8		1.2	3.8
Sample 19 N	1	66.7	0.1	0.5	0.7	10.6	0.0	0.0	0.9	0.3	Dil	7.2	0.1	64.9	8.6	0.0	0.9	0.3	6.6	0.4	14.1	0.0	16.2	0.1	0.6	2.4
Sample 19 N	10	66.9	0.1	0.6	0.7	10.8	0.0	0.0	0.9	0.3	290.4	7.8	0.1	63.8	9.0	0.1	-0.8	0.3	6.7	0.4	15.5	0.0	16.4		0.6	2.6
Sample 20 A	5	0.1	0.1	0.0	0.0	8.6	0.0	0.0	2.0	0.0	0.0	2.0	0.0	6.1	0.0	0.0	2.6	0.0	0.2	0.0	5.1	0.1	1.0	0.0	0.0	0.0
Sample 20 B	1	0.0	0.0	0.0	0.0	10.5	0.0	0.0	2.7	0.0	0.0	1.2	0.0	6.8	0.0	0.0	0.9	0.0	0.0	0.0	3.5	0.0	0.8	0.0	0.0	0.0
Sample 20 C	1	0.0	0.0	0.0	0.2	135.1	0.0	0.0	1.8	0.0	0.0	2.0	0.0	52.6	0.0	0.0	0.8	0.0	0.0	0.0	2.5	0.0	1.2	0.2	0.0	0.0
Sample 20 D	1	0.0	0.0	0.0	0.4	164.0	0.0	0.0	1.2	0.0	0.0	1.2	0.0	43.8	0.0	0.0	0.6	0.0	0.0	0.0	1.8	0.0	2.0	0.3	0.0	0.0

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 20 E	1	0.0	0.0	0.1	1.7	Dil	0.0	0.0	1.7	0.0	0.0	1.3	0.0	77.1	0.1	0.0	1.1	0.0	0.0	0.0	2.6	0.0	5.5	1.2	0.0	0.0
Sample 20 E	20	0.0	0.1	0.2	1.8	844.8	0.0	0.0	1.7	0.0	0.3	1.2	0.0	79.8	0.1	0.1	0.7	0.0	0.0	0.1	3.5	-0.1	5.1	1.1	0.0	0.0
Sample 20 F	1	0.0	0.0	0.1	1.8	Dil	0.0	0.0	1.6	0.0	0.0	1.0	0.0	77.7	0.1	0.0	1.2	0.1	0.0	0.0	2.4	0.0	7.6	1.2	0.0	0.0
Sample 20 F	20	0.0	0.1	0.1	1.9	914.5	0.0	0.0	1.6	0.0	0.1	0.8	0.0	79.0	0.1	0.0	6.4	0.1	0.0	0.0	3.4	-0.1	6.9	1.1	-0.1	0.0
Sample 20 G	1	0.2	0.0	0.1	3.5	Dil	0.0	0.1	4.5	0.0	0.1	1.1	0.0	114.2	5.4	0.0	2.4	0.3	0.0	0.0	4.7	0.0	15.5	2.0	0.9	0.0
Sample 20 G	50	0.3	0.1	0.2	3.6	1753	0.0	0.1	4.8	0.0	0.2	0.9	0.0	120.0	5.9	0.1	4.9	0.4	-0.1	0.0	7.3	-0.4	13.9	1.8	0.8	0.0
Sample 20 H	1	1.6	0.0	0.1	4.0	Dil	0.0	0.2	5.1	0.0	0.1	1.0	0.0	127.7	9.1	0.0	2.3	0.7	0.0	0.0	3.5	0.0	20.0	1.9	0.9	0.7
Sample 20 H	50	2.7	0.1	0.1	4.1	1739	0.0	0.2	5.5	0.0	0.3	0.9	0.0	134.2	10.0	0.1	9.4	0.7	0.1	0.1	5.9	-0.5	18.5	1.8	0.9	1.3
Sample 20 I	1	Dil	0.3	0.6	Dil	Dil	0.1	2.1	60.8	5.7	Dil	2.9	0.1	Dil	32.7	0.0	7.7	10.3	7.9	18.5	6.7	0.0	Dil	3.7	5.4	23.5
Sample 20 I	5	Dil	0.3	0.6	11.3	Dil	0.1	2.2	66.5	5.7	222.5	2.4	0.1	1518	35.4	0.0	5.8	11.2	7.8	20.0	6.8	0.0	Dil	3.8	5.8	25.8
Sample 20 I	50	626.0	0.3	1.0	14.9	5198	0.1	3.1	88.4	7.3	285.9	2.9	0.2	1946	47.1	0.0	-5.4	15.2	10.1	27.8	11.2	0.0	392.3	5.0	7.5	35.9
Sample 20 J	1	Dil	0.2	0.7	6.8	Dil	0.0	2.5	67.2	3.5	Dil	3.9	0.2	Dil	27.9	0.0	9.2	13.9	3.2	9.8	16.4	0.0	Dil	2.3	4.8	18.8
Sample 20 J	50	914.2	0.1	1.0	9.9	3608	0.1	3.9	104.8	4.9	254.5	4.1	0.4	4028	42.4	0.0	0.6	22.6	4.5	16.0	25.6	-0.1	501.7	3.2	7.1	31.2
Sample 20 K	1	Dil	2.8	Dil	6.5	Dil	0.1	1.4	Dil	9.4	Dil	5.2	Dil	Dil	33.4	0.0	5.1	7.1	37.5	Dil	28.9	0.0	Dil	0.1	Dil	15.0
