## University of Strathclyde

## Department of Pure and Applied Chemistry

# Determination and Fractionation of Metals in Urban Soils from the City of Glasgow, UK

by

**Graham J. Urquhart**

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

May 2005

# ACKNOWLEDGEMENTS

The list of people that I would like to thank for their support, help, guidance, tolerance, humour, patience, good looks and tea making is even longer than the list of things I would like to thank them for, but as it is unlikely many of them will actually read this I will stick to the main contenders.

All those that helped with sampling, mainly Iain Hossack, Christine Davidson, Andy Hursthouse, and an especially big thanks to Andrew Briton who came away from retirement to brave the challenging Glasgow environment for nothing more than great conversation with myself and Iain. To those that helped process the samples, thank you, especially Thibault Rehn and Laura Poggio, and all the project students that have helped at various times, and provided 'entertainment' in the laboratory. A huge thanks to David Stirling from UoP for help with the running of the ICPOES.

When I started my Ph.D. I never thought I would get this far, and I know I wouldn't have without lots of prodding in the right direction from Christine and I hope she knows how much I appreciate all her help as well as friendship. Barbara Balfour has also helped out far more than her fair share.

Everyone at Strathclyde has been great; I fear I will miss someone out if I mention names so thank you one and all, especially Luke Bellamy who helped show me the meaning of hard work, and the playstation 2. Alison has also been a great help, especially with the PCA. Everyone past and present from the office have been great too!

There are also those that have had to put up with me away from the lab and I have to thank them. How could I not mention my family who are super supportive of anything I do and I love them all to bits, thank you Mum, Dad and Brother Kelsang Rabzang, formerly Iain. My former flatmates Lesley Watson and Jennifer Walsh have been lovely for the whole 3 years. I will never forget how kind they both were to me, even when Ms. Walsh decided to lock me out, pour wine on my lap, but generally they are amazing friends.

Most importantly many thanks to the EU for funding the URBSOIL project, contract EVK4-CT-2001-0053.

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# ABSTRACT

Potentially toxic elements have been measured and fractionated in soil samples from public-access areas in Glasgow, UK as part of the EU URBSOIL project (EVK4-CT-2001-00053). The spatial variability of analyte concentrations has been studied (a) within two urban parks (Glasgow Green and Alexandra Park) and (b) across 94 sites (including parks, roadsides, riverbanks and ornamental gardens) within the city. Levels of analytes were broadly similar to those reported in previous studies of large, industrial cities. A few soils contained chromium, nickel or lead concentrations in excess of the UK CLEA soil guideline values.

Distribution profiles, and variability in analyte concentrations, were assessed in order to distinguish elements arising mainly from natural sources from those influenced more strongly by Man. Aluminium, iron, lithium, magnesium and manganese levels were least variable and more frequently normally distributed, indicating that these elements are predominantly natural in origin. Barium, calcium, copper, chromium, lead and zinc were characterised by higher variability and non-normal concentration distributions, suggesting anthropogenic sources are important. Principal component analysis confirmed these relationships, grouping the "natural" elements separately from the "urban" metals, and revealed that chromium behaved differently from either group.

Comparison of the revised (4-step) BCR sequential extraction with a modified scheme using acidic ammonium oxalate at step 2 indicated that improved dissolution of iron-containing minerals was offset by losses due to precipitation of oxalate salts. Continued use of the BCR scheme was therefore recommended. When applied to soils from Glasgow, sequential extraction revealed no differences between analyte fractionation patterns in park and roadside soils, nor between samples with markedly different pseudototal (aqua-regia soluble) metal concentrations. Chromium and nickel were found predominantly in association with the residual phase of the soils, but ~ 73% of the lead content was released in step 2, indicating this element has high potential mobility.

# 1 INTRODUCTION

## 1.1 Soil

### 1.1.1 Soil Definition

It is necessary to adopt a formal system of soil description and classification in order to describe the various materials found in ground investigations. Traditionally soils have been described and classified as natural media supporting the growth of plants and often divided into distinct layers or horizons. One definition of soil is as follows[1]:

"*Soil in this text is a natural body comprised of solids (minerals and organic matter), liquid, and gases that occurs on the land surface, occupies space, and is characterized by one or both of the following: horizons, or layers, that are distinguishable from the initial material as a result of additions, losses, transfers, and transformations of energy and matter or the ability to support rooted plants in a natural environment. The upper limit of soil is the boundary between soil and air, shallow water, live plants, or plant materials that have not begun to decompose. Areas are not considered to have soil if the surface is permanently covered by water too deep (typically more than 2.5 m) for the growth of rooted plants. The horizontal boundaries of soil are areas where the soil grades to deep water, barren areas, rock, or ice. In some places the separation between soil and non-soil is so gradual that clear distinctions cannot be made.*"

### 1.1.2 Soil Classification

Soils are classed into groups with similar chemical or physical properties. The properties selected to classify soils will depend upon the objective of the study or survey. For example, for agricultural purposes, chemical parameters such as nutrient availability might be measured and related to suitability for growth of specific crops[2], or an area of land might be classified on a basis of crop productivity[3]. For engineering purposes classification is more likely to be defined by physical parameters relating to suitability for building on, in, or with[4]. Urban soils have been classed on the basis of land use rather than measurement of any specific property[5]. There are many descriptors of general soil that can be used to classify them; some of the common properties measured are discussed in section 1.1.3.

### 1.1.3 Soil Description

Soil is made up of solid particles of various sizes with water- and air-filled voids between grains. The solid material is made up of minerals and organic matter, with strong interaction between all components. Soil conditions are constantly changing, altering these interactions and the soil status.

The size of the particles making up a soil will have a large influence on its properties. Various size ranges are used to classify soils. Table 1.1 shows the British Standard (BS) soil classification based on particle size[6].

| | | | |
|---|---|---|---|
| Very coarse soils | BOULDERS | | > 200 mm |
| | COBBLES | | 63 – 200 mm |
| Coarse Soils | GRAVEL | Coarse | 20 – 63 mm |
| | | Medium | 6.3 – 20 mm |
| | | Fine | 2 – 6.3 mm |
| Medium soils | SAND | Coarse | 0.63 – 2.0 mm |
| | | Medium | 0.2 – 0.63 mm |
| | | Fine | 0.063 – 0.2 mm |
| Fine soils | SILT | Coarse | 0.02 – 0.063 mm |
| | | Medium | 0.0063 – 0.02 mm |
| | | Fine | 0.002 – 0.0063 mm |
| | CLAY | | < 0.002 mm |

*Table 1.1: British standard classification of soils on particle size[6].*

Organic matter content and mineralogy are other main descriptors used to classify soils. Soil chemistry is strongly affected by mineralogy and this is discussed in section 1.1.4. Soil organic matter is discussed in section 1.1.5. General parameters that are measured to describe soils can be split into two groups: physical e.g. strength, water permeability and texture, and chemical e.g. pH, cation exchange capacity or concentrations of specific elements and molecules.

### 1.1.4 Soil Mineralogy[7]

Minerals are natural inorganic compounds. They often have complicated formulas. The most important class of rock forming minerals are the silicates, which can be used to classify rock types by silicon dioxide content. There are many different silicate structures incorporating various metal atoms within their matrix, mainly magnesium, iron, calcium and aluminium.

The formation of primary minerals occurs at high temperature and pressure in reducing conditions. Primary minerals are unstable at the surface of the earth; chemical weathering is the alteration of the principle minerals to more stable secondary minerals. The products of aluminosilicate weathering are the clay minerals[8]. The clay minerals are layered structures containing sheets of tetrahedrally co-ordinated silicon atoms and octahedrally co-ordinated aluminium atoms. Some have a unit layer in a ratio of 1:1 e.g. kaolinite[9]. Layers are held together by hydrogen bonding. Some have unit layers of two tetrahedral sheets sandwiching one octahedral sheet, 2:1 clays e.g. montmorillonite. The unit layers are not held together by hydrogen bonding and 2:1 clays are capable of expanding to accept water molecules or other species between layers. Both types of clay undergo isomorphous substitution by cations of similar size but lower charge. This means they become overall negatively charged and adsorb more cations on surfaces or in the case of 2:1 clays between layers to maintain neutrality.

The most important mineral phases are:

i. Carbonates

   The carbonates are mainly of magnesium and calcium. Acidification reactions can lead to the dissolving of the carbonates.

ii. Iron, aluminium and manganese oxides.

   Large metal oxide lattices are stable in oxidising conditions. Hydroxide groups are usually found at the surface of the lattices. Deprotonation of the hydroxides allows cation adsorption; these cations are often only weakly adsorbed and released readily. Cations can also be incorporated into the lattice itself, becoming unavailable. The iron oxide/hydroxides have lattice structures ranging from highly ordered (crystalline) to highly disordered (amorphous).

iii. Stable mineral lattices

Stable oxide frameworks of silicon are resistant to degradation. Elements bound within stable frameworks are not readily available.

### 1.1.5 Soil Organic Matter[10]

Soil organic matter (SOM) can be divided into 3 classes:

i. Living soil biota - microorganisms, roots and animals.
ii. Decomposing residues of soil biota.
iii. Resistant organic matter.

Some of the SOM present in soils is labile in the form of small organic molecules and polysaccharides and is used by the living soil biota. Most SOM consists of resistant matter that is chemically or physically protected. The resistant organic fraction is called humus. Humus is a general group of high molecular weight macromolecules rich in aromatic groups and hydrocarbons. Humic materials are capable of adsorbing xenobiotics and of ligating cations.

### 1.1.6 Metals in Soils[11,12,13,14,15,16]

There are ten major elements present in soil. Carbon, silicon and oxygen are the non-metallic major elements. Aluminium, calcium, iron, magnesium, potassium, sodium and titanium are the metallic major elements. The non-major elements occurring in soil are normally found at concentrations below 1000 mg $kg^{-1}$. Some elements found in soil are essential to living organisms. These essential elements can often be toxic above critical values, as can other non-essential elements. Metals can be associated with all components of the soil system and how they are associated will vary with soil type and environmental conditions. Certain changes in conditions will bring about the release or binding of certain metals to different degrees and phases. The soil is capable of adsorbing many elements by several mechanisms, cation exchange, specific adsorption[17], organic complex formation and co-precipitation. Assessing which mechanism dominates the adsorption characteristics for any metal is not possible. Interpreting the results of soil analysis requires an understanding of how the analytes behave, their common anthropogenic and natural sources in the soil, and their effect on the biosphere. This is discussed below for the major and non-major elements studied in this project.

#### 1.1.6.1 Aluminium

Aluminium is the most abundant metal in the Earth's crust, and is commonly a major constituent of soils. Aluminosilicate minerals play an important role in geochemical cycling of many trace elements. Typical concentrations range from 10 000 mg $kg^{-1}$ - 300 000 mg $kg^{-1}$.

Aluminium is used in a variety of industrial processes especially in aviation fuels, flocculants, foundries, gas works and tanning industries. Aluminium toxicity has been related to chronic renal failure and aluminium appears to accumulate in brain tissue of individuals with Alzheimer's disease. The main organs indicative of aluminium toxicity are the lungs and nervous system.

#### 1.1.6.2 Barium

In rocks, barium concentrations range from 1 mg $kg^{-1}$ (ultrabasic) to 800 mg $kg^{-1}$ (acid metamorphic) on average. Parent rock material strongly influences concentration of barium in soil but environmental evolution can also result in a wide range of barium levels in soil formed on the same rock type. Concentrations in Scottish soils have been reported from 250 to 3000 mg $kg^{-1}$ accumulating in lower horizons.

#### 1.1.6.3 Cadmium

Geochemically, cadmium is associated with zinc but is found at much lower concentrations than zinc in the Earth's crust. High levels of cadmium and other heavy metals are found in rocks produced from organic rich sediments under anaerobic conditions where they accumulate as sulfides and organic complexes. Unpolluted soils developed on this type of material have been reported to have concentrations up to approximately 22 mg $kg^{-1}$ cadmium. Where this type of parent material is not found and there is no source of cadmium pollution, typical levels of less than 1 mg $kg^{-1}$ would be expected. Elevated levels of cadmium in the topsoil, where cadmium tends to accumulate, are indicative of pollution.

Cadmium tends to be more mobile in soils than many other heavy metals. Precipitation mechanisms rarely effect cadmium distribution at typical levels though in highly polluted areas precipitation might become important. Adsorption mechanisms generally dominate the way in which cadmium is bound in the soil. Adsorption is inhibited by competition from other metal ions such as calcium, cobalt, chromium, copper, nickel and lead. Cadmium is unlikely to have an adverse effect on plants but can be accumulated in crops at levels that pose a serious risk to man.

The major sources of anthropogenic cadmium in the environment are from metallurgic industries, sewage sludge application, waste disposal and fossil fuel burning. The main uses of cadmium are for protective plating, alloys, pigments, plastic stabilizers and batteries.

Cadmium is not an essential element but is highly toxic to man, though does not usually occur at high concentrations in soil. In man cadmium accumulates in the kidney causing renal dysfunction and in bone tissue by calcium substitution. Exposure to high levels of cadmium over several years can lead to major weakening of the bones and eventual death.

The most severe case of recorded cadmium poisoning arose from elevated cadmium levels in the water and soil of an area in Japan. The area was polluted by a nearby lead and zinc mine. Crops tended to be consumed locally resulting in high exposure to cadmium, which in conjunction with poor diet (low calcium intake specifically) led to chronic effects. Another incident occurred in Somerset when houses were built on old mines and showed similarly elevated levels of cadmium, zinc and lead in soils and local crops. However there was no evidence of adverse health effects in this population, which was attributed to less local food being consumed and a better diet overall.

### 1.1.6.4 Calcium

Calcium is an essential element and a major constituent of the soil. It is required for cell walls, enzyme activation and to facilitate other mineral uptake. In soil it is an exchangeable cation due to its ability to be replaced by hydrogen and aluminium ions. Calcium is incorporated in many mineral forms, often with aluminium and silicon or as calcium carbonate. Most calcium minerals are unstable in acidic conditions, with the exchange of $H^+$ releasing $Ca^{2+}$ into the soil solution. In alkaline soils $CaCO_3$ is often present and has a dominating role in many soil properties. Calcareous soils can buffer many compounds but increasing the $CO_2$ in the soil air might lower pH. Agricultural soils are often treated with soluble liming minerals of calcium to help increase pH. Calcium minerals are also heavily used in construction (cement), production of paper, plastics, glasses, paint, steel and various water treatment stages.

### 1.1.6.5 Chromium

Chromium is abundant in the Earth's crust and is most commonly associated with iron oxides as chromite in soil. Geometric mean soil chromium concentration of 62 mg $kg^{-1}$ has been reported in a survey of 2944 Scottish soil samples[18]. The most common oxidation states of chromium in soil are III and VI. Chromium (VI) exists as an anion of chromate and dichromate in equilibrium, with $CrO_4^{2-}$ the predominant form at pH > 6. Chromium (III) is much less mobile and adsorbs to particulates much more strongly than chromium (VI). Chromium (III) precipitates at pH > 5.5. Chromium (VI) is the more stable form in equilibrium with atmospheric oxygen but is reduced by soil organic matter to chromium (III). This occurs more rapidly in acidic conditions and the insoluble chromium (III) is usually the major form in soils. Most chromium in soils is usually unavailable.

Chromium is resistant to oxidation and is mainly used in corrosion resistant alloys. Its refractory properties are exploited to line kilns. Chromium chemicals are found in many products and used in many processes, antifouling pigments, fungicides, catalysts, magnetic tapes, high temperature batteries, pyrotechnics, phosphate fertilizers, tanning products and preservatives. The major anthropogenic source of chromium in the soil is from atmospheric deposition from metallurgic industries, especially iron and chromium production. Other large sources include disposal of fly ash, wearing of brake lining and catalysts for treating exhaust fumes from vehicles.

Chromium is an essential element and is required for sugar and fat metabolism. Chromium deficiency in the diet leads to symptoms indistinguishable from diabetes, patients previously diagnosed as having 'maturity' diabetes have often been successfully treated with long-term doses of trivalent chromium. Chromium has a vital role in cholesterol metabolism, protein synthesis and appears to be present in newborn babies at elevated levels, thought to be beneficial. Some chromium (VI) salts are skin irritants, pulmonary irritants, carcinogens, cause renal and mild hepatic damage and adversely affect reproductive organs, especially in animals. Chromium (III) is essential and chromium (VI) toxic so conditions affecting the oxidation state of metals in the soil will have a major effect on the risk associated with release of chromium.

#### 1.1.6.6 Copper

Copper is often highly associated with organic matter and crystalline phases in soil, potentially leading to non-availability and deficiencies. In soil with high organic matter, available copper is usually low due to stable complex formation. Copper (II) and copper (I) readily form complexes with many different types of ligands and their interactions in soils are complicated. Copper becomes more mobile (and potentially phytotoxic) at lower pH but this release tends to be reduced in soils with high organic matter content. Total soil copper concentrations range from trace levels up to 250 mg $kg^{-1}$ and typically from 20 – 30 mg $kg^{-1}$.

Major sources of anthropogenic copper are from coal ash, smelter emissions and agrochemical applications. Copper is principally used in switches, wire, production of brass and bronze, plumbing, electroplating, undercoating for chromium, nickel and zinc cooking utensils.

Copper is an essential trace element, forming the functional part of enzymes or being involved in metabolic pathways. Copper is only toxic at high levels, cases have been reported in sheep where copper has been accidentally introduced at very high levels in their feed. Elevated, but not toxic, amounts of copper in soil has been linked to high levels of copper in tissues of primary herbivores living near an old copper mine. This provides a potential exposure route to carnivorous birds at higher trophic levels[19].

#### 1.1.6.7 Iron

Much of the iron present in soil is incorporated into mineral lattice structures. Initial precipitation of soluble iron salts results in amorphous or poorly ordered crystal lattices. Crystallization of these structures slowly develops more ordered mineral structures. Iron (III) is the major oxidation state involved in iron minerals. Lowering redox potential and pH increases the amount of iron (II), which is more soluble, therefore increasing the available iron. This is an oversimplification as iron (II) minerals will also form and the degree to which iron (II) is subjected to reduction will depend upon its form in the soil. Stable complex formation will affect iron solubility, which is also pH dependant. Generally highly weathered alkaline soils will have lowest iron mobility. Average iron in soil has been estimated at 3.8 %, with typical values ranging from 1 to 10 %.

Iron is unusual in that it is an essential micronutrient but a major constituent of the Earth's crust and soil. Iron is required for enzyme activity and growth. Specifically iron is a vital component of haemoglobin, which is essential for oxygen transport in mammals. Iron is only toxic at high levels; problems arising from high levels of iron in soil are uncommon. There has been much concern over the effects of too little iron in the diet, especially in children, leading to anaemia. Therefore iron is often found in supplements and multi vitamins. This is the most common source of iron poisoning.

#### 1.1.6.8 Lead

The accumulation of lead in topsoil is primarily a function of the rate of deposition from the atmosphere. Parent materials have lead concentrations up to about 30 mg kg$^{-1}$ and results of topsoil studies have reported natural levels of up to 110 mg kg$^{-1}$ [20]. The fate of lead in soil is affected by specific or exchange adsorption at mineral interfaces, the precipitation of sparingly soluble solid phases, and the formation of relatively stable, insoluble organo-metal complexes or chelates with the organic matter in soil. Microbial uptake of lead is limited and so lead residence times in soil tend to be long. The downward movement of lead from soil by leaching is very slow under most natural conditions. Leaching can be induced if lead is present at concentrations that either approach or exceed the sorption capacity of the soil, in the presence of materials that are capable of forming soluble chelates with lead, and due to a decrease in the pH of the leaching solution (e.g., acid rain)[21].

Lead is used in batteries, solders, electronics, TV tubes, glass, radiation shielding, ballast, soundproofing and ammunition. Lead is introduced into the environment from many anthropogenic sources; from lead piping, industrial output and petrol combustion. Since 1989 most vehicles manufactured have used unleaded petrol and in the European market all vehicles sold since 1994 have not required leaded petrol. Paint is a major source of lead in soil.

Lead is a non-essential element and one of the most widely studied toxic metals. Its metabolic effects are well understood[22] and much data have been obtained on health effects of different levels of lead in the blood.

### 1.1.6.9 Lithium

Lithium is correlated with fluorine content of igneous rocks, and in most parent material has concentration range from 17 to 65 mg $kg^{-1}$. In topsoils developed from various parent materials lithium content has been reported from 8 (sandstone) to 80 (granite) mg $kg^{-1}$. Lithium concentration in soils depends more upon processes of soil formation than parent material[23]. Lithium mobility decreases with soil weathering due to its firm binding with clay minerals. Levels of lithium in sandy soils are lower (approximately 1 mg $kg^{-1}$) than in alluvial soils (98 mg $kg^{-1}$). The main uses of lithium are battery production, medicines and in the nuclear industry. Most lithium poisoning occurs through its use as an antidepressant.

### 1.1.6.10 Magnesium

The average magnesium content of parent material has been estimated at 2.1 % compared to average soil content of 0.5 %[14]. Magnesium forms soluble complexes in soil solutions and therefore tends to be more mobile than other metals. Magnesium interacts with most minerals present in soil including aluminosilicates, iron minerals and calcite. Magnesium (II) is the only important oxidation state present in soils, therefore redox changes in the soil will not directly alter magnesium solubility.

### 1.1.6.11 Manganese

Manganese is found in many different forms in soil, usually derived by the weathering of the parent material. Much of the manganese in the soil is bound in mineral lattices and not available to plants. The highest concentrations of manganese can be found in basic igneous rocks. Levels vary widely in acidic igneous rocks and metamorphic rocks. The average manganese concentration in the Earth's crust is between 900 and 1000 mg $kg^{-1}$. In soil, manganese concentrations range from 20 to 3000 mg $kg^{-1}$ with levels mainly dependent on parent material. The major anthropogenic source of this element in soil is from fertilization, usually using $MnSO_4$ or MnO where a deficiency has previously been found. Availability of manganese is strongly affected by the supply of electrons and $H^+$ ions, which reduce the insoluble higher valence states to manganese (II). Available

$Mn^{2+}_{(aq)}$ can be oxidized by microorganisms into insoluble higher states. Air-drying of the soil can dramatically increase the $CaCl_2$ extractable form. Manganese solubility is affected by redox conditions in a similar way to iron but the chemistry is more complicated due to the increased number of stable oxidation states available ((I), (II), (III), (IV), (VI) and (VII)).

Manganese is principally used in the manufacture of alloys, especially steel, as well as in batteries and glass production. The powerful oxidizing properties of potassium permanganate are utilized for disinfecting, deodorizing and decolouring as well as an important analytical reagent.

Manganese is a major soil constituent and is an essential element. It is required for enzyme activity and growth. Manganese is believed to be toxic to man only at high concentrations, but can cause serious neurological health problems and has been linked to adverse respiratory and reproductive effects. Cases of manganese poisoning are rare and normally limited to occupational exposure.

#### 1.1.6.12 Nickel

In the Earth's crust nickel is mainly found as sulfide and oxide ores often associated with iron. Igneous rocks rich in ferromagnesium and sulfide minerals are also rich in nickel. Nickel (II) is the stable form found in soils and often substitutes for magnesium in minerals and highly weathered soils leaving concentrated residues of nickel and silica from which silicate minerals form. The mean concentration of nickel in Scottish soils of 27 mg $kg^{-1}$ has been reported[18].

Nickel is used in many corrosion resistant alloys, vehicle parts, electronic components and batteries. The major sources of nickel in the environment are from the burning of fuel, oil and coal, and from metallurgic industries. Disposal of fly ash and emissions from smelters are the major anthropogenic sources of nickel in soil.

Nickel is thought to be essential to some organisms, though not humans. Nickel is thought to play a vital role in the metabolic pathways of certain plants, especially legumes but only at a very low concentration so deficiency is extremely rare. Its ability to replace essential metals in enzymes can lead to metabolic disruptions and is thought to be carcinogenic and toxic to humans. The presence of nickel in many alloys has been linked with allergic contact dermatitis to damaged areas of skin, though susceptibility to skin irritation might be reduced by oral intake of nickel[24].

#### 1.1.6.13 Vanadium

Vanadium concentration in rocks is usually below 200 mg kg$^{-1}$. Alluvial areas are likely to show more natural variability. Vanadium concentration in soil is often similar to parent material levels, an average concentration of 60 mg kg$^{-1}$ has been reported in Scotland.

The major use of vanadium is in the production of steel, as a pentoxide catalyst. It is also found in some crude oil. Vanadium is essential in humans. Vanadium compounds can be irritants and long-term exposure can cause respiratory problems.

#### 1.1.6.14 Yttrium

Yttrium levels in rocks is usually below 50 mg kg$^{-1}$ and tends to be similar in various rock types, though acid rocks tend to be at the upper end of this range. Yttrium is known to be incorporated into mineral lattices, especially silicates, phosphates and oxides. Yttrium is not thought to be bound strongly by organic matter. Mean concentrations of 9.4 mg kg$^{-1}$ and 48 mg kg$^{-1}$ yttrium in Scottish top-soils have been reported[25].

#### 1.1.6.15 Zinc

Zinc is present in many different minerals in soils. Levels usually depend on parent material composition. The amount of zinc available is strongly affected by pH and interactions with iron species in the soil. The common range for total zinc in soils is from 10 – 300 mg kg$^{-1}$, with an average of about 50 mg kg$^{-1}$. Solubility of zinc increases at low pH when it is rapidly leached or taken up by certain plants. Zinc mobility can be increased by high levels of chelating fulvic and humic matter and decreased in the presence of clay minerals, which strongly bind zinc.

Zinc has many uses including protective coating, alloy production, in plastics and rubbers, automotive parts, batteries, in oils and greases and in some medicines. The major sources of anthropogenic zinc in the environment are from mining activities, burning of fossil fuels and use of agrochemicals. These activities have led to elevated zinc levels in many areas, often exceeding phytotoxic levels.

Zinc is an essential trace element. Adverse health effects from zinc deficiency are more likely, rather than high levels leading to toxicity problems. Cases of zinc poisoning from ingestion are rare. Severe exposure might give rise to gastritis with vomiting due to swallowing of zinc dusts. Short-term exposure to very high levels of zinc is linked to lethargy, dizziness, nausea, fever, diarrhoea, and reversible pancreatic and neurological damage. Long-term zinc poisoning causes irritability, muscular stiffness and pain, loss of appetite, and nausea.

### 1.1.7 Metals in Urban Soils

There have been previous urban soil studies investigating many different parameters and assessing soil quality in different ways. Studies into roadside soils[26,27], parks[28,29], flowerbeds[30], census tracts[31], and complete cities[32] assessing metal contents and fractionation have been performed. Different fractionation schemes have been applied to soils form Glasgow[33], Naples[34], Hong Kong[35], China[36] and Hawaii[37] looking at the heavy metal distribution within urban soils. Other methods of assessing availability of heavy metals from urban soils have included consideration of plant availability[26,38] and simulation of gastric conditions (physiologically based extraction tests)[39,40] to estimate potential exposure. Table 1.2 shows the average total trace element concentrations from previous urban soil studies, together with selected soil legislative values. The table is expanded from a recent paper comparing results from previous urban soil studies.

| City | Average concentrations (mg kg$^{-1}$) | | | | | | | | | | | Ref | Year |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cd | Cr | Co | Cu | Hg | Pb | Mn | Ni | Sb | V | Zn | | |
| Rome | 0.31 | | | | | 331 | | | | | | 41 | 1995 |
| Pittsburg | 1.2 | | | | 0.51 | 398 | | | | | | 41 | 1980 |
| Boston | | | | | | 800 | | | | | | 41 | 1979 |
| Warsaw | 0.73 | 32 | 5.1 | 12 | | 57 | 337 | 12 | | | 166 | 41 | 1980 |
| Hamburg | 2.0 | 95.4 | | 62.5 | | 218 | 750 | 62.5 | | | 516 | 41 | 1986 |
| Salamanca | 0.53 | | | | | 53.1 | | | | | | 41 | 1994 |
| Coruna | 0.3 | 39 | 11 | 28 | | 309 | | 28 | 3 | | 206 | 41 | 2001 |
| Central Madrid | | | | | | 621 | | | | | | 41 | 1985 |
| Madrid | | 74.7 | 6.42 | 14.1 | | 161 | 437 | 14.1 | | 30 | 210 | 41 | 1998 |
| Bangkok | 0.29 | 26.4 | | 24.8 | | 47.8 | 340 | 24.8 | | | 118 | 41 | 1998 |
| Birmingham | | | | | | 570 | | | | | | 41 | 1982 |
| Glasgow | 0.53 | | | | | 216 | | | | | 207 | 41 | 1986 |
| Central London | | | | | | 647 | | | | | | 41 | 1980 |
| Greater London | | | | | | 250 | | | | | | 41 | 1980 |
| Outer London | | | | | | 322 | | | | | | 41 | 1979 |
| London boroughs | 1.0 | | | | | 294 | | | | | 183 | 41 | 1988 |
| London | 1.0 | | | | | 294 | | | | | 183 | 41 | 1991 |
| Hong Kong | 2.18 | | | | | 93.4 | | | | | 168 | 41 | 2001 |
| | 1.89 | | | | | 100 | | | | | 93.9 | 41 | 1996 |
| | 0.94 | | | | | 89.9 | | | | | 58.8 | 41 | 1997 |
| Manila | 0.57 | 114 | | 20.9 | | 214 | | 20.9 | | | 440 | 41 | 1988 |
| Palermo | 0.68 | 34 | 5.2 | 63 | 0.68 | 202 | 519 | 17.8 | 3.0 | 54 | 138 | 41 | 2002 |
| Aberdeen (Parks) | | 23.9 | 6.4 | 27.0 | | 94.4 | 286 | 14.9 | | | 58.4 | 42 | 1996 |
| Aberdeen (Roadside) | | 22.9 | 6.2 | 44.6 | | 173 | 264 | 15.9 | | | 113 | | |
| Athens (Park edge) | 1.43 | | | | | 413 | | | | | | 28 | 1997 |
| (20 m from park) | 0.62 | | | | | 187 | | | | | | | |
| Berlin | 0.92 | 35.0 | | 79.5 | 0.42 | 119 | | 10.7 | | | 243 | 43 | 2000 |
| Honolulu (0-2.5 cm) | | | 66 | 122 | | 56 | 1570 | 294 | | | 282 | 37 | 2000 |
| (7.5-10cm) | | | 76 | 137 | | 40 | 1690 | 311 | | | 238 | | |
| Napoli | 0.6 | 15 | | | | 204 | | | 2.9 | | 223 | 30 | 2003 |
| Naples | | 11 | | 74 | | 262 | | | | | 251 | 34 | 2003 |
| Nanjing | | 107 | | 84.7 | | 163 | | | | | 66.1 | 36 | 2003 |
| Oslo | 0.41 | 32.5 | 9.98 | 31.7 | 0.13 | 55.6 | 486 | 28.4 | | 51.3 | 160 | 44 | 2002 |
| Seville (0-10cm) | | 39.4 | | 68.2 | | 137 | 471 | 21.9 | | | 145 | 38 | 2002 |
| (10-20cm) | | 40.7 | | 77.3 | | 163 | 510 | 23.2 | | | 131 | | |
| Tyneside | | | | | | 129 | | | | | 282 | 29 | 2001 |
| ICRCL threshold (parks) | | 1000 | | 130* | 20 | 2000 | | 70* | | | 300* | 45 | 1987 |
| CLEA soil guideline values | 30 | 200 | | | 15 | 450 | | 75 | | | | 46 | 2002 |
| Dutch tables (target) | 1 | 100 | 20 | 50 | 0.5 | 50 | | 50 | | | 200 | 47 | 1986 |
| Dutch tables (investigation) | 5 | 250 | 50 | 100 | 2 | 150 | | 100 | | | 500 | | |

*Table 1.2: Summary results of previous studies on urban soil and indicative values,* * *any land use where plants are grown.*

Lead and zinc are the metals most studied; cadmium, copper, chromium, nickel and manganese are also widely reported. Typical values and maximum values for uncontaminated land are also shown. The ICRCL thresholds were used in the UK to indicate contaminated parks and open spaces. These have been replaced by CLEA guideline values, which assess risk to human health and should be used on a site specific basis. Concentrations less than the Dutch target values are at levels not thought to affect soil processes and concentrations greater than the investigation values suggest the land might be contaminated. The Dutch values suggest further investigation into lead levels in Rome, Pittsburg, Boston, Hamburg, Coruna, Madrid, Birmingham, Glasgow, London, Manila, Athens, Napoli, Naples, Nanjing and Seville might be required. Cadmium, chromium and mercury levels reported from all cities are less than the CLEA guideline values. Lead CLEA guideline values are exceeded by the studies in Birmingham, Central London and Madrid. Very high nickel concentrations are reported in the Honolulu study but are not discussed in any detail.

Data is available for other metals not included in this table, e.g. the platinum group metals[30]. The platinum group metals are associated with catalytic converters and have increased in concentration in soil over the last ten years[48], but are at very low levels, detection requiring sensitive analytical techniques.

Many different depth ranges of soils have been studied, commonly from the top 2.5 cm down to 20 cm. The different methods used in the various studies makes quantitative comparisons difficult.

There are many factors that affect the levels of metals in soil. Several techniques have been used to assess anthropogenic input of metals in city soils[49]. Background levels have been estimated by studying soils on the edge of urban areas[40,41] and analysing parent material[50]. These values can then be used to calculate enrichment or pollution load factors. The relationship between enrichment factors and pollution should be treated with care[51].

Pearson correlation co-efficients are often shown to try and indicate possible common sources and relationships between metals[30,34,36,52]. Grouping of the main influence on levels of metals by principle factor analysis has been used to assess human input and effects, and natural factors. Data has been processed into 2,3,4,6 and 7 factors[41,44,53, 54, 55, 56]. Further statistical treatments are also used to analyse data from urban soil studies, including cluster analysis[57] and kriging[56]. The amount of pollutants areas are exposed to will vary depending upon environmental conditions, for example areas with high elevation are less likely to be exposed to airborne pollutants[35]. Environmental conditions will also strongly influence the fate of pollutants in the soil. Elements that have a normal distribution within a city are thought to be less influenced by anthropogenic activities than elements not normally distributed[44]. Elements with a greater variation in a study area are thought to be more affected by anthropogenic activities than elements with less variation[38,53].

The main anthropogenic sources of metals reported are traffic and industry[58]. The application of compost and agrochemicals to maintained parks has also been reported as a major source of metals in urban soil[49]. Metals most often used as indicative of anthropogenic input are lead, copper and zinc [52,59,60,61]. High levels of cadmium and chromium have also been reported arising from anthropogenic influence, but these metals have also been related to parent material. Manganese and nickel have been related to both anthropogenic and natural sources. Aluminium and iron are elements more related to natural sources. Calcium spatial variability has been reported as mainly arising from cement dust[49].

Models have also been used to relate metal concentrations to risk[62]. Several models have been reported taking into account different land uses, exposure routes and receptors. These models can also take into account exposure from other sources.

## 1.2 Atomic Spectrometry

In 1860 Kichoff and Bunsen discovered that the interactions of light with atoms can be related to atom concentration. This led to the development of three main atomic spectrometry techniques, based on atomic emission (AE), atomic fluorescence (AF) and absorption (AA). Atomic fluorescence spectrometry was not used in this project, and so is not discussed further.

### 1.2.1 Atomic Absorption Spectrometry[63]

Atomic absorption spectrometry (AAS) is mostly a single element detection technique. This is because atom production conditions, analysis wavelength and light source are all element specific. These conditions can be altered rapidly in a carefully controlled manner by only a few instruments to allow multi elemental analysis. Figure 1.1 is a schematic diagram of AAS apparatus.

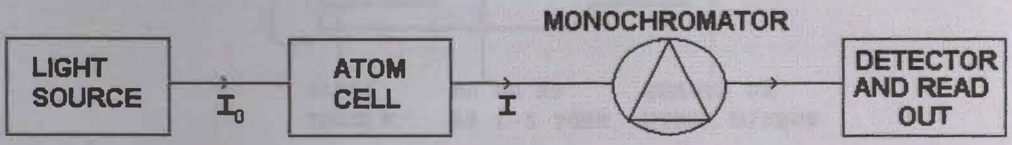


*Figure 1.1: Diagram of main components of an AAS system.*

Absorbance can be calculated:

$$A = \log_{10}[I_0/I] = e^{-(k.b)} \qquad \text{Equation 1.1}$$

Where A = Absorbance,

k = absorption co-efficient of the analyte,

b = average vapour thickness.

The value of k is related to concentration by the number of atoms/cm$^3$ ($N_v$):

$$\int k_\nu d\nu = (\pi e^2 / mc) N_\nu f \qquad \text{Equation 1.2}$$

Where m and e are the mass and charge of the electron, and f is the number of electrons per atom capable of being excited.

### 1.2.1.1 Light Source

It is necessary to provide an intense light source at the wavelength associated with each analyte absorption. Line emission spectra of the elements to be determined are produced by hollow cathode lamps (HCL). Figure 1.2 shows a schematic diagram of a HCL.

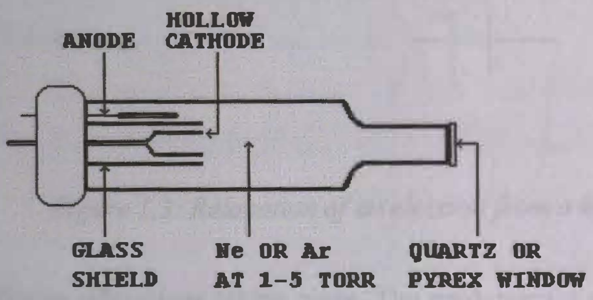


*Figure 1.2: Schematic diagram of a basic hollow cathode lamp.*

The cathode is made of or contains a high concentration of the analyte hence, is element specific. The lamp is filled with an inert gas (argon or neon). Upon application of current the inert gas atoms form cations at the anode, which bombard the cathode. This causes atoms of the cathode to be ejected in a process called sputtering. These atoms are excited by further collisions with electrons. Atom excitation involves the transition of an electron to a vacant higher energy level. The excited electron spontaneously relaxes back to the ground state releasing a photon. The wavelength of the photon is inversely proportional to the energy of the photon. The energy is derived from the difference in atomic energy levels. The number of protons in the nucleus defines the element and in conjunction with electron interactions determines the energy levels an electron can occupy. Therefore there are unique energy level differences for different elements. Hence the energy of the photons released will be unique for every element. Figure 1.3 shows a representation of an electron relaxing and the subsequent release of a photon.

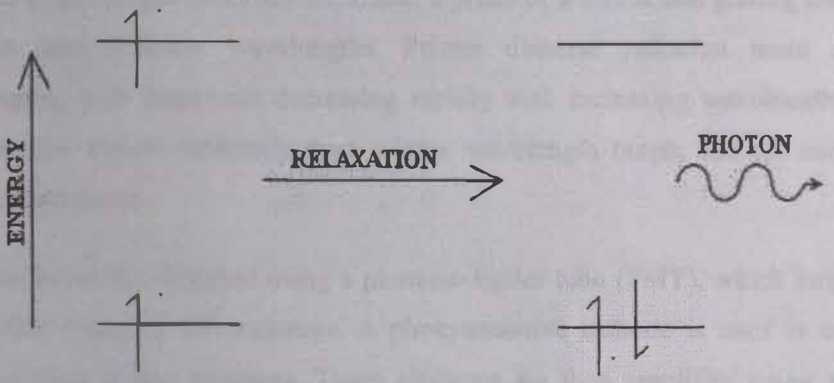


*Figure 1.3: Relaxation of an electron from a higher energy level.*

There are many different relaxations taking place. The predominant relaxation involves the return of the atom to its ground state, this produces the most intense or resonance line, which is usually the analysis wavelength chosen.

The reverse process can occur whereby an electron is excited by the absorption of a photon. The photon needs to have the correct energy to exactly match the difference in energy levels. Therefore only atoms of the analyte element will efficiently absorb the HCL light.

The natural width of the emitted HCL line is about $10^{-5}$ nm. This is broadened in proportion to temperature (Doppler effects) and pressure (Lorentz or collisional effects). Temperature and pressure are both low in the HCL, increasing the natural line width by only a factor of $10^2$. The absorption profile width is broadened in the atom cell but to a much greater extent ($10^3$) due to the high temperatures used. This ensures the light emitted by the HCL is absorbed very efficiently.

### 1.2.1.2 Monochromator, Detector and Modulation

The function of the monochromator is to isolate the measured line from the other emission lines of the cathode material and filler gas. There are two slits that narrow the wavelength bandpass to between 0.001 nm and 2 nm, although this range is not normally achieved in one single spectrometer. Either a prism or a diffraction grating disperses the radiation into different wavelengths. Prisms disperse radiation more at shorter wavelengths, with dispersion decreasing rapidly with increasing wavelength. Gratings disperse light almost uniformly over a large wavelength range, and are used in most modern instruments.

Radiation is usually detected using a photomultiplier tube (PMT), which amplifies one photon into typically $10^6$ electrons. A photo-emissive cathode is used to convert the protons hitting it into electrons. These electrons are then amplified using a series of anodes of increasing voltage. The gain is proportional to the inter-anode voltage, and the number of anodes. Increasing the voltage will also increase the dark noise caused by the statistical fluctuation of the photocurrent. This will have a direct effect on the signal to noise ratio and thereby the detection limit.

The optical signal falling on the PMT consists of the resonance line emission radiation from the HCL and background emission from the atomizer. To remove the non-resonance radiation the HCL signal is modulated. The frequency of modulation is synchronized with the amplifier at the detector, improving signal to noise.

### 1.2.1.3 Flame Atomisation (FAAS)

Atoms are produced by the thermal dissociation of molecules and reduction reactions on particle surfaces in a flame. If the analyte particles are in a form with a low boiling point and low metal oxide bond strength, atoms are mainly produced by thermal dissociation. The sample is sprayed into the flame in the form of an aerosol generated by a nebuliser. An air acetylene flame is the most common type of flame used. It provides sufficient thermal energy (about 2 400 K) to dissociate most elements to their atomic state. If elements which form refractory oxides (e.g. aluminium, zirconium and tantalum) are to be determined a higher temperature flame might be required (e.g. $N_2O$ acetylene at 3 200 K).

FAAS is a relatively rapid technique, ideal for determining concentrations in the µg $mL^{-1}$ range. The sensitivity is limited owing to the high dilution of atoms by the flame gases and the short residence time of atoms in the HCL beam. Where lower detection limits are required a graphite furnace atomiser can be used.

#### 1.2.1.4 Interference Effects

Calibration standards are prepared to allow calculation of analyte concentrations. To ensure accuracy the same atomisation processes that are taking place in the samples must also occur in the standards. Matrix matched calibration standards assist in maintaining constant atomisation conditions. Interference can occur due to co-extracted material from the sample altering the atomisation processes.

##### 1.2.1.4.1 Spectral Interferences

Spectral interferences generally cause less HCL light to be transmitted and hence an overestimation of analyte concentration. The reduction of light is either due to molecular absorption or particle scattering. Molecular absorptions tend to be worse in the UV-vis region (i.e. shorter wavelengths) and scattering is inversely proportional to the fourth power of the wavelength (i.e. shorter wavelength light is scattered more).

These are non-specific or background effects. They can be corrected for by instrumentation:

i. Deuterium ($D_2$) lamp background correction
The $D_2$ lamp is a continuum light source, emitting constant radiation intensity across the spectral bandpass. The HCL emission line width is narrow as described in section 1.2.1.1. The use of a beam splitter allows both light sources to be aligned along exactly the same path, which is important if accurate correction is to be obtained. Light sources are pulsed to allow the detector to differentiate HCL and $D_2$ light absorption.

The absorption calculated from the $D_2$ lamp will be the non-specific absorption and can be subtracted from the HCL or total absorption to give the corrected absorption. This corrects the average molecular absorption across the bandpass, and is adequate for most interference. The atomic absorption line is in fact affected by molecular absorption at a specific wavelength; if the molecular absorption is highly structured within the band pass then over- or under-correction can occur depending upon the emission line (analytical) wavelength. Species which give rise to structured background include InCl and $P_2$.

ii. Zeeman effect background correction

The use of a strong magnet and polarized light allows the background absorption to be calculated on the analytical wavelength. This technique was not used in this work so is not discussed further.

###### 1.2.1.4.2 Chemical Interferences

Chemical interferents tend to react with the analyte to reduce atom formation and hence lead to an underestimate of concentration. There are two main mechanisms of chemical interference in flame atomisation cells[64]:

i. Vaporization interference when a component of the sample alters the rate of vaporization of salt particles that contain the analyte. The formation of thermally stable analyte compounds also reduces the amount of atomisation. The use of a hotter flame can help reduce this type of interference, elements that form refractory oxides are more susceptible, e.g. aluminium and titanium.

ii. Ionisation interferences for atoms with low ionization potentials. This can be overcome by addition of an easily ionisable element to standards and samples to suppress analyte ionisation.

Various reagents can be added to overcome most of these interferences. Reagents can stabilise the analyte, volatilise the interferent or both. Care must be taken to ensure modifiers will not introduce interferent effects of their own.

### 1.2.2 Inductively Coupled Plasma Optical Emission Spectrometry

Here, atoms are excited in a plasma. The radiation emitted upon relaxation is monitored. Section 1.2.1.1 describes the electronic transitions associated with excited atomic species. Ionic emission lines can also be detected. Simultaneous monitoring of many emission lines is possible with inductively coupled plasma optical emission spectrometry (ICPOES), which is the major advantage over AAS.

#### 1.2.2.1 Inductively Coupled Plasma (ICP)

The first laboratory plasma was produced in 1891[65] but plasmas weren't used in optical emission spectrometry until 1964[66]. A plasma is a discharge of high temperature and high electron concentration[67]. In a plasma there is a lot of energy available to atomise, ionise and excite atoms. An inductor coil is used to produce an oscillating electromagnetic field that interacts with argon gas to produce a self-sustaining plasma[68]. Seed electrons produced from a spark initiate the plasma. The electrons are accelerated by the electromagnetic field and collide with argon atoms, ionising them to release more electrons. Some argon atoms and electrons collide and recombine releasing excess energy as heat and light.

A quartz torch is designed to deliver three separate argon gas flows. In addition to the plasma gas flow a central gas flow carries the sample into the plasma and a coolant gas flow prevents the quartz from melting. The coolant gas flows in a circular motion perpendicular to the axis of the plasma. As well as cooling the torch some of this flow helps sustain the plasma. The torch is designed with an optimum outer tube diameter to create a ring plasma with a central hole. This provides a central channel for sample introduction into the plasma. The plasma is not in thermal equilibrium and the concept of temperature in an ICP is not simple, but the kinetic temperature of the main plasma is about 8 000 K compared to the central channel where the temperature is thought to be about 4 000 – 6 000 K.

Analyte atoms are excited mainly by collisions with metastable and excited argon atoms of the plasma. Atoms can also be ionised and the degree of ionisation and atomisation varies at different points in the plasma. Figure 1.4 shows the different zones of plasma.

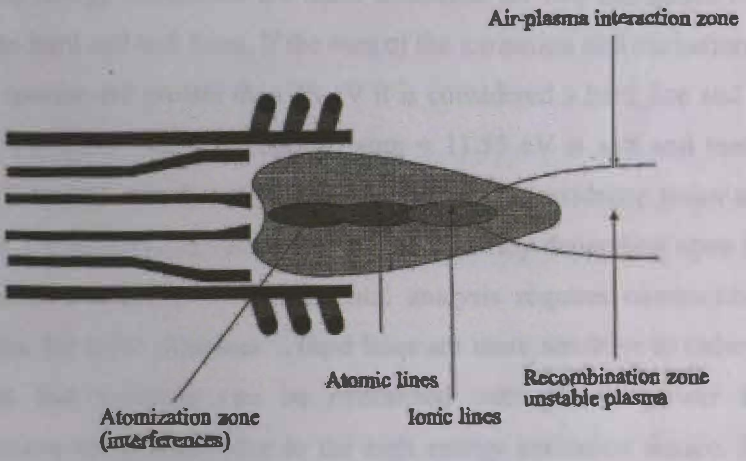


*Figure 1.4: Diagram showing different zones of plasma*[69].

### 1.2.2.2 Optical Emission Spectrometry (OES)

In ICPOES the optical window used for analysis falls just above the apex of the primary plasma core and just under the base of the flame-like after glow. Monitoring of this area excludes the current-carrying zone of the plasma and reduces background emission. Simultaneous monitoring of many different wavelengths allows multi-element analysis. This requires the use of high resolution spectrometers to separate different emission lines, such as an echelle polychromator. Light passing through an entrance slit is collimated and directed to an echelle grating which has a low density of shaped grooves to produce high order diffraction patterns. The diffracted beam is directed to a second, crossed grating with a higher density of grooves, or a prism, which separates the orders into a two-dimensional pattern. This pattern is focused onto a two-dimensional detecting surface, which can be configured to detect the individual spectral lines. An echelle polychromator disperses the radiation twice to give excellent dispersion and resolution over a wide wavelength range: to produce similar resolution with single dispersion polychromator would dramatically increase instrument size. A charge coupled device (CCD) can be used to detect the dispersed light.

#### 1.2.2.3 Interferences and Condition Optimisation

Optimum energy conditions are often described for two categories of analyte species, known as hard and soft lines. If the sum of the ionisation and excitation potentials for the analyte species are greater than 18 eV it is considered a hard line and if the sum is less than 16 eV a soft line e.g. copper I sum = 11.55 eV is soft and manganese II sum = 20.59 eV is hard. Hard analyte lines require longer residence times and higher plasma energies. Optimum observation height will also vary depending upon the analytical line being atomic or ionic. Multi-elemental analysis requires compromising of optimum conditions for some elements[70]. Hard lines are more sensitive to radio frequency power flux but this variation can be minimized with plasma power feedback control. Interferences are minimal due to the high energy excitation source. Matrix effects are mainly due to the physical properties of the test solutions and are overcome by matrix matching of standards with samples. Spectral interferences are also minimal in modern high-resolution instruments.

## 1.3 The URBSOIL Project

URBSOIL is an acronym for the project "Urban soils as a source and sink for pollution, towards a common European methodology for the evaluation of their environmental quality as a tool for sustainable resource management." The project is funded by the European Union 5th Framework, Energy, Environment and Sustainable Development programme under Key Action 4: "City of Tomorrow and Cultural Heritage" and is targeted at the area of sustainable city planning and rational resource management[71].

The overall aim of the project is to identify soil quality parameters and their use in urban areas to provide local, national and European authorities with decision support tools for the correct planning and sustainable management of the soil resource in the towns and cities of Europe[72].

The role of soils within the environment is important. They provide mechanical support and nutrients for plants. Nutrients and pollutants are both buffered by soil. Many previous soil studies were aimed at assessing the availability of nutrients and pollutants in soils for agricultural purposes. Soils in urban areas are less studied and understood. Human health will be directly affected by the status of the soil within a city, as will urban biodiversity and landscaping. Urban activities will tend to expose soils to extreme levels of potentially harmful species over relatively short time scales. Extreme conditions might alter the buffering capacity of the soil and cause the release of toxic materials into the biosphere. A greater understanding of soils in cities is required to assess the risk associated with the release of pollutants.

Several studies in European, American and Asian cities have been carried out on urban soils but a lack of common methodology makes inter comparisons impossible[73]. A common approach is required to study and evaluate soils in different urban settings. The adaptation and validation of procedures used previously in soil quality definitions, to ensure their applicability in urban environments, is also needed.

There are many factors that will influence the behaviour of an urban soil. Cities are dynamic environments with development decisions based on the needs of the population and economic factors. Regulations governing acceptable levels of pollutants in soils for various applications are also in place and must be considered. Climate and conditions unique to individual cities will also alter soil behaviour. All these factors need to be taken into account if the best decisions are to be made on urban planning options that will alter the soil status.

The URBSOIL project aimed to develop a decision support tool (DST) that could be used for the assessment of the quality of the soil resource in view of its sustainable use. To achieve this, soils in various cities across Europe have been studied. The cities have been chosen to represent a wide range of cultures, climates and geographical locations. Table 1.3 shows some of the key data from the partner cities involved in the URBSOIL project.

| Partner | Population (reported 2001) | Mean annual temperature (°C) | Mean annual precipitation (mm) | Geological substrate | Green areas (ha) |
|---|---|---|---|---|---|
| Turin | 900 000 | 12.6 | 750 | Alluvial | 125 |
| Glasgow | 600 000 | 8.9 | 991 | Basalt<br>Alluvial | n.a. |
| Seville | 706 000 | 18.2 | 540 | Alluvial | 278 |
| Aviero | 68 000 | 17.5 | 1000 | Alluvial | n.a. |
| Uppsala | 187 000 | 5.6 | 550 | Granite, glacial and postglacial deposits | 900 |
| Ljubljana | 486 000 | 10.0 | n.a. | n.a. | n.a. |

*Table 1.3: Summary of key data on partner cities of URBSOIL project, (n.a.=not available).*

The DST allows different data types to be displayed in a flexible and informative manner. Access to information, which facilitates an improved understanding of the scientific background on the available data, is also provided as part of the DST. URBSOIL research indicated authorities did not require models giving them an answer but required information on how that answer was created and if it was justified. The importance of soil as a resource is not a high priority to planning authorities. There are many stakeholders that have interests in urban soil, including legislative bodies, city inhabitants and workers, authorities and landowners. Often their interests are very different and in conflict. URBSOIL has incorporated a questionnaire into the DST to allow authorities to gather opinion and understanding from stakeholders and experts.

For each city, soil has been collected and analysed to populate a database of information that feeds into the DST allowing results to be viewed statistically and geographically. The main roles of Strathclyde in generating these results were (a) the production of a soil sampling protocol, (b) providing advice on the use of suitable reference materials and quality control samples and (c) the analysis of soil samples for metal content.

The work undertaken at Strathclyde as part of the URBSOIL project is presented in this thesis. The work described in this thesis is presented in a further 6 chapters:

i. Chapter 2 describes the general procedures that are broadly applicable to the experimental work carried out.

ii. Chapter 3 describes the quality control aspects of the work.

iii. Chapter 4 presents results from an investigation into variability, distribution and associations between metals in soil samples collected from points within two Glasgow parks.

iv. Chapter 5 presents results from analysis of metal content in composite soil samples collected from Glasgow parks, roadsides, ornamental gardens and riversides.

v. Chapter 6 compares different sequential extraction methods.

vi. Chapter 7 describes the results of the BCR sequential extraction of Glasgow park and roadside samples.

## 1.4 Aims

The overall aim of the work in this thesis was to improve knowledge about metal concentrations and partitioning in urban soils from the city of Glasgow, UK. Specific objectives included:

- measurement of a suite of metals in soils from different types of land surface: parks, roadsides, ornamental gardens and riverbanks
- application of chemometric approaches to obtain information on associations between elements and their origins
- evaluation of sequential extraction methodology based on the modified protocol developed under the auspices of the EU Community Bureau of Reference (BCR)
- application of the selected sequential extraction method to urban soil

# 2 GENERAL EXPERIMENTAL PROCEDURES

## 2.1 Sampling

A 30 m tape measure, 100 m string marked at 10 m intervals, map and compass were used to correctly space sampling points, which were marked with canes. Details of sampling locations were recorded on a standard sampling sheet. Equipment used to collect samples was cleaned with distilled water and wiped with paper towels between sampling points. Samples were placed in labelled plastic bags and transported to the laboratory in a cool box.

## 2.2 Sample Pre-treatment and Characterization

Upon return to the laboratory samples were spread out in labelled aluminium trays or on plastic sheets. Samples were dried in an oven at 26 °C until change in mass was less than 5 %. Periodically aggregates were broken up by hand to assist the drying process. Samples were then sieved to 2 mm and the two factions weighed, the less than 2 mm faction was retained in plastic bags or amber glass bottles for analysis.

Sub-samples of approximately 1 g were dried and ashed to allow calculation of moisture content and loss on ignition (LOI). Accurately weighed sub-samples were spread in a layer of about 1 mm depth in ceramic crucibles. The crucibles were then put in an oven at 105 °C overnight. After being left to cool, the masses of the oven dried sub-samples were determined.

Moisture content (%) was determined as:

$$\frac{\text{air dried weight - oven dried weight}}{\text{air dried weight}} \times 100 \qquad \text{Equation 2.1}$$

Values obtained were used to convert all results reported to a dry weight basis. The sub-samples were then ashed in a muffle furnace at 550 °C, cooled and re-weighed.

Percent loss on ignition (LOI) was determined as:

$$\frac{\text{oven dried weight} - \text{muffle furnace weight}}{\text{oven dried weight}} \times 100 \qquad \text{Equation 2.2}$$

LOI values are an indication of the soil organic matter content.

## 2.3 Microwave Assisted Digestion

Pseudo total digestion was performed in a CEM MDS-2000 sample preparation system (CEM corp., Bucks, UK). Microwave power can be adjusted from 0 – 630 W depending upon quantity of material for digestion. Samples were placed in 'Advanced Composite Vessels' (ACV) for digestion. Up to 12 vessels can be accommodated in the microwave in each run. A pressure sensor attached to one of the vessels and feedback electronics control energy input. Up to 5 different pressure stages can be programmed into a digestion sequence.

Nitric and hydrochloric acids (extra pure) were obtained from Sigma-Aldrich (Gillingham, UK). Aqua regia is a mixture of $HCl:HNO_3$, 3:1 and was used for all pseudo total digestions.

20 mL of aqua regia was added to approximately 1 g sample in an ACV. Table 2.1 shows the pressure program used to digest the samples in the microwave.

| | STAGE 1 | STAGE 2 |
|---|---|---|
| Pressure (p.s.i.) | 60 | 120 |
| Time (minutes) | 20 | 30 |
| Time at pressure (minutes) | 5 | 20 |

*Table 2.1: Microwave heating program for soil digestion.*

The digest was then filtered (Whatman 541 filter paper) into 100 mL flasks. The residues in the ACV's were rinsed with distilled water and filtered into flasks, solutions were then made up to 100 mL with distilled water. Triplicate portions of each sample were digested in parallel.

## 2.4 Sequential Extraction

Extractions were performed using an end over end shaker (G.F.L ® 3040) at a speed of 30 ± 10 r.p.m and separation of solid and liquid was achieved by centrifuging at 3000×g for 10 minutes (CEM MDS 2000).

Hydrogen peroxide (8.8 mol $L^{-1}$) was from Fischer chemicals (Manchester, UK). Acetic acid was from Sigma-Aldrich (Gillingham, UK). Ammonium acetate, ammonium oxalate, oxalic acid and hydroxylammonium hydrochloride (GPR grade) were obtained from BDH (Poole, UK). Extractions were performed on triplicate portions of each sample in parallel.

### 2.4.1 Reagent Preparation

Solution A

25 mL of glacial acetic acid was diluted to 1 L with distilled water to make 0.43 mol $L^{-1}$ acetic acid. 250 mL of this was then diluted to 1 L to make solution A, 0.11 mol $L^{-1}$ acetic acid.

Solution B1

34.75 g of hydroxylammonium hydrochloride was dissolved in 400 mL distilled water and transferred to a 1 L volumetric flask. 25 mL of 2 mol $L^{-1}$ nitric acid was then added by means of a pipette and the solution made up to 1 L. Solution B1 is 0.5 mol $L^{-1}$ hydroxylammonium hydrochloride and was prepared on the same day of use.

Solution B2[74]

14.2 g ammonium oxalate was dissolved in 500 mL distilled water. 9.6 g oxalic acid was dissolved in 382 mL distilled water. These 2 solutions were mixed and pH adjusted to pH 3 with concentrated nitric acid to make solution B2. Extraction using solution B2 was performed in the dark by wrapping the sample tubes in aluminium foil.

Solution C

Hydrogen peroxide solution as supplied at 30 % (8.8 mol $L^{-1}$) is solution C.

Solution D

77.08 g of ammonium acetate was dissolved in 800 mL distilled water, pH was adjusted to pH 2.0 ± 0.1 with concentrated nitric acid and the solution made up to 1 L.

### 2.4.2 Extraction Procedure

Two different sequential extraction procedures were used. The procedure using solution B1 was the modified BCR extraction[75] and the alternative procedure replaced solution B1 with B2 in the second step. There was minimal delay between extractant addition and commencement of shaking for steps 1 to 3.

Step 1

40 mL of solution A was added to 1 g sample in a 100 mL centrifuge tube and shaken for 16 h on the mechanical shaker at 23 r.p.m. The extract was separated from the residue by centrifugation at 3000×g, then the liquid decanted into a clean labelled polyethylene bottle and stored at 4 °C. The residue was washed to remove any reagent left over. Washing was performed by adding 20 mL distilled water, followed by 15 min of shaking, and 10 min centrifuging. The wash supernatant was then discarded.

Step 2

40 mL of freshly prepared solution B was added to the residue from step 1. Shaking and washing was carried out as above.

Step 3

To avoid violent reaction, 10 mL of solution C was added to the residue from step 2 in small aliquots. The samples were digested for 1 h at room temperature with loosely fitted caps and occasional manual shaking. The centrifuge tubes were then placed in a water bath at 85 °C for 1 h. The volume was reduced to less than 3 mL by continuing heating with the caps removed. A further 10 mL of solution C was added. The vessels were again heated 85 °C for 1 h, loosely covered with occasional manual shaking. The volume was reduced to less than 1 mL and then allowed to cool. 50 mL of solution D was then added to the cool moist residue. Shaking and washing was carried out as above.

Step 4

The residue from step 3 was washed from the centrifuge tube into an ACV using 20 mL aqua regia. Microwave assisted digestion was performed as described in section 2.3.

## 2.5 Measurement of Metals Concentration in Soils

### 2.5.1 Flame Atomic Absorption Spectrometry

Flame atomic absorption measurements were obtained using a Philips PU9100 AAS instrument (Thermo Electron Spectroscopy, Cambridge, UK), run by an IBM personal computer. Absorbance values were integrated over a 4 second period. Three repeat measurements were performed for each solution. Each time a different solution was analysed the spectrometer was autozeroed with blank solution.

The sample was introduced into the flame by a narrow capillary tube to provide continuous sample nebulisation at an average rate of 5 mL $\text{min}^{-1}$. Optimum conditions for burner height and fuel flow were used to give maximum sensitivity. Analysis was performed for each element separately. A spectral bandpass of 0.2, 0.5 or 1 nm could be selected.

### 2.5.2 Inductively Coupled Plasma Optical Emission Spectrometry

ICPOES measurements were obtained using a Perkin Elmer Optima 3000 ICPOES instrument (Perkin Elmer, Bucks, UK). The sample was introduced into the pumping tubing by an AS91 autosampler. A peristaltic pump delivered a constant flow (1 mL $\text{min}^{-1}$) of sample through a cross flow nebuliser into the spray chamber. Larger droplets were removed and any pulses from the pump smoothed out by the spray chamber. Figure 2.1 shows the spray chamber design.

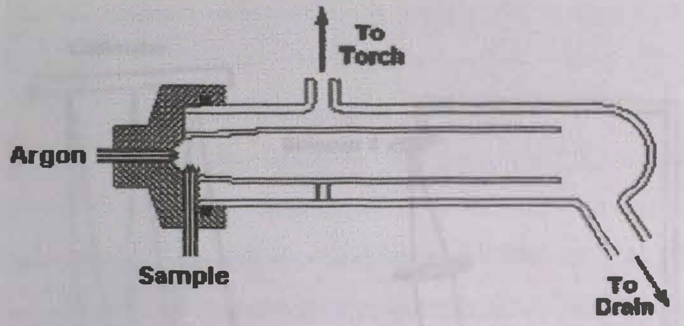


*Figure 2.1: Scott type spray chamber*[76].

A free running radio frequency plasma generator (40 MHz) enables efficient plasma coupling using feedback electronics to monitor electrical characteristics of the plasma and adjust RF power accordingly (750 – 1500 W). The plasma torch is a one-piece quartz tube. There are three argon gas flows into the torch, with flow rates of 15, 0.5 and 0.8 L min$^{-1}$ for plasma generation, auxiliary flow and nebulisation, respectively.

Figure 2.2 shows the optical configuration of the spectrometer. Initially radiation is dispersed with a 79 line mm$^{-1}$ grating with blaze angel of 63.4°. Cross dispersion by a 375 line mm$^{-1}$ grating, with Schmidt correction incorporated into the surface (aberration correction for 400 mm camera sphere), further separates the light which is then reflected to the first detector. Approximately 20 % of the radiation dispersed from the first grating is allowed to pass through a central hole in the second grating to a 60° fused quartz prism. This prism then cross disperses this radiation, which is focused on the second detector. Automatic mercury emission line monitoring between each sample data acquisition calibrates the spectrometer.

