A STUDY OF TOXIC METALS

IN

KERB-SIDE SOILS

by

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Supervised

by

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PREFACE

The following report describes the work that was done at the Durban Institute of Technology, ML Sultan Campus, Department of Chemistry to investigate the levels of the toxic metals: lead, cadmium, copper, nickel, chromium and aluminium, in the vicinity of major/minor traffic routes around the City of Durban in KwaZulu-Natal, South Africa.

DECLARATION

I declare that this dissertation is my own unaided work. It has not been submitted before for any degree or examination in any other institution.

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JOHANNES THEMBA MSUKWINI

________ day of__________________ 2003

ABSTRACT

In urban environments motor vehicles are by far the largest source of lead. In areas subjected to heavy and slow moving vehicular traffic, the amount of lead exhausted may be quite high. Since exhaust fumes settle on kerb-sides, soil samples from these areas may not only give a good measure of the accumulation of lead but also eliminate the need to risk expensive sampling equipment in collecting air samples. In order to determine the levels of lead and other toxic metals such as chromium, cadmium, nickel, copper and aluminium, soil samples were collected from kerb-sides and road islands around the City of Durban and along the national road N3 in the vicinity of Shongweni. City, peri-urban and rural roads were selected for sampling. In a preliminary study, kerb-side dust from one of the streets with very heavy vehicular traffic was collected. It is also a street where many vendors have food stalls.

The horizontal distribution of metals as a function of distance from the kerb was determined by analyzing samples which were collected at various distances from the edge of a road. The determination of vertical distribution of metals in the soil was also performed. Samples for this work were collected by digging 0 to 2 cm, 10 to 15 cm and 20 to 25 cm deep at various points along the National Highway (N3).

Some sub-samples were leached at pHs found in soils using a Hazardous Waste Filtration System while other sub-samples from the same gross sample were acid-digested in a Microwave Digester. The analyses were done using ICP-AES, AAS and GF-AAS.

As expected the values for lead were the highest for urban sites and lowest for rural ones and values from leaching experiments were lower than those for digested samples from the same site. Taken over all sites, the values for lead ranged from 0.02 to 298 ppm for leached samples and from 25 to 1900 ppm for digested samples. In

general, the results do show that the concentrations of lead from kerb-side soils is a fairly good indicator of pollution from motor vehicle emissions.

To get an assessment of the distribution of metals, particularly toxic metals, the samples were also analyzed for chromium, cadmium, nickel, copper and aluminium. The concentrations of these metals as well as those for lead were compared to concentrations reported in the literature and with the natural abundances of these elements.

DEDICATION

To my deceased parents, Thoko and Losi Msukwini, who brought me up under very difficult circumstances, my brother, Smangaliso Msukwini, for his generous helping hands that are always extended to the advancement of my studies and my aunt, Zodwa Komane, for standing by me through thick and thin.

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LIST OF ABBREVIATIONS

${}^0C$	degrees Celcius
AAS	atomic absorption spectrometry
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-OES	inductively coupled plasma-optical emission spectrometry
GF-AAS	graphite furnace-atomic absorption spectrometry
ET-AAS	electrothermal atomic absorption spectrometry
HWFS	hazardous waste filtration system
ppm	parts per million
g	grams
mg	milligrams
mg/L	milligrams per liter
mg/kg	milligrams per kilogram
L	liters
mL	milliliters
SD	standard deviation
RSD	relative standard deviation
ND	not detected
CL	confidence limits
WHO	World Health Organization
Av	average
L/day	liters per day

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LIST OF SAMPLES AND SAMPLING SPOTS

BRD = Digested sample collected from the Victoria Bus Rank

BRL = Leached sample collected from the Victoria Bus Rank

BGED = Digested sample collected from the Botanic Gardens Entrance

BGEL = Leached sample collected from the Botanic Gardens Entrance

BGPD = Digested sample collected from the Botanic Gardens Premises

BGPL = Leached sample collected from the Botanic Gardens Premises

CTD = Digested sample collected from the Centenary road island at the front of ML Sultan Technikon

CTL = Leached sample collected from the Centenary road island at the front of ML Sultan Technikon

SAHL = Leached sample collected from the Centenary road island at the front of St' Aidans Hospital

SAHD = Digested sample collected from the Centenary road island at the front of St' Aidans Hospital

1m - A = 1 meter from the edge of the road at point A (2m-A, 4m-A, 8m-A and 12m-A are also defined the same way)

1m - B = 1 meter from the edge of the road at point B which is 20 m along the road from point A (2m-B, 4m-B, 8m-B and 12m-B are also defined the same way)

1m - C = 1 meter from the edge of the road at point C which is 20 m along the road from point B (2m-C, 4m-C, 8m-C and 12m-C are also defined the same way)

1m - D = 1 meter from the edge of the road at point D which is 20 m along the roadfrom point C (2m-D, 4m-D, 8m-D and 12m-D are also defined the same way)

p1 = Dust sample from Market street opposite Victoria Bus Rank at point 1

p2 = Dust sample from Market street opposite Victoria Bus Rank at point 2 which is 8 m from point 1

p3 = Dust sample from Market street opposite Victoria Bus Rank at point 3 which is 8 m from point 2

p4 = Dust sample from Market street opposite Victoria Bus Rank at point 4 which is 8 m from point 3

P5 = Dust sample from Market street opposite Victoria Bus Rank at point 4 which is 8 m from point 4

CRM = Certified Reference Material

A-TOP = 1 meter from the edge of the road at point A, sample collected 0 - 2 cm deep (B-TOP, C-TOP, D-TOP and E-TOP are separated by 20 m from one another along the road and defined the same way).

A 10 - 15 = 1 meter from the edge of the road at point A, sample collected 10 - 15 cm deep (B-10, C-10, D-10 and E-10 are separated by 20 m from one another along the road and defined the same way).

A 20 - 25 = 1 meter from the edge of the road at point A, sample collected 20 - 25 cm deep (B-20, C-20, D-20 and E-20 are separated by 20 m from one another along the road and defined the same way).

C 30 - 35 = 1 meter from the edge of the road at point C, sample collected 30 - 35 cm deep.

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Chapter 6 - General discussions, conclusions and recommendations

Chapter 1

Introduction

Toxic metals in the environment have received increasing attention in recent years, partly because of the growing scientific and public awareness of environmental issues, and partly because of the improvement in the analytical techniques for accurately measuring their concentrations [1].

A well publicised source of toxic metals is industrial emissions. A relatively less documented source of metals is exhaust emissions from motor vehicles. The latter comprise of particulates and gases. The main metal constituent of the particulate is lead. The exhaust emissions from motor cars may settle on ground adjacent to road ways (kerb-sides). From initial point of deposit, the metals can be transported to water bodies, such as streams, rivers and dams. In view of the fact that exhaust emission pollute the air, soil and water, a brief survey of toxic metals is given prior to the description of the scope of this study and the objectives of this project.

1.1 Brief survey of toxic metals in the environment

1.1.1 Toxic metals in air

Over the last few decades, the concentrations of many trace metals in the atmosphere have risen dramatically to the point where industrial emissions now dominate the natural bio-geochemical cycle [2] and may pose a threat to human health. A study on cancer risk factors implicated a number of trace elements including chromium, arsenic and cadmium as important cancer risk factors in urban air in the United States [3].

The health effects of a trace metal such as lead are well known and have led to ambient air standards for this metal, and to restrictions on the use of leaded gasoline, the most important source of lead in urban air [3]. These restrictions have resulted in dramatic declines in ambient urban concentrations of lead.

Meteorological and physical features play a major determinant role in the concentrations of lead in the air [4]. Where wind velocities are high, particulate material will be more rapidly transported to points distant from the primary pollutant site. Migration of particulates from air to soil is dependent on its size and mass. The particulates with heavier density land closer to areas of initial emission.

1.1.2 Toxic metals in soil

Soil chemistry is an area of environmental chemistry often neglected by chemists [5]. However, it has great importance in environmental science; for example, soil is used for food production as well as for disposal of hazardous wastes. Successful management of these conflicting uses requires an understanding of how soil characteristics affect the mobility and fate of soil contaminants and soil nutrients [5].

Soil can also become contaminated by settling atmospheric pollutants. These include, lead particulates in exhaust emissions which are deposited on roadside soils and vegetation. Coal combustion too gives rise to atmospheric emissions of metals in fly ash that are subsequently deposited in the surrounding area. Once in the soil, it is of interest to know how easily the deposited metals are retained or leached from the soils, and what factors will influence their availability to growing vegetation.

Investigations of toxic metals in soil are essential in giving an idea of the levels of these metals in comparisons with limits set by the international health organizations, such as the World Health Organisation (WHO). Lead uptake by vegetation from soils is highly variable and is governed by the mobility of the cation in the soil. The mobility of a cation in soil may be thought of as being some function of its solution concentration as it is affected by movement of water through the soil profile [6]. Thus any factor that is likely to increase solubility is also likely to affect cation movement. Furthermore, any factors that increase the mobility of cations may possibly enhance cation availability to growing vegetation and increase the likelihood of leaching to local rivers. This in turn may lead to a variety of pollution problems [7].

1.1.3 Toxic metals in water

The determination of trace metals in natural waters is important from different points of view. The first is the inorganic pollution of the waters in which metals have reached concentrations which may be deleterious to aquatic life and ultimately man. The second is that of micronutrient requirements for various life forms [8]. The trace metal content of natural waters must therefore be monitored to determine if the concentrations have reached toxic proportions or have been depleted below the micronutrient requirement levels.

A wide range of human activities contribute to the trace element pollution of the aquatic environment [9]. The major activities include mining and ore processing, coal and fuel combustion, industrial processing (chemical, metal, alloys, petroleum), domestic and agricultural effluents or sewage, transportational (urban and motorway run-off) and nuclear activity.

Elemental or heavy metal input can be from atmospheric fallout, leaching or dumping from the lithosphere, or direct to the aquatic environment. Other sources of contamination could be smoke and ash from ship's smokestacks, sewage discharge from the ship and paint leached from the ship itself [10]. Many aquatic organisms bioconcentrate toxic metals [11]. For example, oysters and mussels can contain levels of mercury and cadmium that are 100 000 times greater than those in the water in which they live. The concentrations of most heavy metals that humans encounter in drinking water are usually small and cause no direct health problems. As is the case with toxic organic chemicals, the amount of metals that are ingested through our food supply are usually of much greater concern than is the intake attributable to drinking water. Paradoxically, the heavy metals in the fish that we ingest usually originate from fresh water.

1.2 Motivation for study

This study has been motivated by the following considerations:-

- ◊ the direct and indirect hazards for health due to metals from vehicular emission.
- ◊ desire to eliminate problems associated with sampling vehicular emissions.
- ◊ the feasibility of using kerb-side soils as an indicator for metal pollution from vehicles.

1.2.1 Health hazards

A number of studies have found a significant neuropsychological impairment in young children [11] due to environmental lead absorbed either before or after birth. In adults lead tends to replace calcium in bones because of the similar size of the two ions which leads to calcium deficiency. In the long run, this can produce toxic effects as a result of remobilization of the bone-stored lead back into the bloodstream [11].

As mentioned earlier a major source of lead pollution is leaded petrol. The use of this has decreased in North America and in parts of Europe. However, there has not been a significant decrease in the use of leaded petrol in South Africa. This is borne out by a survey conducted around the City of Durban as part of the preliminary work for this project. The information obtained from different filling stations revealed that an average of 88.9 percent of petrol driven vehicles use leaded petrol, this is shown in Table 1.1 on the next page. The large traffic volumes shown in appendices A1 to A5 suggest the amount of lead and other toxic metals that settle on kerb-side soils may be quite high.

Direct uptake by vegetables growing on the polluted sites accumulate these metals as well as animals such as cows grazing on infected area. Hamon *et al* [12] conducted a study that showed that increases in soil cadmium led to an increase in the cadmium content of wheat that was grown in the soil. Toxic metals could enter also the human body directly via the inhalation of soil dust during windy days into the lungs or indirectly as in the case of children playing and eating soil which may lead to ingesting a considerable amount of these metals [11].

1.2.2 Sampling problems

While it would be desirable to collect the emissions from vehicles using air samplers, there are problems associated with this approach. Since the cost of air sampling equipment is relatively high, the number of sampling sites would have to be limited. In order to be effective, samplers have to be placed on sampling sites for several days at a time. This would require a continuous protection of the sampling equipment to avoid vandalism and theft. Thus, there is a need for using soil as an indicator of pollution from vehicles.

Table 1.1: **Information on the sales of petrol from different filling stations in the City of Durban**

CALTEX NO.1				
Av. Petrol sold (L)/day	Av. Leaded	Av. Unleaded	% Leaded	% Unleaded
19 000	18 000	1 000	94.7	5.3
CALTEX NO.2				
Av. Petrol sold (L)/day	Av. Leaded	Av. Unleaded	% Leaded	% Unleaded
14 000	12 000	2 000	85.7	14.3

ENGEN NO.1				
Av. Petrol sold (L)/day	Av. Leaded	Av. Unleaded	% Leaded	% Unleaded
7 000	6 000	1 000	85.7	14.3
ENGEN NO.2				
Av. Petrol sold (L)/day	Av. Leaded	Av. Unleaded	% Leaded	% Unleaded
11 000	9 500	1 500	86.4	13.6

BP NO.1				
Av. Petrol sold (L)/day	Av. Leaded	Av. Unleaded	% Leaded	% Unleaded
7 500	7 000	500	93.3	6.7
BP NO.2				
Av. Petrol sold (L)/day	Av. Leaded	Av. Unleaded	% Leaded	% Unleaded
8 000	7 000	1 000	87.5	12.5

Av. % Leaded petrol sold per day = 88.9 %

Av. % Unleaded petrol sold per day = 11.1%

1.2.3 Feasibiliy of using kerb-side soil to analyze metal pollution

Soil serves as a sink for metals that land on it from the atmosphere. Thus, its analysis can give a reasonable idea of the levels of toxic metals in the environment. However, there are problems associated with the analysis of soil for metals, as metals may migrate from points of initial deposit. The mobility of toxic metals such as, lead, chromium, nickel, copper, cadmium and aluminium in soil has previously been investigated [13 - 14].

These studies have shown that low pH values, low soil organic matter content, and the presence of ligands like chloride ions may increase the mobility of a cation through soil during heavy rains. At high pH values, some metal ions may form insoluble hydroxides and carbonates, whilst in acidic conditions, metals can easily be leached from the top soil to local rivers [15] used by a large sector of population especially from rural areas which do not have access to potable water for consumption.

1.3 Aims and Objectives

This investigation was undertaken to:-

◇ determine the total concentrations of lead, chromium, nickel, copper, cadmium and aluminium found in soil samples from selected kerb-sides.

◇ determine the leachable levels of these metals.

◇ determine the distribution of these metals horizontally (distribution from the kerb-side) and vertically (distribution from sampling surface).

◇ determine the levels of lead and other metals on dust particles.

◇ correlate the distribution with volume of traffic and other factors.

◊ establish a database of toxic metals in soils.

1.4 Structure of the thesis

The following chapters will include the detailed discussion of the literature review, background theory of instruments, experimental, results, discussion of results, and general conclusions and recommendations.

Chapter 2

Literature review

This chapter will include the publicised methods of digestion and leaching of metals in soil. A brief background of the sources and the toxicity of elements that were selected for this study is also included.

2.1 Publicised methods of digestion and leaching

Previous studies by Gzyl [16] determined the concentration of lead, cadmium, and zinc in soil around the vicinity of a smelter, these concentrations were compared to Polish hygienic standards. This study involved the collection of samples using an Egner sampling stick , crushing, mixing and air drying at 60^0C. A portion of each sample was then extracted with a solution consisting of 10% HNO_3. The acid suspension was filtered and washed with double distilled water and the analysis was done using AAS. The results of these studies revealed that zinc concentration in soil ranged from 180.80 to 10643.90 mg/kg, cadmium ranged from 3.30 to 102.20 mg/kg and lead ranged from 128.90 to 1996.40 mg/kg. These concentrations were compared with admissible values in Poland, and found to far exceed these set limits; lead was up to 20 times, cadmium was up to 34 times, and zinc was up to 36 times. This method has also been used by the Institute for Ecology of Industrial Areas since 1975 [16].

Amrheln *et al* [17] reported in their studies that emissions from vehicles have resulted in high levels of trace metals in roadside soils. In this study, total trace metals were determined using a hot $HNO_3 / HC\ell O_4$ digest and atomic absorption spectrometry as well as graphite furnace-atomic absorption spectrometry. The use of $HC\ell O_4$ was supported due to its very strong oxidizing nature, it is capable of extracting some of the metal from silicate lattice[18].

Amrheln *et al* [17] also conducted soil column leaching experiments, to evaluate the mobility of metals and organic matter through reconstructed soil profiles. Soils were packed into plastic syringes in layers. The depth of each layer in the column did not necessarily correspond to the actual horizon depth measured in the field. Road dust/sand swept from the road's shoulder within 0.5 m of the road and adjacent to the sampling site was also added to the surface of the column to simulate trace metal pickup from road runoff. Leaching was done using a mechanical vacuum extractor at a constant rate. The results of Pb, Cd, Cu, Cr, Ni and Fe obtained by using de-ionized water as a solvent in Albany soil were 0.44, 0.04, 3.10, 0.22, 0.67 and 48.00 ppm respectively.

Meteorogical factors strongly influence the concentration of lead in the atmosphere. Where wind velocities are high, the particulates will be transported more rapidly and further. Al-Saleh and Taylor [19] conducted a study that determined the concentrations of lead in both the soil and air. In this study, an air sampler was placed in the same sites where soil samples were collected. A soil auger was used to collect 10 cm deep soil including the top layer into clean polyethylene bags. Samples were also collected from high density traffic locations and residential locations. After removal of stones, the samples were ground with a pestle and mortar, dried overnight at 80^0C and stored in a vacuum desiccator at room temperature until they were analyzed. A portion of each soil sample was accurately weighed and treated with nitric acid. After heating on a hot-plate for one hour, the mixture was allowed to cool at room temperature. To the cool mixture, 30% hydrogen peroxide was added and the sample was heated again for an hour. After cooling and filtration, standard solutions were used to establish the calibration curve. The analysis was done using electrothermal-atomic absorption spectrometry. The results from high density traffic locations were much higher (ranging from 0.62 to 6.04 $\mu g/m^3$ in the morning and 0.54 to 5.34 $\mu g/m^3$ in the evening in air, and 29.77 to 219.51 $\mu g/m^3$ in soil) than those from residential locations (ranging from 0.21 to 1.09 $\mu g/m^3$ in the morning and

0.23 to 0.74 in the evening in air, and 5.58 to 77.73 $\mu g/m^3$ of lead in soil).

The traditional open beakers or the more classic alkaline fusion have been the dominant methods for the digestion of soils and sediments [20]. In this procedure the material present in soils and sludges was extracted by refluxing with *aqua regia* on a hot plate. However, these methods have been found to be prone to environmental contamination and do not guarantee complete recovery for many elements, therefore, other methods are becoming more attractive.

Bettinelli *et al* [20] working in collaboration with ENEL DP Central Laboratory of Piacenza and the Institute of Agricultural and Environmental Chemistry, Catholic University of Piacenza, Italy, investigated the setup and optimization of "*aqua regia-soluble*" and "*total*" content of trace metals in soils and sediments. The aim was to evaluate, optimize, and validate a procedure for the dissolution of the sample using microwave with subsequent ICP-OES, GF-AAS and ICP-MS analysis. *Aqua regia* and HF / HNO_3 / $HC\ell$ microwave procedures were used for the analysis of the metals cadmium, cobalt, chromium, copper, magnesium, nickel, lead and zinc. *Aqua regia* procedure seemed to be a valid alternative to the conventional reflux extraction procedure. Sample preparation time was shorter, level of contamination was greatly reduced and the results for the certified standard materials were in good agreement with the certified values. The use of HF / HNO_3 / $HC\ell$ allowed the determination of the total analyte concentrations in soil and sediments without problems with respect to *aqua regia* dissolution.

In another study Robbat jr and Simpson III [21] used *aqua regia* on a closed vessel microwave-assisted acid extraction and ICP-OES in the analysis of the metals magnesium, zinc, copper, iron, arsenic, cadmium, lead, silver and antimony, and concluded that closed vessel microwave digestion allows parameters such as pressure, temperature, and time to be optimized and reliably controlled, thus producing excellent measurement precision in the recovery studies.

Cook *et al* [22] performed a comparative study using HNO_3 / H_2O_2 and HNO_3 / $HC\ell O_4$ for soil digestion, and AAS, GF-AAS and ICP-AES for the analysis of cadmium, copper, nickel, lead and zinc in oil and grease contaminated soils. Nitric acid acts as a strong oxidizer and hydrogen peroxide destroys the organic matter and releases the associated metals. In the HNO_3 / H_2O_2 soil digestion method, the cadmium concentrations were often below detection limit by AAS but were measurable in the HNO_3 / $HC\ell O_4$ digests. For individual samples, the two methods did not always give the same result but these differences may be due to many factors including errors due to sample homogenization or contamination.

Sulphuric acid is not recommended for simultaneous extraction of different metals, especially in sediments rich in alkaline earth metals, because of the formation of insoluble sulphate salts [23, 24]. Perchloric acid always poses a danger of explosion especially when the perchlorate vapour is trapped in wooden or plasticware of the fume exhaust system [23]. On the other hand, hydrofluoric acid requires special attention to handle as it is dangerous and highly corrosive.

Tam and Yao [1] performed a comparative study of three digestion methods. Microwave digestion of air dried sediments in nitric acid using a closed vessel, digestion using *aqua regia* was used whereby a glass funnel and a marble were placed on the mouth of the digestion tube which was heated in a boiling water bath to provide a kind of partially closed reflux condition which enhanced the digestion efficiency, and a third method was a blocked digestion procedure which involved the use of concentrated nitric acid instead of *aqua regia*. The concentrations of the metals copper, zinc, magnesium, nickel, chromium, cadmium, lead, and iron in acid digests were determined by the AAS. The accuracy and reproducibility of the three digestion methods examined in this study were acceptable.