Sample 20 K	20	963.1	3.1	5.4	7.8	1410	0.1	1.8	294.9	9.9	Dil	4.8	0.4	1121	41.7	0.0	-1.4	9.4	44.9	53.8	36.5	-0.2	Dil	0.1	14.0	20.8
Sample 20 K	50	1106	3.5	6.5	9.1	1647	0.1	2.0	348.8	11.7	4332	5.4	0.6	1307	48.9	0.0	-5.1	11.2	53.5	63.5	43.8	-0.6	889.6	0.1	16.4	24.9
Sample 20 L	1	Dil	0.9	0.7	2.3	224.0	0.0	0.2	50.2	1.4	Dil	2.0	0.1	91.4	7.0	0.0	1.7	0.8	9.0	6.1	8.9	0.0	Dil	0.3	1.6	4.4
Sample 20 L	20	124.4	0.9	1.0	2.5	243.0	0.0	0.2	54.6	1.5	459.9	2.0	0.1	98.4	7.7	0.3	1.6	0.9	9.5	7.0	11.0	-0.1	44.7	0.3	1.6	5.0
Sample 20 M	1	29.0	1.7	0.6	1.5	28.9	0.0	0.1	27.9	0.9	Dil	1.8	0.0	13.6	3.0	0.0	-0.1	0.4	9.5	2.6	12.0	0.0	23.3	0.1	1.0	1.7
Sample 20 M	20	31.6	1.9	0.8	1.6	32.1	0.0	0.1	30.3	0.9	388.9	2.1	0.0	14.9	3.2	0.1	-2.2	0.4	9.9	2.9	15.1	0.0	20.9	0.0	0.9	1.9
Sample 20 N	1	92.4	0.6	1.0	1.5	27.0	0.0	0.2	36.9	1.2	Dil	3.8	0.1	48.8	6.6	0.0	1.6	0.7	6.7	2.5	12.1	0.0	8.7	0.3	0.8	3.8
Sample 20 N	20	110.8	0.7	1.4	1.8	35.2	0.0	0.3	46.7	1.5	798.8	5.0	0.1	62.3	8.3	0.1	-0.2	0.9	8.2	3.3	17.1	-0.1	10.2	0.3	1.0	4.9
Sample 20																										
Sample 21 A	5	0.2	0.4	-0.1	0.0	7.9	0.0	0.0	0.0	0.1	0.5	4.5	0.0	0.9	0.0	-0.1	0.6	0.0	0.9	0.1	6.0	0.2	1.9	0.0	0.0	0.0
Sample 21 B	1	0.0	0.0	0.0	0.0	9.7	0.0	0.0	0.0	0.0	0.1	4.8	0.0	1.0	0.0	0.0	1.3	0.0	0.3	0.0	1.6	0.0	0.9	0.0	0.0	0.0
Sample 21 C	1	0.0	0.0	0.0	0.4	159.1	0.0	0.0	0.0	0.0	0.0	15.5	0.0	15.8	0.0	0.0	1.9	0.0	0.0	0.0	0.7	0.0	3.9	0.6	0.0	0.0
Sample 21 D	1	0.1	0.0	0.1	0.4	179.1	0.0	0.0	0.0	0.0	0.0	13.0	0.0	15.4	0.2	0.0	0.7	0.0	1.0	0.0	0.7	0.0	5.9	0.7	0.0	0.1
Sample 21 E	1	11.2	0.1	0.2	5.2	Dil	0.0	0.0	0.0	0.1	0.3	19.5	0.0	36.3	3.8	0.0	1.7	0.1	4.6	0.1	1.3	0.0	Dil	3.8	0.0	7.4
Sample 21 E	5	12.2	0.1	0.2	5.6	876.3	0.0	0.0	0.0	0.1	0.4	19.7	0.0	39.3	4.1	0.0	0.7	0.1	4.9	0.2	1.9	0.0	32.3		0.0	8.4
Sample 21 F	1	39.7	0.1	0.2	Dil	Dil	0.1	0.1	0.0	0.5	1.3	17.9	0.0	28.6	8.6	0.0	3.4	0.3	10.1	1.3	1.6	0.0	Dil	4.0	0.1	19.3
Sample 21 F	5	41.4	0.1	0.2	11.0	790.5	0.1	0.1	0.0	0.6	1.4	18.2	0.0	31.3	9.5	0.0	0.3	0.3	10.8	1.5	2.2	0.0	63.4		0.1	21.6
Sample 21 G	1	Dil	0.2	0.3	Dil	Dil	0.2	0.8	0.1	3.8	7.9	17.9	0.1	30.6	54.0	0.0	6.4	0.9	39.6	15.1	3.1	0.0	Dil	4.6	1.9	39.7
Sample 21 G	10	177.6	0.3	0.3	23.7	817.0	0.2	0.9	0.1	4.0	9.4	17.4	0.1	33.0	62.4	0.0	4.2	1.0	44.6	16.4	4.6	0.1	96.5		2.1	44.3
Sample 21 H	1	Dil	0.2	0.2	Dil	389.2	0.1	0.3	0.1	6.1	14.4	11.2	0.1	34.3	18.6	0.0	4.9	0.6	36.8	Dil	3.3	0.0	Dil	2.1	1.0	21.6
Sample 21 H	10	154.9	0.2	0.2	13.5	383.4	0.1	0.3	0.1	6.1	15.5	10.7	0.1	35.3	20.5	0.0	0.2	0.7	40.1	23.3	4.6	0.1	103.6		1.1	23.5