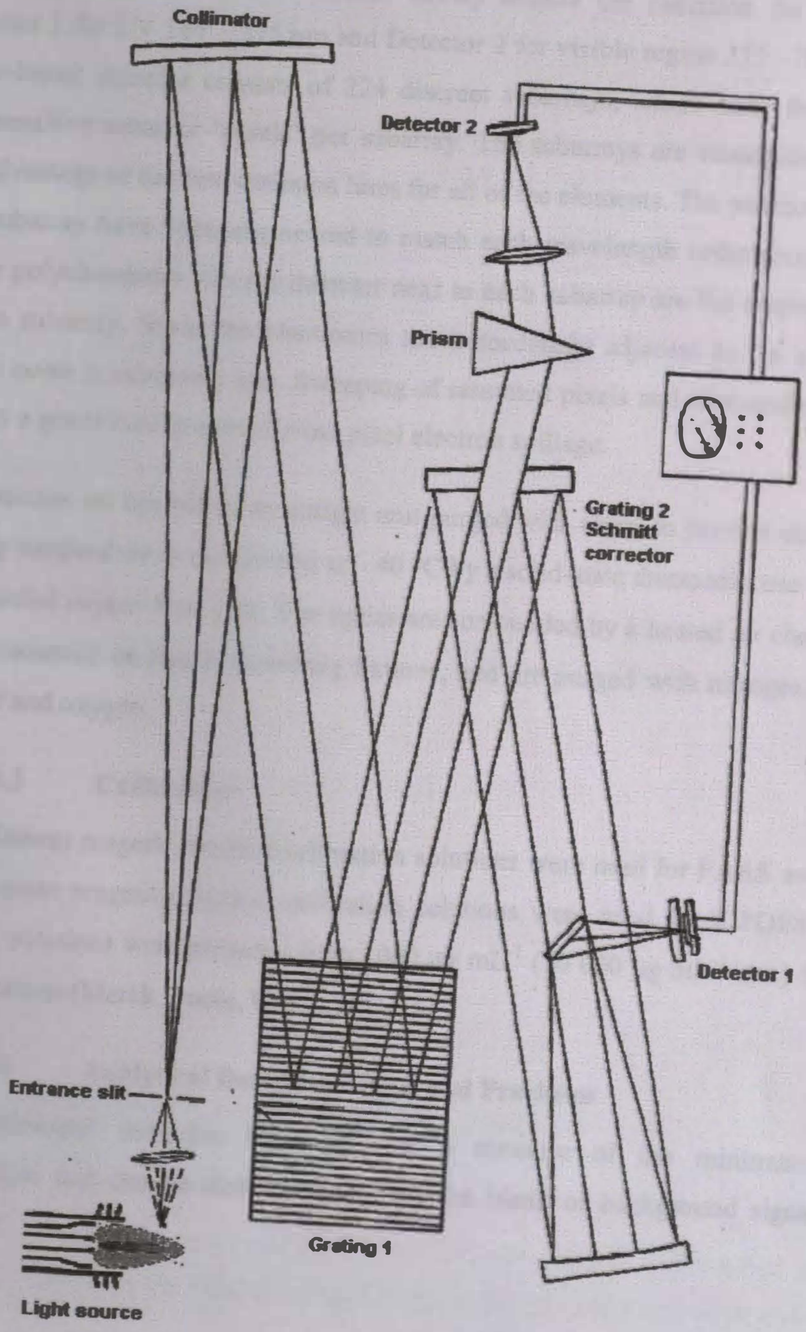


*Figure 2.2: Schematic diagram of optical configuration*[77].

A segmented charge coupled device (SCD) detects the radiation for each region (Detector 1 for UV 167 – 375 nm and Detector 2 for visible region 375 –782 nm). Each silicon-based detector consists of 224 discreet subarrays, which have from 20 to 80 photosensitive areas or "pixels" per subarray. The subarrays are strategically placed to take advantage of the best emission lines for all of the elements. The position and size of each subarray have been engineered to match each wavelength order produced by the echelle polychromator. On the detector next to each subarray are the output electronics for that subarray. Since the electronics are immediately adjacent to the subarray, the readout noise is extremely low. Sweeping of saturated pixels and surrounding each subarray by a guard band prevents cross pixel electron spillage.

The detectors are housed in an airtight unit purged with argon to prevent condensation. Housing temperature is maintained at – 40 °C by a solid-state thermoelectric cooler with water-cooled copper heat sink. The optics are surrounded by a heated air chamber at 38 °C and mounted on shock absorbing fixtures, and are purged with nitrogen to remove moisture and oxygen.

### 2.5.3 Calibration

Single element reagent matched calibration solutions were used for FAAS analysis and multi element reagent matched calibration solutions were used for ICPOES analysis. Calibrant solutions were prepared from 1000 μg $mL^{-1}$ (10 000 μg $mL^{-1}$ iron) Spectrosol stock solutions (Merck, Poole, UK).

### 2.5.4 Analytical Detection Limits and Precision

The instrumental detection limit (DL) is a measure of the minimum analyte concentration that can be distinguished from the blank or background signal. DL is defined as:

$$DL = \frac{3 \times S}{\text{gradient of the calibration slope}}$$ Equation 2.3

Where S = standard deviation of 10 replicate analyses of a blank (or low calibration standard) and is defined as:

$$S = \sqrt{\frac{\Sigma_i (x_i - \bar{x})^2}{N-1}}$$ Equation 2.4

$x_i$ = the $i^{th}$ result

N = the number of replicates

The instrumental detection limit is used to calculate the method or procedural detection limit ($DL_{pro}$). $DL_{pro}$ is the minimum concentration of analyte that can be detected in the original sample, allowing for dilution or digestion procedures performed. $DL_{pro}$ is calculated:

$$DL_{pro} = \frac{DL \text{ x volume of extractant}}{\text{mass of sample}}$$ Equation 2.5

The precision is often expressed as the percent relative standard deviation (RSD):

$$RSD = 100 \times \frac{S}{\bar{x}}$$ Equation 2.6

for a specified number of replicate measurements or samples.

### 2.5.5 Spectrometer Wavelengths and Detection Limits

Detection limits for each analytical wavelength were determined as described in section 2.5.4. Table 2.2 shows the detection limits for the different analytes in aqua regia.

| Element | Analyte $\lambda$ (nm) | $D_L$ inst. (ng $L^{-1}$) | $D_L$ pro. (mg $kg^{-1}$) |
|---|---|---|---|
| Al | 308.211 | 38 | 3.8 |
| Al | 396.147 | 22 | 2.2 |
| Ba | 233.527 | 3.5 | 0.35 |
| Ba | 455.403 | 0.091 | 0.091 |
| Cd | 214.440 | 2.6 | 0.26 |
| Cd | 228.802 | 7.4 | 0.74 |
| Ca | 315.887 | 13 | 1.3 |
| Ca | 396.847 | 4.0 | 0.4 |
| Ca | 422.7 (FAAS) | 87 | 8.7 |
| Cr | 205.560 | 8.8 | 0.88 |
| Cr | 267.716 | 9.0 | 0.90 |
| Cu | 224.700 | 18 | 1.8 |
| Cu | 324.752 | 9.6 | 0.96 |
| Cu | 325 (FAAS) | 19 | 1.9 |
| Fe | 238.204 | 22 | 2.2 |
| Fe | 239.562 | 24 | 2.4 |
| Fe | 248.3 (FAAS) | 140 | 14 |
| Li | 670.784 | 5.7 | 0.57 |
| Mg | 279.077 | 41 | 4.1 |
| Mg | 285.213 | 1.2 | 0.12 |
| Mn | 257.610 | 1.5 | 0.15 |
| Mn | 260.568 | 1.2 | 0.12 |
| Mn | 279.5 (FAAS) | 42 | 4.2 |
| Ni | 221.648 | 14 | 1.4 |
| Ni | 232.003 | 28 | 2.8 |
| Pb | 217.000 | 220 | 22 |
| Pb | 220.353 | 33 | 3.3 |
| Pb | 217 (FAAS) | 120 | 12 |
| V | 292.402 | 3.6 | 0.36 |
| V | 310.230 | 4.2 | 0.42 |
| Y | 360.073 | 1.5 | 0.15 |
| Y | 371.029 | 0.65 | 0.065 |
| Zn | 206.200 | 18 | 1.8 |
| Zn | 213.857 | 16 | 1.6 |
| Zn | 213.9 (FAAS) | 41 | 4.1 |

*Table 2.2: Detection limits in 20 % aqua regia.*

## 2.6 Data Analysis

### 2.6.1 Statistics[78]

#### 2.6.1.1 Normality

Distribution of data was tested for normality using the software in Minitab, by the Kolmogorov-Smirnov method. This method compares the cumulative frequency curve of the data with that of a normal distribution. Probability (P-value) that the data is normally distributed can then be estimated. If $P > 0.05$ then the distribution passes as being normally distributed with 95 % confidence. In soil studies if an analyte passes the normality test it indicates analyte concentrations are influenced by the same factors to a similar degree at all sampling locations[79], and that the samples are from the same statistical population for that analyte. Failing the normality test indicates samples are not from the same population, and that analytes at some sites are probably affected by specific factors. The presence of outlier values, which might originate from sites affected differently than most sites, strongly influences the results of the normality test.

#### 2.6.1.2 Outliers

There are several different types of outliers in soil studies[80]. Outlier values might arise for a single variable and can be tested using many simple statistical methods such as Grubb's test or range tests. The rejection of results based on a univariate outlier tests might lead to loss of information that is of interest[81]. Outlier samples might also exist with several variables of unusually high or low values. Outliers in soil studies often highlight areas that might be of particular environmental interest. Range outliers were indicated by Minitab when plotting boxplots as being more than 1.5 times the inter-quartile range below the first quartile or above the third quartile. Outlier sites should only be rejected if they are thought to represent areas that are influenced by specific factors that are not important to an investigation, or if there is a mistake that has resulted in the outlier value. Where there are samples with several outlier analytes it is likely the factors that have resulted in these high or low values are of interest and so should not be removed. Outliers will have a greater influence on summary statistics and might distort the overall picture. However if it is thought outliers are representative of the underlying nature of the data they should be included. To reduce the influence of the outliers, and try to gain an insight into the overall general trends in data, the median and inter quartile range can also be examined.

#### 2.6.1.3 Paired t-test

The paired t-test compares two sets of results that originate from the same sample. In this work this corresponds to the results from the same sample point at different depths. The result from the deeper sample is subtracted from the surface result to give the differences in analyte concentration at each site. The distribution of the differences is then statistically tested at 95 % confidence to have a mean = zero. If the distribution of the differences is not approaching normal (see section 2.6.1.1) the test is not valid. The influence of outliers in the differences will also alter the reliability of the paired t-test. Where a differences distribution failed the normality test it often passed after outliers were removed. Performing the paired t-test with all values and then again with outliers removed gives two statistical results. If both results agree, and in one case the distribution of the differences is normal there is reasonable confidence that the result is generally applicable. Where the test statistics do not agree upon removal of outlier(s) this indicates the outlier values are having a large effect on the test result. The importance of this depends upon the P-values found and the number of outliers that were removed. This case is more complicated and it is likely there is insufficient information to significantly conclude if there is a difference in analyte concentration between depths.

### 2.6.2 Principal Component and Factor Analysis (PCA and PFA)[82]

A sample with a large number of variables (e.g. 8 metal concentrations) measured can be uniquely defined by the combination of different variable values (concentrations). Where there is correlation between variables in different samples, principal component analysis (PCA) can be used to reduce the number of variables required to define each sample. Instead of defining the data on axes corresponding to variable measurements new axes are defined to explain the maximum variation of the data. Principal component one (PC1) always explains the most variation, PC2 is orthogonal to PC1 and explains the next most variation and so on. In datasets with strong correlation between variables the correlated variables are effectively combined to define a new PC or latent variable. This allows all the data to be defined by fewer variables and simplifies data handling.

Where there are large differences in magnitude of the variables measured, data must be scaled or PC1 is likely to relate to only the variable with the highest magnitude. Results can be scaled in many different ways. PCA will produce very different results depending upon how the data is scaled. Data is commonly scaled by subtracting the mean and dividing by the standard deviation to give a new data distribution with mean = zero and unit variance (autoscaling). This weights each analyte with equal variation and therefore removes the potential relationship, for metal concentration in soils, of increased variability with anthropogenic input. Autoscaling allows potentially common sources and relationships between analytes to be investigated. An alternative method of scaling is dividing by the mean, which will maintain differences in variation between analytes whilst removing the differences in magnitude of concentration (relative results). Using relative results allows the relationship between variability and analytes to be investigated.

PCA produces arrays of scores and loadings. Eigenvalues are used to calculate the scores matrix from the singular value decomposition of the original (scaled) data matrix. The eigenvalues are related to the amount of variation captured by each PC. The scores give information on the samples' relationship to each PC and the loadings are the correlation co-efficients between the original analytes concentrations and the PCs. Examination of loadings provides information about the relationships between the analytes. Examination of the scores provides information about the sample sites.

Previous literature studying urban soil has often used principal factor analysis to study relationships between analytes and relate that to anthropogenic input. PFA requires the data to be autoscaled before performing PCA. The desired number of PCs to use in further calculations is then estimated from a plot of eigenvalues. A balance between use of as few PCs as possible and loss of information is required: for example if four PCs capture 95 % of the variation in the data and five PCs capture 98 % of the variation it is probably not worth including the fifth PC. The reduced data set can then be defined on a new set of axes to meet different criteria. The method used in literature is a varimax rotation. This type of rotation maximises the loadings in any factor with as few original variables as possible. Mathematically this is done by maximising the simplicity (variance of the values squared) of the new matrix. This produces new scores and loadings data sets related to new principal factors, instead of PCs. These principal factors no longer capture the most variation possible, but usually capture almost as much as the equivalent PC.

The loading matrix produced by PFA can then be studied to give information on possible common sources related to the factors, in terms of real events and situations compared to the mathematical abstract space PCA often works in. It has been reported PFA is not valid where data is not distributed normally[83]. The mathematical argument for this is unclear but caution must be used when using this method where data is not normally distributed.

# 3 QUALITY CONTROL

## 3.1 Sampling and Sample Pre-treatment

The uncertainty due to soil sampling has been reported as being in general ten times greater than the uncertainty due to analysis[84]. It is therefore important to minimize variability between sampling procedures applied. A standard soil sampling protocol was proposed for use throughout the URBSOIL project. The sampling protocol detailed all steps, from collection and labelling of soil samples, to preparation of samples for chemical analysis. The proposal was discussed, modified and then used as a guide by all URBSOIL partners.

In Glasgow, soil sampling was always performed by the same individuals. Detailed sampling records were completed on-site and care taken to ensure the same procedures were followed for all sites of the same type (land use). Where procedural alterations were required these were recorded.

## 3.2 Analytical Line Agreement

Analysis of solutions by ICPOES allows simultaneous determination of analyte concentration at different wavelengths. Any interference is unlikely to affect different wavelengths to the same extent. Comparison of concentrations determined at different wavelengths therefore allows potential inaccuracies to be highlighted. Near the start of the work, concentrations of an analyte determined at one wavelength were divided by the concentrations found at the other wavelength to give a percentage agreement. Table 3.1 shows the average percent agreement found for the different analytes.

|  | Percent agreement (%) |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | Al | Ba | Ca | Cr | Cu | Fe | Mg |
| Average | 102 | 102 | 99 | 103 | 113 | 99 | 98 |
| SD | 3 | 3 | 2 | 2 | 15 | 3 | 3 |
| N | 294 | 294 | 294 | 294 | 190 | 294 | 294 |
|  | Mn | Ni | Pb | V | Y | Zn |  |
| Average | 100 | 104 | 116 | 105 | 103 | 104 |  |
| SD | 2 | 12 | 27 | 4 | 3 | 2 |  |
| N | 294 | 128 | 154 | 294 | 294 | 294 |  |

*Table 3.1: Agreement between solution concentrations determined at different wavelengths by ICP-OES, SD=standard deviation, N=number of replicates.*

The average percent agreement was excellent for most analytes. Only copper and lead showed poorer agreement between lines, and high standard deviations indicating a wider range of ratios. To investigate whether interferences were affecting measurement of these elements by ICPOES sample solutions were also analysed for copper and lead concentrations by flame atomic absorption spectrometry (FAAS). It was found that the most sensitive ICPOES wavelengths (Cu 324.725 nm, Pb 220.353 nm) were in better agreement with the FAAS results. Therefore, although poor agreement between concentrations calculated at different ICPOES lines was shown for only some samples, results from one line only were used to calculate copper and lead concentrations throughout this work.

The ratio of the concentrations of nickel obtained at the two wavelengths also showed a high standard deviation (although average agreement itself was good). It was noted that the spectral regions used to detect nickel emissions were not flat, possibly due to iron and silicon emissions. Unfortunately, comparative analysis was not possible because nickel concentrations were too low to be determined by FAAS. However, measured nickel concentrations in CRM143R were in excellent agreement with target values, and it was therefore decided to use average results from both nickel analytical wavelengths in calculation of analyte concentrations.

## 3.3 Method Quality Control

### 3.3.1 Analysis of Method Blanks

Every set of samples extracted or digested included a method blank. The concentrations of most analytes in the blanks were low, usually below detection limits. Where this was not the case samples from the same batch were blank corrected. Calcium concentration in the blank solutions was usually above detection limits. Table 3.2 shows the concentration of calcium in two soil samples digested in three batches. The concentrations of calcium in solutions and method blanks are also shown. The first batch included soil A, the second batch included soil B. The third digestion batch contained soils A and B and was performed to check whether the presence of a significant method blank affected the measured analyte concentrations in soil.

| Batch | Sample | Calcium concentration in | |
|---|---|---|---|
| | | Digestate or blank ($mg\ L^{-1}$) | soil * ($mg\ kg^{-1}$) |
| 1 | Blank 1 | 5.76 | - |
| | Soil A - 1 | 13.7 | 956 |
| | Soil A - 2 | 15.0 | 1110 |
| | Soil A - 3 | 15.3 | 1020 |
| 2 | Blank 2 | 5.22 | - |
| | Soil B - 1 | 81.5 | 6850 |
| | Soil B - 2 | 80.7 | 7220 |
| | Soil B - 3 | 81.6 | 7330 |
| 3 | Blank 3 | 5.73 | - |
| | Soil A - 4 | 20.9 | 1360 |
| | Soil A - 5 | 19.5 | 1200 |
| | Soil A - 6 | 18.7 | 1230 |
| | Soil B - 4 | 74.1 | 7160 |
| | Soil B - 5 | 68.2 | 7080 |
| | Soil B - 6 | 78.5 | 6900 |

*Table 3.2: Concentrations of calcium in blanks, extracts and soils (A and B), *blank corrected results.*

There was always a measurable amount of calcium in the method blanks, but there was fair agreement between concentrations of calcium found in soils A and B when digested on two different occasions (81 and 104 % recovery respectively). These results indicate blank correction effectively compensates for differences in background analyte levels between different batches. The accuracy of results from reference material analysis adds further weight to the validity of blank subtraction.

### 3.3.2 Reference Materials

A certified reference material (CRM) has target results and stated uncertainty that can be traced to an accurate realisation of the unit in which the property values are expressed. Results from the analysis of suitable CRMs allow experimental accuracy to be assessed. CRMs as supplied are highly homogeneous. Soil is intrinsically heterogeneous. Therefore soils must be treated to reduce heterogeneity if they are to be used as CRMs. The material is usually ground (typically to < 90 μm) to reduce the size range of particles and mixed thoroughly.

CRMs are expensive and the range of matrices and analyte levels available is limited. No urban soil CRMs currently exist certified for extractable trace metals. Further, when using CRMs, it is desirable to have a matrix matched reference material containing levels of analytes similar to those in the actual samples. In the URBSOIL project, production of an internal, urban soil reference material (URM) was undertaken by each partner to provide soil with similar matrix composition and trace element concentrations to those studied, which could be used in the place of a CRM. The Glasgow URM was obtained from sample site GLA.PO.34 (Glasgow Green). Target values for aqua regia soluble metal contents were established by replicate analysis of the URM in parallel with BCR CRM143R. Portions of soil were then included in all batches of digestion (see below).

Results obtained for analysis of reference materials were presented in the form of multi-element control charts. Results were autoscaled by subtraction of the target mean and division by the target precision. Hence, autoscaled results have a target of zero and a y-axis measured in acceptable standard deviations from this target. This allows results for different analytes, with different target values, to be plotted on one chart. The analytical procedure was deemed to be under statistical control provided results were within three standard deviations of the target values.

### 3.3.3 Microwave Digestion

#### 3.3.3.1 Certified Reference Material

There are several soils certified for trace element content, but these often do not have information on aqua regia soluble levels. BCR CRM143R was deemed the most suitable CRM available. Certified values are available for the aqua regia soluble content of cadmium, chromium, lead, manganese, nickel and zinc, and indicative values for copper. Table 3.3 shows the target values and precision for trace metals soluble in aqua regia for CRM143R.

| Target values of CRM143R (mg kg$^{-1}$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cd | | Cr | | Cu | | Mn | | Ni | | Pb | | Zn | |
| Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| 72.0 | 1.7 | 426 | 13 | 128 | 7 | 858 | 13 | 296 | 4 | 174 | 5 | 1060 | 20 |

*Table 3.3: Certified and indicative values of CRM143R aqua regia soluble metal content*[85].

Aqua regia digestion was performed as described in Section 2.3. The method used evolved during the project and three versions were applied at different stages. Method 1 was the original procedure and was used for the digestion of the pilot study samples discussed in Chapter 4. Method 2 included a closed overnight pre-digestion. Method 3 included an open overnight pre-digestion and was the method used for the digestion of samples discussed in Chapter 5. The method was altered to improve accuracy as assessed by comparison of results of CRM analysis with target values. Figure 3.1 shows the results of the digestion and analysis of CRM143R following the different procedures.

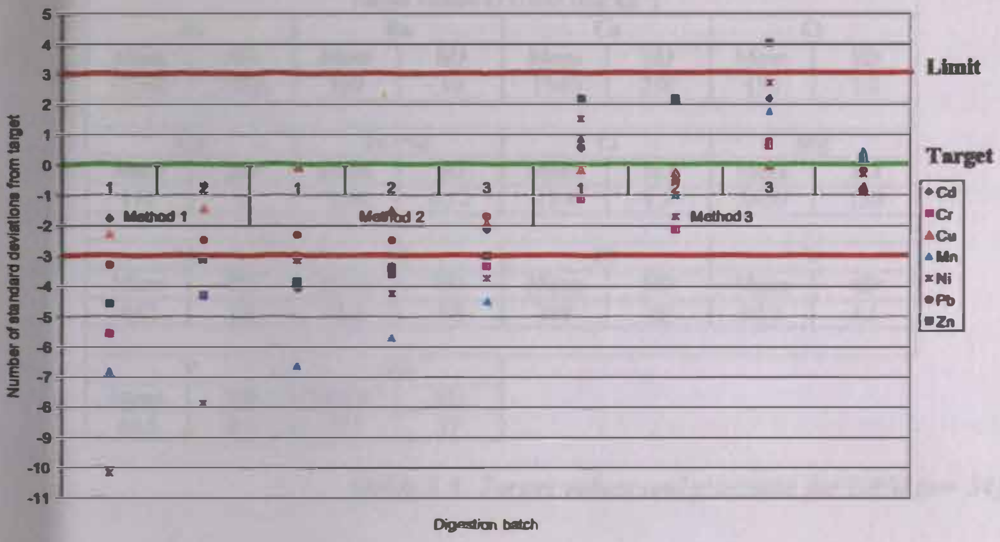


*Figure 3.1: Control chart showing autoscaled average results from the analysis of aqua regia soluble metals in CRM143R (n=2).*

Copper and lead levels obtained for the CRM were close to target values irrespective of digestion method. Cadmium concentrations were also generally close to the target value except in some batches where digestion Method 2 was applied. Zinc extraction efficiency was low when Method 1 was used but slightly high when Method 3 was used. Chromium, manganese and nickel were the metals whose extraction efficiency was lowest by Method 1 (> 5 SD from target). Overall Method 3 was the most accurate procedure as results for nearly all metals were within three standard deviations of the target values.

### 3.3.3.2 Urban Soil Reference Material

Table 3.4 shows the target values and standard deviations that were obtained for the Glasgow URM.

| Target values of URM (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Al | | Ba | | Ca | | Cr | |
| Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| 12300 | 1460 | 169 | 10 | 1540 | 250 | 43.2 | 3.0 |
| Cu | | Fe (%) | | Li | | Mg | |
| Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| 111 | 5 | 3.06 | 0.12 | 12.4 | 1.3 | 2810 | 150 |
| Mn | | Ni | | Pb | | V | |
| Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| 442 | 18 | 48.8 | 7.0 | 389 | 25 | 85.0 | 4.1 |
| Y | | Zn | | | | | |
| Mean | SD | Mean | SD | | | | |
| 10.5 | 0.6 | 177 | 11 | | | | |

*Table 3.4: Target values and precision for URM,(n= 34).*

Figure 3.2 shows the results of digestion and analysis of the Glasgow URM following the three different digestion procedures (discussed above).

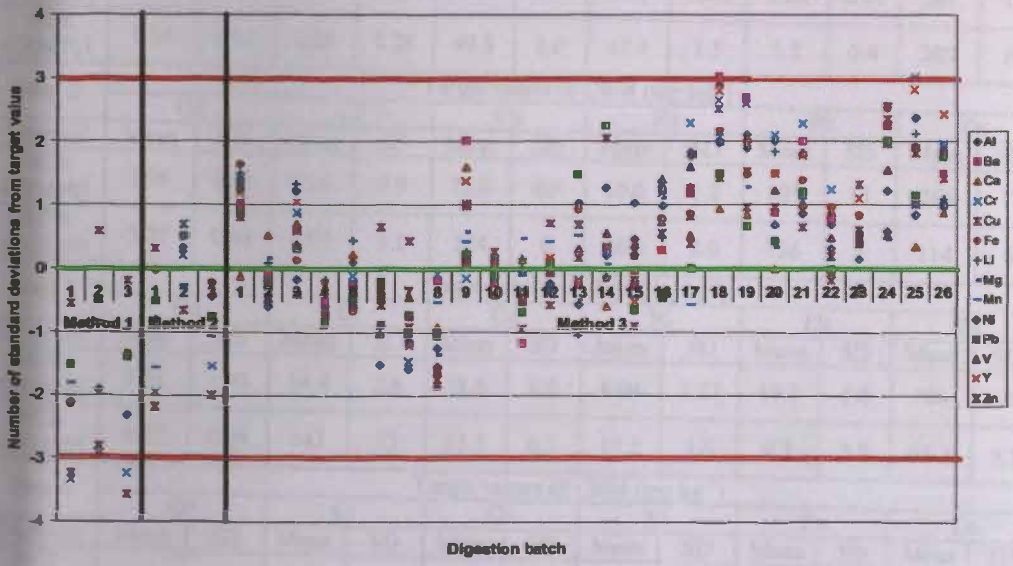


*Figure 3.2: Control chart showing autoscaled average results from the analysis of aqua regia soluble metals in Glasgow URM (n=2).*

Chromium and zinc showed low recovery when the samples were extracted following Method 1, but otherwise, results were close to target values for all analytes regardless of the method used. Nevertheless, due to the low recovery of some metals from CRM143R by digestion Methods 1 and 2, (see section 3.3.3.1) digestion Method 3 was preferred. The results after batch 15 were consistently above target values indicating a trend towards high extraction for most metals.

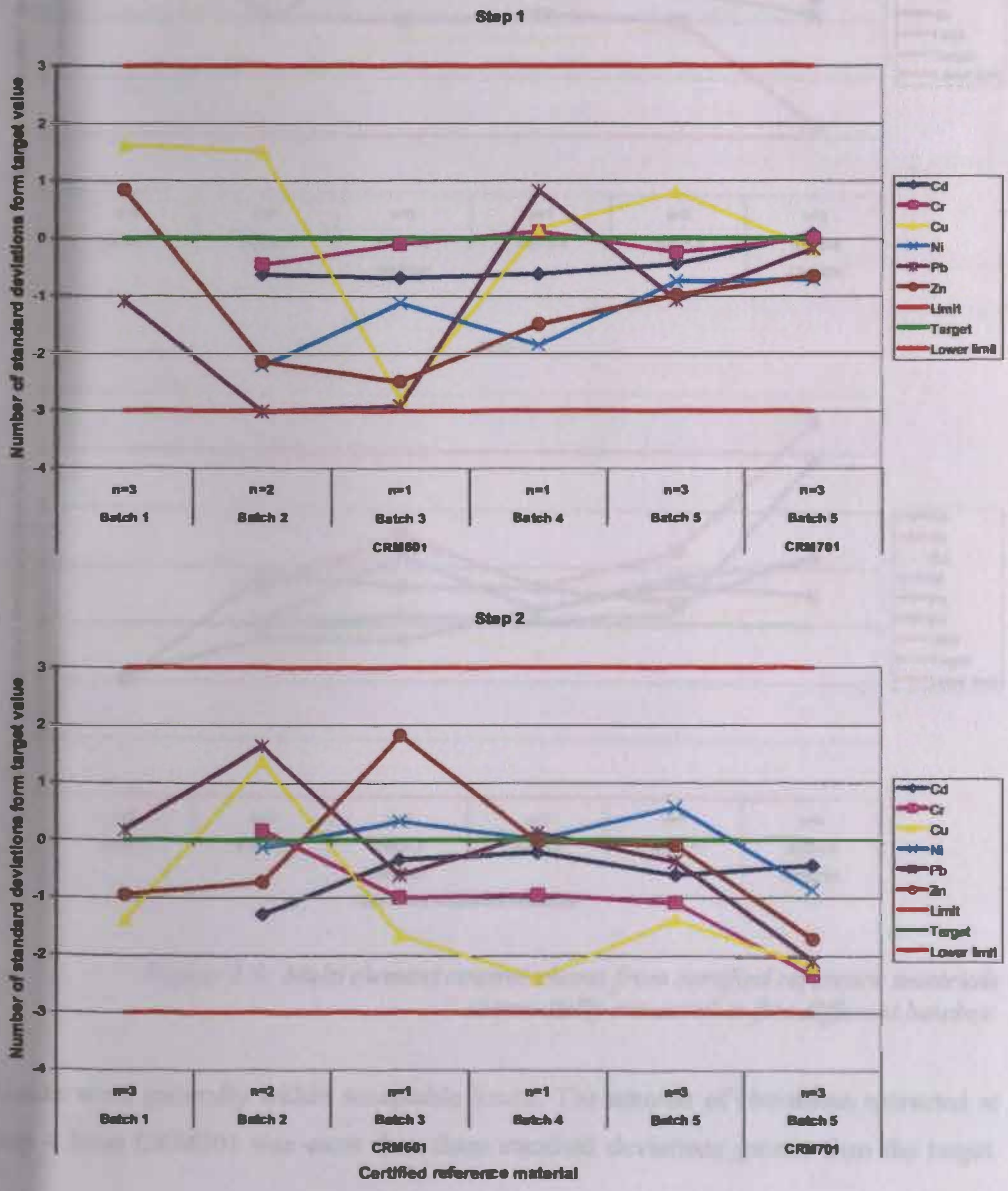
### 3.3.4 Sequential Extraction

One or more test portion of CRM was included in every sequential extraction batch for validation purposes. Table 3.5 shows the target means and acceptable precision from the BCR sequential extraction of CRM601 and CRM701.

| Step 1 | Target values of CRM (mg kg$^{-1}$) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cd | | Cr | | Cu | | Ni | | Pb | | Zn | |
| Material | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| BCR CRM601 | 4.45 | 0.67 | 0.35 | 0.08 | 10.5 | 0.8 | 7.82 | 0.84 | 2.28 | 0.44 | 261 | 13 |
| BCR CRM701 | 7.34 | 0.61 | 2.26 | 0.28 | 49.3 | 3.0 | 15.4 | 1.5 | 3.2 | 0.4 | 205 | 10 |
| Step 2 | Target values of CRM (mg kg$^{-1}$) | | | | | | | | | | | |
| | Cd | | Cr | | Cu | | Ni | | Pb | | Zn | |
| Material | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| BCR CRM601 | 3.95 | 0.53 | 10.6 | 0.9 | 72.8 | 4.9 | 10.6 | 1.2 | 205 | 11 | 266 | 17 |
| BCR CRM701 | 3.77 | 0.48 | 45.7 | 3.1 | 124 | 6 | 26.2 | 2.0 | 126 | 5 | 114 | 8 |
| Step 3 | Target values of CRM (mg kg$^{-1}$) | | | | | | | | | | | |
| | Cd | | Cr | | Cu | | Ni | | Pb | | Zn | |
| Material | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| BCR CRM601 | 1.91 | 1.43 | 14.4 | 2.6 | 78.6 | 8.9 | 6.04 | 1.27 | 19.7 | 5.8 | 106 | 11 |
| BCR CRM701 | 0.27 | 0.09 | 143 | 23 | 55.2 | 6.1 | 15.3 | 1.5 | 9.3 | 3.0 | 45.7 | 5.1 |
| Step 4 | Target values of CRM (mg kg$^{-1}$) | | | | | | | | | | | |
| | Cd | | Cr | | Cu | | Ni | | Pb | | Zn | |
| Material | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD |
| BCR CRM601 | 1.3 | 2.2 | 78.2 | 6.5 | 60.4 | 4.9 | 50.5 | 6.1 | 38 | 9 | 161 | 14 |
| BCR CRM701 | 0.13 | 0.08 | 62.5 | 7.4 | 38.5 | 11.2 | 41.4 | 4.0 | 11 | 5.2 | 95 | 13 |

*Table 3.5: Certified and indicative values for trace element BCR sequential extraction metal content of CRM601[86] and 701[87].*

In total, five batches of sequential extraction were performed. The first batch was part of a method comparison, results of which are presented in Chapter 6. Sequential extraction batches two – five contained urban soils from Glasgow. Results are presented in Chapter 7. Batch 5 included both BCR CRM601 and CRM701. Figure 3.3 shows the autoscaled results obtained from the sequential extractions of certified reference materials.



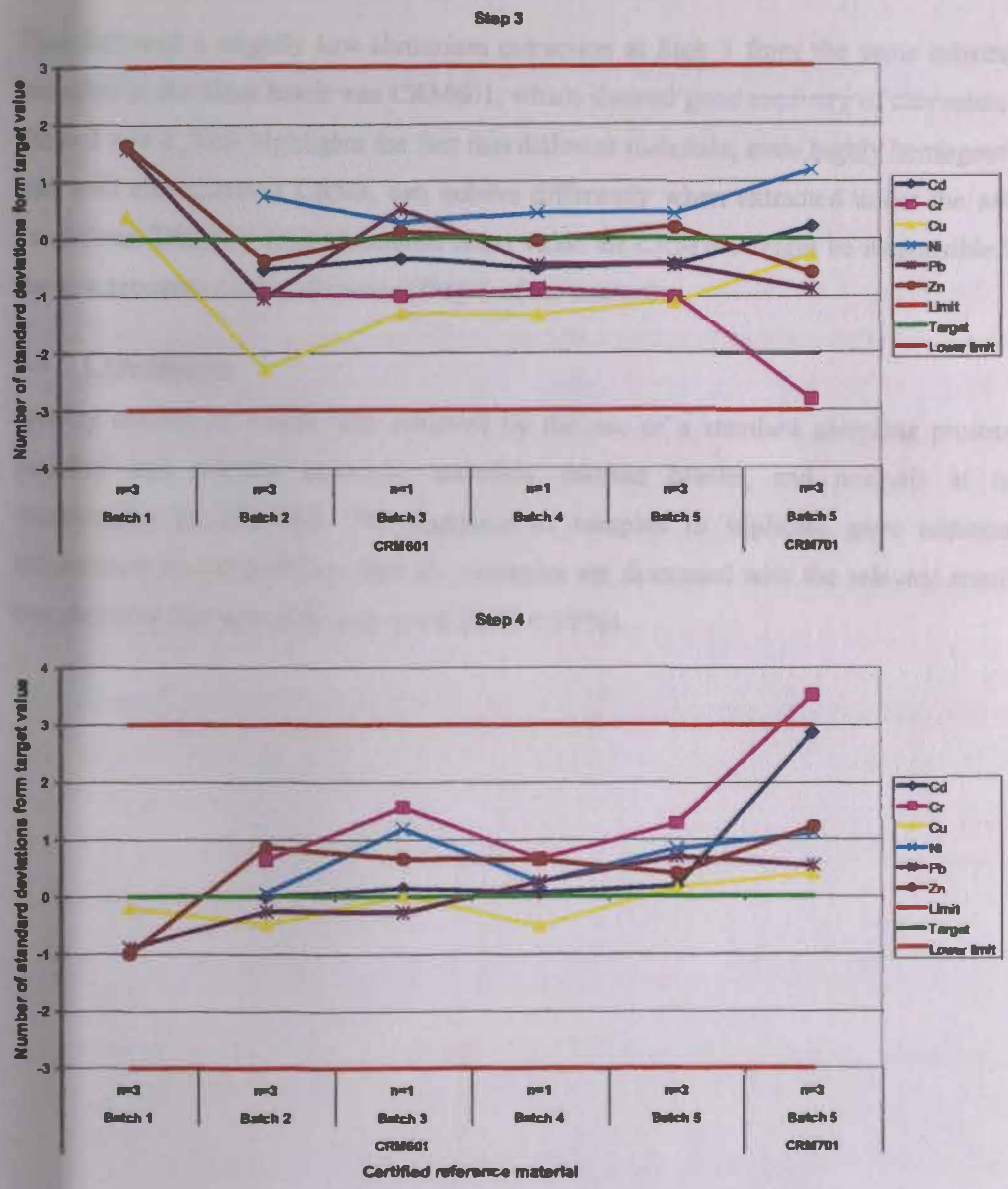


*Figure 3.3: Multi element control charts from certified reference materials sequentially extracted in five different batches.*

Results were generally within acceptable limits. The amount of chromium extracted at Step 4 from CRM701 was more than three standard deviations greater than the target.

This followed a slightly low chromium extraction at Step 3 from the same substrate. Included in the same batch was CRM601, which showed good recovery of chromium at Steps 3 and 4. This highlights the fact that different materials, even highly homogenous and well characterized CRMs, can behave differently when extracted under the same conditions. The very high chromium target value for CRM701 might be responsible for the low recovery of this element at Step 3 of the extraction.

## 3.4 Conclusions

Quality control of results was achieved by the use of a standard sampling protocol, certified and internal reference materials, method blanks, and analysis at two wavelengths by ICPOES. The digestion of samples in triplicate gave additional information on repeatability. Specific examples are discussed with the relevant results, but precision was generally very good (RSD < 10 %).

# 4 INVESTIGATION OF METAL VARIABILITY AND DISTRIBUTION IN TWO URBAN PARKS

## 4.1 Introduction

Previous studies on metals in urban soils are described in section 1.1.7. Assessment of metal concentrations across a city have reported highly variable results. In general, literature indicates that elements with a normal distribution and low variation in concentration are likely to have been less strongly affected by anthropogenic input than those with non-normal distributions and higher variability in concentration. However, most studies on urban soil used a sampling density of only one sample per km$^2$. It would also be of interest to study metal distribution in greater density over a smaller area e.g. a single urban park. No such detailed studies have been reported.

It was therefore decided to investigate the distribution of several metals within visually homogeneous land in parks, with a 50 m resolution, to give an indication of the variability in the metal content of the soil at this sampling density. Taking soil from two depths at each point was also considered useful to assess any differences between surface and sub-surface samples.

## 4.2 Aims

To assess levels and variability in metal content in soil within two parks in Glasgow.

## 4.3 Experimental

Chapter 2 explained the general procedures used. This section covers the aspects specific for this study.

### 4.3.1 Apparatus and Sample Preparation

The surface vegetation was removed with stainless steel shears. Samples were collected with a stainless steel corer containing a plastic sheath. The corer was hammered into the ground at the point defined by a 50 m grid to a depth of about 30 cm. The corer was then pulled from the ground and the plastic sheath containing the core removed. A plastic 30 cm ruler was used to measure and separate the 0 – 10 cm (0 = top of core after vegetation removed) and the 10 – 20 cm sections from the core. Each sample was given a unique letter and number code, GLA.AP.SF.01 indicated a sample from Glasgow, Alexandra Park, 0 – 10 cm, position 1.

Upon return to the laboratory samples were prepared as described in Section 2.2. Subsequently each pre-treated sample was coned and quartered to obtain approximately 10 g sub samples, which were ground in a mortar and pestle to pass through a 150 μm sieve. This material was then digested following the method described in Section 2.3.

### 4.3.2 Sampling Sites

Two parks from Glasgow were sampled at points defined by a 50 m grid. 13 sample points in Glasgow Green and 14 points in Alexandra Park were selected. Originally it had been hoped to obtain 25 samples from Glasgow Green, since all other URBSOIL partners sampled only a single park in their respective cities. However the presence of sub-surface structures (see section 4.3.2.1) made it necessary to divide the sampling between two parks.

#### 4.3.2.1 Glasgow Green

Glasgow Green is just south of the centre of Glasgow and is one of the oldest parks in Scotland. There are records of land use and developments in this area dating back to 581 A.D. The area was mainly used as a market, and from 1189, hosted the annual Glasgow fair which still runs. From 1450 to the end of the 18th century the area was designated for common grazing land. The Green was drained, levelled and pathways laid down in the early 1800's and in 1806 Nelson's Monument was erected. The construction of a swimming pool started in 1939 but was postponed for the duration of the war and then abandoned in 1948. During the Second World War air raid shelters were built under large areas of the Green. Figure 4.1 is adapted from a recent geophysical survey of the

Green showing the areas where construction of the pool was started and the shelters built.

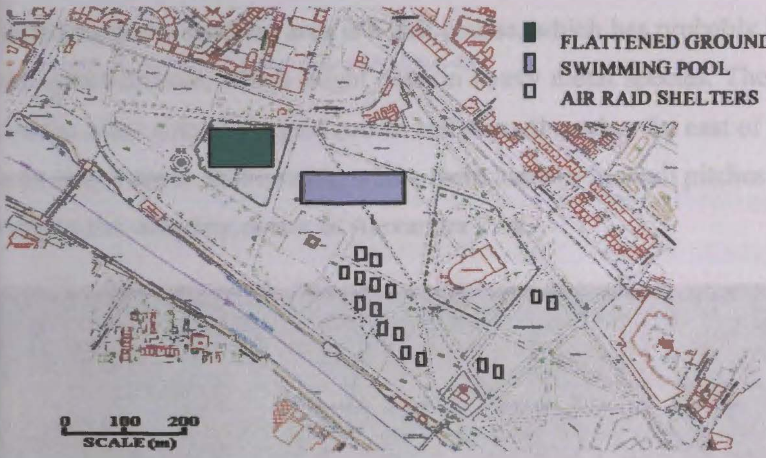


*Figure 4.1: Summary of geophysical surveys of Glasgow Green*[88].

The sampled area was quite flat and is divided by several paths but there are no main roads directly adjacent to the sample site. Figure 4.2 shows where samples were taken from; recently disturbed (World War II) areas were avoided.

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*Figure 4.2: Sampling points from Glasgow Green.*

#### 4.3.2.2 Alexandra Park

Alexandra Park is just east of the centre of Glasgow and was established in 1870. To the north and uphill from the sampled area is a golf course, which has probably been treated with various agrochemicals, which might contain heavy metal species. There is a busy motorway on the other side of the golf course and a small road to the east of the sampled area. The area slopes down to the south, where there are two football pitches and a pond. Figure 4.3 shows the sampling points in Alexandra Park.

*Figure 4.3: Sampling points from Alexandra Park.*

### 4.3.3 Digestion and Analysis

Samples were digested following the procedure described in Section 2.3. Analysis was performed as described in Section 2.5 by ICPOES for cadmium, calcium, chromium, copper, iron, lead, manganese, nickel, lead and zinc. Cadmium results were below detection limits for all samples, hence none are reported.

## 4.4 Results and Discussion

### 4.4.1 Glasgow Green

#### 4.4.1.1 Descriptive Statistics

Mean concentration and precision (as % RSD) results of pseudo total metal content and loss on ignition (LOI) in the soil samples from Glasgow Green are shown in appendix A. Table 4.1 shows the summary statistics of the Glasgow Green results. The distribution of results was tested for normality as described in section 2.6.1.1. Table 4.1 also shows the P-value normality test results.

| | Loss on ignition (%) | |
|---|---|---|
| | SF (0 – 10 cm) | SB (10 – 20 cm) |
| Min. | 10.1 | 6.70 |
| Median | 13.0 | 11.7 |
| Mean | 14.4 | 11.2 |
| Max. | 20.8 | 14.5 |
| IQR | 5.8 | 4.3 |
| SD | 3.6 | 2.6 |
| RSD (%) | 25 | 23 |
| K-S, p-value | 0.113 | 0.037 |

| | Ca (mg kg$^{-1}$) | | Cr (mg kg$^{-1}$) | | Cu (mg kg$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | SF | SB | SF | SB | SF | SB | SB* |
| Min. | 1 730 | 1 120 | 23.9 | 22.5 | 23.8 | 34.3 | 34.3 |
| Median | 3 410 | 3 820 | 30.1 | 27.7 | 87.8 | 98.7 | 97.4 |
| Mean | 3 600 | 3 730 | 28.9 | 28.0 | 85.1 | 133 | 84.0 |
| Max. | 6 260 | 7 170 | 33.5 | 32.7 | 113 | 678 | 110 |
| IQR | 2 340 | 1 910 | 7.5 | 3.2 | 26.5 | 49.3 | 55.0 |
| SD | 1 490 | 1 520 | 3.7 | 2.8 | 22.9 | 174 | 28.1 |
| RSD (%) | 41 | 41 | 13 | 10 | 27 | 130 | 33 |
| K-S, p-value | 0.064 | >0.15 | >0.15 | 0.128 | >0.15 | <0.01 | <0.01 |

|  | Fe (%) |  | Pb (mg $kg^{-1}$) |  | Mn (mg $kg^{-1}$) |  | Ni (mg $kg^{-1}$) |  | Zn (mg $kg^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 2.07 | 2.14 | 98.4 | 143 | 333 | 430 | 21.0 | 24.5 | 102 | 94.0 |
| Median | 2.29 | 2.40 | 279 | 314 | 460 | 512 | 33.4 | 37.9 | 174 | 200 |
| Mean | 2.35 | 2.44 | 307 | 330 | 458 | 502 | 35.2 | 36.5 | 199 | 196 |
| Max. | 2.81 | 2.83 | 676 | 894 | 559 | 557 | 52.6 | 50.7 | 377 | 317 |
| IQR | 0.37 | 0.30 | 169 | 182 | 142 | 85.5 | 15.1 | 12.5 | 122 | 108 |
| SD | 0.23 | 0.19 | 146 | 197 | 75.7 | 45.1 | 9.0 | 7.8 | 80.7 | 66.7 |
| RSD (%) | 10 | 8 | 48 | 60 | 17 | 9 | 26 | 21 | 40 | 34 |
| K-S, p-value | >0.15 | >0.15 | >0.15 | <0.01 | >0.15 | >0.15 | >0.15 | >0.15 | 0.042 | >0.15 |

*Table 4.1: Summary statistics for Glasgow Green, SF = 0 – 10 cm (n=13), SB = 10 – 20 cm (n = 12),* Result from sample point 7 removed as an outlier (n = 11), (IQR = interquartile range, SD = standard deviation, K-S = Kolmogorov-Smirnov normality test, P-value = probability of normal distribution).*

Most metals are within typical ranges found in soil (Section 1.1.6). Chromium levels are slightly lower and lead levels are higher than typical concentrations. Chromium, copper, manganese, nickel and zinc have similar concentrations in Glasgow Green as the results from previous urban studies shown in Table 1.2. Lead levels are slightly higher in Glasgow Green soil compared to most previous studies, with the exceptions of studies from some large cities. Lead exceeds the CLEA guideline value (450 mg $kg^{-1}$) at points four (SF=458 mg $kg^{-1}$) and 13 (SF=676 mg $kg^{-1}$, SB=894 mg $kg^{-1}$), but on average is below this limit.

There is an extremely high copper SB value from sample point seven. There is no obvious point source near this location, or any experimental error that might explain the high value. This value will dominate all copper results and was therefore removed for the purpose of further discussion.

Most of the metals were normally distributed in Glasgow Green. A non-normal metal distribution indicates a metal that is influenced in a highly variable way or by several factors within Glasgow Green, more likely to be caused by anthropogenic activities. Copper and lead in the sub-surface layers showed non-normal distributions, but the surface distributions were normal despite high concentrations of lead. The variability at depth might be due to historically high variations in deposition of substances containing these elements. Zinc distribution was close to the critical P-value from the normality test in the SF depth while passing the normality test in the SB layer. The elements most often described as anthropogenic in urban soil studies are copper, lead and zinc which is confirmed by these observations.

Analyte variability has also been linked to anthropogenic activity. A measure of variability is the RSD. The metal contents in the SF samples have increasing RSD in the order Fe<Cr<Mn<Ni<Cu<Zn<Ca<Pb. The elements can be grouped into three sets, chromium, iron and manganese have low variability (RSD < 20 %), copper and nickel have medium variability (RSD 20 – 30 %) and calcium, lead and zinc have high variability (RSD > 30 %) in the SF Glasgow Green samples.

The SB samples' metal contents have increasing RSD in the order Fe<Mn<Cr<Ni<Cu <Zn<Ca<Pb. Similar groups can be seen in the SB samples as were shown in the SF samples: low variability for chromium, iron and manganese, medium variability for nickel and high variability for calcium, copper, lead and zinc. Copper shows a greater variability in the SB samples compared to that shown in the SF samples.

Figure 4.4 shows the box plots of relative concentrations (i.e. concentration/mean concentration) for all analytes. This allows the distributions of different analytes to be compared on the same scale and shows the trends in variability discussed above.

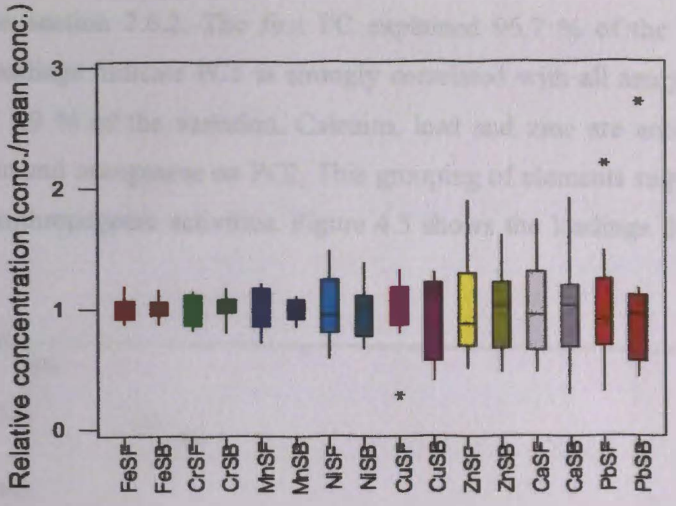

*Figure 4.4: Variability of metal concentration in Glasgow Green.*

### 4.4.1.2 Comparison between Metal Concentrations at Different Depths

The concentration in the SB layer was subtracted from the concentration in the corresponding SF layer to give a set of differences for each analyte. The distribution of the differences was tested for normality and outliers as described in section 2.6.1. Iron differences failed the normality test, due to outlier values. These values were removed and the normality test repeated, and passed.

The paired t-test was applied to all elements. Manganese was the only one that failed (P = 0.025). Manganese has significantly higher concentration in the SB depth than in the SF depth. There was no significant difference in concentration between the depths for all the other elements.

### 4.4.1.3 Principal Component and Factor Analysis

PCA was performed on the relative metal concentrations for the SF samples i.e. concentrations divided by mean concentration. The reason for the use of relative values is discussed in section 2.6.2. The first PC explained 96.7 % of the variation in the results. The loadings indicate PC1 is strongly correlated with all analytes. The second PC explained 1.9 % of the variation. Calcium, lead and zinc are anti-correlated with iron, chromium and manganese on PC2. This grouping of elements suggests PC2 might be related to anthropogenic activities. Figure 4.5 shows the loadings from PC1 plotted against PC2.

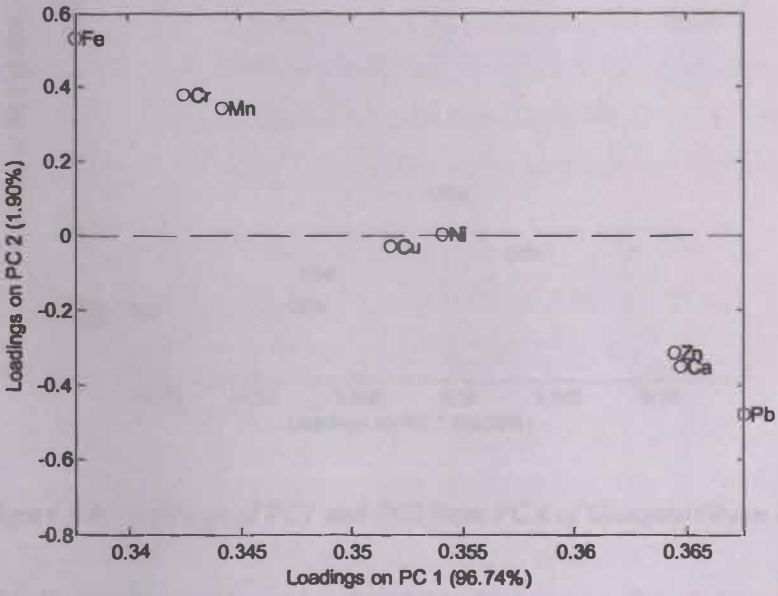

*Figure 4.5: Loadings of PC1 and PC2 from PCA of Glasgow Green SF samples.*

Figure 4.5 indicates the metals can be placed into three groups. Group A is made up of chromium, iron and manganese. Group B is composed of copper and nickel, and group C is composed of calcium, lead and zinc. This grouping corresponds to that already identified (Section 4.4.1.1) on the basis of relative analyte variability at the Glasgow Green site.

PCA was also performed on the relative results for the SB samples. The first PC explained 94.4 % of the variation in the results. The loadings indicate PC1 is strongly correlated with all original analytes. The second PC explained 2.9 % of the variation.

Lead is anti-correlated with calcium, chromium, iron and manganese. PC2 is dominated by the variation in lead between Glasgow Green SB samples. Figure 4.6 shows the loadings from PC1 plotted against PC2.

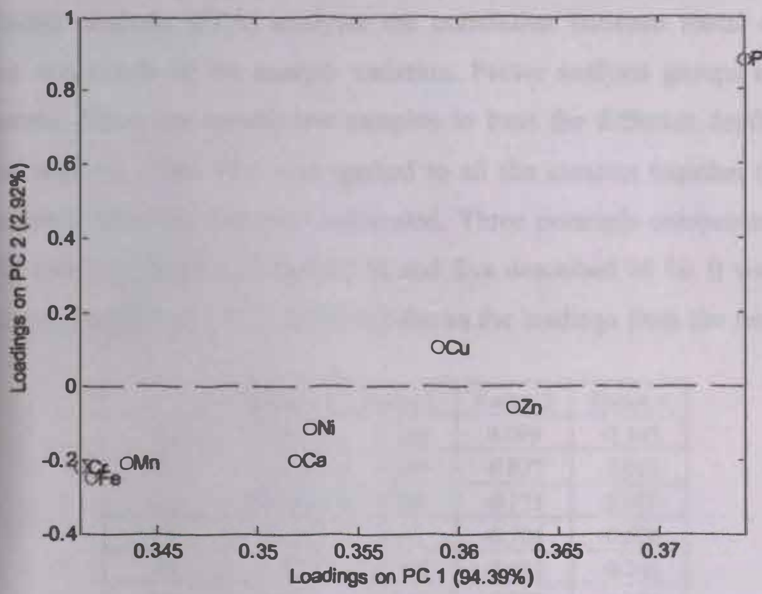

*Figure 4.6: Loadings of PC1 and PC2 from PCA of Glasgow Green SB samples.*

Figure 4.6 indicates the metals can be placed into four groups. Group A is composed of chromium, iron and manganese. Group B is made up of calcium and nickel. Group C is made up of copper and zinc. Group D is lead. These groupings are again similar to the groups seen based upon variability.

Although this method of PCA groups elements on the basis of their variability and hence shows similar patterns to those seen when examining the RSDs of the metals within Glasgow Green, it allows better visualization of results and takes into account the multivariate nature of the data set. In general, it is thus preferred.

Chromium, iron and manganese are grouped together, have low variability and are not likely to have been largely influenced by anthropogenic activity in Glasgow Green.

Nickel levels might have been affected by anthropogenic activities to a small degree. Calcium, copper, lead and zinc levels are all likely to have been affected by anthropogenic activity, though to differing extents in the different depths.

Principal factor analysis (PFA) analyses the correlation between metal distributions, ignoring the magnitude of the analyte variation. Factor analysis groups analytes with similar sources. There are insufficient samples to treat the different depths separately using factor analysis. Thus PFA was applied to all the samples together (both surface and sub-surface), after the data was autoscaled. Three principle components described 85 % of the variance, four described 93 % and five described 96 %. It was decided to apply the factor analysis to 4 PCs. Table 4.2 shows the loadings from the factor analysis.

| | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|---|---|---|---|---|
| Ca | 0.918 | -0.184 | 0.099 | -0.145 |
| Cr | 0.309 | -0.284 | -0.877 | -0.036 |
| Cu | 0.446 | -0.800 | -0.173 | 0.147 |
| Fe | -0.218 | 0.063 | -0.704 | -0.620 |
| Pb | 0.238 | -0.880 | -0.101 | -0.266 |
| Mn | 0.333 | -0.142 | -0.092 | -0.882 |
| Ni | 0.814 | -0.430 | -0.300 | -0.124 |
| Zn | 0.862 | -0.373 | -0.235 | -0.144 |
| % Variation | 34 | 24 | 18 | 16 |

*Table 4.2: Factor loadings for Glasgow Green, (n = 24).*

Calcium, nickel and zinc are most strongly related to Factor 1, but the other elements also have positive loadings with the exception of iron, which has a negative loading. Factor 1 might be associated with elements that are influenced by both natural and anthropogenic factors. A negative correlation might reflect the natural influences on analyte levels.

Copper and lead are most associated with Factor 2. Though copper is found in many minerals, increased levels in urban soils have been attributed to anthropogenic activities. Lead is thought to be mainly of anthropogenic origin in urban soils. Factor 2 is thus probably related to mainly anthropogenic influences.

Chromium and iron are the main elements associated with Factor 3, and are commonly associated together in natural parent material. Iron and manganese are the major elements associated with Factor 4, these elements (in the form of oxyhydroxides) constitute a major mineral phase in many soils. Factors 3 and 4 are probably indicative of natural sources of these metals in Glasgow Green.

### 4.4.2 Alexandra Park

#### 4.4.2.1 Descriptive Statistics

Mean concentration and precision (as % RSD) results of pseudo total metal content and LOI in the soil samples from Alexandra Park are shown in appendix A. Table 4.3 shows the summary statistics of the Alexandra Park results.

| | Loss on ignition (%) | |
|---|---|---|
| | SF | SB |
| Min. | 9.2 | 5.4 |
| Median | 14.8 | 8.3 |
| Mean | 14.4 | 8.7 |
| Max. | 18.9 | 14.7 |
| IQR | 3.7 | 3.1 |
| SD | 2.6 | 2.4 |
| RSD (%) | 18 | 28 |
| K-S, p-value | >0.15 | >0.15 |

| | Ca (mg kg$^{-1}$) | | Cr (mg kg$^{-1}$) | | Cu (mg kg$^{-1}$) | |
|---|---|---|---|---|---|---|
| | SF | SB | SF | SB | SF | SB |
| Min. | 580 | 490 | 21.3 | 16.8 | 33.4 | 24.2 |
| Median | 1 120 | 955 | 39.7 | 22.4 | 59.4 | 42.9 |
| Mean | 1 470 | 1 650 | 44.9 | 32.2 | 62.3 | 50.5 |
| Max. | 4 770 | 6 900 | 131 | 107 | 113 | 151 |
| IQR | 630 | 873 | 22.3 | 15.6 | 20.0 | 17.1 |
| SD | 1 160 | 1 820 | 27.1 | 25.0 | 20.5 | 30.4 |
| RSD (%) | 78 | 110 | 60 | 78 | 33 | 60 |
| K-S, p-value | <0.01 | <0.01 | 0.036 | <0.01 | 0.085 | <0.01 |

|  | Fe (%) |  | Pb (mg kg$^{-1}$) |  | Mn (mg kg$^{-1}$) |  | Ni (mg kg$^{-1}$) |  | Zn (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 2.04 | 2.30 | 114 | 41.2 | 163 | 292 | 18.0 | 16.2 | 66.9 | 64.0 |
| Median | 2.63 | 2.53 | 179 | 130 | 377 | 611 | 26.4 | 21.1 | 103 | 114 |
| Mean | 2.65 | 2.60 | 194 | 142 | 398 | 606 | 28.6 | 23.9 | 122 | 125 |
| Max. | 3.35 | 3.15 | 414 | 432 | 724 | 840 | 52.7 | 39.0 | 305 | 298 |
| IQR | 0.24 | 0.35 | 51.8 | 46.7 | 310 | 285 | 12.0 | 8.9 | 41.7 | 64.7 |
| SD | 0.29 | 0.23 | 71.4 | 90.5 | 181 | 165 | 9.9 | 7.4 | 65.2 | 60.3 |
| RSD (%) | 11 | 9 | 37 | 64 | 46 | 27 | 35 | 31 | 53 | 48 |
| K-S, p-value | >0.15 | >0.15 | 0.020 | <0.01 | >0.15 | >0.15 | 0.141 | 0.092 | <0.01 | >0.15 |

*Table 4.3: Summary statistics for Alexandra Park, SF = 0 – 10 cm, SB = 10 – 20 cm (n = 14).*

Average metal contents are within typical ranges found in soils. Chromium, copper, lead, manganese, nickel and zinc have similar concentrations in Alexandra Park as the results from previous urban studies shown in Table 1.2.

There are outlier values for all elements except manganese. These values are from sample locations two and seven. There is no obvious environmental factor close to these locations that might explain the high results.

Calcium, chromium and lead in both depths, copper in the 10 – 20 cm layer and zinc in the 0 – 10 cm layer have non-normal distributions, indicating a variety of factors, most probably anthropogenic in origin, affect their distribution.

The SF samples' metal concentrations have increasing RSD in the order Fe<Cu<Ni<Pb <Mn<Zn<Cr<Ca. Iron shows low variability (RSD < 20 %), copper, nickel, lead, calcium, chromium, manganese and zinc show high variability (RSD > 30 %) in the Alexandra Park SF samples.

The metal contents in the SB samples have increasing RSD in the order Fe<Mn<Ni<Zn <Cu<Pb<Cr<Ca. Iron again shows lower variability, manganese and nickel show intermediate variability, calcium, chromium, copper, lead and zinc show higher variability in the Alexandra Park SB samples. Manganese shows lower variability,

copper and lead show higher variability in the 10 – 20 cm depth samples than in the 0 – 10 cm samples.

Figure 4.7 shows the relative box plots of results for all analytes. This allows the distributions of different analytes to be compared on the same scale and shows the trends in spread discussed above.

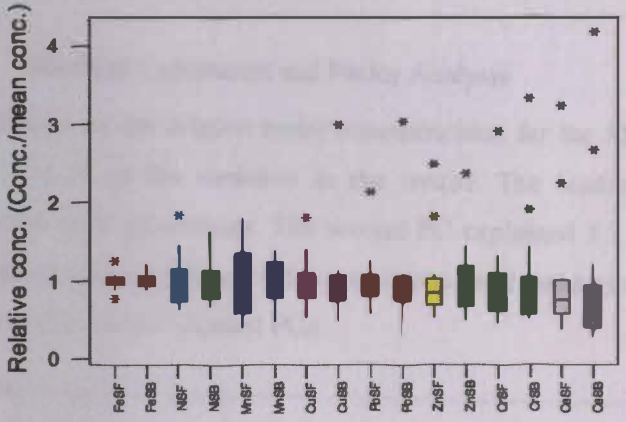

*Figure 4.7: Variability of metal concentration in Alexandra Park.*

### 4.4.2.2 Comparison between Metal Concentrations at Different Depths

The concentration in the SB layer was subtracted from the concentration in the corresponding SF layer to give a set of differences for each analyte. Calcium and iron differences failed the normality test. Calcium, copper and iron differences had outlier values. These values were removed and the normality test repeated, and passed.

The result of the paired t-test for calcium and iron differences did not change when outlier sites were not included. There is no significant difference in calcium, iron and zinc concentrations between depths. The result of the paired t-test changed when two copper outlier sites were not included (P = 0.060 for all sites, P = 0.003 for 12 sites). There might be higher concentrations of copper in the SF layer than in the SB layer in Alexandra Park. Chromium, lead, manganese and nickel differences all failed the paired t-test (P = 0.000, 0.002, 0.002 and 0.005 respectively). Chromium, lead and nickel levels were higher in the SF samples than the SB samples and manganese levels were higher in the SB than the SF samples. Chromium, lead and nickel might possibly be introduced to the surface layer from atmospheric sources in Alexandra Park. However there is insufficient data for this to be stated conclusively. Further work, testing the top few centimetres of soil might clarify this theory.

### 4.4.2.3 Principal Component and Factor Analysis

PCA was performed on the relative metal concentrations for the SF samples. The first PC explained 92.4 % of the variation in the results. The loadings indicate PC1 is strongly correlated with all analytes. The second PC explained 3.7 % of the variation. Calcium and zinc are anti-correlated with copper, iron, lead and nickel. Figure 4.8 shows the loadings from PC1 plotted against PC2.