Leaching experiments were carried out by Ellis and Revitt [25] using a 1 : 10 weight / volume ratio of sediment in rain water of pH 6.5. Constant agitation of all suspensions at 25^{0}C was achieved using a shaking water bath thus enabling simulation of turbulent runoff conditions during storm drainage from the roadside surface. After allowing a settling time, aliquots were removed at 1, 5, 11 and 28 day intervals. The levels of the metals cadmium, copper, iron, magnesium, lead and zinc were determined after filtration by using atomic absorption spectrophotometer and for the lower levels in the leachates a Digital Flameless Atomiser was employed. This method is related to the leaching method that was employed in this study.

Nitric acid has been used either on its own or in combination with hydrochloric acid and proved to be effective [23]. The use of either concentrated nitric acid alone or concentrated nitric-hydrochloric acid mixture is a common digestion practice for metal determination in most accredited routine laboratories [1]. This method is also used in this study, nitric acid was used alone in the microwave digestion of soil and dust samples.

2.2 Background of selected elements

2.2.1 Lead

Tetraethyllead in gasoline is the major source of lead in roadside soils [17]. The natural lead content of soil is inherited from the parent rocks. An upper limit for the content of a normal soil was established by the World Health Organization (WHO) as 50 ppm [26]. However, due to widespread lead pollution, most soils are likely to be enriched with this metal, especially the top layers. Anthropogenic lead in soils has recently received much attention because this metal is hazardous to man and animals from three main sources; the food chain, soil dust inhalation and water. The main lead pollutants is emitted from smelters in mineral forms, contamination from vehicle exhausts and lead paint. Lead is poisonous, it may cause mental impairment especially in young children. The first visible sign of lead poisoning in adults is amnesia [26].

2.2.2 Chromium

The main sources of elevated chromium content in surface soil are industrial effluents from works such as electroplating sludge, chromium pigment and tannery waste and municipal sewage sludge. Previous studies [26] suggest that chromium added to soils is usually accumulated on the top layer.

Chromium can exist in an number of oxidation states, and the most stable and common forms of chromium are Cr(VI) and Cr(III) [1]. These two forms have sharply contrasting chemical properties, and Cr(VI) is more toxic and readily extracted from sediment particles whereas Cr(III) is less mobile and tightly adsorbed to siliceous material. The other sources of chromium which are a result of human activities are coal and fuel power generation, transport and aerosol sprays as shown in Table 6.4.

2.2.3 Cadmium

Environmental pollution is an inevitable consequence of metal mining, manufacture and disposal. The major sources of cadmium in soil is a result of anthropogenic and natural activities [27]. Anthropogenic sources comprise industrial processes such as mining and metallurgy, urban and industrial wastes, and sewage and fertilizer applications. Cadmium has no essential biological function, and is highly toxic to plants and animals. The main toxic effects of cadmium are renal tubular dysfunction and disturbances of the calcium homeostasis and bone metabolism [28]. The major hazard to human health from cadmium is its chronic accumulation in the kidneys where it can cause dysfunction if the concentration in the kidney cortex exceeds 200 mg/kg fresh weight [26].

Cadmium containing fertilizers can introduce this metal into the food chain and hence food is the main route by which cadmium enters the body. Cadmium also enters the body through exposure to tobacco smoking. The World Health Organization (WHO) [26] recommended maximum tolerable intake of cadmium is 400 to 500 μg/week, which is equivalent to about 70 μg/day. Sources of soil contamination by cadmium are mining and smelting of cadmium and zinc, atmospheric pollution from metallurgical industries, the disposal of waste containing cadmium, such as incineration of plastic containers and batteries, sewage sludge application to land and the burning of fossil fuels [26].

Cadmium may also, at least partially, be transferred via routes other than the food chain, such as dust inhalation during gardening or via licking of fingers contaminated by the polluted soil during childhood [24]. Other sources of cadmium is diesel oil and tyre attrition [17].

2.2.4 Copper

The wear of bearing and bushings in automobiles contribute metals such as copper into roadside soil [17], but on the other hand, high concentration of copper in the surface horizon of a soil is an indication of additions from smelters, fertilizers, sewage sludges and other wastes fungicides or bactericides. Manure from swine poultry fed selected copper containing compounds for increased feed efficiency and greater growth rates is also a source of copper. Atmospheric inputs of copper to soils from rain and dry deposition varies considerably according to the proximity of industries emitting fumes containing copper [26].

2.2.5 Nickel

Nickel in the body can replace essential metals in metalloenzymes and cause disruption of metabolic pathways [26]. Recent studies suggest that nickel is also a possible carcinogen [26].

Steel parts attrition (nickel, chromium, vanadium, tungsten, molybdenum) contribute trace metals to roadside soils [17]. More recent uses of nickel include batteries and electronic compounds.

Combustion of coal is the next most important emission, followed by nickel mining and smelting sites. Whilst there are vast differences in the amounts of different metals produced, soil concentrations of most metals, especially nickel, chromium and cadmium have increased over the past years [26].

2.2.6 Aluminium

Aluminium is the most abundant metal on the earth and moon, its concentration is as high as 81300 ppm in the earth's crust as shown in appendix I. It has been found to have a mean concentration of 71000 mg/Kg in the surface of uncontaminated soils of the world as shown in Table 5.4. Aluminium comprises 8.1% of the earth's crust by mass and owing to its lightness, a lesser 6.4% on an atom basis [29]. Weathering and leaching out of the silica produces the main ore bauxite.

Plants can take up the mobile aluminium in acid soil and it creates a problem of chemical stress in the plants. This metal can also enter the food chain by the same route. Aluminium in brain can cause Alzheimer's disease which is a progressive senile dementia characterized by a complete memory loss of input from a memory bank so that the sufferer becomes forgetful [29].

Chapter 3

Background theory of instruments

3.1 Inductively coupled plasma - atomic emission spectrometry

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) have been the Environmental Protection Agency (EPA) methods of choice for the elemental analysis of soil extracts and aqueous samples, because of their utility, sensitivity and reliability. These methods can rapidly determine trace levels of metals in different types of matrices [30]. The former method is based on AES coupled with an ICP source. The ICP source produces a stream of high-energy ionized gas known as a plasma by inductively coupling an inert gas (most commonly argon) with a high-frequency field. The resulting plasma has an internal temperature of up to 10 000 K which desolvates, dissociates, atomizes and excites the elements present when a sample is injected through its centre. This results in the emission of light of unique frequencies for the given elements. The plasma is formed by a tangential stream of argon gas flowing between two quartz tubes as shown in Figure 3.1.

The intensity of light emitted from the plasma is proportional to the concentration of the element(s) in the sample. The light is transferred to an emission spectrometer which has the capability of separating the unique frequencies into discrete wavelengths (each wavelength or frequency being a function of the element present) [30]. The intensity of light is measured at a wavelength which is unique to each element, for instance the intensities of lead, cadmium, chromium, nickel, copper and aluminium were measured at 220.353, 228.802, 283.563, 221.647, 224.700 and 309.271 nm respectively. Since the concentration of an element is proportional to the intensity of the light produced, the

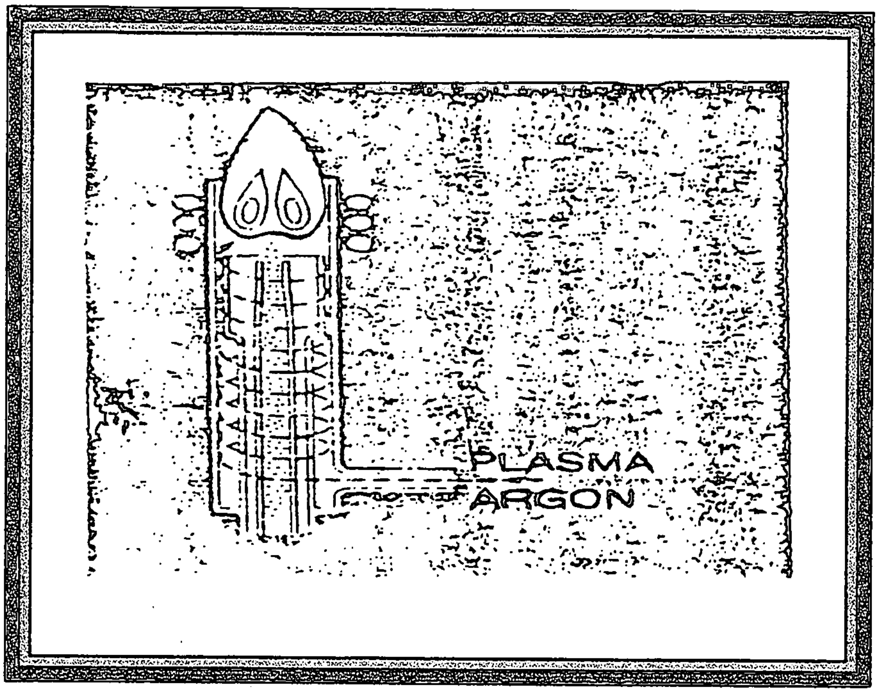

Figure 3.1 The Plasma

electronics of the spectrometer calculates the correlation and quantifies the results.

Atomic spectra are emitted by atoms and they are a form of radiation which is measured as energy per unit time. If an atom is to emit radiation, it follows from the law of conservation of energy that the atom must first absorb a corresponding amount of energy.

In 1913 Bohr postulated that any atom is allowed only certain discrete and characteristic energy values, and that emission or absorption of radiation by atom occurs when it undergoes a transition between these stationary states or energy levels. These energy levels are directly proportional to the empirical spectral terms of the atom. The frequency of radiation corresponding to a transition of an atom between a higher energy level, E_m, and a lower energy level, E_n is related by

$$\nu = \Delta E / h \quad (1)$$

Where E is energy, $\Delta E = E_m - E_n$, h is Planck's constant, and ν is frequency. In terms of wavelength λ,

$$\lambda = c / \nu = hc/\Delta E \quad (2)$$

where c is the velocity of light.

ICP-AES is an elemental analysis technique using spectra emitted by free atoms or ions generated within a source such as an ICP. The basic elements of an ICP-AES instrument are:-

(a) Source - which produces the emission spectra characteristic of the elements present in a sample.
(b) Optics - the spectrometer which optically collects light from the source (plasma) and separates the spectral details of the elements present in a sample.
(c) Detector - generally a photo-multiplier with associated electronics.
(d) Processor - signal processing.
(e) Data analysis and output or usually a printer.

3.1.1 Interferences

Not a single analytical technique can be claimed free of interferences for qualitative analysis [13]. Some common interferences which can affect an analysis are:-

(a) Matrix interference

The overall efficiency of the ICP-AES sample introduction system is influenced by the surface tension, viscosity, and dissolved solid content of samples. Differences in these properties among samples and standards may cause differences in the nebulizer uptake rate and in the efficiency of sample aerosol transport to the plasma. Results can be erroneously high or low depending on how the overall efficiency of the sample introduction system is affected. This was avoided by using dilute solutions, using a blank solution that has the same components as the standard solutions and samples except the analyte for both leaching and digestion. Filtration of the samples was performed to maintain clear solutions.

(b) Chemical and physical interference

ICP-AES is relatively free from chemical interferences due to the high operating temperature of the argon plasma (8000 to 10 000 K), which is high enough to cause dissociation of most chemical bonds and compounds to the atomic state.

Physical interferences are due to sample consumption and alteration of sample transport or droplet formation processes. ICP - AES tends to be more independent of physical interferences due to the relatively small sample consumption rate. The sample flow rate in ICP - AES is also controlled by a peristaltic pump which makes the uptake rate independent of the viscosity of the sample liquid and minimizes chemical and matrix effects.

(c) Ionization interference

These interferences arise from donation of electrons by concomitant species in the sample which alters the atom or ion concentration of the species being determined. The ionizing effect of the high-temperature environment appears to be buffered by the electron-rich nature of the ionized argon gas. Ionization does occur, but the degree of ionization is constant within the overall reproducibility of ICP - AES measurements.

(d) Spectral or background interference

In ICP-AES, background shifts due to light emission at the analyte wavelength by the excitation source or some component of the sample can cause interference, for example, a spectral interference occurs when the spectrometer is set to determine the emission of an element (A) at a particular wavelength, and another element (B) is also present in the sample and has an emission line very close to the analyte wavelength. The measured amount of element (A) will be higher than present in the sample because the spectrometer detects the emission from both elements (A and B), but ascribes the total only to element (A). There are three types of spectral interference:

(i) Stray light
(ii) Partial overlap of nearby or wing-broadened spectral lines
(iii) Direct overlap of unresolved spectral lines

These interferences may arise from emission of unwanted light from several sources, including the

(i) Matrix - the sample matrix including other wavelengths of the analyte
(ii) Solvent - including OH bands from water and emission from acids or fusion salts used to dissolve the sample
(iii) Air - entrained air in the plasma discharge
(iv) Gases - the carrier and plasma gases (usually argon)

3.2 Atomic absorption spectroscopy

If energy of the right magnitude is applied to an atom, the energy will be absorbed by an atom and an outer electron will be promoted to a less stable configuration, the excited state, and thereafter, the atom will immediately and spontaneously return to its ground state configuration. The electron will return to its initial, stable orbital position, and radiant energy equivalent to the amount of energy initially absorbed in the excitation process will be emitted. Since every element has unique electron structure, the wavelength of light emitted is a unique property of each individual element. For instance, in the present analysis the wavelengths of lead, chromium, cadmium, nickel, copper and aluminium are different. Atomic absorption methods rely on the absorption of light by atoms. All atoms can absorb light, but only at certain wavelengths corresponding to the energy requirements of the particular atom.

3.2.1 Qualitative and quantitative analysis by atomic absorption

Light at the resonance wavelength of the initial intensity I_0 is focused on the flame cell containing ground state atoms. The initial light intensity is decreased by an amount determined by the atom's concentration in the flame cell. The light is then directed onto the detector where the reduced intensity, I, is measured. The amount of light absorbed is determined by comparing I to I_0.

Several related terms are used to define the amount of light absorption which has taken place. The 'transmittance' is defined as the ratio of the final intensity to the initial intensity

$$T = I / I_0 \tag{3}$$

Transmittance is an indication of the fraction of initial light which passes through the flame cell to fall on the detector. The percent transmission is simply the transmittance expressed in percentage terms.

$$\%T = 100 \times (I / I_0) \tag{4}$$

The 'percent absorption' is the complement of percent transmission defining the percentage of the initial light intensity which is absorbed in the flame. These terms are easy to visualize on a physical basis. 'Absorbance' is purely a mathematical quantity.

$$A = \log (I_0 / I) \tag{5}$$

Absorbance is the most convenient term for characterizing light absorption in absorption spectrophotometry, as this quantity follows a linear relationship with concentration. Beer-Lamberts law defines this relationship as follows:

$$A = kc\ell \tag{6}$$

where 'A' is the absorbance; 'k' is the absorption coefficient, a constant which is characteristic of the absorbing species; 'c' is the concentration of the absorbing species in the absorption cell, 'ℓ' is the path length of light intercepted by cell. The equation simply states that the absorbance is directly proportional to the concentration of the absorbing species for a given set of instrumental conditions. The calculation of the concentration of the analyte will be shown in the results.

3.2.2 Calibration

The calibration method used is an interpolation method, which means that the readings of all the sample solutions must lie between the lowest and highest readings of the standard solutions.

3.2.3 Interference

If the atomic absorption profile for an element overlaps the emission line of another, a spectral interference is said to exist. This is an infrequent occurrence, because of the very wavelength - specific nature of atomic absorption. Even if an absorption line for a diverse element falls within the spectral bandpass for the determination of another element, an interference will occur only if an emission line of precisely the same wavelength is present in the source. As the typical emission line width may be only 0,002 nanometres, actual overlap is extremely rare. The chances for spectral interference increase when multi-element lamps are used, where the source may contain close emission lines for several elements. Multi-element lamps were not used in this study, however, the procedures used for circumventing spectral interference include narrowing the monochromator slit width or using an alternate wavelength. Atoms have extremely narrow absorption lines and there are few problems involving spectral interferences where one element absorbs at identical wavelength to another [31].

3.2.4 The main components of an Atomic Absorption Spectrometer

The instrument functions as follows:-

(i) The radiation source (a hallow cathode) or an EDL (electrodeless discharge lamp) emits a sharp line spectrum characteristic of the analyte element,

(ii) The emission beam from the radiation source is modulated,

(iii) The modulated signal passes through the atomic vapour where the atoms of the analyte absorb radiation of the line-like radiation source,

(iv) The desired spectral line (usually resonance line) is selected by the monochromator,

(v) The isolated analyte line falls onto the detector (a photomultiplier) where the light signal is converted into the electric signal,

(vi) The modulated signal is amplified by a selective amplifier,

(vii) The signal is finally recorded by a read out device (printer).

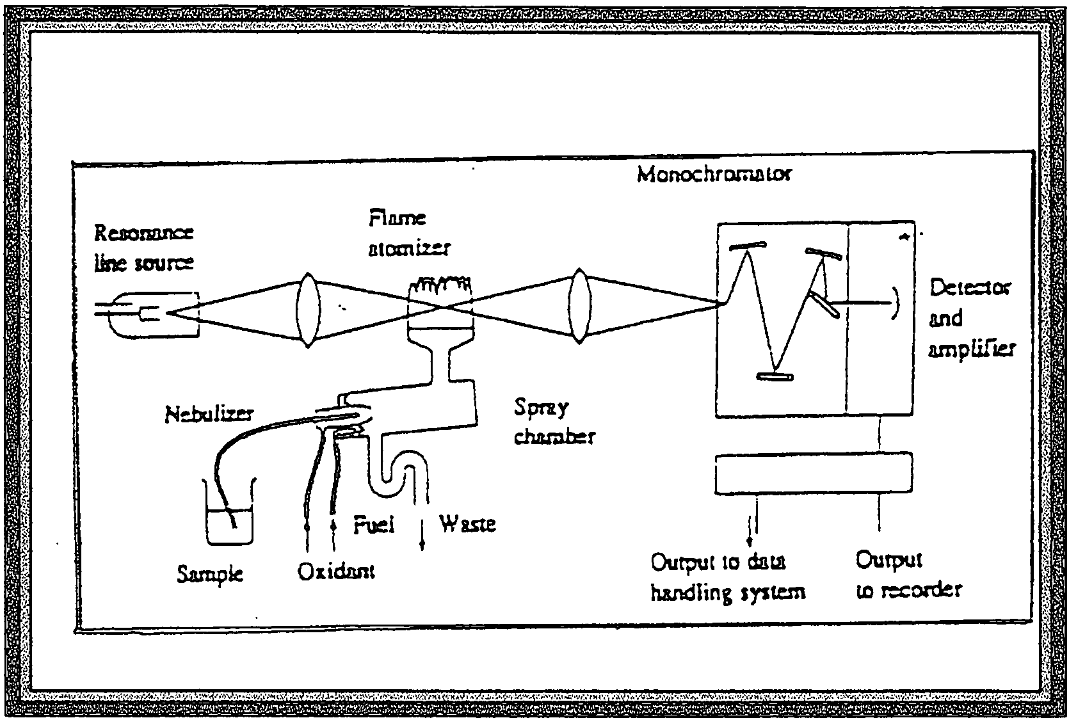

Figure 2.2 Components of an Atomic Absorption Spectrometer

3.3 Graphite furnace

Electrical heating as an alternative to the flame has become more and more widely used [32]. Several types of heaters have been proposed of which the most successful consist of a small tube of graphite, heated by passing a large current of 500 A through it at low voltage. The graphite tube (in the Varian model) is a few millimeters in the inside diameter and about a centimetre in length. It has a small orifice (an opening) in its upper surface through which the dissolved sample can be inserted. The internal surface is coated with an impervious form of carbon called pyrolytic carbon. The tube, often called graphite furnace, must be surrounded with an atmosphere of an inert gas, such as nitrogen, to prevent oxidation of both the sample and the hot carbon. The temperature of the graphite atomizer, as is used with liquid samples, is generally programmed in three steps. It is first raised to 90 ^{0}C, and held there for a minute to evaporate the solvent. Any organic matter is next removed by charring at about 300 ^{0}C for another minute or so depending on the element that is being analyzed (The details are shown in appendices C1, C2 and C3). Only after this, is the temperature increased to the point needed to dissociate inorganic compounds into atoms, this may require as high as 2500 ^{0}C. Each of these time intervals and temperatures can, in most models, be varied by the operator, to meet the requirements of different samples. The trace on a time-based recorder will often show an extraneous absorption peak during the drying period, due to the solvent vapour. A peak may also appear during the charring step if much organic matter is present. Analytical information is obtained from a measurement of the peak height as observed at the final temperature [32].

3.3.1 Advantages of graphite furnace

The advent of flameless atomization, in particular the pyrolytic coated graphite tube furnace (or carbon rod type) atomizer, greatly reduced physical and chemical limitations imposed by the flame atomization process [33].

(a) with the graphite atomizer, a discrete volume of sample solution is vaporized and wastage is virtually eliminated.

(b) although the ground state atom population is still subject to interferences, these are of a different nature to those found in flame atomization, but are amenable to control by proper choice of analytic conditions and chemical pre-treatment.

(c) the graphite tube is in effect a confined furnace chamber where pulse vaporization of the element is achieved by raising the temperature with a programmed sequence of electrical power. Consequently, a dense population of ground state atoms is produced for a longer time interval in contrast to the low atom density and short residence time of the flame.

The major advantage of a Graphite Furnace - Atomic Absorption Spectrometry is lower detection limits.

3.3.2 Stages involved in the analysis

Although there are different approaches to the construction of high temperature furnaces, they are all designed to perform the same function - generate a population of free atoms so that atomic absorption can be measured. This is generally achieved in three stages:

(a) A DRYING stage during which the solvent is removed from the sample in the furnace.

(b) AN ASHING stage which removes organic molecules or inorganic material.

(c) AN ATOMIZATION stage in which free atoms are generated within a confined zone.

The absorption signal produced in the atomization stage is a sharp peak, the height (or area) of which can be related to the amount of analyte element present.