Sample 21 I	1	Dil	0.5	0.5	Dil	466.8	0.1	0.2	0.2	17.6	Dil	13.5	0.1	61.0	14.9	0.0	6.8	0.7	71.7	Dil	8.9	0.0	Dil	2.2	0.9	22.1
Sample 21 I	20	229.3	0.5	0.5	13.1	430.9	0.1	0.2	0.2	16.7	165.0	12.2	0.1	60.3	15.7	0.0	2.7	0.8	74.2	70.9	11.2	0.0	162.3		0.9	23.5
Sample 21 J	1	Dil	0.4	0.4	6.4	245.6	0.0	0.1	0.2	9.4	Dil	8.6	0.1	47.2	8.4	0.0	3.9	0.5	33.0	Dil	7.8	0.0	Dil	1.2	0.6	13.4
Sample 21 J	10	170.2	0.4	0.4	6.2	239.0	0.0	0.1	0.2	9.0	142.5	8.1	0.1	46.9	9.0	0.0	1.4	0.5	34.6	28.8	8.6	0.0	128.0		0.6	14.2

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 21 K	1	Dil	0.4	0.5	4.7	166.0	0.0	0.1	0.2	7.4	Dil	7.1	0.1	41.8	5.9	0.0	3.0	0.4	23.6	18.8	9.9	0.0	Dil	0.9	0.6	9.7
Sample 21 K	10	136.1	0.4	0.5	4.7	169.1	0.0	0.1	0.2	7.4	206.2	6.9	0.1	41.6	6.3	0.0	0.9	0.5	24.9	19.0	10.8	0.0	110.8		0.6	10.3
Sample 21 L	1	Dil	0.3	0.4	3.3	120.0	0.0	0.1	0.3	4.6	Dil	5.4	0.1	37.9	4.6	0.0	1.4	0.4	13.5	9.6	9.5	0.0	Dil	0.7	0.5	7.9
Sample 21 L	10	107.0	0.3	0.4	3.3	117.6	0.0	0.1	0.3	4.4	185.9	5.3	0.1	37.4	4.9	0.0	0.3	0.4	14.1	9.8	10.3	0.0	86.7		0.5	8.3
Sample 21 M	1	Dil	1.0	0.9	2.8	104.9	0.0	0.1	0.9	6.8	Dil	7.0	0.1	49.5	7.6	0.1	1.0	0.9	23.1	13.8	22.1	0.1	Dil	0.6	1.3	11.1
Sample 21 M	10	130.5	1.0	1.0	3.0	108.4	0.0	0.1	0.9	7.0	539.6	7.6	0.1	52.2	8.5	0.1	0.2	1.0	24.2	14.9	24.0	0.0	80.9		1.4	12.6
Sample 21 N	1	Dil	0.8	Dil	4.1	181.1	0.0	0.3	1.4	5.8	Dil	14.2	0.3	149.8	15.9	0.1	3.2	1.5	18.4	16.3	30.2	0.0	Dil	1.5	1.9	22.0
Sample 21 N	20	326.7	0.9	1.9	4.5	198.6	0.0	0.4	1.6	6.0	1023	15.3	0.3	165.2	18.7	0.1	-3.7	1.8	21.2	18.7	35.4	0.1	43.5		2.0	26.7
Sample 22 A	1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.6	0.0	0.3	0.0	2.0	0.1	0.0	0.0	0.0	0.0
Sample 22 B	1	0.0	0.0	0.0	0.0	7.6	0.0	0.0	0.0	0.0	0.0	1.8	0.0	0.9	0.0	0.0	0.3	0.0	0.3	0.0	0.7	0.0	0.4	0.0	0.0	0.0
Sample 22 C	1	0.1	0.0	0.0	0.5	183.3	0.0	0.0	0.0	0.0	0.0	3.5	0.0	13.3	0.3	0.0	0.5	0.0	0.4	0.0	1.1	0.0	3.0	0.4	0.0	0.1
Sample 22 D	1	0.1	0.0	0.0	0.7	196.3	0.0	0.0	0.0	0.0	0.0	2.2	0.0	10.2	0.8	0.0	0.2	0.0	0.3	0.0	1.4	0.0	4.9	0.5	0.0	0.3
Sample 22 E	1	26.4	0.1	0.1	6.7	Dil	0.2	0.0	0.1	1.8	2.9	3.0	0.0	17.9	4.9	0.0	2.5	0.4	2.8	3.2	1.6	0.0	15.8	1.3	0.4	7.5
Sample 22 E	5	54.4	0.2	0.2	13.6	1039	0.3	0.1	0.2	3.7	6.2	5.9	0.0	38.3	10.4	-0.1	1.0	0.7	5.8	6.5	3.6	0.0	35.2		0.8	Dil
Sample 22 F	1	37.5	0.1	0.1	2.8	198.3	0.1	0.1	0.2	2.4	7.7	2.0	0.0	30.2	8.4	0.0	2.6	0.6	3.0	5.0	1.1	0.0	23.9	0.5	0.5	7.3
Sample 22 G	1	50.5	0.2	0.1	1.9	110.5	0.1	0.3	0.3	3.8	28.3	1.7	0.0	31.3	32.4	0.0	1.1	1.0	7.2	10.3	1.4	0.0	26.7	0.3	1.8	6.6