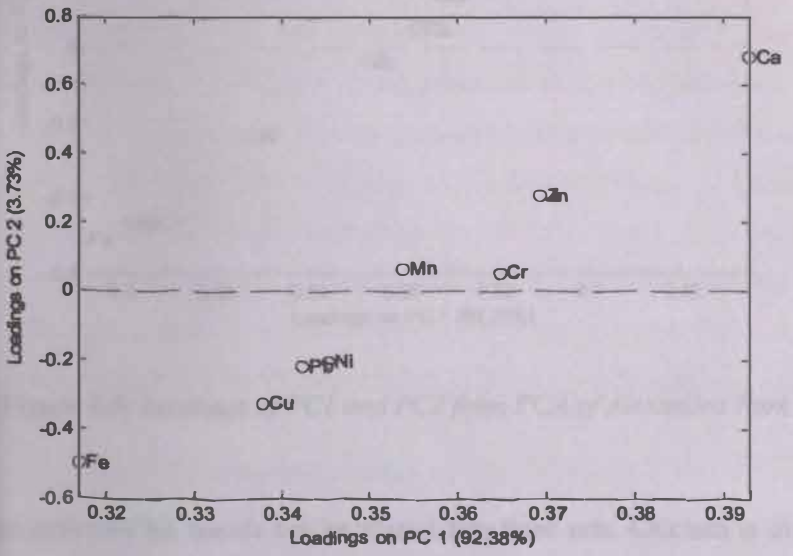

*Figure 4.8: Loadings of PC1 and PC2 from PCA of Alexandra Park SF samples.*

This figure indicates the metals can be placed into four groups. Iron and calcium are in opposite groups alone. Copper, lead and nickel make up another group. Chromium, manganese and zinc make up the final group. These groups follow a similar pattern to that obtained by comparison of RSD's shown in Section 4.4.2.1.

PCA was also performed on the relative results for the SB samples. The first PC explained 89.2 % of the variation in the results. The loadings indicate PC1 is strongly correlated with all analytes. The second PC explained 6.1 % of the variation. Calcium is anti-correlated with iron and manganese on PC2. Figure 4.9 shows the loadings from PC1 plotted against PC2.

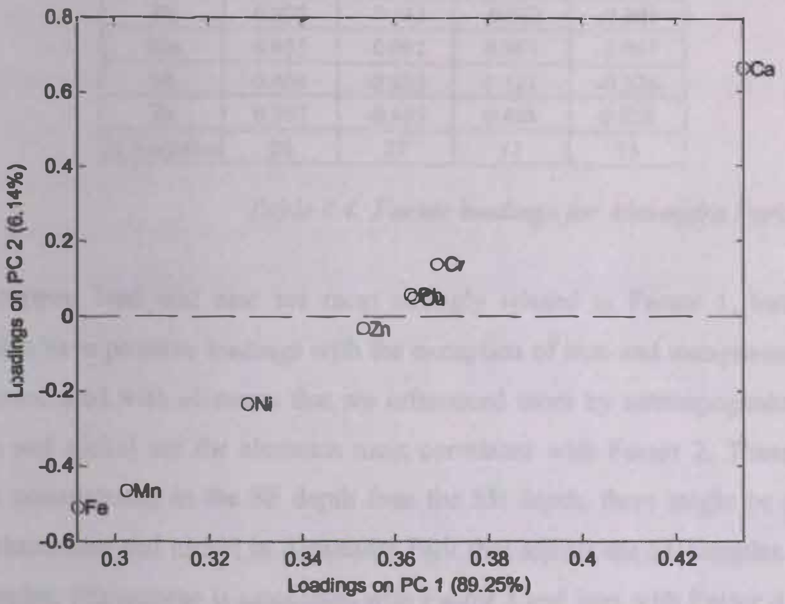

*Figure 4.9: Loadings of PC1 and PC2 from PCA of Alexandra Park SB sample results.*

This figure indicates the metals can be placed into three sets. Calcium is distinct from the other metals. Copper, chromium, lead and zinc comprise a group. Iron and manganese make up the third group. Nickel is between the latter two groups. The variability in metal concentrations (RSD values) showed the same trend as in the loadings plot, from least variable iron to most variable calcium.

PFA was applied to all the samples, after the data was autoscaled. Three principle components described 87 % of the variance, four described 95 % and five described 98 %. It was decided to apply the factor analysis to 4 PCs. Table 4.4 shows the loadings from the factor analysis.

| | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|---|---|---|---|---|
| Ca | 0.691 | -0.494 | 0.396 | 0.160 |
| Cr | 0.185 | -0.964 | 0.078 | -0.099 |
| Cu | 0.946 | -0.230 | 0.001 | -0.083 |
| Fe | 0.006 | -0.160 | -0.006 | -0.981 |
| Pb | 0.975 | -0.161 | -0.027 | -0.007 |
| Mn | 0.035 | -0.092 | 0.981 | -0.007 |
| Ni | 0.406 | -0.833 | 0.122 | -0.226 |
| Zn | 0.707 | -0.465 | 0.468 | 0.028 |
| % Variation | 38 | 27 | 17 | 13 |

*Table 4.4: Factor loadings for Alexandra Park, (n = 28).*

Calcium, copper, lead and zinc are most strongly related to Factor 1, but the other elements also have positive loadings with the exception of iron and manganese. Factor 1 might be associated with elements that are influenced more by anthropogenic activities. Chromium and nickel are the elements most correlated with Factor 2. These elements were more concentrated in the SF depth than the SB depth; there might be a common source of chromium and nickel in Alexandra Park that affects the SF samples more than the SB samples. Manganese is associated with Factor 3 and iron with Factor 4. Factors 3 and 4 are probably associated with elements less affected by anthropogenic activities.

### 4.4.3 Comparison between Parks

Table 4.5 summarises which metals passed the normality test in which sample set.

| | Normality test passed (P) or failed (F) | | | |
|---|---|---|---|---|
| | Glasgow Green | | Alexandra Park | |
| **Analyte** | Surface | Sub-surface | Surface | Sub-surface |
| **Calcium** | P | P | F | F |
| **Chromium** | P | P | F | F |
| **Copper** | P | F | P | F |
| **Iron** | P | P | P | P |
| **Lead** | P | F | F | F |
| **Manganese** | P | P | P | P |
| **Nickel** | P | P | P | P |
| **Zinc** | F | P | F | P |

*Table 4.5: Summary of analytes passing or failing the normality test.*

Copper results were normally distributed from the SF depth but not normally distributed from the SB depth in Glasgow Green and Alexandra Park. Iron, manganese and nickel results were normally distributed in both depths and both parks. In both parks zinc levels from the SF layer were not normally distributed but were normally distributed in the SB depth. Calcium and chromium results were normally distributed in both depths at Glasgow Green but not in Alexandra Park. Lead results were normally distributed from Glasgow Green SF samples but not normally distributed from Glasgow Green SB samples or in either depth in Alexandra Park.

Chromium levels in the 0 – 10 cm depth and iron levels in both depths were higher in Alexandra Park than in Glasgow Green. Manganese SB levels were higher in Alexandra Park than Glasgow Green while manganese SF levels were similar in both parks. Calcium, copper, lead, nickel and zinc levels were higher in Glasgow Green than in Alexandra Park.

Iron showed the least overall variation in concentration and, within both parks, is probably an element little affected by anthropogenic activities. Calcium results were highly varied within both parks. Few previous studies on urban soils have reported calcium results, though calcium levels in roadside soils have been attributed to application of grit to roads. The ubiquitous nature of calcium e.g. in building materials suggests there are many potential sources of calcium in urban soils, and therefore calcium levels are likely to vary even within a site. Copper, lead and zinc showed greater variability in Glasgow Green than in Alexandra Park. This, in conjunction with higher concentrations, indicates Glasgow Green is more affected by anthropogenic activities than Alexandra Park. Chromium had greater variability and higher concentration in Alexandra Park than Glasgow Green that might indicate exposure to a specific source containing chromium at Alexandra Park. Generally it is more likely Glasgow Green is more polluted than Alexandra Park shown by higher levels and variability of metals associated with anthropogenic input.

Manganese levels were higher in the SB depth than the SF depth in both parks. Calcium, iron and zinc levels showed no significant difference between depths in both parks. Chromium, copper, lead and nickel concentrations were greater in the Alexandra Park surface samples than the sub-surface samples, whereas there was no statistical difference in metal concentrations between depths in the metal concentrations in Glasgow Green samples.

Principal component analysis indicated some different trends between metals in Alexandra Park and Glasgow Green. Chromium from both depths and manganese from the SF samples in Alexandra Park were grouped with higher variability metals whereas in Glasgow Green chromium and manganese were grouped with iron (and lower variability).

Principal factor analysis showed similar associations between metals in both parks. PFA of the Alexandra Park results indicated a strong correlation between chromium and nickel, which was not shown in the Glasgow Green factor analysis.

## 4.5 Conclusions

The levels of chromium, copper, manganese, nickel and zinc in both parks were similar to levels from previous urban soil studies. Lead levels from some sample points in Glasgow Green were above CLEA guideline values. Further investigation in Glasgow

Green might be required to assess if the land is sufficiently contaminated to pose a health risk.

The variation of metal concentrations within both parks was high. There were large differences between parks in terms of both average metal concentrations and ranges suggesting different factors and influences dominate metal behaviour in Glasgow Green than in Alexandra Park.

Iron levels were similar in all samples collected from the same park. Iron levels were slightly higher in Alexandra Park compared to Glasgow Green. Iron levels in soil are probably not largely influenced by anthropogenic activities, which confirms conclusions from previous studies.

Copper, lead and zinc levels were highly varied in samples collected from the same park. This also confirms previous literature results that suggest these elements are 'urban'. Calcium also showed high variability and might also be classed as urban.

Calcium, copper, lead and zinc average levels were much greater in Glasgow Green than in Alexandra Park, and generally showed greater variability in Glasgow Green than in Alexandra Park. This suggests Glasgow Green is more polluted than Alexandra Park.

Chromium and manganese average levels were greater in Alexandra Park than in Glasgow Green, and showed higher variability. Higher variability has been related to anthropogenic activities but these elements are not commonly associated with general urban pollution.

Chromium was also associated with nickel by principal factor analysis of Alexandra Park metal concentrations, and both chromium and nickel failed the normality test in Alexandra Park surface samples. There might possibly be a common source of chromium and nickel in the Alexandra Park soil.

The results of this study highlight some important relationships between metals in both parks. Although metal levels are different there are some similarities in metal associations in both parks. Some metals show different behaviours in Glasgow Green compared to Alexandra Park. This suggests the extrapolation of observations from one site to another is not applicable. The next stage of the URBSOIL project was to sample different park, roadside, riverbank and ornamental garden soils to examine metal levels and variabilities between different locations and land uses in Glasgow.

# 5 DISTRIBUTION OF METALS IN GLASGOW SOIL

## 5.1 Introduction

Previous studies assessing metal levels in urban soils have been discussed in Section 1.1.7. Various methods were used to choose the sampling sites in previous studies, including regular grids, census tracts, prevailing wind transects and land use. For this work it was decided to select sample sites so as to be as evenly as possible distributed within the Glasgow City boundary. Sites were classified according to land use. The land uses thought to be most common amongst the cities in the URBSOIL project were park and open space (PO), roadside (RD), riverbank (RB) and ornamental garden (OG).

In Glasgow it was decided to concentrate mainly upon PO and RD sample sites although RB and OG samples were collected. Composite samples were collected from each sample site to reduce the effect of spatial heterogeneity (see section 5.3). To improve discrimination between natural and anthropogenic inputs of metals, the range of analytes was increased to include aluminium, barium, lithium, magnesium, vanadium and yttrium. Aluminium, lithium and yttrium levels in soil are thought to be less likely to have been affected by anthropogenic activities. Barium and vanadium have been linked with traffic emissions and therefore might be more indicative of anthropogenic activities, especially near busy roads.

## 5.2 Aims

To assess the levels, variability and associations of metals in soils from different land types within Glasgow.

## 5.3 Experimental

### 5.3.1 Apparatus and Sample Preparation

The surface vegetation was removed with stainless steel shears. A stainless steel shovel was used to extract a cube of soil approximately 20 X 20 X 20 cm. Plastic trowels were used to remove a portion of soil from the surface 0 – 10 cm (SF) and the sub-surface 10

– 20 cm (SB). PO samples were collected from five points defined by a 10 m cross from a central location within each site. Figure 5.1 shows the composite sample point's configuration for each park and open space sample site.

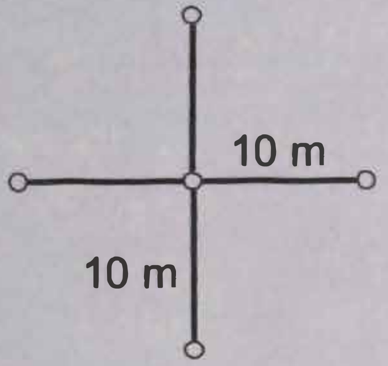

*Figure 5.1: Park and open spaces composite sample points.*

Roadside and riverbank samples were collected from five points on a 40 m transect at 10 m intervals. Ornamental garden samples were grab samples from a random selection of flowerbeds within a park. Approximately equal volumes of soil were collected from each point and combined to give a composite sample for each depth and location. Samples were given a unique code corresponding to land type and location.

Upon return to the laboratory samples were prepared as described in Section 2.2 i.e. dried and sieved to < 2 mm. Subsequently each sample was coned and quartered to obtain approximately 10 g sub-samples. Grab samples were taken from the 10 g sub-samples for digestion following the method described in Section 2.3.

### 5.3.2 Sampling Sites

A total of 94 sampling sites were chosen in Glasgow. There were 39 PO sites, 30 RD sites, 13 RB sites and 12 OG sites making a total of 188 samples from 94 locations. The approximate grid references of the sample locations are shown in appendix B. Figure 5.2 shows a map of Glasgow with the sample locations indicated.

This image has been removed from the digital version of the thesis for copyright reasons.

*Figure 5.2: Map of Glasgow showing location of sampling sites by land use category.*

### 5.3.3 Digestion and Analysis

Samples were digested following the procedure described in Section 2.3 with an open overnight digestion before being heated in the microwave. Various operators performed the digestion procedures. Analysis was performed as described in Section 2.5 by ICPOES for aluminium, barium, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, lead, vanadium, yttrium and zinc. Cadmium results were below detection limits for all samples, hence none are reported.

## 5.4 Results and Discussion

### 5.4.1 Descriptive Statistics

#### 5.4.1.1 Parks and Open Spaces

Mean concentration and precision (as % RSD) results of pseudo total metal content in the soil samples from Glasgow park and open spaces (PO) and loss on ignition results are shown in appendix B. Table 5.1 shows the summary statistics of the PO results. The distribution of results was tested for normality as described in Section 2.6.1.1. Table 5.1 shows the P-value normality test results.

| | LOI (%) | |
|---|---|---|
| | SF | SB |
| Min. | 3.89 | 3.51 |
| Median | 13.2 | 9.05 |
| Mean | 13.4 | 9.80 |
| Max. | 24.0 | 23.5 |
| IQR | 4.1 | 2.9 |
| SD | 3.8 | 3.5 |
| RSD (%) | 29 | 35 |
| K-S, P-value | >0.15 | 0.038 |

| | Al (mg kg$^{-1}$) | | Ba (mg kg$^{-1}$) | | Ca (mg kg$^{-1}$) | | Cr (mg kg$^{-1}$) | | Cu (mg kg$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 6 700 | 7 000 | 62.4 | 58.9 | 870 | 470 | 22.0 | 16.8 | 18.3 | 20.3 |
| edian | 14 200 | 14 900 | 116 | 134 | 2 180 | 2 060 | 35.2 | 36.0 | 48.9 | 48.6 |
| Mean | 15 000 | 16 100 | 139 | 164 | 2 490 | 2 733 | 53.3 | 53.3 | 61.3 | 84.1 |
| Max. | 26 400 | 37 400 | 452 | 752 | 5 460 | 7 680 | 229 | 232 | 194 | 504 |
| IQR | 5 100 | 6 000 | 61 | 84 | 1 990 | 2 370 | 32.0 | 31.2 | 29.0 | 35.0 |
| SD | 4 180 | 5 160 | 78.9 | 123 | 1 250 | 1 740 | 43.0 | 44.5 | 37.1 | 103 |
| SD (%) | 28 | 32 | 57 | 75 | 50 | 64 | 81 | 83 | 61 | 122 |
| -S, P-value | >0.15 | >0.15 | <0.01 | <0.01 | 0.046 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |

|  | Fe (%) |  | Li (mg kg$^{-1}$) |  | Mg (mg kg$^{-1}$) |  | Mn (mg kg$^{-1}$) |  | Ni (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 1.61 | 1.84 | 7.4 | 7.9 | 1 090 | 1 090 | 94 | 171 | 19.6 | 13.6 |
| Median | 2.73 | 3.20 | 12.9 | 14.1 | 2 470 | 2 660 | 425 | 512 | 33.6 | 34.2 |
| Mean | 2.85 | 3.19 | 14.0 | 14.9 | 2 600 | 2 690 | 463 | 541 | 39.4 | 42.3 |
| Max. | 4.94 | 4.70 | 25.3 | 32.7 | 6 550 | 6 760 | 1 050 | 1 140 | 131 | 202 |
| IQR | 0.70 | 0.78 | 5.70 | 6.00 | 1 030 | 970 | 193 | 264 | 16.8 | 21.8 |
| SD | 0.74 | 0.70 | 4.06 | 4.84 | 1 050 | 1 030 | 206 | 226 | 20.4 | 30.3 |
| RSD (%) | 26 | 22 | 29 | 32 | 40 | 38 | 44 | 42 | 52 | 72 |
| K-S, P-value | 0.122 | >0.15 | 0.148 | >0.15 | 0.025 | <0.01 | 0.098 | >0.15 | <0.01 | <0.01 |

|  | Pb (mg kg$^{-1}$) |  | V(mg kg$^{-1}$) |  | Y(mg kg$^{-1}$) |  | Zn (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 38.0 | 43.0 | 33.1 | 33.3 | 4.66 | 5.12 | 67 | 28 |
| Median | 159 | 159 | 59.9 | 57.7 | 7.99 | 8.28 | 151 | 156 |
| Mean | 197 | 196 | 63.7 | 65.4 | 8.45 | 9.21 | 189 | 204 |
| Max. | 618 | 831 | 135 | 183 | 19.5 | 29.5 | 621 | 855 |
| IQR | 142 | 106 | 25.0 | 19.7 | 2.44 | 2.69 | 84 | 92 |
| SD | 113 | 140 | 20.2 | 26.1 | 2.66 | 4.00 | 117 | 175 |
| RSD (%) | 58 | 71 | 32 | 40 | 32 | 43 | 62 | 86 |
| K-S, P-value | 0.016 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |

*Table 5.1: Summary results from Glasgow park and open spaces (n=39, IQR=interquartile range, SD = standard deviation, K-S = Kolmogorov-Smirnov normality test, P-value = probability of normal distribution).*

Average metal levels are generally within typical soil values, as discussed in Section 1.1.6. Generally chromium, copper, lead, manganese, nickel and zinc levels are similar to levels reported in previous urban studies, shown in Table 1.2. The CLEA soil guideline values (SGV) are exceeded at several PO sample sites. The chromium SGV (200 mg kg$^{-1}$) is exceeded at sites 18 (SB = 232 mg kg$^{-1}$) and 32 (SF = 229 mg kg$^{-1}$), the nickel SGV (75 mg kg$^{-1}$) is exceeded at sites 24 (SF = 131, SB = 202 mg kg$^{-1}$) and 26 (SF = 85.4, SB = 92.6 mg kg$^{-1}$) and the lead SGV (450 mg kg$^{-1}$) is exceeded at sites 15 (SF = 474, SB = 477 mg kg$^{-1}$) and 24 (SF = 618, SB = 831 mg kg$^{-1}$).

Aluminium, iron, lithium and manganese metal concentrations in PO samples are the only elements that pass the normality test. This indicates that, as expected, these elements are unlikely to have been influenced strongly by anthropogenic activities. Yttrium levels would also have been expected to be less influenced by anthropogenic activities and therefore normally distributed. However yttrium results were not normally distributed due to high outlier values. This indicates either that normality alone might be an unreliable indication of elements not greatly influenced by anthropogenic activity, or that yttrium levels are more affected by Man than previously suspected. All the analytes have outlier values (as identified by MINITAB i.e. where a value is more than 1.5 X the IQR below the first quartile or above the third quartile). The sample sites that have been indicated as outliers for each analyte in each depth are shown in table 5.2.

| Analyte | High outlier PO sample sites | |
|---|---|---|
| | SF | SB |
| Aluminium | 24 | 24 |
| Barium | 16, 24, 26, 29, 34 | 16, 24, 26 |
| Calcium | | 16 |
| Chromium | 6, 15, 18, 32 | 6, 15, 18, 32 |
| Copper | 15, 24, 26, 28 | 6, 15, 24, 26, 28 |
| Iron | 25, 26 | |
| Lithium | 24 | 24 |
| Magnesium | 1, 25, 26 | 1, 26 |
| Manganese | 25, 26, 27 | 26 |
| Nickel | 15, 24, 26 | 24, 26 |
| Lead | 15, 24 | 15, 24, 34 |
| Vanadium | 24 | 1, 15, 24, 26 |
| Yttrium | 15, 24, 26 | 15, 24, 26 |
| Zinc | 15, 24, 26, 29 | 15, 24, 26, 29 |

*Table 5.2: Outlier sample sites from Glasgow parks and open spaces.*

Sample sites 15, 24 and 26 are identified as outlier sites for many elements. This might indicate these sites have been particularly contaminated by anthropogenic activities.

The metal contents in the SF samples have increasing RSD in the order Fe<Al<Li<V=Y <Mg<Mn<Ca<Ni<Ba<Pb<Cu<Zn<Cr. The metal levels in the SB samples have increasing RSD in the order Fe<Al<Li<Mg<V<Mn<Y<Ca<Pb<Ni<Ba<Cr<Zn<Cu.

Two groups of analytes can be distinguished. Group A elements have lower variability (RSD < 50 %). Group A is composed of aluminium, iron, lithium, manganese, magnesium, vanadium and yttrium. Group B is made up of barium, calcium, chromium, copper, nickel, lead and zinc, elements with higher variability (RSD > 50 %). Group B elements include copper, lead and zinc which agrees with literature classing these elements as 'urban'. This also suggests barium, calcium, chromium and nickel levels might be significantly influenced by anthropogenic activities.

The LOI results also have low variability between PO sites and would be included in group A. Site 24 has very high loss on ignition values in both depths (LOI from SF sample = 23.6 % and from SB sample = 23.5 %) compared to other sites (mean LOI from SF samples = 13.4 % and 9.8 % from SB samples). Higher LOI suggests higher organic matter, which may contribute to the higher metal concentrations at this site by chelating metals.

Many analytes did not pass the normality test so a non-parametric measure of variability was also examined. The inter-quartile range was divided by the median to give a relative inter-quartile range. Although the exact order of analyte variability altered the two groups of analytes remained the same. This means the same trends are seen when the influence of outlier values is reduced.

### 5.4.1.2 Roadsides

Mean concentration and precision (as % RSD) results of pseudo total metal content in the soil samples from Glasgow roadside soils (RD) and LOI results are shown in appendix B. Table 5.3 shows the summary statistics of the RD results.

| | LOI (%) | |
|---|---|---|
| | SF | SB |
| Min. | 6.11 | 3.83 |
| Median | 10.9 | 8.88 |
| Mean | 11.5 | 9.42 |
| Max. | 19.3 | 22.6 |
| IQR | 3.96 | 3.10 |
| SD | 2.78 | 3.21 |
| RSD (%) | 24 | 34 |
| K-S, P-value | >0.15 | 0.059 |

|  | Al (%) |  | Ba (mg kg$^{-1}$) |  | Ca (mg kg$^{-1}$) |  | Cr (mg kg$^{-1}$) |  | Cu (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 6 770 | 8 110 | 72.6 | 58 | 2 500 | 1 520 | 20.3 | 20.9 | 36.6 | 25.7 |
| Median | 13 200 | 12 000 | 143 | 151 | 4 455 | 3 880 | 39.8 | 38.2 | 73.1 | 64.4 |
| Mean | 13 280 | 12 900 | 166 | 210 | 4 791 | 4 830 | 43.7 | 43.6 | 92.0 | 97.5 |
| Max. | 21 600 | 20 200 | 682 | 1 780 | 10 600 | 13 500 | 117 | 105 | 444 | 585 |
| IQR | 4 380 | 5 350 | 57 | 81 | 2 240 | 2 610 | 20.3 | 19.7 | 49.2 | 63.5 |
| SD | 3 320 | 3 440 | 115 | 301 | 1 950 | 2 830 | 21.3 | 22.2 | 80.1 | 114 |
| RSD (%) | 25 | 27 | 69 | 144 | 41 | 59 | 49 | 51 | 87 | 117 |
| K-S, P-value | >0.15 | 0.141 | <0.01 | <0.01 | 0.051 | <0.01 | 0.017 | <0.01 | <0.01 | <0.01 |

|  | Fe (%) |  | Li (mg kg$^{-1}$) |  | Mg (mg kg$^{-1}$) |  | Mn (mg kg$^{-1}$) |  | Ni (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 1.92 | 2.07 | 7.40 | 7.84 | 2 210 | 1 890 | 339 | 366 | 23.2 | 21.4 |
| Median | 2.97 | 2.90 | 12.4 | 11.7 | 3 280 | 3 120 | 597 | 603 | 32.4 | 31.6 |
| Mean | 3.09 | 3.12 | 12.6 | 12.0 | 3 620 | 3 360 | 659 | 688 | 37.0 | 41.8 |
| Max. | 4.55 | 4.79 | 20.6 | 18.6 | 6 530 | 7 620 | 1 370 | 1 510 | 100 | 158 |
| IQR | 0.88 | 1.13 | 3.60 | 5.05 | 1 680 | 1 150 | 281 | 362 | 12.7 | 14.0 |
| SD | 0.63 | 0.70 | 3.04 | 3.18 | 1 200 | 1 250 | 230 | 246 | 17.2 | 31.8 |
| RSD (%) | 21 | 22 | 24 | 26 | 33 | 37 | 35 | 36 | 46 | 76 |
| K-S, P-value | 0.052 | 0.014 | >0.15 | >0.15 | 0.137 | <0.01 | 0.019 | 0.047 | <0.01 | <0.01 |

|  | Pb (mg kg$^{-1}$) |  | V(mg kg$^{-1}$) |  | Y(mg kg$^{-1}$) |  | Zn (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 57.0 | 42.0 | 35.4 | 37.7 | 4.66 | 5.33 | 103 | 82.0 |
| Median | 226 | 193 | 58.6 | 57.6 | 7.61 | 7.63 | 211 | 179 |
| Mean | 273 | 283 | 61.9 | 64.2 | 7.91 | 8.46 | 285 | 258 |
| Max. | 1 330 | 2 050 | 140 | 181 | 16.0 | 20.4 | 1 340 | 1 740 |
| IQR | 183 | 142 | 16.9 | 18.3 | 1.54 | 2.46 | 111 | 110 |
| SD | 246 | 370 | 20.6 | 28.3 | 1.97 | 2.89 | 247 | 302 |
| RSD (%) | 90 | 131 | 33 | 44 | 25 | 34 | 87 | 117 |
| K-S, p-value | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |

*Table 5.3: Summary results from Glasgow roadside soils (n=30).*

Average metal levels are generally within typical soil values. Generally chromium, copper, lead, manganese, nickel and zinc levels are similar to those reported in previous studies, shown in Table 1.2. The CLEA soil guideline values (SGV) are exceeded at several RD sample sites. The nickel SGV (75 mg kg$^{-1}$) is exceeded at sites 13 (SF = 100, SB = 148 mg kg$^{-1}$), and 19 (SF = 83.4, SB = 158 mg kg$^{-1}$), the lead SGV (450 mg kg$^{-1}$)

is exceeded at sites 12 (SF = 636, SB = 501 mg kg$^{-1}$), 13 (SF = 1 330, SB = 2 050 mg kg$^{-1}$) and 19 (SF = 692, SB = 859 mg kg$^{-1}$).

Aluminium, lithium, calcium (SF depth only), iron (SF depth only) and magnesium (SF depth only) are the only elements that passed the normality test. This indicates these elements are less likely to have been influenced by anthropogenic activities. The results from Chapter 3 indicate calcium might be expected to be non-normally distributed. All the analytes except aluminium and iron have outlier values identified by MINITAB. Table 5.4 shows the sample sites that have been indicated as outliers for each analyte in each depth.

| Analyte | High outlier RD sample sites | |
|---|---|---|
| | SF | SB |
| Aluminium | | |
| Barium | 12, 13 | 13 |
| Calcium | 13, 17 | 13, 17 |
| Chromium | 17, 19 | 1, 7, 17 |
| Copper | 12, 13, 19 | 13, 19 |
| Iron | | |
| Lithium | 8 | |
| Magnesium | | 1, 6 |
| Manganese | 17 | 17 |
| Nickel | 13, 19 | 2, 13, 19 |
| Lead | 12, 13, 19 | 12, 13, 19 |
| Vanadium | 1, 13 | 1, 13 |
| Yttrium | 22 (low) | |
| Zinc | 12, 13, 19, 24 | 13, 19, 24 |

*Table 5.4: Outlier sites from Glasgow roadside soils (n=30).*

Sample sites 12, 13 and 19 are identified as outlier sites for many elements. This indicates potential contamination of sites 12, 13 and 19 compared to the other RD sites in Glasgow.

The SF samples' metal contents have increasing RSD in the order Fe<Li<Al=Y<V<Mg <Mn<Ca<Ni<Cr<Ba<Cu=Zn<Pb. The metal concentrations in the SB samples have increasing RSD in the order Fe<Li<Al<Y<Mn<Mg<V<Cr<Ca<Ni<Cu<Zn<Pb. Two groups of analytes can be distinguished based on their variability. Group A elements

have lower variability (RSD < 40 %) and the group is made up of aluminium, iron, lithium, manganese, magnesium, vanadium and yttrium. Group B is composed of barium, calcium, chromium, copper, nickel, lead and zinc, elements with higher variability (RSD > 40 %). Again group B includes copper, lead and zinc, which agrees with literature classing these elements as 'urban'.

The LOI results from RD samples also show low variability and if included in the metal comparison would be in group A. Site 13 has comparatively high LOI values at both depths. (LOI from SF sample = 19.3 % and from SB sample = 22.6 %) compared to other sites (mean LOI from SF samples = 11.5 % and 9.42 % from SB samples).

Many analytes did not pass the normality test so a non-parametric measure of variability was also examined. The order of variability did change but aluminium, iron, lithium and yttrium remained in the low variability group and copper, lead and zinc remained in the high variability group.

### 5.4.1.3 Riverbanks

Mean concentration and precision (as % RSD) results of pseudo total metal content in the soil samples from Glasgow riverbank soils (RB) and LOI results are shown in appendix B. Table 5.5 shows the summary statistics of the RB results.

| | LOI (%) | |
|---|---|---|
| | SF | SB |
| Min. | 4.49 | 5.23 |
| Median | 8.71 | 8.39 |
| Mean | 9.03 | 8.96 |
| Max. | 15.2 | 13.1 |
| IQR | 2.64 | 3.60 |
| SD | 2.78 | 2.39 |
| RSD (%) | 31 | 27 |
| K-S, P-value | 0.11 | >0.15 |

|  | Al (%) |  | Ba (mg kg$^{-1}$) |  | Ca (mg kg$^{-1}$) |  | Cr (mg kg$^{-1}$) |  | Cu (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 6 600 | 7 600 | 135 | 118 | 2 990 | 2 660 | 20.8 | 27.7 | 19.0 | 28.0 |
| Median | 12 500 | 15 400 | 175 | 189 | 4 020 | 4 020 | 48.0 | 54.5 | 40.0 | 45.0 |
| Mean | 12 260 | 14 960 | 176 | 193 | 4 500 | 4 750 | 59.3 | 69.4 | 53.4 | 57.3 |
| Max. | 18 200 | 22 100 | 229 | 285 | 8 280 | 11 800 | 117 | 178 | 102 | 119 |
| IQR | 4 850 | 6 900 | 19 | 23 | 2 200 | 2 240 | 56.6 | 49.0 | 44.0 | 45.5 |
| SD | 3 390 | 4 500 | 31 | 47 | 1 520 | 2 350 | 32.5 | 46.2 | 26.9 | 31.3 |
| RSD (%) | 28 | 30 | 18 | 24 | 34 | 49 | 55 | 67 | 50 | 55 |
| K-S, P-value | >0.15 | >0.15 | >0.15 | >0.15 | 0.063 | <0.01 | >0.15 | 0.109 | 0.062 | >0.15 |

|  | Fe (%) |  | Li (mg kg$^{-1}$) |  | Mg (mg kg$^{-1}$) |  | Mn (mg kg$^{-1}$) |  | Ni (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 2.68 | 2.71 | 7.00 | 7.50 | 2 560 | 2 600 | 546 | 543 | 18.3 | 22.1 |
| Median | 3.35 | 3.46 | 11.1 | 13.0 | 3 640 | 3 600 | 806 | 829 | 35.8 | 40.5 |
| Mean | 3.64 | 3.72 | 11.3 | 13.3 | 4 000 | 4 130 | 814 | 808 | 39.5 | 41.8 |
| Max. | 5.00 | 5.31 | 14.9 | 19.3 | 6 020 | 6 640 | 1 190 | 1 300 | 59.2 | 60.5 |
| IQR | 1.59 | 1.67 | 2.15 | 3.20 | 2 090 | 2 240 | 350 | 319 | 28.3 | 31.7 |
| SD | 0.85 | 0.88 | 2.37 | 3.43 | 1 150 | 1 260 | 202 | 218 | 14.8 | 15.0 |
| RSD (%) | 23 | 24 | 21 | 26 | 29 | 31 | 25 | 27 | 38 | 36 |
| K-S, P-value | >0.15 | >0.15 | >0.15 | >0.15 | 0.049 | 0.037 | >0.15 | 0.103 | >0.15 | >0.15 |

|  | Pb (mg kg$^{-1}$) |  | V(mg kg$^{-1}$) |  | Y(mg kg$^{-1}$) |  | Zn (mg kg$^{-1}$) |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SB* |
| Min. | 59.0 | 79.0 | 31.6 | 32.8 | 4.98 | 5.28 | 153 | 162 | 162 |
| Median | 109 | 110 | 50.2 | 57.8 | 7.58 | 7.98 | 238 | 254 | 238 |
| Mean | 141 | 153 | 55.3 | 59.2 | 7.71 | 8.12 | 230 | 316 | 233 |
| Max. | 335 | 426 | 85.3 | 94.7 | 10.5 | 11.2 | 310 | 1310 | 337 |
| IQR | 76.0 | 100 | 28.2 | 30.6 | 2.22 | 2.25 | 103 | 89 | 76 |
| SD | 77.5 | 100 | 16.8 | 19.6 | 1.59 | 1.76 | 53 | 302 | 53 |
| RSD (%) | 55 | 65 | 30 | 33 | 21 | 22 | 23 | 96 | 23 |
| K-S, P-value | 0.018 | <0.01 | >0.15 | >0.15 | >0.15 | >0.15 | >0.15 | <0.01 | >0.15 |

*Table 5.5: Summary statistics for Glasgow riverbanks (n=13).*

Average metal levels are generally within typical soil values. Generally chromium, copper, lead, manganese, nickel and zinc levels are similar to levels reported in previous urban studies, shown in Table 1.2.

Most analyte levels passed the normality test, except calcium, magnesium, lead and zinc. This might indicate calcium, magnesium, lead and zinc are affected by different factors at the different sites. Outlier values will have a significant affect on the normality test result. Outlier sites were identified by MINITAB for calcium (SB depth only) at site five, chromium (SB depth only) at site two, lead (both depths) and zinc (SB depth only) at site 13.

The metal levels in the SF samples have an increasing RSD in the order Ba<Li=Y <Fe=Zn<Mn<Al<Mg<V<Ca<Ni<Cu<Cr=Pb. The SB samples' metal concentrations have an increasing RSD in the order Y<Ba=Fe<Li<Mn<Al<Mg<V<Ni<Ca<Cu<Pb<Cr <Zn. Examination of a non-parametric measure of spread showed generally the same trend. A major difference was seen for the SB samples where zinc appeared at the low variability end. This indicates the very large zinc outlier is causing the high RSD. Ideally this sample would be re-analysed or the site re-sampled, but this was not practical. Three groups of metals can be distinguished in the RB samples. Group A is composed of aluminium, barium, iron, lithium, manganese, yttrium and zinc with lower variability (RSD < 30 %). Group B is made up of calcium, magnesium, nickel and vanadium with intermediate variability (30 ≤ RSD < 40 %). Group C is made up of chromium, copper and lead with higher variability (RSD > 40 %). Zinc is in the group with low variability, which is not expected. This might be due to different influences on the RB sample sites than on the parks or roadside sites, more samples would be required to confirm this.

### 5.4.1.4 Ornamental Gardens

Mean concentration and precision (as % RSD) results of pseudo total metal content and LOI results from Glasgow ornamental garden soils (OG) are shown in appendix B. Table 5.6 shows the summary statistics of the OG results.

| | LOI (%) | |
|---|---|---|
| | SF | SB |
| Min. | 3.84 | 6.20 |
| Median | 11.1 | 8.50 |
| Mean | 10.1 | 9.60 |
| Max. | 18.1 | 16.8 |
| IQR | 6.8 | 5.3 |
| SD | 4.40 | 3.44 |
| RSD (%) | 43 | 36 |
| K-S, P-value | >0.15 | 0.021 |

|  | Al (%) |  | Ba (mg kg$^{-1}$) |  | Ca (mg kg$^{-1}$) |  | Cr (mg kg$^{-1}$) |  | Cu (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 8 860 | 7 860 | 35.3 | 76.0 | 1 780 | 2 340 | 23.6 | 25.1 | 23.8 | 30.1 |
| Median | 11 000 | 14 200 | 101 | 112 | 7 560 | 6 910 | 31.8 | 40.1 | 36.1 | 44.3 |
| Mean | 12 500 | 15 500 | 103 | 117 | 9 900 | 9 040 | 45.6 | 46.4 | 41.3 | 46.7 |
| Max. | 27 800 | 30 900 | 177 | 195 | 22 700 | 19 700 | 181 | 117 | 77.9 | 82.7 |
| IQR | 4 000 | 5 100 | 46.8 | 46.5 | 11 200 | 10 600 | 12.8 | 20.0 | 20.5 | 24.8 |
| SD | 5 200 | 6 940 | 36.0 | 33.3 | 7 160 | 6 050 | 43.5 | 24.8 | 15.0 | 16.3 |
| RSD (%) | 42 | 45 | 35 | 28 | 72 | 67 | 95 | 53 | 36 | 35 |
| K-S, P-value | 0.05 | 0.019 | >0.15 | 0.142 | >0.15 | >0.15 | <0.01 | 0.024 | >0.15 | 0.134 |

|  | Fe (%) |  | Li (mg kg$^{-1}$) |  | Mg (mg kg$^{-1}$) |  | Mn (mg kg$^{-1}$) |  | Ni (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 1.96 | 2.08 | 6.13 | 5.56 | 2 200 | 1 990 | 376 | 414 | 20.9 | 19.6 |
| Median | 2.70 | 2.70 | 9.50 | 11.4 | 3 190 | 3 150 | 503 | 520 | 26.2 | 33.2 |
| Mean | 2.74 | 2.97 | 9.50 | 11.5 | 3 880 | 4 120 | 495 | 541 | 32.4 | 37.3 |
| Max. | 5.07 | 4.96 | 12.6 | 16.6 | 10 700 | 10 500 | 742 | 727 | 82.0 | 80.3 |
| IQR | 0.63 | 0.59 | 2.63 | 3.92 | 1 360 | 1 440 | 146 | 81.4 | 14.1 | 15.6 |
| SD | 0.80 | 0.89 | 2.06 | 3.05 | 2 290 | 2 710 | 102 | 89.6 | 16.8 | 16.8 |
| RSD (%) | 29 | 30 | 22 | 27 | 59 | 66 | 21 | 17 | 52 | 45 |
| K-S, P-value | <0.01 | <0.01 | >0.15 | >0.15 | <0.01 | <0.01 | >0.15 | >0.15 | 0.029 | 0.044 |

|  | Pb (mg kg$^{-1}$) |  | V(mg kg$^{-1}$) |  | Y(mg kg$^{-1}$) |  | Zn (mg kg$^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|
|  | SF | SB | SF | SB | SF | SB | SF | SB |
| Min. | 12.4 | 38.6 | 38.9 | 35.7 | 5.06 | 5.44 | 53.7 | 98.1 |
| Median | 94.1 | 102 | 49.5 | 53.0 | 6.31 | 7.05 | 134 | 149 |
| Mean | 109 | 127 | 49.5 | 56.9 | 6.41 | 7.14 | 147 | 175 |
| Max. | 236 | 264 | 80.0 | 85.4 | 7.96 | 8.37 | 251 | 321 |
| IQR | 102 | 127 | 12.2 | 16.7 | 1.73 | 2.35 | 80.0 | 119 |
| SD | 67.4 | 75.7 | 11.2 | 14.0 | 0.96 | 1.12 | 57.0 | 70.2 |
| RSD (%) | 62 | 59 | 23 | 25 | 15 | 16 | 39 | 40 |
| K-S, P-value | >0.15 | 0.138 | 0.135 | 0.113 | >0.15 | 0.149 | >0.15 | >0.15 |

*Table 5.6: Summary statistics from Glasgow ornamental gardens (n=12).*

Average metal levels are generally within typical soil values, barium levels are slightly lower than expected. Generally chromium, copper, lead, manganese, nickel and zinc levels are similar to levels reported in previous studies, shown in Table 1.2. Nickel exceeds the CLEA guideline value at site two (SF=82.0 mg kg$^{-1}$) and at site six (SB=80.3 mg kg$^{-1}$).

Most analytes pass the normality test, except aluminium (SB depth), chromium, iron, magnesium and nickel. These elements are elements less likely to have been influenced by anthropogenic activities so this is an unusual result. It could be due to OG soil being regularly changed or imported from different sources of soil in different parks. Outlier values will have a significant affect on the normality test result. Outlier sites were identified by MINITAB for aluminium at sites two and six (SB depth), chromium at site 12, iron and magnesium at sites two and six (SB depth), manganese site two (SB depth), nickel at sites two (SF depth) and six (SB depth), and vanadium at site two (SF depth). There are several metals with high outlier values at sites two and six.

The SF samples have an increasing RSD in the order Y<Mn<Li<V<Fe<Ba<Cu<Zn<Al <Ni<Mg<Pb<Ca<Cr. The SB samples have an increasing RSD in the order Y<Mn<V< Li<Ba<Fe<Cu<Zn<Al=Ni<Cr<Pb<Mg<Ca.

Iron, lithium, manganese, vanadium and yttrium metal concentrations in OG samples have lower variability (RSD < 30 %). Aluminium, barium, copper, nickel and zinc levels show intermediate to high variability (30 < RSD < 50 %). Calcium, chromium, magnesium and lead show higher variability (RSD > 50 %).

These trends do not generally agree well with what would be expected. This might be due to different treatments being used in different OG sites, potentially with high turnover of soil.

#### 5.4.1.5 Differences between Land Types

Figure 5.3 shows the boxplots of metal concentrations in soil from different land uses.

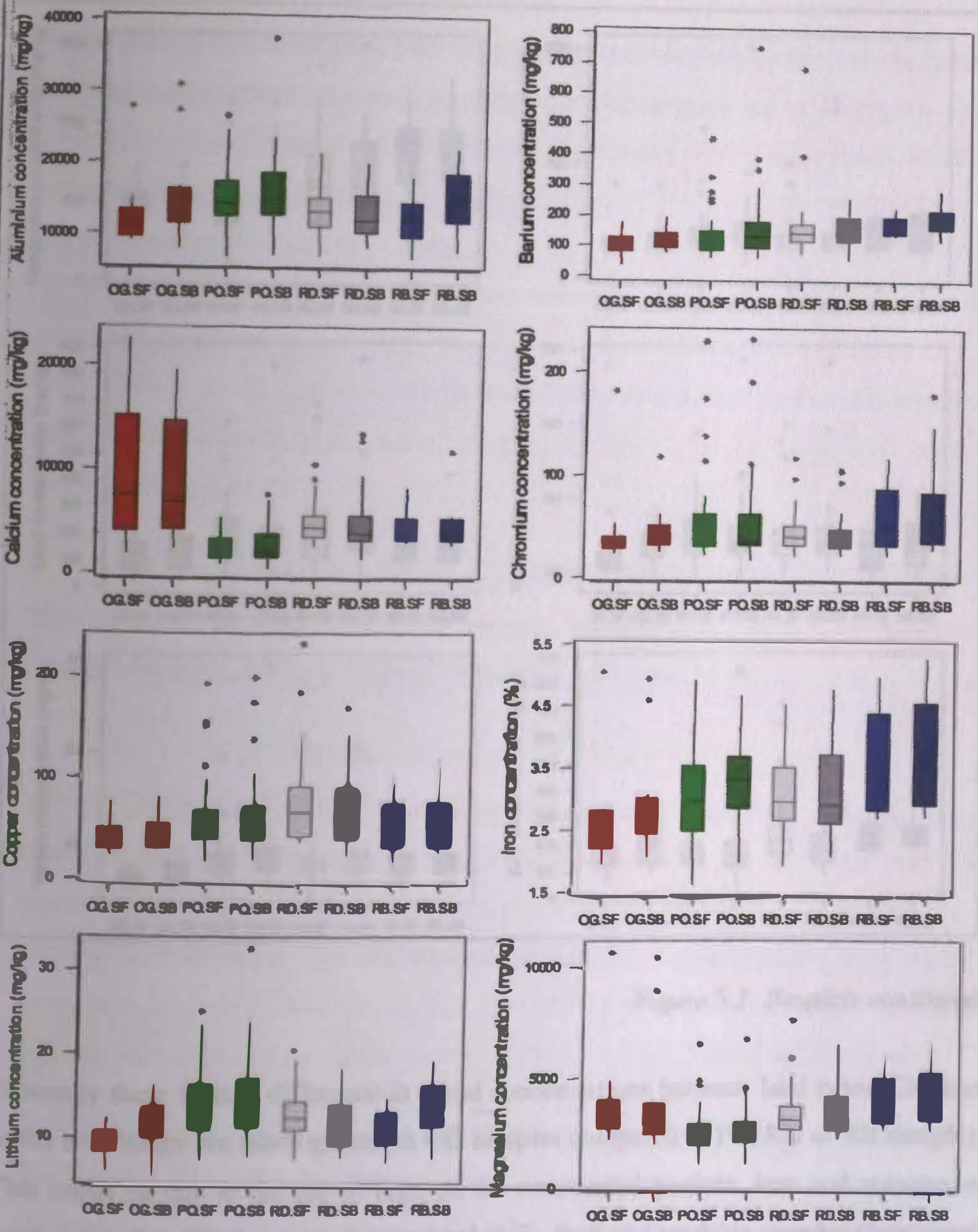

*Figure 5.3: Boxplots showing metal concentrations in soil from different land uses.*

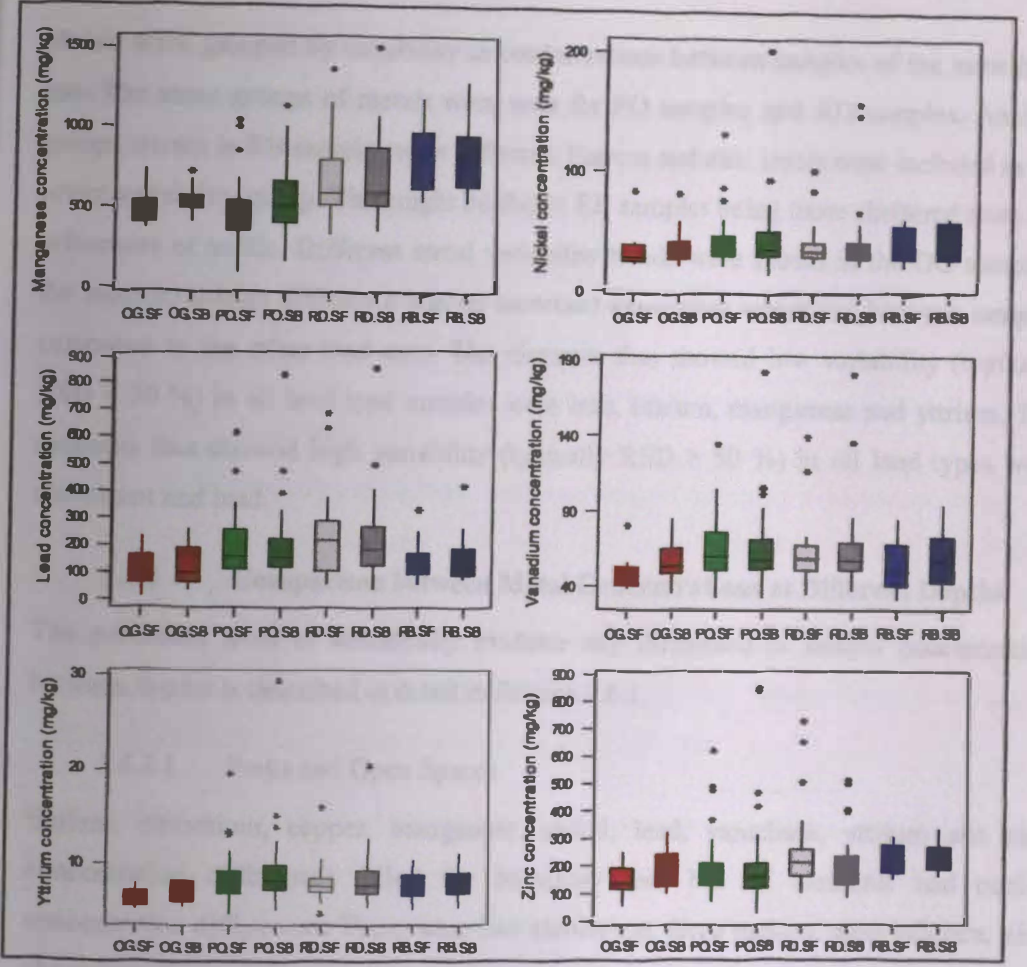

*Figure 5.3: Boxplots continued.*

Generally there is little difference in metal concentrations between land types. Calcium levels and ranges are much greater in OG samples compared to PO, RD or RB samples. This might be due to the use of lime on the ornamental gardens. Iron and manganese levels might be slightly greater in riverbank soils. Park and roadside samples show many more outlier concentrations for barium, chromium, copper, nickel, lead, vanadium, yttrium and zinc than riverbank or ornamental garden samples, i.e. there are more high metal concentrations in PO and RD samples.

Metals were grouped by variability in concentrations between samples of the same land use. The same groups of metals were seen for PO samples and RD samples. Analyte groups shown in RB samples were different. Barium and zinc levels were included in the lower variability group. This might be due to RB samples being more sheltered from the influences of traffic. Different metal variability trends were shown in the OG samples, the most noticeable difference was an increased aluminium variability between samples compared to the other land uses. The elements that showed low variability (typically RSD < 30 %) in all land type samples were iron, lithium, manganese and yttrium. The elements that showed high variability (typically RSD > 50 %) in all land types were chromium and lead.

### 5.4.2 Comparison between Metal Concentrations at Different Depths

The procedure used to statistically evaluate any difference in analyte concentration between depths is described in detail in Section 2.6.1.

#### 5.4.2.1 Parks and Open Spaces

Barium, chromium, copper, manganese, nickel, lead, vanadium, yttrium and zinc concentration differences failed the normality test, but all elements had outlier concentration differences. There were two aluminium, three barium, three calcium, nine chromium, four copper, two lithium, one magnesium, three manganese, three nickel, six lead, four vanadium, two yttrium and two zinc concentration difference outliers. The outliers were removed and the normality test repeated, and passed for all metals.

The result of the paired t-test changed when three calcium differences outlier sites were not included ($P = 0.035$ for all sites, $P = 0.237$ for 36 sites). The result of the paired t-test changed when six lead differences outlier sites were not included ($P = 0.880$ for all sites, $P = 0.005$ for 33 sites). The outlier sites have a large influence on the results of the paired test for calcium and lead which means it is unclear if there is, overall, a significant difference in calcium or lead concentration between depths. The result of the paired t-test for aluminium, barium, chromium, copper, lithium, magnesium, manganese, nickel, vanadium, yttrium and zinc did not change when outlier sites were not included.

There was a significantly greater concentration in the SB depth compared to the SF depth of aluminium, barium, iron, lithium, manganese and yttrium. With the exception of barium these elements showed low variability and are likely to be less influenced by anthropogenic activity. Barium is thought to accumulate in lower horizons, which support barium concentrations being higher in the 10 – 20 cm layer than in the surface 10 cm. There was no significant difference in chromium, copper, magnesium, nickel, vanadium and zinc concentrations between depths.

#### 5.4.2.2 Roadsides

Barium, chromium, copper, nickel, lead, vanadium and zinc differences failed the normality test. Aluminium and iron were the only elements that had no outlier concentration differences. There were two barium, three calcium, three chromium, five copper, one lithium, one magnesium, two manganese, three nickel, four lead, five vanadium, one yttrium and five zinc differences outliers. Upon removal of outlier differences all analyte differences passed the normality test.

The result of the paired t-test changed when two barium outlier sites were not included ($P = 0.245$ for all sites, $P = 0.013$ for 28 sites). A similar trend was shown by lead ($P = 0.714$ for all sites, $P = 0.003$ for 26 sites) and zinc ($P = 0.176$ for all sites and $P < 0.001$ for 25 sites). These outlier sites had a large influence on the paired t-test result and it was unclear if there was significant difference in barium, lead and zinc concentrations between depths. Upon removal of outlier sites the result of the paired t-test did not change for calcium, chromium, copper, lithium, magnesium, manganese, nickel, vanadium or yttrium. There was no statistical difference in concentration of aluminium, calcium, chromium, copper, iron, lithium, magnesium, manganese, nickel or vanadium between depths. There was a significantly greater concentration of yttrium in the SB depth compared to the SF depth.

### 5.4.2.3 Riverbanks

Calcium, chromium, manganese and zinc differences failed the normality test. There were one calcium, three chromium, one copper, one lithium, two manganese, one lead, and one zinc concentration difference outliers.

Upon removal of outlier sites the result of the paired t-test changed for chromium making it unclear if there was a statistical difference in chromium concentration between depths. There was no statistical difference in concentration of barium, calcium, copper, iron, magnesium, manganese, nickel, lead or zinc between depths. There was a significantly greater concentration of aluminium, lithium, vanadium and yttrium in the SB depth compared to the SF depth.

### 5.4.2.4 Ornamental Gardens

Barium, calcium, chromium, iron, magnesium, vanadium and zinc differences failed the normality test. There were one aluminium, one barium, one calcium, one chromium, one iron, four magnesium, two nickel and two vanadium differences outliers.

Upon removal of outlier sites the result of the paired t-test changed for calcium, chromium and magnesium making it unclear if there was a statistical difference in these metals' concentration between depths. There was no statistical difference in concentration of aluminium, barium, copper, iron, manganese, nickel, lead, yttrium or zinc between depths. There was a significantly greater concentration of lithium and of vanadium in the SB depth compared to the SF depth.

### 5.4.2.5 Summary of Differences between Depths

The analytes that show a significant difference between depths appear to be analytes that would not be expected to have been influenced by anthropogenic activities, regardless of land use. This could be due to a dilution effect from pollutant deposition at the surface, but a significantly greater SF concentration for 'urban' metals would then have been expected. This trend was not shown and to investigate further would require re-sampling at greater depth or greater resolution (for example 0 – 2.5 cm and 7.5 – 10 cm).

### 5.4.3 Principal Component Analysis

Principal component analysis was performed on the relative (concentration/mean concentration) SF sample results then relative SB sample results as described in Section 2.6.2.

#### 5.4.3.1 Parks and Open spaces

##### 5.4.3.1.1 Variance Explained and Analyte Loadings

Initially the SF samples were considered. The first PC explained 90.8 % of the variation in the results. The loadings indicated PC1 was strongly correlated with all analytes. The second PC explained 3.5 % of the variation. The loadings on PC2 showed anti-correlation of chromium with calcium, magnesium and manganese. The third PC explained 2.8 % of the variation. Barium, copper, nickel, lead and zinc were anti-correlated with aluminium, chromium, iron, lithium, magnesium and manganese on PC3. Figure 5.4 shows the loadings on PC1 plotted against the loadings on PC2, whilst Figure 5.5 shows the loadings on PC1 vs. PC3.

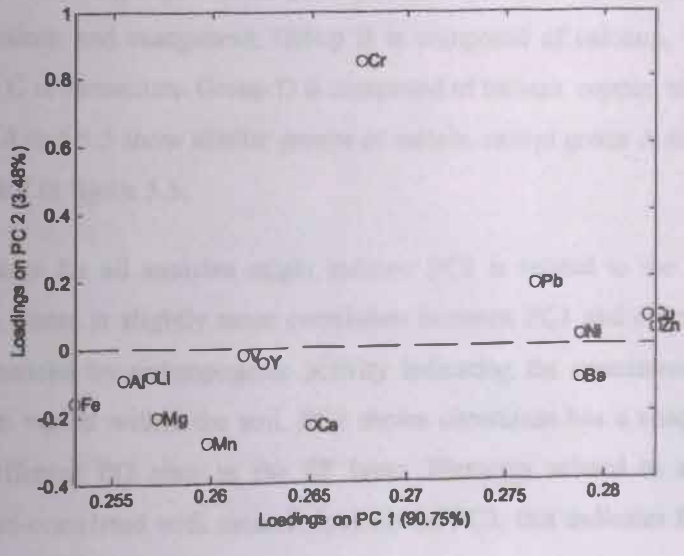

*Figure 5.4: Loadings from POSF on PC1 vs. loadings on PC2 (n=39).*

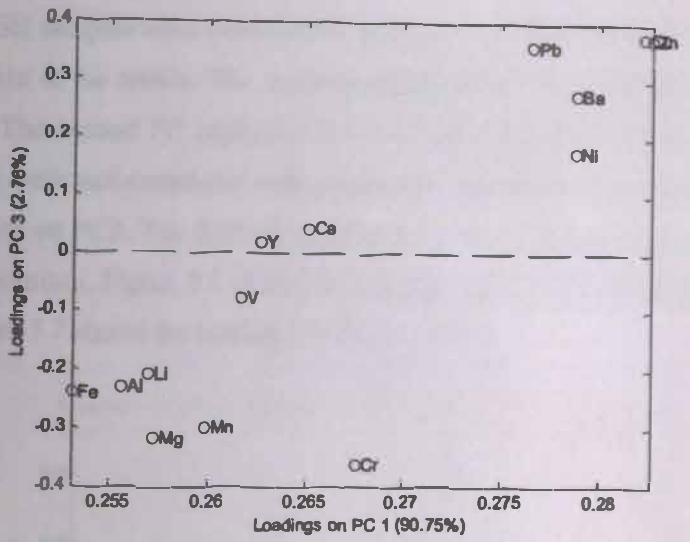

*Figure 5.5: Loadings from POSF on PC1 vs. loadings on PC3 (n=39).*

Figure 5.4 shows three groups of analytes. Group A is made up of aluminium, calcium, iron, lithium, magnesium, manganese, vanadium and yttrium. Group B is chromium. Group C is composed of barium, copper, nickel, lead and zinc.

Figure 5.5 shows four groups of analytes. Group A is made up of aluminium, iron, lithium, magnesium and manganese. Group B is composed of calcium, vanadium and yttrium. Group C is chromium. Group D is composed of barium, copper, nickel, lead and zinc. Figures 5.4 and 5.5 show similar groups of metals, except group A shown in figure 5.4 is sub-divided in figure 5.5.

The high loadings for all analytes might indicate PC1 is related to the heterogeneity within the soil. There is slightly more correlation between PC1 and elements likely to have been influenced by anthropogenic activity indicating the concentrations of these metals are more varied within the soil. PC2 shows chromium has a unique behaviour between the different PO sites in the SF layer. Elements related to anthropogenic activities are anti-correlated with natural elements on PC3, this indicates PC3 is related to anthropogenic activities.

The relative SB samples were processed in the same way. The first PC explained 86.8 % of the variation in the results. The loadings indicated PC1 was strongly correlated with all analytes. The second PC explained 5.4 % of the variation. Barium, copper, nickel, lead and zinc were anti-correlated with aluminium, chromium, iron, lithium, magnesium and manganese on PC2. The third PC explained 3.1 % of the variation and was strongly related to chromium. Figure 5.6 shows the loadings on PC1 plotted against the loadings on PC2. Figure 5.7 shows the loadings on PC1 vs. PC3.

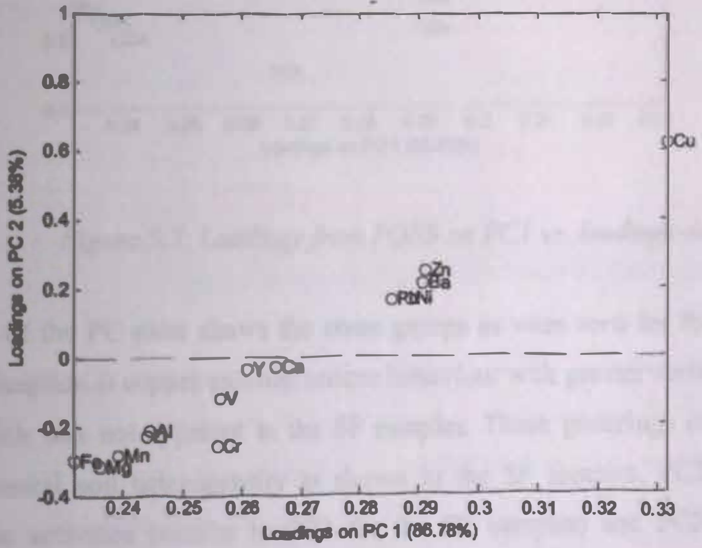

*Figure 5.6: Loadings from POSB on PC1 vs. loadings on PC2 (n=39).*

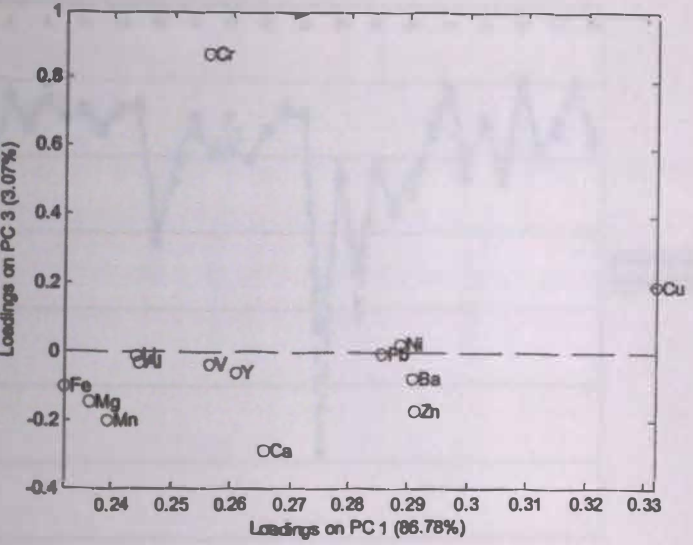

*Figure 5.7: Loadings from POSB on PC1 vs. loadings on PC3 (n=39).*

Examination of the PC plots shows the same groups as were seen for the SF samples. The major exception is copper exhibits unique behaviour with greater variation in the SB samples, which was not apparent in the SF samples. These groupings indicate PC1 is related to general soil heterogeneity as shown in the SF samples, PC2 is related to anthropogenic activities (similar to PC3 for the SF samples) and PC3 is related to chromium variability (similar to PC2 from the SF samples).

#### 5.4.3.1.2 Sample Scores

The scores show the relationship between the samples and the PC's. Figure 5.8 shows the scores on PC1.

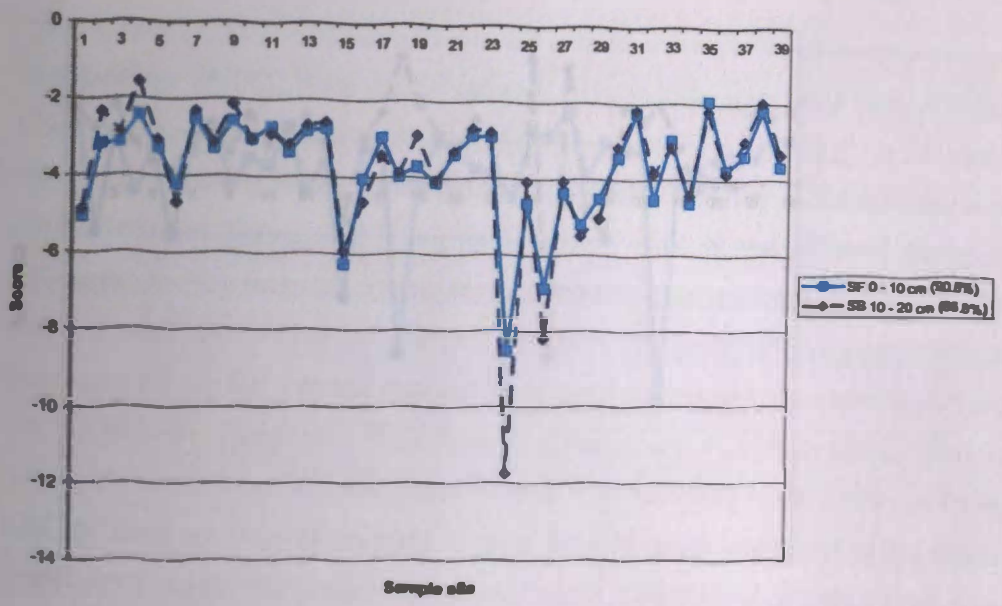

*Figure 5.8: Scores from POSF and POSB samples on PC1.*

Sample sites 15, 24 and 26 have the highest influence in PC1. The same trends are shown in the SF and SB depths on PC1. Figure 5.8 suggests site 24 is the most contaminated PO site. This site was identified as having several metal outlier values in section 4.4.1. Identifying outliers for each element ignored the relationships between metals and was time consuming. Figure 5.9 shows the scores on PC2 and PC3.