3.3.3 Interferences

Many interference effects have been described in the literature and they can generally be categorized as being physical or chemical by the mechanism through which they are produced [33]. Physical effects of viscosity and surface tension are less important than with flame AAS, but nevertheless they can affect the reproducibility of sample dispensing. The main effect is in the degree to which the sample spreads inside the graphite tube. Chemical interference effects can be categorized as follows:

(i) Volatile compound formation, where the analyte element is lost at a relatively low temperature, perhaps during a dry or ashing stage, without undergoing atomization [33].

(ii) Stable compound formation in which one or more relatively stable compounds of the analyte element are formed. More than one atomization peak could result because the appearance temperature will depend on the nature of the intermediate chemical form of the element [33].

The most common spectral interference encountered in GF - AAS is that of non-specific attenuation of the source radiation by the products of the vaporization or decomposition of the sample matrix, an effect usually referred to as background absorption. This non-specific attenuation of the source radiation may result from scattering of light by particulate matter or absorption by molecular species having broad-band and line absorption spectra. When this non-specific attenuation overlaps with the atomic absorption of the analyte, the absorption measured with the analyte hollow-cathode lamp will contain a contribution due to the background absorption [33]. Finally, the smoke signal was eliminated by setting high temperatures for each element so that the smoke is gone by the time the highest temperature of a particular analysis is attained.

3.4 The hazardous waste filtration system

A Millipore Corporation hazardous waste filtration system of maximum 100 psi inlet,124 mm diameter prefilter and 142 mm dia meter filter was used in order to make sure that all the leachates a filtered through the soil. This instrument was assembled as illustrated on the following section.

3.4.1 Assemble of a hazardous waste filtration system

The top-plate of holder assembly shown in figure 2.3 was removed by disconnecting the handwheel bolts. A Whatman filter paper (wetted by floating in a pan of deionized water) was placed on a base support screen and the stainless steel cylinder was centered onto filter paper to assure an even seal. A prefilter was installed by lowering it through the top of the cylinder onto the membrane. A top-plate of filter holder was placed on top of the cylinder rim and the handwheel bolts were replaced on top of the unit by screwing tightly. The PVC tubing was fitted over the Tri-Clover hose adapter and secured with a hose clamp. The end of the PVC tubing was attached to a nitrogen tank regulator outlet and secured with a hose clamp.

3.4.2 Operation of a hazardous waste filtration system

A mixture of a homogenous sample and the solvent were poured into the unit through the inlet by using a funnel. The Tri-Clover (TC) hose adapter shown in figure 2.3 was attached to the Tri-Clover connection of the top plate. A receiving vessel was placed below the sanitary outlet. Pressure was slowly increased and liquid flow began from the outlet into the receiving vessel. After the whole sample was filtered, pressure was shut from the nitrogen tank regulator outlet valve and the vent valve was opened gradually to release pressure from cylinder. The inlet TC hose connector and handwheel bolts were removed, then top plate and extension cylinder of holder. The liquid was kept under refrigeration for future analysis. This liquid was clear of particulate matter. The prefilter, filter and a solid cake were removed and the instrument was cleaned.

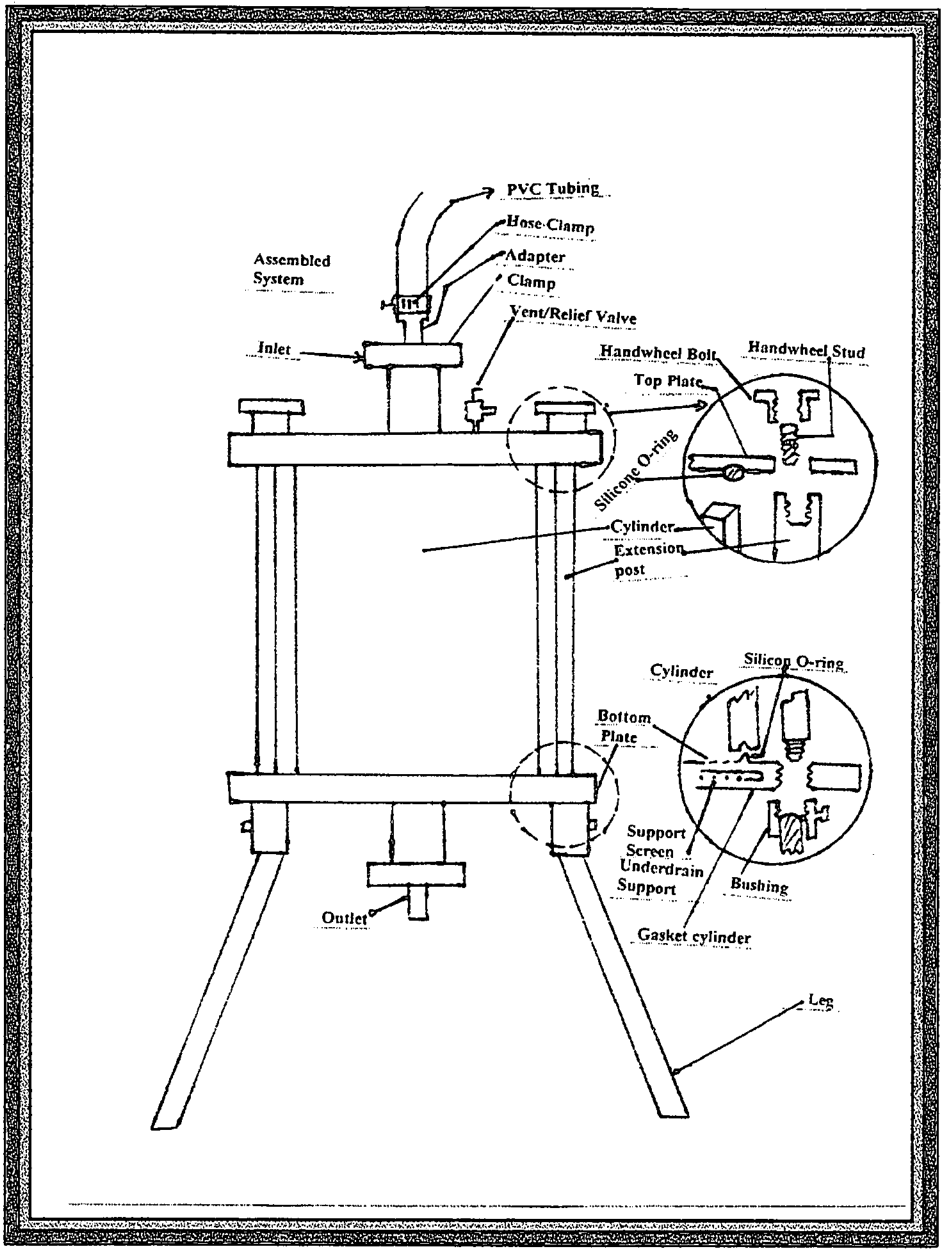

Figure 3.3 A Hazardous waste filtration system

Chapter 4

Experimental

4.1 Materials

The following materials were used as purchased. A 70% analar grade nitric acid from Riedel-deHaen and standard solutions of lead, chromium, cadmium, copper, nickel and aluminium from Saarchem (Pty) LTD. Nitrogen(minimum purity = 99.999%), compressed air(minimum purity = 99.000%), acetylene(minimum purity = 99.000%) and argon(minimum purity = 99.999%) were obtained from Afrox. Millipore glass fibre prefilters of 124 mm diameter and 142 Whatman hardened filter papers of medium speed were used in filtration. Buffer solutions (phosphate) of pH 4 and pH 7 were purchased from BDH Laboratory. Certified reference material of soil obtained from Industrial Analytical (NCS DC 73320) certified in 1986 and revised in 1998. Double de-ionized water from Milli-Q water system was used in all preparations of solutions.

4.2 Selection of sampling sites

As described below, some of the sampling sites were chosen for preliminary work purposes. This was done in order to test the availability of analytes and the effectiveness of the method of analysis. The selection was based on sites which have roads with very low traffic volumes, and they were referred to as sites with "zero" pollution, that is, control sites for comparison purposes, and sites with large traffic volumes. The sites were chosen around the City of Durban, the N3 freeway from Durban and Eshongweni rural area. This work is focused on top layers about 2 cm deep on surface horizons changing the distance from the road. Samples were collected in new polyethylene bags using a hard plastic scoop. In order to determine the seepage or vertical distribution of the analytes at the N3 freeway, samples were collected from the top 0 to 2 cm, 10 to 15 cm and 20 to 25 cm deep at point A, B, C, D and E that are separated by a distance of 20 m from one another and 1 m from the edge of the road using a soil auger and new polyethylene bags.

4.2.1 Centenary Road island in front of ML Sultan Technikon and St' Aidans Hospital

This is an island that was undisturbed for a very long time. Pollution is from both sides of the road. This spot was chosen for preliminary work. The traffic volume is very high as shown in Appendix A1, it consist of motor vehicular traffic to the technikon, the neighboring hospital and high schools. In the mornings and afternoons a lot of vehicles stop and idle along this sampling spot. Students of the technikon and people from the hospital use this spot during their free times on daily basis. This makes them susceptible to dust inhalation. The location of this site is shown in Figure 4.1(a) as S1 and S2.

4.2.2 Victoria Bus Rank

Victoria bus rank is adjacent to the Market (shown as S3 in Figure 4.1(a)). It is surrounded by the Market, Warwick, Old Dutch and Leopold Streets, the traffic volume is very high as shown in Appendices A2 and A3. At the same time the bus is situated next to the very busy Inanda Taxi Rank. The population of people who are living there consist of street kids and adults, and there are several hawkers who are there on daily basis exposed to the pollution from vehicles. Soil samples were collected from this site and pavement dust particles were also swept and collected from Market Street opposite the bus rank.

4.2.3 Botanic Gardens

In this sampling site, samples were collected from the entrance of the gardens in St' Thomas Road (shown as S4 in Figure 4.1(a)) where the traffic flow is very low as compared to the highways and again for comparison purposes, samples were also collected from the centre of the garden (shown as S5 in Figure 4.1(a)). Fertilizers that are used in the garden may add a considerable amount of metals such as cadmium which is found as an impurity in phosphate fertilizers [26].

4.2.4 Umgeni/Goble Road intersection

This site is towards the north side of the city of Durban, (shown as S6 in Figure 4.1(b)). The spot is at Umgeni Road about ± 300 m from the Goble Road crossing. The traffic volume is also very high as shown in Appendix A4. Due to the presence of pavements, samples were collected at 4.6, 10 and 13 m from the road on the north side and 7 m from the south side. It is of interest to note that the north side is ascending, which might not give the expected sequence of results.

Some samples were also collected from the island. Another sample was collected 9 km from the initial spot next to Umgudluli informal settlement 1 m from the road. This spot was chosen because it is flat and the results will be compared to those that were obtained from the initial sampling spot.

4.2.5 N3 freeway next to Shongweni off-ramp

N3 is a freeway from Durban to Johannesburg which has a very large traffic volume of fast and slow vehicles as shown in Appendix A5. The site next to Shongweni off-ramp was chosen because it is flat and open, therefore it provides an access to sample collection in a straight line perpendicular to the road from both sides. The initial set was collected following the sequence of 1, 2, 4, 8 and 12 m from the edge of the road on the north side. The next set of samples was collected after heavy rains, the distances were varied following the sequence 2, 10, 20, 30 m from both the north and the south side of the freeway. Finally, the last set was collected from the same site following the sequence of 1, 2, 4, 8 and 12 m from points A, B, C and D which were separated by 20 m. The location of this site is shown in Figure 4.2 as S7.

4.2.6 Shongweni rural route D356

This route is on the inside of Eshongweni, about 5 kilometers away from the highway. There is less vehicular contribution in this area. A sample was collected to be used for comparison purposes.

4.3 Sample Treatment

Preparations were always done in fume cupboards. Each sample that was collected weighed about 1 to 2 kg. On arrival at the laboratory the samples were dried in the oven at 105 ^{0}C for one day each, cooled and then sieved through King Test 2.00 mm and 425 μm stainless steel sieves. The material that remained in the sieves was ground using pestle and mortar and sieved again to exclude stones and plant roots. For homogeneity, each ground sample was thoroughly mixed in a clean plastic box. Sub-samples were obtained from the homogeneous samples by taking half of the sample (i.e. scooping out from the middle) and mixing it again. This was done three times and all samples were stored in clean plastic bags at room temperature.

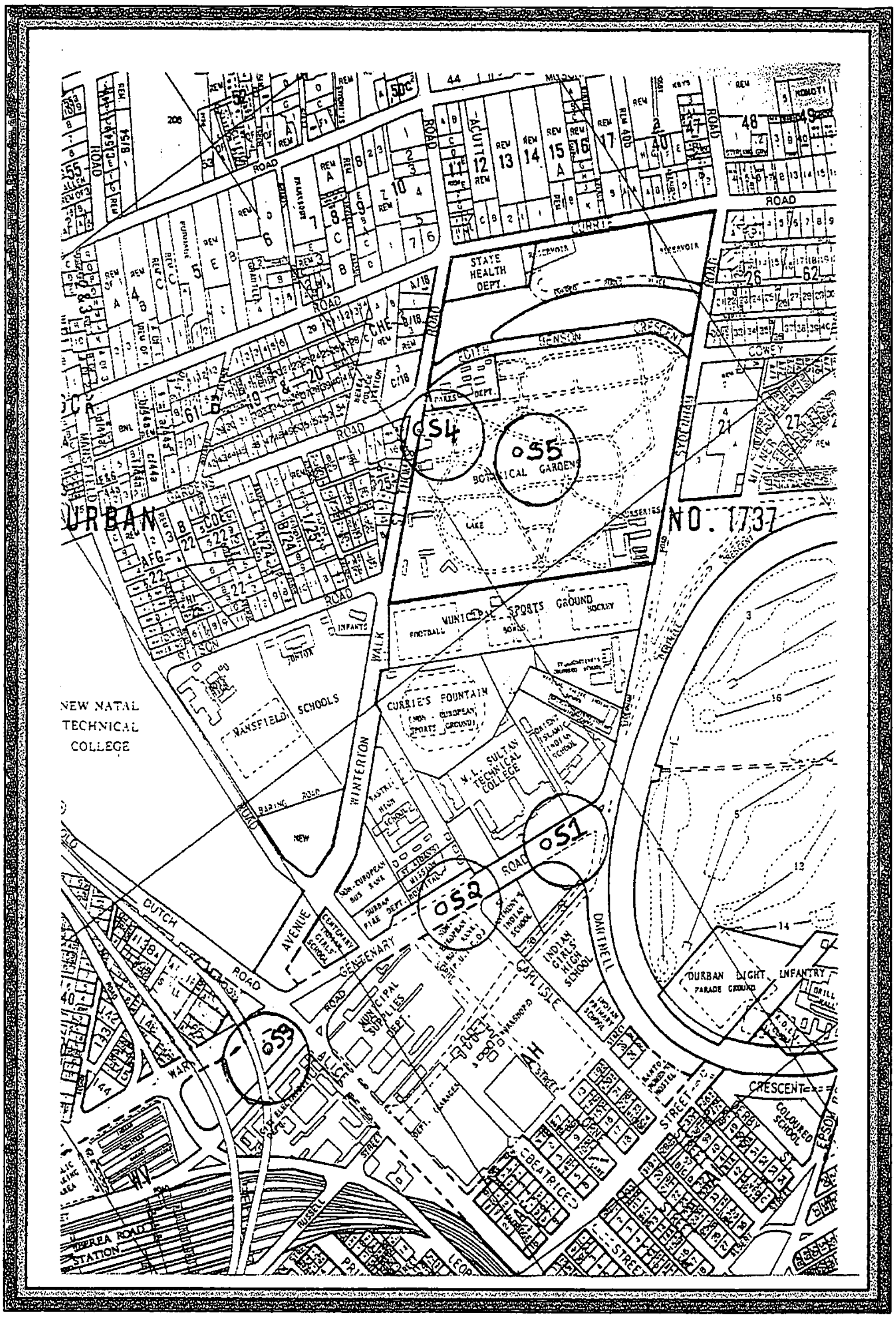

Figure 4.1(a): Map of Durban

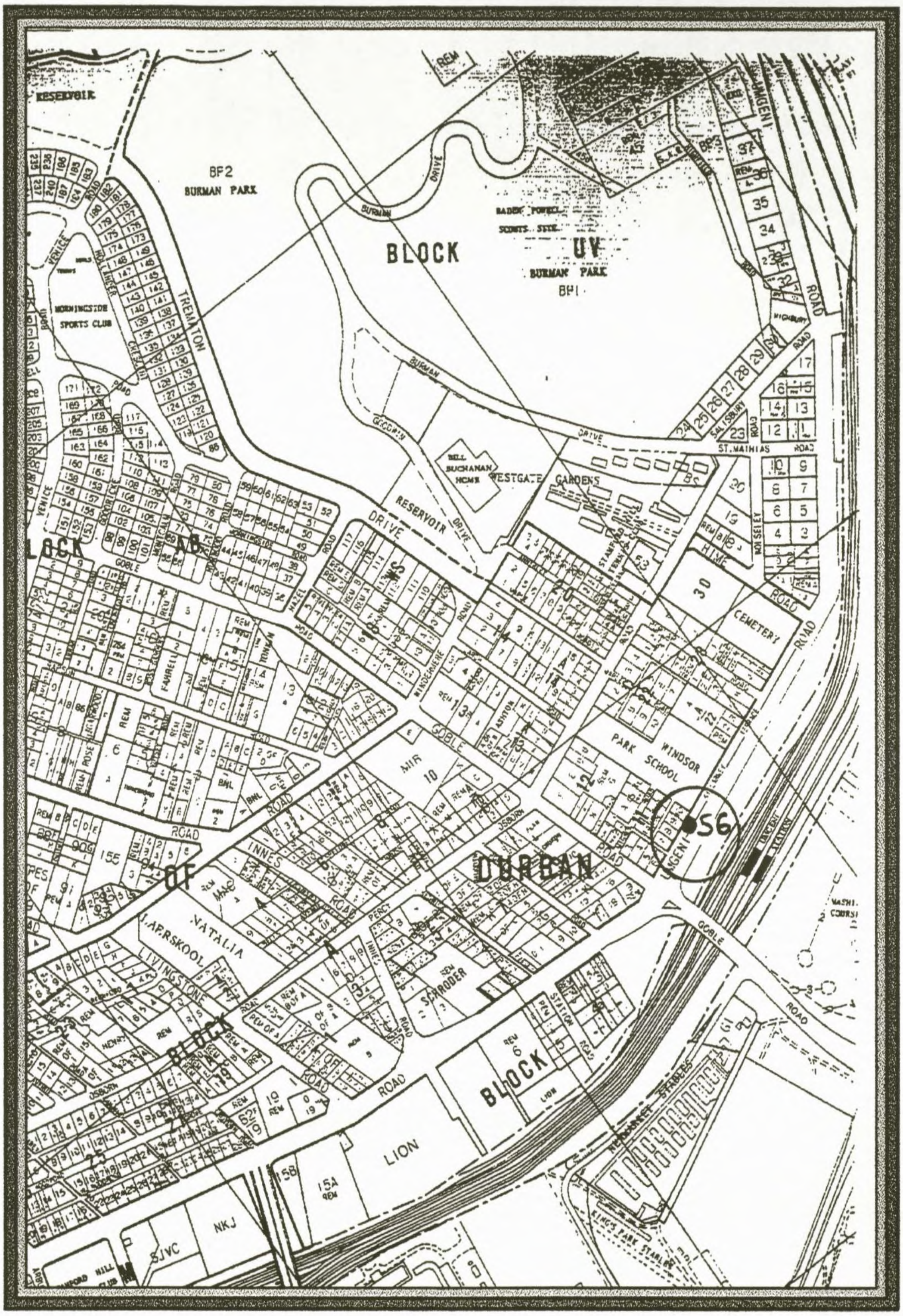

Figure 4.1(b): Map of Durban

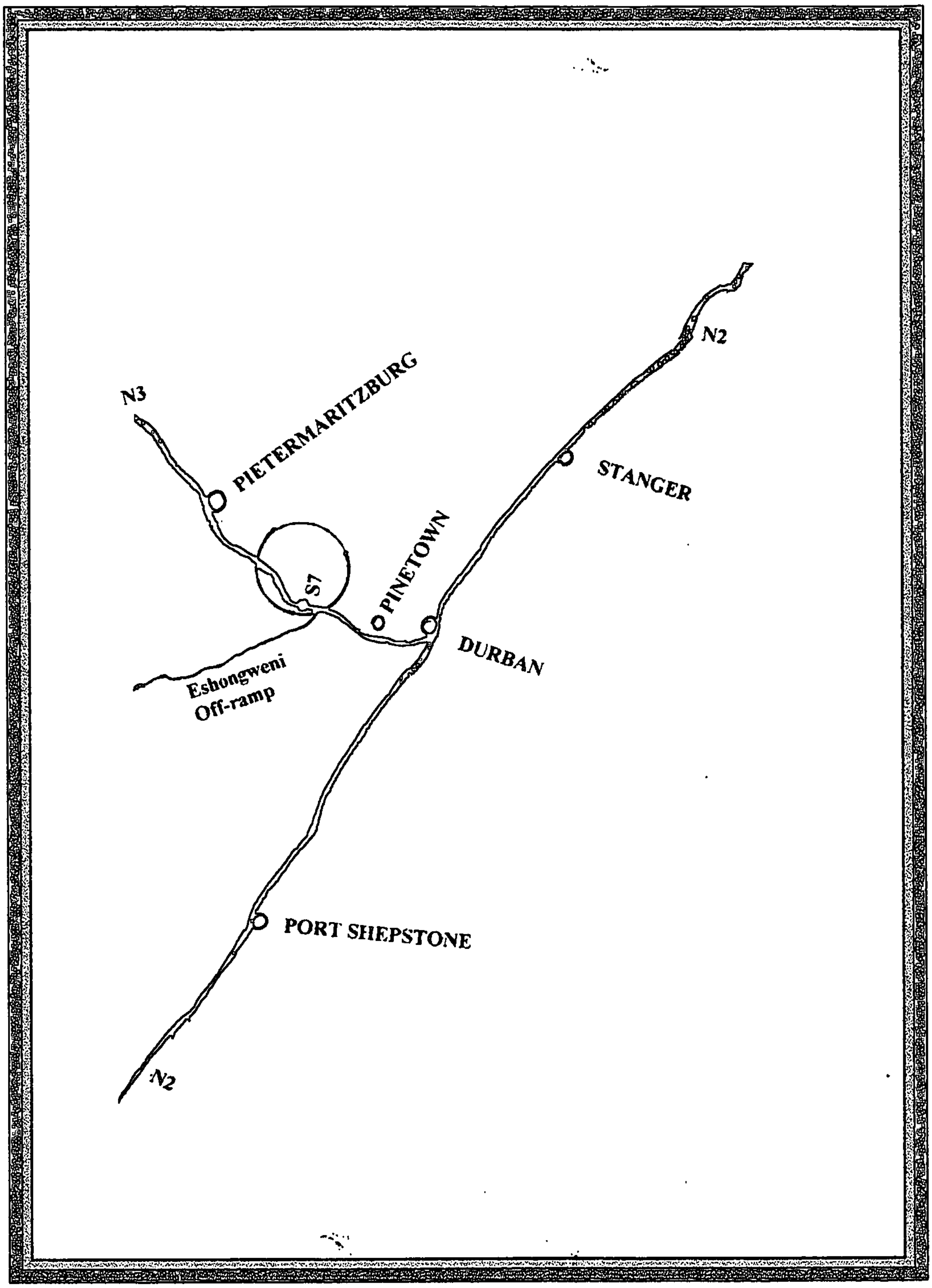

Figure 4.2: Map of the N3 freeway

4.3.1 Digestion

The sub-samples were weighed into acid-washed teflon vessels of Milestone High Performance Microwave Digestion Unit, MLS 1200 mega model level 3.7, Rotor type MDR 1000/6/100/110 (6 closed-vessels of 100 ml). Each vessel contained 1 g of soil and 2 ml of 15.78 M concentrated nitric acid and digestion program was as described in Table 4.1.