Sample 22 H	1	42.3	0.1	0.1	0.9	51.1	0.0	0.1	0.3	2.1	24.6	1.3	0.0	23.0	10.1	0.0	1.4	0.5	6.5	5.6	1.3	0.0	22.7	0.2	1.0	4.1
Sample 22 I	1	74.2	0.4	0.2	1.0	57.8	0.0	0.1	0.6	2.6	Dil	1.8	0.0	22.2	10.9	0.1	2.5	0.6	18.8	7.2	3.5	0.0	Dil	0.2	1.2	4.2
Sample 22 I	2	92.3	0.4	0.2	1.2	72.1	0.0	0.1	0.8	3.2	137.5	2.2	0.0	28.7	14.2	0.1	1.7	0.8	23.7	9.2	4.5	0.0	Dil		1.5	Dil
Sample 22 J	1	68.3	0.2	0.2	0.7	56.9	0.0	0.1	0.8	1.4	93.4	1.6	0.0	16.1	9.7	0.2	1.8	0.5	11.7	2.9	2.7	0.0	Dil	0.1	0.9	2.8
Sample 22 J	2	85.9	0.3	0.2	0.9	71.5	0.0	0.1	1.1	1.7	122.7	2.0	0.0	20.7	12.6	0.2	2.0	0.6	14.6	3.6	3.6	0.0	48.8		1.2	Dil
Sample 22 K	1	Dil	0.3	0.3	1.0	143.0	0.0	0.1	2.4	1.5	Dil	2.8	0.0	46.5	24.0	0.9	4.5	0.8	14.1	3.1	6.5	0.0	Dil	0.4	1.8	3.3
Sample 22 K	5	134.2	0.4	0.3	1.4	192.1	0.0	0.2	3.3	2.1	315.3	4.0	0.1	63.2	32.8	1.1	4.0	1.1	18.3	4.2	9.5	0.0	57.9		2.4	Dil
Sample 22 L	1	89.3	0.2	0.4	1.1	108.4	0.0	0.1	3.1	1.3	Dil	2.3	0.1	52.1	29.5	0.9	1.8	0.7	10.4	2.5	6.0	0.0	23.6	0.5	1.8	2.3
Sample 22 L	5	110.9	0.3	0.4	1.4	141.3	0.0	0.1	4.1	1.7	438.6	3.1	0.1	69.2	39.4	1.2	1.1	0.9	13.3	3.4	8.8	0.0	35.7		2.3	Dil
Sample 22 M	1	17.7	0.7	0.4	0.3	19.4	0.0	0.0	1.8	0.8	Dil	1.1	0.0	17.2	19.8	0.8	-0.2	0.4	14.8	1.2	8.3	0.1	11.7	0.0	0.6	0.8
Sample 22 M	5	20.2	0.8	0.4	0.4	23.2	0.0	0.0	2.0	0.9	324.8	1.3	0.0	20.3	23.1	0.9	-1.5	0.4	16.3	1.5	10.7	0.0	14.8		0.7	Dil
Sample 22 N	1	61.6	0.5	Dil	0.8	23.3	0.0	0.2	3.4	1.5	Dil	2.3	0.1	55.7	41.6	1.4	0.1	0.9	10.2	2.1	8.0	0.0	8.6	0.2	1.1	3.2
Sample 22 N	10	67.8	0.5	1.1	0.9	28.2	0.0	0.2	3.9	1.7	1210	2.8	0.1	66.1	51.2	1.4	-3.6	1.1	11.6	2.5	11.2	0.0	11.3		1.3	Dil
Sample 23 A	5	0.0	0.2	0.0	0.1	17.4	0.0	0.0	0.0	0.1	0.4	2.8	0.0	1.9	0.0	-0.1	2.0	0.0	0.4	0.0	4.2	0.1	0.7	0.0	0.0	0.0
Sample 23 B	1	0.0	0.0	0.0	0.0	9.6	0.0	0.0	0.0	0.0	0.0	2.0	0.0	1.0	0.0	0.0	0.6	0.0	0.2	0.0	1.0	0.0	0.4	0.0	0.0	0.0
Sample 23 C	1	0.1	0.0	0.0	1.4	183.6	0.0	0.0	0.0	0.0	0.0	4.5	0.0	13.2	0.4	0.0	0.4	0.0	0.1	0.0	0.7	0.0	2.4	0.6	0.0	0.5
Sample 23 D	1	0.4	0.0	0.0	2.0	201.9	0.0	0.0	0.0	0.0	0.1	3.1	0.0	10.2	1.1	0.0	0.4	0.0	0.1	0.0	0.8	0.0	4.8	0.6	0.0	1.7
Sample 23 E	1	19.8	0.0	0.1	Dil	Dil	0.1	0.1	0.0	5.5	2.2	5.0	0.0	13.0	4.3	0.0	2.3	0.2	1.8	16.1	0.8	0.0	10.0	1.6	0.1	20.5
Sample 23 E	5	19.1	0.0	0.1	15.7	448.0	0.1	0.1	0.0	5.5	2.1	4.5	0.0	12.7	4.2	0.0	0.7	0.2	1.7	15.5	0.8	0.0	9.5	1.5	0.1	20.0
Sample 23 F	1	46.3	0.0	0.0	8.4	173.0	0.0	0.1	0.1	6.0	5.0	3.1	0.0	23.0	7.4	0.0	2.7	0.2	2.2	Dil	0.6	0.0	22.1	0.7	0.1	21.4
Sample 23 F	2	43.5	0.0	0.0	7.4	164.8	0.0	0.1	0.1	5.9	4.8	2.9	0.0	22.2	7.0	0.0	2.3	0.2	2.0	22.3	0.5	0.0	22.8	0.7	0.1	20.5