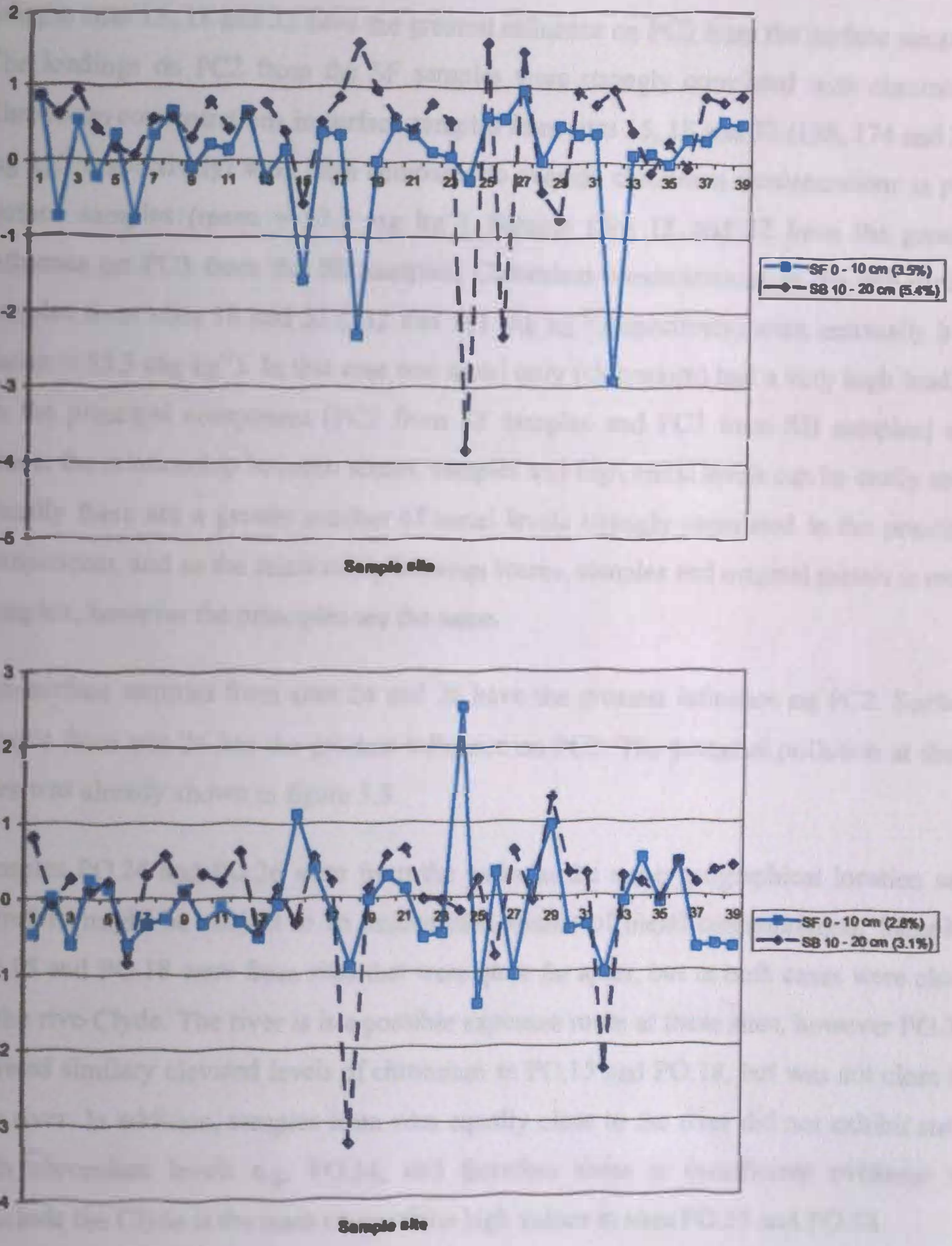

*Figure 5.9: Scores from POSF and POSB samples on PC2 and PC3.*

Sample sites 15, 18 and 32 have the greatest influence on PC2 from the surface samples. The loadings on PC2 from the SF samples were strongly correlated with chromium. Chromium concentrations in surface samples from sites 15, 18 and 32 (138, 174 and 229 mg $kg^{-1}$ respectively) were high compared to average chromium concentrations in park surface samples (mean = 53.3 mg $kg^{-1}$). Sample sites 18 and 32 have the greatest influence on PC3 from the SB samples. Chromium concentrations in the sub-surface samples from sites 18 and 32 (232 and 191 mg $kg^{-1}$ respectively) were unusually high (mean = 53.3 mg $kg^{-1}$). In this case one metal only (chromium) had a very high loading on the principal component (PC2 from SF samples and PC3 from SB samples) and hence, the relationship between scores, samples and high metal levels can be easily seen. Usually there are a greater number of metal levels strongly correlated to the principal components, and so the relationship between scores, samples and original metals is more complex, however the principles are the same.

Sub-surface samples from sites 24 and 26 have the greatest influence on PC2. Surface sample from site 24 has the greatest influence on PC3. The potential pollution at these sites was already shown in figure 5.8.

Samples PO.24 and PO.26 were from the parks in the same geographical location and therefore might be subject to an unidentified source of metal contamination. Samples PO.15 and PO.18 were from sites that were quite far apart, but in both cases were close to the rive Clyde. The river is is a possible exposure route at these sites, however PO.32 showed similary elevated levels of chromium as PO.15 and PO.18, but was not close to any river. In addition, samples from sites equally close to the river did not exhibit such high chromium levels e.g. PO.34, and therefore there is insufficient evidence to conclude the Clyde is the main cause of the high values at sites PO.15 and PO.18.

### 5.4.3.2 Roadsides

#### 5.4.3.2.1 Variance Explained and Analyte Loadings

Initially the SF samples were processed. The first PC explained 88.9 % of the variation in the results. The loadings indicate PC1 was strongly correlated with all analytes. The second PC explained 7.6 % of the variation. Barium, copper, lead and zinc were anti-correlated with aluminium, chromium, iron, lithium, magnesium and manganese on PC2. The third PC explained 1.2 % of the variation. Chromium was anti-correlated with aluminium, barium and lithium on PC3. Figure 5.10 shows the loadings on PC1 plotted against the loadings on PC2. Figure 5.11 shows the loadings on PC1 plotted against the loadings on PC3.

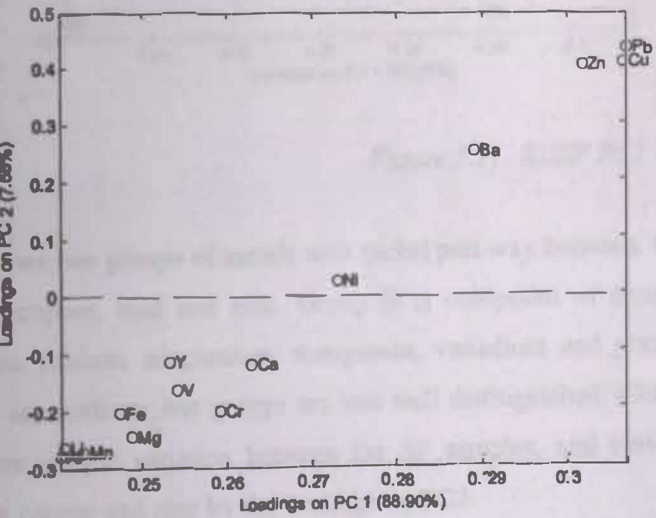

*Figure 5.10: RDSF PC1 vs PC2 loadings.*

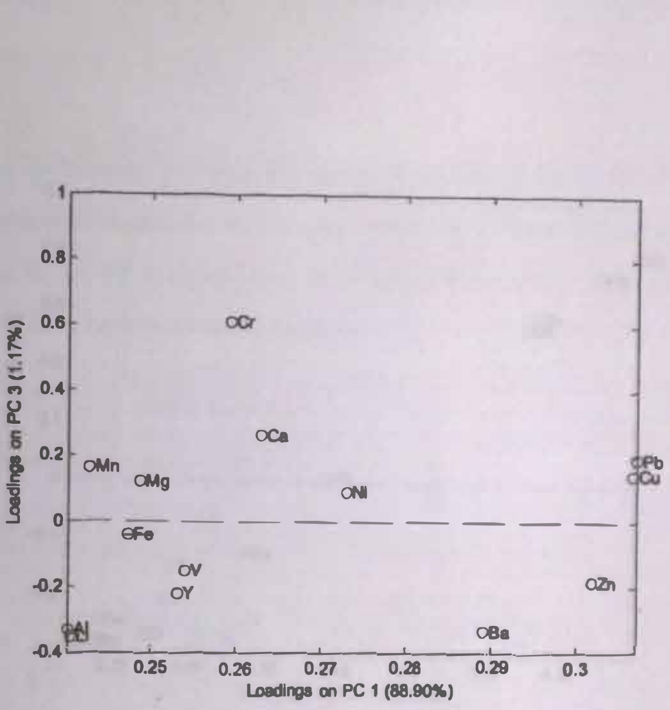

*Figure 5.11: RDSF PC1 vs PC3 loadings.*

Figure 5.10 shows two groups of metals with nickel part way between. Group A is made up of barium, copper, lead and zinc. Group B is composed of aluminium, calcium, chromium, iron, lithium, magnesium, manganese, vanadium and yttrium. Figure 5.11 shows similar associations, but groups are less well distinguished. Chromium is shown to have a more unique variation between the SF samples, and barium and zinc are separated from copper and zinc by the loadings on PC3.

Next the relative RDSB sample results were processed using PCA. The first PC explained 82.4 % of the variation in the results. The loadings indicated PC1 was correlated with all analytes. The second PC explained 13.1 % of the variation. Barium, copper, lead and zinc were anti-correlated with aluminium, chromium, iron, magnesium, manganese and vanadium on PC2. The third PC explained 1.8 % of the variation. Barium was anti-correlated with copper and nickel on PC3. Figure 5.12 shows the loadings on PC1 plotted against the loadings on PC2. Figure 5.13 shows the loadings on PC1 plotted against the loadings on PC3.

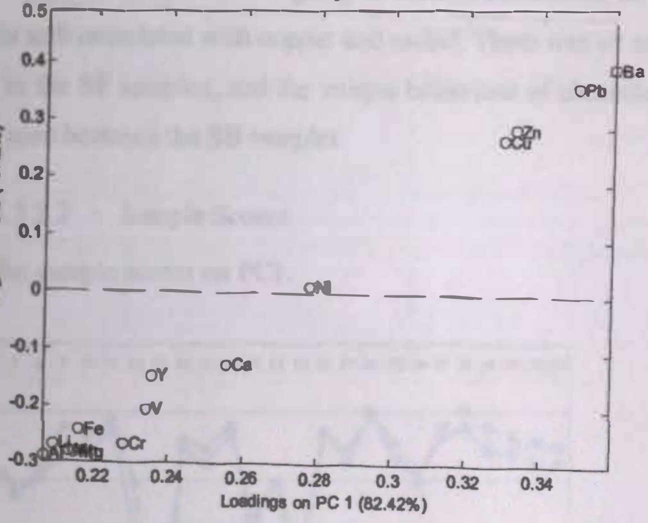

*Figure 5.12: RDSB PC1 vs PC2 loadings.*

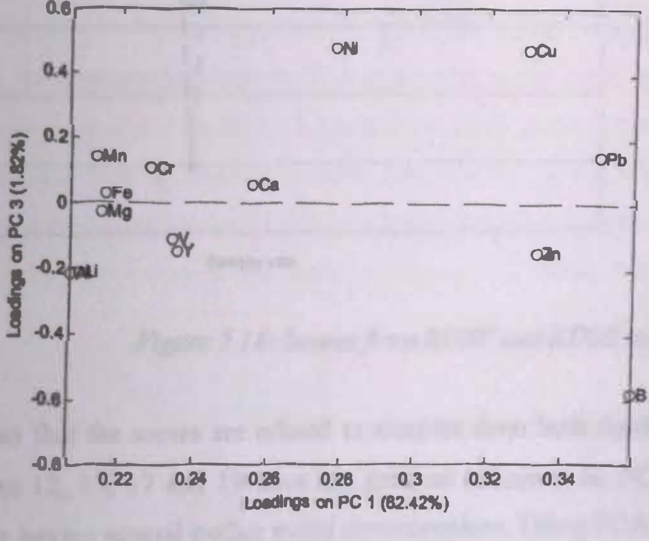

*Figure 5.13: RDSB PC1 vs PC3 loadings.*

Figure 5.12 shows two clear groups of metals. Group A is made up of aluminium, calcium, chromium, iron, lithium, magnesium, manganese, vanadium and yttrium. Group B is composed of barium, copper, lead and zinc. Nickel is between these groups.

Figure 5.13 shows differences between the group B metals, association of copper with nickel, and barium is anti-correlated with copper and nickel. There was no association of copper with nickel in the SF samples, and the unique behaviour of chromium shown in figure 5.11 was not seen between the SB samples.

#### 5.4.3.2.2 Sample Scores

Figure 5.14 shows the sample scores on PC1.

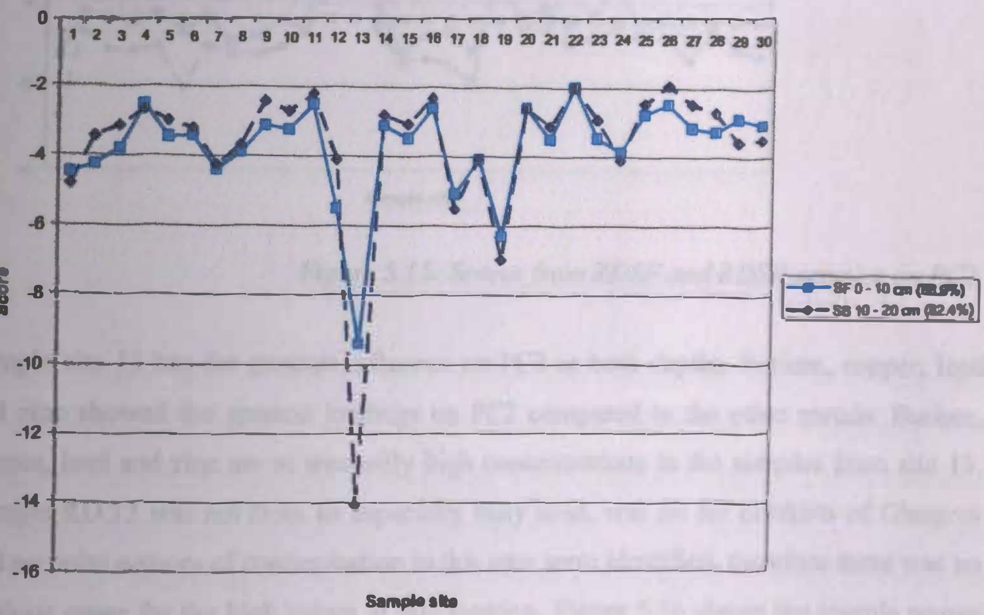

*Figure 5.14: Scores from RDSF and RDSB samples on PC1.*

Figure 5.14 shows that the scores are related to samples from both depths in a similar way. Sample sites 12, 13, 17 and 19 have the greatest influence on PC1. These sites were identified as having several outlier metal concentrations. Using PCA to analyse the results saved time, considered the relationships between metals and improved display of results. Figure 5.15 shows the sample scores on PC2.

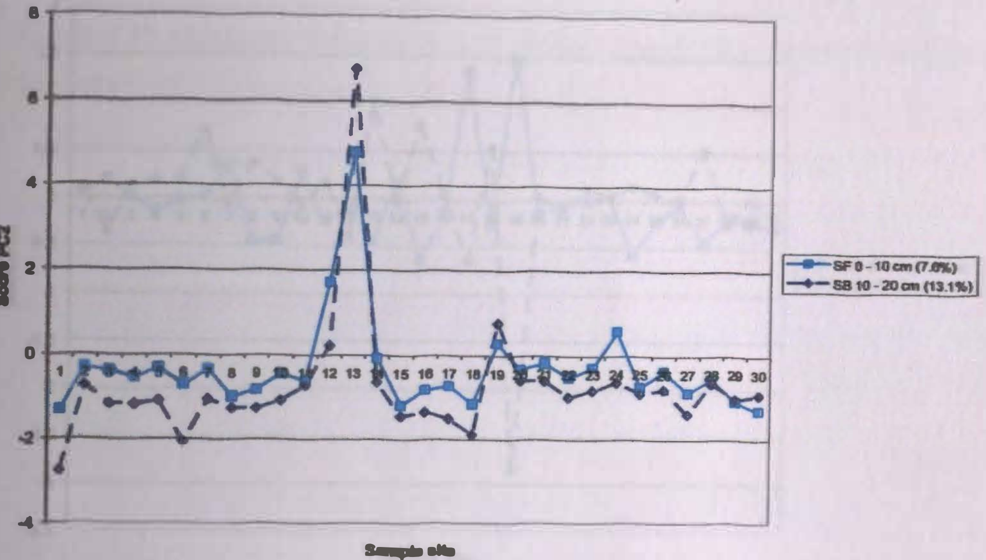

*Figure 5.15: Scores from RDSF and RDSB samples on PC2.*

Sample site 13 has the greatest influence on PC2 in both depths. Barium, copper, lead and zinc showed the greatest loadings on PC2 compared to the other metals. Barium, copper, lead and zinc are at unusually high concentrations in the samples from site 13. Sample RD.13 was not from an especially busy road, was on the outskirts of Glasgow and no point sources of contamination in this area were identified, therefore there was no obvious cause for the high values at this location. Figure 5.16 shows the sample scores on PC3.

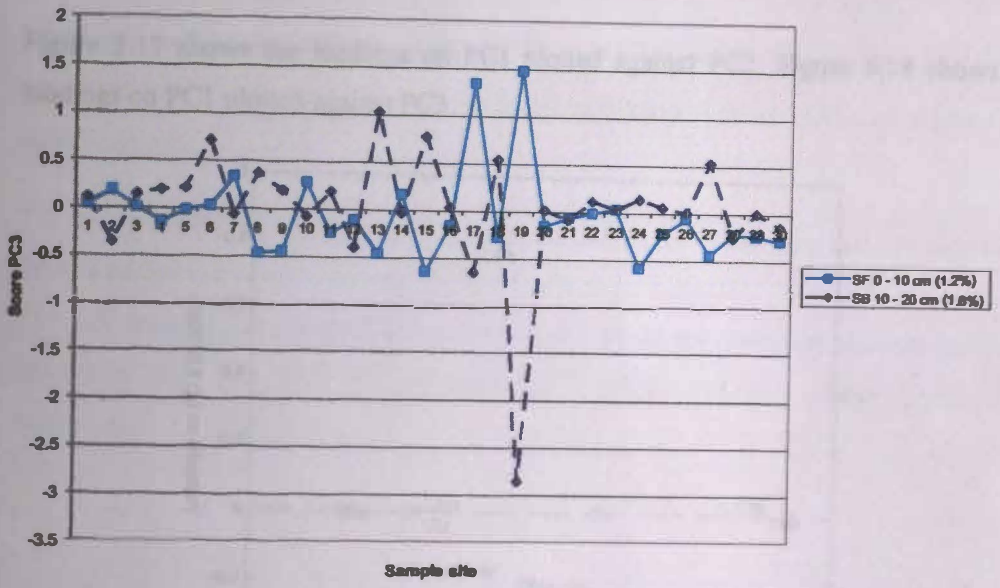

*Figure 5.16: Scores from RDSF and RDSB samples on PC3.*

Surface sample sites 17 and 19 have the greatest relationship with PC3 indicating potential chromium contamination. Sub-surface site 19 has the greatest relationship with PC3 which is due to high copper (382 mg $kg^{-1}$) and nickel (158 mg $kg^{-1}$) concentrations compared to the other roadside soil copper and nickel concentrations (mean = 97.5 and 41.8 mg $kg^{-1}$ respectively). There were no obvious environmental sources, particular to these locations, which might explain the high values.

### 5.4.3.3 Riverbanks

#### 5.4.3.3.1 Variance Explained and Analyte Loadings

The relative RBSF sample results were analysed using PCA. The first PC explained 95.2 % of the variation in the results. The loadings indicate PC1 is correlated with all analytes. The second PC explained 2.3 % of the variation. Copper and lead are anti-correlated with aluminium, calcium, iron, magnesium, and manganese on PC2. The third PC explained 1.4 % of the variation and showed a strong relation to chromium results.

Figure 5.17 shows the loadings on PC1 plotted against PC2. Figure 5.18 shows the loadings on PC1 plotted against PC3.

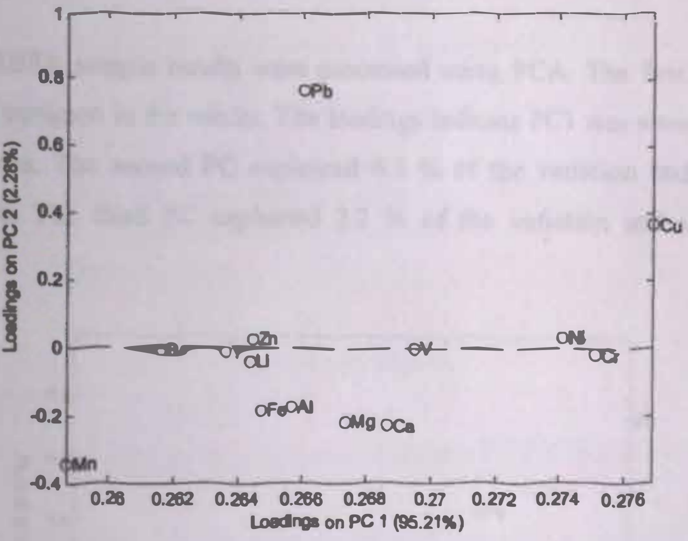

*Figure 5.17: RBSF PC1 vs PC2 loadings.*

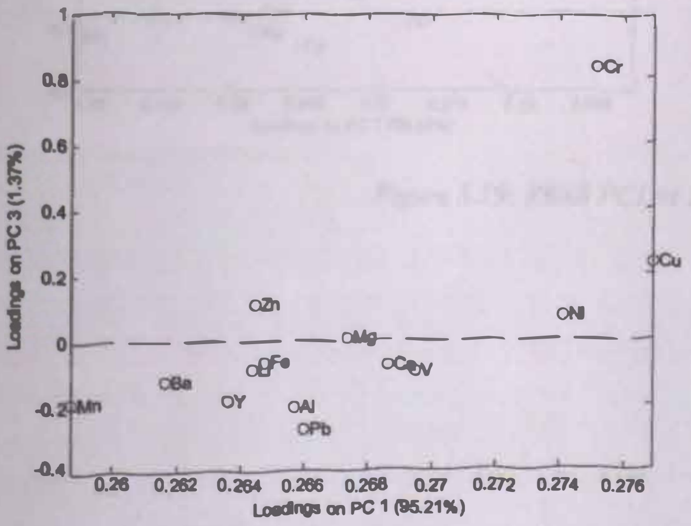

*Figure 5.18: RBSF PC1 vs PC3 loadings.*

There are no distinct groups of elements. Chromium, copper, manganese and lead are separated from the other elements indicating these elements show unique trends between RBSF samples.

The relative RBSB sample results were processed using PCA. The first PC explained 89.6 % of the variation in the results. The loadings indicate PC1 was strongly correlated with all analytes. The second PC explained 6.3 % of the variation and was strongly related to zinc. The third PC explained 2.2 % of the variation and was related to chromium.

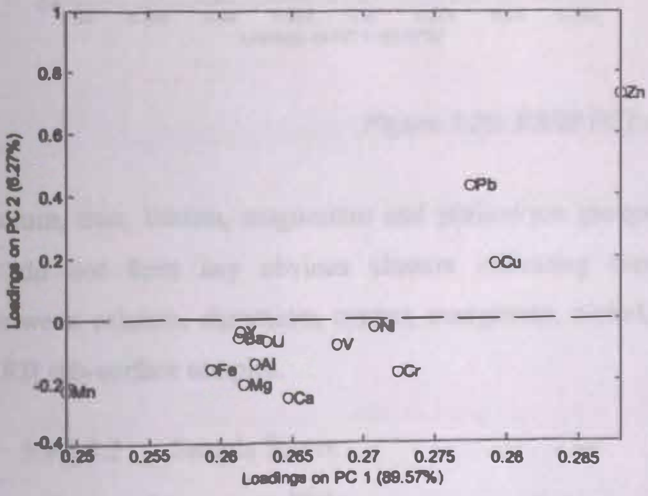

*Figure 5.19: RBSB PC1 vs PC2 loadings.*

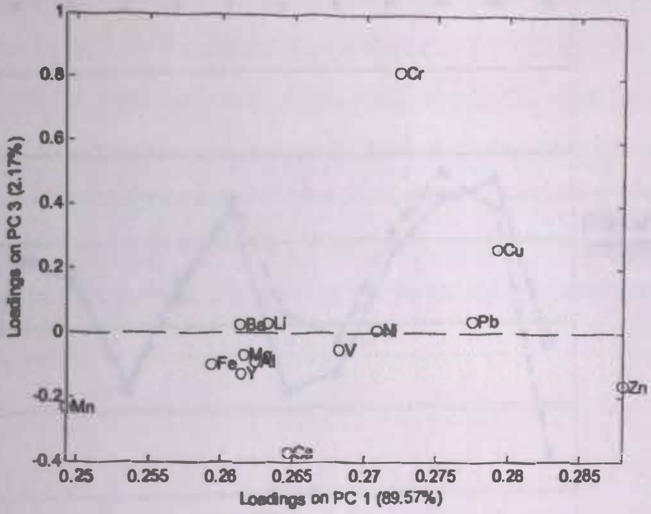

*Figure 5.20: RBSB PC1 vs PC3 loadings.*

Aluminium, barium, iron, lithium, magnesium and yttrium are grouped together. The other analytes do not form any obvious clusters indicating there are different relationships between calcium, chromium, copper, manganese, nickel, lead, vanadium and zinc in the RB sub-surface samples.

#### 5.4.3.3.2 Sample Scores

Figure 5.21 shows the sample scores on PC1.

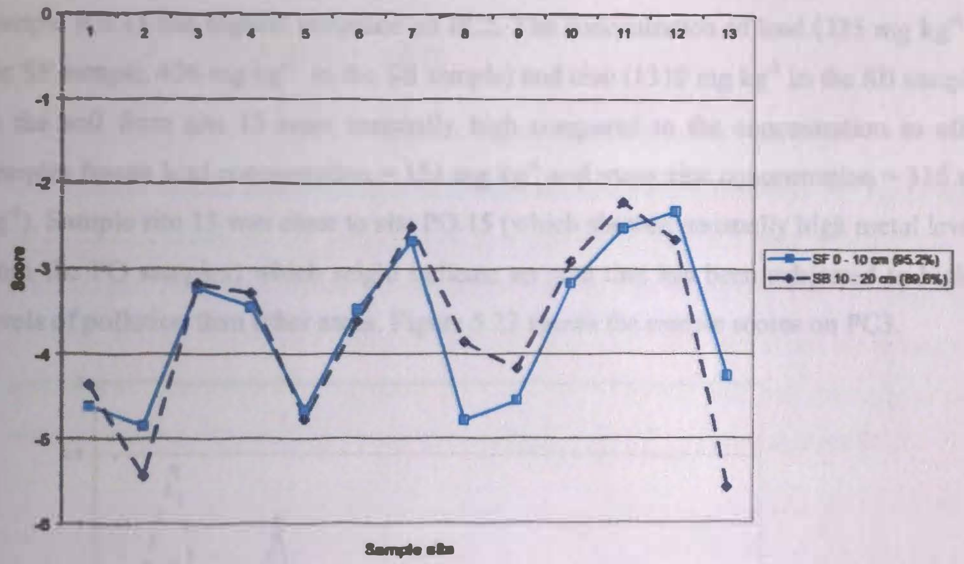

Figure 5.21: Scores from RB.SF and RB.SB samples on PC1.

The sample scores show there is no clear domination of any one sample on PC1. Figure 5.22 shows the sample scores on PC2.

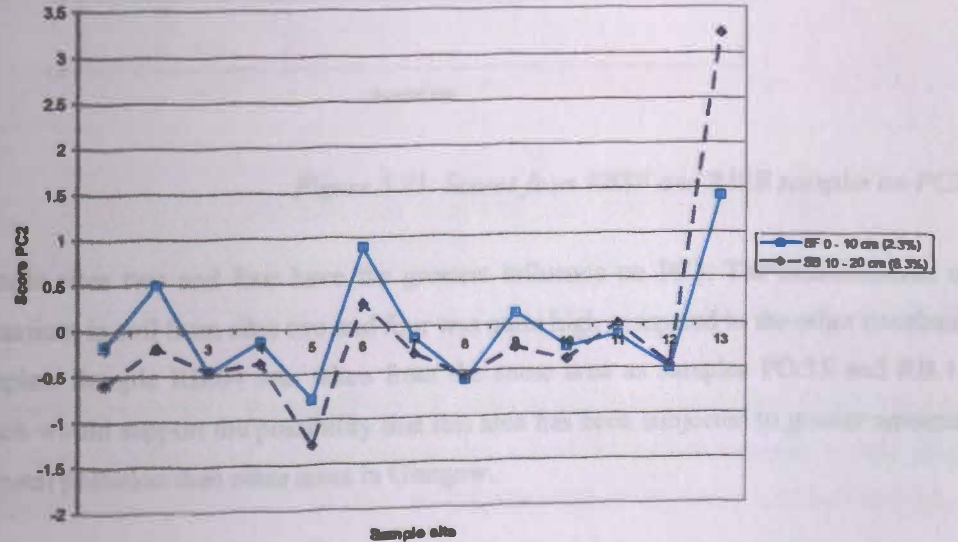

*Figure 5.22: Scores from RBSF and RBSB samples on PC2.*

Sample RB.13 has highest influence on PC2. The concentration of lead (335 mg $kg^{-1}$ in the SF sample, 426 mg $kg^{-1}$ in the SB sample) and zinc (1310 mg $kg^{-1}$ in the SB sample) in the soil from site 13 were unusually high compared to the concentration in other samples (mean lead concentration = 153 mg $kg^{-1}$ and mean zinc concentration = 316 mg $kg^{-1}$). Sample site 13 was close to site PO.15 (which showed unusually high metal levels from the PO samples) which might indicate an area that has been subjected to higher levels of pollution than other areas. Figure 5.23 shows the sample scores on PC3.

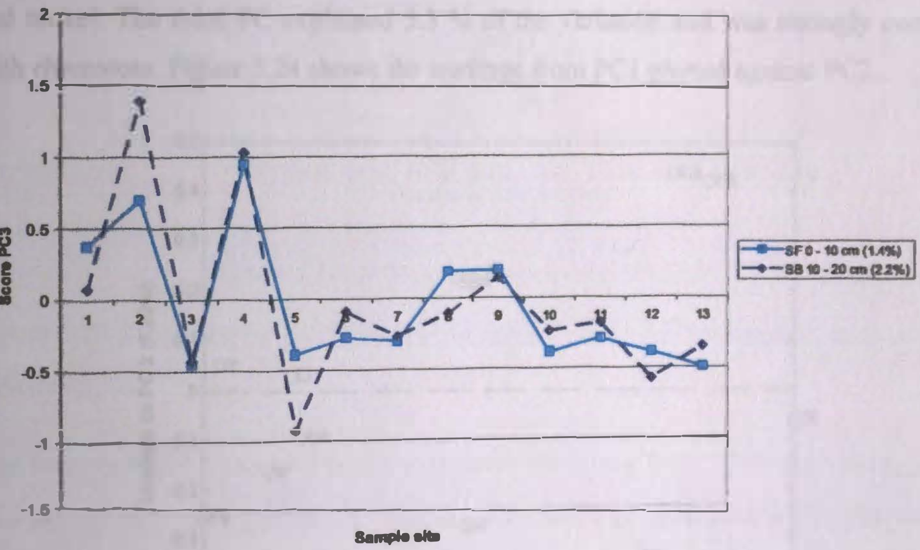

*Figure 5.23: Scores from RBSF and RBSB samples on PC3.*

Sample sites two and four have the greatest influence on PC3. The concentration of chromium in soil from sites two and four was quite high compared to the other riverbank samples. Sample RB.04 was taken from the same area as samples PO.15 and RB.13 which would support the possibility that this area has been subjected to greater amounts of metal pollution than other areas in Glasgow.

### 5.4.3.4 Ornamental Gardens

#### 5.4.3.4.1 Variance Explained and Analyte Loadings

The relative OGSF sample results were analysed using PCA. The first PC explained 87.4 % of the variation in the results. The loadings indicated PC1 was strongly correlated with all analytes. The second PC explained 5.8 % of the variation. The loadings on PC2 showed strong correlation between calcium and lead, anti-correlated with magnesium and nickel. The third PC explained 5.3 % of the variation and was strongly correlated with chromium. Figure 5.24 shows the loadings from PC1 plotted against PC2.

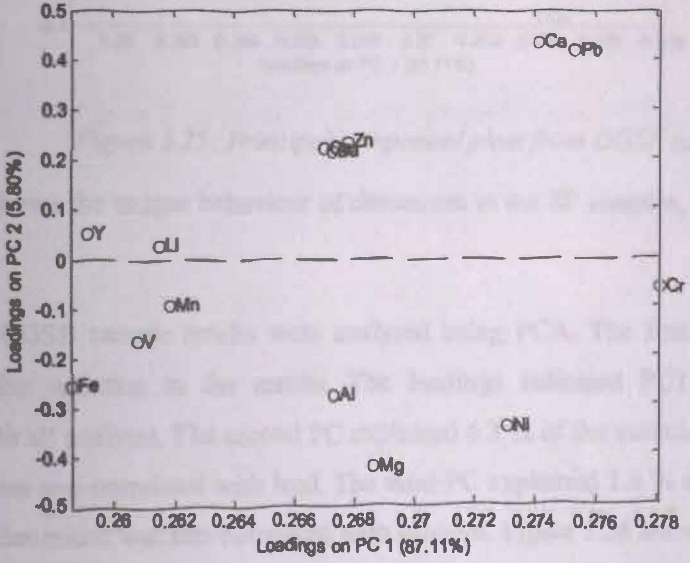

*Figure 5.24: OGSF PC1 vs. PC2 loadings.*

Figure 5.24 shows 5 groups of metals. Aluminium, magnesium and nickel are loosely grouped together. Iron, lithium, manganese, vanadium and yttrium are loosely grouped together. Barium, copper and zinc are closely grouped together. Calcium and lead are closely grouped together. Chromium is not grouped with any other metal. Figure 5.25 shows the loadings on PC1 plotted against PC3.

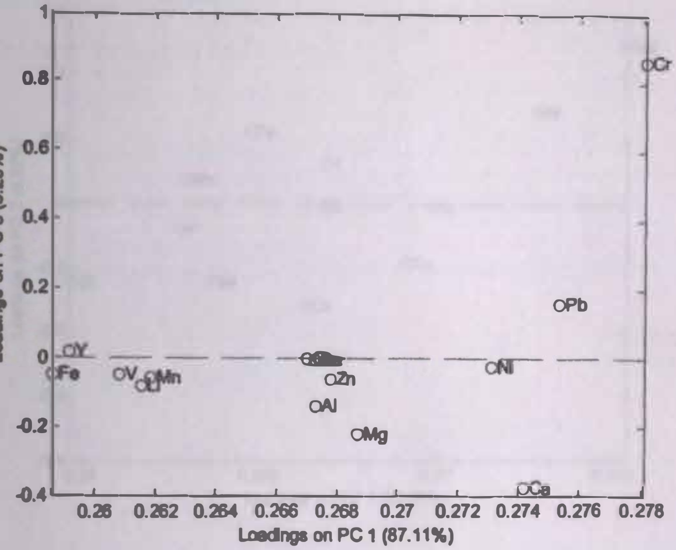

*Figure 5.25: Principal component plots from OGSF sample analysis.*

Figure 5.25 shows the unique behaviour of chromium in the SF samples, anti-correlated with calcium.

The relative OGSB sample results were analysed using PCA. The first PC explained 88.6 % of the variation in the results. The loadings indicated PC1 was strongly correlated with all analytes. The second PC explained 6.3 % of the variation and showed magnesium was anti-correlated with lead. The third PC explained 2.6 % of the variation and showed chromium was anti-correlated with calcium. Figure 5.26 shows the loadings from PC1 plotted against PC2. Figure 5.27 shows the loadings from PC1 vs. PC3.

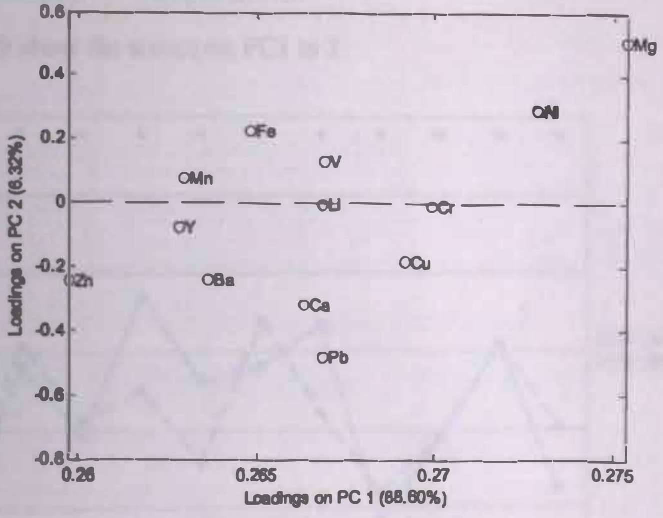

*Figure 5.26: Loadings on PC1 plotted against PC2 from OGSB PCA.*

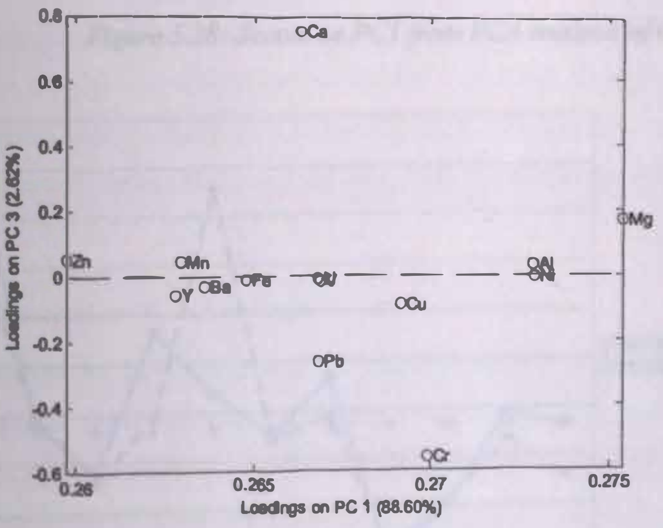

*Figure 5.27: Loadings on PC1 plotted against PC3 from OGSB PCA.*

The metals are not clearly grouped in either figures 5.26 or 5.27. Aluminium and nickel are grouped together, possibly with magnesium. Zinc levels show unique behaviour between OG samples. Similar to SF results calcium and chromium are ant-correlated but any relationships of these groups of metals to environmental influences are not clear.

### 5.4.3.4.2 Sample Scores

Figure 5.28 to 4.29 show the scores on PC1 to 3.

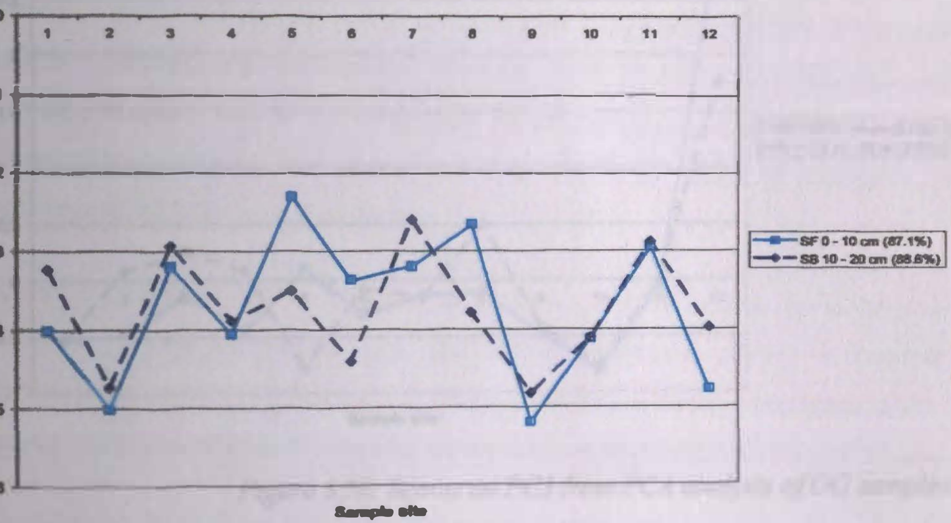

*Figure 5.28: Scores on PC1 from PCA analysis of OG samples.*

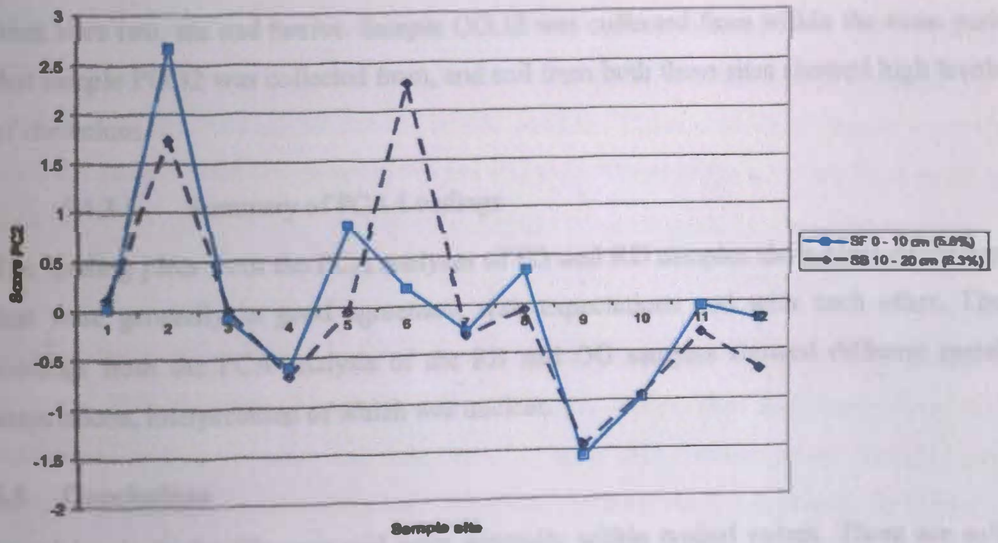

*Figure 5.29: Scores on PC2 from PCA analysis of OG samples.*

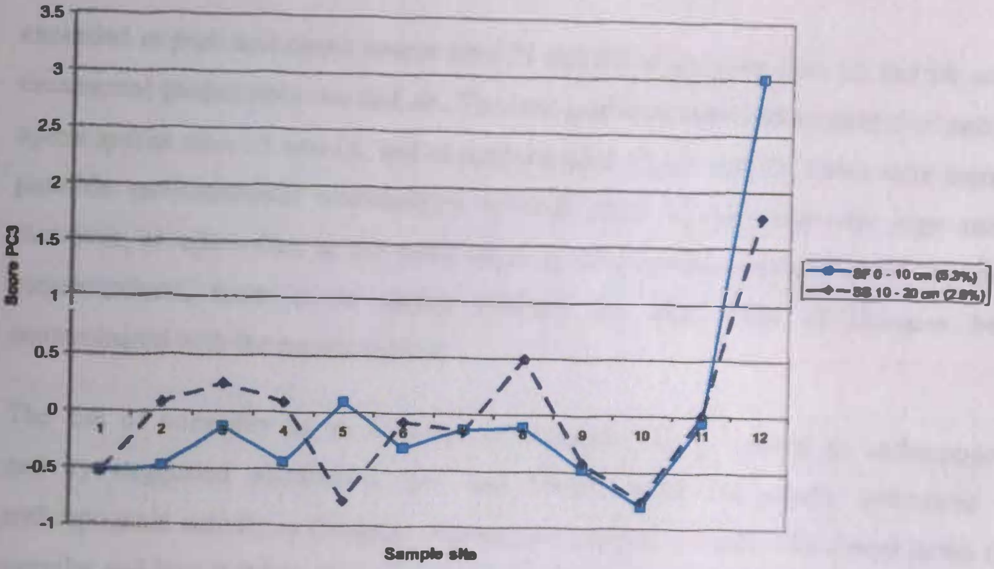

*Figure 5.30: Scores on PC3 from PCA analysis of OG samples.*

There is no strong relationship between any particular sample and PC1, but similar patterns are shown in results from both depths. Figures 5.29 and 5.30 highlight samples from sites two, six and twelve. Sample OG.12 was collected from within the same park that sample PO.32 was collected from, and soil from both these sites showed high levels of chromium.

#### 5.4.3.5 Summary of PCA Loadings

The loading plots from the PCA analyses of PO and RD samples show clear groupings that were generally in good agreement with expectations and with each other. The loadings from the PCA analysis of the RB and OG samples showed different metal associations, interpretation of which was unclear.

## 5.5 Conclusions

Metal levels in the Glasgow soil were generally within typical values. There are soil guideline values (SGV) based upon risk to human health for chromium, nickel and lead. Results from all samples were generally significantly below SGV's. The SGV for chromium was exceeded at park and opens spaces sites 18 and 32. The nickel SGV was exceeded at park and opens spaces sites 24 and 26, at roadside sites 13 and 19, and at ornamental garden sites two and six. The lead guideline value was exceeded at park and opens spaces sites 15 and 24, and at roadside sites 12, 13 and 19. There were tentative possible environmental relationships between some of the sites with high values. However, as other sites in the same areas as contaminated points showed low metal concentrations, there is no strong evidence for large areas of Glasgow being contaminated with the metals studied.

The use of normality as an indicator of elements less influenced by anthropogenic activity suggested aluminium, iron and lithium were not greatly influenced by anthropogenic activity in Glasgow. Aluminium was not normally distributed in the OG samples and is probably indicative of a varied origin of and treatments to the OG soils.

The variability of analytes within soil types was a better indication of metals more likely to have been influenced by anthropogenic activity. This confirmed that aluminium, iron and lithium were less likely to have been influenced by anthropogenic activity, as they showed low variability between sites. Copper, lead and zinc showed high variability confirming copper, lead and zinc are more likely to be of anthropogenic origin. These trends were not seen for the RB or the OG samples. There were significantly fewer OG and RB sample sites compared to PO and RD sites. There might not have been sufficient RB or OG samples to fully explore relationships between metal levels in these soils.

The range of analyte concentrations in soils from all land types was generally similar. Data analysis using PCA of relative results for each land use showed similar trends for PO and RD samples. Aluminium, iron, lithium, magnesium and manganese were associated with each other and less likely to have been influenced by anthropogenic activities. Chromium showed unique behaviour between sites, which may be indicative of anthropogenic inputs affecting chromium levels in Glasgow soils. Barium tended to be associated with copper, lead and zinc generally, indicating barium levels in the soils were affected by anthropogenic activities, possibly traffic related. However, calcium, nickel, vanadium and yttrium showed different associations and behaviour in the PO samples compared to the RD samples. Different groups of metals were seen from the PCA processing of RB and OG sample results compared to each other and to PO and RD samples. The loadings calculated from the PCA analysis allowed improved visualization of analyte variability, and consideration of the multivariate properties of the data. The sample scores on the principal components were plotted to highlight sample sites that might be more contaminated. This information was also obtained by examining the outliers one element at a time. The graphical representation provided by the score plots was preferred as it displayed a similar amount of information with fewer components than analytes. The scores could be plotted using a Geographical Information System, to assist in decision making in relation to land use by Local Authorities.

# 6 APPLICATION OF DIFFERENT SEQUENTIAL SCHEMES TO DETERMINE THE METAL FRACTIONATION IN SOILS

## 6.1 Introduction

### 6.1.1 Chemical Speciation

A chemical species is defined as a specific form of an element with respect to isotopic composition, electronic or oxidation state, and/or complex or molecular structure. Speciation analysis is defined as analytical activities to identify and/or measure the quantities of one or more individual chemical species in a sample. Speciation is defined as the distribution of an element amongst defined chemical species in a system[89]. The behaviour and toxicity of elements is dependant upon their chemical species. Therefore assessments of health hazards, toxicity and bioavailability must be based on concentrations of specific chemical species rather that total (or pseudo total) element levels.

The main difficulties of speciation analysis are sample preservation, isolating the species in their natural states and species stability[90]. Alterations in metal speciation after samples have been collected cannot be prevented but efforts must be made to minimize problems associated with sampling and storage[91,92,93].

Soil is required to be extracted to isolate the chemical species in soluble form, for analysis. The extract is then selectively analysed for the chemical species of interest (e.g. free ions[94], oxidation states[95] or isotopes[96]). Soil may be extracted using acidified organic solvents or by supercritical fluid extraction. The determination of the chemical species of an element in soil often uses chromatographic separation but is not possible for all samples[97]. The determination of chemical species is more common from water samples than from soil samples[98].

### 6.1.2 Chemical Fractionation

Fractionation is defined as the process of classification of an analyte or a group of analytes from a sample according to physical or chemical properties[89].

The treatment of soil with reagents chosen to nominally target specific soil compartments (e.g. organic matter) although sometimes referred to as 'operational speciation', is in fact an example of a fractionation procedure. The phases that are targeted by reagents vary. Extracts have been chosen to simulate gastric conditions to yield information on bioavailability[99]. Plant-available trace metal concentrations have been estimated using several reagents, chosen to isolate analytes by cation exchange, complexation and/or acidification[100,101,102]. The relationship between metal mobility and risk assessment has also been reported[103], as well as an overview of extraction tests for risk assessment of contaminated land[104]. It is recommended that the mobility of the contaminant(s) is considered when performing a risk assessment.

The availability of trace elements in soil solution is ultimately controlled by soil minerals. Hence, reagents are often selected to target specific geochemical soil phases. Target phases include water soluble, exchangeable, organically bound, carbonate bound, manganese oxides, iron oxides, residual and mineral lattices. Different reagents have been used to target the same phase (e.g. the carbonate phase can be targeted by acetic acid, sodium acetate or EDTA)[105] and considerable debate exists in the literature over the preferred reagent for a specific target. Sometimes a sample is treated with a series of reagents, where each reagent is chosen to target different phases.

### 6.1.3 Sequential Extraction

The treatment of a sample with a series of reagents is a sequential extraction. A large number of different schemes have been used to sequentially extract soils and sediments, for example references[106,107,108,109]. The number of steps (from 2 to 8) and the target phases vary between protocols. Consequently results from different schemes are not directly comparable, though generally similar trends in analye recovery from target phases have been observed between different schemes[110].

The three-stage BCR sequential extraction was developed in an attempt to standardize different schemes[109]. Three different sequential extraction schemes were compared. Results of extractions following the different procedures were crudely converted to three target phases (exchangeable/carbonate, reducible/organic/sulfide and residual). Differences in amounts extracted between different protocols were shown, but also between different laboratories following the same procedure. This again highlighted the need for a harmonized extraction procedure and also the need for a certified reference material for use in method validation. Certified values of the extractable content of cadmium, chromium, copper, nickel, lead and zinc from a sediment reference material (CRM601) following the three step BCR sequential extraction were the result of an inter-laboratory trial[111].

The original BCR procedure has been used with good reproducibility within laboratories. The use of a sediment standard reference material showed excellent reproducibility except from analytes close to detection limits and analytes heterogeneously distributed within the reference material[112]. The original procedure was also applied to sewage sludge and showed good reproducibility (RSD's < 7 %, n = 8)[113]. Good agreement between (a) the sum of metal extracted at each step of the BCR sequential extraction plus the residual fraction and (b) pseudo total metal content for lake sediment has been reported[114]. Good reproducibility was also shown from an application of the BCR sequential extraction to in house reference materials and to different soil samples collected from the same locations annually for a period of over a decade[115].

However inter-laboratory trials highlighted unacceptable variation between laboratory results. When, major sources of variability in the different steps were assessed[116], variability in extraction efficiency at step 2 was found to be unacceptable. The major source of variability was related to differences in pH of the hydroxylammonium hydrochloride used at step 2[117]. The original BCR procedure was thus modified to improve reproducibility at step 2. To acidify the step 2 reagent a fixed volume of nitric acid was recommend to be added, as an alternative to adjustment of the extractant to a prescribed pH. The concentration of hydroxylammonium hydrochloride was also increased (from 0.1 mol $L^{-1}$ to 0.5 mol $L^{-1}$) in the modified procedure. The modified protocol also recommended inclusion of an additional, residual, extraction stage (step 4) to allow comparison with pseudo total digestion results for validation purposes.

The original and the modified BCR sequential extractions have been compared. An inter-laboratory comparison using a certified reference material as a substrate showed lower inter-laboratory RSD's for extraction of cadmium, chromium, copper, nickel and lead in step 2 following the modified pocedure[118]. This was attributed to the increased amount of metals extracted at step 2 by the lower pH and higher extractant concentration used in the modified procedure. The original and the modified procedure have also been compared using sediments and industrial soil[119]. The modified procedure was thought to dissolve similar amounts of manganese oxides but significantly greater amounts of iron oxides at step 2 compared to the original procedure. When the original and the old BCR schemes were compared to other schemes extracting standard reference materials[120], the study highlighted the importance of using harmonized sequential extraction procedures due to element, substrate and protocol specific differences in extraction efficacy.

### 6.1.4 Target Phases of the BCR Sequential Extraction

Section 2.4 describes reagent preparation and extraction procedures used in the BCR protocol. The phases targeted in each extraction step are described below.

#### 6.1.4.1 Exchangeable, Water and Acid Soluble Phases

The water-soluble fraction is essentially the soil solution. The exchangeable fraction includes metals weakly adsorbed on the surfaces of mineral and organic matter particles (see section 1.1.4 and 1.1.5). Some sequential extraction schemes attempt to isolate these phases separately but a relevantly short extraction procedure was desired by BCR and so these were considered together. The acetic acid used will also dissolve carbonates and release bound metals.

### 6.1.4.2 Reducible Phase

Iron and manganese oxyhyroxides are the major reducible mineral phases in soil. Iron oxides are dissolved by acidic attack, reduction and chelation[121]. Different reagents have been used to target the reducible phase, mainly based upon hydroxylammonium hydrochloride, dithionite/citrate or oxalate. Dithionite/citrate extraction introduces problems of sulfide re-precipitation, reagent purity and blockages during analysis[107]. 0.1 M hydroxylammonium hydrochloride has been shown to efficiently dissolve manganese from sediments[106]. Increasing concentration of hydroxylammonium hydrochloride up to 0.25 M increased extraction of iron, but not significantly. Less than 8 % of total iron was dissolved.

The use of oxalate reagents provides a more efficient dissolution of the iron oxide phase[122]. The use of 0.2 M ammonium oxalate and 0.2 M oxalic acid in the dark has been used to target the amorphous iron oxides[123]. Adding a strong reducing agent (e.g. ascorbic acid) and extracting in the light provides sufficiently severe conditions to dissolve even the crystalline iron oxide. Table 6.1 shows the reagents used to target the reducible fractions separately in a sequential extraction.

| Target Phase | Reagent |
|---|---|
| Manganese oxide | 0.1 M $NH_2OH.HCl$, 30 min |
| Amorphous iron oxides | 0.2 M ammonium oxalate and 0.2 M oxalic acid, 4 h in dark |
| Crystalline iron oxides | 0.2 M ammonium oxalate, 0.2 M oxalic acid and 0.1 M ascorbic acid, 30 min 80 °C |

*Table 6.1: Target reducible phases from a sequential extraction scheme*[124].

The BCR sequential extraction uses hydroxylammonium hydrochloride to target the reducible phase. As the oxalate reagent is able to dissolve greater amounts of iron it can be argued that an oxalate extraction at step 2 might be more specific, or in fact is less specific and is dissolving iron from other, non-target soil fractions.

#### 6.1.4.3 Oxidizable Phase

An oxidising agent is chosen in order to dissolve organic matter and sulfides, thereby releasing associated metals. A second medium (ammonium acetate) is required to then retain the released metals in solution for analysis.

#### 6.1.4.4 Residual or Pseudo-total

True total metal concentrations require dissolution of soil by use of acids such as hydrofluoric acid (HF). However, for pollution studies, the increased information gained does not generally warrant the risk associated with handling HF. Instead concentrated acids such as HCl or $HNO_3$ are used under high temperature and/or pressure. This dissolves nearly all the material, excluding primary silicates thus releasing most metals present in the sample. If performed after the BCR extraction, aqua regia digestion gives residual values. These can be compared to values obtained from a separate digestion of the same soil for mass balance and method validation.

### 6.1.5 Limitations of Sequential Extraction

Method validity, re-adsorption of analytes and phase specificity are the major critisms of sequential extraction schemes[125,126,127].

#### 6.1.5.1 Validation

Section 6.1.3 discussed some previous work generally showing good reproducibility within laboratories using the BCR sequential extraction procedure and the alterations that were made to improve inter-laboratory comparability. The production and use of certified reference materials has also helped give confidence in the results of sequential extractions. However few appropriate CRM's are available (only BCR CRM 601 and 701, both certified for use with the BCR extraction protocol).

To obtain additional reference data, a variety of reference materials not originally intended for validation of sequential extractions have been extracted using a variety of protocols. Different reference materials certified for total metal content were extracted following a five step sequential extraction based on the Tessier procedure[128]. Recovery of most analytes from the samples was approximately 92 %. Potassium was the element with the lowest recovery (65.3 %) and lead the highest recovery (138 %). The low potassium recovery was from one out of four materials extracted and the high lead recovery from one out of three materials extracted. Recoveries of potassium and lead from the other materials were close to 100 %. The Tessier extraction was also applied to three NIST standard reference materials certified for total element content[129]. Recoveries were typically between 90 and 105 %. The concentrations of 20 elements from 10 reference materials were determined after a 5 step sequential extraction, developed by the Geological Survey of Canada[130]. Recoveries were again in good agreement with certified total values but the amount of metals released from the target phases was different to those released following the Tessier scheme. The modified BCR sequential procedure was used to extract a sewage sludge amended soil (CRM483R) as part of an inter-laboratory comparison[131]. Generally results produced by the six laboratories were in good agreement (RSD of laboratory means typically < 20 %). The modified BCR procedure was also applied to a range of certified and standard reference materials[132]. Again results were in good agreement with target values of extractable metals from CRM601 and CRM483R. Table 6.2 shows target phase extraction results for iron, manganese and lead by three different methods applied to three different materials. Method A is the Tessier scheme, Method B is the Geological Survey of Canada scheme and Method C is the modified BCR sequential extraction.

| Nominal phase | Concentration of iron extracted at each target phase (mg $kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SRM2709 | | SRM2710 | | | SRM2711 | | |
| | A[129] | B[130] | A[129] | B[130] | C[132] | A[129] | B[130] | C[132] |
| Exchangeable | 2.9 | 60 | 37 | 90 | 16 | 6.4 | 40 | 19 |
| Carbonate | 60 | | 168 | | | 32.2 | | |
| Amorphous Fe(OH)x | 1 930 | 5 240 | 5 150 | 9 420 | 4 510 | 1 440 | 4 080 | 1390 |
| Crystalline Fe | | 17 000 | | 7 330 | | | 7 620 | |
| Organic matter/sulfide | 133 | 4 210 | 468 | 5 110 | 1 080 | 104 | 4 000 | 298 |
| Residual | 32 000 | 8 020 | 28 100 | 8 610 | 25 400 | 26 900 | 9 880 | 26 200 |
| Sum | 34 100 | 34 500 | 33 900 | 30 600 | 31 000 | 28 500 | 25 600 | 27 900 |
| Target | 35 000 ± 1 100 | | 33 800 ± 1 000 | | | 28 900 ± 600 | | |

*Table 6.2a: Sequential extraction results for iron extracted from three NIST reference materials, by Method A ($MgCl_2$, NaOAc, $NH_2OH.HCl$ @96 °C, $H_2O_2$@85 °C, HF), Method B (NaOAc, $NH_2OH.HCl$ @60 °C, $NH_2OH.HCl$ @90 °C, acidic $KClO_3$, HF) and Method C ($CH_3CO_2H$, $NH_2OH.HCl$, $H_2O_2$@85 °C,aqua regia).*

| Nominal phase | Concentration of manganese extracted at each target phase (mg $kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SRM2709 | | SRM2710 | | | SRM2711 | | |
| | A[129] | B[130] | A[129] | B[130] | C[132] | A[129] | B[130] | C[132] |
| Exchangeable | 16.7 | 135 | 912 | 1005 | 2 780 | 16.7 | 236 | 577 |
| Carbonate | 93 | | 395 | | | 167 | | |
| Amorphous Fe(OH)x | 182 | 166 | 4 660 | 4522 | 6 590 | 170 | 124 | 204 |
| Crystalline Fe | | 103 | | 1525 | | | 58 | |
| Organic matter/sulfide | 41.8 | 25 | 629 | 165 | 2 120 | 26.2 | 23 | 43 |
| Residual | 244 | 63 | 3 830 | 1851 | 6 640 | 265 | 129 | 317 |
| Sum | 578 | 492 | 10 400 | 9068 | 18 130 | 645 | 570 | 1 140 |
| Target | 538 ± 17 | | 10 100 ± 400 | | | 638 ± 28 | | |

*Table 6.2b: Sequential extraction results for manganese extracted from three NIST reference materials, by Methods A, B and C.*

| Nominal phase | Concentration of lead extracted at each target phase (mg $kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SRM2709 | | SRM2710 | | | SRM2711 | | |
| | $A^{129}$ | $B^{130}$ | $A^{129}$ | $B^{130}$ | $C^{132}$ | $A^{129}$ | $B^{130}$ | $C^{132}$ |
| Exchangeable | <d.l. | 1.00 | 553 | 2 797 | 624 | 2.3 | 843 | 280 |
| Carbonate | <d.l. | | 1 300 | | | 506 | | |
| Amorphous Fe(OH)x | <d.l. | 4.68 | 1 250 | 2 021 | 4 240 | 372 | 235 | 774 |
| Crystalline Fe | | 6.70 | | 359 | | | 48.2 | |
| Organic matter/sulfide | <d.l. | 0.653 | 900 | 63.0 | 250 | 116 | 3.68 | 108 |
| Residual | 24.2 | 7.17 | 1 080 | 217 | 458 | 90 | 13.4 | 51 |
| Sum | 24.2 | 20.2 | 5 080 | 5 457 | 5 570 | 1 090 | 1 144 | 1 210 |
| Target | 18.9 ± 0.5 | | 5 532 ± 80 | | | 1 162 ± 31 | | |

*Table 6.2c: Sequential extraction results for lead extracted from three NIST reference materials, by Methods A, B and C.*

Table 6.2 shows generally excellent agreement between target values of the three SRM's and total amounts of metal extracted by the three different procedures. However agreement between metal concentrations extracted at the step(s) supposedly targeting the same phase by different reagents is poor. This reinforces the fact that sequential extractions are not necessarily phase specific and that the fractionation pattern produced is operationally defined. Even within the same procedure small details such as the type of mechanical shaker have been reported to have a large influence on extraction results[133].

The sequential extraction of industrial contaminated soil highlighted potential problems of method validation on material likely to contain interfering species[134]. Problems with unpolluted soils where metals might be present at low concentrations have also been reported[135]. The validation of metal determination in sample extracts is also important to ensure accurate results. The need for modifiers when using AAS to determine chromium, copper or lead content extracted at steps 1 and 2 by the BCR procedure[136,137], matrix effects on calibration curves[136,137], and the requirement to calibrate by standard additions when using GFAAS for cadmium concentration determination in ammonium acetate extracts[101] have been reported.

#### 6.1.5.2 Re-adsorption during Sequential Extractions and Phase Specificity

The dissolution of the target soil phase should release trace metals originally bound within that phase. However the possibility exists that the released metal might re-adsorb to a different phase of the solid before they can be isolated for analysis, resulting in low recovery from the target phase. The amount of re-adsorption has been assessed kinetically[138]. A soil was extracted with hydroxylammonium hydrochloride to dissolve the reducible soil phase. Approximately 50 % of lead originally bound to the reducible soil phase (amount calculated kinetically) was not measured in the extract. The addition of radiotracers to the first extraction solution has also been used to assess cadmium and zinc re-adsorption[139]. Approximately 20 – 30 % of the added tracers were recovered at later extraction steps. Model minerals with known trace element distribution have also been used, and has often shown very poor specificity[140]. An example compared the application of the Tessier and BCR schemes to model substrates for lead fractionation and concluded alterations in lead distribution between phases was unacceptable[141]. A recent study comparing three sequential extraction procedures indicated the BCR reagent used at step 2 also released metals bound to organic matter and sulfides from some sediments[142]. Attempts to prevent re-adsorption using chelating agents have been reported. The addition of nitrilotriacetic acid (NTA) to the reagents used in the Tessier extraction may reduce re-adsorption[143]. Authors estimated an improved recovery of 18 % lead, 30 % nickel and 19 % zinc when the extraction was performed with NTA, and attributed this improvement to prevention of re-adsorption. Samples with high organic matter content were also found likely to be more susceptible to greater re-adsorption problems.