Table 4.1: Programme of digestion

1st Step	2nd Step	3rd Step
250 Watts	400 Watts	500 Watts
5 minutes	5 minutes	10 minutes

Digestion time is also a function of particle size of the sample, the finer the sample, the larger the reaction surface and the faster is the digestion. After allowing to cool, samples were transferred into an acid-washed beaker and filtered using Millipore glass fibre pre-filters and Whatman filter papers of medium speed inserted into a Millipore Corporation hazardous waste filtration system, max 100 psi inlet, filter diameter 142 mm, pre-filter diameter 124 mm. Prior to the filtration, 50 ml of 1 M nitric acid was passed through filter papers to remove any contaminating material present in the filter and the receiving vessel. These samples were filtered, the volume was measured and diluted to 1 M nitric acid with double de-ionised water and transferred into acid-washed 500 ml polyethylene bottles. The final volume of the samples was 250 ml. These samples were stored in a freezer to prevent any chemical reaction until they were analyzed. The filtration system was rinsed with double de-ionised water before it was used for the next sample.

4.3.2 Leaching

Parallel soil sub-samples were weighed and transferred into acid-washed 800 ml beakers, each beaker contained 100 g of soil and 500 ml of pH 4 double de-ionised water to simulate rainwater conditions. The mixture was stirred from time to time using a glass rod to simulate rainwater flow, sealed with a Shalom Laboratory Parafilm and left to leach for 20 hours. Filtration was done using Millipore glass fibre prefilters and Whatman filter papers of medium speed inserted into a Millipore corporation hazardous waste filtration system, max 100 psi inlet, filter diameter 142 mm, prefilter diameter 124 mm. Prior to the filtration 50 ml of pH 4 de-ionised water was passed through filter papers to remove any contaminating material present from filter and the receiving vessel, the volume was made up to 500 ml and transferred into acid-washed 500 ml polyethylene bottles. Samples were stored in a freezer to prevent any chemical reactions until the analysis was done. The filtration system was rinsed with double de-ionised water before it was used for the next sample.

4.3.3 Method validation

The validation of the analytical and sample digestion technique has been undertaken by comparing the concentrations obtained from a certified reference material, NCS DC 73320 (Soil obtained from Industrial Analytical (Pty) Ltd, approved by China National Analysis Center for Iron and Steel), using the above-mentioned method of digestion together with the ICP-AES with those that are reported on the certificate of certified reference materials in Table 4.2.

It should be noted that the values obtained by the suppliers of the reference material rely upon $HC\ell/HF/HNO_3/HC\ell O_4$ sample digestion methods to completely digest the refractory alumino-silicate compounds, whilst the HNO_3 method used in this report is unable to completely solubilise these compounds. Thus any elements associated with the alumino-silicate compounds will be slightly under-estimated by the technique employed on this analysis. The method of determination that is outlined on this report is derived from three replicates.

Table 4.2: A comparison of toxic metal content in ppm in the reference material NCS DC 73320 and as determined by the method outlined in this report

Element	**NCS DC 73320 Quoted Concentration**	**Concentration by method of this report**	**% Recovery**
Ni	19.40 ± 1.90	20.92 ± 1.28	107.84
Cu	16.30 ± 1.40	18.28 ± 0.83	112.15
Pb	20.00 ± 4.00	18.99 ± 1.87	94.95
Cr	47.00 ± 6.00	42.50 ± 1.04	90.43
Cd	0.07 ± 0.02	0.07 ± 0.00	100.00
Al	5.46 ± 0.15	5.42 ± 1.59	99.26

4.4 Instrument reliability

In order to determine the reliability of the ICP-AES, 25 ppm standard solutions of copper were prepared and ran as samples during an analysis. The results obtained are shown in table 4.3. It should be noted that an alternate instrument was used in cases where one instrument was unstable or unreliable. For instance in cases where the AAS was unreliable, the ICP-AES was used and vice versa. The GF-AAS was used only when the samples had very low concentrations of analytes.

Table 4.3 Standard solutions that were read as samples

Element	Concentration(ppm)			Average	SD	% RSD	95% CL
Copper	24.23	24.44	24.95	24.54	0.37	1.51	24.54 ± 0.92

4.5.1 pH meter

A Metrohm 691 pH meter was used to measure pH values of solutions and mixtures. For instance the pH of acidic water that was used for leaching experiments was adjusted by using the pH meter. It was optimized and calibrated using BDH Laboratory buffer solutions (phosphate) of pH 4 and pH 7.

4.5.2 pH of soil samples

The acidity or basicity of soil samples was measured to determine the mobility or immobility of cations. A homogenous soil sample of 10.00 g was transferred into a beaker and slurried with 10.00 ml of double deionized water. The slurry was allowed to stand for five minutes and the pH was measured using a pH meter. Some of the pH values of different samples that revealed the acidic nature of the soil samples and hence the mobility of [15] cations are shown in Table 4.4.

4.6 Calibration of ICP - AES, AAS and GF - AAS

A multi-point calibration was employed in the optimization and the calibration of the Perkin-Elmer Plasma 400 Emission Spectrometer. A blank and five standard solutions of each of the elements viz:- lead, cadmium, nickel, chromium, copper and aluminium were prepared from 10 to 50 ppm in multiples of ten in order to determine the linearity of the calibration line as shown in Figure 4.3. In cases of elements that were expected to have low concentrations in the samples, the range of the five standard solutions was reduced accordingly. The regression output of the calibration line in Figure 4.3 is shown in Table 4.5.

In all cases, it was maintained that the sample concentration should not exceed the highest standard since the error in extrapolation is always higher than in interpolation. Consequently the samples were diluted accordingly. With the Varian AA-1275 series of AAS, a multipoint calibration was performed. The range of standard solution was prepared to commensurate the quantity of the analyte. For instance, a range of 1, 2, 3, 4, 5 ppm was used to analyze samples that had an analyte with a level that is less than 5 ppm. This range was increased to cater for samples with higher levels of the analyte, this was done in such a way that the linearity of the calibration was maintained. A Varian Graphite Tube Atomizer (GTA-95) coupled with AAS was used to analyze metals of low concentrations. The range of standard solutions that was used is 0.005 to 0.025 ppm in multiples of five and again samples that were outside this range were diluted accordingly.

4.6.1 Principle of the calibration line

This principle is based on Beer-Lambert's law that was mentioned in equation (6). Since a direct proportion implies a straight line, then Beer-Lambert's law represents an equation of a straight line graph as follows:-

$$Y = MX + C \tag{7}$$

were M is the gradient and C is the constant. A direct substitution of equation (6) is done as follows:-

$$A = Y; \; k\ell = M; \; c = X; \tag{8}$$

Hence the straight line equation takes the form:-

$$A = Mc + C \quad (9)$$

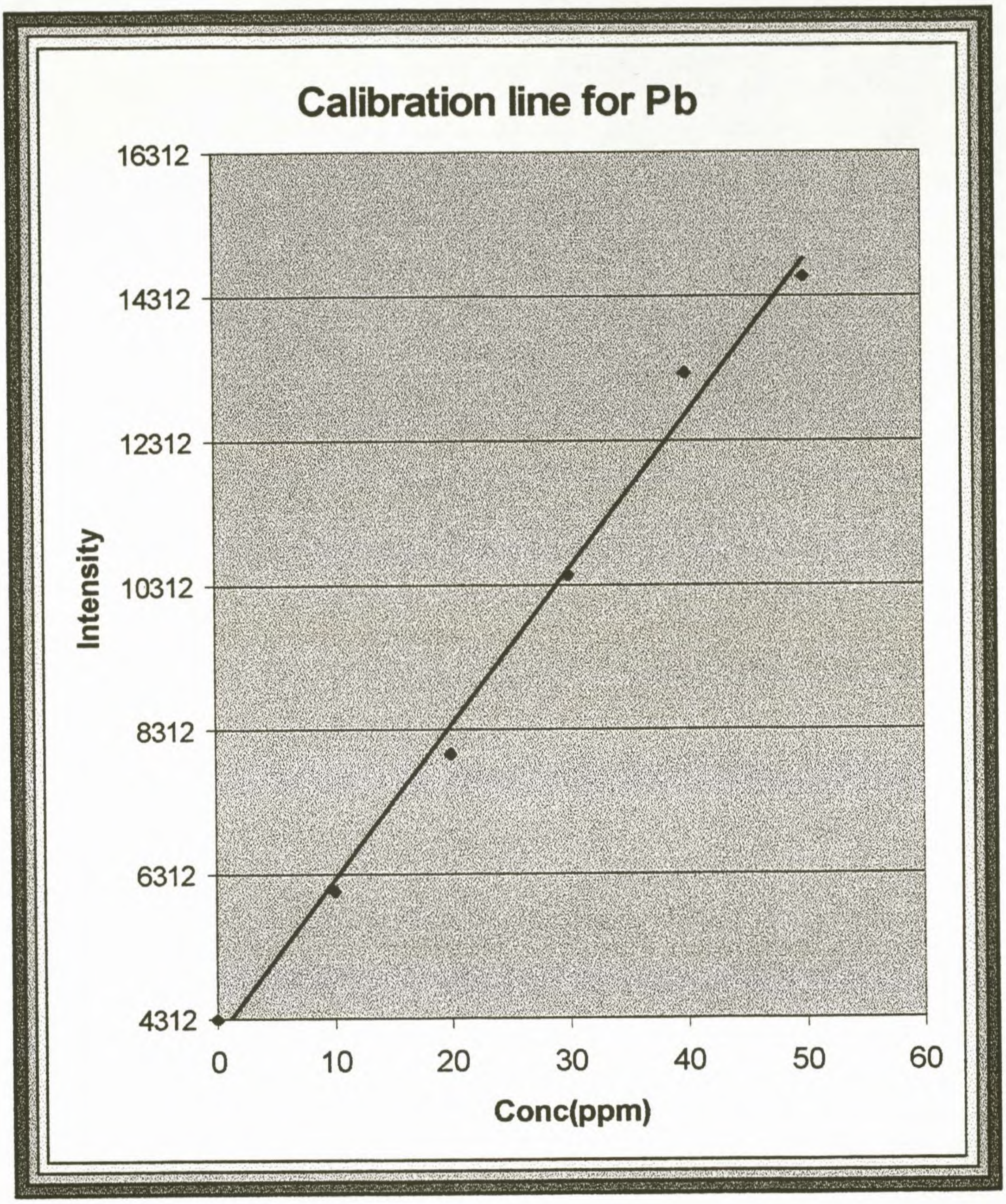

Figure 4.3: Calibration line of lead by ICP-AES

Table 4.5 **Regression output of the calibration line of lead**

Concentration(ppm)	Intensity	Regression Output	
0.00	4312.00	Constant	4059.52
10.00	6092.30	Std Err of Y Est	396.218
20.00	7967.00	R Squared	0.992
30.00	10456.00	No. of observations	6
40.00	13253.30	Degrees of freedom	5
50.00	14603.30	X coefficient(s)	215.506
		Std Err of coefficients	9.471

4.6.2 Analysis of lead, copper, nickel by AAS

A set of frozen samples was left at room temperature to defrost. Standard solutions were prepared by dilution using a Saarchem (Pty) Ltd 1000 ppm metal w/v 1 N HNO_3. A Varian AA-1275 atomic absorption spectrometer with a hollow cathode lamp of a specific element was optimized and calibrated using standard solutions. Samples were run under the instrument parameters listed in table 3.6 in three replicates. Samples that were outside the calibration line were diluted and analyzed again.

4.6.3 Analysis by GF-AAS

The concentrations of lead and cadmium were found to be below the detection limit in some samples, hence it was impossible to analyze by atomic absorption technique. This necessitated the use of a more sensitive technique such as the graphite furnace. The range of standard solutions that were prepared was from 0.005 to 0.025 ppm in multiples of 0.005. The analysis was performed using a Varian AA-1275 atomic absorption spectrometer with a hollow cathode lamp of a specific element coupled to a GTA-95 electrothermal atomizer and a programmable sample dispenser (Varian Techtron Pty. Ltd). Table 4.7 describes the optimized heating programme of lead that was used. The heating programme of cadmium is shown in Appendix C1.

Table 4.6: AA-1275 Parameters for the analysis of lead

Working conditions are fixed	
Lamp current	4 mA
Fuel	Acetylene
Support	air
Flame stoichiometry	oxidising
Working conditions are variable	
Wavelength	232.0 nm
Slit width	0.2 nm
Optimum working range	3 - 12 ppm

The AAS parameters of nickel and copper are listed in appendix B1.

Table 4.7: GTA-95 Parameters for the analysis of lead

Step No.	Temp (^0C)	Time (s)	Gas flow (L/min)	Gas Type	Read Command
1	75	5.0	3.0	N_2	
2	90	60.0	3.0	N_2	
3	400	10.0	3.0	N_2	
4	400	2.0	0		
5	2000	1.0	0		yes
6	2000	2.0	0		yes
7	2000	1.0	3.0	N_2	

AA Instrument parameters	
Lamp current	5 mA
Spectral Bandwidth	1.0 nm
Wavelength	217.0 nm
Background correction	OFF

Each element was analyzed under the sampler parameters that are described in Table 4.8 whereby the blank solution for digested samples was 1 M solution of nitric acid and pH 4 double de-ionized water for the leached samples.

Table 4.8: Sampler Parameters.

TYPE	LOCATION	VOLUME OF SAMPLE AND STD (μL)	BLANK VOLUME (μL)
Blank	-	-	20
Std 1	51	4	16
Std 2	51	8	12
Std 3	51	12	8
Std 4	51	16	4
Std 5	51	20	0
Samples	-	20	0

Last sample no. = 10	Multiple injections = 1
No of replicates = 3	Last dry step = 2
Reslope rate = 0	Injection temperature = 3
First sample no = 1	

The total volume of material that is analyzed in the atomizer is 20 μL.

4.6.4 Analysis of aluminium, lead, copper, nickel, cadmium and chromium by ICP-AES.

Inductively coupled plasma was introduced in this investigation for two reasons; the first one is that the number of samples at this stage of analysis was high and a technique that could analyze all six elements simultaneously was needed, secondly the levels of aluminium in soil is very high therefore it was necessary to find a technique that could be used for the analysis using higher standard solutions without disturbing the linearity of the calibration line to avoid error that could be obtained from a high dilution factor in samples. A 50 ppm standard solution of aluminium, lead, copper, nickel, cadmium and chromium was prepared as a single multi-element standard solution. An element file of each analyte was created on the Perkin-Elmer Plasma 40 Emission Spectrometer that operates by an argon plasma. The photo-multiplier tube was optimized for each element. The wavelength of each element was set as described in Table 4.9.

Table 4.9: Wavelengths of Cr, Pb, Ni, Cu, Cd and Al analyzed on the ICP-AES

Element	**Wavelength (nm)**
Cr	205.522
Pb	220.353
Ni	221.647
Cu	224.700
Cd	228.802
Al	309.271

A method file in which the instrument was programmed to read the blank followed by the standard solution and the samples was also created. Although this instrument Perkin-Elmer Plasma 40 Emission Spectrometer is fitted with an auto-sampler, the analysis was done on a manual basis.

Chapter 5

Results and discussions

This chapter will include schematic diagrams of sampling sites, a description of the use of a calibration line to calculate the final results and the discussion of the results of obtained from various sampling sites.

5.1 Typical calibration plot

The absorbance values of the standard solutions of concentrations 1, 2, 3, 4 and 5 ppm of lead were obtained using atomic absorption spectrophotometer(Varian AA-1275). An average of three replicate values of absorbance per standard solution was taken as shown in Table 5.1.

Table 5.1: **Absorbance values of lead standard solutions**

Replicate 1	**Replicate 2**	**Replicate 3**	**Average**	**Concentration(ppm)**
0.000	0.000	0.000	0.000	0.00
0.026	0.026	0.026	0.026	1.00
0.048	0.048	0.048	0.048	2.00
0.071	0.070	0.071	0.071	3.00
0.094	0.094	0.092	0.093	4.00
0.117	0.117	0.117	0.117	5.00

The calibration line obtained by plotting data that is given in Table 5.1 is shown in Figure 5.1, together with the regression output in Table 5.2.

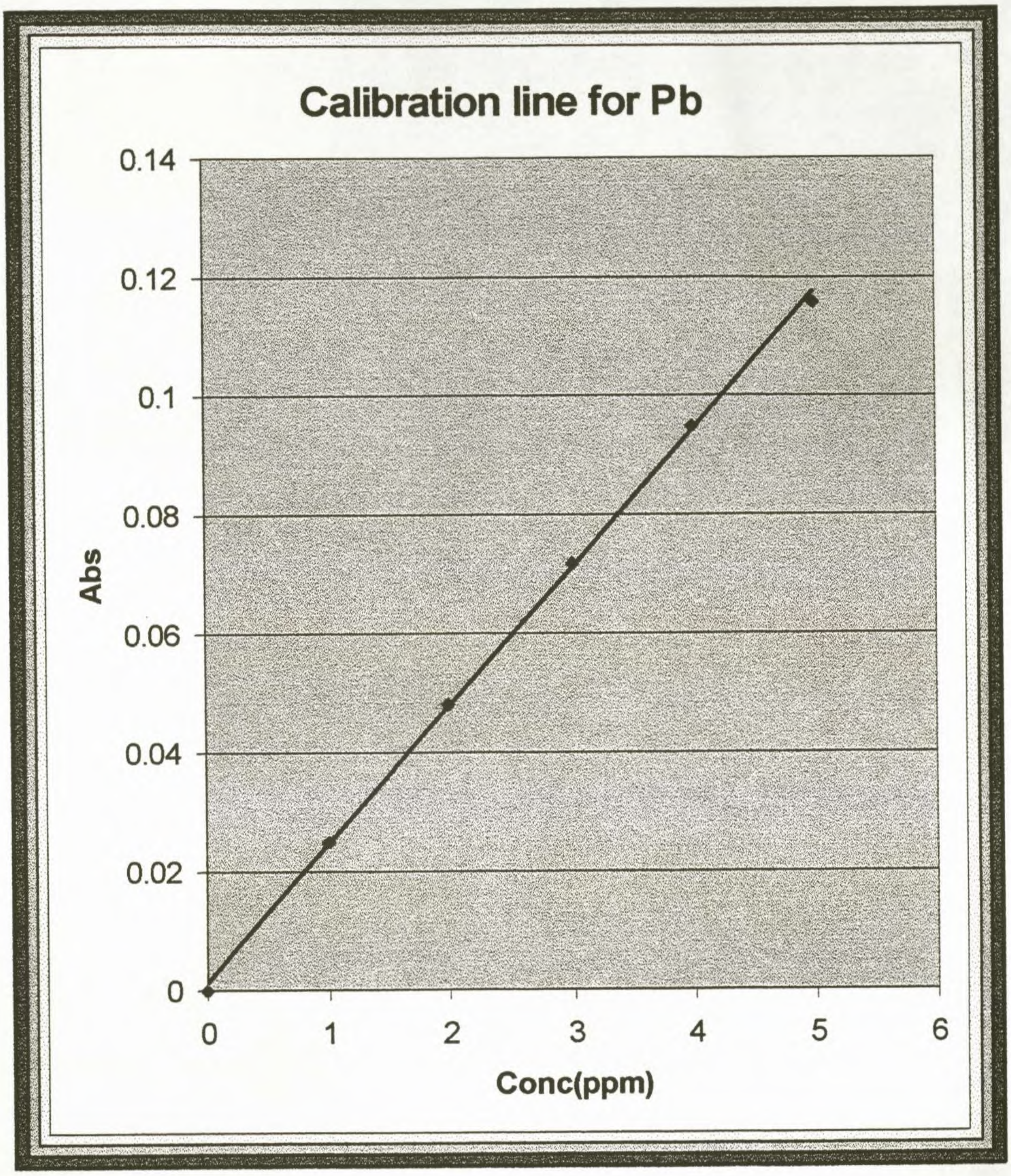

Figure 5.1: Calibration line for Pb standard solutions analyzed by the AAS

Table 5.2: Regression output for lead calibration line

Constant	0.001
Std Err of Y Est	0.0008
R squared	0.999
No of observations	6
Degrees of Freedom	4
X Coefficient(s)	0.0232
Std Err of Coef.	0.0002

All samples that had an absorbance value that was above range of values obtained by standard solutions were diluted accordingly in both leaching and digestion.