Sample 23 F	5	58.8	0.0	0.1	10.1	225.1	0.1	0.2	0.1	7.8	6.6	4.3	0.0	30.4	9.9	0.0	1.0	0.3	2.7	30.7	1.2	0.0	34.2		0.2	28.4
Sample 23 G	1	65.4	0.1	0.1	5.6	106.0	0.0	0.5	0.1	8.5	25.4	2.3	0.0	21.9	33.9	0.0	2.5	0.3	5.8	Dil	1.1	0.0	22.8	0.5	0.5	14.5

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 23 G	5	58.6	0.1	0.1	4.9	97.3	0.0	0.5	0.1	8.3	23.5	2.1	0.0	20.8	32.3	0.0	0.8	0.3	5.2	40.3	1.1	0.0	22.2	0.4	0.5	13.6
Sample 23 H	1	51.3	0.1	0.1	3.2	57.3	0.0	0.1	0.1	5.2	25.7	1.6	0.0	17.1	7.6	0.0	1.5	0.2	5.4	Dil	1.3	0.0	19.7	0.3	0.3	7.5
Sample 23 H	2	49.5	0.1	0.1	3.1	56.1	0.0	0.1	0.1	5.2	25.3	1.5	0.0	17.0	7.5	0.0	0.8	0.1	5.1	23.3	1.2	0.0	20.9	0.3	0.3	7.4
Sample 23 H	5	56.6	0.1	0.1	3.7	66.7	0.0	0.1	0.1	6.1	29.2	1.8	0.0	19.8	9.0	0.0	0.3	0.2	5.9	27.2	1.9	0.0	27.0		0.4	8.7
Sample 23 I	1	86.9	0.2	0.2	4.1	64.6	0.0	0.1	0.2	7.8	Dil	2.1	0.0	18.0	5.3	0.0	0.6	0.2	18.0	Dil	4.5	0.0	Dil	0.4	0.5	7.0
Sample 23 I	5	79.4	0.2	0.2	3.8	62.8	0.0	0.1	0.2	7.2	118.5	1.9	0.0	17.8	5.1	0.0	0.2	0.2	17.2	25.2	4.7	0.0	30.2	0.3	0.4	6.7
Sample 23 J	1	83.0	0.2	0.2	3.4	46.8	0.0	0.1	0.3	4.2	Dil	1.7	0.0	14.8	4.5	0.0	0.8	0.2	13.2	10.0	4.2	0.0	Dil	0.3	0.4	5.4
Sample 23 J	5	76.1	0.2	0.2	3.2	45.6	0.0	0.1	0.3	4.1	120.0	1.6	0.0	14.6	4.5	0.0	0.9	0.2	12.5	9.6	4.3	0.0	33.0	0.3	0.4	5.2
Sample 23 K	1	Dil	0.2	0.4	3.9	80.1	0.0	0.1	0.7	4.5	Dil	3.4	0.1	35.8	13.3	0.0	2.0	0.4	17.8	12.0	11.0	0.0	Dil	0.8	0.9	11.6
Sample 23 K	5	141.7	0.2	0.4	3.5	76.7	0.0	0.1	0.7	4.3	285.6	3.2	0.1	34.9	12.8	0.0	1.2	0.4	16.7	11.5	11.1	0.0	43.0	0.7	0.9	11.3
Sample 23 L	1	Dil	0.1	0.5	2.8	41.7	0.0	0.1	0.8	2.8	Dil	3.0	0.1	27.7	11.4	0.0	1.5	0.4	13.4	8.3	10.6	0.0	20.1	0.6	0.9	7.8
Sample 23 L	5	109.5	0.1	0.6	2.7	41.7	0.0	0.1	0.8	2.8	414.0	3.0	0.1	28.1	11.5	0.0	-0.7	0.4	13.0	8.3	11.1	0.0	20.4	0.6	0.9	7.8
Sample 23 M	1	19.4	0.5	0.3	1.5	5.4	0.0	0.0	0.4	1.2	Dil	1.9	0.0	5.0	4.6	0.0	-0.3	0.2	23.6	2.8	12.2	0.0	9.8	0.1	0.2	1.6
Sample 23 M	5	18.9	0.5	0.4	1.4	5.6	0.0	0.0	0.4	1.2	216.1	2.0	0.0	5.1	4.6	0.1	-1.0	0.2	23.3	2.8	13.2	0.0	9.6	0.0	0.2	1.6
Sample 23 N	1	77.2	0.3	0.8	1.9	11.0	0.0	0.1	1.1	1.5	Dil	3.9	0.1	24.5	14.2	0.1	0.7	0.5	13.7	4.1	13.6	0.0	7.1	0.2	0.5	6.9
Sample 23 N	5	71.8	0.3	0.9	1.8	11.1	0.0	0.0	1.1	1.5	Dil	4.1	0.1	25.1	14.2	0.1	-0.4	0.5	13.3	4.1	14.3	0.0	6.9	0.2	0.4	7.0
Sample 23 N	10	76.1	0.3	1.0	1.9	11.3	0.0	0.0	1.1	1.5	593.0	4.3	0.1	25.6	15.1	0.1	-2.4	0.5	13.8	4.4	15.5	0.0	8.5		0.4	7.6
Sample 24 A	5	0.1	0.2	0.0	0.0	15.6	0.0	0.0	0.0	0.0	0.3	3.4	0.0	3.5	0.0	-0.1	2.3	0.0	1.0	0.0	4.7	0.1	3.2	0.0	0.0	0.0