### 6.1.6 Adaptations and Alternatives

A further limitation of the sequential extraction approach is amount of time it requires. Adaptations to sequential extraction procedures have been investigated to reduce extraction time using ultrasound[144] and microwave energy[145]. Overall extraction time was reduced from approximately 50 h to less than 5 h, with comparable metal fractionation between the BCR procedure and a faster ultrasound method[146]. Further investigation indicated the sonication conditions required to produce similar results as found by the conventional BCR procedure were substrate specific. The use of microwaves was shown to reduce the extraction time even more dramatically from hours to seconds (at each step of the BCR protocol) but chromium was the only analyte investigated in this work, and so the modified method may not be more generally applicable[147].

Miniaturization of sequential extraction procedures has also been investigated, when the approach was applied to airborne particulate matter using sonication and capillary electrophoresis[148]. This might be useful where only small amounts of sample are available for sequential extraction.

Alternative approaches to determine element associations with geochemical phases have been investigated. The BCR sequential extraction has been compared to kinetic extraction methods. The use of at least one non-specific reagent to classify metal leachability was used to characterize sediment[149]. Non-specific dissolution studies using chemometric data processing have also been reported but this method requires the determination of many analytes[150]. The amounts of major elements extracted at different chemometric components can be used to indicate major mineral associations.

The target phase of the 2nd step in the BCR sequential extraction is the reducible phase. As has been discussed in the previous sections extractants are not phase specific. However alternative, more specific alternatives to hydroxylammonium hydrochloride have commonly been used to target the iron oxide phases, specifically the oxalate-based reagents[91,108,124,127]. Potential problems of cadmium and lead precipitation in oxalate solutions exist, as was demonstrated using solubility tests at 120 mg $L^{-1}$ metal concentration[117]. An investigation into phase specificity of hydroxylammonium hydrochloride and oxalate for manganese and iron oxide phases studied three soils[151]. A buffered oxalate or hydroxylammonium hydrochloride extraction at room temperature was used to target the manganese and amorphous iron oxide phases. Similar solutions were used at higher temperatures to target the crystalline iron oxide phase. The oxalate reagents used to target these phases were found to be more phase specific than the hydroxylamine hydrochloride alternatives. However possible problems due to precipitation of cadmium and lead oxalate were shown. The potential for nickel or zinc precipitation was also mentioned. The solubility product of the oxalate salt, and oxalate complex formation constant were thought to have the major effect on re-precipitation.

## 6.2 Aims

The work in this chapter was a comparison of the revised BCR sequential extraction with an alternative procedure in which acidic ammonium oxalate replaced hydroxylammonium hydrochloride in step 2.

## 6.3 Experimental

### 6.3.1 Samples

Three different materials were studied. A certified reference material CRM601 as supplied. CRM601 was originally sediment from lake Flumendosa, Italy. A sewage-sludge amended soil from Great Billing sieved to < 1 mm (Northampton, UK) and an industrial contaminated soil sieved to < 2 mm (from a derelict chemical manufacturing site in SW Scotland, UK) were also extracted.

### 6.3.2 Extraction and Analysis

Samples were extracted following the procedure described in Section 2.4. The procedure using 0.5 mol $L^{-1}$ hydroxylammonium hydrochloride in step 2 is the modified BCR extraction and is referred to henceforth in the text as 'BCR'. The procedure using acidic ammonium oxalate in step 2 is referred to henceforth in the text as the 'Oxalate' extraction. Analysis of extracts was performed as described in section 2.5 by FAAS for calcium (rarely previously studied); iron and manganese (to obtain information on oxyhydroxy phases targeted at step 2); copper, lead and zinc (potentially toxic 'urban' metals).

### 6.3.3 Pulse Nebulisation FAAS

Continuous nebulisation of samples in extract solution B2 (oxalate) rapidly resulted in the burner head becoming partially blocked with precipitating salt. This caused flame instability and loss of precision. The problem was overcome by introducing the sample in 200 µL aliquots. Integration time was increased to 6 seconds to allow all of the aliquot to pass through the flame during read-out. A plastic adapter was fitted to the end of the nebuliser to allow the aliquot to be injected using a 1000 µL micropipette. This resulted in a loss of sensitivity but the burner head remained clear and the precision improved.

### 6.3.4 Detection Limits

Detection limits for elements in aqua regia are shown in Section 2.5.4. In this work extracts were analysed against matrix-matched standards by FAAS and GFAAS. Table 6.3 shows the detection limits found in the different extracts analysed.

| | | Step 1 | Step 2 BCR | Step 2 oxalate | Step 3 |
|---|---|---|---|---|---|
| | | Solution A | Solution B1 | Solution B2 | Solution D |
| Calcium<br>423 nm | $D_L$ inst. (ng mL$^{-1}$) | 27 | 110 | - | 32 |
| | $D_L$ pro. (mg kg$^{-1}$) | 1.1 | 4.4 | - | 1.6 |
| Copper<br>325 nm | $D_L$ inst. (ng mL$^{-1}$) | 22 | 23 | $69^{b}$ | 25 |
| | $D_L$ pro. (mg kg$^{-1}$) | 0.88 | 0.91 | $2.8^{b}$ | 1.2 |
| Iron<br>248 nm | $D_L$ inst. (ng mL$^{-1}$) | 21 | 51 | $270^{b}$ | 22 |
| | $D_L$ pro. (mg kg$^{-1}$) | 0.84 | 2.0 | $11^{b}$ | 1.1 |
| Lead<br>217 nm | $D_L$ inst. (ng mL$^{-1}$) | $6.0^{a}$ | 67 | $7.7^{a}$ | 71 |
| | $D_L$ pro. (mg kg$^{-1}$) | 0.24 | 2.7 | $0.31^{a}$ | 3.6 |
| Manganese<br>280 nm | $D_L$ inst. (ng mL$^{-1}$) | 12 | 15 | $130^{b}$ | 8.9 |
| | $D_L$ pro. (mg kg$^{-1}$) | 0.48 | 0.59 | $5.1^{b}$ | 0.44 |
| Zinc<br>214 nm | $D_L$ inst. (ng mL$^{-1}$) | 6.1 | 12 | $7.0^{b}$ | 8.5 |
| | $D_L$ pro. (mg kg$^{-1}$) | 0.24 | 0.49 | $0.28^{b}$ | 0.42 |

*Table 6.3: Detection limits in different matrices by conventional nebulization and FAAS, (except a = GFAAS, b = pulse nebulization).*

## 6.4 Results and Discussion

### 6.4.1 Calcium

Table 6.4 shows the results obtained for calcium sequential extraction and pseudo total analysis of the soil samples. Figure 6.1 shows the average amount of calcium extracted at each step of the sequential extraction as a percent of the pseudo total concentration, plotted as a bar graph. This allows results to be compared between materials with different total calcium concentrations. Perfect mass balance will result in the bar reaching 100 %.

| | | Step 1 | | Step 2 | | Step 3 | | Step 4 | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Scheme | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % |
| CRM601 | BCR | 26 500 | 1.9 | 2 480 | 2.6 | 22.7 | 13 | 449 | 22 |
| CRM601 | Oxalate | 26 000 | 4.3 | <d.l. | - | 5 180 | 2.5 | 465 | 14 |
| G.Billing | BCR | 10 000 | 2.5 | 3 460 | 4.4 | 22.1 | 12 | 35.5 | 49 |
| G.Billing | Oxalate | 10 100 | 5.4 | <d.l. | - | 3 570 | 1.4 | 278 | 20 |
| Industrial | BCR | 780 | 3.0 | 417 | 17 | 69.1 | 13 | 799 | 19 |
| Industrial | Oxalate | 891 | 7.8 | <d.l. | - | 970 | 18 | 938 | 50 |
| | | Sum of 1 to 4 | | | | Pseudo total | | | |
| | | $\bar{x}$ (µg g$^{-1}$) | | *RSD % | | $\bar{x}$ (µg g$^{-1}$) | | RSD % | |
| CRM601 | BCR | 29 500 | | 1.9 | | 18 500 | | 6.1 | |
| CRM601 | Oxalate | 31 700 | | 4.0 | | | | | |
| G.Billing | BCR | 13 600 | | 2.6 | | 13 400 | | 2.4 | |
| G.Billing | Oxalate | 13 900 | | 4.6 | | | | | |
| Industrial | BCR | 2 060 | | 9.8 | | 1 290 | | 14.3 | |
| Industrial | Oxalate | 2 800 | | 26 | | | | | |

*Table 6.4: Average amounts of calcium extracted by two different sequential extraction procedures and pseudo total values (*calculated from sum of extraction steps of each replicate), n=3.*

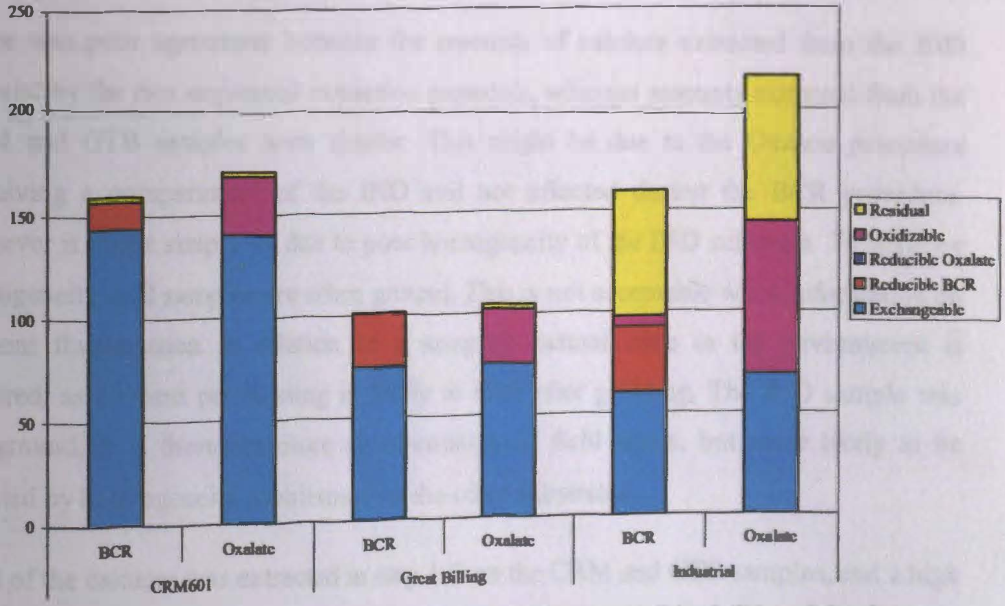

*Figure 6.1: Average amounts of calcium extracted in the steps of the BCR and Oxalate sequential extraction procedures expressed as percentages of pseudo total concentrations.*

Precision of results was generally very good (RSD $< 10$ %), but worsened in the later extraction steps (RSD $\approx 25$ %). The sum of the extraction steps showed low RSD's for the CRM and Great Billing (GTB) soil (RSD $< 5$ %) but poorer precision was obtained for the industrial soil (IND), especially for the Oxalate procedure (RSD = 26 %). Much more calcium was released in the sequential extractions of the CRM and IND materials than the pseudo total value. Poor mass balance might be due to inefficient microwave digestion. The ISO standard method for pseudo total digestion with aqua regia allows the sample to digest for 16 hours at room temperature before refluxing[152]. The mass balance for the GTB material was good (103 %). Therefore microwave efficiency is probably not low when applied to the GTB samples. The CRM has the highest total calcium concentration ($\approx$ 26 000 mg kg$^{-1}$). The IND soil has the lowest calcium concentration but is the coarsest material. It is possible total calcium level and particle size of the samples has a strong influence on microwave efficiency.

There was poor agreement between the amounts of calcium extracted from the IND material by the two sequential extraction protocols, whereas amounts extracted from the CRM and GTB samples were similar. This might be due to the Oxalate procedure dissolving a compartment of the IND soil not affected during the BCR procedure. However it might simply be due to poor homogeneity of the IND substrate. To improve homogeneity, soil samples are often ground. This is not acceptable when information on element fractionation in relation to a sample's natural state in the environment is required, as element partitioning is likely to alter after grinding. The IND sample was not ground. It is therefore more representative of field status, but more likely to be affected by heterogeneity problems than the other substrates.

Most of the calcium was extracted in step 1 from the CRM and GTB samples, and a high proportion of the calcium was extracted from the IND sample at step 1. The oxalate solution did not extract enough calcium in step 2 for the analyte to be detected. In contrast, the BCR reagent extracted most of the calcium left in the samples after step 1, except from the industrial soil. The calcium not extracted by the oxalate reagent was recovered at step 3. Very little calcium was extracted from the CRM and GTB samples in step 4, but the industrial soil had quite a high percent of calcium released at step 4.

Calcium oxalate has a low solubility product (2.57 x $10^{-9}$ mol $L^{-1}$)[153] and low complex formation constant (log $K_1$ = 1.66)[154]. Re-precipitation of the calcium released by oxalate reagent attack on the soil matrix might explain the low amount extracted when reagent B2 was used.

### 6.4.2 Copper

Table 6.5 shows the results obtained for copper sequential extraction and pseudo total analysis of the soil samples. Figure 6.2 shows the average amount of copper extracted at each step of the sequential extraction as a percent of the pseudo total concentration, plotted as a bar graph.

|  |  | Step 1 |  | Step 2 |  | Step 3 |  | Step 4 |  |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Scheme | $\bar{x}$ (µg $g^{-1}$) | RSD % | $\bar{x}$ (µg $g^{-1}$) | RSD % | $\bar{x}$ (µg $g^{-1}$) | RSD % | $\bar{x}$ (µg $g^{-1}$) | RSD % |
| CRM601 | BCR | 11.8 | 4.7 | 66.0 | 1.9 | 82.1 | 3.4 | 59.4 | 0.4 |
| CRM601 | Oxalate | 11.2 | 8.0 | 121 | 0.6 | 49.1 | 1.3 | 43.2 | 4.4 |
| G.Billing | BCR | 16.0 | 6.4 | 137 | 6.2 | 178 | 1.7 | 41.7 | 15 |
| G.Billing | Oxalate | 17.0 | 1.5 | 377 | 8.8 | 46.8 | 5.9 | 17.5 | 3.7 |
| Industrial | BCR | 4.87 | 8.1 | 22.8 | 6.4 | 27.4 | 3.0 | 28.0 | 32 |
| Industrial | Oxalate | 4.64 | 7.8 | 74.3 | 12.6 | 9.30 | 24 | 22.9 | 39 |

|  |  | Sum of 1 to 4 |  | Pseudo total |  |
|---|---|---|---|---|---|
|  |  | $\bar{x}$ (µg $g^{-1}$) | RSD % | $\bar{x}$ (µg $g^{-1}$) | RSD % |
| CRM601 | BCR | 219 | 1.3 | 210 | 1.5 |
| CRM601 | Oxalate | 225 | 1.5 |  |  |
| G.Billing | BCR | 372 | 1.7 | 419 | 1.8 |
| G.Billing | Oxalate | 458 | 7.5 |  |  |
| Industrial | BCR | 83.1 | 12 | 93.0 | 5.0 |
| Industrial | Oxalate | 111 | 18 |  |  |

*Table 6.5: Average amounts of copper extracted by two different sequential extraction procedures and pseudo total values (n=3).*

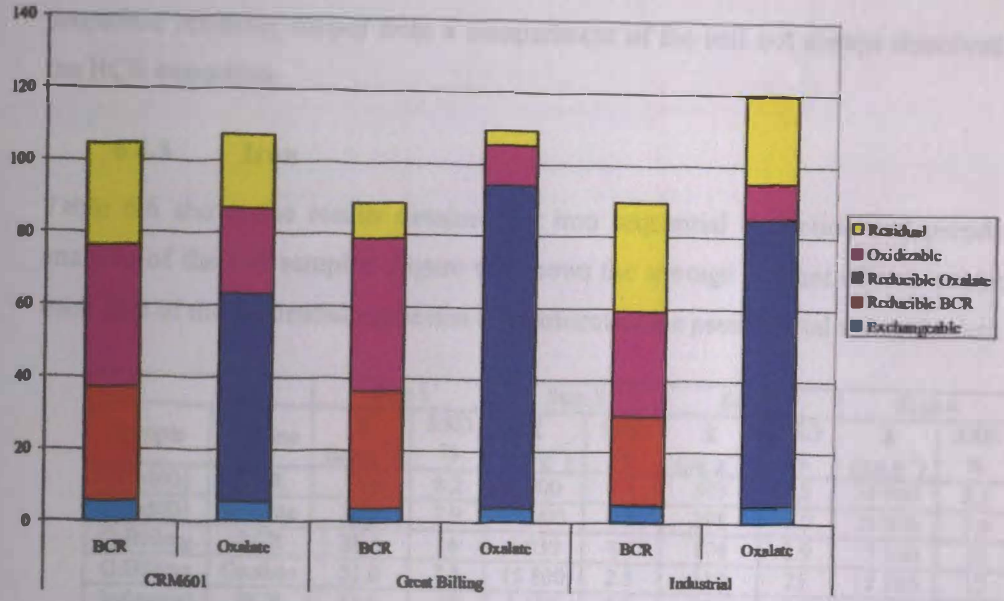

*Figure 6.2: Average amounts of copper extracted in the steps of the BCR and Oxalate sequential extraction procedures expressed as percentages of pseudo total concentrations.*

Precision of results was generally very good (RSD < 10 %), but worsened in the later extraction steps, especially for the IND sample (RSD > 30 %). The sum of the extraction steps showed low RSD's for the CRM and GTB samples (RSD ≈ 5 %) but poorer precision from the industrial soil (RSD ≈ 15 %). The extraction mass balance for all samples was good (89 - 120 %).

Step 1 extracted a small percentage of copper from all samples. In step 2 the oxalate reagent consistently extracted more copper than the BCR reagent. The copper not extracted by the BCR reagent in step 2 appeared to be released in step 3. Copper oxalate solubility is low ($2.87 \times 10^{-9}$ mol $L^{-1}$). Instead of the insoluble salt formation it is possible the oxalate forms a soluble copper-oxalate complex ($\log K_1 = 6.23$ and $\log K_2 = 4.04$). Slightly lower overall amounts of copper are extracted following the BCR protocol compared to the oxalate extraction. This might be indicative of the oxalate procedure releasing copper from a compartment of the soil not always dissolved using the BCR extraction.

### 6.4.3 Iron

Table 6.6 shows the results obtained for iron sequential extraction and pseudo total analysis of the soil samples. Figure 6.3 shows the average amount of iron extracted at each step of the sequential extraction as a percent of the pseudo total concentration.

| | | Step 1 | | Step 2 | | Step 3 | | Step 4 | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Scheme | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % |
| CRM601 | BCR | 33.4 | 8.2 | 4 700 | 1.1 | 303 | 0.8 | 34 900 | 5.5 |
| CRM601 | Oxalate | 28.2 | 7.9 | 11 900 | 4.3 | 298 | 1.0 | 25 800 | 3.9 |
| G.Billing | BCR | 28.4 | 16 | 6 030 | 4.4 | 174 | 2.9 | 17 100 | 10 |
| G.Billing | Oxalate | 31.0 | 7.3 | 15 800 | 2.1 | 113 | 21 | 12 100 | 12 |
| Industrial | BCR | 11.6 | 13 | 1 630 | 5.3 | 255 | 9.5 | 16 900 | 18 |
| Industrial | Oxalate | 10.0 | 13 | 8 820 | 14 | 190 | 3.4 | 15 200 | 27 |
| | | Sum of 1 to 4 | | | | Pseudo total | | | |
| | | $\bar{x}$ ($\mu g\ g^{-1}$) | | RSD % | | $\bar{x}$ ($\mu g\ g^{-1}$) | | RSD % | |
| CRM601 | BCR | 40 000 | | 4.7 | | 35 300 | | 3.4 | |
| CRM601 | Oxalate | 38 000 | | 3.3 | | | | | |
| G.Billing | BCR | 23 300 | | 8.3 | | 26 100 | | 1.0 | |
| G.Billing | Oxalate | 28 000 | | 6.1 | | | | | |
| Industrial | BCR | 18 800 | | 16 | | 22 700 | | 4.8 | |
| Industrial | Oxalate | 24 200 | | 22 | | | | | |

*Table 6.6: Average amounts of iron extracted by two different sequential extraction procedures and pseudo total values (n=3).*

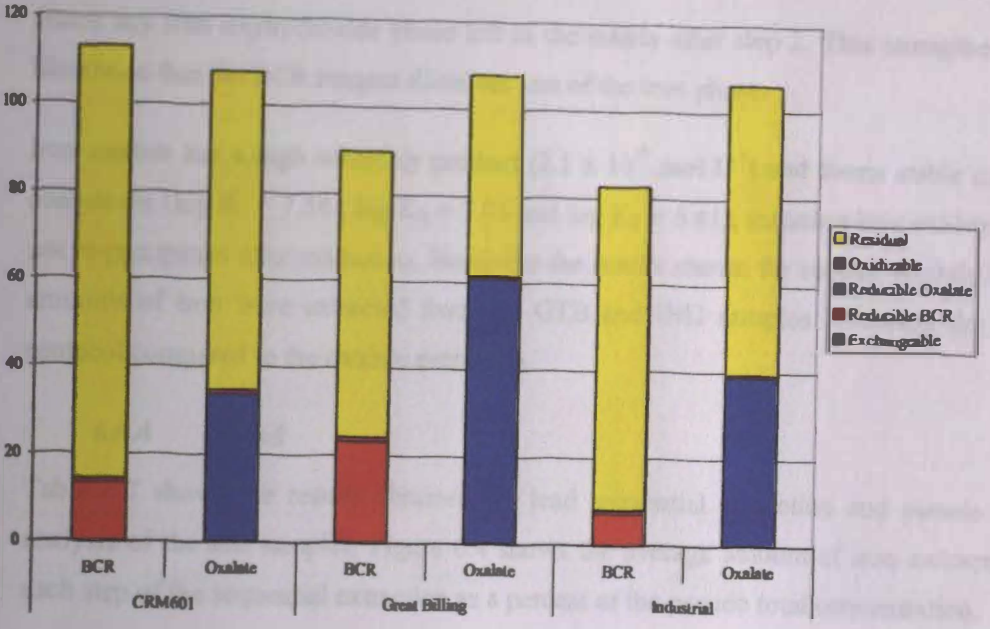

*Figure 6.3: Average amounts of iron extracted in the steps of the BCR and Oxalate sequential extraction procedures expressed as percentages of pseudo total concentrations.*

Precision of results was generally very good (RSD < 10 %), but was worse at the later extraction steps and from the industrial soil (RSD > 20 %). The sum of the extraction steps showed low RSD's from the CRM and GTB samples but poorer precision from the industrial soil, probably due to sample heterogeneity, as discussed previously. The extraction mass balance for all samples was good (83 - 113 %).

Step 1 extracted very little iron from all samples. In step 2 the oxalate reagent extracted considerably more iron than the BCR reagent. Previous literature suggests oxalate is able to dissolve iron oxide phases that are not accessable to hydroxylammonium hydrochloride (see sections 6.1.4.2 and 6.1.6).

The iron that oxalate recovers, but is inaccessible to the BCR reagent, was either released in step 4 (as suggested by CRM601 results) or not at all (as suggested by GTB and IND results). The strong oxidizing agent used in step 3 would not significantly attack any iron oxyhydroxide phase left in the matrix after step 2. This strengthens the likelihood that the BCR reagent dissolves less of the iron phase.

Iron oxalate has a high solubility product (2.1 x $10^{-7}$ mol $L^{-1}$) and forms stable oxalate complexes (log $K_1 = 7.54$ , log $K_2 = 7.05$ and log $K_3 = 5.41$), meaning iron oxalate does not re-precipitate after extraction. Similar to the results shown for copper, slightly lower amounts of iron were extracted from the GTB and IND samples following the BCR protocol compared to the oxalate extraction.

### 6.4.4 Lead

Table 6.7 shows the results obtained for lead sequential extraction and pseudo total analysis of the soil samples. Figure 6.4 shows the average amount of iron extracted at each step of the sequential extraction as a percent of the pseudo total concentration.

| | | Step 1 | | Step 2 | | Step 3 | | Step 4 | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Scheme | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % |
| CRM601 | BCR | 1.80 | 8.3 | 207 | 0.8 | 28.8 | 18 | 30.2 | 33 |
| CRM601 | Oxalate | 1.70 | 7.6 | 9.00 | 8.0 | 217 | 1.8 | 26.2 | 41 |
| G.Billing | BCR | <d.l. | - | 334 | 4.6 | 96.0 | 9.8 | 129 | 12 |
| G.Billing | Oxalate | <d.l. | - | 32.1 | 1.7 | 469 | 14 | 80.6 | 10 |
| Industrial | BCR | 8.96 | 12 | 192 | 0.3 | 36.2 | 14 | 57.0 | 37 |
| Industrial | Oxalate | 8.64 | 1.1 | 100 | 9.7 | 139 | 20 | 50.8 | 26 |

| | | Sum of 1 to 4 | | Pseudo total | |
|---|---|---|---|---|---|
| | | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % |
| CRM601 | BCR | 268 | 4.4 | 269 | 1.9 |
| CRM601 | Oxalate | 254 | 4.8 | | |
| G.Billing | BCR | 560 | 3.6 | 599 | 0.3 |
| G.Billing | Oxalate | 581 | 9.6 | | |
| Industrial | BCR | 295 | 6.5 | 288 | 6.3 |
| Industrial | Oxalate | 299 | 13 | | |

*Table 6.7: Average amounts of lead extracted by two different sequential extraction procedures and pseudo total values (n=3).*

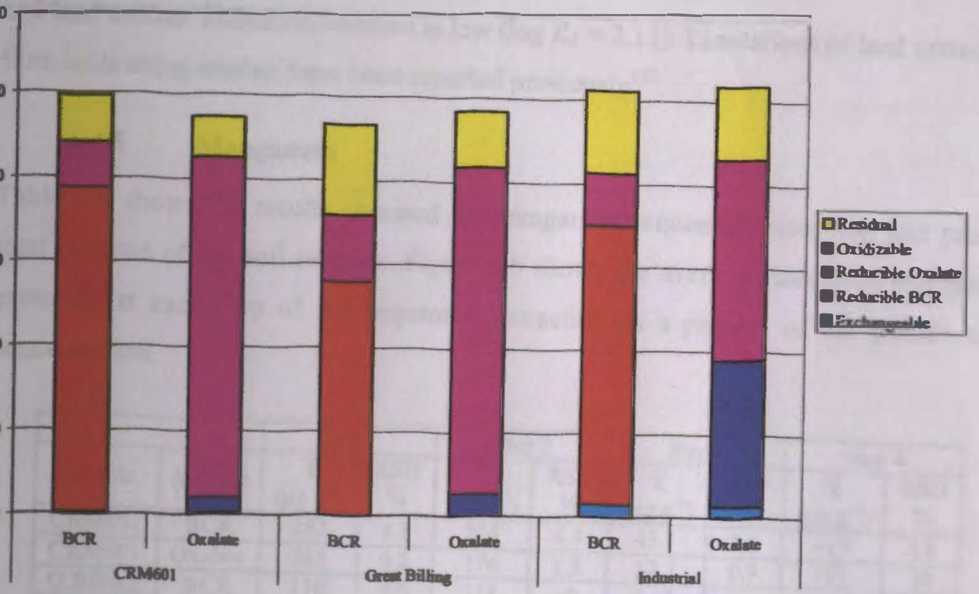

*Figure 6.4: Average amounts of lead extracted in the steps of the BCR and Oxalate sequential extraction procedures expressed as percentages of pseudo total concentrations.*

Precision of results was generally very good (RSD < 5%), but worsened in the later extraction steps (RSD ≈ 30 %). The total lead extracted from the GTB and IND samples showed poorer precision between replicates than when they were extracted following the BCR protocol (e.g. RSD = 6.5 cf. 13 %). There might be soil compartments that the Oxalate procedure is releasing metals from that are not accessible to the BCR extraction. Lead might be associated with this compartment in the GTB and IND samples. If this compartment was heterogeneously distributed within the GTB and IND samples it might explain the poorer precision when the Oxalate procedure is used. The extraction mass balance for all samples was very good (93 - 104 %).

Step 1 extracted very little lead from all samples. In step 2 the oxalate reagent extracted much less lead than the BCR reagent. The lead not extracted by the oxalate reagent appeared to be extracted at step 3. Lead oxalate has low solubility ($2.74 \times 10^{-11}$ mol $L^{-1}$)

and lead oxalate formation constant is low (log $K_1 = 2.11$). Limitations of lead extraction from soils using oxalate have been reported previously[151].

### 6.4.5 Manganese

Table 6.8 shows the results obtained for manganese sequential extraction and pseudo total analysis of the soil samples. Figure 6.5 shows the average amount of manganese extracted at each step of the sequential extraction as a percent of the pseudo total concentration.

| | | Step 1 | | Step 2 | | Step 3 | | Step 4 | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Scheme | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % |
| CRM601 | BCR | 282 | 4.1 | 214 | 4.4 | 43.1 | 3.4 | 425 | 4.8 |
| CRM601 | Oxalate | 285 | 0.2 | 176 | 1.3 | 52.7 | 0.9 | 352 | 10 |
| G.Billing | BCR | 110 | 3.9 | 114 | 10 | 5.12 | 22 | 48.9 | 16 |
| G.Billing | Oxalate | 113 | 1.6 | 81.0 | 4.4 | 24.5 | 1.4 | 48.7 | 18 |
| Industrial | BCR | 30.9 | 7.8 | 121 | 9.0 | 9.00 | 7.4 | 93.5 | 16 |
| Industrial | Oxalate | 33.1 | 12 | 142 | 6.0 | 16.0 | 21 | 81.1 | 30 |

| | | Sum of 1 to 4 | | Pseudo total | |
|---|---|---|---|---|---|
| | | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % | $\bar{x}$ ($\mu g\ g^{-1}$) | RSD % |
| CRM601 | BCR | 964 | 4.3 | 865 | 4.1 |
| CRM601 | Oxalate | 865 | 4.5 | | |
| G.Billing | BCR | 278 | 5.3 | 293 | 2.5 |
| G.Billing | Oxalate | 267 | 1.5 | | |
| Industrial | BCR | 254 | 4.6 | 266 | 4.2 |
| Industrial | Oxalate | 272 | 14 | | |

*Table 6.8: Average amounts of manganese- extracted by two different sequential extraction procedures and pseudo total values (n=3).*

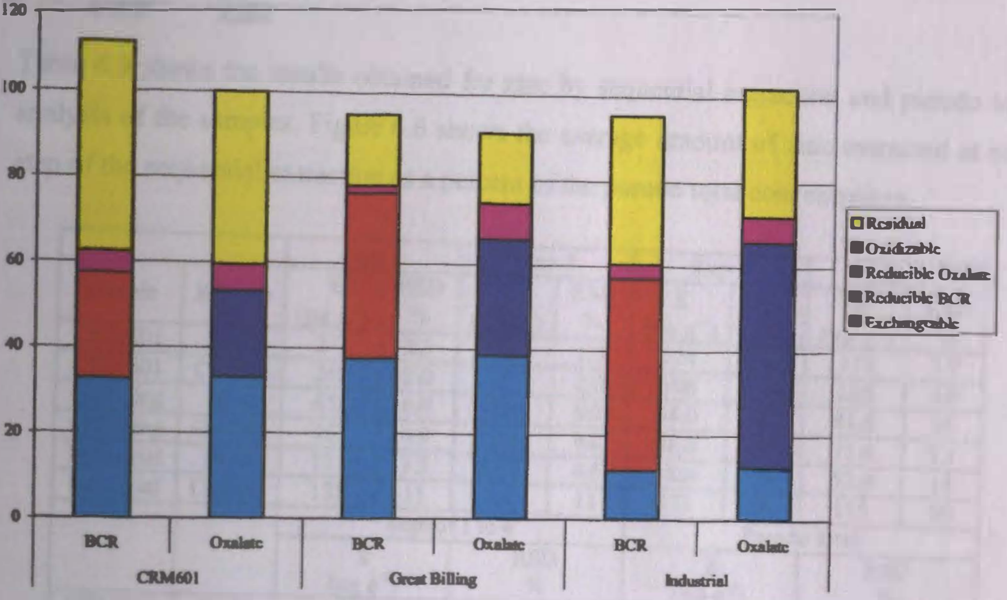

*Figure 6.5: Average amounts of manganese extracted in the steps of the BCR and Oxalate sequential extraction procedures expressed as percentages of pseudo total concentrations.*

Precision of results was generally very good (RSD < 10 %), but worsened at the later extraction steps (RSD ≈ 15 %). The sum of the extraction steps showed low RSD's from the CRM and GTB samples (RSD < 5%) but poorer precision from the industrial soil extracted by the Oxalate procedure (RSD = 14 %). The extraction mass balance for all samples was very good (91 - 111 %).

A significant amount of manganese was extracted at step 1. There appeared to be little difference between manganese extracted by either the BCR or the oxalate reagent in step 2, and it is therefore likely both reagents are dissolving similar amounts of manganese oxides. Hydroxylammonium hydrochloride has previously been shown to dissolve manganese containing minerals efficiently. Approximately 85 % of the total manganese content could be recovered from sediments using 0.025 – 2.5 mol $L^{-1}$ $NH_2OH.HCl$, with no increase in release of manganese with increasing extractant concentration[106].

### 6.4.6 Zinc

Table 6.9 shows the results obtained for zinc by sequential extraction and pseudo total analysis of the samples. Figure 6.6 shows the average amount of zinc extracted at each step of the sequential extraction as a percent of the pseudo total concentration.

|  |  | Step 1 |  | Step 2 |  | Step 3 |  | Step 4 |  |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Scheme | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % |
| CRM601 | BCR | 272 | 2.2 | 250 | 1.3 | 124 | 3.9 | 147 | 3.7 |
| CRM601 | Oxalate | 265 | 2.0 | 251 | 2.0 | 108 | 3.5 | 136 | 4.0 |
| G.Billing | BCR | 452 | 6.0 | 444 | 6.0 | 44.0 | 3.2 | 81.0 | 38 |
| G.Billing | Oxalate | 467 | 4.9 | 368 | 9.0 | 98.0 | 2.5 | 71.0 | 9.1 |
| Industrial | BCR | 121 | 3.3 | 62.0 | 4.6 | 58.0 | 14 | 52.0 | 14 |
| Industrial | Oxalate | 131 | 11 | 151 | 11 | 373 | 74 | 115 | 90 |

|  |  | Sum of 1 to 4 |  | Pseudo total |  |
|---|---|---|---|---|---|
|  |  | $\bar{x}$ (µg g$^{-1}$) | RSD % | $\bar{x}$ (µg g$^{-1}$) | RSD % |
| CRM601 | BCR | 794 | 1.3 | 698 | 1.9 |
| CRM601 | Oxalate | 760 | 1.2 |  |  |
| G.Billing | BCR | 1 020 | 5.7 | 1 150 | 1.4 |
| G.Billing | Oxalate | 1 000 | 5.7 |  |  |
| Industrial | BCR | 292 | 2.7 | 307 | 9.6 |
| Industrial | Oxalate | 768 | 46 |  |  |

*Table 6.9: Average amounts of zinc extracted by two different sequential extraction procedures and pseudo total values (n=3).*

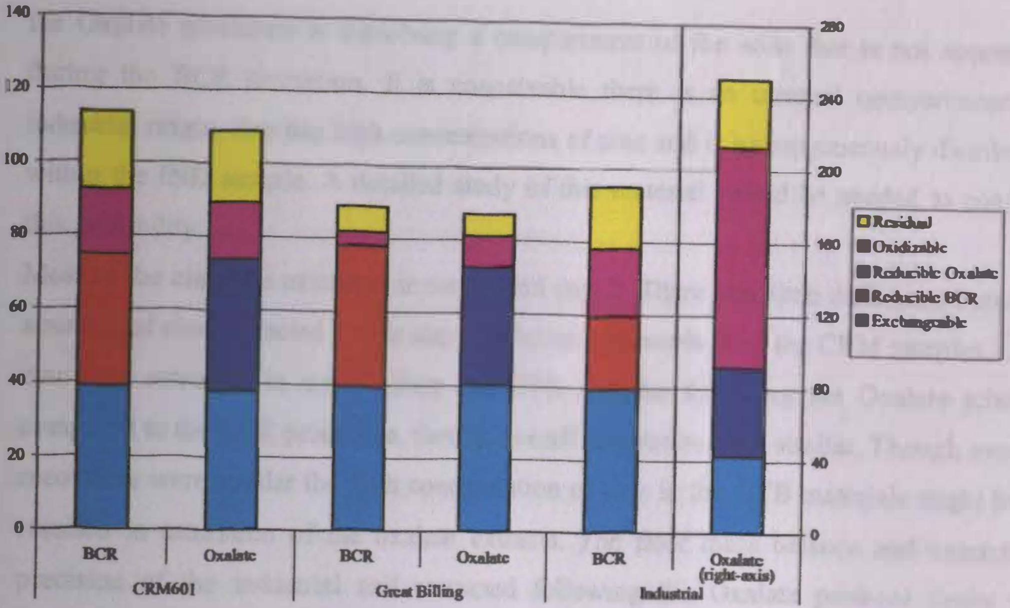

*Figure 6.6: Average amounts of zinc extracted in the steps of the BCR and Oxalate sequential extraction procedures expressed as percentages of pseudo total concentrations.*

Precision of results was generally very good (RSD < 5 %), but worsened at the later extraction steps. The sum of the extraction steps showed low RSD's from the CRM and GTB samples (RSD < 10 %) but poorer precision from the IND soil extracted following the Oxalate procedure. The extraction mass balance for all samples was good (recovery of 87 - 114 %) apart from zinc extraction from the IND soil following the Oxalate procedure (250 %). The amount of zinc extracted at step 3 was greater than the pseudo total concentration which might indicate there was a problem with the analysis of these samples. The industrial soil extracted following the Oxalate protocol showed poor precision between triplicate portions at steps 3 and 4. This might indicate either poor soil homogeneity or a problem with zinc contamination of these samples. Results obtained for the industrial samples have generally shown poorer precision than those for the CRM and GTB samples. This would suggest there is a higher probability that the poor agreement in zinc extraction is due to the heterogeneity of these samples. It is possible the Oxalate procedure is dissolving a compartment of the soils that is not accessible during the BCR extraction. It is conceivable there is an unusual compartment, of industrial origin, that has high concentrations of zinc and is heterogeneously distributed within the IND sample. A detailed study of this material would be needed to confirm this possibility.

Most of the zinc was extracted in step 1 and step 2. There was little difference between amounts of zinc extracted by the steps of the two protocols from the CRM samples. Less zinc was extracted in step 2 from the GTB samples following the Oxalate scheme compared to the BCR procedure, though overall recoveries were similar. Though overall recoveries were similar the high concentration of zinc in the GTB materials might have resulted in saturation of the oxalate extracts. The poor mass balance and extraction precision of the industrial soil extracted following the Oxalate protocol limits the reliability of comparing results from the different protocols.

Zinc oxalate solubility product is low ($1.35 \times 10^{-9}$ mol $L^{-1}$) but the element does form stable oxalate complexes in solution (formation constant log $K_1 = 4.85$). These results indicate that zinc oxalate re-precipitation does not occur at low zinc concentrations.

## 6.5 Conclusions

### 6.5.1 Mass Balance and Precision

Amounts extracted following both sequential extractions and pseudo total digestions were well matched for most analytes. This suggests the sequential extraction methods employed are equally efficient overall. Poor mass balance shown by some of the calcium results might be due to inefficient microwave digestion. Poor mass balance for zinc, in the industrial soil, following the Oxalate extraction procedure might be due to unevenly distributed particles with high zinc concentration in this substrate.

Precision was generally good, but appeared to deteriorate in the later extraction steps, due to propagation of errors. Precision was good for the sum of the 4 steps showing good extraction repeatability between sub-samples. The industrial soil appeared to be the most heterogeneous material extracted in this work.

### 6.5.2 Substitution of BCR Step 2 Reagent with Acidic Ammonium Oxalate

The BCR step 2 reagent has been shown to be selective for the manganese oxide phase of soil[106]. The oxalate solution extracted similar amounts of manganese to the BCR reagent implying a similar specificity for the manganese oxide phase. Zinc extraction from CRM601 was not significantly different between protocols. Zinc oxalate precipitation might occur at higher levels of zinc as in fraction two of the Great Billing material.

The oxalate solution extracted more iron and copper than the BCR reagent. Oxalate is a good chelating ligand. It is probably the chelating properties of the oxalate solution that assisted attack on the iron phase of the materials, increasing phase specificity[155]. Formation of stable copper oxalate complexes $[Cu(C_2O_4)]_{aq}$ and $[Cu(C_2O_4)_2]^{2-}{}_{aq}$ prevented precipitation of the poorly soluble copper oxalate.

The oxalate solution extracted less calcium and lead than the BCR reagent. Calcium extraction was particularly low but lead levels were also significantly reduced in the oxalate extracts. Calcium and lead oxalate have low solubility constants and are not well complexed by oxalate. Precipitation of metal oxalates thus limits the analytes for which the Oxalate extraction is suitable.

The oxalate reagent is probably more phase specific for iron oxides phases than the reagent used in the BCR procedure. However problems for certain analytes have been reported using the oxalate solution due to precipitation and the current work confirms those findings[117,151]. Poor metal oxalate solubility can be compensated for by stable complex formation. The distribution of the analyte and the overall concentration of the analyte within the material studied will also influence the effect of using the oxalate reagent as an alternative.

### 6.5.3 Recommendation

The validity of sequential extractions has been confirmed, and the potential problems associated with highly heterogeneous samples highlighted. The chosen reagents of the BCR extraction can be broadly related to potential alterations in environmental conditions. The use of an acidic oxalate alternative to the hydroxylammonium hydrochloride increases the amount of iron extracted, which may indicate a more efficient dissolution of the iron oxide phase of the soil. However, the increase in phase specificity is offset by the problems of calcium and lead oxalate re-precipitation. Therefore the general substitution of hydroxylammonium hydrochloride with acid ammonium oxalate in step 2 of the BCR sequential extraction is not recommended.

# 7 SEQUENTIAL EXTRACTION OF URBAN SOILS

## 7.1 Introduction

There have been a number of previous investigations into metal fractionation in urban soils. Even though the literature clearly shows sequential extractions do not target specific mineral phases, some articles do not always make this clear. The following review uses the phase terms as they are employed by previous authors and as a general indication of the phase that has been targeted. However it must be recognized that the extraction schemes are not in fact entirely phase specific.

Ninety topsoil (0-5 cm) samples from Glasgow, UK were sequentially extracted using a six step procedure[33]. Cadmium, copper, lead and zinc concentrations were determined. Average partitioning patterns indicated association of cadmium with exchangeable and carbonate fractions, association of lead with the reducible fraction and association of copper and zinc with the organic fraction. The order of mobility was Cd>>Pb>Cu>Zn. The low levels of lead in the residual fraction, compared with earlier fractions was considered as being indicative of lead pollution in the Glasgow soils.

A study of soil in Warsaw, Poland used a five step sequential extraction targeted at exchangeable, soluble, organically bound, inorganically bound and residual phases[156]. The metals studied were cadmium, chromium, copper, manganese, lead and zinc. Cadmium was associated mainly with exchangeable (21.2 %), organically bound (28.1 %) and the residual phases (31.3 %). Chromium (51.1 %) and copper (47.1 %) were mainly associated with the residual phase. Manganese (57.3 %) and lead were mainly associated with the inorganically bound phase. Zinc was mainly associated with the inorganically bound (39.5 %) and residual phases (41.2 %). The order of mobility was given as Pb>Cd>Mn>Zn>Cu>Cr.

A sequential extraction scheme based on the Tessier method, but significantly different (water used to target exchangeable lead and EDTA to target organically bound lead), was used to assess lead fractionation in soil from Falun, Sweden[39]. Mineral phases were also investigated using microscopy and X-ray diffraction analysis. Results indicated a high association of lead with several mineral phases, and low lead availability. A more recent study followed the original Tessier scheme, investigating metal partitioning in soil from Nanjing, China[36]. Chromium was mainly extracted in the residual phase, copper mainly in the residual and organic matter phases. Zinc was more evenly distributed between phases but the residual phase on average included the greatest percentage zinc. Lead was present mainly in the residual and iron/manganese phases. The order of mobility was Pb>Zn>Cu>Cr.

A sequential extraction of seven steps was applied to soils from Bangkok, Thailand[60]. Aluminium, cadmium, chromium, copper, iron, manganese, nickel, lead and zinc levels were determined. PCA was applied to the log transformed total metal concentrations and indicated that aluminium, chromium, iron, manganese and nickel levels were dominated by the parent material composition. Cadmium, copper, lead and zinc levels were thought to have been more affected by anthropogenic activity. The elements more associated with parent material were generally the least mobile, except for manganese. The order of mobility was Mn>Pb>Zn>Cd>Cu>Fe>Ni>Cr>Al.

Metal speciation analysis was performed on soil solutions from Montreal, Canada[157]. This study indicated copper, lead and zinc tended to form organic complexes in the soil solution. The amounts of free copper, lead, nickel and zinc in the soil solution were related to pH and total soil metal concentrations by regression analysis. The concentrations of dissolved and total metal in the soil solution were found not to be good predictors of plant availability.

The modified BCR sequential extraction has been applied to urban roadside soils from Honolulu, USA[37]. Aluminium fractionation between different samples was similar, while lead fractionation between samples was more varied. Analyte variability in terms of fractionation pattern between samples was linked to anthropogenic activity. The original BCR procedure was applied to soils from Naples, Italy[34]. Chromium and copper were associated with the organic fraction, lead with the residual fraction and zinc with all fractions except the organic phase.

Because many different sequential extraction schemes have been used in different studies direct comparisons between results is not possible. However, some similarities could be seen in the trends described irrespective of method used. For example lead was mainly associated with reducible or residual phases, copper and chromium were mainly associated with organic matter/sulfide and residual phases and aluminium, iron and nickel were mainly associated with the residual phase.

Another issue which makes inter-comparison between studies difficult, is the way in which results are presented. This depends, to a certain degree, upon the aim of the study but also on the data processing conducted. The use of chemometric data analysis techniques is becoming more common and has been applied to sequential extraction results. Ten soil samples collected from an urban vegetable garden in Kayseri, Turkey were tested following the original BCR sequential extraction[158]. Vegetable samples were also collected from the same garden. Chemometric methods indicated no relationship between vegetable metal levels and metal extracted in step 1 of the BCR sequential extraction for any metal except nickel. The Tessier scheme was used to extract a sewage sludge; the extracts were analysed for cadmium, cobalt, chromium, copper, iron, magnesium, manganese, nickel, lead and zinc[159]. The amounts of analytes extracted at each step were normalized before manipulation by PCA. Most analytes were found to be strongly correlated with PC1. The scores on PC1 increased from negative for fraction one to positive for fraction five in ascending order, thereby indicating PC1 was inversely related to extractability. This was an example of PCA applied to one sample. Most studies involve the sequential extraction of several samples. This essentially introduces another mathematical dimension to the dataset of results. Mathematical tools have been developed to assist in data interpretation from large sets of multi-dimensional data (e.g. parallel factor analysis - PARAFAC)[160]. When the BCR procedure was used to sequentially extract 13 sediment samples and extracts were analysed for 11 metals, various methods of data interpretation were examined including PARAFAC. The use of

PARAFAC to manipulate results allowed consideration of the interactions between extraction steps, analytes and samples to be displayed[161].

## 7.2 Aims

The aim of this work was to determine the fractionation pattern of metals in a sub-set of the URBSOIL Glasgow surface samples by means of the BCR sequential extraction procedure.

## 7.3 Experimental

### 7.3.1 Samples

The modified BCR sequential extraction was applied to 20 surface (SF) samples selected from the main samples discussed in Chapter 4. In Glasgow it was decided to select 14 parks and open spaces (PO) and 6 roadsides (RD) sites; and to include both pilot study sites. Other sites were chosen to cover Glasgow as evenly as possible. Preliminary PO pseudo total data was available at the time of selection and prompted the inclusion of sites 15 and 24 due to their relatively high metal content. Figure 7.1 shows the location of the selected sites. Table 7.1 shows the corresponding park and road names.

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*Figure 7.1: Glasgow sites sampled for sequential extraction analysis.*

| Sample reference | Easting (approx.) | Northing (approx.) | Description |
|---|---|---|---|
| RD.04 | 251750 | 670250 | Great Western Road, close to Glasgow boundary |
| RD.05 | 255250 | 668250 | Great Western Road |
| RD.06 | 260250 | 666750 | Sprinburn Road |
| RD.07 | 260750 | 665750 | Between M8 and Alexandra Parade |
| RD.14 | 264750 | 666250 | Edinburgh Road |
| RD.23 | 255250 | 661250 | Barrhead Road |
| PO.04 | 261250 | 668750 | Springburn Park |
| PO.07 | 256250 | 670250 | Maryhill Park |
| PO.10 | 264250 | 667250 | Hogganfield Loch |
| PO.14 | 266750 | 663250 | Mount Vernon |
| PO.15 | 260250 | 663250 | Richmond Park |
| PO.18 | 254750 | 665750 | Elder Park |
| PO.20 | 257250 | 666750 | Kelvingrove Park |
| PO.24 | 252750 | 661250 | Househill Park |
| PO.31 | 252250 | 671250 | Drumchapel |
| PO.32 | 258250 | 665750 | Blythswood Square |
| PO.33 | 262250 | 665750 | Alexandra Park |
| PO.34 | 259750 | 664250 | Glasgow Green |
| PO.38 | 259250 | 665250 | George Square |
| PO.39 | 259750 | 665750 | Strathclyde University, (Steelhendge) |

*Table 7.1: Sites from which samples were obtained for sequential extraction.*

### 7.3.2 Extraction and Analysis

Samples were extracted following the modified BCR sequential extraction procedure described in section 2.4. Analysis was performed as described in Section 2.5 by ICPOES for cadmium, calcium, chromium, copper, iron, lead, manganese, nickel and zinc. Cadmium results were below detection limits and are not discussed further.

### 7.3.3 Detection Limits

Detection limits for elements in aqua regia are shown in Section 2.5.4. In this work extracts were analysed in matrix-matched standards by ICPOES. Table 7.2 shows the detection limits found in the different extracts analysed.

| | Analyte λ (nm) | Step 1 | | Step 2 | | Step 3 | |
|---|---|---|---|---|---|---|---|
| | | $D_L$ inst. (ng mL$^{-1}$) | $D_L$ pro. (mg kg$^{-1}$) | $D_L$ inst. (ng mL$^{-1}$) | $D_L$ pro. (mg kg$^{-1}$) | $D_L$ inst. (ng mL$^{-1}$) | $D_L$ pro. (mg kg$^{-1}$) |
| Cd | 214.440 | 9.1 | 0.36 | 11 | 0.43 | 7.8 | 0.39 |
| | 228.802 | 9.0 | 0.36 | 16 | 0.66 | 7.2 | 0.36 |
| Ca | 315.887 | 460 | 18 | 460 | 18 | 14 | 0.72 |
| | 396.847 | 230 | 9.1 | 420 | 17 | 50 | 2.5 |
| Cr | 205.560 | 9.9 | 0.40 | 16 | 0.65 | 14 | 0.72 |
| | 267.716 | 9.5 | 0.38 | 9.5 | 0.38 | 8.5 | 0.42 |
| Cu | 224.700 | 11 | 0.42 | 15 | 0.60 | 9.2 | 0.46 |
| | 324.752 | 5.1 | 0.21 | 8.8 | 0.35 | 6.2 | 0.31 |
| Fe | 238.204 | 34 | 1.4 | 460 | 18 | 18 | 0.88 |
| | 239.562 | 27 | 1.1 | 440 | 18 | 20 | 1.0 |
| Mn | 257.610 | 12 | 0.47 | 31 | 1.2 | 9.7 | 0.49 |
| | 260.568 | 15 | 0.59 | 34 | 1.4 | 13 | 0.66 |
| Ni | 221.648 | 18 | 0.72 | 19 | 0.75 | 23 | 1.2 |
| | 232.003 | 33 | 1.3 | 23 | 0.91 | 25 | 1.2 |
| Pb | 217.000 | 160 | 6.6 | 240 | 9.4 | 170 | 8.6 |
| | 220.353 | 38 | 1.5 | 47 | 1.9 | 54 | 2.7 |
| Zn | 206.200 | 14 | 0.56 | 46 | 1.8 | 32 | 1.6 |
| | 213.857 | 19 | 0.76 | 42 | 1.7 | 23 | 1.2 |

*Table 7.2: Detection limits in different matrices by ICPOES analysis.*

As expected detection limits obtained by ICPOES were generally lower than detection limits by FAAS, but greater than detection limits for GFAAS for lead analysis, in the relevant steps (see Table 6.3). The detection limits were generally similar in all reagents although calcium and iron detection limits (in step 3 and step 2 respectively) were unusual. The cause for these differences was unknown.

## 7.4 Results and Discussion

### 7.4.1 Calcium

Average results and RSD values for the measurement of calcium in sequential extracts are shown in appendix C. Precision was generally very good (average RSD's are 6.2 % at step 1, 13 % at steps 2 and 3, 18 % at step 4 and 8.0 % from the sum of steps 1 to 4). Figure 7.2a shows the results of the sequential extraction of 20 surface soils from Glasgow, together with corresponding pseudo total concentrations.

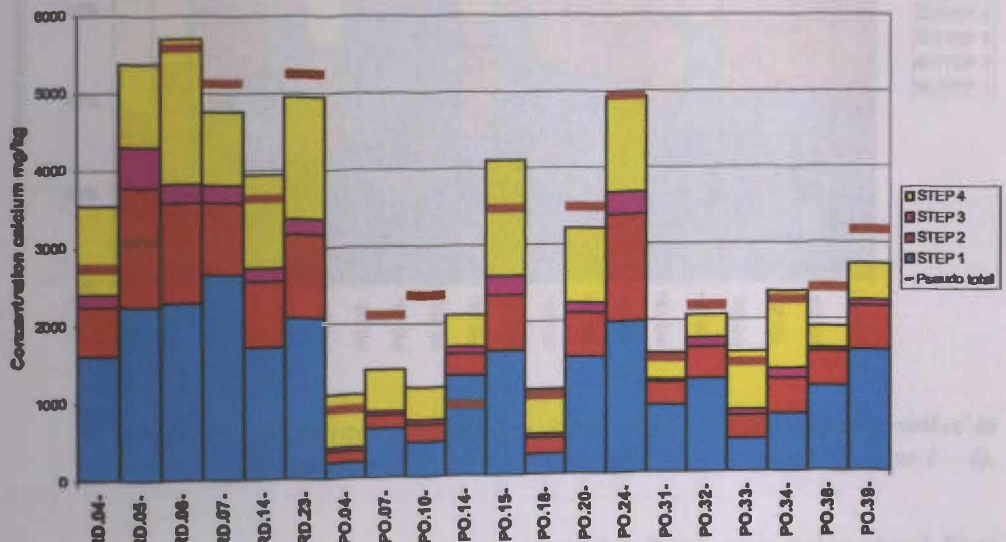

*Figure 7.2a: Average concentration of calcium in sequential extracts and pseudo total concentrations (n=3).*

Average calcium recovery, calculated on the basis of the sum of steps 1 to 4 compared to pseudo total concentrations, was acceptable (108 %), although samples RD.05 and PO.14 were over extracted by the BCR sequential extraction compared to the pseudo total concentrations, (recoveries of 174 % and 227 % respectively) and samples PO.07 and PO.10 were under extracted (67 % and 49 % respectively). Figure 7.2a shows that, in general, roadside soil samples contain more extractable calcium than those from parks, though samples PO.15 and PO.24 appear more similar to the roadside group.

Figure 7.2b shows the same results ranked in order of increasing overall extractable analyte content (i.e. increasing sum of steps 1 to 4) and with fractionation shown on a percentage basis. This allows any trends in fractionation pattern with increasing total extractable metal content more easily to be seen.

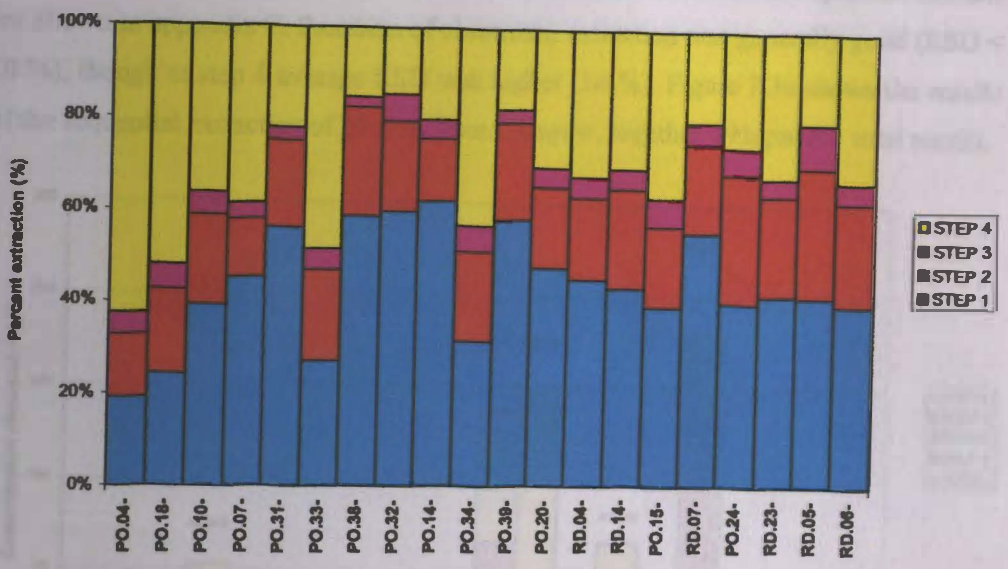

*Figure 7.2b: Average fractionation of calcium (%) in soil samples ranked in order of increasing overall extractable metal content (∑ steps 1 – 4).*

There is a slight indication of lower amounts of calcium being extracted at step 1 from soils with lower total extractable calcium levels but samples PO.33 and PO.34 also have lower than average calcium in this step. Similar percentages of calcium were extracted at steps 2 and 3 in all samples. Where a lower percent of calcium was extracted at step 1, a greater percentage was generally extracted at step 4.

Calcium was mainly extracted from the Glasgow soils in steps 1 and 4 of the BCR sequential extraction. There was a wide range in the proportion of calcium extracted in step 1 (19 – 62 %) and step 4 (14 – 62 %) between different samples. Previous results (see Chapters 4 and 5) indicated calcium concentration in soil was highly varied between and within sample sites, hence likely to have been influenced by anthropogenic activities. The variable amounts released at different stages in the sequential extraction also support this conclusion.

### 7.4.2 Chromium

Average results and RSD values for the measurement of chromium in sequential extracts are shown in appendix C. Precision of chromium extraction was generally good (RSD < 10 %), though at step 4 average RSD was higher (14 %). Figure 7.3a shows the results of the sequential extraction of 20 soils from Glasgow, together with pseudo total results.

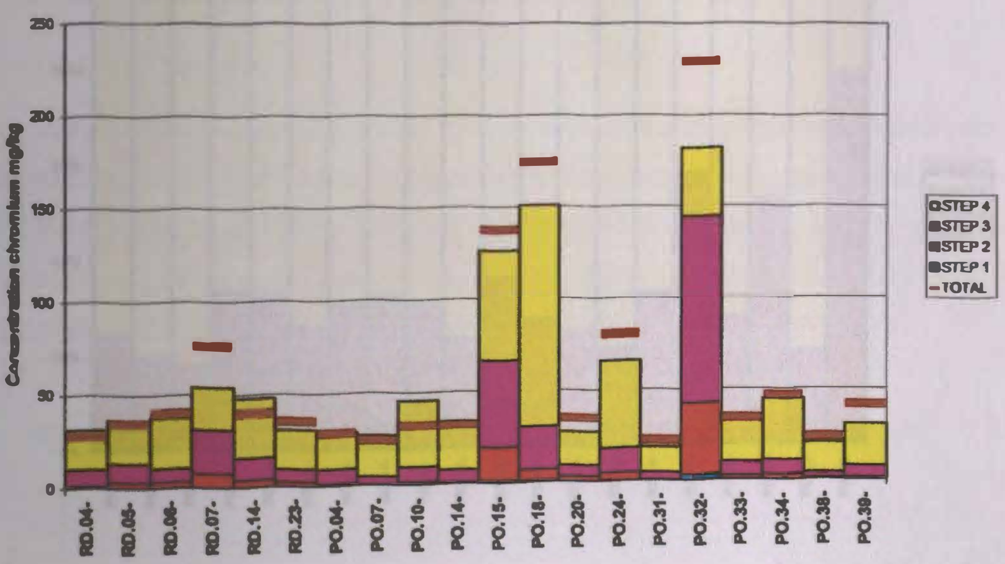

*Figure 7.3a: Average concentration of chromium in sequential extracts and pseudo total concentrations (n=3).*

The recovery of chromium by sequential extraction was on average 96 %. Sample PO.10 was over extracted by the sequential extraction compared to the pseudo total digestion (143 %). Sample RD.07 was under extracted by the BCR sequential extraction (71 %). Figure 7.3a does not show any distinction between RD and PO sample sites in terms of amount of chromium released. The CLEA soil guideline value (SGV) for chromium is 200 mg kg$^{-1}$, based on total chromium concentration. The pseudo total chromium concentration in the sample from site PO.32 was greater than the SGV. Though the amount of chromium released by the sequential extraction was less than the SGV, it should be noted that there was almost 150 mg kg$^{-1}$ chromium that was extracted in steps 1 – 3 and so could be potentially labile. A more detailed risk assessment at site PO.32 might be required, as chromium can be highly toxic.

Figure 7.3b shows the same results, on a percentage basis, in order of overall extractable analyte content.

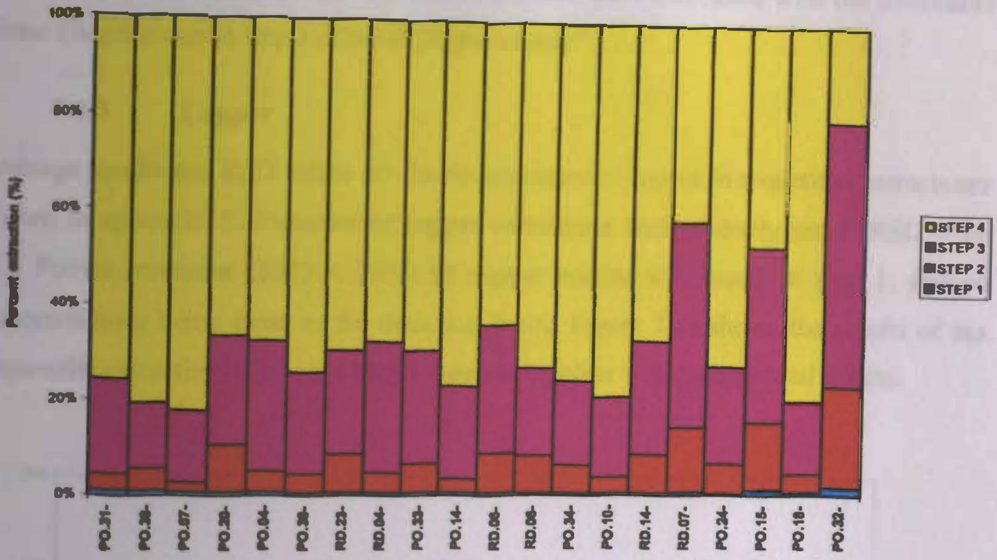

*Figure 7.3b: Average fractionation of chromium in soil samples ranked in order of increasing overall extractable metal content (∑ steps 1 – 4).*

At most sites progressively greater amounts of chromium were released through the extraction steps (i.e. chromium concentration in step 1 < step 2 < step 3 < step 4). Generally almost 80 % of the total chromium was extracted in step 4. A smaller proportion of chromium was extracted at step 4 from samples RD.07, PO.15 and PO.32 than from the other samples. These samples contained a larger amount of chromium associated with the exchangeable, reducible and especially the oxidisable phases than other samples. The greater percent of potentially labile chromium at sites RD.07, PO.15 and PO.32 might be indicative of chromium contamination (though at site RD.07 the amount of chromium is unlikely to be of concern). Samples PO.18 and PO.24 also had high chromium levels, most of which was released at step 4 which might indicate a natural source of chromium at these sites. This suggests chromium fractionation is highly dependant upon location within the city.

Results were in good agreement with previous work obtained by application of sequential extractions to urban soils (see Section 7.1), in which chromium was generally extracted in the residual phase. Chromium has also been associated with the oxidisable phase (target phase at step 3 of the BCR procedure)[34].