5.2.1 Method of calculation of the final result

The regression output reveals that the constant (C) and the gradient (M) are equal to 0.001 and 0.0232 respectively. Substitution into equation (9) gives the following:-

$$A = 0.0232\ c + 0.001 \qquad (10)$$

The concentration measured in parts per millions (ppm) in the sample was calculated by substituting for A and making c the subject of the equation. To calculate the mass of the analyte, the milliliters (mL) were converted to litres (L) and milligrams (mg) were converted to grams (g) as follows:-

$$1\ \text{L} = 1\ 000\ \text{mL} \qquad (11)$$

$$1\ \text{g} = 1\ 000\ \text{mg} \qquad (12)$$

The following equation,

$$\text{mass (analyte)} = c\ (\text{mg/L})\ \times\ V\ (\text{mL}) \qquad (13)$$

where V (mL) is the volume of the sample (leachate or digest) used. Substituting the conversions from equations (11) and (12) into equation (13) produced the following equation:-

$$\text{mass (analyte in grams)} = \frac{c \ x \ \dfrac{V}{1000}}{1000} \qquad (14)$$

Finally, the concentration c of the analyte in soil was converted to parts per million using equation (15) below:-

$$\text{c [analyte (ppm)]} = \frac{\text{mass [analyte (grams)]}}{\text{mass [soil (grams)]}} \times 1\ 000\ 000 \qquad (15)$$

This equation was used for both leached and digested samples throughout this analysis.

5.2.2 Example of calculations using the results from preliminary work

In the analysis for lead on samples collected for a preliminary study, a sample labeled BRL in Appendix D1 was leached. The diluted solution which was analyzed by AAS had an average absorbance of 0.034 (obtained from three replicates). The concentration (c) of lead was calculated by substituting the average absorbance (0.034) into equation (10) as follows:-

$$0.034 = 0.0232\text{ c} + 0.001 \qquad (16)$$

Hence,

$$\text{c(diluted)} = 1.42\text{ ppm} \qquad (17)$$

The dilution of this sample was ten fold due to the fact that it had absorbance values that were outside the range of the calibration line. The concentration of lead was obtained by multiplying the result in equation (17) by ten:-

$$\text{c(original)} = 14.2\text{ ppm} \qquad (18)$$

The mass of lead in the sample was calculated by substituting the concentration c from equation (18) and the volume (V) of the original sample which was 500 mL into equation (14), hence,

$$\text{mass(Lead)} = 0.00711\text{ g} \qquad (19)$$

Finally, the concentration (c) of lead in the soil samples was calculated by substituting its mass from equation (19) and the mass of soil sample which was weighed to be 99.87 g into equation (15) to obtain that

$$c\ (\text{Lead}) = 71.1\ \text{ppm}. \qquad (20)$$

This value is shown on the fifth column of the first row in Table 5.3. This method was also employed for the digested samples using the data obtained.

Table 5.3: Results of Pb for preliminary work on leached samples

Sample	Mass used(g)	Average Absorbance	Dilution factor	Concentration (ppm)
BRL	99.87	0.034	10	71.1
CTL (1st sampling)	100.04	0.086	5	91.5
CTL (2nd sampling)	100.09	0.059	12.5	156

The analysis was done in three replicates, that is, three portions of the same soil sample were digested. Leaching was also performed on three portions of the same soil sample. This can be seen in Appendices D1 to H12.

5.2.3 The use of confidence limits

The average concentration or the mean, standard deviation (s), relative standard deviation (%RSD), and the 95% confidence limits (95% CL) were calculated using equations and tables given in appendix G. For example, the average concentration of lead on the digested sample labeled BRD was calculated to be 162.88 ± 0.85 ppm as shown in Appendix D1. This means that we are 95% confident that the true value lies within this interval. It was duly noted that deviations from the mean increased the confidence interval of the mean.

5.3 Results from the preliminary study

Soil samples for the preliminary study were collected from an island in Centenary Road at the sites in front of ML Sultan campus (shown in Figure 4.1(a) as S1), in front of St' Aidans Hospital (shown in Figure 4.1(a) as S2) and also from Victoria Bus Rank (shown in Figure 4.1(a) as S3). The sampling was done on two occassions from the each sites. Dust samples were also swept and collected from the pavement in Centenary Road opposite Victoria Bus Rank.

5.3.1 Soil from the island in Centenary Road and Victoria Bus Rank

In the sketch shown in Figure 5.2 the sampling spots are marked CT, SAH and BR. The highest concentration of lead on the island of Centenary road was initially found to be 223 ppm (rounded off) on the sample labeled CTD that was collected from the front of the ML Sultan campus and 337 ppm (rounded off) on the sample labeled SAHD that was collected from the spot in front of St' Aidans Hospital. The analysis of the samples that were collected on the second sampling revealed an increase of lead on the sample from the front of ML Sultan campus and a decrease of lead on the sample from the front of St' Aidan's Hospital. The concentration was found to be 243 ppm (rounded off) on the sample labeled CTD and 212 ppm (rounded off) on the sample labeled SAHD. It is possible that due to factors such as wind and the different velocities of vehicles, emission may accumulate at sites unevenly.

As mentioned earlier, soil samples from the Victoria Bus Rank were also analyzed. The highest concentration of lead was found to be 163 ppm (rounded off). This sampling site is surrounded by roads of large traffic volumes as discussed in Section 4.2.2.

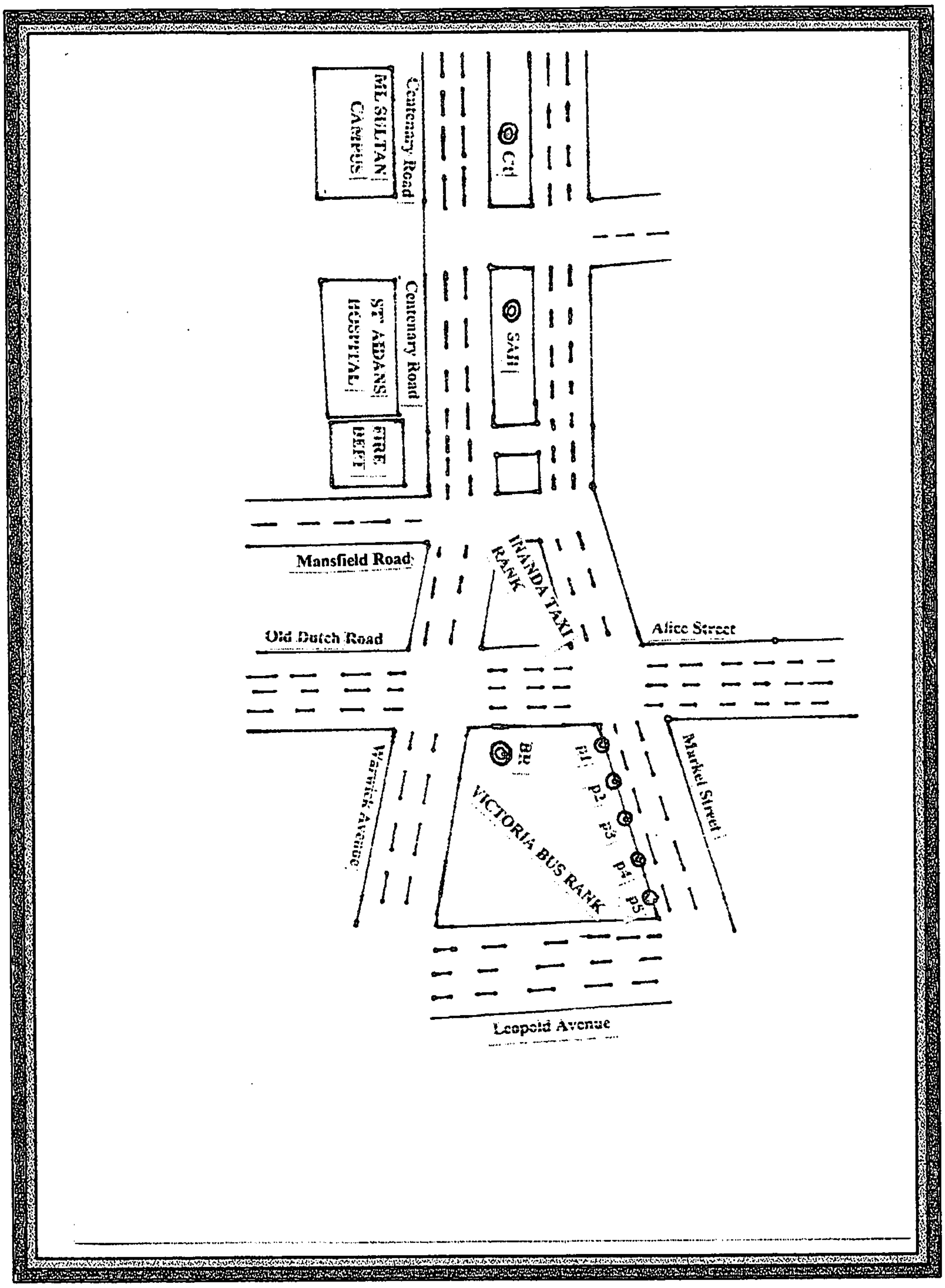

Figure 5.2: Sketch of sampling sites in Centenary and Market Streets

All the samples described above were also analyzed for chromium, cadmium, nickel, copper and aluminium. In general, these metals were found to have a slight increase in concentrations when comparing the first and the second sample collection. This is can be seen in Appendices D1 and D2.

5.3.2 Dust samples from Market Street opposite Victoria Bus Rank

This site is also shown in Figure 5.2. The sampling spots are labeled p1, p2, p3, p4 and p5. These spots are separated by 8 m from one another. All six metals viz lead, aluminium, copper, nickel, chromium and cadmium were found to be present (see Appendix D3). The bus rank is surrounded by the roads of very high traffic volumes (see Section 4.2.2). As expected, the concentrations of aluminium are the highest ranging from 3030.14 ± 763.86 to1821.11 ± 84.44 ppm in digested samples and 5.20 ± 0.32 to 4.02 ± 0.19 ppm on leached samples. This is followed by lead which ranges between 250.90 ± 20.12 and 115.63 ± 11.16 ppm in digested and 2.52 ± 0.26 and 2.12 ± 0.46 ppm on leached samples. These concentrations are less than the concentrations of lead which range from 923.31 ± 81.11 to 407.82 ± 14.14 ppm and 4.97 ± 0.53 to 1.59 ± 0.20 ppm (shown in Appendices G1 and G2) found in soils from the N3 near Shongweni off-ramp in digested and leached samples respectively. This is due to the fact that dust from pavements indicates recent pollution whereas kerbside soil serves as a sink for metals from automobiles. Again the concentrations of digested samples are much higher than the concentrations of the leached samples. Cadmium has the lowest concentration in digested samples and it was not detected in leached samples although higher concentrations of this element were expected opposite Victoria Bus Rank due to the fact that a lot of paving sweepings were expected to contain a large volume of cigarette ash from smokers. The sampling sites were expected to have more or less the same concentrations for each metal but in most cases they have shown independent sets of results due to uneven distribution of metals by vehicles as shown in Appendix D13.

5.4 Levels of lead and other metals from the site near Umgeni/Goble Road intersection

This sampling site is labeled S6 in Figure 4.1(b). A sketch of this site and the sampling spots chosen is shown in Figure 5.3, to facilitate the discussion of the results.
As shown in Figure 5.3 samples were taken from the spots marked A, B and C which are 4.6, 10 and 13 m (due to concrete pavings) along the bank above the road level.

Samples were also taken from the spot marked D on the island between the north and the south bound lanes. The concentration of Pb obtained from the sampling spot shown above are given in Appendix E. To illustrate the effect of distance from kerb-side on the concentration of the lead a bar chart of concentration versus distance for leached and digested samples is given in Figure 5.4.

It is seen from Figure 5.4 that the concentration of lead increases with increasing distance from the road. This is contrary to the expectation that most of the emission will land fairly close to the kerbside. However, consideration of the terrain suggests that emissions are lofted up before they land.

The sampling spot D, on the island gave a concentration of 200 ppm (rounded off) whereas the highest concentration from the kerb was found to be 268 ppm (rounded off). Again, one would have expected an opposite result in view of the fact that the island is subjected to vehicle emissions from both sides of the Umgeni Road and also from Goble Road traffic as well.

Figure 5.4 also shows the concentrations of leached and digested samples side by side. As expected, the values of lead concentrations of digested samples are generally higher than those for the leached samples. The relative closeness of the values for leached and digested samples appears to suggest that a relatively high percentage of the lead from the vehicles is exhausted as soluble species.

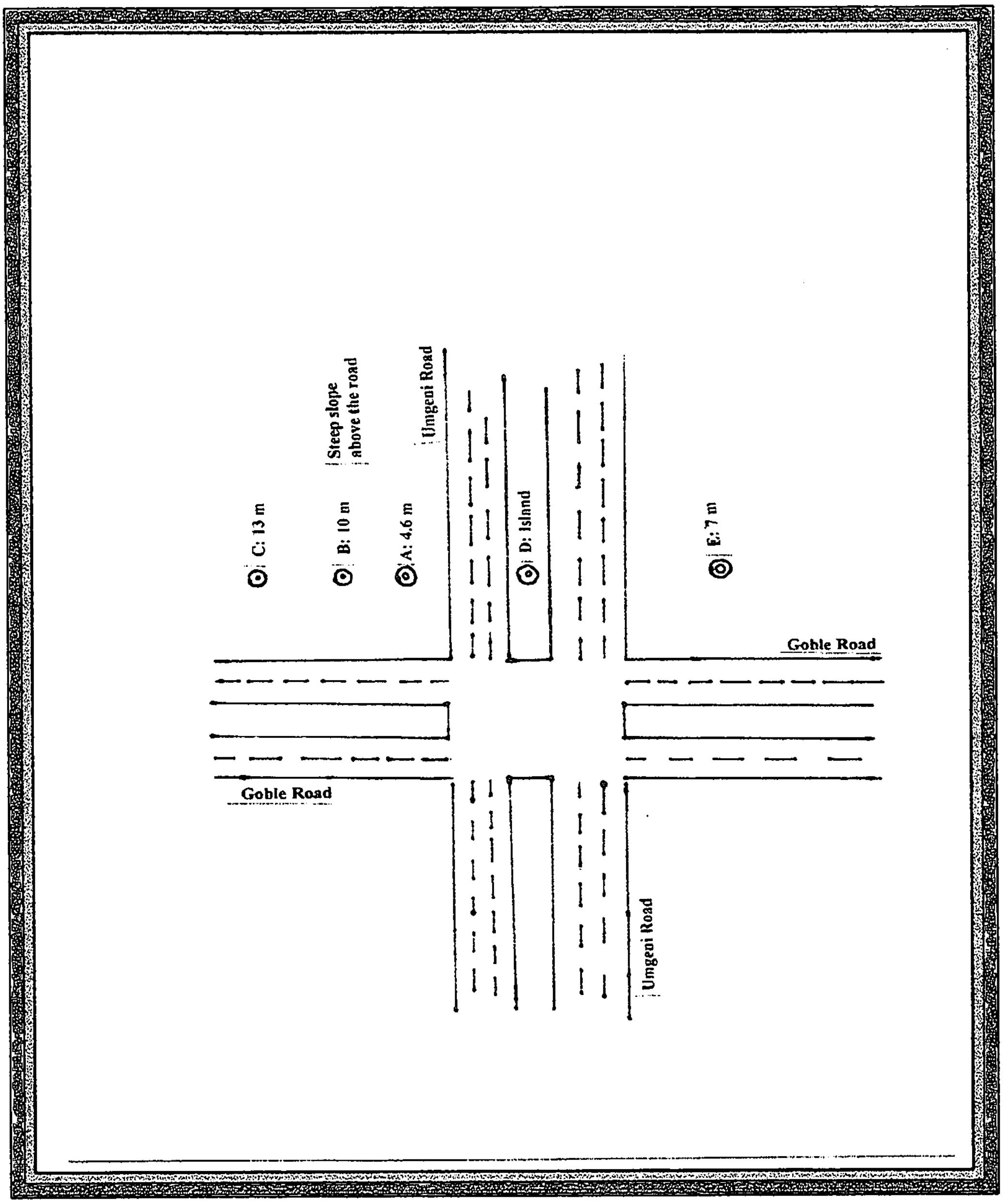

Figure 5.3: A sketch of Umgeni/Goble Road intersection sampling site

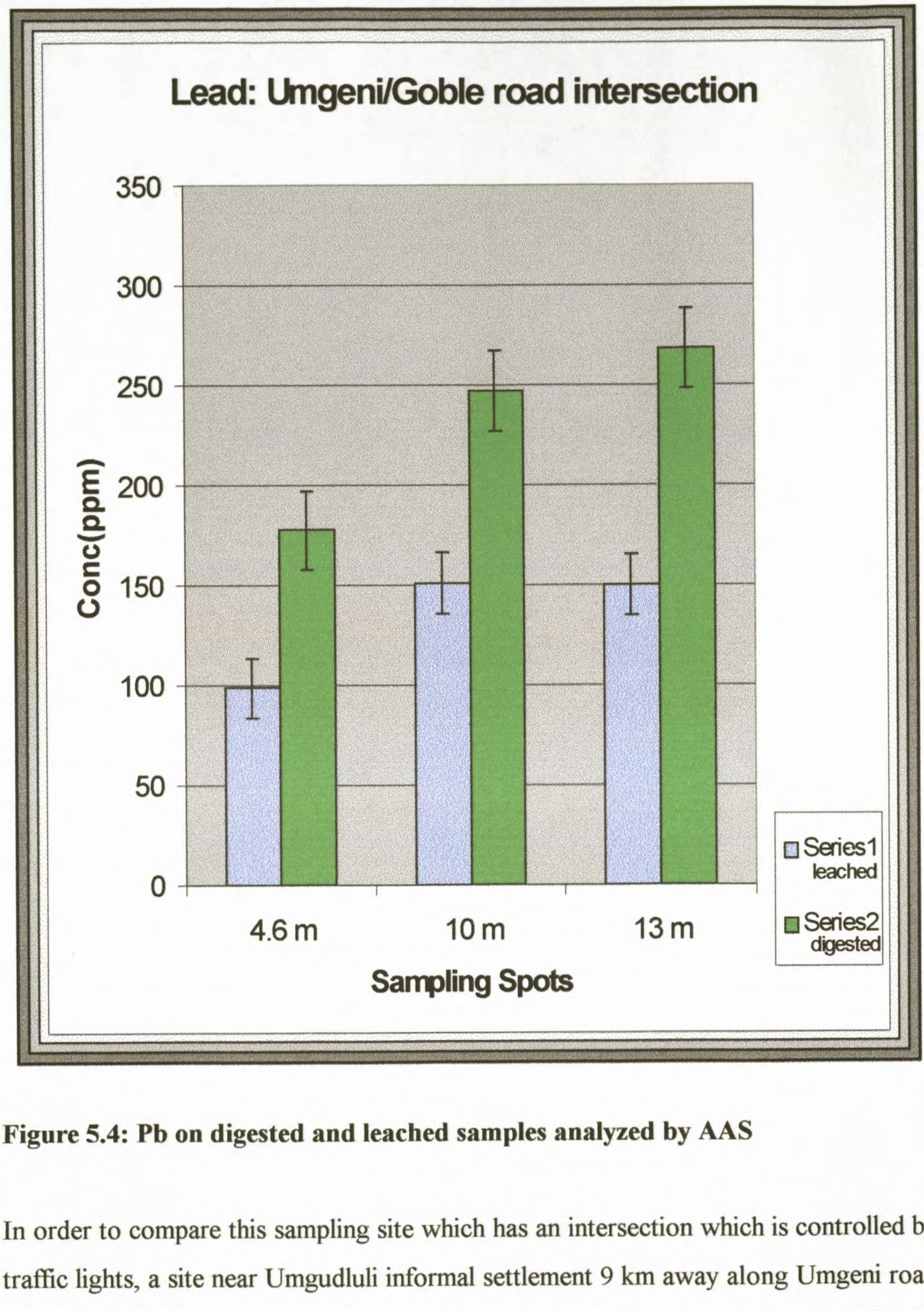

Figure 5.4: Pb on digested and leached samples analyzed by AAS

In order to compare this sampling site which has an intersection which is controlled by traffic lights, a site near Umgudluli informal settlement 9 km away along Umgeni road was chosen. It was hoped that this site where traffic flows freely would contrast with the stop-start nature of traffic at the Umgeni/Goble Road intersection. Moreover, these samples were collected 1 m from the edge of the road which could not be done for the samples near Umgeni/Goble Road intersection due to concrete pavings. The subsampling and analysis was repeated three times.

The results for lead at the Umgudluli informal settlement were found to be higher that the highest value at the Umgeni/Goble Road intersection. The concentration of lead at this spot was as high as 276 ppm for leached samples and 596 ppm for digested samples (rounded off). This is lower than the concentrations of lead on samples which were collected 1 m from the edge of the road along the freeway (N3) (see Appendix G1). The other selected metals were also anlayzed in all spots and the results are shown in Appendix E.