Sample 24 B	1	0.0	0.0	0.0	0.0	6.9	0.0	0.0	0.0	0.0	0.0	2.3	0.0	1.6	0.0	0.0	1.1	0.0	0.3	0.0	1.0	0.0	0.6	0.0	0.0	0.0
Sample 24 C	1	0.0	0.0	0.0	0.3	158.5	0.0	0.0	0.0	0.0	0.0	5.8	0.0	25.0	0.0	0.0	0.5	0.0	0.0	0.0	0.8	0.0	1.6	0.3	0.0	0.0
Sample 24 D	1	0.0	0.0	0.0	0.4	187.3	0.0	0.0	0.0	0.0	0.0	3.8	0.0	19.5	0.6	0.0	0.3	0.0	0.0	0.0	0.9	0.0	2.5	0.4	0.0	0.0
Sample 24 E	1	12.6	0.0	0.1	5.3	Dil	0.0	0.1	0.3	0.2	1.5	5.9	0.0	27.4	4.0	0.0	0.5	0.2	1.5	0.2	0.8	0.0	6.2	1.5	0.1	1.1
Sample 24 E	5	12.2	0.0	0.0	4.7	623.2	0.0	0.1	0.3	0.2	1.5	5.3	0.0	26.9	3.7	0.0	-0.3	0.2	1.4	0.2	0.9	0.0	5.8	1.4	0.1	1.1
Sample 24 F	1	45.5	0.0	0.0	3.7	283.5	0.0	0.1	1.3	0.5	3.7	3.3	0.0	32.1	6.3	0.0	0.7	0.3	3.3	0.6	0.6	0.0	15.8	0.7	0.2	1.2
Sample 24 G	1	Dil	0.0	0.1	2.7	165.6	0.0	0.7	2.9	1.1	22.9	2.3	0.0	40.0	36.6	0.0	0.5	0.5	11.3	2.8	1.2	0.0	22.0	0.5	0.9	1.3
Sample 24 H	1	98.3	0.0	0.1	1.2	74.2	0.0	0.3	3.5	0.8	27.3	1.4	0.0	34.8	13.5	0.0	0.5	0.4	10.7	2.6	1.7	0.0	24.3	0.3	0.8	1.0
Sample 24 I	1	Dil	0.1	0.2	1.1	58.0	0.0	0.2	9.2	1.3	Dil	1.8	0.0	37.9	10.5	0.0	0.0	0.4	33.5	5.9	6.9	0.0	Dil	0.3	1.4	1.2
Sample 24 I	5	162.6	0.1	0.2	1.0	54.2	0.0	0.2	8.6	1.2	142.0	1.6	0.0	35.8	9.9	0.0	0.3	0.4	30.7	5.5	6.9	0.0	47.1	0.2	1.2	1.1
Sample 24 J	1	Dil	0.1	0.3	0.7	39.7	0.0	0.1	10.3	0.7	Dil	1.5	0.0	17.5	7.8	0.0	0.1	0.3	25.2	2.8	8.2	0.0	Dil	0.1	1.2	1.0
Sample 24 J	5	169.9	0.1	0.3	0.6	38.1	0.0	0.1	9.9	0.6	166.0	1.3	0.0	17.1	7.5	0.0	-0.3	0.3	23.4	2.7	8.3	0.0	56.3	0.1	1.1	1.0
Sample 24 K	1	Dil	0.1	0.6	0.9	208.8	0.0	0.2	25.8	0.6	Dil	2.3	0.0	33.6	14.8	0.0	1.3	0.4	32.9	2.3	26.1	0.0	Dil	0.2	1.7	1.5
Sample 24 K	10	226.6	0.1	0.7	0.9	200.0	0.0	0.2	25.4	0.6	440.2	2.1	0.0	33.7	14.5	0.0	-1.6	0.4	31.4	2.3	27.0	0.0	50.1	0.2	1.7	1.5
Sample 24 L	1	Dil	0.1	0.8	0.9	98.9	0.0	0.2	28.1	0.5	Dil	2.3	0.1	50.6	13.7	0.0	0.1	0.5	28.8	1.9	30.7	0.0	Dil	0.2	2.2	1.7
Sample 24 L	10	203.8	0.1	0.8	0.8	94.9	0.0	0.2	27.6	0.5	561.0	2.1	0.1	50.0	13.3	0.0	-0.1	0.5	27.2	1.9	31.3	-0.1	30.5	0.2	2.1	1.7
Sample 24 M	1	54.0	0.3	0.5	0.3	11.5	0.0	0.0	11.7	0.3	Dil	1.4	0.0	11.7	4.3	0.0	-0.1	0.3	36.5	1.0	26.7	0.0	15.6	0.0	0.8	0.6
Sample 24 M	10	52.0	0.3	0.6	0.3	11.7	0.0	0.0	12.0	0.3	374.7	1.6	0.0	12.2	4.4	0.0	-1.5	0.3	49.6	1.0	29.0	0.0	15.8	0.0	0.8	0.7
Sample 24 N	1	Dil	0.2	0.8	0.9	15.8	0.0	0.2	12.1	0.5	Dil	3.0	0.1	83.0	11.0	0.0	-0.1	0.7	18.1	1.3	20.5	0.0	9.8	0.1	1.2	2.1
Sample 24 N	10	153.5	0.2	1.0	0.8	16.0	0.0	0.2	12.0	0.5	593.0	3.1	0.1	82.3	10.9	0.2	-3.2	0.7	21.5	1.3	22.3	0.0	9.6	0.0	1.1	2.2