### 7.4.3 Copper

Average results and RSD values for the measurement of copper in sequential extracts are shown in appendix C. Precision of copper extractions was generally good (RSD < 10 %). Poorer precision (RSD < 20%) of copper results was found at step 1, due to concentrations being close to the detection limits. Figure 7.4a shows the results of the sequential extraction of 20 soils from Glasgow, together with pseudo total results.

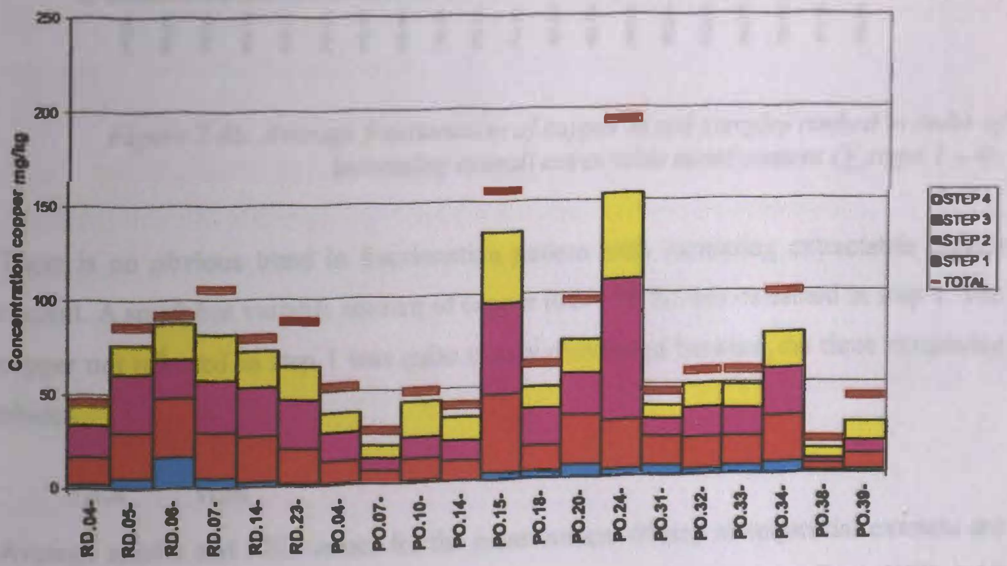

*Figure 7.4a: Average concentration of copper in sequential extracts and pseudo total concentrations (n=3).*

Average recovery of copper was fair (83 %) following the BCR procedure, though always lower than corresponding pseudo total results, the reason for this is unclear. The lowest recoveries were from samples RD.23, PO.04, PO.07 and PO.38 (< 75 %).

Figure 7.4b shows the fractionation of copper in soil samples in order of increasing extractable content.

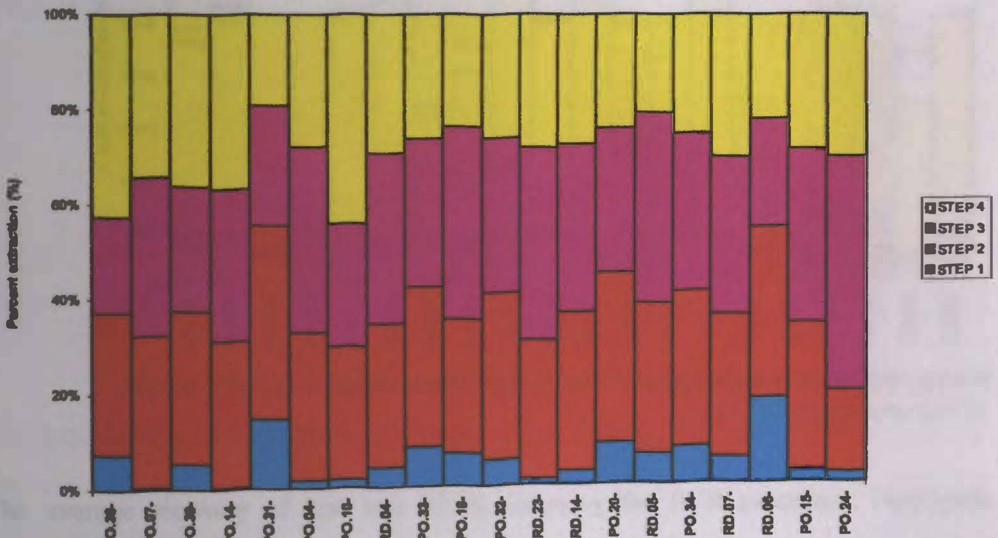

*Figure 7.4b: Average fractionation of copper in soil samples ranked in order of increasing overall extractable metal content (∑ steps 1 – 4).*

There is no obvious trend in fractionation pattern with increasing extractable copper content. A small but variable amount of copper (0.3 - 18 %) was extracted in step 1. The copper not released in step 1 was quite evenly distributed between the three remaining phases.

### 7.4.4 Iron

Average results and RSD values for the measurement of iron in sequential extracts are shown in appendix C. Precision of iron extractions was generally excellent (RSD < 10 %), except for analysis of some step 1 extracts where concentrations were close to detection limits. Figure 7.5a shows the results of the sequential extraction of 20 surface soils from Glasgow and pseudo total results for iron.

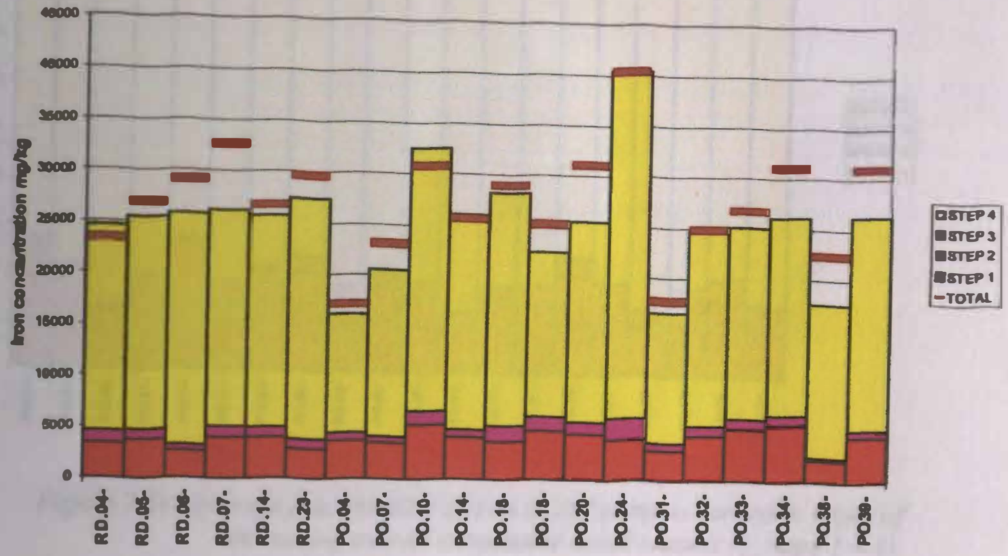

*Figure 7.5a: Average concentration of iron in sequential extracts and pseudo total concentrations (n=3).*

The average recovery of iron was 93 % following the BCR procedure. Negligible amounts of iron were released in step 1 and the concentrations of iron extracted in step 3 were also quite low. Larger amounts of iron were released in step 2, but the fractionation pattern was dominated by step 4. The release of large amounts of iron at step 4 might be indicative of soils with high crystalline iron oxide content. As discussed in Chapter 6, the reagent used in step 2 of the BCR procedure is unlikely to target efficiently the more refractory iron oxide minerals.

Figure 7.5b shows the fractionation of iron in order of increasing extractable content.

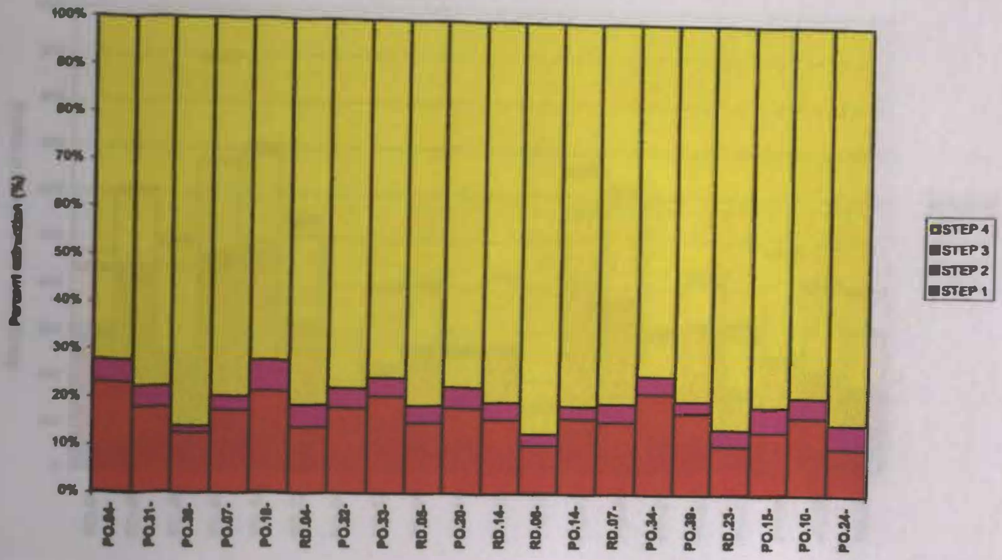

*Figure 7.5b: Average fractionation of iron in soil samples ranked in order of increasing overall extractable metal content ($\sum$ steps 1 – 4).*

The fractionation patterns are very similar between samples with 10 – 23 % released in step 2, 1 – 6 % released in step 3 and 72 – 87 % in step 4. This, together with the dominance of the residual phase would confirm previous indications (Chapters 4 and 5) that the major inputs of iron to Glasgow city soils are from natural sources. The small differences in fractionation between samples might possibly be indicative of different degrees of weathering.

### 7.4.5 Manganese

Average results and RSD values for the measurement of manganese in sequential extracts are shown in appendix C. Precision of manganese extractions was generally excellent (RSD < 10 %). Figure 7.6a shows the results of the sequential extraction of 20 soils from Glasgow, together with corresponding pseudo total concentrations.

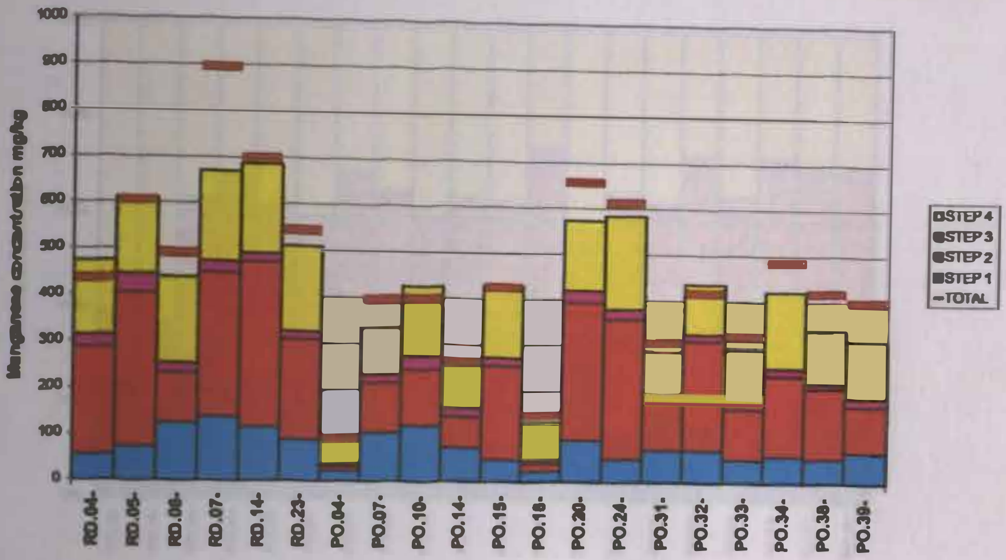

*Figure 7.6a: Average concentration of manganese in sequential extracts and pseudo total concentrations (n=3).*

The recovery of manganese following the BCR procedure was good (average 93 %). Samples contained a large range of extractable manganese concentrations. Smaller amounts of manganese were extracted from samples PO.04 and PO.18 than from other soils.

Figure 7.6b shows the fractionation in order of increasing extractable content.

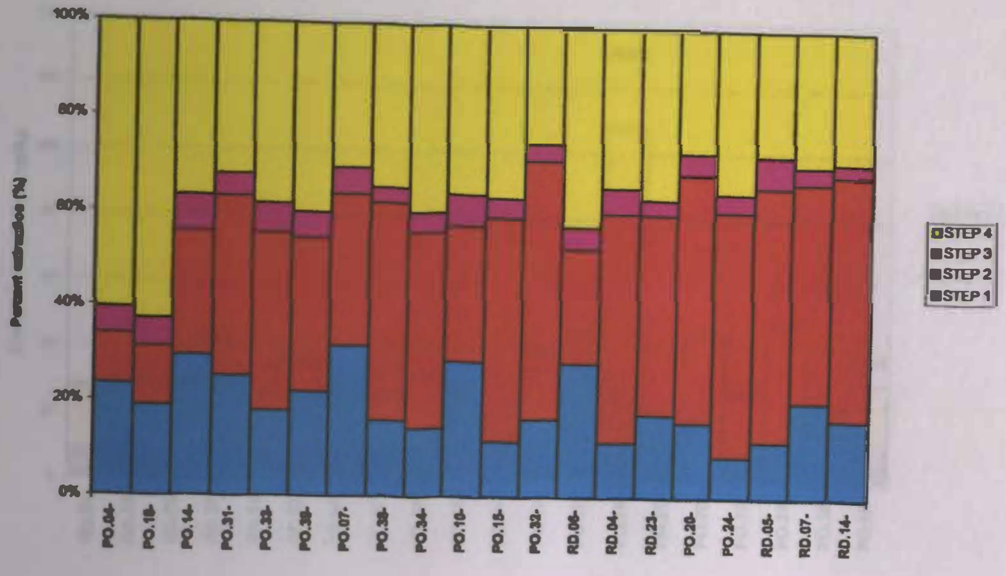

*Figure 7.6b: Average fractionation of manganese in soil samples ranked in order of increasing overall extractable metal content.*

A significant proportion of manganese was extracted at step 2 which is as expected since manganese oxides are amongst the mineral phases targeted by hydroxylammonium hydrochloride. The two samples with noticeably lower overall manganese content than the others (PO.04 and PO.18) also contained lower proportions of manganese associated with the reducible phase.

Figure 7.6b may indicate a slight increase in the percentage manganese extracted at step 2 with increasing total manganese content, accompanied by a corresponding decrease in steps 1 and 4. This suggests the total amount of manganese in the soil is strongly related to the manganese oxide content.

### 7.4.6 Nickel

Average results and RSD values for the measurement of nickel in sequential extracts are shown in appendix C. Precision of nickel extractions were generally excellent (RSD < 10 %). Figure 7.7a shows the results of the sequential extraction of 20 soils from Glasgow, together with corresponding pseudo total concentrations.

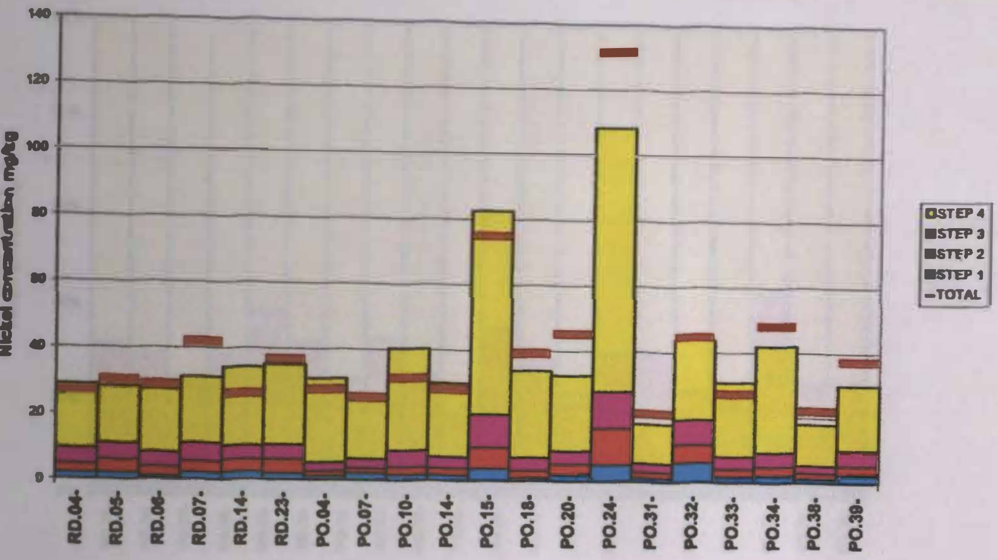

*Figure 7.7a: Average concentration of nickel in sequential extracts and pseudo total concentrations (n=3).*

The average recovery of nickel was excellent (98 %) following the BCR procedure, although there are some discrepancies with pseudo total values for some samples e.g. 131 % for RD.14 recovery. More nickel was released by the BCR sequential extraction than the CLEA nickel SGV (75 mg kg$^{-1}$) from samples PO.15 and PO.24. However the low amounts of nickel released in steps 1 to 3 (potentially labile phases) indicates there is minimal risk of nickel mobilisation at these sites.

Figure 7.7b shows the fractionation of nickel in order of increasing BCR sequential extractable content.

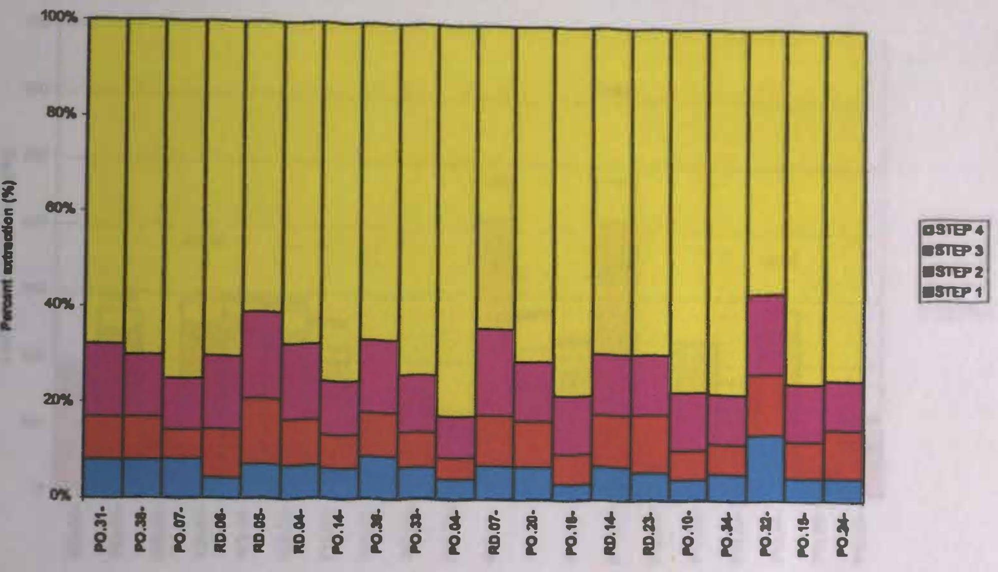

*Figure 7.7b: Average fractionation of nickel in soil samples ranked in order of increasing overall extractable metal content.*

Figure 7.7b shows similar nickel fractionation patterns in almost all samples. Progressively larger amounts of nickel were released by succeeding steps of the sequential extraction, i.e. 7 % in step 1, 9 % in step 2, 13 % in step 3 and 71 % in step 4. This trend was also shown for chromium. An association between chromium and nickel was previously identified in samples from Alexandra Park during the URBSOIL pilot study (see Table 4.3). The explanation of the relationship between chromium and nickel is unclear.

### 7.4.7 Lead

Average results and RSD values for the measurement of lead in sequential extracts are shown in appendix C. Precision of lead extractions was generally good (RSD < 10 %). Figure 7.8a shows the results of the sequential extraction of 20 soils from Glasgow and corresponding pseudo total results.

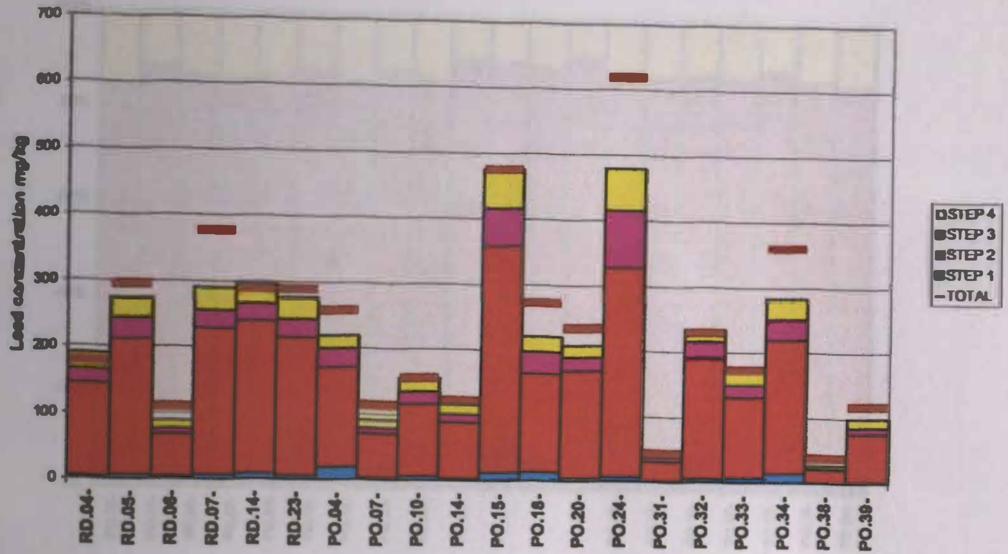

*Figure 7.8a: Average concentration of lead in sequential extracts and pseudo total concentrations (n=3).*

The recovery of lead was good (average = 90 %) following the BCR procedure. There was a wide range of total lead levels in the 20 Glasgow samples. The lead CLEA SGV (450 mg kg$^{-1}$) was exceeded by the sum of the sequential extraction steps in samples PO.15 and PO.24. In both these samples more than 400 mg kg$^{-1}$ lead was released in steps 1 to 3 and is therefore potentially labile. A more detailed risk assessment would be needed at sites PO.15 and PO.24 to help decide if soil remediation is required.

Figure 7.8b shows the fractionation of lead in order of increasing BCR analyte content.

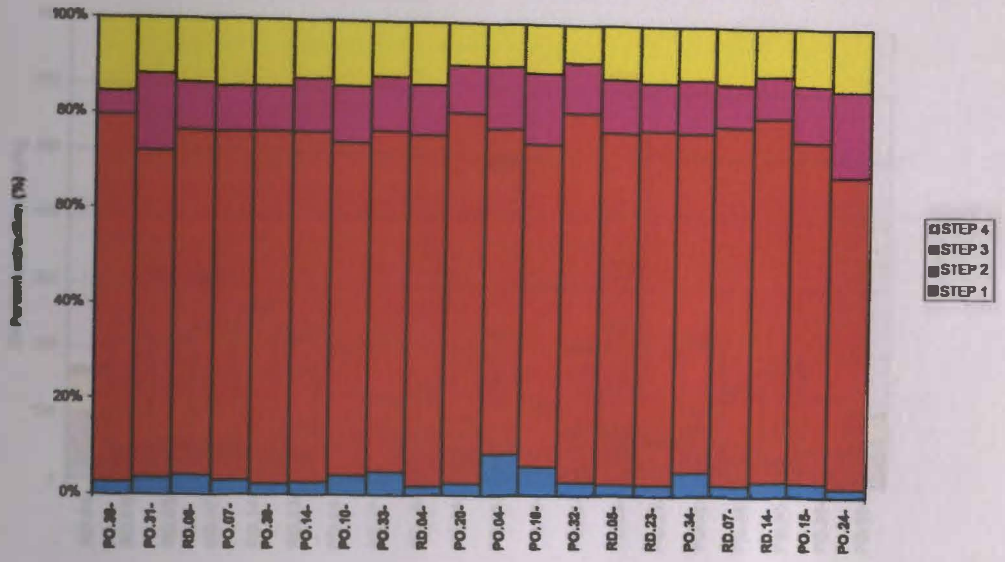

*Figure 7.8b: Average fractionation of lead in soil samples ranked in order of increasing overall extractable metal content.*

Similar lead fractionation patterns were obtained from all samples. Small amounts of analyte were measured in step 1 (3 %), slightly larger amounts in step 3 and 4 (11 and 12 % respectively), but the majority of lead (73 %) was always found in step 2. The extraction of lead at the reducible step of sequential extractions is common for urban soils (see Section 7.1).

### 7.4.8 Zinc

Average results and RSD values for the measurement of zinc in sequential extracts are shown in appendix C. Precision of zinc extractions were on average quite poor at steps 1 and 2 (average RSD = 17 % and 21 %). This was due to some samples having zinc concentration close to the detection limits in these extracts. Precision of zinc extracted at steps 3 and 4 was generally excellent. Figure 7.9a shows the results of the sequential extraction of 20 soils from Glasgow and corresponding pseudo total concentrations.

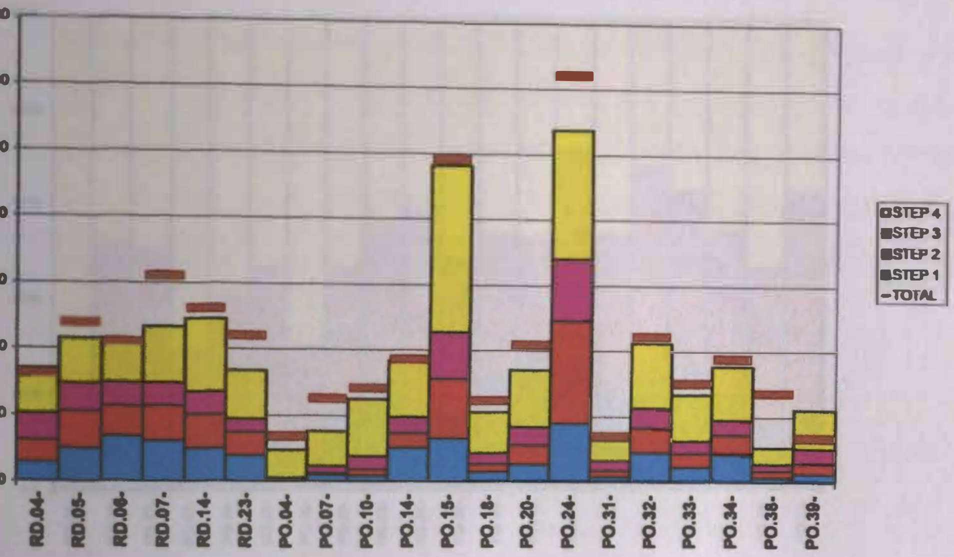

*Figure 7.9a: Average concentration zinc in sequential extracts and pseudo total concentrations (n=3).*

The average recovery of zinc was generally good following the BCR procedure (89 %). Sample PO.39 was over extracted by the BCR procedure compared to the pseudo total digestion, (recovery = 165 %), and samples PO.04, PO.07 and PO.38 were under extracted (recoveries = 70 %, 60 % and 39 % respectively). Figure 7.b shows the fractionation of zinc in order of increasing extractable content.

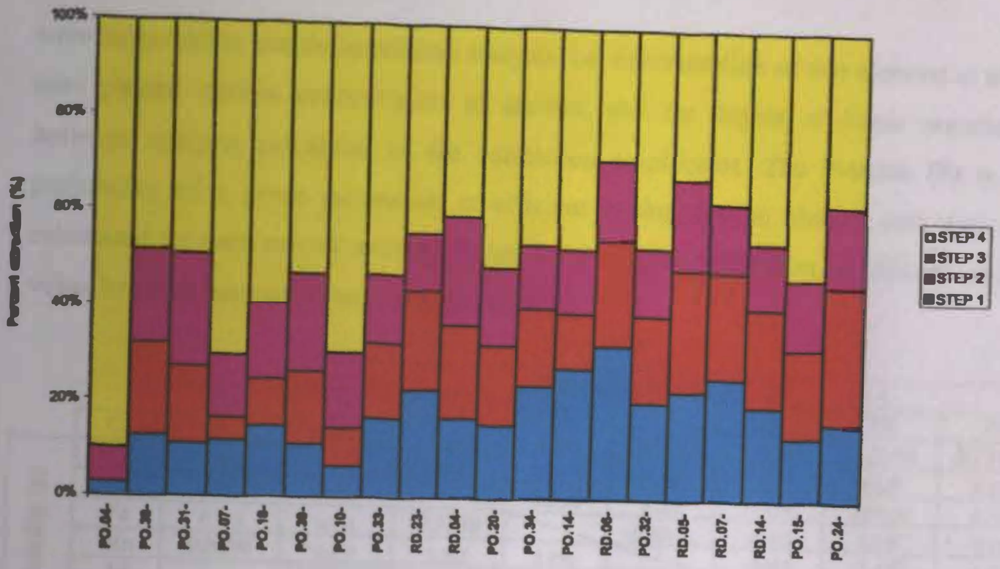

*Figure 7.9b: Average fractionation of zinc in soil samples ranked in order of increasing overall extractable metal content.*

Zinc was released in all steps of the sequential extraction from nearly all samples, but the proportions varied considerably. There is some evidence of an increase in release of zinc at step 1, and a decrease in step 4, as total concentration increases. This would indicate that soils with higher total zinc content also contain a higher proportion of the element in potentially labile forms.

### 7.4.9 Correlations between Metals

Previous work presented in this thesis has shown high correlations between pseudo total concentrations of certain metals in Glasgow soils. It is interesting also to compare and assess relationships between amounts of metals extracted from the operationally defined phases of the BCR sequential extraction. In addition to highlighting analytes that are associated with the same soil compartments, these may provide further insight into elements with common origins (natural and/or anthropogenic). Detailed investigation of correlation between metals extracted from urban soils following the BCR procedure, have not previously been reported. Results for each step of the sequential extraction were subjected to simple correlation analysis, i.e. concentration of one element at all 20 sites plotted against concentration of another, and the degree of linear association between analytes calculated as the correlation co-efficient. The P-value (P) is the probability of a given correlation co-efficient arising due to chance and was also calculated for each pair of analytes. Table 7.3 shows the correlation co-efficient and P-value between pairs of metals extracted at step 1.

| | | | Correlation co-efficient (R) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ca | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
| | Ca | | -0.0445 | 0.362 | -0.363 | **0.48813** | 0.23185 | -0.32418 | **0.72064** |
| Probability (p) | Cr | 0.852 | | 0.0378 | -0.0176 | -0.162 | **0.679** | 0.220 | 0.220 |
| | Cu | 0.117 | 0.874 | | **0.502** | 0.252 | -0.114 | -0.0154 | 0.395 |
| | Fe | 0.115 | 0.941 | **0.0240** | | -0.00893 | -0.423 | 0.248 | -0.172 |
| | Mn | **0.0290** | 0.494 | 0.283 | 0.970 | | -0.093 | **-0.455** | 0.229 |
| | Ni | 0.325 | **0.000480** | 0.633 | 0.0630 | 0.697 | | 0.0980 | **0.519** |
| | Pb | 0.163 | 0.350 | 0.949 | 0.292 | **0.0440** | 0.681 | | 0.105 |
| | Zn | **0.000338** | 0.350 | 0.0845 | 0.468 | 0.332 | **0.0189** | 0.661 | |

*Table 7.3: Assessment of correlation between elements isolated in step 1 of the BCR sequential extraction, (correlation co-efficients and probability of chance occurrence of correlation; values in bold are significant at 95 % confidence).*

Calcium was correlated with manganese and zinc at step 1. These three metals showed the highest percent extraction at step 1. Chromium and nickel concentrations were correlated. Both elements were poorly extracted at step 1, indeed chromium levels were typically below detection limits. Nickel levels were also correlated with zinc levels but zinc concentration was not correlated with chromium concentration. There are possibly common sources contributing to chromium and nickel, and to nickel and zinc extracted at step 1. Copper levels were correlated with iron concentrations in step 1 extracts, manganese concentrations were anti-correlated with lead concentrations, the explanation for these correlations is unclear.

Table 7.4 shows the correlation co-efficients between pairs of metals extracted at step 2.

|  |  |  | Correlation co-efficient (R) |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Ca | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|  | Ca |  | -0.0118 | **0.595** | -0.320 | **0.667** | **0.597** | **0.479** | **0.722** |
| Probability (p) | Cr | 0.961 |  | 0.291 | 0.132 | 0.226 | 0.409 | 0.381 | 0.245 |
|  | Cu | **0.00565** | 0.213 |  | 0.0589 | **0.511** | **0.552** | **0.726** | **0.677** |
|  | Fe | 0.168 | 0.578 | 0.80508 |  | -0.02861 | 0.0501 | 0.258 | -0.0288 |
|  | Mn | **0.00131** | 0.338 | **0.0212** | 0.90468 |  | **0.558** | **0.592** | **0.620** |
|  | Ni | **0.00549** | 0.0732 | **0.0116** | 0.83378 | **0.0106** |  | **0.769** | **0.942** |
|  | Pb | **0.0326** | 0.0970 | **0.000290** | 0.27136 | **0.00592** | **0.0000751** |  | **0.762** |
|  | Zn | **0.000327** | 0.297 | **0.00105** | 0.90395 | **0.00357** | **$<10^{-7}$** | **0.0000935** |  |

*Table 7.4: Assessment of correlation between elements isolated in step 2 of the BCR sequential extraction, (correlation co-efficients and probability of chance occurrence of correlation; values in bold are significant at 95 % confidence).*

Chromium levels showed no correlation with any other metals extracted at step 2; nor did iron which is unexpected given that the amorphous iron/manganese oxyhydroxides are the phase targeted at step 2. The lack of correlation between iron levels and other metals might be indicative of other sources dominating metal release at step 2 in these soils. The high percentage of lead extracted at step 2 (see Figure 7.b) might indeed indicate there is a specifically anthropogenic compartment that is being attacked at step 2. Concentrations of calcium, copper, manganese, nickel, lead and zinc in extract two were all correlated with each other. Manganese levels showed the greatest correlation with calcium and zinc concentrations; these metal levels were also correlated at step 1. This might be due to a natural relationship between these elements in the more labile soil mineral phases. Copper concentrations were most strongly correlated with lead and zinc levels, which might be due to similar anthropogenic influences on these three metals in these soils. Nickel levels were most strongly correlated with amounts of lead and zinc extracted at step 2 which might also be indicative of an anthropogenic influence on nickel levels in these soils.

Table 7.5 shows the correlation co-efficients between metals extracted at step 3.

| | | | Correlation co-efficient (R) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ca | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
| | Ca | | 0.0895 | **0.619** | 0.307 | **0.719** | **0.501** | **0.474** | **0.645** |
| Probability (p) | Cr | 0.707 | | 0.164 | 0.259 | -0.102 | **0.520** | 0.246 | 0.249 |
| | Cu | **0.00363** | 0.4901 | | **0.799** | 0.266 | **0.865** | **0.954** | **0.913** |
| | Fe | 0.189 | 0.271 | **0.0000237** | | 0.223 | **0.797** | **0.866** | **0.730** |
| | Mn | **0.000354** | 0.670 | 0.257 | 0.34425 | | 0.250 | 0.128 | 0.403 |
| | Ni | **0.024327** | **0.0188** | **$<10^{-7}$** | **0.0000262** | 0.28876 | | **0.858** | **0.914** |
| | Pb | **0.034662** | 0.295 | **$<10^{-7}$** | **$<10^{-7}$** | 0.59086 | **0.00000128** | | **0.827** |
| | Zn | **0.002133** | 0.289 | **$<10^{-7}$** | **0.000258** | 0.078241 | **$<10^{-7}$** | **0.00000691** | |

*Table 7.5: Assessment of correlation between elements isolated in step 3 of the BCR sequential extraction, (correlation co-efficients and probability of chance occurrence of correlation; values in bold are significant at 95 % confidence).*

Calcium concentrations were correlated with amounts of copper, manganese, nickel, lead and zinc extracted at step 3. Chromium was correlated with nickel, as in step 1. Copper levels were strongly correlated with amounts of iron, nickel, lead and zinc extracted at step 3. Iron concentrations were correlated with nickel, lead and zinc concentrations. Nickel levels were strongly correlated with concentrations of lead and zinc. Lead and zinc levels were strongly correlated.

The phases targeted at step 3 are organic matter and sulfide minerals. The organic matter will chelate a variety of metals from both anthropogenic and natural sources and so it is expected that there might be a high correlation between most of the metals extracted at step 3. The very high correlation between the three so called ' urban' metals (copper, lead and zinc) might indicate the phase targeted at step 3 is a common reservoir for many anthropogenic metals. The correlation between iron, an element indicated throughout this work to be associated with natural influences in Glasgow soils, and the urban metals, shows there may also be natural pool of these elements that is extracted at step 3, or indeed a small amount of anthropogenic iron is released in step 3. Table 7.6 shows the correlation co-efficients between pairs of metals extracted at step 4.

|  |  |  | Correlation co-efficient (R) |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Ca | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|  | Ca |  | 0.0267 | **0.603** | **0.478** | **0.733** | 0.360 | 0.568 | 0.436 |
| Probability (p) | Cr | 0.911 |  | 0.262 | 0.118 | -0.119 | 0.388 | 0.331 | 0.341 |
|  | Cu | **0.00491** | 0.265 |  | **0.806** | **0.667** | **0.898** | **0.921** | **0.891** |
|  | Fe | **0.0331** | 0.621 | **0.0000178** |  | **0.736** | **0.706** | **0.693** | **0.654** |
|  | Mn | **0.000235** | 0.617 | **0.00132** | **0.000219** |  | 0.354 | **0.589** | 0.435 |
|  | Ni | 0.119 | 0.0909 | **$<10^{-7}$** | **0.000498** | 0.126 |  | **0.862** | **0.881** |
|  | Pb | **0.00894** | 0.154 | **$<10^{-7}$** | **0.000708** | **0.00628** | **0.00000107** |  | **0.869** |
|  | Zn | 0.0549 | 0.141 | **$<10^{-7}$** | **0.00177** | 0.0552 | **$<10^{-7}$** | **$<10^{-7}$** |  |

*Table 7.6: Assessment of correlation between elements isolated in step 4 of the BCR sequential extraction, (correlation co-efficients and probability of chance occurrence of correlation; values in bold are significant at 95 % confidence).*

Chromium concentration was not correlated with any other metal extracted at step 4, nor in step 2, and was correlated only with nickel in steps 1 and 3. This, supports previously discussed PCA findings that suggested chromium behaved differently from the other analytes (see Section 5.4.3). Calcium levels were correlated with amounts of copper, iron and manganese extracted. Manganese concentrations were correlated with copper, iron and lead levels. Nickel concentrations were correlated with amounts of copper, iron, lead and zinc. All other metal levels were correlated with each other. Lead concentration were correlated with copper, iron, manganese, nickel and zinc levels. The percentage of lead associated with the residual phase was very low. This might indicate there is only a small amount of natural lead present in the soil, which is correlated with other naturally occurring metals.

## 7.5 Discussions

### 7.5.1 Precision and Mass Balance

Generally, the precision of metal extractions was excellent (RSD < 10 %, n = 3). Metals at concentrations close to the detection limit showed poorer precision, which is expected. Mass balance was generally excellent, as shown by average recoveries of between 89 % and 108 % for most analytes in most samples. Copper recovery was consistently low from the sequential extraction procedure, on average 83 %, and there is some evidence of low recovery from the sequential extraction procedure for some other analytes. A small amount of dissolved metals might be lost at each wash stage of the sequential extraction. However, the generally high average recovery suggest any loss was not significant.

### 7.5.2 General Trends in Metal Fractionation

Average fractionation patterns, over all samples, for each element give information on average mobility and are commonly reported in literature. Figure 7.10 shows the average fractionation patterns from sequential extraction of the 20 Glasgow surface soils.

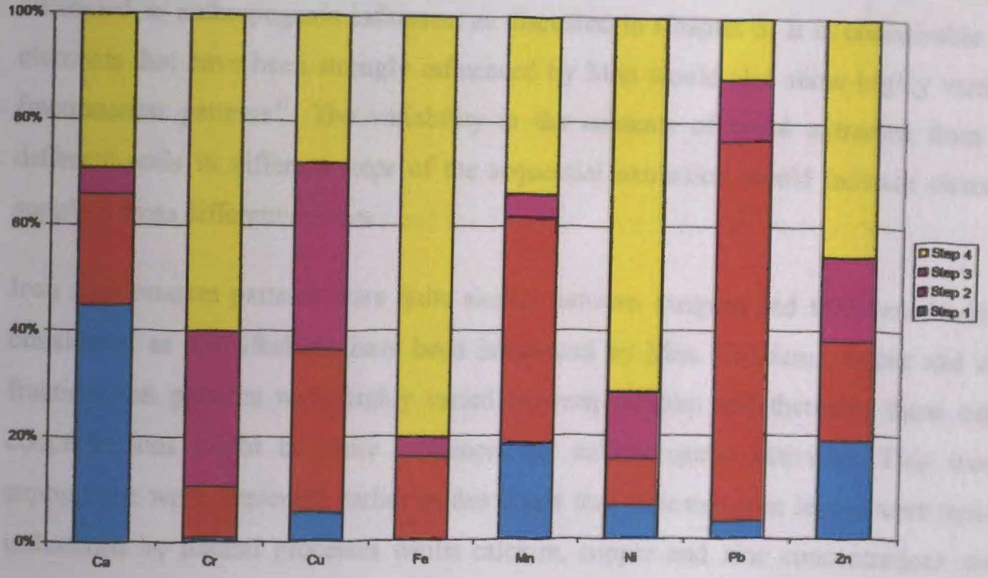

*Figure 7.10: Average fractionation of analytes in surface soils from Glasgow, (n=20).*

Relative potential mobility for different elements is often assessed on the basis of the percentage of analyte recovered in steps 1 – 3. The average results for the 20 Glasgow samples indicated mobility decreasing in the order Pb>Cu>Ca>Mn>Zn>Cr>Ni>Fe. This agrees with previous general mobility orders where elements less likely to have been influenced by anthropogenic activity are more strongly bound in the soil mineral matrix than elements associated with anthropogenic factors. However, this method of assessing mobility suggests lead is the most mobile metal, though it is generally accepted that lead is in fact not very mobile in soil at all. Therefore it is unlikely extractability from steps 1 to 3 is a good indicator of metal mobility. Another method of assessing mobility is to compare percent metal extracted in the first step. This gave a very different result. The mobility decreased in the order Ca>Mn=Zn>Ni>Cu>Pb>Cr>Fe. The major difference using this approach is that copper and lead would be expected to have much lower mobility than when steps 1 – 3 are considered together.

A highly variable pseudo total concentration of an element in soil from Glasgow may be attributed to anthropogenic influence, as discussed in Chapter 5. It is conceivable that elements that have been strongly influenced by Man would also show highly variable fractionation patterns[37]. The variability in the amounts of metal extracted from the different soils in different steps of the sequential extraction would indicate elements supplied from different sources.

Iron fractionation patterns were quite similar between samples and therefore could be considered as less likely to have been influenced by Man. Calcium, copper and zinc fractionation patterns were highly varied between samples and therefore these metal concentrations might be more influenced by anthropogenic activities. This would support the work presented earlier in this thesis that indicated iron levels were mainly influenced by natural processes whilst calcium, copper and zinc concentrations were more influenced by anthropogenic processes.

Manganese fractionation patterns were highly varied between samples whilst lead fractionation patterns were uniform across all samples. Given that lead was previously identified as an 'anthropogenic' element and manganese as mainly natural in origin, the high manganese fractionation variability and low lead fractionation variability are the opposite to what would be expected. The relationship between fractionation pattern and analyte source will depend upon several factors. These include the form in which the analyte was deposited in the soil; the analyte mobility within the soil; the number of anthropogenic sources that significantly increase analyte concentration; the amount of metal naturally present in the soil, and general soil properties such as mineral composition, that can influence metal binding and re-distribution. The concept that there is a relationship between fractionation pattern variability and anthropogenic input does not account for all the factors that affect metal behaviour in soils and appears to be too simplistic to be applicable in the present study. The complex chemistry of manganese in soil might explain the high variation in fractionation between samples, whilst the major anthropogenic sources of lead in Glasgow soils might all be deposited in a form that can be dissolved in hydroxylammonium hydrochloride.

A higher percentage of metal extracted at step 4 is commonly related to a strong natural influence on a metal concentration in soils. This might generally be the case but it is also important to consider the form that the anthropogenic metals are in when they enter the soil system. If the input species are unreactive they might not be released until the residual step of the sequential extraction. This might be the case for chromium in Glasgow soils.

### 7.5.3 Correlation between Metals

Similar to the pseudo total results presented in chapters 4 and 5 there was high correlation between metals extracted in the different steps of the BCR sequential extraction. It was hoped that these correlations might have hinted at common sources of metals in the soils which, in turn, might have been related to natural or anthropogenic sources. However, some correlations were found that were not expected (e.g. chromium concentrations correlated with amount of nickel released in step 1) and, where some correlations might have been expected, there were none (e.g. iron levels not correlated with any other metal at step 2). Therefore, confidence in the usefulness of this approach was limited. The measurement of a greater number of analytes and/or samples, or the application of more sophisticated data analysis methods e.g. PCA or PARAFAC, might be necessary to provide more definitive information and greater confidence about the major sources and relationships between metals in the sequential extracts of Glasgow samples.

### 7.5.4 Environmental Interpretation

The sometimes very high amounts of lead extracted in the first three steps of the BCR sequential extraction suggest the risk of mobilisation of lead from the soil at some sites is of concern. Most of the lead in all the soils was released in step 2, which suggests an increase in reducing conditions in the soil at certain sites could release large amounts of lead. Chromium was generally not released from the samples until step 4 of the extraction and therefore might be less likely to be released from the soil. However, some samples with very high chromium concentration showed an increase in the proportion of chromium extracted at step 3 indicating chromium fractionation is very site specific, and chromium might be mobilised under oxidising conditions. Nickel was generally not extracted until step 4 of the sequential extraction and therefore, even at high concentrations, the risk of nickel mobilisation is minimal.

## 7.6 Conclusions

The additional information obtained from the sequential extraction of soils allowed the relationship between metals and their behaviour in the soil to be studied. Generally results of phase associations with metals were similar to previous literature studies, but the inference of highly varied fractionation pattern being indicative of anthropogenic influence on metal levels was shown to be too simplistic in the case of the Glasgow samples.

Chromium, iron and nickel were most strongly associated with the residual phase indicating these elements are mostly bound in the ordered mineral phases. Chromium was also highly associated with the organic/sulfide phase, as was copper. Copper was quite evenly distributed between the phases extracted at step 2 to 4. Lead was mainly associated with the reducible phase which is in good agreement with literature results. Manganese was largely associated with the reducible phase, but was also released to a significant degree in the exchangeable and residual phases. Zinc was more evenly distributed between all phases, though the residual phase did extract the greatest average percent.

# 8 CONCLUSIONS AND FURTHER WORK

## 8.1 Conclusions

Soil samples were collected at points defined by a 50 m grid, from two parks in Glasgow, Glasgow Green and Alexandra Park. Two depths of soil were sampled, the surface (0 – 10 cm) and the sub-surface (10 – 20 cm). Aqua regia soluble metal content in the soil samples was determined for cadmium, calcium, chromium, copper, iron, manganese, nickel, lead and zinc. Metal levels in soil from Glasgow Green were usually greater than in soil from Alexandra Park, with the exception of chromium concentration which was greater in Alexandra Park. The distribution profile and variability in metal concentration within each park appeared to be indicative of anthropogenic influences on some analytes. Metals with non-normal distributions and/or high variability (calcium, copper, lead and zinc) were thought to be more associated with anthropogenic activities than metals with normal distributions and/or low variability (iron and manganese).

The next stage of the work was to collect soil samples from various areas in Glasgow. Composite samples were again collected from two depths, either within a park or open spaces (PO), along a roadside (RD) or riverbank (RB) or from within ornamental gardens (OG). Aqua regia soluble metal content in the soils was determined for aluminium, barium, calcium, cadmium, chromium, copper, iron, lithium, magnesium, manganese, nickel, lead, vanadium, yttrium and zinc. Metal levels in soil from Glasgow were similar to other large cities. There was no marked difference in metal concentrations between different land uses in Glasgow. Similar to the findings from the study within two parks, relationships could be seen between analyte distribution, variability and anthropogenic influence.

Aluminium, iron, lithium and perhaps manganese had distributions approaching normality and hence their concentrations in Glasgow soil would appear to be governed mainly by geochemical factors. Relative variability in analyte concentration between samples seemed to better distinguish metals more likely to have been influenced by anthropogenic activities from those less likely to have been influenced by Man.

Relationships between levels and variabilities of analytes were investigated using principal component analysis (PCA), this generally confirmed implications shown by examination of distribution and variability. Overall, the elements commonly grouped together were aluminium, iron, lithium, magnesium and manganese with low variability and levels probably dominated by natural influences. Barium, copper, lead and zinc were grouped and showed high variability; these metal levels were likely to be most influenced by anthropogenic activities. Calcium, vanadium and yttrium were grouped together and these metal concentrations seemed to be of intermediate variability. Nickel levels were generally highly to moderately variable. Chromium concentrations were consistently highly varied, but chromium levels were not strongly related with any other analyte. In addition to exploring relationships between analytes, PCA allowed most of the variation from all analytes to be explained on one principal component. This first component was always strongly related to all analytes, but the small differences in loadings between analytes might be indicative of elements more influenced by anthropogenic activities. Subsequent principal components might also have been indicative of anthropogenic input, often showing anti-correlation between 'natural' and 'urban' metals.

The loadings indicated metal levels in soil from parks and roads were related in similar ways, whilst metals were inter-related differently in soil from riverbanks and differently again in soils from ornamental gardens. Although metal concentrations were similar in soil regardless of land use, the different patterns seen in the loadings, after application of PCA, might be capable of differentiating between land types.

The scores showed the relationship between samples and principal components. The scores on three principal components were plotted to allow rapid identification of samples with high metal content and, therefore, potentially contaminated sites. This might be a useful data reduction technique to produce a smaller, more easily managed and displayed, data set that could be loaded into a geographic information system and used by local authorities involved in decision making in relation to land use.

The reliability of the four stage modified BCR sequential extraction was confirmed and the importance of following a standardised procedure highlighted. An acidic ammonium oxalate reagent released more iron, from three substrates, than the hydroxylammonium hydrochloride recommended by the BCR protocol. However, the use of an oxalate replacement at step 2 of the BCR sequential extraction appeared unlikely to offer any substantial benefit due to problems with oxalate salt precipitation.

The application of the BCR sequential extraction to urban soil allowed further investigation into the relationships between metal levels, mobilities and variabilities. Risk assessment at contaminated land sites needs to consider the mobility of any potentially toxic elements. The first three steps of the BCR sequential extraction can be related to potential release of elements under different environmental conditions (e.g. step 1 is related to acidification) and hence, the results from the sequential extraction of soils can be useful for risk assessment. A sub-set of 14 PO and 6 RD samples from Glasgow were extracted following the BCR protocol. Some of the soil samples from Glasgow exceeded soil guideline values (SGV) for chromium, nickel and lead concentrations. Results of the sequential extractions indicated chromium and nickel were not mobile and therefore unlikely to be released from the soil whereas lead mobility was much greater. Most of the lead (73 %) in the Glasgow samples was released at step 2 of the BCR sequential extraction and therefore there is a potential for release of high amounts of lead under reducing conditions (e.g. from waterlogged soil) at contaminated sites.

Generally there appeared to be no relation of fractionation pattern with total extractable metal content. For no element studied was there a distinct difference in fractionation pattern between the park soils and the roadside soils. Variability in fractionation pattern has been proposed in the literature as an indicator of elements more likely to be influenced by Man's activities. This was observed in the current study for some elements indicated previously to be anthropogenic in origin (copper and zinc) but not for others (lead). In contrast, low variability in fractionation pattern between samples has been suggested as indicative of elements dominated by natural effects. This suggestion was confirmed for iron, but contradicted for manganese, in the Glasgow soils. Correlations between metals extracted in the steps of the sequential extraction were statistically significant but often difficult to interpret.

Overall metal levels in soils from various land uses were similar to previous levels reported in soils from other cities. It was not possible to differentiate between soil from different land uses on the basis of metal concentrations or sequential extraction patterns. Several methods were used to distinguish elements dominated by natural or anthropogenic processes and indicated copper, lead and zinc were more influenced by anthropogenic influences, which confirmed previous work suggesting these are 'urban' metals.

## 8.2 Future Work

Analyte variability in soil could be investigated further, to assess temporal or seasonal differences in metal concentrations. Variability of metal levels at different scales could be investigated e.g. spatial variability could be examined at different scales, from less than millimetres up to several metres. The exact physical meaning of the high correlation of all analytes with the first principal component should be explored further, possibly with the use of X-ray diffraction to try and determine if PC1 could be directly related to intrinsic soil heterogeneity.

An increased understanding of metal concentrations in Glasgow soils could be gained by sampling more sites and increasing the number of analytes determined in the samples. The analysis of samples for organic pollutants in addition to metals might give stronger evidence for contamination and anthropogenic input. More information on the distribution of metals with depth could be interesting. To better assess the impact of surface deposition on metal concentrations in the soil, the top few centimetres of soil could be sampled.

The application of the BCR sequential extraction to more samples might show differences between soils from different land uses in terms of metal fractionation pattern (e.g. riverbanks). The formal integration of the sequential extraction results with risk assessment might allow better decisions on contaminated land to be made. The use of extraction conditions chosen to mimic physiological compartments should also be investigated and considered for risk assessments.

The use of non-specific reagents and chemometric data processing might offer more phase specific information and should be investigated further on urban soils. The improvement of data interpretation using chemometric processing (e.g. PARAFAC) should be further studied, for the results of sequential extractions. A guideline for the format of presentation of sequential extraction results could also be useful.

Overall more information on urban soils is needed, to help improve risk assessment models and definition of soil quality in an urban context. An improved level of understanding should help increase the value given to soil by local authorities and assist with urban planning decisions.

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# APPENDIX A

Table A.1 – table A.5 show the aqua regia soluble metals content and LOI (%) from Glasgow Green soil samples.

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Calcium | | | | Chromium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 1880 | NA | 1120 | 5.4 | 32.1 | NA | 27.1 | 3.3 |
| 2 | 3310 | 11.6 | 3770 | 0.9 | 24.5 | 2.1 | 27.6 | 1.0 |
| 3 | 3610 | 2.8 | 2490 | 2.1 | 23.9 | 4.2 | 24.3 | 3.0 |
| 4 | 6260 | 3.8 | 7170 | 4.4 | 32.5 | 2.7 | 28.5 | 3.2 |
| 5 | 1750 | 8.5 | 2530 | 1.9 | 28.3 | 1.8 | 27.2 | 1.1 |
| 6 | 3760 | 5.2 | 3280 | 9.5 | 32.4 | 4.9 | 32.7 | 6.1 |
| 7 | 3410 | 3.8 | 4440 | 0.6 | 30.1 | 3.5 | 30.9 | 1.0 |
| 8 | 5650 | 2.7 | 4760 | 1.5 | 33.5 | 3.2 | 28.1 | 0.4 |
| 9 | 1730 | 5.1 | 2640 | 10.8 | 25.9 | 3.0 | 31.5 | 5.2 |
| 10 | 3530 | 5.4 | NA | | 24.2 | 3.1 | NA | |
| 11 | 2840 | 3.1 | 4480 | 1.6 | 30.1 | 2.0 | 22.5 | 1.4 |
| 12 | 3370 | 2.3 | 4230 | 2.9 | 25.5 | 1.2 | 27.3 | 2.7 |
| 13 | 5770 | 3.2 | 3880 | 2.3 | 33.1 | 2.6 | 27.8 | 3.2 |

*Table A.1: Average and RSD aqua regia soluble calcium and chromium content in soil samples from Glasgow Green, (n = 3).*

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Copper | | | | Iron (%) | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 97.1 | NA | 88.9 | 2.9 | 2.42 | NA | 2.43 | 3.8 |
| 2 | 92.2 | 2.7 | 103 | 0.5 | 2.13 | 1.2 | 2.49 | 1.2 |
| 3 | 69.0 | 1.1 | 47.6 | 1.4 | 2.27 | 2.3 | 2.3 | 1.7 |
| 4 | 113 | 0.9 | 100 | 2.7 | 2.29 | 1.4 | 2.26 | 3.7 |
| 5 | 23.8 | 1.6 | 43.2 | 1.0 | 2.81 | 1.5 | 2.83 | 1.0 |
| 6 | 87.8 | 1.1 | 97.4 | 3.5 | 2.67 | 1.3 | 2.66 | 4.2 |
| 7 | 76.2 | 2.9 | 678 | 1.0 | 2.33 | 1.2 | 2.37 | 3.3 |
| 8 | 104 | 2.4 | 100 | 1.2 | 2.48 | 3.1 | 2.33 | 2.0 |
| 9 | 72.0 | 1.3 | 90.5 | 2.3 | 2.07 | 2.0 | 2.63 | 3.1 |
| 10 | 86.5 | 1.9 | NA | | 2.23 | 3.0 | NA | |
| 11 | 82.6 | 0.8 | 34.3 | 1.4 | 2.16 | 2.7 | 2.14 | 2.2 |
| 12 | 92.2 | 0.4 | 110 | 0.7 | 2.14 | 0.5 | 2.33 | 1.9 |
| 13 | 110 | 0.5 | 109 | 1.8 | 2.55 | 2.5 | 2.52 | 1.1 |

*Table A.2: Average and RSD aqua regia soluble copper and iron content in soil samples from Glasgow Green, (n = 3).*

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lead | | | | Manganese | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 368 | NA | 261 | 2.3 | 356 | NA | 513 | 2.6 |
| 2 | 292 | 3.3 | 325 | 1.1 | 376 | 2.0 | 430 | 0.6 |
| 3 | 230 | 1.4 | 160 | 0.6 | 526 | 1.1 | 519 | 1.2 |
| 4 | 458 | 1.3 | 386 | 2.7 | 496 | 1.8 | 478 | 3.0 |
| 5 | 98.4 | 1.8 | 143 | 0.5 | 460 | 1.4 | 510 | 0.7 |
| 6 | 331 | 0.9 | 342 | 2.8 | 559 | 1.2 | 553 | 3.7 |
| 7 | 279 | 3.4 | 324 | 1.7 | 457 | 2.2 | 494 | 0.9 |
| 8 | 398 | 2.7 | 376 | 2.2 | 547 | 2.7 | 557 | 2.2 |
| 9 | 198 | 0.3 | 304 | 2.5 | 333 | 1.4 | 453 | 2.2 |
| 10 | 233 | 1.1 | NA | | 420 | 2.1 | NA | |
| 11 | 193 | 2.7 | 144 | 3.1 | 413 | 2.1 | 433 | 0.8 |
| 12 | 240 | 0.4 | 298 | 0.3 | 468 | 1.6 | 538 | 1.3 |
| 13 | 676 | 1.5 | 894 | 2.1 | 549 | 0.2 | 547 | 2.1 |

*Table A.3: Average and RSD aqua regia soluble lead and manganese content in soil samples from Glasgow Green, (n = 3).*

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Nickel | | | | Zinc | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 33.9 | NA | 27.4 | 6.6 | 144 | NA | 105 | 3.5 |
| 2 | 30.1 | 4.3 | 36.5 | 2.6 | 169 | 2.9 | 197 | 1.0 |
| 3 | 31.0 | 5.6 | 30.3 | 3.0 | 160 | 3.0 | 165 | 2.9 |
| 4 | 52.6 | 4.9 | 50.7 | 4.4 | 377 | 2.1 | 317 | 2.2 |
| 5 | 21.0 | 0.9 | 24.5 | 3.0 | 102 | 1.7 | 122 | 1.3 |
| 6 | 44.2 | 5.5 | 45.6 | 7.5 | 244 | 3.1 | 246 | 5.3 |
| 7 | 36.2 | 3.6 | 38.2 | 1.4 | 174 | 4.0 | 190 | 1.2 |
| 8 | 46.5 | 3.0 | 40.8 | 0.6 | 314 | 2.8 | 267 | 1.7 |
| 9 | 26.8 | 4.3 | 38.3 | 6.5 | 131 | 2.2 | 203 | 4.5 |
| 10 | 33.4 | 4.3 | NA | | 183 | 3.1 | NA | |
| 11 | 26.9 | 5.4 | 27.5 | 0.9 | 128 | 2.1 | 94.0 | 1.8 |
| 12 | 31.8 | 0.5 | 37.5 | 2.9 | 189 | 0.9 | 224 | 2.0 |
| 13 | 43.1 | 4.4 | 40.3 | 3.2 | 274 | 1.6 | 223 | 2.5 |

*Table A.4: Average and RSD aqua regia soluble nickel and zinc content in soil samples from Glasgow Green, (n = 3).*

| Sample point | Loss on ignition at 550 °C (%) | | | |
|---|---|---|---|---|
| | Surface | | Sub surface | |
| | Mean | RSD | Mean | RSD |
| 1 | 20.1 | 1.0 | 11.8 | 1.7 |
| 2 | 12.7 | 7.5 | 12.7 | 1.4 |
| 3 | 10.1 | 3.6 | 6.7 | 4.8 |
| 4 | 20.8 | 4.9 | 14.5 | 6.2 |
| 5 | 10.9 | 1.9 | 6.9 | 6.2 |
| 6 | 15.8 | 5.2 | 11.2 | 1.5 |
| 7 | 13 | 0.8 | 11.4 | 4.8 |
| 8 | 18.2 | 1.7 | 13.7 | 3.2 |
| 9 | 11.9 | 5.4 | 13.4 | 4.8 |
| 10 | 11.5 | 4.7 | NA | NA |
| 11 | 13.6 | 12.5 | 8.1 | 8.8 |
| 12 | 11.9 | 4.0 | 12.5 | 3.9 |
| 13 | 16.8 | 4.7 | 11.6 | 2.4 |

*Table A.5: Average and RSD of LOI (%) from Glasgow Green soil samples, (n = 3).*

Table A.6 – table A.10 show the aqua regia soluble metals content and LOI (%) from Alexandra Park samples.