5.5 Results of samples from the Botanical Gardens

Two sampling spots marked BGE and BGP were chosen from this site as shown in Figure 5.5. This site is bound by Sydenham Road and Botanic Gardens Avenue. These roads carry heavy traffic especially in the mornings and afternoons. The concentrations of lead on samples BGEL, BGED, BGPL and BGPD was found to be 35.86 ± 7.68, 92.78 ± 1.65, 45.42 ± 9.08 and 88.95 ± 0.27 ppm respectively as shown in Figure 5.6. This is two or three times lower when compared to the concentration of lead in Centenary road and Umgeni/Goble road intersection. Moreover, there is no significant difference between the total concentration of lead in the sample from the entrance labeled BGED and the total concentration of the sample from the premises of the Botanical Gardens labeled BGEP. This can be attributed to the fact that the Botanical Gardens is surrounded by three busy roads. Contributions are from Sydenham road which has a very large traffic volume and is about ± 200 m from the sampling spot, Botanic gardens avenue which is ± 100 m and St' Thomas which is 168 m from the spot. The results obtained for the second sampling (shown in Appendix F2) were more or less the same as the results of the first sampling in almost all the samples. All other selected metals were found to be present as shown in Appendices F1 and F2.

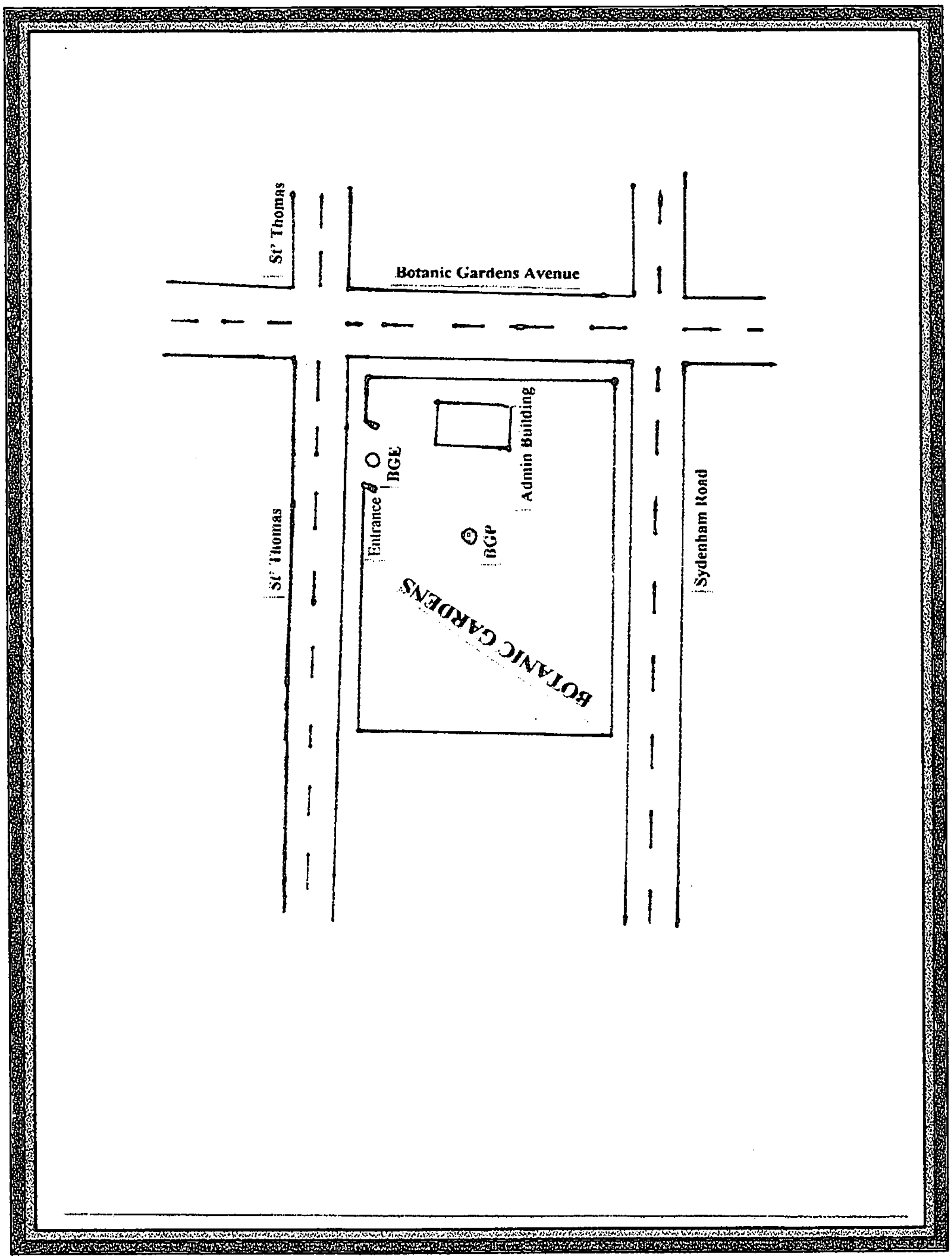

Figure 5.5: A sketch of the Botanic Gardens

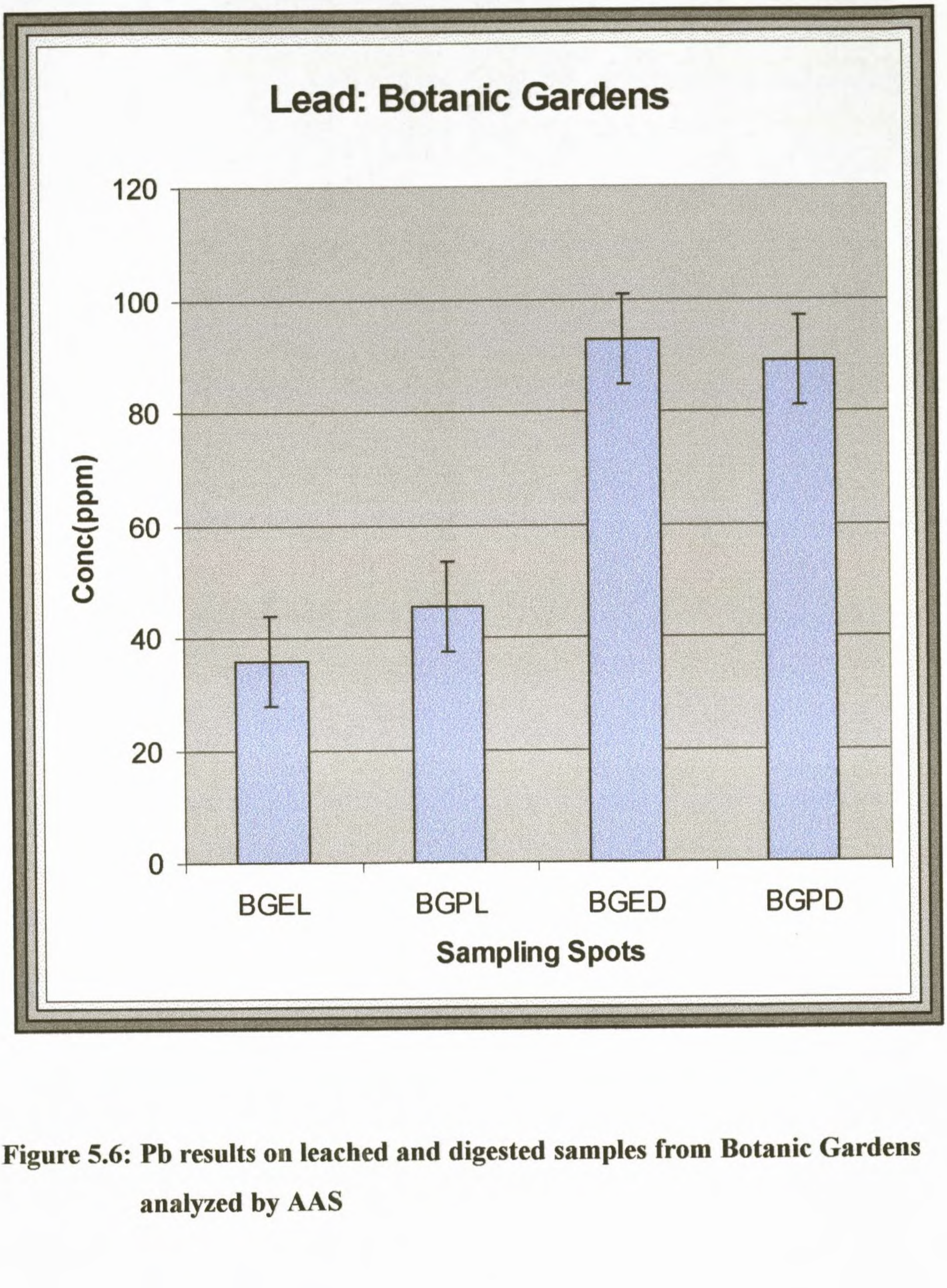

Figure 5.6: Pb results on leached and digested samples from Botanic Gardens analyzed by AAS

5.6 Results of lead and other metals from the N3 freeway near Shongweni off-ramp

Soil samples were also collected from the N3 freeway near the off-ramp to Shongweni. This site was chosen because it has large volume of free-flowing traffic as shown in Appendix D5. It is also is flat, open (it allows for a collection of samples at varying distances from the kerb) and fairly undisturbed.. The sampling plan used is shown in Figure 5.9.

5.6.1 Lead on the site near Shongweni off-ramp

The first set of samples was collected 1, 2, 4, 8 and 12 m from the edge of the road. The results of lead obtained by leaching ranged from 8.73 ± 0.84 to 3.01 ± 0.39 ppm. Parallel portions of these samples were also digested and the concentration of lead was found to be high, ranging from 852.88 ± 7.11 to 189.05 ± 4.21 ppm. The results for the digested samples have been depicted in Figure 5.7. It is seen that the concentrations of lead decrease with distance from the kerb.

In order to investigate the concentrations of lead further away from the edge of the road, a second set of samples was collected from the same site seven months later. The distance was varied as follows 2, 10, 20 and 30 m from both the north and the south side of the road. This sampling was done after heavy rains. The lead results were found to range from 0.065 ± 0.003 to 0.025 ± 0.002 ppm. These results are shown in bar chart form in Figure 5.8. There is no significant difference in the concentrations of the corresponding samples on the north and south side of the road. For instance, the concentration of lead on sample that was collected 2 m from the road on the south side is 0.029 ± 0.001 ppm whereas on the north side, the concentration of lead on the sample

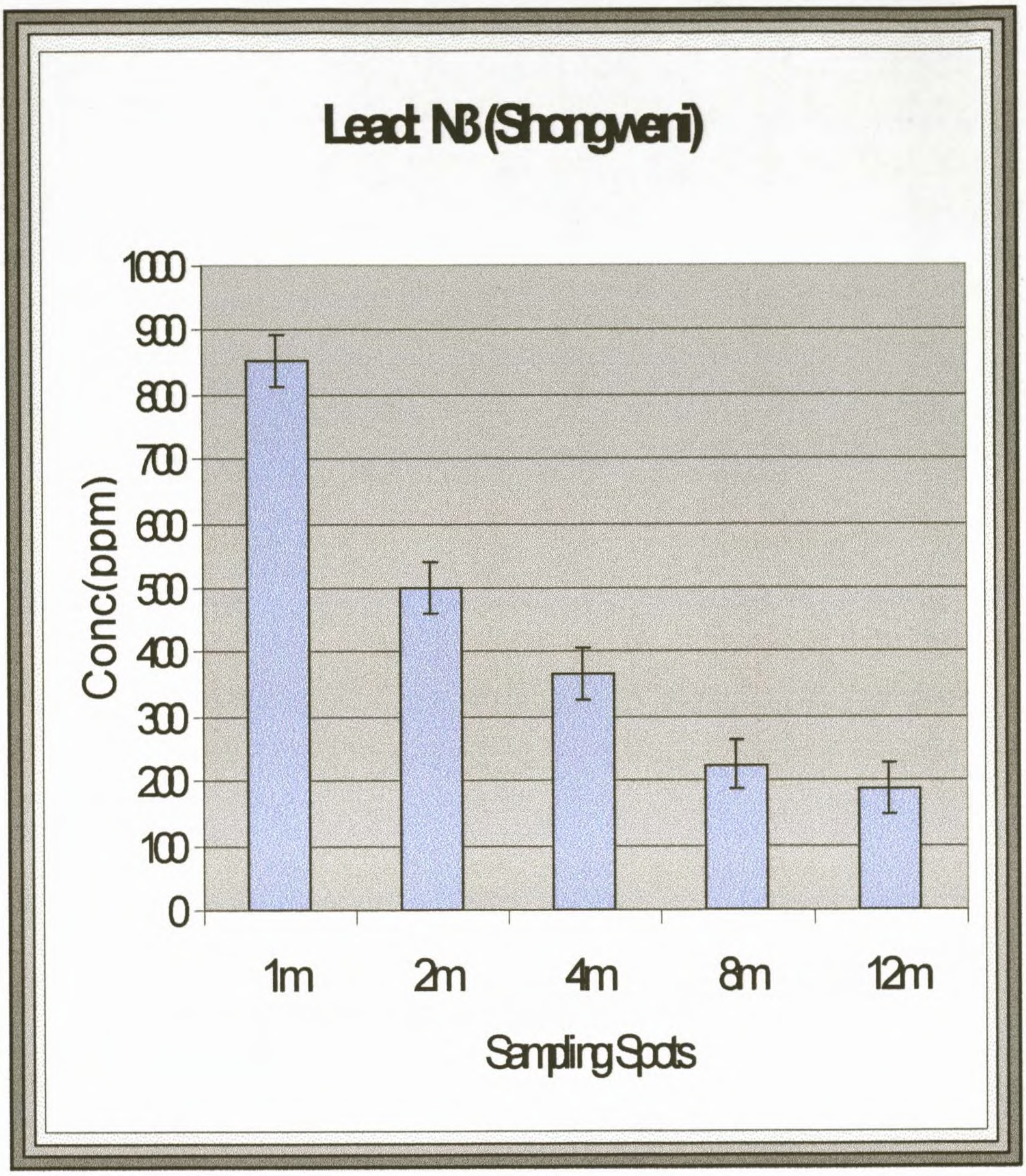

Figure 5.7: Pb results on digested samples from the N3 analyzed by ICP-AES

that was collected 2 m from the edge of the road is 0.028 ± 0.002 ppm. The samples that were collected 10 m from the road show an increase in the concentration of lead on both sides. This is may be due to the input made by vehicles from Hilcrest and Shongweni that are joining the N3 freeway. It is possible that the most of contribution of these vehicles land onto the 10 m spot since the concentrations were found to decrease for samples collected 20 m and 30 m from the road. Samples from the island were also analysed and the concentrations were found to be 0.049 ± 0.005 ppm on the north side and 0.026 ± 0.003 ppm on the south side.

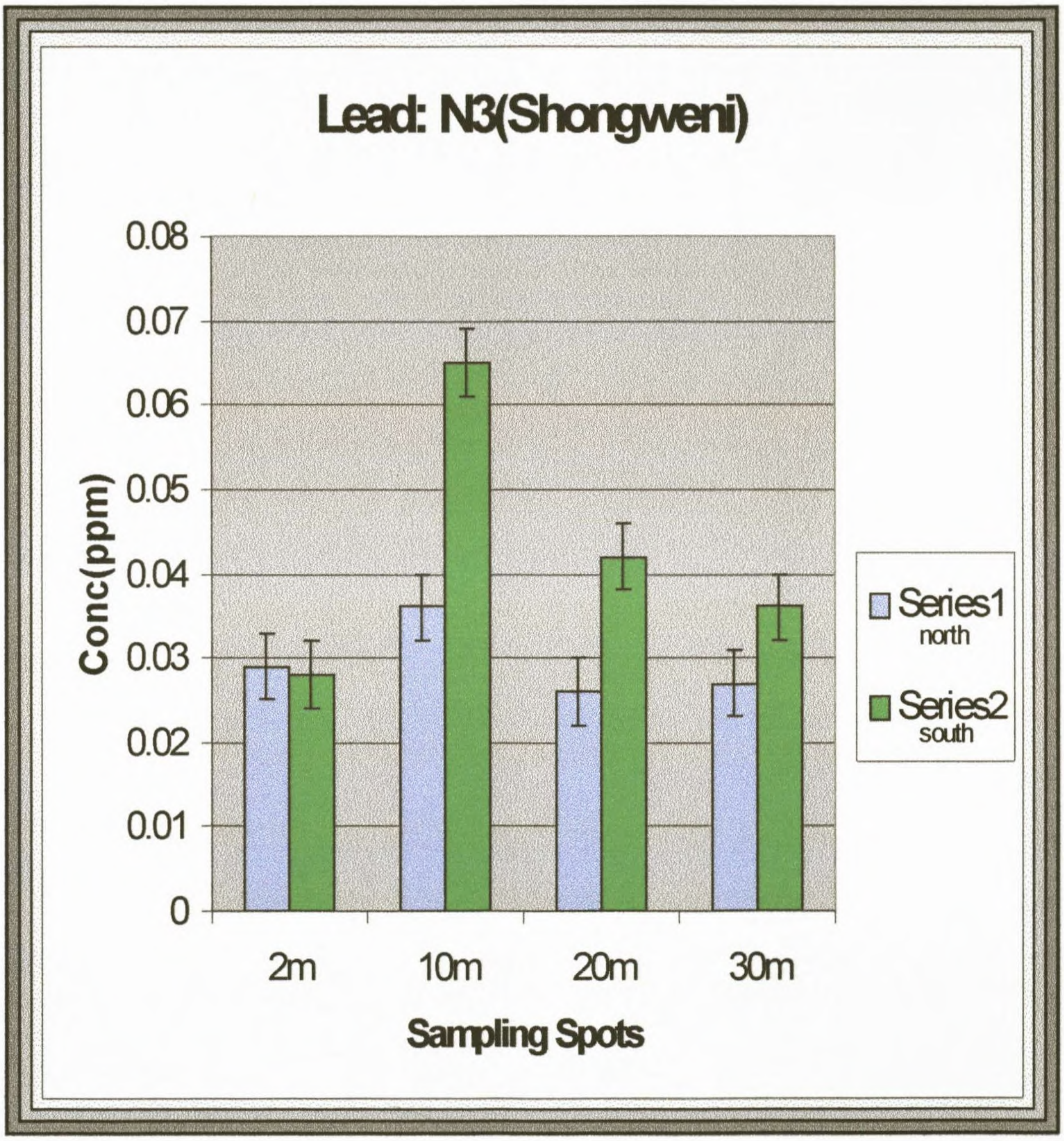

Figure 5.8: Pb results on leached samples analyzed by GF-AAS

The final sampling was done at points A, B, C and D along the N3 freeway in the same area next to Shongweni off-ramp. These points were separated by 20 m from one another. Samples were collected 1, 2, 4, 8 and 12 m at point A, these were labeled 1m-A, 2m-A, 4m-A, 8m-A and 12m-A respectively. The same was done for points B, C and D as shown in the sketch of the sampling site in Figure 5.9.

The full set of results is given in Appendix G1. Again, the concentration of lead on digested samples followed a decreasing trend where the highest concentration was for the sample collected 1 m from the edge of the road. This can clearly be seen on the samples collected at point C as shown in Figure 5.10. The concentration of the first sample labeled 1m-C is 923.31 ± 81.11 ppm, followed by samples 2m-C, 4m-C, 8m-C and 12m-C which are 674.99 ± 20.60, 193.36 ± 21.41, 171.89 ± 3.92 and 162.71 ± 8.46 ppm respectively. It has been noted that the concentrations of lead on the last samples at point A and B (samples 12m-A and 12m-B) are greater than the concentrations of lead for samples 8m-A and 8m-B. There is no logical explanation for this observation. Moreover, the concentration of lead for the sample that was taken 1 m away from the edge of the road at point D (sample 1m-D) is 407.82 ± 14.14 ppm. This is very low compared to concentration of lead on corresponding samples 1m-A, 1m-B and 1m-C which are 762.96 ± 76.30, 850.00 ± 54.85 and 923.31 ± 81.11 ppm respectively. It is noted that the concentrations of other metals analyzed in this study were also lower for point D compared to the other three points.