Sample 25 A	5	0.1	0.1	0.1	0.0	6.7	0.0	0.0	0.0	0.0	0.2	1.4	0.0	0.7	0.1	0.0	2.0	0.0	0.9	0.1	3.7	0.1	0.9	0.0	0.0	0.0

CISED Extraction Concentrations

All units are mg/L. Dil = Over range, dilution required

Sample ID	Dil	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Si	Sr	V	Zn
Sample 25 B	1	0.1	0.0	0.0	0.0	2.4	0.0	0.0	0.0	0.0	0.1	1.0	0.0	0.3	0.0	0.0	1.0	0.0	0.5	0.0	0.8	0.0	0.4	0.0	0.0	0.0
Sample 25 C	1	0.9	0.0	0.0	2.0	172.1	0.0	0.0	0.0	0.0	0.1	4.7	0.0	12.6	2.2	0.0	1.1	0.0	0.1	0.3	0.4	0.0	0.7	1.0	0.0	0.9
Sample 25 D	1	2.7	0.0	0.0	4.0	159.9	0.0	0.0	0.0	0.2	0.3	3.7	0.0	7.2	2.8	0.0	0.6	0.1	1.3	3.7	0.4	0.0	2.0	1.1	0.0	1.7
Sample 25 E	1	27.8	0.0	0.0	Dil	250.1	0.0	0.1	0.0	1.8	3.0	4.2	0.0	6.3	4.8	0.0	1.2	0.2	7.0	Dil	0.5	0.0	3.5	2.0	0.1	3.7
Sample 25 E	10	25.5	0.0	0.1	11.3	221.8	0.0	0.1	0.0	1.7	2.8	3.7	0.0	6.0	4.4	0.0	0.3	0.2	6.4	60.3	0.8	0.0	3.4	1.8	0.0	3.5
Sample 25 F	1	40.6	0.0	0.0	8.1	115.7	0.0	0.1	0.0	1.6	3.9	2.7	0.0	2.5	4.2	0.0	1.8	0.2	8.4	Dil	0.5	0.0	7.5	1.0	0.1	2.5
Sample 25 F	10	37.1	0.0	0.0	6.8	106.5	0.0	0.1	0.0	1.5	3.6	2.4	0.0	2.4	4.1	0.0	1.2	0.2	7.7	61.0	0.8	-0.1	6.9	0.9	0.1	2.4
Sample 25 G	1	61.2	0.0	0.0	5.6	66.5	0.0	0.7	0.0	2.5	21.2	2.0	0.0	1.7	33.3	0.0	1.6	0.2	16.7	Dil	1.1	0.0	9.0	0.6	0.4	2.0
Sample 25 G	10	55.2	0.0	0.1	5.0	62.8	0.0	0.6	0.0	2.5	20.2	1.8	0.0	1.6	31.7	0.0	0.1	0.2	15.5	101.8	1.4	0.0	8.3	0.5	0.3	1.9
Sample 25 H	1	50.9	0.0	0.1	2.5	36.1	0.0	0.2	0.0	1.7	27.7	1.3	0.0	2.0	9.1	0.0	1.2	0.1	15.3	Dil	1.5	0.0	9.7	0.3	0.3	1.2
Sample 25 H	10	46.1	0.0	0.1	2.3	34.4	0.0	0.2	0.0	1.7	25.3	1.2	0.0	1.8	8.5	0.0	1.3	0.1	13.9	57.3	1.8	0.0	8.9	0.2	0.3	1.1
Sample 25 I	1	83.1	0.1	0.3	2.1	33.4	0.0	0.1	0.2	2.6	Dil	1.7	0.0	3.5	5.3	0.0	0.6	0.1	42.0	Dil	4.5	0.0	15.0	0.3	0.5	1.3
Sample 25 I	10	73.0	0.1	0.3	1.9	31.9	0.0	0.1	0.1	2.5	171.8	1.5	0.0	3.3	5.1	0.0	0.7	0.1	39.2	59.3	4.7	0.0	14.0	0.2	0.4	1.3
Sample 25 J	1	79.2	0.1	0.3	1.3	22.9	0.0	0.1	0.2	1.4	Dil	1.4	0.0	5.8	7.3	0.0	0.6	0.1	33.7	Dil	4.1	0.0	20.2	0.2	0.6	1.5
Sample 25 J	5	70.3	0.1	0.3	1.2	22.0	0.0	0.1	0.2	1.4	191.6	1.2	0.0	5.6	6.9	0.0	-0.5	0.1	31.4	19.3	4.1	-0.1	19.4	0.1	0.6	1.4
Sample 25 K	1	Dil	0.2	0.5	1.8	55.6	0.0	0.2	0.5	1.5	Dil	3.2	0.0	28.0	12.8	0.0	1.7	0.4	41.9	16.6	9.8	0.0	Dil	0.4	1.5	3.8
Sample 25 K	10	162.5	0.2	0.5	1.7	52.9	0.0	0.2	0.5	1.4	336.5	2.9	0.0	27.0	12.1	0.0	-0.3	0.3	39.3	15.6	10.0	-0.1	32.8	0.4	1.3	3.7
Sample 25 L	1	Dil	0.1	0.5	1.4	33.0	0.0	0.1	0.6	1.1	Dil	3.3	0.1	24.3	5.6	0.0	0.5	0.4	26.8	7.8	8.5	0.0	18.9	0.4	1.2	3.3