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Calcium | | | | Chromium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 920 | 19.6 | 550 | 18.2 | 39.2 | 2.3 | 17.5 | 1.7 |
| 2 | 3310 | 3.0 | 4420 | 2.3 | 131 | 1.1 | 107 | 11.2 |
| 3 | 900 | 13.3 | 750 | 8.0 | 42.3 | 3.5 | 25.5 | 2.7 |
| 4 | 580 | 5.2 | 490 | 10.2 | 43.1 | 2.3 | 24.0 | 2.5 |
| 5 | 1180 | 11.9 | 1400 | 12.9 | 53.2 | 1.3 | 29.7 | 4.4 |
| 6 | 710 | 14.1 | 580 | 15.5 | 35.5 | 2.5 | 26.5 | 1.5 |
| 7 | 4770 | 4.6 | 6900 | 1.9 | 59.6 | 1.2 | 61.6 | 2.3 |
| 8 | 1500 | 10.0 | 1360 | 8.8 | 48.6 | 6.6 | 46.4 | 4.5 |
| 9 | 750 | 26.7 | 730 | 16.4 | 40.1 | 3.5 | 17.5 | 2.9 |
| 10 | 1210 | 3.3 | 1270 | 0.8 | 21.3 | 2.8 | 18.7 | 1.1 |
| 11 | 1490 | 9.4 | 830 | 12.0 | 24.8 | 1.2 | 16.8 | 15.5 |
| 12 | 1150 | 7.8 | 720 | 8.3 | 35.2 | 5.1 | 18.5 | 0.0 |
| 13 | 1100 | 5.5 | 2030 | 21.2 | 27.7 | 0.0 | 20.8 | 5.3 |
| 14 | 1050 | 3.8 | 1080 | 2.8 | 26.7 | 1.1 | 20.0 | 3.5 |

*Table A.6: Average and RSD aqua regia soluble calcium and chromium content in soil samples from Alexandra Park, (n = 3).*

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Copper | | | | Iron (%) | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 87.8 | 7.1 | 31.2 | 2.9 | 2.77 | 2.5 | 2.75 | 1.8 |
| 2 | 66.1 | 1.2 | 54.7 | 1.3 | 2.86 | 0.3 | 2.81 | 0.7 |
| 3 | 79.6 | 4.1 | 55.2 | 3.8 | 2.78 | 2.9 | 2.65 | 2.6 |
| 4 | 62.5 | 1.0 | 24.2 | 4.5 | 2.55 | 0.8 | 2.51 | 2.0 |
| 5 | 62.9 | 2.2 | 57.4 | 3.8 | 2.78 | 1.1 | 2.77 | 3.2 |
| 6 | 53.6 | 0.4 | 47.9 | 1.3 | 2.66 | 0.8 | 3.15 | 1.0 |
| 7 | 113 | 0.8 | 151 | 3.3 | 2.52 | 1.6 | 2.45 | 2.4 |
| 8 | 40.7 | 7.1 | 41.2 | 3.2 | 2.54 | 5.5 | 2.45 | 3.7 |
| 9 | 64.9 | 3.2 | 44.6 | 3.6 | 2.55 | 2.7 | 2.36 | 3.4 |
| 10 | 44.3 | 2.9 | 42.3 | 0.7 | 2.35 | 1.7 | 2.41 | 1.2 |
| 11 | 33.4 | 1.2 | 31.7 | 6.0 | 2.04 | 0.5 | 2.30 | 5.2 |
| 12 | 56.3 | 1.8 | 39.8 | 0.8 | 3.35 | 2.1 | 2.55 | 0.8 |
| 13 | 56.3 | 0.5 | 43.4 | 2.8 | 2.77 | 0.7 | 2.78 | 4.0 |
| 14 | 51.2 | 2.0 | 42.4 | 0.7 | 2.6 | 1.5 | 2.43 | 1.2 |

*Table A.7: Average and RSD aqua regia soluble copper and iron content in soil samples from Alexandra Park, (n = 3).*

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lead | | | | Manganese | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 213 | 0.9 | 41.2 | 4.9 | 229 | 2.2 | 715 | 2.4 |
| 2 | 183 | 3.8 | 125 | 0.0 | 724 | 1.9 | 630 | 1.9 |
| 3 | 245 | 3.3 | 155 | 1.9 | 339 | 3.2 | 829 | 1.7 |
| 4 | 175 | 1.1 | 55.6 | 0.0 | 258 | 1.9 | 840 | 2.9 |
| 5 | 179 | 0.6 | 150 | 2.0 | 569 | 1.4 | 616 | 2.4 |
| 6 | 175 | 1.1 | 134 | 3.0 | 163 | 1.8 | 292 | 1.4 |
| 7 | 414 | 1.0 | 432 | 2.5 | 670 | 0.9 | 782 | 3.1 |
| 8 | 134 | 6.0 | 122 | 3.3 | 446 | 5.6 | 418 | 2.6 |
| 9 | 208 | 3.8 | 153 | 3.3 | 207 | 2.4 | 476 | 2.1 |
| 10 | 147 | 2.7 | 138 | 1.4 | 534 | 2.2 | 573 | 1.0 |
| 11 | 114 | 0.9 | 107 | 6.5 | 280 | 0.7 | 507 | 4.7 |
| 12 | 178 | 1.7 | 97.9 | 0.0 | 414 | 2.2 | 605 | 0.8 |
| 13 | 196 | 1.0 | 151 | 4.0 | 509 | 0.4 | 747 | 4.1 |
| 14 | 161 | 2.5 | 125 | 1.6 | 234 | 1.7 | 454 | 1.5 |

*Table B.8: Average and RSD aqua regia soluble lead and manganese content in soil samples from Alexandra Park, (n = 3).*

| Sample point | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Nickel | | | | Zinc | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 24.4 | 5.3 | 18.0 | 3.3 | 74.3 | 1.9 | 64.0 | 1.6 |
| 2 | 52.7 | 0.9 | 38.3 | 6.0 | 224 | 0.5 | 181 | 2.0 |
| 3 | 30.6 | 4.9 | 24.0 | 1.7 | 98.9 | 4.9 | 133 | 5.1 |
| 4 | 27.5 | 8.4 | 19.6 | 5.6 | 66.9 | 0.7 | 70.0 | 3.3 |
| 5 | 41.8 | 1.4 | 32.5 | 7.4 | 123 | 1.5 | 152 | 4.1 |
| 6 | 23.2 | 3.4 | 22.7 | 0.9 | 83.7 | 2.2 | 102 | 1.8 |
| 7 | 39.0 | 2.1 | 39.0 | 3.3 | 305 | 1.3 | 298 | 3.3 |
| 8 | 26.1 | 7.7 | 25.5 | 4.7 | 133 | 6.8 | 126 | 4.6 |
| 9 | 30.8 | 6.5 | 18.0 | 3.9 | 90.9 | 5.4 | 92.6 | 1.8 |
| 10 | 18.6 | 0.5 | 18.5 | 1.6 | 116 | 2.7 | 120 | 2.3 |
| 11 | 18.0 | 5.0 | 16.2 | 10.5 | 82.8 | 1.0 | 70.7 | 10.6 |
| 12 | 26.7 | 3.4 | 20.6 | 1.9 | 120 | 5.3 | 89.8 | 2.2 |
| 13 | 21.2 | 2.8 | 21.6 | 2.8 | 108 | 2.0 | 149 | 2.4 |
| 14 | 19.8 | 1.5 | 20.4 | 4.9 | 88.3 | 2.9 | 108 | 2.4 |

*Table A.9: Average and RSD aqua regia soluble nickel and zinc content in soil samples from Alexandra Park, (n = 3).*

| Sample point | Loss on ignition at 550 °C (%) | | | |
|---|---|---|---|---|
| | Surface | | Sub surface | |
| | Mean | RSD | Mean | RSD |
| 1 | 18.9 | 4.4 | 5.4 | 6.3 |
| 2 | 16.0 | 4.2 | 10.5 | 7.1 |
| 3 | 16.1 | 1.6 | 7.7 | 2.0 |
| 4 | 14.7 | 1.0 | 5.5 | 3.1 |
| 5 | 12.6 | 3.2 | 9.6 | 2.9 |
| 6 | 14.4 | 10.2 | 7.2 | 2.3 |
| 7 | 16.5 | 2.9 | 14.7 | 7.1 |
| 8 | 12.6 | 6.9 | 10.2 | 3.6 |
| 9 | 15.0 | 1.7 | 8.0 | 2.9 |
| 10 | 10.7 | 4.0 | 8.3 | 0.6 |
| 11 | 9.2 | 0.9 | 6.3 | 4.6 |
| 12 | 17.3 | 4.1 | 10.1 | 1.8 |
| 13 | 14.8 | 2.7 | 8.2 | 8.3 |
| 14 | 12.3 | 3.6 | 9.7 | 18.0 |

*Table A.10: Average and RSD of LOI (%) from Alexandra Park soil samples, (n = 3).*

# APPENDIX B

Table B.1 shows the sample site locations from Glasgow parks and open spaces.

| Sample reference | Easting (approx.) | Northing (approx.) | Description |
|---|---|---|---|
| PO.01 | 254250 | 667250 | Victoria Park |
| PO.02 | 258250 | 662250 | Queens Park |
| PO.03 | 259500 | 660500 | Kings Park |
| PO.04 | 261250 | 668750 | Springburn Park |
| PO.05 | 254750 | 663750 | Bellahoustoun Park |
| PO.06 | 265500 | 664500 | Cranhill Park |
| PO.07 | 256250 | 670250 | Maryhill Park |
| PO.08 | 255750 | 669750 | Dawsholm Park |
| PO.09 | 258000 | 668250 | Ruchill Park |
| PO.10 | 264250 | 667250 | Hogganfield Loch |
| PO.11 | 263500 | 663750 | Tolcross Park |
| PO.12 | 265250 | 663500 | Sandyhill Park |
| PO.13 | 264500 | 664750 | Greenfield Park |
| PO.14 | 266750 | 663250 | Mount Vernon |
| PO.15 | 260250 | 663250 | Richmond Park |
| PO.16 | 259500 | 661000 | Toryglen Park |
| PO.17 | 258500 | 659250 | Linn Park |
| PO.18 | 254750 | 665750 | Elder Park |
| PO.19 | 257250 | 666750 | Kelvingrove Park (near river) |
| PO.20 | 257250 | 666750 | Kelvingrove Park (top of hill) |
| PO.21 | 263250 | 668250 | Robroyston Park |
| PO.22 | 259750 | 666500 | Sighthill Park |
| PO.23 | 253250 | 669750 | Knightswood Park |
| PO.24 | 252750 | 661250 | Househill Park |
| PO.25 | 252250 | 663000 | Rosshall Park |
| PO.26 | 253500 | 662750 | Lochar Park |
| PO.27 | 252750 | 659750 | Woodcroft Quad |
| PO.28 | 256500 | 661250 | Near Auldhouse Road |
| PO.29 | 258500 | 666500 | Open space near St. Georges Rd and M8 |
| PO.30 | 256750 | 667500 | Botanic Gardens |
| PO.31 | 252250 | 671250 | Drumchapel |
| PO.32 | 258250 | 665750 | Blythswood Square |
| PO.33 | 262250 | 665750 | Alexandra Park |
| PO.34 | 259750 | 664250 | Glasgow Green |
| PO.35 | 255500 | 662250 | Pollock Park |
| PO.36 | 256750 | 663250 | Maxwells Park |
| PO.37 | 257000 | 660500 | Newlands Park |
| PO.38 | 259250 | 665250 | George Square |
| PO.39 | 259750 | 665750 | Strathclyde University, (Steelhendge) |

*Table B.1: Park and open spaces sample site locations.*

Table B.2 to B.9 show the results from Glasgow park and open spaces samples.

| Sample point GLA.PO | Loss on ignition at 550 °C (%) | | | |
|---|---|---|---|---|
| | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 17 | 4.3 | 13.3 | 11.6 |
| 2 | 24 | 1.2 | 8.36 | 8.5 |
| 3 | 12.5 | 9.3 | 9.1 | 2.5 |
| 4 | 17.1 | 2.6 | 6.68 | 10.9 |
| 5 | 11.9 | 7.3 | 9.05 | 4.5 |
| 6 | 15.3 | 7.9 | 17.9 | 14.2 |
| 7 | 11.2 | 4.9 | 9.23 | 6.8 |
| 8 | 11.5 | 7.5 | 9.77 | 8.3 |
| 9 | 12.3 | 9.1 | 8.4 | 7.3 |
| 10 | 15.8 | 10.2 | 11.6 | 10.1 |
| 11 | 10.6 | 2.7 | 8.72 | 7.0 |
| 12 | 11.4 | 5.4 | 6.87 | 8.3 |
| 13 | 11.2 | 7.0 | 8.5 | 2.5 |
| 14 | 11 | 8.9 | 8.08 | 9.3 |
| 15 | 17 | 0.9 | 11 | 4.7 |
| 16 | 13.9 | 5.3 | 10.7 | 8.8 |
| 17 | 14.9 | 3.7 | 11.2 | 6.9 |
| 18 | 17 | 8.9 | 7.59 | 4.3 |
| 19 | 13.2 | 2.8 | 8.67 | 3.2 |
| 20 | 11.8 | 6.6 | 10.2 | 8.7 |
| 21 | 14.5 | 9.5 | 10.7 | 1.6 |
| 22 | 13.3 | 5.3 | 9.37 | 6.3 |
| 23 | 14.3 | 1.5 | 8.52 | 0.9 |
| 24 | 23.6 | 4.5 | 23.5 | 1.6 |
| 25 | 11.3 | 8.3 | 8.43 | 5.8 |
| 26 | 13.4 | 3.4 | 13.1 | 6.4 |
| 27 | 13.8 | 1.2 | 9.97 | 4.6 |
| 28 | 18.5 | 5.5 | 13.7 | 5.7 |
| 29 | 9.91 | 3.9 | 8.37 | 3.7 |
| 30 | 13.6 | 7.2 | 9.97 | 3.6 |
| 31 | 8.06 | 3.4 | 5.04 | 10.2 |
| 32 | 10.1 | 8.0 | 7.81 | 8.1 |
| 33 | 11.7 | 2.8 | 7.24 | 2.5 |
| 34 | 14.4 | 2.7 | 12.1 | 0.5 |
| 35 | 10.3 | 18.9 | 6.61 | 15.8 |
| 36 | 17.6 | 5.7 | 14.1 | 2.9 |
| 37 | 9.82 | 3.4 | 8.29 | 1.3 |
| 38 | 3.89 | 3.2 | 3.51 | 16.7 |
| 39 | 9.18 | 4.2 | 7.43 | 6.0 |

*Table B.2: LOI (%) from park and open spaces samples.*

| Sample point GLA.PO | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Aluminium | | | | Barium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 18400 | 5.3 | 18600 | 7.0 | 142 | 4.7 | 160 | 12 |
| 2 | 11800 | 14.0 | 14500 | 6.2 | 88.2 | 6.6 | 67.5 | 1.2 |
| 3 | 17400 | 5.5 | 18200 | 4.4 | 141 | 6.7 | 154 | 8.2 |
| 4 | 10800 | 5.7 | 9900 | 11.3 | 62.4 | 6.5 | 58.9 | 5.3 |
| 5 | 12900 | 15.6 | 13800 | 6.3 | 148 | 3.6 | 140 | 2.1 |
| 6 | 16900 | 9.6 | 16900 | 5.8 | 153 | 5.2 | 247 | 31 |
| 7 | 12800 | 10.6 | 12200 | 10.4 | 84.0 | 2.3 | 93.5 | 5.2 |
| 8 | 13600 | 17.2 | 12600 | 2.6 | 143 | 7.4 | 162 | 5.3 |
| 9 | 9900 | 2.9 | 10000 | 6.2 | 85.9 | 7.2 | 69.1 | 8.4 |
| 10 | 16100 | 10.0 | 17500 | 12.3 | 84.7 | 6.5 | 108 | 7.3 |
| 11 | 11100 | 19.2 | 12600 | 12.2 | 92.4 | 6.6 | 120 | 7.1 |
| 12 | 13100 | 5.5 | 12200 | 5.8 | 139 | 12 | 118 | 1.0 |
| 13 | 11000 | 6.0 | 12600 | 21.7 | 112 | 1.4 | 134 | 8.6 |
| 14 | 13200 | 5.7 | 14500 | 19.1 | 78.1 | 2.4 | 90.0 | 2.7 |
| 15 | 16300 | 2.2 | 19500 | 24.4 | 185 | 3.2 | 205 | 14 |
| 16 | 11300 | 3.4 | 14800 | 12.9 | 277 | 4.1 | 352 | 12 |
| 17 | 14300 | 10.4 | 21300 | 36.3 | 98.0 | 2.6 | 138 | 10 |
| 18 | 16500 | 6.8 | 18800 | 24.2 | 88.4 | 4.0 | 94.4 | 16 |
| 19 | 16200 | 5.2 | 18800 | 12.6 | 116 | 3.5 | 92.4 | 4.3 |
| 20 | 13300 | 4.3 | 17200 | 6.6 | 157 | 3.0 | 182 | 6.5 |
| 21 | 14600 | 30.4 | 12800 | 8.0 | 105 | 6.5 | 112 | 11 |
| 22 | 13600 | 11.2 | 14900 | 7.3 | 97.0 | 14 | 101 | 5.9 |
| 23 | 18800 | 11.4 | 17100 | 2.9 | 78.7 | 4.5 | 94.8 | 6.7 |
| 24 | 26400 | 5.7 | 37400 | 4.6 | 452 | 10 | 752 | 2.4 |
| 25 | 24300 | 5.9 | 23500 | 14.0 | 140 | 2.8 | 135 | 4.6 |
| 26 | 24600 | 4.3 | 23300 | 4.4 | 327 | 6.1 | 387 | 9.8 |
| 27 | 21300 | 3.2 | 22100 | 9.9 | 147 | 8.0 | 148 | 4.4 |
| 28 | 18100 | 4.2 | 19800 | 14.9 | 185 | 5.3 | 236 | 2.1 |
| 29 | 13000 | 2.0 | 12400 | 4.5 | 256 | 4.2 | 296 | 4.6 |
| 30 | 15900 | 6.4 | 18200 | 6.2 | 87.6 | 6.7 | 95.5 | 1.8 |
| 31 | 11000 | 11.9 | 12200 | 8.5 | 80.4 | 7.9 | 98.1 | 16 |
| 32 | 14200 | 14.6 | 11800 | 7.2 | 144 | 8.6 | 138 | 6.4 |
| 33 | 14200 | 3.8 | 16300 | 7.9 | 101 | 4.8 | 127 | 1.6 |
| 34 | 15200 | 5.6 | 14700 | 3.8 | 244 | 18 | 284 | 13 |
| 35 | 9500 | 1.1 | 11600 | 7.7 | 64.0 | 3.6 | 84.9 | 18 |
| 36 | 12300 | 0.6 | 13200 | 2.4 | 149 | 6.6 | 179 | 2.5 |
| 37 | 17600 | 5.3 | 16300 | 18.8 | 96.8 | 0.4 | 101 | 2.9 |
| 38 | 6700 | 1.5 | 7000 | 1.1 | 71.4 | 6.9 | 80.0 | 3.8 |
| 39 | 17500 | 4.6 | 16300 | 5.4 | 127 | 2.6 | 153 | 7.8 |

*Table B.3: Average and RSD aluminium and barium aqua regia soluble content in park and open spaces samples, (n = 3).*

| Sample point GLA.PO | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Copper | | | | Iron (%) | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 77.4 | 3.1 | 93.0 | 6.6 | 3.87 | 2.6 | 4.22 | 4.3 |
| 2 | 69.4 | 2.6 | 44.7 | 10 | 2.14 | 2.9 | 3.09 | 10 |
| 3 | 26.9 | 3.8 | 27.7 | 6.6 | 2.84 | 4.8 | 3.44 | 4.6 |
| 4 | 52.4 | 4.4 | 27.2 | 5.6 | 1.71 | 5.6 | 1.84 | 8.0 |
| 5 | 69.4 | 4.6 | 96.1 | 3.0 | 3.21 | 2.1 | 3.56 | 1.7 |
| 6 | 54.5 | 1.1 | 139 | 3.1 | 2.68 | 5.3 | 2.96 | 3.7 |
| 7 | 28.3 | 3.1 | 30.9 | 4.5 | 2.31 | 3.2 | 2.56 | 5.8 |
| 8 | 40.2 | 11 | 47.0 | 1.7 | 2.70 | 9.9 | 3.32 | 16 |
| 9 | 48.1 | 4.7 | 48.6 | 29 | 2.61 | 2.8 | 3.16 | 12 |
| 10 | 48.8 | 1.3 | 45.3 | 3.1 | 3.08 | 0.7 | 3.39 | 0.6 |
| 11 | 41.1 | 3.2 | 48.0 | 4.0 | 2.41 | 1.8 | 2.79 | 2.6 |
| 12 | 48.9 | 3.4 | 73.9 | 19 | 2.83 | 4.8 | 3.34 | 3.8 |
| 13 | 34.6 | 5.2 | 36.9 | 4.8 | 2.49 | 3.0 | 2.90 | 18 |
| 14 | 40.5 | 1.9 | 45.6 | 2.8 | 2.56 | 2.4 | 2.61 | 3.0 |
| 15 | 156 | 2.9 | 176 | 16 | 2.90 | 0.3 | 3.24 | 5.4 |
| 16 | 57.2 | 6.2 | 61.6 | 3.4 | 2.2 | 7.8 | 2.60 | 2.4 |
| 17 | 40.0 | 3.8 | 51.7 | 5.0 | 2.97 | 2.3 | 3.81 | 5.9 |
| 18 | 61.8 | 4.8 | 59.4 | 4.9 | 2.52 | 2.8 | 2.85 | 2.4 |
| 19 | 63.7 | 2.4 | 40.1 | 4.2 | 3.23 | 1.8 | 3.37 | 3.1 |
| 20 | 96.0 | 3.0 | 75.3 | 3.8 | 3.11 | 3.6 | 3.57 | 2.7 |
| 21 | 54.2 | 1.9 | 55.0 | 11 | 2.73 | 1.8 | 3.53 | 6.2 |
| 22 | 28.9 | 13 | 29.1 | 5.9 | 1.76 | 8.9 | 2.19 | 8.0 |
| 23 | 42.0 | 2.5 | 55.7 | 8.2 | 2.69 | 3.0 | 2.98 | 3.5 |
| 24 | 194 | 3.2 | 471 | 8.9 | 4.04 | 2.9 | 4.64 | 0.7 |
| 25 | 39.8 | 1.2 | 40.3 | 3.7 | 4.64 | 1.3 | 4.49 | 3.6 |
| 26 | 152 | 0.1 | 504 | 26 | 4.94 | 3.4 | 4.70 | 2.2 |
| 27 | 39.3 | 3.0 | 43.7 | 7.4 | 3.83 | 1.4 | 4.32 | 4.2 |
| 28 | 113 | 6.2 | 200 | 0.4 | 3.56 | 4.4 | 3.60 | 1.6 |
| 29 | 56.8 | 5.4 | 75.4 | 5.8 | 2.81 | 6.2 | 2.97 | 4.7 |
| 30 | 47.9 | 8.3 | 42.1 | 5.6 | 3.09 | 3.9 | 3.71 | 7.3 |
| 31 | 45.6 | 7.3 | 26.4 | 7.8 | 1.77 | 9.0 | 1.97 | 2.1 |
| 32 | 56.4 | 7.6 | 53.3 | 6.1 | 2.48 | 10 | 2.92 | 3.7 |
| 33 | 56.5 | 6.9 | 70.5 | 6.0 | 2.68 | 8.9 | 3.11 | 5.6 |
| 34 | 99.5 | 4.5 | 107 | 2.2 | 3.11 | 2.3 | 3.20 | 2.7 |
| 35 | 32.3 | 4.0 | 46.7 | 7.6 | 1.61 | 3.3 | 2.00 | 6.8 |
| 36 | 72.3 | 2.2 | 90.2 | 5.9 | 2.27 | 4.4 | 2.37 | 2.3 |
| 37 | 43.3 | 1.4 | 44.6 | 4.5 | 3.59 | 1.2 | 3.61 | 1.9 |
| 38 | 18.3 | 6.5 | 20.3 | 7.8 | 2.24 | 14 | 2.30 | 1.9 |
| 39 | 41.9 | 30 | 37.9 | 4.4 | 3.11 | 0.6 | 3.33 | 4.8 |

*Table B.4: Average and RSD copper and iron aqua regia soluble content in park and open spaces samples, (n = 3).*

| Sample point GLA.PO | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Calcium | | | | Chromium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 3730 | 9.2 | 3840 | 6.7 | 38.4 | 2.2 | 35.9 | 5.1 |
| 2 | 1920 | 40 | 820 | 8.6 | 76.4 | 8.5 | 35.2 | 3.1 |
| 3 | 2390 | 49 | 1730 | 9.9 | 35.2 | 4.7 | 35.5 | 3.5 |
| 4 | 900 | 2.0 | 470 | 18.5 | 28.2 | 3.9 | 16.8 | 9.5 |
| 5 | 2180 | 4.4 | 2060 | 6.8 | 29 | 14 | 29.7 | 7.5 |
| 6 | 2350 | 6.2 | 2930 | 9.0 | 114 | 3.4 | 111 | 3.9 |
| 7 | 1310 | 5.1 | 1600 | 7.7 | 24.2 | 8.1 | 22.9 | 9.4 |
| 8 | 2690 | 0.8 | 2690 | 3.3 | 26.8 | 14 | 27.6 | 5.9 |
| 9 | 870 | 3.6 | 910 | 28 | 32.5 | 4.9 | 22.5 | 7.5 |
| 10 | 920 | 6.1 | 1410 | 2.7 | 31.8 | 9.0 | 30.9 | 10 |
| 11 | 1590 | 3.5 | 1900 | 6.5 | 32.6 | 14 | 34.5 | 10 |
| 12 | 3260 | 1.6 | 3890 | 6.2 | 29.5 | 2.7 | 26.1 | 0.8 |
| 13 | 1340 | 2.9 | 1330 | 8.6 | 62.0 | 3.1 | 69.6 | 7.0 |
| 14 | 2100 | 7.0 | 2050 | 3.1 | 31.7 | 4.8 | 32.4 | 12 |
| 15 | 3470 | 3.4 | 4230 | 12 | 138 | 3.5 | 92.3 | 17 |
| 16 | 5460 | 8.2 | 7680 | 15 | 48.9 | 3.9 | 68 | 29 |
| 17 | 2050 | 6.1 | 2720 | 15 | 29.0 | 9.8 | 42.5 | 27 |
| 18 | 1030 | 7.3 | 930 | 31 | 174 | 3.8 | 232 | 16 |
| 19 | 1610 | 5.1 | 1030 | 2.4 | 44.5 | 4.4 | 38.2 | 10 |
| 20 | 3480 | 1.4 | 3000 | 10 | 34.6 | 4.9 | 36 | 3.9 |
| 21 | 3030 | 0.9 | 3810 | 10 | 30.0 | 21 | 26.5 | 9.7 |
| 22 | 3420 | 8.6 | 3270 | 7.1 | 53.4 | 10 | 54.6 | 6.0 |
| 23 | 1080 | 10 | 1470 | 4.4 | 37.9 | 6.2 | 38.3 | 7.1 |
| 24 | 4930 | 3.1 | 7130 | 3.5 | 80.2 | 28 | 108 | 24 |
| 25 | 2160 | 1.6 | 2220 | 5.2 | 65.4 | 2.5 | 62.1 | 5.4 |
| 26 | 4190 | 7.2 | 5170 | 10 | 71.0 | 2.7 | 105 | 59 |
| 27 | 4620 | 4.7 | 4050 | 3.4 | 44.9 | 2.2 | 45.9 | 9.1 |
| 28 | 3180 | 10 | 4020 | 6.8 | 66.6 | 2.9 | 69.3 | 7.3 |
| 29 | 4660 | 7.7 | 6390 | 4.3 | 35.1 | 3.4 | 36.4 | 3.2 |
| 30 | 1940 | 11 | 1530 | 13 | 34.4 | 5.4 | 33.8 | 4.6 |
| 31 | 1500 | 8.3 | 1680 | 2.8 | 22.0 | 11 | 24.0 | 5.9 |
| 32 | 2180 | 10 | 1930 | 6.1 | 229 | 12 | 191 | 13 |
| 33 | 1430 | 20 | 1600 | 7.7 | 33.8 | 3.8 | 31.8 | 4.0 |
| 34 | 2250 | 5.9 | 1940 | 17 | 46.5 | 4.4 | 44.5 | 4.5 |
| 35 | 940 | 9.1 | 1230 | 31 | 26.3 | 2.5 | 30.9 | 3.0 |
| 36 | 4170 | 1.9 | 4710 | 9.2 | 34.2 | 0.8 | 35.8 | 2.1 |
| 37 | 1100 | 7.9 | 1390 | 15 | 40.9 | 3.8 | 38.0 | 13 |
| 38 | 2400 | 6.8 | 2310 | 8.3 | 23.6 | 6.2 | 23.8 | 1.1 |
| 39 | 3160 | 2.3 | 3530 | 7.3 | 41.2 | 6.0 | 40.2 | 3.4 |

*Table B.5: Average and RSD calcium and chromium aqua regia soluble content in park and open spaces samples, (n = 3).*

| Sample point GLA.PO | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lithium | | | | Magnesium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 18.0 | 5.7 | 18.1 | 5.3 | 6550 | 2.2 | 6760 | 5.8 |
| 2 | 10.6 | 17 | 13.8 | 11 | 1580 | 9.7 | 1760 | 2.0 |
| 3 | 16.6 | 4.5 | 17.3 | 4.1 | 2410 | 7.0 | 2370 | 3.9 |
| 4 | 10.2 | 5.2 | 8.60 | 16 | 1310 | 6.4 | 1270 | 13 |
| 5 | 12.9 | 19 | 13.6 | 5.7 | 1640 | 9.0 | 1700 | 4.3 |
| 6 | 14.2 | 6.1 | 14.3 | 3.8 | 2830 | 5.0 | 2730 | 3.4 |
| 7 | 11.7 | 11 | 10.4 | 15 | 1930 | 5.8 | 1840 | 8.1 |
| 8 | 11.7 | 19 | 11.3 | 6.4 | 2630 | 12 | 2690 | 4.4 |
| 9 | 8.60 | 9.6 | 8.50 | 9.0 | 1090 | 5.1 | 1090 | 6.9 |
| 10 | 12.8 | 11 | 14.1 | 11 | 2350 | 6.7 | 2680 | 6.9 |
| 11 | 9.9 | 17 | 11.3 | 12 | 1790 | 8.0 | 2040 | 8.8 |
| 12 | 12.6 | 5.9 | 12.3 | 7.8 | 3120 | 6.2 | 3630 | 12.0 |
| 13 | 10.9 | 8.1 | 11.8 | 18 | 2060 | 6.6 | 2060 | 8.3 |
| 14 | 10.6 | 5.3 | 11.6 | 15 | 1740 | 2.9 | 1730 | 7.1 |
| 15 | 16.3 | 2.2 | 18.8 | 22 | 3110 | 1.5 | 3800 | 9.9 |
| 16 | 12.2 | 4.0 | 15.4 | 6.8 | 2240 | 2.6 | 2930 | 12 |
| 17 | 13.3 | 20 | 20.4 | 35 | 1750 | 6.6 | 2050 | 14 |
| 18 | 18.5 | 5.9 | 21.8 | 17 | 2490 | 2.0 | 2620 | 11 |
| 19 | 14.2 | 5.6 | 16.7 | 12 | 2080 | 4.3 | 1970 | 3.3 |
| 20 | 12.4 | 4.0 | 15.9 | 5.3 | 2670 | 0.2 | 2990 | 3.0 |
| 21 | 13.6 | 36 | 11.5 | 10 | 1930 | 8.7 | 2870 | 10 |
| 22 | 10.7 | 11 | 11.3 | 3.2 | 2220 | 9.6 | 2390 | 4.6 |
| 23 | 17.3 | 11 | 16.3 | 2.9 | 2630 | 3.2 | 2660 | 3.4 |
| 24 | 25.3 | 5.7 | 32.7 | 4.5 | 2960 | 2.6 | 2840 | 4.9 |
| 25 | 18.9 | 6.8 | 18.6 | 13 | 4650 | 4.0 | 4410 | 6.2 |
| 26 | 22.0 | 2.7 | 21.1 | 2.9 | 4880 | 2.3 | 4540 | 2.9 |
| 27 | 23.6 | 3.4 | 24.1 | 10 | 2870 | 2.2 | 3030 | 8.2 |
| 28 | 18.1 | 3.5 | 19.3 | 12 | 3260 | 2.6 | 3600 | 5.7 |
| 29 | 13.8 | 4.0 | 13.0 | 3.2 | 2740 | 4.9 | 2830 | 3.5 |
| 30 | 14.6 | 5.1 | 16.2 | 5.8 | 2860 | 6.4 | 2410 | 1.7 |
| 31 | 10.2 | 9.1 | 11.2 | 5.6 | 2470 | 8.6 | 2750 | 2.1 |
| 32 | 12.7 | 13 | 10.2 | 7.7 | 2060 | 7.1 | 1960 | 6.7 |
| 33 | 11.2 | 5.1 | 12.7 | 5.4 | 2030 | 13 | 2210 | 6.2 |
| 34 | 14.9 | 5.4 | 15.0 | 2.8 | 3450 | 4.0 | 3020 | 4.9 |
| 35 | 9.40 | 0.1 | 11.2 | 6.8 | 1100 | 2.0 | 1290 | 9.2 |
| 36 | 11.1 | 0.8 | 12.0 | 3.9 | 2170 | 1.1 | 2380 | 4.0 |
| 37 | 17.7 | 3.5 | 16.3 | 16 | 2720 | 0.6 | 2540 | 5.2 |
| 38 | 7.40 | 2.2 | 7.90 | 0.8 | 3010 | 5.8 | 3010 | 1.5 |
| 39 | 16.3 | 4.3 | 14.8 | 3.6 | 3970 | 4.0 | 3580 | 2.6 |

*Table B.6: Average and RSD lithium and magnesium aqua regia soluble content in park and open spaces samples, (n = 3).*

| Sample point GLA.PO | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Manganese | | | | Nickel | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 643 | 0.9 | 672 | 1.7 | 52.0 | 1.6 | 56.2 | 3.6 |
| 2 | 245 | 3.9 | 213 | 6.3 | 31.1 | 8.2 | 21.3 | 4.1 |
| 3 | 503 | 2.5 | 457 | 7.1 | 25.5 | 3.8 | 27.7 | 5.3 |
| 4 | 94 | 1.9 | 276 | 12 | 27.7 | 3.8 | 13.6 | 5.7 |
| 5 | 435 | 6.6 | 512 | 7.0 | 27.8 | 12 | 27.6 | 4.3 |
| 6 | 590 | 3.6 | 653 | 2.7 | 41.3 | 3.8 | 49.8 | 1.6 |
| 7 | 396 | 1.8 | 409 | 5.3 | 25.3 | 0.9 | 24.9 | 8 |
| 8 | 652 | 13 | 679 | 7.9 | 27.1 | 11 | 30.5 | 4.9 |
| 9 | 353 | 7.9 | 330 | 17 | 24.7 | 1.2 | 22.8 | 22 |
| 10 | 399 | 6.7 | 621 | 9.5 | 31.3 | 7.1 | 33.9 | 4.9 |
| 11 | 364 | 3.0 | 465 | 3.9 | 28.8 | 8.8 | 32.8 | 10 |
| 12 | 509 | 5.2 | 552 | 2.4 | 30.3 | 4.1 | 28.6 | 1.2 |
| 13 | 397 | 4.3 | 400 | 10 | 27.9 | 4.3 | 27.6 | 8.7 |
| 14 | 263 | 1.4 | 277 | 2.6 | 27.8 | 2.4 | 29.0 | 6.4 |
| 15 | 425 | 2.8 | 442 | 2.2 | 74.9 | 2.3 | 72.0 | 16 |
| 16 | 431 | 4.0 | 741 | 59 | 34.6 | 3.3 | 39.8 | 0.7 |
| 17 | 420 | 2.2 | 575 | 5.9 | 32.4 | 3.4 | 45.5 | 7.7 |
| 18 | 145 | 3.8 | 194 | 2.6 | 39.1 | 4.7 | 37 | 10 |
| 19 | 483 | 5.3 | 705 | 3.6 | 42.7 | 3.8 | 33.4 | 3.3 |
| 20 | 656 | 0.6 | 943 | 14 | 45.1 | 4.4 | 52.1 | 8.0 |
| 21 | 372 | 3.4 | 412 | 6.3 | 33.6 | 7.2 | 37.1 | 9.9 |
| 22 | 467 | 12 | 389 | 24 | 32 | 8.7 | 33.7 | 8.0 |
| 23 | 185 | 19 | 171 | 2.6 | 36 | 3.8 | 36.5 | 2.4 |
| 24 | 612 | 2.5 | 657 | 6.0 | 131 | 4.1 | 202 | 7.8 |
| 25 | 1006 | 6.8 | 1007 | 8.2 | 55.7 | 1.9 | 53.3 | 5.8 |
| 26 | 1049 | 3.8 | 1140 | 21 | 85.4 | 1.7 | 92.6 | 5.4 |
| 27 | 860 | 4.0 | 972 | 8.9 | 37.1 | 0.4 | 37.9 | 4.2 |
| 28 | 692 | 5.0 | 745 | 9.7 | 58.8 | 4.2 | 63.1 | 4.5 |
| 29 | 473 | 5.4 | 536 | 5.1 | 34.1 | 3.2 | 38.2 | 3.5 |
| 30 | 546 | 8.3 | 719 | 14 | 35.9 | 6.9 | 34.2 | 1.5 |
| 31 | 307 | 10 | 418 | 0.4 | 20.9 | 8.4 | 23.3 | 5.8 |
| 32 | 416 | 8.6 | 461 | 6.9 | 44.6 | 8.7 | 42.0 | 9.5 |
| 33 | 323 | 17 | 612 | 4.7 | 27.3 | 2.8 | 30.5 | 2.7 |
| 34 | 486 | 4.4 | 619 | 4.3 | 48.1 | 2.6 | 49.5 | 2.4 |
| 35 | 176 | 6.7 | 257 | 14 | 19.6 | 5.4 | 25.1 | 6.5 |
| 36 | 334 | 3.0 | 408 | 8.4 | 47.7 | 1.2 | 50.7 | 1.3 |
| 37 | 525 | 2.7 | 569 | 3.8 | 33.1 | 1.9 | 32.3 | 15 |
| 38 | 418 | 7.0 | 436 | 1.3 | 22.2 | 5.9 | 22.9 | 2.9 |
| 39 | 398 | 7.7 | 442 | 3.0 | 37.3 | 4.6 | 36.5 | 1.6 |

*Table B.7: Average and RSD manganese and nickel aqua regia soluble content in park and open spaces samples, (n = 3).*

| Sample point GLA.PO | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lead | | | | Vanadium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 278 | 1.3 | 320 | 9.8 | 105 | 2.2 | 105 | 2.8 |
| 2 | 248 | 5.8 | 110 | 4.0 | 61 | 6.3 | 52 | 1.0 |
| 3 | 97 | 5.7 | 99 | 3.1 | 48.8 | 3.3 | 51.8 | 3.7 |
| 4 | 257 | 2.2 | 97 | 7.7 | 58.1 | 3.2 | 34.5 | 8.1 |
| 5 | 157 | 6.0 | 140 | 2.9 | 52.2 | 7.2 | 51.7 | 3.1 |
| 6 | 162 | 2.2 | 229 | 4.8 | 61.1 | 4.5 | 66.1 | 1.9 |
| 7 | 114 | 2.0 | 123 | 6.5 | 50.4 | 3.3 | 50.9 | 6.4 |
| 8 | 156 | 5.3 | 177 | 7.7 | 50.6 | 9.1 | 53.9 | 7.0 |
| 9 | 231 | 3.0 | 160 | 9.1 | 53.4 | 2.1 | 47.8 | 10.5 |
| 10 | 156 | 3.5 | 145 | 3.4 | 59.9 | 3.6 | 58.6 | 4.9 |
| 11 | 143 | 2.9 | 171 | 5.9 | 51.3 | 7.3 | 55.5 | 6.0 |
| 12 | 115 | 3.6 | 104 | 0.3 | 53.3 | 4.8 | 53.3 | 8.2 |
| 13 | 99 | 1.2 | 93 | 0.8 | 47.9 | 4.1 | 46.7 | 11.3 |
| 14 | 122 | 1.3 | 126 | 6.2 | 51.9 | 3.9 | 54.2 | 6.3 |
| 15 | 474 | 2.1 | 477 | 14 | 99.6 | 1.7 | 102 | 14.1 |
| 16 | 204 | 8.4 | 221 | 12 | 61.7 | 4.6 | 78.4 | 11.2 |
| 17 | 144 | 5.5 | 148 | 2.1 | 48.3 | 6.5 | 57.5 | 13.5 |
| 18 | 272 | 5.0 | 177 | 6.0 | 77.2 | 4.4 | 70 | 9.4 |
| 19 | 287 | 4.7 | 136 | 2.2 | 75.6 | 3.8 | 57.2 | 3.5 |
| 20 | 234 | 2.2 | 243 | 9.6 | 62.4 | 3.5 | 71.4 | 6.2 |
| 21 | 159 | 3.6 | 165 | 10 | 56.4 | 12.6 | 62.1 | 2.7 |
| 22 | 96 | 13 | 96 | 6.9 | 42.2 | 10.5 | 46.6 | 4.8 |
| 23 | 139 | 5.1 | 159 | 9.1 | 57.6 | 4.0 | 55.6 | 3.2 |
| 24 | 618 | 28 | 831 | 4.8 | 135 | 3.0 | 183 | 1.7 |
| 25 | 114 | 2.0 | 116 | 5.5 | 81.2 | 1.8 | 79.2 | 5.5 |
| 26 | 301 | 0.7 | 332 | 11 | 94.1 | 1.7 | 106 | 8.0 |
| 27 | 97 | 3.6 | 123 | 39 | 88.8 | 0.9 | 92.4 | 5.1 |
| 28 | 306 | 5.5 | 333 | 4.1 | 83.5 | 4.7 | 85 | 6.4 |
| 29 | 277 | 5.8 | 290 | 5.6 | 46.3 | 3.5 | 46.7 | 2.3 |
| 30 | 211 | 7.2 | 174 | 2.2 | 66.2 | 4.6 | 62.1 | 2.8 |
| 31 | 44 | 7.9 | 47 | 19 | 39.8 | 8.8 | 43.1 | 2.1 |
| 32 | 230 | 7.2 | 216 | 4.3 | 61.1 | 7.3 | 57.7 | 6.6 |
| 33 | 173 | 4.3 | 171 | 1.3 | 59.7 | 5.1 | 61.3 | 3.8 |
| 34 | 360 | 6.1 | 396 | 6.9 | 78.6 | 3.9 | 78.5 | 1.5 |
| 35 | 108 | 5.0 | 134 | 12 | 38.7 | 2.9 | 47.1 | 5.7 |
| 36 | 208 | 4.3 | 234 | 6.1 | 66.1 | 2.5 | 68.8 | 3.1 |
| 37 | 141 | 1.9 | 138 | 5.3 | 62.1 | 1.5 | 59.4 | 5.4 |
| 38 | 38 | 8.5 | 43 | 13 | 33.1 | 9.6 | 33.3 | 4.1 |
| 39 | 118 | 2.6 | 135 | 7.8 | 65.9 | 2.8 | 65.6 | 3.0 |

*Table B.8: Average and RSD lead and vanadium aqua regia soluble content in park and open spaces samples, (n = 3).*

| Sample point GLA.PO | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Yttrium | | | | Zinc | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 10.1 | 1.6 | 10.9 | 5.3 | 224 | 1.5 | 239 | 1.9 |
| 2 | 6.99 | 4.6 | 8.18 | 3.6 | 123 | 8.6 | 97 | 3.0 |
| 3 | 7.2 | 3.8 | 7.82 | 6.1 | 141 | 5.3 | 133 | 4.4 |
| 4 | 7.83 | 5.7 | 5.12 | 6.2 | 68 | 3.6 | 52 | 6.8 |
| 5 | 7.58 | 6.4 | 7.78 | 4.5 | 180 | 4.0 | 159 | 1.7 |
| 6 | 10.0 | 3.9 | 11.6 | 3.2 | 246 | 3.5 | 273 | 4.2 |
| 7 | 5.83 | 3.3 | 6.15 | 6.0 | 125 | 3.8 | 121 | 3.9 |
| 8 | 6.94 | 6.2 | 7.14 | 3.7 | 168 | 9.1 | 185 | 4.2 |
| 9 | 5.89 | 1.8 | 5.8 | 8.4 | 124 | 13 | 88 | 8.6 |
| 10 | 7.99 | 7.1 | 8.32 | 3.6 | 141 | 5.3 | 156 | 0.8 |
| 11 | 7.03 | 8.4 | 8.28 | 7.5 | 146 | 4.0 | 177 | 4.4 |
| 12 | 7.94 | 2.0 | 8.43 | 1.2 | 156 | 1.9 | 139 | 5.5 |
| 13 | 7.49 | 5.7 | 7.46 | 7.3 | 121 | 4.3 | 119 | 6.7 |
| 14 | 6.79 | 2.8 | 7.2 | 5.8 | 186 | 21 | 159 | 0.7 |
| 15 | 13.1 | 3.3 | 13.97 | 12 | 490 | 3.9 | 468 | 14 |
| 16 | 8.93 | 1.1 | 10.4 | 4.9 | 184 | 11 | 189 | 6.1 |
| 17 | 6.8 | 5.3 | 8.13 | 11 | 149 | 5.4 | 130 | 5.8 |
| 18 | 6.83 | 6.4 | 7.26 | 12 | 124 | 8.0 | 106 | 7.2 |
| 19 | 8.43 | 2.6 | 7.5 | 3.1 | 151 | 10 | 113 | 3.4 |
| 20 | 8.23 | 4.1 | 9.89 | 4.9 | 208 | 4.3 | 197 | 4.9 |
| 21 | 8.19 | 11 | 8.8 | 1.8 | 243 | 4.4 | 245 | 5.5 |
| 22 | 5.55 | 10 | 6.06 | 7.7 | 111 | 11 | 115 | 13.4 |
| 23 | 6.27 | 4.5 | 6.89 | 5.5 | 107 | 1.6 | 117 | 6.5 |
| 24 | 19.5 | 4.0 | 29.5 | 1.9 | 621 | 3.2 | 855 | 21 |
| 25 | 9.22 | 3.8 | 9.48 | 2.7 | 182 | 0.5 | 170 | 2.1 |
| 26 | 13.4 | 3.0 | 15.2 | 6.6 | 367 | 1.6 | 417 | 7.0 |
| 27 | 9.29 | 1.6 | 9.64 | 2.6 | 151 | 2.2 | 151 | 5.3 |
| 28 | 11.4 | 5.1 | 12.5 | 4.8 | 293 | 5.3 | 313 | 4.5 |
| 29 | 8.77 | 4.0 | 9.19 | 7.4 | 477 | 3.3 | 845 | 17 |
| 30 | 8.63 | 4.7 | 9.09 | 0.8 | 124 | 6.3 | 138 | 7.6 |
| 31 | 6.13 | 9.2 | 7 | 3.8 | 69 | 7.2 | 72 | 9.9 |
| 32 | 8.34 | 8.1 | 7.7 | 8.7 | 222 | 7.0 | 209 | 7.2 |
| 33 | 7.37 | 4.2 | 8.54 | 4.2 | 151 | 6.5 | 188 | 2.6 |
| 34 | 11.2 | 4.6 | 11.4 | 3.2 | 188 | 4.1 | 222 | 8.0 |
| 35 | 4.66 | 2.5 | 5.97 | 10 | 91 | 5.6 | 107 | 16 |
| 36 | 10.2 | 2.5 | 11.4 | 1.4 | 189 | 3.5 | 208 | 5.8 |
| 37 | 8.15 | 0.6 | 8.1 | 3.9 | 136 | 2.5 | 133 | 5.0 |
| 38 | 5.89 | 7.2 | 6.45 | 5.1 | 67 | 11 | 28 | 12 |
| 39 | 9.27 | 3.6 | 9.15 | 1.1 | 128 | 10 | 129 | 4.0 |

*Table B.9: Average and RSD yttrium and zinc aqua regia soluble content in park and open spaces samples, (n = 3).*

Table B.10 shows the sample site locations from Glasgow roadsides.

| Sample reference | Easting (approx.) | Northing (approx.) | Description |
|---|---|---|---|
| RD.01 | 251750 | 661250 | Hurlet Road B762 |
| RD.02 | 252750 | 661250 | Hurlet Road B762 |
| RD.03 | 255750 | 661250 | Hurlet Road B762 |
| RD.04 | 251750 | 670250 | Great Western Road, close to Glasgow boundary |
| RD.05 | 255250 | 668250 | Great Western Road |
| RD.06 | 260250 | 666750 | Sprinburn Road |
| RD.07 | 260750 | 665750 | Between M8 and Alexandra Parade |
| RD.08 | 262250 | 668500 | 237 Wallacewell Road |
| RD.09 | 252250 | 662750 | Brockburn Road |
| RD.10 | 268250 | 664250 | Edinburgh Road |
| RD.11 | 257500 | 667750 | Maryhill Road (near fire station) |
| RD.12 | 256000 | 666500 | Beith Street |
| RD.13 | 264750 | 667500 | Cumbernauld Road |
| RD.14 | 264750 | 666250 | Edinburgh Road |
| RD.15 | 268000 | 662500 | London Road (near City border) |
| RD.16 | 266000 | 663750 | Ballieston Road |
| RD.17 | 265500 | 662500 | London Road |
| RD.18 | 259500 | 658750 | Carmunnock Road |
| RD.19 | 253500 | 662250 | Shieldhall Road |
| RD.20 | 260250 | 669250 | Ashgill Road |
| RD.21 | 254500 | 666750 | Expressway |
| RD.22 | 252500 | 659750 | Nitshill Road |
| RD.23 | 255250 | 661250 | Barrhead Road |
| RD.24 | 260750 | 668750 | Balgray Hill Road |
| RD.25 | 259500 | 667250 | Kepochill Road |
| RD.26 | 254750 | 670500 | Switchback Road |
| RD.27 | 251750 | 670750 | Duntreath Avenue |
| RD.28 | 253250 | 669750 | 2017 Great Western Road |
| RD.29 | 254250 | 660250 | Boydstone Road |
| RD.30 | 253500 | 663750 | Paisley Road West |

*Table B.10: Roadside sample site locations.*

Table B.11 to B.18 show the results from Glasgow roadside samples.

| Sample point GLA.RD | Loss on ignition at 550 °C (%) | | | |
|---|---|---|---|---|
| | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 10.7 | 1.1 | 10.3 | 5.2 |
| 2 | 13.6 | 3.1 | 10.5 | 12 |
| 3 | 9.3 | 5.8 | 9.75 | 51 |
| 4 | 11.1 | 8.6 | 6.9 | 11 |
| 5 | 10.5 | 9.6 | 7.92 | 2.4 |
| 6 | 6.11 | 24 | 3.83 | 4.9 |
| 7 | 14.2 | 30 | 12.9 | 14 |
| 8 | 15.1 | 9.1 | 11.7 | 6.0 |
| 9 | 10.5 | 4.0 | 8.59 | 6.2 |
| 10 | 10.5 | 2.3 | 7.43 | 5.1 |
| 11 | 14.7 | 2.7 | 7.2 | 7.2 |
| 12 | 15.5 | 5.8 | 8.56 | 3.3 |
| 13 | 19.3 | 5.0 | 22.6 | 1.7 |
| 14 | 11.9 | 0.6 | 10.6 | 5.9 |
| 15 | 10 | 4.6 | 8.01 | 3.9 |
| 16 | 8.14 | 5.8 | 5.9 | 10 |
| 17 | 7.46 | 9.2 | 9.12 | 6.1 |
| 18 | 12.9 | 4.2 | 9.23 | 7.9 |
| 19 | 9.74 | 9.1 | 11.8 | 10 |
| 20 | 13.6 | 1.4 | 9.88 | 6.8 |
| 21 | 11.4 | 9.0 | 8.41 | 0.8 |
| 22 | 9.34 | 3.3 | 6.42 | 0.8 |
| 23 | 14 | 2.2 | 8.64 | 2.2 |
| 24 | 14.4 | 5.7 | 12 | 5.7 |
| 25 | 9.74 | 3.7 | 8.47 | 9.5 |
| 26 | 11.2 | 5.8 | 7.28 | 4.8 |
| 27 | 10.1 | 4.4 | 7.39 | 2.0 |
| 28 | 12 | 6.1 | 10.1 | 2.8 |
| 29 | 10.4 | 3.2 | 11.8 | 3.0 |
| 30 | 8.55 | 3.2 | 9.49 | 1.5 |

*Table B.11: LOI (%) from roadside samples.*

| Sample point GLA.RD | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Aluminium | | | | Barium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 16900 | 12 | 19900 | 2.4 | 158 | 5.3 | 179 | 4.9 |
| 2 | 13200 | 13 | 10500 | 12 | 172 | 5.6 | 189 | 4.3 |
| 3 | 14100 | 21 | 15300 | 20 | 163 | 14 | 160 | 6.3 |
| 4 | 9890 | 6.3 | 12600 | 14 | 83.8 | 7.6 | 105 | 2.5 |
| 5 | 13200 | 16 | 15800 | 7.8 | 138 | 4.4 | 140 | 4.9 |
| 6 | 12300 | 15 | 19000 | 10 | 166 | 26 | 196 | 3.4 |
| 7 | 15600 | 19 | 13200 | 4.2 | 193 | 7.2 | 231 | 15 |
| 8 | 21600 | 6.6 | 16100 | 7.6 | 127 | 1.7 | 191 | 3.6 |
| 9 | 13300 | 4.6 | 11900 | 7.9 | 165 | 59 | 101 | 2.4 |
| 10 | 10600 | 13 | 9680 | 9.2 | 97.4 | 5.3 | 92.5 | 2.1 |
| 11 | 10700 | 12 | 8670 | 9.3 | 108 | 8.0 | 124 | 3.8 |
| 12 | 13700 | 16 | 9560 | 14 | 397 | 43 | 226 | 11 |
| 13 | 13100 | 10 | 14600 | 7.8 | 682 | 3.0 | 1780 | 19 |
| 14 | 8380 | 7.5 | 8950 | 6.1 | 130 | 3.2 | 133 | 7.6 |
| 15 | 19100 | 16 | 18100 | 24 | 219 | 3.3 | 222 | 5.6 |
| 16 | 14700 | 4.2 | 12000 | 5.3 | 83.1 | 1.2 | 81 | 2.5 |
| 17 | 10800 | 13 | 11900 | 10 | 170 | 1.9 | 215 | 3.0 |
| 18 | 18900 | 19 | 20200 | 14 | 172 | 2.2 | 235 | 5.8 |
| 19 | 15000 | 4.4 | 10800 | 4.2 | 204 | 4.8 | 261 | 4.8 |
| 20 | 9200 | 20 | 9010 | 16 | 116 | 10 | 127 | 14 |
| 21 | 11800 | 8.4 | 11700 | 14 | 145 | 5.5 | 142 | 8.8 |
| 22 | 6770 | 3.1 | 8110 | 5.3 | 72.6 | 3.0 | 83.8 | 10 |
| 23 | 11700 | 18 | 11800 | 12 | 141 | 2.1 | 133 | 7.4 |
| 24 | 12400 | 7.3 | 13800 | 23 | 176 | 8.9 | 197 | 16 |
| 25 | 13700 | 19 | 10200 | 13 | 119 | 4.3 | 122 | 3.3 |
| 26 | 9510 | 14 | 9440 | 13 | 73.5 | 5.6 | 58 | 6.0 |
| 27 | 17000 | 8.1 | 16900 | 9.0 | 152 | 3.5 | 129 | 8.1 |
| 28 | 16200 | 16 | 11200 | 8.6 | 117 | 5.8 | 119 | 8.9 |
| 29 | 11800 | 19 | 13800 | 10 | 111 | 7.6 | 161 | 2.8 |
| 30 | 13300 | 7.1 | 13000 | 24 | 116 | 3.1 | 160 | 7.4 |

*Table B.12: Average and RSD aluminium and barium aqua regia soluble content in roadside samples, (n = 3).*

| Sample point GLA.RD | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Calcium | | | | Chromium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 6330 | 1.5 | 6930 | 6.2 | 56.2 | 9.9 | 105 | 44 |
| 2 | 5670 | 4.9 | 4570 | 4.3 | 56.9 | 46 | 31.5 | 4.5 |
| 3 | 5610 | 25 | 5090 | 7.7 | 42.5 | 20 | 39.6 | 16 |
| 4 | 2740 | 14 | 3050 | 6.2 | 27.5 | 4.0 | 31.8 | 12 |
| 5 | 5470 | 14 | 3090 | 7.3 | 34.3 | 9.4 | 36.6 | 6.5 |
| 6 | 5580 | 3.6 | 4060 | 3.6 | 40 | 11 | 47.3 | 8.6 |
| 7 | 5120 | 5.6 | 6160 | 13 | 75.9 | 5.5 | 93.3 | 21 |
| 8 | 4670 | 1.7 | 4330 | 5.8 | 47.9 | 4.6 | 40.9 | 2.1 |
| 9 | 3560 | 6.6 | 2750 | 4.5 | 32.4 | 3.6 | 28.4 | 4.1 |
| 10 | 2840 | 9.6 | 2590 | 5.4 | 50.1 | 13 | 44.2 | 6.7 |
| 11 | 4240 | 3.7 | 3820 | 1.9 | 26.5 | 8.5 | 24.1 | 5.2 |
| 12 | 5160 | 0.9 | 6040 | 12 | 56.9 | 35 | 37.6 | 11 |
| 13 | 9100 | 2.8 | 12900 | 3.5 | 43.6 | 11 | 58.7 | 11 |
| 14 | 3630 | 17 | 3000 | 16 | 39.6 | 2.2 | 43 | 5.7 |
| 15 | 4920 | 18 | 3920 | 9.5 | 50 | 4.9 | 47.3 | 13 |
| 16 | 2500 | 1.3 | 2950 | 4.5 | 44.1 | 4.2 | 52 | 30 |
| 17 | 10600 | 3.5 | 13500 | 3.6 | 96 | 8.9 | 104 | 8.9 |
| 18 | 6600 | 3.2 | 9480 | 15 | 46.5 | 7.6 | 44.5 | 8.6 |
| 19 | 8540 | 3.2 | 7700 | 5.8 | 117 | 82 | 63.6 | 2.4 |
| 20 | 3350 | 9.2 | 3490 | 19 | 24.4 | 23 | 23.7 | 22 |
| 21 | 4740 | 4.7 | 4040 | 4.3 | 34.2 | 4.8 | 30.7 | 9.0 |
| 22 | 3190 | 13 | 3530 | 6.7 | 20.3 | 2.9 | 22.1 | 4.8 |
| 23 | 5240 | 10 | 3840 | 5.7 | 35.1 | 12 | 35 | 14.0 |
| 24 | 3830 | 7.6 | 5570 | 14 | 33 | 9.3 | 50 | 30 |
| 25 | 3330 | 3.3 | 3320 | 6.4 | 30.1 | 12 | 25.6 | 10 |
| 26 | 2530 | 5.3 | 1520 | 8.3 | 23.3 | 10 | 20.9 | 13 |
| 27 | 4150 | 1.0 | 3410 | 22 | 32.7 | 7.6 | 28 | 4.7 |
| 28 | 2830 | 3.7 | 2390 | 9.2 | 41.4 | 22 | 25.8 | 11 |
| 29 | 4000 | 6.3 | 4020 | 2.2 | 23.5 | 13 | 38.7 | 9.5 |
| 30 | 3650 | 8.1 | 3760 | 8.7 | 28.5 | 9.1 | 35 | 15.9 |

*Table B.13: Average and RSD calcium and chromium aqua regia soluble content in roadside samples, (n = 3).*

| Sample point GLA.RD | Analyte concentration (mg $kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Copper | | | | Iron (%) | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 78.2 | 5.5 | 65 | 5.1 | 4.22 | 4.2 | 4.79 | 2.0 |
| 2 | 120 | 0.5 | 109 | 5.4 | 3.36 | 9.1 | 2.89 | 9.8 |
| 3 | 93.4 | 12.5 | 62.9 | 4.4 | 3.05 | 14 | 2.57 | 8.7 |
| 4 | 45.7 | 5.4 | 41.9 | 2.7 | 2.33 | 5.7 | 2.61 | 3.7 |
| 5 | 85.5 | 3.6 | 65.9 | 6.8 | 2.68 | 6.1 | 2.8 | 6.1 |
| 6 | 91.5 | 17.7 | 28.6 | 1.0 | 2.91 | 5.2 | 2.94 | 2.7 |
| 7 | 105 | 5.9 | 84.8 | 4.9 | 3.26 | 11 | 3.72 | 3.8 |
| 8 | 68 | 10.0 | 63.5 | 3.9 | 3.02 | 6.8 | 3.28 | 9.0 |
| 9 | 41.7 | 6.0 | 35.5 | 2.4 | 2.63 | 2.7 | 2.62 | 9.0 |
| 10 | 66.3 | 4.9 | 50.1 | 2.3 | 2.97 | 4.6 | 2.9 | 2.2 |
| 11 | 43.6 | 10.8 | 39.9 | 5.4 | 2.65 | 7.6 | 2.66 | 3.5 |
| 12 | 233 | 5.4 | 171 | 4.9 | 3.77 | 3.3 | 3.59 | 2.4 |
| 13 | 444 | 23.5 | 585 | 6.9 | 4.05 | 11 | 4.03 | 11 |
| 14 | 78.7 | 1.8 | 64.5 | 1.4 | 2.67 | 5.4 | 2.48 | 5.1 |
| 15 | 38.8 | 7.2 | 35.5 | 0.6 | 3.23 | 0.8 | 3.25 | 7.5 |
| 16 | 55.7 | 1.9 | 47 | 2.0 | 2.74 | 2.1 | 2.75 | 7.9 |
| 17 | 146 | 9.3 | 145 | 6.0 | 3.87 | 5.8 | 4.5 | 7.3 |
| 18 | 65.8 | 1.7 | 54.8 | 1.5 | 3.51 | 2.6 | 3.77 | 11 |
| 19 | 186 | 5.9 | 382 | 80.9 | 4.55 | 2.2 | 3.96 | 0.8 |
| 20 | 55.2 | 6.0 | 70.7 | 28.1 | 2.6 | 5.0 | 2.69 | 8.3 |
| 21 | 92.9 | 7.3 | 106 | 28.6 | 3.02 | 1.9 | 2.97 | 12 |
| 22 | 36.6 | 4.3 | 29.1 | 14.7 | 1.92 | 4.2 | 2.07 | 7.2 |
| 23 | 88 | 4.8 | 64.3 | 7.8 | 2.96 | 5.8 | 2.73 | 16 |
| 24 | 88.9 | 8.0 | 95.4 | 10.1 | 2.8 | 11 | 3.03 | 10 |
| 25 | 41.5 | 4.8 | 42.7 | 3.3 | 2.4 | 2.9 | 2.46 | 5.1 |
| 26 | 55.9 | 2.7 | 38.9 | 3.7 | 2.48 | 2.5 | 2.43 | 2.1 |
| 27 | 43.3 | 2.0 | 25.7 | 7.0 | 2.73 | 5.3 | 2.45 | 1.4 |
| 28 | 90.9 | 5.0 | 133 | 6.8 | 2.54 | 2.2 | 2.4 | 7.3 |
| 29 | 40.5 | 3.5 | 81.6 | 2.9 | 3.59 | 4.8 | 4.07 | 5.6 |
| 30 | 38.1 | 3.1 | 105 | 2.6 | 4.2 | 4.9 | 4.05 | 13 |

*Table B.14: Average and RSD copper and iron aqua regia soluble content in roadside samples, (n = 3).*

| Sample point GLA.RD | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lithium | | | | Magnesium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 12.9 | 10 | 15.8 | 5.8 | 5910 | 3.4 | 5910 | 4.0 |
| 2 | 12.8 | 16 | 10.8 | 12 | 4230 | 6 | 2830 | 12 |
| 3 | 12.1 | 18 | 11.7 | 20 | 4180 | 15.8 | 4040 | 4.0 |
| 4 | 10.6 | 6.3 | 12.5 | 10 | 3300 | 7.3 | 3610 | 6.2 |
| 5 | 11.5 | 12 | 14 | 5.3 | 3620 | 2.6 | 3120 | 3.7 |
| 6 | 10.9 | 7.8 | 17.4 | 6.4 | 6330 | 2.7 | 7620 | 3.6 |
| 7 | 14.2 | 17 | 11.9 | 2.7 | 3020 | 3.9 | 2890 | 5.2 |
| 8 | 20.6 | 2.6 | 17.5 | 8.5 | 4380 | 1.3 | 3500 | 7.8 |
| 9 | 14.5 | 2.1 | 13.2 | 6.7 | 4090 | 5.8 | 3460 | 3.8 |
| 10 | 9.5 | 11 | 8.1 | 9.2 | 2670 | 5 | 2730 | 21.0 |
| 11 | 10.7 | 10 | 7.84 | 15 | 2570 | 4.7 | 2050 | 4.6 |
| 12 | 14.4 | 16 | 8.73 | 22 | 2880 | 2.3 | 2540 | 5.8 |
| 13 | 13.1 | 9.4 | 15.1 | 6.5 | 4320 | 1.2 | 4020 | 2.9 |
| 14 | 7.67 | 5.8 | 7.89 | 7.0 | 2540 | 5.6 | 2150 | 1.4 |
| 15 | 19.4 | 10 | 18.6 | 20 | 3410 | 6.5 | 3150 | 8.5 |
| 16 | 12.4 | 4.0 | 10.1 | 4.9 | 2540 | 1.4 | 2570 | 8.2 |
| 17 | 11.1 | 15 | 10.9 | 7.3 | 5450 | 2.0 | 5130 | 3.6 |
| 18 | 17.3 | 15 | 17.6 | 12 | 4740 | 3.8 | 4470 | 4.1 |
| 19 | 14.1 | 4.1 | 11.1 | 0.5 | 6530 | 4.4 | 4900 | 0.3 |
| 20 | 8.31 | 23 | 7.89 | 18 | 2210 | 7 | 2190 | 10.1 |
| 21 | 12.4 | 9.0 | 11.7 | 19 | 3250 | 0.9 | 3050 | 6.3 |
| 22 | 7.4 | 2.6 | 9.15 | 6.6 | 3120 | 0.6 | 3440 | 3.8 |
| 23 | 10.8 | 14 | 11.1 | 13 | 3750 | 7.1 | 2850 | 9.5 |
| 24 | 11.8 | 9.2 | 12.7 | 22.8 | 2470 | 2 | 2340 | 14.2 |
| 25 | 11.9 | 15 | 8.94 | 14 | 2240 | 3.1 | 1960 | 6.6 |
| 26 | 8.8 | 15 | 7.96 | 16 | 2410 | 6.0 | 1890 | 5.9 |
| 27 | 14.4 | 5.1 | 14.5 | 6.0 | 3960 | 1.1 | 3340 | 4.2 |
| 28 | 14.8 | 12 | 10.5 | 7.2 | 3170 | 5.4 | 2600 | 7 |
| 29 | 12.5 | 24 | 13.2 | 10 | 2900 | 13.8 | 3300 | 4.5 |
| 30 | 14.5 | 9.5 | 12.2 | 27 | 2570 | 8.7 | 3110 | 9.1 |