5.6.2 Rural road in Shongweni

This sampling site was chosen because it is a rural setting and experiences relatively lower traffic volume. It was hoped that the results of lead would provide an indication of vehicular contribution of this metal. The concentration of lead in the sample obtained from Shongweni rural area Route D356 which is used by relatively few vehicles was found to be 0.037 ± 0.002 ppm on leached samples and 0.79 ± 0.02 ppm on digested

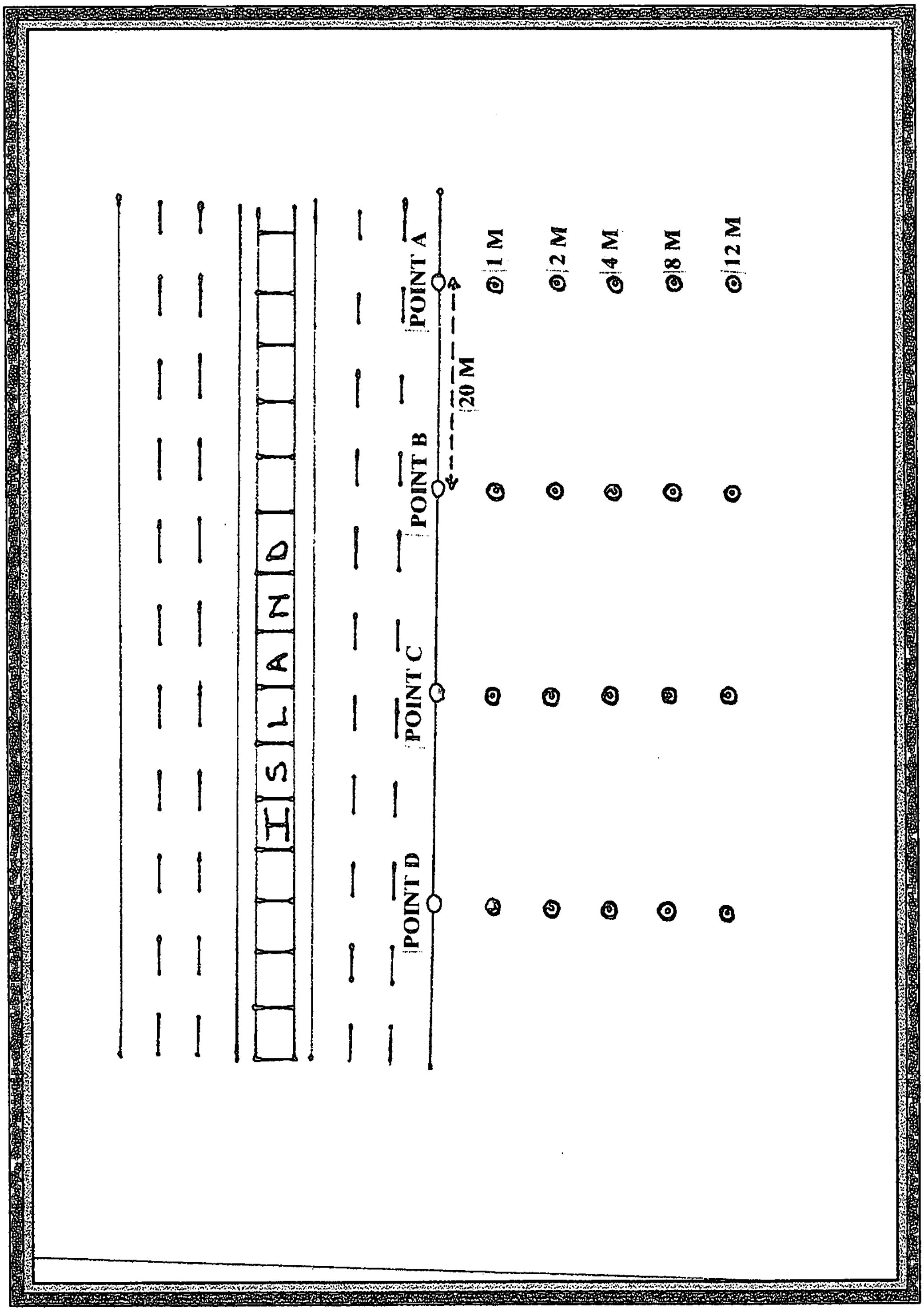

Figure 5.9: A sketch of site along the freeway (N3) near Shongweni off-ramp

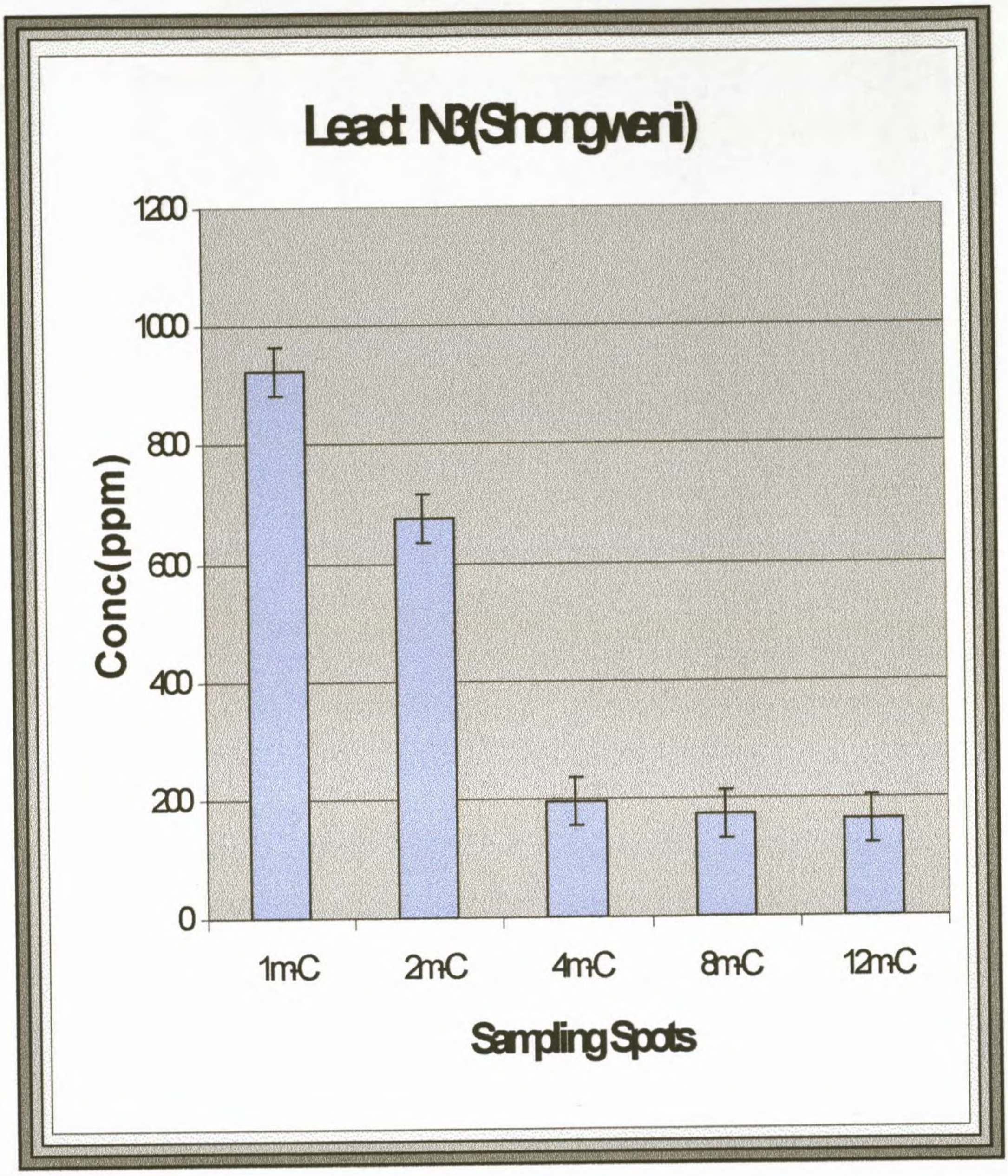

Figure 5.10: Pb results from N3 freeway near Shongweni off-ramp at point C

samples. This is very low as compared to the concentration of lead on leached and digested samples from all other sampling sites. This sample was collected with the first set of samples from the N3. Due to the low levels of lead, this analysis was done using GF-AAS.

5.6.3 Other metals on the site near Shongweni off-ramp

The other metals, namely, chromium, copper, nickel, cadmium and aluminium were also analyzed and the results are given in Appendices G3 to G13 . The concentration of these metals shows neither a decreasing nor an increasing trend. This may suggest that a large percentage of the concentration of these metals does not come from vehicles. The source could be natural abundance.

The levels of chromium were found to be within the range of the concentrations of metals in the surface of uncontaminated soils of the world that are shown in Table 5.4. Chromium ranges from 28.67 ± 3.86 to 79.51 ± 8.35 ppm in digested samples (see Appendix G3). This is within the range 20 to 100 ppm found for uncontaminated soils of the world [34]. On leached samples chromium concentrations were very low and did not follow any trend as shown by results in Appendix G4.

The levels of cadmium and nickel for the digested samples were outside the range of metals of uncontaminated soils of the world. These concentrations range from 4.18 ± 0.19 to 19.56 ± 1.02 ppm and 91.93 ± 9.53 to 270.31 ± 18.68 ppm respectively (see Appendices G5 and G7), whereas the range of concentrations of metals in uncontaminated soils is from 0.01 to 1.1 ppm for cadmium and 5 to 35 ppm for nickel as shown in Table 5.4. The observed concentrations of these two metals may be attributed to tyre and steel parts attrition respectively as explained in Chapter 2. Given the large traffic volume using this road (see Appendix A5) one would expect the levels to be high. The other aspect that should be considered is natural abundance of these elements in the soil.

As in all cases, the concentrations cadmium and nickel on leached samples were also low (see appendices G6 and G8). Once more, an independent trend is observed for cadmium on leached samples as shown in Figure 5.10 by using point B from Appendix G6.

Table 5.4: Heavy metals/metalloids in the surface of uncontaminated soils of the world [34]

	CONCENTRATION(mg/kg)	
METAL/METALLOID	MEAN	RANGE
Aluminium	71 000	-
Arsenic	8	0.7 - 30
Beryllium	0.3	-
Cadmium	0.5	0.01 - 1.1
Chromium	60	10 - 100
Copper	23	1 - 80
Lead	30	9 - 84
Manganese	550	10 - 1 500
Mercury	0.11	0.01 - 0.1
Nickel	20	5 - 35
Selenium	0.4	0.1 - 1.0
Silver	0.05	-
Tin	4	-
Uranium	2	-
Vanadium	87	10 - 460
Zinc	60	15 - 220

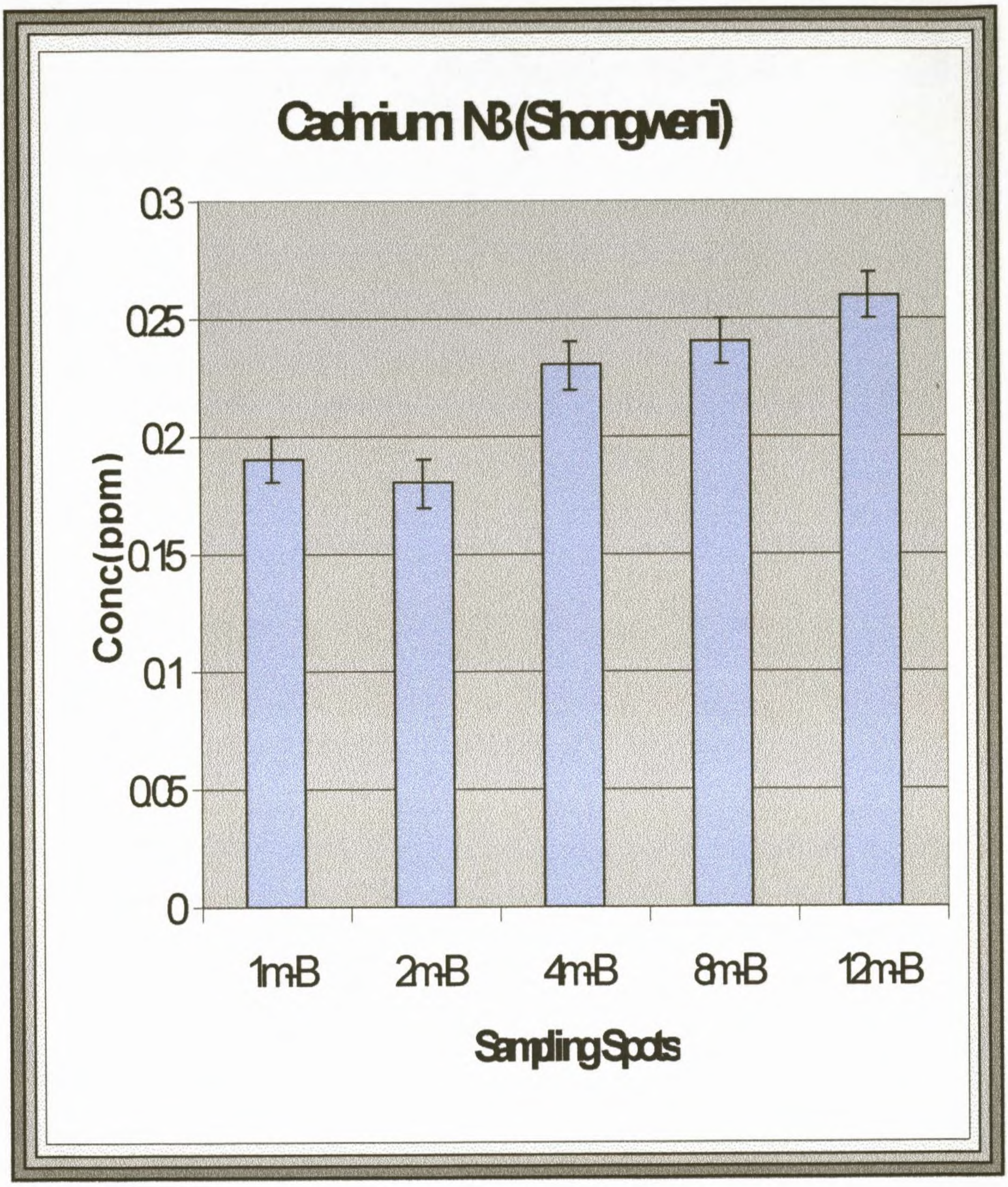

Figure 5.11: Cd results on leached samples analyzed by ICP-AES

The concentration of copper ranges from 3.10 ± 0.36 to 44.24 ± 8.38 ppm as shown in Appendix G9. This is also within the range 1 to 80 ppm from the uncontaminated soils of the world [34]. These concentrations show no trend. The sample labeled 1m-A which was collected 1 m from the edge of the road has the highest concentration. There is no significant difference between the concentrations of samples 2m-A and 4m-A. The concentration of sample 8m-A is less than the concentration of sample 12m-A.

Aluminium was found to have extremely high concentrations in soil. Its abundance on the earth's crust is 81 300 as shown in Table 5.5. The range of the concentration of this metal along the N3 freeway is from 5869.86 ± 280.00 to 37710.42 ± 460.97 ppm in digested samples where point A has the lowest concentration as shown in Appendix D11. The range of concentration on leached samples is from 3.42 ± 0.31 to 12.52 ± 1.78 ppm. No trend is observed in these results.

Table 5.5: Abundances of metals [29 and 35]

Metal	**Earth's crust(ppm)**
Aluminium	81 300
Chromium	122
Copper	68
Cadmium	0.16
Nickel	99

5.7 Vertical distribution of toxic metals along the N3 freeway near Shongweni off-ramp

Soil samples were also collected at varying depths from the surface to investigate the seepage of metals. These samples were collected from the site along the N3 freeway near Shongweni off-ramp. The sampling was done 1 m from the edge of the road and ± 2 cm, 10 to 15 cm and 20 to 25 cm deep at points A, B, C, D and E which are separated by 20 m from one another.

In order to compare the concentration of lead at each point on top soil a bar chart was plotted as shown in Figure 5.12. This plot represents the levels of lead on digested samples along the N3 freeway 1 m from the road as they appear in Appendix H1. As mentioned, these samples viz A-TOP, B-TOP, C-TOP, D-TOP and E-TOP were collected from top layers ± 2 cm deep at points A, B, C, D and E. The concentrations show a staggered kind of a situation where by point A has the lowest lead concentration. There is a reasonable difference between points B, C and E. Again, point D was expected to be more or less the same as points B, C and E but that it is not the case. It is puzzling to note that this time, point D has the highest concentration.

The concentration of lead in samples that were collected from 0 to 2 cm , 10 to 15 cm and 20 to 25 cm deep showed a decreasing trend with increasing depth. This is shown in Figures 5.13(a) and 5.13(b) which represent the concentrations of lead on digested samples from point A and point E respectively. There is no significant difference between the samples that were collected 10 to 15 cm and 20 to 25 cm for sampling spot A. The decrease was observed in samples from sampling spot E where the concentration of E-TOP is 1449.10 ± 46.49 ppm, and for E 10-15 and E20-25 are 294.93 ± 17.77 and 26.18 ± 5.16 ppm (see Appendix E1) respectively.

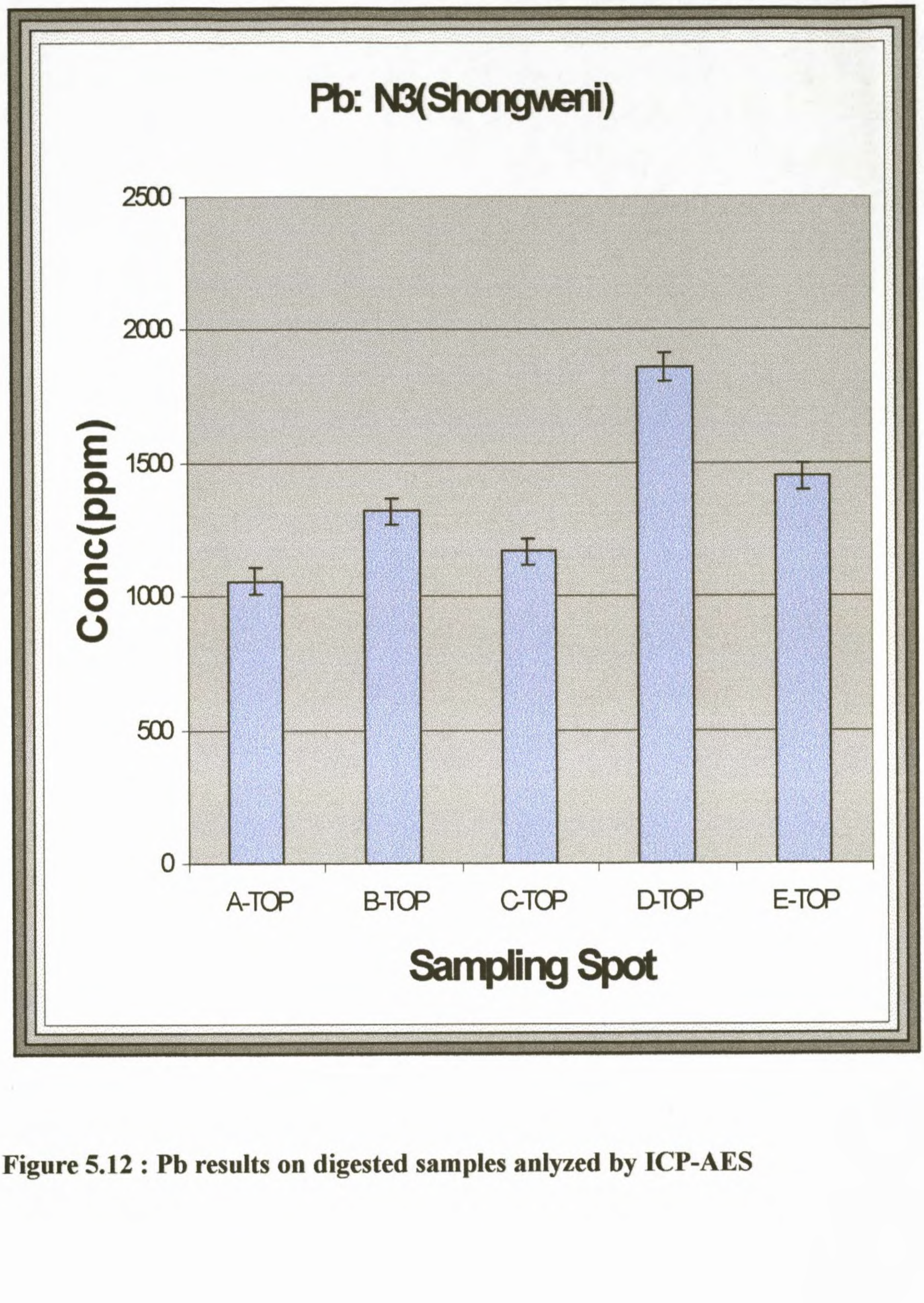

Figure 5.12 : Pb results on digested samples anlyzed by ICP-AES

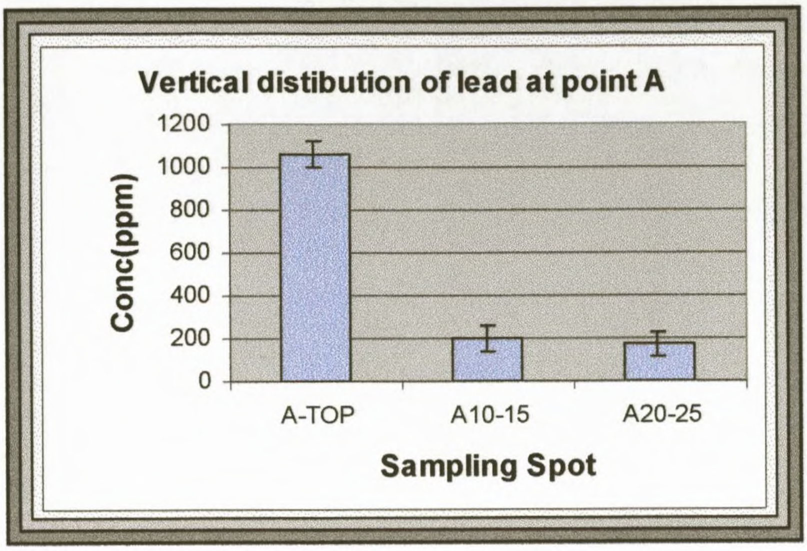

Figure 13(a): Pb result on digested samples at point A analyzed by ICP-AES

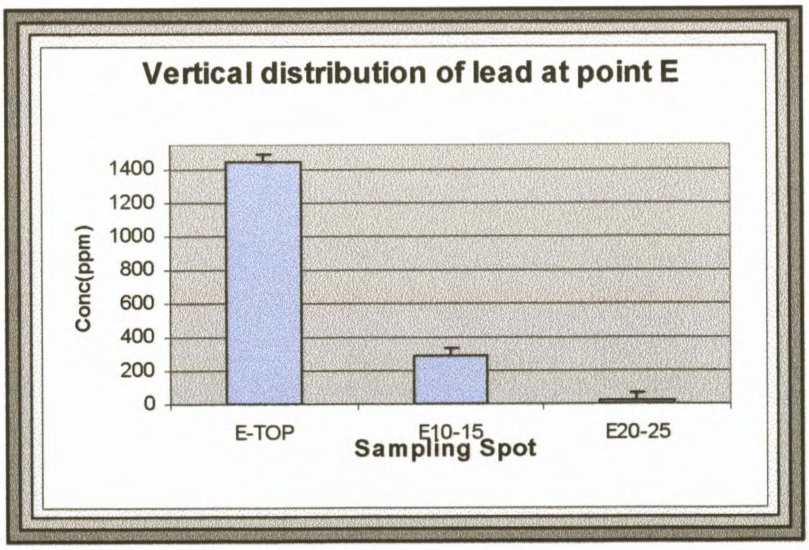

Figure 13(b): Pb result on digested samples at point E analyzed by ICP-AES

In general, the concentrations of the other metals viz lead, chromium, nickel, cadmium and copper were found to show decreasing trends on digested samples. This may suggest that these metals were deposited on the top layer. Since the pH of soil was found to be acidic in this area (see Table 6.1) it appears that a percentage of these metals may be carried downwards by rain water (see Appendices H1 to H112). Aluminium shows no trend at all (see Appendix H11).