Sample 25 L	10	146.0	0.1	0.5	1.4	33.0	0.0	0.1	0.6	1.0	318.5	3.4	0.1	24.0	5.7	0.0	-1.4	0.4	25.0	7.8	9.4	0.0	21.9		1.2	3.3
Sample 25 M	1	27.8	0.3	0.3	0.4	4.3	0.0	0.0	0.4	0.7	Dil	2.0	0.0	3.4	1.2	0.0	-0.3	0.1	39.1	2.2	11.8	0.0	10.5	0.0	0.3	0.7
Sample 25 M	5	28.1	0.3	0.3	0.4	4.6	0.0	0.0	0.4	0.7	203.2	2.3	0.0	3.6	1.2	0.0	-2.2	0.1	43.0	2.4	13.4	0.0	12.8		0.3	0.8
Sample 25 N	1	Dil	0.2	0.6	0.8	9.5	0.0	0.1	0.7	0.7	Dil	3.7	0.1	19.8	5.0	0.0	0.0	0.4	22.3	2.2	9.3	0.0	7.5	0.1	0.5	2.7
Sample 25 N	10	125.5	0.2	0.8	1.0	12.1	0.0	0.1	0.9	0.9	489.4	5.2	0.1	24.8	6.4	0.2	-2.6	0.5	27.1	2.8	13.1	0.0	10.7		0.6	3.5
Sample 26 A	5	0.1	0.2	0.0	0.0	6.3	0.0	0.0	0.0	0.0	1.0	1.9	0.0	0.9	0.1	-0.1	0.9	0.0	0.5	0.0	4.3	0.1	2.7	0.0	0.0	0.0
Sample 26 B	1	0.0	0.0	0.0	0.0	2.3	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.3	0.0	0.0	0.5	0.0	0.1	0.0	1.0	0.0	0.4	0.0	0.0	0.0
Sample 26 C	1	2.8	0.0	0.0	3.2	162.6	0.0	0.0	0.0	0.3	0.1	5.5	0.0	11.5	3.5	0.0	0.7	0.2	0.5	0.0	0.5	0.0	3.6	1.1	0.0	1.4
Sample 26 D	1	13.5	0.0	0.0	4.9	107.3	0.0	0.1	0.0	1.6	0.5	3.9	0.0	6.1	4.3	0.0	0.6	0.2	1.0	0.2	0.4	0.0	5.9	0.9	0.1	1.9
Sample 26 E	1	43.9	0.1	0.1	6.0	88.7	0.0	0.1	0.0	5.0	8.8	3.2	0.0	5.4	6.0	0.0	0.4	0.3	7.1	4.3	0.5	0.0	8.9	0.9	0.7	2.0
Sample 26 F	1	38.9	0.1	0.1	2.9	54.6	0.0	0.1	0.0	2.6	9.6	2.0	0.0	7.2	7.4	0.0	0.5	0.2	4.5	3.7	0.5	0.0	13.7	0.5	0.5	1.6
Sample 26 G	1	43.3	0.1	0.1	2.6	42.6	0.0	0.5	0.0	3.0	34.8	1.6	0.0	6.7	29.6	0.0	0.4	0.4	8.4	7.2	0.8	0.0	16.5	0.5	1.4	1.5
Sample 26 H	1	39.8	0.1	0.1	1.8	33.6	0.0	0.1	0.0	2.1	38.0	1.2	0.0	6.6	6.1	0.0	0.3	0.2	7.0	4.8	1.0	0.0	18.0	0.4	1.1	1.0
Sample 26 I	1	66.0	0.5	0.3	2.3	40.3	0.0	0.1	0.1	2.8	Dil	1.5	0.0	8.2	4.9	0.0	0.2	0.2	23.1	7.5	3.4	0.0	Dil	0.5	1.6	1.3
Sample 26 I	5	61.3	0.5	0.3	2.2	39.4	0.0	0.1	0.1	2.8	153.0	1.4	0.0	8.1	4.8	0.0	-0.6	0.2	22.2	7.3	3.5	0.0	30.1	0.5	1.6	1.3
Sample 26 J	1	72.9	0.5	0.4	2.1	37.3	0.0	0.1	0.1	2.0	Dil	1.3	0.0	8.5	4.5	0.0	-0.2	0.2	18.2	4.6	3.4	0.0	Dil	0.5	1.6	1.4
Sample 26 J	5	68.8	0.5	0.5	2.0	37.7	0.0	0.1	0.1	2.0	218.9	1.3	0.0	8.7	4.5	0.1	-0.8	0.2	18.0	4.6	3.7	0.0	43.0	0.5	1.6	1.4
Sample 26 K	1	Dil	0.8	0.6	3.7	114.0	0.0	0.1	0.3	2.4	Dil	3.6	0.1	22.0	9.0	0.0	1.0	0.5	26.0	5.0	8.1	0.0	Dil	1.8	2.0	2.2
Sample 26 K	10	158.4	0.8	0.7	3.5	113.7	0.0	0.1	0.2	2.5	342.5	3.5	0.1	22.9	9.3	0.1	0.2	0.5	26.0	5.1	8.9	0.0	88.0	1.8	2.0	2.3
Sample 26 L	1	Dil	0.6	0.7	4.1	129.4	0.0	0.2	0.3	2.3	Dil	4.6	0.1	19.6	15.6	0.0	2.2	0.5	26.9	5.3	7.9	0.0	Dil	2.8	2.4	2.0
Sample 26 L	10	202.6	0.5	0.7	3.8	130.1	0.0	0.2	0.3	2.3	400.4	4.5	0.1	20.1	15.6	0.1	2.6	0.5	26.2	5.4	8.6	0.0	95.2	2.7	2.4	2.1