*Table B.15: Average and RSD lithium and magnesium aqua regia soluble content in roadside samples, (n = 3).*

| Sample point GLA.RD | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Manganese | | | | Nickel | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 798 | 3.3 | 1080 | 25 | 53.2 | 14 | 55.2 | 4.5 |
| 2 | 648 | 8.3 | 619 | 7.8 | 54.5 | 7.5 | 65.7 | 4.7 |
| 3 | 575 | 17 | 534 | 8.2 | 39.2 | 16 | 39.1 | 7.2 |
| 4 | 435 | 5.7 | 499 | 4.5 | 26.8 | 2.8 | 30.9 | 7.1 |
| 5 | 605 | 5.0 | 560 | 1.4 | 30.1 | 14 | 31.6 | 1.7 |
| 6 | 492 | 4.5 | 577 | 3.4 | 28.7 | 8.9 | 31.6 | 5.4 |
| 7 | 894 | 25 | 944 | 9.0 | 41.9 | 4.4 | 39.9 | 3.9 |
| 8 | 528 | 5.5 | 738 | 6.0 | 36.3 | 4.9 | 42.6 | 2.7 |
| 9 | 613 | 15 | 575 | 6.5 | 35.0 | 5.0 | 30.8 | 3.8 |
| 10 | 871 | 8.2 | 898 | 9.2 | 27.4 | 9.8 | 26.2 | 16 |
| 11 | 376 | 2.5 | 402 | 1.6 | 23.3 | 10 | 22.3 | 6.3 |
| 12 | 606 | 0.6 | 659 | 13 | 47.8 | 19 | 32.6 | 12.3 |
| 13 | 652 | 4.9 | 638 | 6.1 | 100 | 8.5 | 148 | 13.2 |
| 14 | 698 | 5.6 | 682 | 11 | 26.1 | 1.9 | 28.3 | 14 |
| 15 | 491 | 1.9 | 513 | 9.8 | 30.2 | 2.6 | 29.3 | 8.5 |
| 16 | 402 | 7.9 | 584 | 20 | 24.1 | 3.8 | 22.4 | 2.5 |
| 17 | 1370 | 15 | 1510 | 3.1 | 39.7 | 3.3 | 47.4 | 5.5 |
| 18 | 792 | 1.1 | 960 | 11.1 | 37.7 | 4.7 | 38.7 | 5.6 |
| 19 | 808 | 1.4 | 935 | 8.5 | 83.4 | 63 | 158 | 97 |
| 20 | 531 | 8.1 | 586 | 14 | 24.3 | 9.8 | 25.3 | 13 |
| 21 | 588 | 37 | 411 | 2.7 | 35.1 | 4.5 | 31.6 | 5.8 |
| 22 | 339 | 7.8 | 366 | 5.4 | 23.2 | 2.9 | 25.4 | 7.9 |
| 23 | 543 | 4.4 | 555 | 21 | 36.8 | 9.3 | 32.8 | 12 |
| 24 | 543 | 7.0 | 900 | 27 | 36.3 | 2.1 | 40.4 | 12 |
| 25 | 823 | 5.3 | 874 | 4.5 | 24.3 | 2.2 | 24.9 | 3.3 |
| 26 | 578 | 7.9 | 519 | 8.2 | 24.4 | 5.5 | 21.4 | 11 |
| 27 | 521 | 0.5 | 452 | 5.5 | 27.3 | 12 | 24 | 1.4 |
| 28 | 513 | 5.0 | 478 | 12 | 33.3 | 7.9 | 30.7 | 2.7 |
| 29 | 987 | 2.9 | 812 | 3.9 | 29.3 | 10 | 38.5 | 1.9 |
| 30 | 1160 | 5.8 | 790 | 6.6 | 31.5 | 4.4 | 38.9 | 11 |

*Table B.16: Average and RSD manganese and nickel aqua regia soluble content in roadside samples, (n = 3).*

| Sample point GLA.RD | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lead | | | | Vanadium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 199 | 5.9 | 175 | 3.3 | 140 | 2.4 | 181 | 5.2 |
| 2 | 273 | 3.1 | 188 | 15 | 69.1 | 3.8 | 58.9 | 6.7 |
| 3 | 291 | 19 | 182 | 4.4 | 63.4 | 16 | 58.5 | 11 |
| 4 | 178 | 4.6 | 165 | 4.3 | 51.1 | 7.1 | 59.9 | 5.4 |
| 5 | 295 | 4.0 | 205 | 7.0 | 59.8 | 7.2 | 61.7 | 4.6 |
| 6 | 109 | 15 | 42 | 6.0 | 57.4 | 4.5 | 58.5 | 4.6 |
| 7 | 377 | 8.7 | 393 | 1.9 | 56.4 | 8.7 | 53.6 | 7.0 |
| 8 | 233 | 7.4 | 215 | 3.3 | 73.5 | 5.8 | 68 | 4.2 |
| 9 | 100 | 4.5 | 89 | 2.7 | 58.8 | 2.5 | 53 | 1.1 |
| 10 | 319 | 6.1 | 198 | 2.8 | 59.9 | 3.0 | 54.7 | 1.0 |
| 11 | 109 | 11 | 121 | 2.3 | 42.6 | 5.4 | 40.4 | 2.8 |
| 12 | 636 | 8.0 | 501 | 37 | 50.1 | 5.0 | 45.6 | 6.3 |
| 13 | 1330 | 3.3 | 2050 | 4.2 | 117 | 4.2 | 136 | 2.4 |
| 14 | 289 | 2.5 | 241 | 5.8 | 52.6 | 2.8 | 50.1 | 1.7 |
| 15 | 57 | 7.3 | 54 | 3.6 | 66.7 | 6.6 | 59.5 | 10 |
| 16 | 104 | 2.7 | 77 | 4.3 | 50.5 | 2.8 | 53.1 | 3.8 |
| 17 | 289 | 20 | 411 | 7.3 | 73.0 | 1.6 | 86.4 | 4.1 |
| 18 | 195 | 3.8 | 152 | 4.2 | 71.4 | 1.9 | 70.6 | 6.0 |
| 19 | 692 | 4.9 | 859 | 12 | 72.9 | 5.9 | 68.9 | 3.7 |
| 20 | 198 | 6.1 | 203 | 7.8 | 48.0 | 8.6 | 48.3 | 10 |
| 21 | 304 | 7.6 | 275 | 3.6 | 58.8 | 0.4 | 56.6 | 4.6 |
| 22 | 91 | 3.1 | 75 | 6.4 | 35.4 | 3.2 | 37.7 | 3.4 |
| 23 | 289 | 5.1 | 251 | 8.1 | 58.4 | 8.5 | 55.2 | 11 |
| 24 | 256 | 4.1 | 280 | 36 | 53.0 | 4.4 | 70.9 | 18 |
| 25 | 170 | 4.4 | 178 | 4.9 | 50.8 | 2.4 | 47.3 | 4.2 |
| 26 | 220 | 5.8 | 141 | 4.9 | 46.5 | 6.9 | 42.2 | 8.6 |
| 27 | 173 | 5.4 | 82 | 9.5 | 62.4 | 4.1 | 55.6 | 3.5 |
| 28 | 231 | 21 | 138 | 7.6 | 61.4 | 4.7 | 51.2 | 3.5 |
| 29 | 91 | 1.2 | 289 | 3.7 | 48.2 | 8.4 | 71.2 | 6.5 |
| 30 | 80.1 | 4.0 | 267 | 2.0 | 48.8 | 1.3 | 70 | 11 |

*Table B.17: Average and RSD lead and vanadium aqua regia soluble content in roadside samples, (n = 3).*

| Sample point GLA.RD | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Yttrium | | | | Zinc | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 8.72 | 4.4 | 9.95 | 3.8 | 196 | 2.7 | 166 | 14 |
| 2 | 9.41 | 2.4 | 10.8 | 3.8 | 319 | 12 | 181 | 13 |
| 3 | 8.43 | 17 | 8.11 | 8.4 | 250 | 23 | 156 | 8.2 |
| 4 | 6.18 | 5.7 | 7.9 | 3.4 | 162 | 6.1 | 144 | 2.7 |
| 5 | 7.58 | 7.0 | 7.48 | 4.0 | 238 | 4.3 | 167 | 4.4 |
| 6 | 6.69 | 4.4 | 9.17 | 5.4 | 210 | 6.0 | 86 | 4.0 |
| 7 | 10.1 | 6.0 | 10.7 | 5.7 | 310 | 13 | 277 | 1.6 |
| 8 | 9.03 | 2.0 | 11.8 | 5.9 | 256 | 6.7 | 259 | 6.9 |
| 9 | 7 | 3.3 | 6.25 | 4.3 | 220 | 6.2 | 118 | 1.9 |
| 10 | 7.76 | 1.8 | 7.6 | 1.3 | 211 | 5.0 | 176 | 4.5 |
| 11 | 6.95 | 1.8 | 6.4 | 5.9 | 152 | 9.1 | 144 | 3.3 |
| 12 | 7.16 | 2.2 | 6.73 | 9.6 | 654 | 6.0 | 400 | 3.7 |
| 13 | 16 | 4.9 | 20.4 | 0.6 | 1340 | 4.1 | 1740 | 2.8 |
| 14 | 7.44 | 8.4 | 7.71 | 3.3 | 261 | 3.0 | 231 | 6.1 |
| 15 | 7.63 | 5.8 | 7 | 9.6 | 197 | 4.0 | 190 | 1.7 |
| 16 | 6.57 | 1.4 | 5.83 | 1.5 | 130 | 1.4 | 82 | 2.7 |
| 17 | 7.86 | 6.6 | 8.88 | 1.3 | 364 | 3.9 | 407 | 2.8 |
| 18 | 10.6 | 2.4 | 12.8 | 5.3 | 211 | 1.0 | 172 | 2.8 |
| 19 | 8.88 | 3.8 | 9.31 | 1.8 | 509 | 5.3 | 503 | 0.9 |
| 20 | 7.27 | 11 | 7.77 | 11 | 166 | 7.9 | 196 | 38 |
| 21 | 7.36 | 2.9 | 7.47 | 8.6 | 259 | 4.3 | 209 | 3.9 |
| 22 | 4.66 | 2.9 | 5.7 | 9.1 | 103 | 2.8 | 93 | 9.5 |
| 23 | 7.83 | 7.3 | 7.51 | 10 | 220 | 7.4 | 185 | 8.5 |
| 24 | 8.46 | 1.1 | 9.51 | 11 | 733 | 4.9 | 514 | 6.7 |
| 25 | 6.03 | 4.8 | 5.99 | 6.6 | 148 | 2.6 | 132 | 4.1 |
| 26 | 5.69 | 6.4 | 5.33 | 8.3 | 161 | 3.8 | 120 | 7.3 |
| 27 | 7.1 | 2.9 | 6.95 | 9.0 | 166 | 1.5 | 97 | 10 |
| 28 | 7.84 | 6.9 | 7.54 | 3.7 | 168 | 5.9 | 134 | 8.1 |
| 29 | 7.23 | 7.0 | 7.6 | 4.0 | 129 | 5.3 | 239 | 3.1 |
| 30 | 7.94 | 3.0 | 7.66 | 12 | 121 | 2.6 | 213 | 6.4 |

*Table B.18: Average and RSD yttrium and zinc aqua regia soluble content in roadside samples, (n = 3).*

Table B.19 shows the sample site locations from Glasgow riverbanks.

| Sample reference | Easting (approx.) | Northing (approx.) | Description |
|---|---|---|---|
| RB.01 | 251750 | 663250 | Cart River |
| RB.02 | 252750 | 662250 | Levern Water |
| RB.03 | 255750 | 669750 | Kelvin (Dawsholm Park) |
| RB.04 | 260250 | 663250 | Clyde (near Richmond Park) |
| RB.05 | 258250 | 659250 | Cathcart River |
| RB.06 | 257250 | 666750 | Kelvin (Kelvingrove Park) |
| RB.07 | 256000 | 670500 | Kelvin (near Killermont) |
| RB.08 | 253500 | 662750 | White Cart Water (Lochar Park) |
| RB.09 | 256500 | 661250 | White Cart Water (near Aulhouse Road) |
| RB.10 | 258000 | 671750 | Kelvin (Balmore Road) |
| RB.11 | 256750 | 667500 | Kelvin (Botanic Gardens) |
| RB.12 | 256250 | 668500 | Kelvin (Kelvindale Road) |
| RB.13 | 259750 | 664250 | Clyde (opposite boathouse) |

*Table B.19: Roadside sample site locations.*

Table B.20 to B.27 show the results from Glasgow riverbank samples.

| Sample point GLA.RB | Loss on ignition at 550 °C (%) | | | |
|---|---|---|---|---|
| | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 8.79 | 4.0 | 8.2 | 8.1 |
| 2 | 8.65 | 7.0 | 9.16 | 10 |
| 3 | 7.21 | 3.8 | 9.49 | 7.0 |
| 4 | 8.9 | 23 | 5.23 | 6.8 |
| 5 | 12.6 | 6.8 | 10.6 | 2.2 |
| 6 | 10.5 | 6.8 | 12.6 | 3.0 |
| 7 | 8.24 | 7.5 | 8.33 | 10 |
| 8 | 8.71 | 4.7 | 6.62 | 6.5 |
| 9 | 8.38 | 1.8 | 7.77 | 4.7 |
| 10 | 10.2 | 3.2 | 8.39 | 4.4 |
| 11 | 4.49 | 6.9 | 5.97 | 13 |
| 12 | 5.5 | 15 | 11.0 | 14 |
| 13 | 15.2 | 1.9 | 13.1 | 6.5 |

*Table B.20: LOI (%) from riverbank samples.*

| Sample point GLA. RB | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Aluminium | | | | Barium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 14200 | 2.4 | 19800 | 18 | 215 | 8.0 | 263 | 30 |
| 2 | 13200 | 7.4 | 20500 | 20 | 204 | 1.5 | 285 | 31 |
| 3 | 12500 | 6.4 | 17500 | 17 | 175 | 3.6 | 189 | 8.3 |
| 4 | 8310 | 6.1 | 10900 | 24 | 143 | 13 | 148 | 18 |
| 5 | 18200 | 13 | 22100 | 17 | 171 | 9.9 | 184 | 1.2 |
| 6 | 9760 | 5.3 | 13500 | 28 | 193 | 5.9 | 215 | 13 |
| 7 | 10000 | 2.5 | 12600 | 21 | 135 | 4.3 | 137 | 6.5 |
| 8 | 17000 | 4.4 | 14500 | 17 | 229 | 1.4 | 199 | 5.2 |
| 9 | 14600 | 5.5 | 15700 | 5.6 | 194 | 5.3 | 201 | 1.5 |
| 10 | 13800 | 1.0 | 16500 | 15 | 171 | 1.9 | 175 | 1.4 |
| 11 | 9250 | 12 | 7620 | 13 | 139 | 13 | 118 | 5.0 |
| 12 | 6580 | 9.0 | 7920 | 10 | 135 | 3.7 | 172 | 36 |
| 13 | 11900 | 3.9 | 15400 | 20 | 187 | 1.2 | 228 | 1.9 |

*Table B.21: Average and RSD aluminium and barium aqua regia soluble content in riverbank samples, (n = 3).*

| Sample point GLA. RB | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Calcium | | | | Chromium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 5550 | 5.0 | 5660 | 4.0 | 87.6 | 4.0 | 90.5 | 5.3 |
| 2 | 4890 | 3.2 | 4950 | 5.0 | 110 | 3.9 | 178 | 9.4 |
| 3 | 4020 | 2.7 | 3800 | 4.9 | 30.7 | 4.3 | 37.7 | 9.1 |
| 4 | 4060 | 9.0 | 3090 | 13 | 117 | 8.0 | 147 | 15 |
| 5 | 8280 | 16 | 11800 | 24 | 59.8 | 11 | 66.0 | 6.8 |
| 6 | 3820 | 2.1 | 5310 | 40 | 48.0 | 8.2 | 54.5 | 7.3 |
| 7 | 3190 | 4.1 | 3050 | 6.3 | 31.1 | 1.4 | 33.1 | 7.0 |
| 8 | 6180 | 3.0 | 5440 | 11 | 87.4 | 8.0 | 74.2 | 11 |
| 9 | 5250 | 2.3 | 4820 | 3.2 | 71.2 | 4.6 | 76.1 | 1.8 |
| 10 | 3200 | 2.2 | 3170 | 1.4 | 35.5 | 0.9 | 35.4 | 3.4 |
| 11 | 3060 | 7.8 | 2660 | 2.2 | 27.2 | 8.4 | 29.5 | 3.4 |
| 12 | 2990 | 5.2 | 4020 | 11 | 20.8 | 5.2 | 27.7 | 8.4 |
| 13 | 3980 | 2.7 | 3970 | 3.4 | 44.9 | 2.2 | 52.5 | 8.3 |

*Table B.22: Average and RSD calcium and chromium aqua regia soluble content in riverbank samples, (n = 3).*

| Sample point GLA. RB | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Copper | | | | Iron (%) | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 74.0 | 4.5 | 65.7 | 6.8 | 4.36 | 2.1 | 4.34 | 1.4 |
| 2 | 102 | 3.1 | 120 | 2.7 | 4.28 | 0.3 | 4.73 | 1.5 |
| 3 | 34.0 | 10 | 34.3 | 4.4 | 3.45 | 7.0 | 3.46 | 2.3 |
| 4 | 33.9 | 7.8 | 32.6 | 15 | 3.15 | 1.9 | 3.05 | 11 |
| 5 | 39.7 | 10 | 41.8 | 1.3 | 5.00 | 8.7 | 5.31 | 3.1 |
| 6 | 53.5 | 3.1 | 57.7 | 8.6 | 2.68 | 7.5 | 2.75 | 6.6 |
| 7 | 30.9 | 5.7 | 27.9 | 18 | 2.71 | 4.8 | 2.74 | 7.6 |
| 8 | 63.5 | 14 | 53.5 | 11 | 4.88 | 2.4 | 4.70 | 2.0 |
| 9 | 95.1 | 2.7 | 90.2 | 1.2 | 4.46 | 1.8 | 4.44 | 0.7 |
| 10 | 38.8 | 4.7 | 45.0 | 4.0 | 3.35 | 2.0 | 3.21 | 3.0 |
| 11 | 28.8 | 2.1 | 32.4 | 4.4 | 2.73 | 5.3 | 2.71 | 1.2 |
| 12 | 19.1 | 14 | 30.6 | 47 | 2.90 | 5.6 | 3.28 | 7.7 |
| 13 | 79.1 | 0.7 | 113 | 9.0 | 3.31 | 4.0 | 3.59 | 9.1 |

*Table B.23: Average and RSD copper and iron aqua regia soluble content in riverbank samples, (n = 3).*

| Sample point GLA.RB | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lithium | | | | Magnesium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 13.1 | 3.1 | 17.0 | 15 | 4980 | 0.7 | 5410 | 3.8 |
| 2 | 12.9 | 4.8 | 19.3 | 17 | 5000 | 1.1 | 5380 | 4.0 |
| 3 | 11.1 | 5.9 | 14.0 | 11 | 3510 | 3.6 | 3580 | 2.8 |
| 4 | 10.7 | 5.8 | 13.0 | 18 | 3640 | 4.9 | 3700 | 7.0 |
| 5 | 13.3 | 13 | 16.3 | 15 | 6020 | 9.8 | 6640 | 7.2 |
| 6 | 9.45 | 4.2 | 12.0 | 22 | 2560 | 2.2 | 2730 | 5.9 |
| 7 | 8.77 | 2.5 | 10.5 | 16 | 2940 | 2.5 | 3050 | 5.0 |
| 8 | 14.9 | 4.5 | 12.7 | 12 | 5480 | 1.9 | 5260 | 3.5 |
| 9 | 12.3 | 4.2 | 13.0 | 5.4 | 5050 | 2.0 | 5030 | 1.7 |
| 10 | 11.1 | 0.6 | 12.8 | 13 | 3650 | 2.1 | 3600 | 0.8 |
| 11 | 8.13 | 9.2 | 7.55 | 11 | 2940 | 4.4 | 2600 | 2.1 |
| 12 | 6.98 | 7.8 | 8.04 | 6.2 | 2790 | 1.7 | 3110 | 4.0 |
| 13 | 13.5 | 3.5 | 16.5 | 14 | 3450 | 2.8 | 3550 | 4.7 |

*Table B.24: Average and RSD lithium and magnesium aqua regia soluble content in riverbank samples, (n = 3).*

| Sample point GLA. RB | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Manganese | | | | Nickel | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 966 | 7.4 | 973 | 1.6 | 59.2 | 27 | 50.9 | 6.8 |
| 2 | 806 | 0.7 | 829 | 3.6 | 48.8 | 0.4 | 59.1 | 6.8 |
| 3 | 978 | 5.6 | 942 | 4.8 | 29.6 | 7.5 | 32.3 | 7.1 |
| 4 | 644 | 5.0 | 646 | 11 | 35.8 | 6.1 | 38.0 | 7.5 |
| 5 | 1030 | 8.3 | 1030 | 2.7 | 56.1 | 8.7 | 60.3 | 3.9 |
| 6 | 601 | 2.0 | 648 | 8.6 | 35.0 | 4.7 | 40.5 | 7.2 |
| 7 | 661 | 2.0 | 631 | 1.9 | 24.0 | 6.1 | 25.8 | 16 |
| 8 | 1190 | 1.9 | 889 | 4.6 | 54.0 | 3.3 | 50.9 | 5.8 |
| 9 | 854 | 1.7 | 844 | 1.1 | 53.9 | 3.7 | 55.1 | 1.2 |
| 10 | 767 | 2.8 | 660 | 3.5 | 27.4 | 2.2 | 25.0 | 4.2 |
| 11 | 571 | 6.8 | 543 | 0.9 | 20.5 | 8.5 | 22.1 | 3.7 |
| 12 | 968 | 2.7 | 1300 | 48 | 18.3 | 1.7 | 23.5 | 10 |
| 13 | 546 | 2.3 | 576 | 4.4 | 51.4 | 0.7 | 60.5 | 4.0 |

*Table B.25: Average and RSD manganese and nickel aqua regia soluble content in riverbank samples, (n = 3).*

| Sample point GLA. RB | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lead | | | | Vanadium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 127 | 6.7 | 124 | 7.5 | 64.7 | 1.8 | 69.4 | 5.7 |
| 2 | 197 | 1.1 | 235 | 5.7 | 75.9 | 1.2 | 88.1 | 5.1 |
| 3 | 86 | 3.0 | 90 | 4.5 | 45.3 | 6.5 | 50 | 5.3 |
| 4 | 109 | 2.7 | 106 | 12 | 40.6 | 2.9 | 43.6 | 8.9 |
| 5 | 118 | 10 | 110 | 3.9 | 85.3 | 11 | 94.7 | 4.9 |
| 6 | 255 | 3.4 | 269 | 8.9 | 50.2 | 1.3 | 57.8 | 11 |
| 7 | 100 | 3.2 | 92 | 6.4 | 39.2 | 0.2 | 41.2 | 7.4 |
| 8 | 107 | 1.7 | 106 | 12 | 65.2 | 3.0 | 61.7 | 5.4 |
| 9 | 148 | 3.5 | 151 | 1.7 | 70.4 | 2.0 | 72 | 1.3 |
| 10 | 101 | 2.1 | 92.9 | 9.0 | 48.5 | 1.5 | 49.1 | 2.4 |
| 11 | 92.3 | 6.8 | 113 | 4.2 | 36.7 | 7.8 | 32.8 | 5.1 |
| 12 | 59.2 | 14 | 79.4 | 2.7 | 31.6 | 3.9 | 35.4 | 4.9 |
| 13 | 335 | 0.9 | 426 | 5.7 | 65.8 | 1.5 | 74.0 | 7.4 |

*Table B.26: Average and RSD lead and vanadium aqua regia soluble content in riverbank samples, (n = 3).*

| Sample point GLA. RB | Analyte concentration ($mg\ kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Yttrium | | | | Zinc | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 8.29 | 5.5 | 8.34 | 3.7 | 310 | 1.7 | 280 | 5.3 |
| 2 | 8.80 | 9.0 | 9.65 | 6.1 | 298 | 1.3 | 337 | 2.5 |
| 3 | 7.29 | 8.2 | 7.98 | 3.7 | 212 | 6.2 | 217 | 3.0 |
| 4 | 6.73 | 8.3 | 7.08 | 11 | 257 | 4.1 | 254 | 8.0 |
| 5 | 10.50 | 12 | 11.2 | 2.5 | 223 | 6.9 | 222 | 3.7 |
| 6 | 6.84 | 0.7 | 7.86 | 11 | 245 | 2.8 | 259 | 7.4 |
| 7 | 6.47 | 0.5 | 6.66 | 5.9 | 164 | 2.6 | 162 | 3.0 |
| 8 | 8.83 | 1.7 | 8.30 | 4.0 | 284 | 5.8 | 255 | 1.1 |
| 9 | 8.55 | 4.5 | 8.58 | 0.8 | 266 | 3.0 | 273 | 1.3 |
| 10 | 7.58 | 1.8 | 7.56 | 1.6 | 167 | 2.5 | 162 | 3.2 |
| 11 | 5.68 | 6.0 | 5.28 | 2.1 | 178 | 5.9 | 186 | 1.1 |
| 12 | 4.98 | 2.7 | 5.97 | 16 | 153 | 4.9 | 188 | 17 |
| 13 | 9.74 | 3.4 | 11.1 | 6.1 | 238 | 3.2 | 1310 | 141 |

*Table B.27: Average and RSD yttrium and zinc aqua regia soluble content in riverbank samples, (n = 3).*

Table B.28 shows the sample site locations from Glasgow ornamental gardens.

| Sample reference | Easting (approx.) | Northing (approx.) | Description |
|---|---|---|---|
| OG.01 | 254250 | 667250 | Victoria Park |
| OG.02 | 258250 | 662250 | Queens Park |
| OG.03 | 259500 | 660500 | Kings Park |
| OG.04 | 261250 | 668750 | Springburn Park |
| OG.05 | 266750 | 666250 | Auchinlea Park |
| OG.06 | 256250 | 670250 | Maryhill Park |
| OG.07 | 258000 | 668250 | Ruchill Park |
| OG.08 | 263500 | 663750 | Tolcross Park |
| OG.09 | 257250 | 666750 | Kelvingrove Park |
| OG.10 | 256750 | 667500 | Botanic Gardens |
| OG.11 | 262250 | 665750 | Alexandra Park |
| OG.12 | 258250 | 665750 | Blythswood Square |

*Table B.28: Ornamental gardens sample site locations.*

Table B.29 to B.36 show the results from Glasgow ornamental garden samples.

| Sample point GLA. OG | Loss on ignition at 550 °C (%) | | | |
|---|---|---|---|---|
| | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 10.8 | 3.0 | 8.49 | 4.3 |
| 2 | 11.5 | 5.3 | 8.04 | 4.1 |
| 3 | 11.6 | 1.5 | 8.51 | 10 |
| 4 | 13.7 | 3.2 | 14.6 | 2.4 |
| 5 | 6.82 | 15 | 6.23 | 3.4 |
| 6 | 3.84 | 1.6 | 8.65 | 10 |
| 7 | 11.5 | 8.4 | 10.9 | 5.2 |
| 8 | 4.4 | 5.4 | 7.23 | 3.1 |
| 9 | 18.1 | 24 | 12.6 | 0.6 |
| 10 | 15.2 | 6.4 | 16.8 | 7.7 |
| 11 | 7.7 | 8.2 | 6.2 | 1.1 |
| 12 | 6.25 | 16 | 6.64 | 5.4 |

*Table B.29: LOI (%) from ornamental garden samples.*

| Sample point GLA. OG | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Aluminium | | | | Barium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 15100 | 7.6 | 11900 | 7.6 | 113 | 7.1 | 95.7 | 2.2 |
| 2 | 27800 | 13 | 30900 | 17 | 78.1 | 21 | 87.9 | 16 |
| 3 | 12200 | 7.9 | 13900 | 26 | 97.7 | 8.4 | 114 | 7.6 |
| 4 | 12600 | 5.6 | 15600 | 23 | 104 | 3.9 | 120 | 7.0 |
| 5 | 8930 | 28 | 14500 | 6.9 | 35.3 | 12 | 109 | 16 |
| 6 | 11200 | 4.3 | 27300 | 19 | 90.4 | 11 | 76 | 19 |
| 7 | 8860 | 13 | 7860 | 12 | 97.7 | 4.0 | 94.2 | 4.8 |
| 8 | 9490 | 7.8 | 16600 | 7.3 | 69.3 | 6.6 | 120 | 2.1 |
| 9 | 13700 | 14 | 15300 | 15 | 177 | 12 | 195 | 8.1 |
| 10 | 10900 | 3.5 | 13000 | 1.1 | 138 | 5.1 | 148 | 4.8 |
| 11 | 9370 | 13 | 8380 | 5.4 | 106 | 8.3 | 95.3 | 7.8 |
| 12 | 10100 | 11 | 11000 | 17 | 133 | 12 | 150 | 19 |

*Table B.30: Average and RSD aluminium and barium aqua regia soluble content in ornamental garden samples, (n = 3).*

| Sample point GLA. OG | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Calcium | | | | Chromium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 15900 | 11 | 12500 | 3.3 | 38.1 | 5.4 | 38.6 | 4.8 |
| 2 | 4880 | 7.1 | 6060 | 15 | 53.7 | 14 | 62.7 | 17 |
| 3 | 6780 | 13 | 3880 | 8.8 | 27.1 | 6.0 | 28.7 | 19 |
| 4 | 13100 | 26 | 8910 | 9.0 | 29.7 | 7.7 | 36.6 | 17 |
| 5 | 1790 | 16 | 15400 | 24 | 33.6 | 23 | 36.6 | 9.7 |
| 6 | 11800 | 10 | 4780 | 14 | 36.5 | 13 | 52.5 | 18 |
| 7 | 8340 | 6.6 | 7750 | 7.7 | 27.5 | 9.5 | 25.1 | 17 |
| 8 | 2970 | 4.9 | 3700 | 2.4 | 23.6 | 11 | 41.7 | 5.3 |
| 9 | 22700 | 35 | 18500 | 49 | 40.6 | 16 | 44.2 | 12 |
| 10 | 21700 | 3.5 | 19700 | 4.6 | 26 | 1.2 | 45.2 | 57 |
| 11 | 5220 | 10 | 4830 | 6.8 | 30 | 7.6 | 27.7 | 9.3 |
| 12 | 3680 | 43 | 2350 | 5.4 | 181 | 8.6 | 117 | 3.5 |

*Table B.31: Average and RSD calcium and chromium aqua regia soluble content in ornamental garden samples, (n = 3).*

| Sample point GLA. OG | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Copper | | | | Iron (%) | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 34.7 | 8.9 | 30.2 | 3.4 | 2.8 | 2.8 | 2.87 | 3.0 |
| 2 | 31.4 | 11 | 55.9 | 12 | 5.07 | 11 | 4.62 | 15 |
| 3 | 37.5 | 7.2 | 36.5 | 8 | 2.88 | 5.2 | 3.11 | 7.8 |
| 4 | 52.2 | 7.9 | 60 | 5 | 2.15 | 4.3 | 2.52 | 16 |
| 5 | 23.8 | 6 | 33.7 | 22 | 2.86 | 5.3 | 2.7 | 11 |
| 6 | 28.5 | 10 | 30.8 | 16 | 2.71 | 8.5 | 4.96 | 14 |
| 7 | 45.8 | 20 | 37.6 | 10 | 2.78 | 4.1 | 2.51 | 5.6 |
| 8 | 32.2 | 9 | 56.2 | 11 | 2.4 | 11 | 2.74 | 0.5 |
| 9 | 77.9 | 20 | 82.7 | 6 | 2.49 | 24 | 2.44 | 9.2 |
| 10 | 48.9 | 3.7 | 51.0 | 6 | 2.12 | 4.2 | 2.4 | 1.8 |
| 11 | 30.4 | 4.4 | 30.1 | 6.9 | 1.96 | 3.7 | 2.08 | 5.9 |
| 12 | 52.0 | 11 | 56.4 | 4.5 | 2.69 | 3.9 | 2.69 | 2.4 |

*Table B.32: Average and RSD copper and iron aqua regia soluble content in ornamental garden samples, (n = 3).*

| Sample point GLA. OG | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lithium | | | | Magnesium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 12.5 | 4.5 | 9.95 | 8.3 | 4070 | 7.3 | 3810 | 1.7 |
| 2 | 10.3 | 14 | 16.6 | 13 | 10700 | 12 | 8980 | 14 |
| 3 | 9.66 | 15 | 12 | 29 | 2200 | 4.2 | 1990 | 13 |
| 4 | 11.2 | 7.8 | 13.7 | 21 | 4980 | 28 | 3160 | 7.5 |
| 5 | 6.18 | 28 | 12 | 10 | 2890 | 10 | 3900 | 9.1 |
| 6 | 9.34 | 3.7 | 10.1 | 19 | 3600 | 9.8 | 10500 | 17 |
| 7 | 6.13 | 23 | 5.56 | 15 | 2640 | 9.6 | 2260 | 6.8 |
| 8 | 9.25 | 8.1 | 14.7 | 6.8 | 3270 | 6.9 | 3060 | 5.3 |
| 9 | 12.6 | 15 | 14 | 10 | 3120 | 4.8 | 3140 | 4.2 |
| 10 | 9.68 | 3.3 | 11 | 2.7 | 3960 | 7.8 | 3650 | 6.2 |
| 11 | 8 | 13 | 7.89 | 4.9 | 2770 | 4.1 | 2980 | 6.2 |
| 12 | 9.29 | 6.7 | 10.3 | 15 | 2350 | 18 | 2090 | 7.4 |

*Table B.33: Average and RSD lithium and magnesium aqua regia soluble content in ornamental garden samples, (n = 3).*

| Sample point GLA. OG | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Manganese | | | | Nickel | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 522 | 3.7 | 519 | 3.4 | 34.7 | 1.8 | 32.9 | 2.3 |
| 2 | 742 | 12 | 678 | 21 | 82 | 11 | 57.5 | 20 |
| 3 | 434 | 4.7 | 512 | 29 | 23 | 3.4 | 23.6 | 9.2 |
| 4 | 399 | 3.0 | 414 | 1.6 | 22.9 | 8.6 | 29.4 | 19 |
| 5 | 376 | 4.9 | 504 | 15 | 21.7 | 10 | 33.4 | 13 |
| 6 | 491 | 14 | 727 | 17 | 31 | 9.2 | 80.3 | 16 |
| 7 | 514 | 15 | 520 | 27 | 24 | 11 | 19.6 | 10 |
| 8 | 413 | 9.9 | 546 | 3.1 | 20.9 | 13 | 40.9 | 6.9 |
| 9 | 566 | 12 | 577 | 4.7 | 37.7 | 22 | 39.7 | 9.6 |
| 10 | 559 | 3.7 | 566 | 3.0 | 27.6 | 3.7 | 32.3 | 2.4 |
| 11 | 402 | 2.8 | 437 | 10 | 24.9 | 6.3 | 23.3 | 3.4 |
| 12 | 517 | 14 | 489 | 1.1 | 39 | 11 | 35.1 | 11 |

*Table B.34: Average and RSD manganese and nickel aqua regia soluble content in ornamental garden samples, (n = 3).*

| Sample point GLA. OG | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lead | | | | Vanadium | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 74.3 | 14 | 60.6 | 9.3 | 55.8 | 1.7 | 52.3 | 2.2 |
| 2 | 40.1 | 41 | 42.4 | 24 | 80.1 | 14 | 85.4 | 16 |
| 3 | 111 | 3.3 | 103 | 7.6 | 45.4 | 2.6 | 48.1 | 13 |
| 4 | 171 | 13 | 193 | 1.4 | 50.8 | 8.1 | 56.9 | 9.6 |
| 5 | 12.4 | 1.3 | 72.6 | 27 | 49.7 | 6.9 | 53.7 | 13 |
| 6 | 57.2 | 14 | 38.6 | 34 | 49.3 | 9.2 | 78.4 | 18 |
| 7 | 118 | 27 | 101 | 9.2 | 39 | 9.4 | 35.7 | 6.1 |
| 8 | 67.6 | 11 | 146 | 8.6 | 38.9 | 6.7 | 67.8 | 1.5 |
| 9 | 236 | 32 | 264 | 15.7 | 52.9 | 19 | 58 | 11 |
| 10 | 137 | 2.6 | 184 | 4.7 | 41.8 | 2.5 | 50.2 | 1.4 |
| 11 | 77.6 | 1.6 | 91.3 | 32 | 39.6 | 4.1 | 45.4 | 24 |
| 12 | 201 | 8.5 | 234 | 3.1 | 50.5 | 3.8 | 51.4 | 4.4 |

*Table B.35: Average and RSD lead and vanadium aqua regia soluble content in ornamental garden samples, (n = 3).*

| Sample point GLA. OG | Analyte concentration (mg kg$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Yttrium | | | | Zinc | | | |
| | Surface | | Sub-surface | | Surface | | Sub-surface | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| 1 | 7.32 | 1.1 | 6.87 | 6.5 | 146 | 7.2 | 126 | 1.7 |
| 2 | 5.75 | 12 | 8.23 | 12 | 113 | 14 | 124 | 14 |
| 3 | 6.27 | 6.8 | 6.67 | 15 | 117 | 17 | 98.1 | 11 |
| 4 | 7.07 | 5.8 | 8.31 | 13 | 214 | 4.9 | 253 | 5.6 |
| 5 | 5.06 | 15 | 7.06 | 15 | 53.7 | 6.7 | 142 | 20 |
| 6 | 6.5 | 14 | 5.64 | 18 | 119 | 13 | 111 | 17 |
| 7 | 6.04 | 11 | 5.44 | 10 | 121 | 4.8 | 122 | 12 |
| 8 | 5.46 | 4.6 | 8.33 | 3.3 | 82.7 | 12 | 180 | 15 |
| 9 | 7.79 | 18 | 8.37 | 13 | 251 | 12 | 255 | 3.5 |
| 10 | 6.34 | 1.5 | 7.03 | 2.3 | 201 | 2.6 | 209 | 4.4 |
| 11 | 5.3 | 3.5 | 5.7 | 3.7 | 174 | 5.4 | 321 | 14 |
| 12 | 7.96 | 10 | 8.06 | 8.0 | 165 | 5.8 | 156 | 6.3 |

*Table B.36: Average and RSD yttrium and zinc aqua regia soluble content in ornamental garden samples, (n = 3).*

# APPENDIX C

Table C.1 – C.8 show the metal concentrations from the sequential extractions of 20 Glasgow surface samples (0-10 cm). The precision (as % RSD) is also shown.

| Sample | Step1 | | Step 2 | | Step 3 | | Step 4 | | Sum | | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | |
| RD.04 | 1610 | 4.2 | 639 | 6.3 | 158 | 3.1 | 1140 | 16 | 3540 | 6.0 | 129 |
| RD.05 | 2250 | 11 | 1530 | 42 | 524 | 54 | 1070 | 22 | 5380 | 21 | 174 |
| RD.06 | 2290 | 9.0 | 1290 | 5.2 | 249 | 11 | 1880 | 18 | 5710 | 2.1 | 102 |
| RD.07 | 2650 | 4.9 | 930 | 16 | 225 | 14 | 950 | 4.7 | 4760 | 1.9 | 93 |
| RD.14 | 1710 | 4.7 | 858 | 14 | 170 | 18 | 1200 | 25 | 3940 | 12 | 109 |
| RD.23 | 2080 | 4.4 | 1090 | 11 | 191 | 10 | 1580 | 11 | 4940 | 7.0 | 94 |
| PO.04 | 211 | 5.7 | 150 | 21 | 50.1 | 12 | 683 | 26 | 1090 | 14 | 122 |
| PO.07 | 640 | 7.5 | 177 | 3.7 | 49.1 | 4.9 | 543 | 18 | 1410 | 7.6 | 67 |
| PO.10 | 459 | 3.9 | 226 | 3.3 | 56 | 6.7 | 421 | 20 | 1160 | 7.9 | 49 |
| PO.14 | 1310 | 12 | 286 | 9.8 | 88.5 | 2.9 | 417 | 5.4 | 2100 | 9.3 | 227 |
| PO.15 | 1620 | 3.2 | 720 | 30 | 256 | 15 | 1500 | 8.7 | 4100 | 10 | 118 |
| PO.18 | 273 | 13 | 202 | 2.0 | 57.7 | 25 | 579 | 30 | 1110 | 16 | 108 |
| PO.20 | 1530 | 3.8 | 571 | 3.4 | 131 | 16 | 969 | 25 | 3210 | 8.7 | 92 |
| PO.24 | 1990 | 6.4 | 1400 | 8.9 | 283 | 10 | 1260 | 2.9 | 4920 | 1.9 | 100 |
| PO.31 | 885 | 5.6 | 299 | 6.4 | 42.2 | 5.3 | 346 | 45 | 1570 | 9.0 | 105 |
| PO.32 | 1230 | 7.5 | 405 | 9.4 | 122 | 9.7 | 298 | 1.4 | 2060 | 5.6 | 94 |
| PO.33 | 432 | 5.5 | 311 | 4.9 | 70.9 | 11 | 762 | 7.1 | 1580 | 4.9 | 110 |
| PO.34 | 752 | 5.3 | 464 | 17 | 128 | 6.7 | 1020 | 3.6 | 2360 | 2.4 | 105 |
| PO.38 | 1120 | 3.6 | 452 | 38 | 37.2 | 22 | 292 | 32 | 1900 | 8.6 | 79 |
| PO.39 | 1590 | 2.8 | 575 | 3.2 | 79 | 3.2 | 477 | 32 | 2720 | 4.8 | 86 |

*Table C.1: Average concentration of calcium in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100 *( ∑steps 1 to 4)/pseudo total content, (n=3).*

| Sample | Step1 | | Step 2 | | Step 3 | | Step 4 | | Sum | | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | |
| RD.04 | 0.19 | <d.l. | 1.34 | 7.6 | 8.64 | 15 | 21.4 | 7.1 | 31.5 | 2.6 | 115 |
| RD.05 | 0.19 | <d.l. | 3.06 | 13 | 9.79 | 22 | 23.2 | 29 | 36.2 | 25 | 105 |
| RD.06 | 0.19 | <d.l. | 2.97 | 8.1 | 7.01 | 13 | 27.7 | 37 | 38.0 | 27 | 95 |
| RD.07 | 0.40 | 17 | 7.38 | 3.3 | 23.4 | 0.7 | 22.6 | 5.2 | 53.8 | 2.0 | 71 |
| RD.14 | 0.19 | <d.l. | 3.88 | 7.5 | 11.6 | 2.2 | 32.3 | 29 | 47.9 | 19 | 121 |
| RD.23 | 0.19 | <d.l. | 2.47 | 9.7 | 6.73 | 8.5 | 21.5 | 8.8 | 30.8 | 8.2 | 88 |
| PO.04 | 0.19 | <d.l. | 1.27 | 4.4 | 7.82 | 2.8 | 19.4 | 27 | 28.6 | 18 | 102 |
| PO.07 | 0.19 | <d.l. | 0.53 | 20 | 4.05 | 7.0 | 22.2 | 7.4 | 26.8 | 6.2 | 111 |
| PO.10 | 0.19 | <d.l. | 1.57 | 2.9 | 7.72 | 1.8 | 36 | 13 | 45.6 | 10 | 143 |
| PO.14 | 0.19 | <d.l. | 0.98 | 5.9 | 6.71 | 5.9 | 26.3 | 3.9 | 34.1 | 4.3 | 108 |
| PO.15 | 1.35 | 1.8 | 18.2 | 1.4 | 47.2 | 5.2 | 59.8 | 6.5 | 127 | 4.8 | 92 |
| PO.18 | 0.99 | 13 | 5.96 | 2.8 | 23.2 | 4.6 | 121 | 13 | 151 | 11 | 87 |
| PO.20 | 0.19 | <d.l. | 2.67 | 4.8 | 6.22 | 1.8 | 18.1 | 10 | 27.3 | 6.6 | 79 |
| PO.24 | 0.19 | <d.l. | 4.24 | 25 | 13.4 | 6.6 | 47.8 | 17 | 65.8 | 14 | 82 |
| PO.31 | 0.19 | <d.l. | 0.66 | 6.5 | 3.65 | 5.3 | 14.1 | 17 | 18.5 | 11 | 84 |
| PO.32 | 3.07 | 13 | 39.1 | 12 | 102 | 7.1 | 37.4 | 3.1 | 182 | 7.4 | 79 |
| PO.33 | 0.19 | <d.l. | 1.98 | 7.6 | 7.82 | 5.0 | 22.8 | 4.1 | 32.9 | 3.3 | 97 |
| PO.34 | 0.19 | <d.l. | 2.61 | 8.8 | 7.94 | 8.7 | 33.8 | 32 | 44.7 | 24 | 96 |
| PO.38 | 0.19 | <d.l. | 0.97 | 44 | 2.86 | 6.2 | 16.8 | 13 | 20.7 | 13 | 88 |
| PO.39 | 0.19 | <d.l. | 1.23 | 5.8 | 6.51 | 5.8 | 22.8 | 7.8 | 30.7 | 5.2 | 75 |

*Table C.2: Average concentration of chromium in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100 *(∑steps 1 to 4)/pseudo total content, < d.l. = below detection limits, mean = 0.5 * $DL_{pro}$,(n=3).*

| Sample | Step1 | | Step 2 | | Step 3 | | Step 4 | | Sum | | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | |
| RD.04 | 2.02 | 11 | 14.4 | 0.4 | 17 | 4.6 | 14 | 6.5 | 47.4 | 3.2 | 104 |
| RD.05 | 4.93 | 12 | 24.4 | 12 | 30.8 | 3.8 | 15.9 | 7.1 | 76.1 | 5.0 | 89 |
| RD.06 | 15.9 | 19 | 31.9 | 4.8 | 20.1 | 12 | 19.5 | 4.3 | 87.4 | 7.7 | 95 |
| RD.07 | 4.49 | 13 | 24.8 | 3.7 | 27.3 | 4.5 | 24.8 | 7.1 | 81.4 | 2.5 | 77 |
| RD.14 | 2.12 | 17 | 24.5 | 1.7 | 25.8 | 5.9 | 20 | 6.0 | 72.4 | 3.1 | 92 |
| RD.23 | 0.85 | 8.0 | 18.7 | 1.1 | 26 | 4.6 | 18.1 | 0.4 | 63.6 | 1.9 | 72 |
| PO.04 | 0.64 | 6.0 | 11.9 | 0.4 | 15 | 2.5 | 10.7 | 8.6 | 38.3 | 1.7 | 73 |
| PO.07 | 0.103 | <dl | 6.61 | 6.4 | 6.9 | 7.4 | 7.1 | 5.8 | 20.6 | 5.6 | 73 |
| PO.10 | 0.81 | 14 | 12.2 | 2.8 | 11.3 | 4.0 | 19.3 | 13.0 | 43.5 | 5.8 | 89 |
| PO.14 | 0.103 | <dl | 10.6 | 3.1 | 11 | 6.6 | 12.7 | 8.3 | 34.2 | 6.1 | 85 |
| PO.15 | 3.43 | 8.9 | 42.2 | 4.5 | 49.3 | 5.4 | 38.4 | 5.4 | 133 | 4.0 | 86 |
| PO.18 | 3.48 | 9.3 | 14 | 3.9 | 20.1 | 2.6 | 11.9 | 4.6 | 49.5 | 3.6 | 80 |
| PO.20 | 6.65 | 18 | 26.8 | 17 | 22.9 | 14 | 18.1 | 11 | 74.5 | 14 | 78 |
| PO.24 | 3.43 | 12 | 26.9 | 18 | 76.5 | 7.7 | 46.5 | 31 | 153 | 16 | 79 |
| PO.31 | 5.59 | 13 | 15.6 | 8.3 | 9.63 | 3.1 | 7.36 | 4.4 | 38.2 | 5.4 | 84 |
| PO.32 | 2.74 | 9.7 | 17.6 | 10 | 16.2 | 8.3 | 13.1 | 8.0 | 49.7 | 8.9 | 88 |
| PO.33 | 4.14 | 9.5 | 16.5 | 7.2 | 15.3 | 4.5 | 12.9 | 7.2 | 48.7 | 2.0 | 86 |
| PO.34 | 6.06 | 14 | 25.4 | 7.2 | 25.7 | 9.2 | 19.5 | 12 | 76.7 | 9.5 | 77 |
| PO.38 | 0.98 | 11 | 3.98 | 1.2 | 2.7 | 3.3 | 5.68 | 4.8 | 13.3 | 3.3 | 73 |
| PO.39 | 1.49 | 6.8 | 8.92 | 5.1 | 7.27 | 2.5 | 10.1 | 4.3 | 27.8 | 0.4 | 66 |

*Table C.3: Average concentration of copper in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100 *(∑steps 1 to 4)/pseudo total content, (n=3).*

| Sample | Step1 | | Step 2 | | Step 3 | | Step 4 | | Sum | | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | |
| RD.04 | 6.48 | 47 | 3450 | 3.5 | 1100 | 8.7 | 20100 | 2.9 | 24700 | 2.6 | 106 |
| RD.05 | 5.17 | 23 | 3790 | 8.3 | 930 | 11 | 20700 | 1.6 | 25500 | 1.4 | 95 |
| RD.06 | 51.7 | 12 | 2640 | 6.0 | 585 | 7.1 | 22600 | 4.7 | 25900 | 4.7 | 89 |
| RD.07 | 8.37 | 24 | 4020 | 1.8 | 1010 | 8.0 | 21100 | 7.5 | 26200 | 5.9 | 80 |
| RD.14 | 7.94 | 9.4 | 4040 | 2.8 | 918 | 8.0 | 20700 | 3.3 | 25600 | 3.0 | 96 |
| RD.23 | 6.76 | 13 | 2880 | 2.4 | 936 | 13 | 23600 | 9.4 | 27400 | 8.7 | 93 |
| PO.04 | 28.3 | 4.8 | 3750 | 0.1 | 728 | 5.1 | 11700 | 8.2 | 16200 | 6.2 | 95 |
| PO.07 | 13.2 | 8.7 | 3570 | 5.4 | 595 | 0.9 | 16400 | 2.5 | 20600 | 2.8 | 89 |
| PO.10 | 30.3 | 12 | 5370 | 3.0 | 1350 | 9.4 | 25800 | 13 | 32500 | 11 | 106 |
| PO.14 | 10.4 | 38 | 4160 | 5.2 | 716 | 11 | 21200 | 8.5 | 26100 | 7.5 | 102 |
| PO.15 | 7.71 | 9.8 | 3800 | 3.9 | 1520 | 14 | 22900 | 2.7 | 28300 | 2.3 | 97 |
| PO.18 | 40.6 | 8.5 | 4790 | 4.4 | 1450 | 14 | 16200 | 7.8 | 22500 | 7.4 | 89 |
| PO.20 | 9.65 | 1.5 | 4600 | 2.9 | 1110 | 2.5 | 19800 | 4.6 | 25500 | 3.7 | 82 |
| PO.24 | 8.25 | 6.2 | 4070 | 3.2 | 2050 | 5.6 | 34300 | 3.4 | 40400 | 3.1 | 100 |
| PO.31 | 11.9 | 13 | 2960 | 5.1 | 733 | 8.3 | 12900 | 4.2 | 16600 | 2.8 | 94 |
| PO.32 | 10.6 | 8.8 | 4450 | 7.1 | 1010 | 6.2 | 19300 | 5.7 | 24800 | 5.9 | 100 |
| PO.33 | 21.2 | 3.4 | 5120 | 5.0 | 984 | 5.5 | 19000 | 7.1 | 25200 | 5.7 | 94 |
| PO.34 | 20.0 | 12 | 5610 | 1.7 | 955 | 9.1 | 19600 | 6.5 | 26200 | 4.6 | 84 |
| PO.38 | 13.2 | 10 | 2210 | 4.9 | 237 | 11 | 15200 | 6.0 | 17600 | 5.8 | 79 |
| PO.39 | 12.5 | 10 | 4540 | 3.3 | 670 | 4.2 | 21100 | 2.6 | 26300 | 1.7 | 85 |

*Table C.4: Average concentration of iron in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100* *( $\sum$*steps 1 to 4)/pseudo total content, (n=3).*

| Sample | Step1 | | Step 2 | | Step 3 | | Step 4 | | Sum | | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | |
| RD.04 | 56.5 | 2.9 | 231 | 2.6 | 25.6 | 3.6 | 162 | 4.6 | 475 | 0.6 | 109 |
| RD.05 | 75.1 | 7.6 | 330 | 22 | 41 | 56 | 164 | 12 | 610 | 18 | 101 |
| RD.06 | 126 | 17 | 108 | 11 | 20.5 | 4.8 | 187 | 10 | 441 | 8.6 | 90 |
| RD.07 | 139 | 7.8 | 312 | 5.6 | 23.6 | 5.5 | 195 | 11 | 669 | 7.2 | 75 |
| RD.14 | 117 | 2.9 | 357 | 4.9 | 18.8 | 6.6 | 194 | 19 | 686 | 8.0 | 98 |
| RD.23 | 90.3 | 7.1 | 217 | 6.9 | 16.4 | 7.0 | 186 | 1.7 | 510 | 4.2 | 94 |
| PO.04 | 22.8 | 7.8 | 10.1 | 66 | 5.41 | 9.6 | 58.8 | 14 | 97.1 | 3.2 | 103 |
| PO.07 | 107 | 8.0 | 107 | 7.0 | 18.7 | 8.9 | 103 | 2.0 | 335 | 4.8 | 85 |
| PO.10 | 123 | 5.4 | 122 | 23 | 27.9 | 2.2 | 153 | 19 | 426 | 10 | 107 |
| PO.14 | 75.5 | 24 | 66.8 | 9.1 | 19 | 7.6 | 94.1 | 3.6 | 255 | 6.1 | 97 |
| PO.15 | 50.9 | 6.8 | 203 | 2.3 | 17.9 | 15 | 157 | 8.9 | 428 | 4.9 | 101 |
| PO.18 | 25.1 | 14 | 16.3 | 15 | 7.61 | 9.3 | 82.7 | 8.3 | 132 | 9.4 | 90 |
| PO.20 | 93.1 | 1.1 | 302 | 6.0 | 25.8 | 6.9 | 152 | 3.3 | 573 | 2.7 | 87 |
| PO.24 | 53.1 | 28 | 304 | 11 | 22.5 | 8.7 | 204 | 8.9 | 584 | 7.8 | 95 |
| PO.31 | 73.5 | 5.7 | 110 | 21 | 13 | 9.1 | 93.6 | 7.3 | 290 | 5.3 | 94 |
| PO.32 | 72.6 | 4.1 | 239 | 6.7 | 15.8 | 4.7 | 109 | 4.5 | 437 | 5.3 | 105 |
| PO.33 | 53 | 5.4 | 110 | 4.9 | 17.8 | 11 | 113 | 8.7 | 294 | 5.9 | 91 |
| PO.34 | 61.1 | 11 | 175 | 5.6 | 17.4 | 8.3 | 168 | 31 | 422 | 11 | 87 |
| PO.38 | 54.6 | 7.8 | 155 | 6.6 | 11 | 9.6 | 117 | 11 | 338 | 7.1 | 81 |
| PO.39 | 69.3 | 1.8 | 103 | 4.3 | 16.4 | 5.3 | 127 | 3.9 | 315 | 3.1 | 79 |

*Table C.5: Average concentration of manganese in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100* *( $\sum$*steps 1 to 4)/pseudo total content, (n=3).*

| Sample | Step1 | | Step 2 | | Step 3 | | Step 4 | | Sum | | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | |
| RD.04 | 1.99 | 11 | 2.77 | 2.8 | 4.6 | 4.8 | 19.5 | 6.2 | 28.9 | 4.7 | 108 |
| RD.05 | 2.04 | 11 | 3.9 | 12 | 5.08 | 3.4 | 17.3 | 4.3 | 28.3 | 3.1 | 94 |
| RD.06 | 1.2 | 8.2 | 2.76 | 5.4 | 4.25 | 6.1 | 19.3 | 22 | 27.5 | 17 | 96 |
| RD.07 | 2.21 | 9.3 | 3.33 | 3.0 | 5.68 | 5.6 | 20 | 7.8 | 31.2 | 6.3 | 75 |
| RD.14 | 2.42 | 2.7 | 3.72 | 2.7 | 4.42 | 4.9 | 23.7 | 11 | 34.3 | 7.9 | 131 |
| RD.23 | 2.03 | 7.4 | 4.36 | 6.4 | 4.44 | 6.5 | 24.3 | 7.7 | 35.1 | 6.1 | 96 |
| PO.04 | 1.36 | 12 | 1.33 | 3.9 | 2.75 | 11 | 25.7 | 15 | 31.1 | 11 | 112 |
| PO.07 | 2.14 | 11 | 1.6 | 7.4 | 2.8 | 3.2 | 19.7 | 3.6 | 26.3 | 3.8 | 104 |
| PO.10 | 1.81 | 8.9 | 2.43 | 5.0 | 5.02 | 6.3 | 31.1 | 13 | 40.4 | 11 | 129 |
| PO.14 | 1.89 | 11 | 2.13 | 8.5 | 3.34 | 8.0 | 22.6 | 4.3 | 29.9 | 4.7 | 108 |
| PO.15 | 3.99 | 1.6 | 6.35 | 4.3 | 10 | 4.0 | 62.2 | 2.9 | 82.6 | 2.9 | 110 |
| PO.18 | 1.14 | 8.6 | 2.13 | 6.7 | 4.16 | 3.4 | 26.5 | 10 | 33.9 | 8.5 | 87 |
| PO.20 | 2.26 | 0.4 | 3.13 | 5.6 | 4.07 | 8.5 | 23 | 9.5 | 32.5 | 7.1 | 72 |
| PO.24 | 5.26 | 6.7 | 11.1 | 4.6 | 11.3 | 2.7 | 80.8 | 14 | 109 | 11 | 83 |
| PO.31 | 1.43 | 10 | 1.62 | 2.7 | 2.72 | 8.4 | 12.2 | 9.8 | 18 | 4.9 | 86 |
| PO.32 | 6.1 | 8.4 | 5.63 | 15 | 7.45 | 6.1 | 24.6 | 4.0 | 43.8 | 6.4 | 98 |
| PO.33 | 2.07 | 5.2 | 2.31 | 8.3 | 3.7 | 9.5 | 22.9 | 16 | 31 | 13 | 113 |
| PO.34 | 2.32 | 7.5 | 2.72 | 5.0 | 4.38 | 8.3 | 32.6 | 8.8 | 42 | 7.8 | 87 |
| PO.38 | 1.43 | 4.1 | 1.64 | 14 | 2.35 | 5.6 | 12.8 | 9.0 | 18.2 | 5.6 | 82 |
| PO.39 | 2.68 | 2.0 | 2.74 | 4.0 | 4.61 | 3.8 | 20.1 | 4.7 | 30.1 | 3.1 | 81 |

*Table C.6: Average concentration of nickel in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100 *( ∑steps 1 to 4)/pseudo total content, (n=3).*

| Sample | Step1 | | Step 2 | | Step 3 | | Step 4 | | Sum | | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | |
| RD.04 | 3.27 | 7.0 | 142 | 3.0 | 20.4 | 2.5 | 25.3 | 2.0 | 190 | 2.5 | 107 |
| RD.05 | 6.69 | 9.2 | 205 | 6.0 | 31 | 3.4 | 31.5 | 8.4 | 274 | 5.0 | 93 |
| RD.06 | 3.6 | 25 | 64.2 | 4.5 | 8.95 | 9.4 | 12 | 7.2 | 88.7 | 5.5 | 81 |
| RD.07 | 6.88 | 20 | 222 | 3.5 | 26.5 | 5.3 | 35.4 | 2.9 | 291 | 3.0 | 77 |
| RD.14 | 8.96 | 7.4 | 230 | 0.2 | 26.6 | 9.6 | 30.7 | 5.4 | 297 | 0.9 | 103 |
| RD.23 | 6.3 | 16 | 209 | 14 | 27.8 | 43 | 33.9 | 17 | 277 | 17 | 96 |
| PO.04 | 18.9 | 5.7 | 151 | 3.4 | 29.2 | 1.6 | 19.8 | 8.4 | 219 | 2.4 | 85 |
| PO.07 | 2.67 | 10 | 67.4 | 4.9 | 8.7 | 7.3 | 13.2 | 18 | 91.9 | 6.1 | 81 |
| PO.10 | 6.19 | 4.5 | 110 | 8.5 | 18.6 | 11 | 21.4 | 13 | 156 | 4.4 | 100 |
| PO.14 | 2.99 | 27 | 85.2 | 4.3 | 12.9 | 6.2 | 14.4 | 9.3 | 116 | 4.6 | 95 |
| PO.15 | 13 | 9.3 | 347 | 2.2 | 56.4 | 15 | 58.5 | 19 | 475 | 3.0 | 100 |
| PO.18 | 13.5 | 5.5 | 151 | 4.2 | 33.2 | 7.8 | 22.9 | 0.5 | 221 | 4.1 | 81 |
| PO.20 | 5.11 | 8.1 | 163 | 0.7 | 20.9 | 11 | 18.9 | 2.2 | 208 | 1.8 | 89 |
| PO.24 | 8.6 | 9.5 | 319 | 5.9 | 87.5 | 6.2 | 63.9 | 1.8 | 479 | 3.2 | 78 |
| PO.31 | 1.49 | 17 | 30 | 5.0 | 6.96 | 7.5 | 5.22 | 14 | 43.7 | 5.6 | 99 |
| PO.32 | 6.75 | 10 | 185 | 9.6 | 25.1 | 7.3 | 18.9 | 1.1 | 235 | 8.2 | 102 |
| PO.33 | 8.31 | 9.4 | 123 | 6.6 | 19.4 | 5.9 | 20 | 6.3 | 170 | 3.8 | 99 |
| PO.34 | 14.4 | 13 | 205 | 6.3 | 32.3 | 4.1 | 32.2 | 6.3 | 284 | 6.2 | 79 |
| PO.38 | 0.75 | <dl | 21.5 | 2.0 | 1.35 | <dl | 4.35 | 9.8 | 27.9 | 2.0 | 73 |
| PO.39 | 2.16 | 25 | 74 | 2.0 | 9.43 | 4.9 | 14.1 | 6.3 | 99.7 | 1.9 | 84 |

*Table C.7: Average concentration of lead in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100 *( ∑steps 1 to 4)/pseudo total content, (n=3).*

| Sample | Step1 |  | Step 2 |  | Step 3 |  | Step 4 |  | Sum |  | R (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD |  |
| RD.04 | 28.6 | 2.3 | 33.3 | 5.5 | 39.4 | 11 | 68.6 | 4.1 | 170 | 3.5 | 105 |
| RD.05 | 49.9 | 13 | 55.6 | 8.9 | 42.1 | 9.9 | 67.7 | 2.8 | 215 | 7.5 | 90 |
| RD.06 | 67.1 | 11 | 45.9 | 5.0 | 35.3 | 35 | 57.1 | 8.2 | 205 | 2.8 | 98 |
| RD.07 | 60.5 | 8.2 | 53 | 1.6 | 34.4 | 6.9 | 85.7 | 5.1 | 234 | 3.1 | 75 |
| RD.14 | 49.0 | 5.4 | 51.6 | 30 | 34.3 | 12 | 111 | 11 | 246 | 13 | 94 |
| RD.23 | 38.4 | 2.5 | 34.9 | 2.1 | 20.5 | 8.8 | 74.3 | 4.6 | 168 | 3.1 | 76 |
| PO.04 | 1.34 | 46 | 0.84 | <dl | 3.44 | 7.3 | 42.9 | 27 | 47.7 | 26 | 70 |
| PO.07 | 8.91 | 7.8 | 3.59 | 146 | 9.91 | 8.0 | 52.9 | 1.5 | 75.3 | 6.9 | 60 |
| PO.10 | 8.16 | 5.5 | 9.99 | 22 | 19.7 | 3.9 | 86.5 | 13 | 124 | 8.7 | 88 |
| PO.14 | 51.3 | 12.8 | 21.5 | 45 | 24.9 | 12 | 86.6 | 4.9 | 184 | 44 | 99 |
| PO.15 | 65.2 | 0.8 | 90.6 | 0.6 | 71.8 | 3.7 | 254 | 3.1 | 482 | 1.2 | 98 |
| PO.18 | 15.6 | 12 | 10.4 | 11 | 17.1 | 4.2 | 62.7 | 6.6 | 106 | 5.0 | 86 |
| PO.20 | 26.3 | 2.2 | 29.1 | 13 | 27.9 | 4.1 | 86.9 | 7.5 | 170 | 6.0 | 82 |
| PO.24 | 89.2 | 7.1 | 157 | 5.1 | 94.1 | 10 | 197 | 9.0 | 537 | 5.7 | 86 |
| PO.31 | 7.03 | 5.0 | 10.4 | 13 | 15.2 | 8.7 | 31.5 | 8.1 | 64.2 | 2.6 | 93 |
| PO.32 | 43.7 | 10 | 39 | 15 | 30.7 | 5.1 | 98.8 | 5.9 | 212 | 8.2 | 96 |
| PO.33 | 22.2 | 4.6 | 21.2 | 6.0 | 19.4 | 8.7 | 70.9 | 3.1 | 134 | 2.4 | 89 |
| PO.34 | 42.3 | 66 | 29.1 | 26 | 23.9 | 4.6 | 81.6 | 6.9 | 177 | 23 | 94 |
| PO.38 | 6.73 | 4.6 | 10.3 | 33 | 10.4 | 13 | 25.7 | 5.6 | 53.1 | 8.6 | 39 |
| PO.39 | 12.3 | 3.0 | 16.9 | 3.9 | 22.6 | 10 | 58.5 | 3.9 | 110 | 2.8 | 165 |

*Table C.8: Average concentration of zinc in sequential extracts of 20 Glasgow samples, RD = roadside, PO = park and open space, Recovery (R) =100 *( ∑steps 1 to 4)/pseudo total content, (n=3).*