The variations of concentrations of lead (on leached samples) with distance from the kerb show a conflicting trend. For instance, concentrations in samples A-TOP, A10-15 and A20-25 are 2.97 ± 0.49, 3.73 ± 0.33 and 4.34 ± 0.72 ppm respectively. This shows an increasing trend. On the other hand the concentrations of lead in the samples E-TOP, E10-15 and E20-25 are 8.78 ± 0.63, 5.21 ± 0.51 and 5.09 ± 0.37 ppm respectively (see Appendix H2). This shows a decreasing trend.

The concentrations of the rest of the metals in this analysis copper, nickel, cadmium, chromium and aluminium have shown an independent trend on leached samples. This is shown in Appendices H1 to H12.

Chapter 6

General discussions, conclusions and recommendations

As expected, the concentrations of the acid digested samples are higher than those of the parallel samples leached with acidic water. The process of digestion enables the analysis or determination of the total analyte, whereas leaching determines concentration of an analyte that is freely available. It is possible for available analytes such as metal to be washed by rain water in acidic soils, or run-off water from the acid rain which is a result of dissolved gases or fumes in the atmosphere; for example, sulphur dioxide and/or nitrogen dioxide that is emitted by industries.

The soil pH was measured in order to determine the acidity or basicity of the soil since these are the factors that influence the mobility of cations in the soil. Low pH values, low soil organic matter content, and the presence of ligands like chloride ions may increase the mobility of cations through soil. At high pH values, some metal ions may form insoluble hydroxides and carbonates [13 - 15]. The soil pH was found to be weakly acidic in all sampling sites with the pH range being 3.66 to 6.01 as shown in Table 6.1 on the next page.

The data shown in Appendices F1 to G12, is for, samples that were collected at varying distances from the edge of road. This serves to show the horizontal distribution of the total and leachable metal concentrations in kerb-side soils. The analysis of the data in Appendices H1 to H12 for samples that were collected by digging vertically into the soil shows the vertical distribution of metals that can take place due to seepage during heavy rains. Also, these may serve as an indication to the origin of the metals.

Dust samples were collected and analysed (result shown in Appendix D3) in order to determine the levels of the selected toxic metals that may be introduced into the body by inhaling dust particles in a given area. This was correlated to the traffic volume on that particular road and it may suggest that vehicles are a source of these toxic metals, mainly lead, on the side of the road.

Table 6.1: **pH values of soil samples**

SAMPLES FROM CENTENARY ROAD AND VICTORIA BUS RANK	
Sample	**pH value**
BRD	3.66
CTD	4.23
SAHD	4.45
SAMPLES FROM THE BOTANIC GARDENS	
BGED	4.40
BGPD	6.01
SAMPLES FROM THE N3 FREEWAY	
1m - A	5.30
1m - B	5.01
1m - C	4.32
1m - D	5.50
1m - E	3.99
SAMPLES FROM UMGENI ROAD	
4.6 m	4.19
10 m	4.35
13 m	4.25
Island	4.02
Umgudluli	3.98

6.1 Comparisons of the results from different sampling sites

6.1.1 Lead

The concentration of lead for the Centenary Road site which was selected for preliminary work ranges from 162.88 ± 0.85 to 337.18 ± 2.62 ppm (see Appendices D1 to D2). The concentrations decreased on the samples that were collected on the second visit. The dust samples from the site opposite Victoria Bus Rank were found to have concentrations ranging from 115.63 ± 11.66 to 250.90 ± 20.12 ppm (see Appendix D3). The range of concentration of lead for samples collected from Botanic Gardens was from 88.69 ± 1.07 to 93.93 ± 1.24 ppm (see Appendix E). There is no significant difference between the concentrations of lead in samples collected initially and those that were collected on the second visit. As mentioned in earlier chapters, samples were also collected from Umgeni/Goble Road intersection and the national freeway (N3) at varying distances from the edge of the road. The results obtained show that the concentration of lead on these two sites range from 177.59 ± 1.40 to 268.00 ± 2.60 and 103.15 ± 8.85 to 923.31 ± 81.11 ppm respectively (see Appendices F and G1). It can be concluded from the results that the national freeway (N3) site contains the highest concentrations of lead and this may be correlated to its high traffic volume.

As shown in Appendix G1 the levels of lead found at different sampling points along the N3 are as follows: 762.96 ± 76.30 to 103.15 ± 8.85 ppm at point A; 850.00 ± 54.85 to 120.08 ± 8.30 ppm at point B; 923.31 ± 81.11 to 162.71 ± 8.46 ppm at point C and 407.82 ± 14.14 to 143.53 ± 11.95 ppm at point D. This suggests that most of the lead emitted by vehicle exhausts settled on kerb-sides next to the road and some of it was blown or distributed by wind to areas further away from the kerb-sides. These levels are lower than the levels of lead in high traffic locations such as the City of Riyadh [19], which ranges between 4.09 and 1676.00 ppm. In many countries the permissible levels of lead concentration in soil amounts to approximately 100 ppm and in Great Britain 300 ppm [19].

The leachable amounts of lead in all of these sampling spots range from 1.45 ± 0.42 to 153.84 ± 5.43 ppm of which the lowest and the highest values of the range was obtained from the national freeway (N3) and Botanic Gardens respectively. This is the amount of lead that is readily available and may be washed by rain water or taken up by plants due to the acidic nature of the soil (see Table 6.1).

6.1.2 Chromium

The total content of chromium in all sampling sites ranges from 5.58 ± 0.17 to 82.15 ± 2.09 ppm of which the lowest levels were obtained from Umgeni/Goble Road island and the highest concentration was obtained from the island of Centenary Road. The concentrations of chromium for the rest of the sites are within this range. This is within the ranges of maximum metal concentrations allowed in soils treated with sewage sludge in different countries (see Table 6.2). Literature describe chromium as one of the elements that are used as heavy metal oxide additives along with organic materials and soot in the manufacture of tyres [36]. Hence, a considerable amount of chromium in kerb-side soil can be attributed to the wearing of tyres.

6.1.3 Cadmium

Cadmium has the lowest concentration range as expected, due to its unavailability or the low natural abundance of this element [25] (see Table 5.5). Its concentration ranges from 19.56 ± 1.02 to 0.43 ± 0.08 ppm in all sampling sites including the dust samples which had the lowest concentration in the range. The highest concentration was found in samples from the national freeway (N3).

Table 6.2: Maximum metal concentrations allowed in soils treated with sewage sludge in different countries (mg/kg) [45]

Country	Cd	Cr	Cu	Hg	Ni	Pb	Zn
European Union	1 - 3	100 - 150	50 - 140	1 - 1.5	30 - 75	50 - 300	150 - 300
France	2	150	100	1	50	100	300
Germany	1.5	100	60	1	50	100	200
Italy	3	150	100	-	50	100	300
UK	3	400	135	1	75	300	300
Denmark	0.5	30	40	0.5	15	40	100
Finland	0.5	200	100	0.2	60	60	150
Norway	1	100	50	1	30	50	150
Sweden	0.5	30	40	0.5	15	40	100
USA	20	1500	750	8	210	150	1400

The maximum permissible level of cadmium in soil in the Netherlands is 0.8 ppm and in many other European countries it is 3 ppm [16]. Inputs of this metal to road surfaces is widely associated with oil spills and tyre wear, and would therefore relate to vehicle volume and braking intensity [16]. In general, the concentrations of this in all sites show no trend. This could be due to the uneven transportation and distribution by run-off water.

The leachable levels of this element are even lower. The range is between 0.11 ± 0.08 and 5.53 ± 1.11 ppm for all sites, and is consistent with studies done by Ellis and Revitt in a collation of levels in sediments and surface runoff from different road types in N.W. London [25].

6.1.4 Nickel

The natural abundance of nickel is 99 ppm (see Table 5.5). This metal is used as an alloy in engine parts [36] including brake linings. Nickel is identified as one of the metals that are added to the atmosphere as a result of transport (see Table 6.4).

In general, the concentration of nickel is observed to be fluctuating in all sites. The range of the total content of this metal was found to be from 35.25 ± 2.71 to 270.31 ± 18.68 ppm. The lowest level of the range was from Botanic Gardens site and the highest was from the national freeway (N3). This is way above the maximum metal concentrations allowed in soils treated with sewage sludge in different countries (see Table 6.2). Also, the concentration of leached samples are more or less the same, that is, there is no significant difference in the levels of nickel on samples with respect to the sampling points.

6.1.5 Copper

Copper is one of the metals that are in soil due to natural abundance (see Table 5.5). Its density is as high as 8.933 g/mL. Literature reveals that emissions from vehicles have resulted in high levels of metals including copper in roadside soils [17]. For instance, copper results from the wear of bearings and bushings. Copper is also identified as one of the metals that are in the atmosphere as a result of transport (see Table 6.4).

The range of the total concentrations from the results of this element is from 8.84 ± 2.10 to 144.10 ± 7.75 ppm in all sampling sites of which the lowest level was obtained from Botanic Gardens site and the highest concentration was obtained from the freeway (N3). The leachable levels of this metal are fairly low in all sites. The range was found to be from 0.17 ± 0.03 to 48.92 ± 2.10 ppm which is outside the range 0.003 to 1.41 ppm shown by Ellis and Revitt in the concentrations ranges of some heavy metals in road sediments and stormwater runoff (see Table 6.4).

Table 6.3: Concentration ranges of some heavy metals in road sediments and stormwater runoff [25]

Metal	Location type	Road sediment levels ($\mu g/g$)	Storm water runoff (total) (mg/l)	Storm water runoff (soluble) ($\mu g/l$)
Pb	Motorway	130 - 10000	0.003 - 14.73	< 3 - 1200
	Urban/Residential	128 - 8300	0.25 - 26	10 - 1800
	Rural	5 - 3900	0.1 - 1.0	16
Zn	Motorway	44 - 480	0.01 - 22	< 15 - 1200
	Urban/Residential	13 - 1110	0.008 - 4.6	
	Rural	7.5 - 710	0.15 - 1.10	
Cd	Motorway	0.22 - 2.2	0.0005 - 13.73	< 0.5 - 5
	Urban/Residential	0.0034 - 10.1	0.0008 - 0.008	
	Rural	0.02 - 5.4		
Cu	Motorway	22 - 200	0.003 - 0.38	4 - 200
	Urban/Residential	25 - 3170	0.007 - 1.41	
	Rural	33 - 150	0.02 - 0.12	
Fe	Motorway	21000	0.67 - 440	0 - 500
	Urban/Residential	1400 - 128000	1.0 - 85	
	Rural	1300 - 43000	20 - 62	

6.1.6 Aluminium

Aluminium is the most natural abundant metal in the soil. This element is toxic as mentioned in earlier sections but it cannot be classified as a heavy metal since its density is only 2.698 g/mL. Moreover, this metal is not identified as one of the elements released into the atmosphere by means of transport (see Table 6.4). The concentration of this metal is high in all sites. The range is from 1821.11 ± 81.44 to 37673.89 ± 273.44 ppm. In general, the concentrations of aluminium in all sampling sites show no trend at all due to high natural abundance (see Table 5.5).

Table 6.4: Trace elements released into the atmosphere from human activities [9]

Element	**Coal and fuel power generation**	**Metal processing and smelting**	**Transport**	**Waste incineration**	**Aerosol sprays**
Aluminium		X		X	X
Vanadium	X	X	X		
Chromium	X	X	X	X	
Iron	X	X			
Nickel		X	X	X	
Copper	X	X	X	X	X
Cobalt		X	X		
Lead		X	X	X	
Zinc	X	X	X	X	X
Manganese	X	X	X		
Silver		X		X	
Cadmium		X	X	X	X

6.2 General conclusions and recommendations

Soil can serve as a good means of determining the levels of the selected toxic metals, mainly lead, especially when the site in question is fairly undisturbed. The reproducibility of results and the low coefficients of variations (%RSD) have supported the feasibility of using kerb-side soils as an indicator for metal pollution from vehicles. This helped to eliminate problems of sampling vehicular emissions associated with using aerosol samplers.

According to Durban Metro's Department of Environmental Health, South Africa does not have its own established maximum permissible values of metals in soil. Therefore the analysis of metals in soil may be useful in producing a data base and formulating permissible limits. On a national scale, the emission of lead from vehicles at the current time is diminishing because of the introduction of unleaded petrol or lower lead petrol. In the UK, the maximum permissible lead content of petrol is 0.4 g/l [19], but in 1985 it was reduced to its present value of 0.15 g/l. In the beginning of the year 1987, the lead content of gasoline produced in Saudi Arabia was reduced from 0.84 g/l to 0.6 g/l [19]. Around the year 1995, Saudi Arabia adopted a plan to phase out lead completely [19].

The indirect hazard for health due to metals from vehicular emission can be attributed to the acidic nature of the selected sites soil as shown in Table 6.1 and the high concentrations of leachable amounts of these elements that was determined on all sites. As mentioned, the acidic nature of soil enhances the mobility of cations which can enable the run-off water to wash and transport these metals to the surrounding rivers and dams, that are used by people from rural areas for domestic purposes. The other danger is that plant can up-take these metals and store the in the leaves and stems. Animals such as cows which ingest the contaminated plants at therefore liable to metal poisoning.

The horizontal distribution of metals shows that, depending on the density of the metal, the highest concentrations of metals are found next to the edge of the road. The concentrations of the metals decrease with distance from the kerb. The results obtained for vertical distribution of metals has shown a decreasing trend with increasing depth (see Appendices H1 to H12). This suggests that in addition to metals that are present in soil due to natural abundance there is another external source of these metals and this could possibly be vehicular emissions.

The direct hazard for health due to metals from vehicular emission can be gauged from the levels of these metals in dust samples collected from Market Street opposite Victoria Bus Rank (see Appendix D3). This area is highly populated by pedestrians, homeless people and hawkers who have stalls from which they sell a variety of "take away" meals. The dust particles containing toxic metals are bound to affect these people directly through inhalation and indirectly through the foods contaminated with the dust (see Appendix D3 for data).

The concentration of lead is very high at sites that have a relatively high traffic volume and low at sites that have little vehicular traffic. This can be shown by comparing a sample that was collected from Shongweni rural area with that from the freeway (N3). The former sample had lead concentration of 0.037 ppm (rounded off) on leached samples whereas samples from the freeway (N3) near Shongweni off ramp had concentrations as high as 4.97 ppm (rounded off) on leached samples.

For future work it is recommended that one needs to undertake the analysis of toxic metals in plants that grow on kerb-side soils, as these plants may take up a considerable amount of these metals in acidic soils. Also, the analyisis of toxic metals from the rivers in the vicinity of pollution "hot spots" could be of importance.

Remediation technologies are now available for treating metal contaminated soils. Although these remedies may not be realistic for kerb-side soils, it is important to take cognisance of their availability. These include ecological as well as engineering technologies [37] which may include steps such as soil excavation followed by washing and subsequent distribution of treated soils. However, soil removal is prohibitively expensive, so more cost effective in-situ technologies that would still be able to satisfy compliance requirements, especially those that are geared to restore the soil's quality and to protect human health, are highly desirable [38].

Another strategy that may be recommended involves immobilization of metals in soil. A number of workers [39 - 41] have investigated the effects of several factors on cation mobility. In all cases their work tends to show that low pH values, low soil organic matter content and the presence of ligands like chloride ions may increase the mobility of a cation through soil. There are several ways of achieving metal immobilization in soil. A common way is to add dolomitic lime, phosphates, or organic matter residues [38]. This could also be achieved by adding other natural or synthetic chemical additives that may not produce any detrimental by-product and would enhance soil ion-exchange capacity; for example, hydrous manganese oxide (HMO) exhibited the most potential in reducing Cd and Pb transfer from the soil to the soil solution and their eventual entry into the food chain via plant uptake [38]. A further option for soil remediation is metal desorption in soil; for example, the removal of metals from soil by the use of rhamnolipid biosurfactant [42]. Low pH values can be adjusted by the addition of limestone $CaCO_3$ or wood ashes [15].

The alternative to immobilization is phytoremediation. In this method plants are used to absorb contaminants from the soil and translocate them to the stems and leaves. These pollutants are then removed by harvesting the above-ground tissue for subsequent volume reduction (i.e. ashing) and storage [43].

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APPENDICES

Appendix A1

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Thursday 26 January 1995 from 06H30 to 17H30 at Centenary Road and Mansfield

(Weather : Fine School Holidays: No Comments: SR IS U/T TO MARKET RD. ASM)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
CARS						
Centenary (North)		3024	957	3981	5678	9659
Centenary (South)	784	4835	100	5719	4256	9975
Mansfield (West)	843		1232	2075	1741	3816
Total	1627	7859	2289	11775	11675	
HEAVIES						
Centenary (North)		148	13	161	303	464
Centenary (South)	25	228	4	257	205	462
Mansfield (West)	75		57	132	38	170
Total	100	376	74	550	546	
BUSES						
Centenary (North)		585	49	634	580	1214
Centenary (South)	163	397	31	591	670	1261
Mansfield (West)	183		85	268	212	480
Total	346	982	165	1493	1462	

Appendix A1 (Continued)

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Thursday 26 January 1995 from 06H30 to 17H30 at Centenary Road and Mansfield

(Weather : Fine School Holidays: No Comments: SR IS U/T TO MARKET RD. ASM)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
P.C.U.S.						
Centenary (North)		4490	1081	5571	7444	13015
Centenary (South)	1160	6085	170	7415	6006	13421
Mansfield (West)	1359		1516	2875	2241	5116
Total	2519	10575	2767	15861	15691	
ALL VEHICLES						
Centenary (North)		3757	1019	4776	6561	11337
Centenary (South)	972	5460	135	6567	5131	11698
Mansfield (West)	1101		1374	2475	1991	4466
Total	2073	9217	2528	13818	13683	

Appendix A2

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Tuesday 04 June 1996 from 06H00 to 18H30 at Market Road and Leopold street

(Weather : Fine School Holidays: No Comments: ACCIDENT 0611- 0615 TAXI BREAKDOWN 1325 - 1330. DELCA)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
CARS						
Market (North)		5772	3281	9053		9053
Leopold (East)	9625	16192		26537		27537
Total	9625	22684	3281	35590		
HEAVIES						
Market (North)		607	129	736		736
Leopold (East)	494	380		874		874
Total	494	987	129	1610		
BUSES						
Market (North)		196	189	385		385
Leopold (East)	364	1803		2167		2167
Total	364	1999	189	2552		

Appendix A2 (Continued)

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Tuesday 04 June 1996 from 06H00 to 18H30 at Market Road and Leopold street

(Weather : Fine School Holidays: No Comments: ACCIDENT 0611- 0615 TAXI BREAKDOWN 1325 - 1330. DELCA)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
P.C.U.S.						
Market (North)		7378	3917	11295		11295
Leopold (East)	11341	21278		32619		32619
Total	11341	28656	3917	43914		
ALL VEHICLES						
Market (North)		6575	3599	10174		10174
Leopold (East)	10483	19095		29578		29578
Total	10483	25670	3599	39752		

Appendix A3

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Thursday 26 January 1995 from 06H30 to 17H30 at Centenary Road and Alice street

(Weather : Fine School Holidays: No Comments: ASM)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
CARS						
Warwick (South)		4538	5635	10173		10173
Old Dutch (West)	2026	15232		17258		17258
Total	2026	19770	5635	27431		
HEAVIES						
Warwick (South)		207	403	610		610
Old Dutch (West)	62	690		752		752
Total	62	897	403	1362		
BUSES						
Warwick (South)		473	844	1317		1317
Old Dutch (West)	201	598		799		799
Total	201	1071	844	2116		

Appendix A3 (Continued)

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Thursday 26 January 1995 from 06H30 to 17H30 at Centenary Road and Alice street

(Weather : Fine School Holidays: No Comments: ASM)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
P.C.U.S.						
Warwick (South)		5898	8129	14027		14027
Old Dutch (West)	2552	17808		20360		20360
Total	2552	23706	8129	34387		
ALL VEHICLES						
Warwick (South)		5218	6882	12100		12100
Old Dutch (West)	2289	16520		18809		18809
Total	2289	21738	6882	30909		

Appendix A4

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Tuesday 18 July 1995 from 06H15 to 17H45 at Umngeni Road and Goble street

(Weather : Fine School Holidays: No Comments: S,E U/T 288,2 VEH ALL DAY RESP ASM)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
CARS						
Umngeni (North)	4751	11467	1627	17845	16018	33863
Umngeni (South)	455	10009	1383	11847	13836	25683
Goble (East)	1794	3789	4357	9940	10226	20166
Goble (West)	1652	4092	575	6319	5871	12190
Total	8652	29357	7942	45951	45951	
HEAVIES						
Umngeni (North)	196	555	22	773	847	1620
Umngeni (South)	15	586	30	631	659	1290
Goble (East)	77	16	217	310	241	551
Goble (West)	44	15	27	86	53	139
Total	332	1172	296	1800	1800	

Appendix A4 (Continued)

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Tuesday 18 July 1995 from 06H15 to 17H45 at Umngeni Road and Goble street

(Weather : Fine School Holidays: No Comments: S,E U/T 288,2 VEH ALL DAY RESP ASM)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
BUSES						
Umngeni (North)	8	1127		1135	1098	2233
Umngeni (South)		1090	9	1099	1140	2239
Goble (East)	13		4	17	18	35
Goble (West)	4	1		5		2
Total	25	2218	13	2256	2256	
P.C.U.S.						
Umngeni (North)	5159	14831	1671	21661	19908	41569
Umngeni (South)	485	13361	1461	15307	17434	32741
Goble (East)	1974	3821	4799	10594	10744	21338
Goble (West)	1748	4124	629	6501	5977	12478
Total	9366	36137	8560	54063	54063	

Appendix A4 (Continued)

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Tuesday 18 July 1995 from 06H15 to 17H45 at Umngeni Road and Goble street

(Weather : Fine School Holidays: No Comments: S,E U/T 288,2 VEH ALL DAY RESP ASM)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
ALL VEHICLES						
Umngeni (North)	4955	13149	1649	19753	17963	37716
Umngeni (South)	470	11685	1422	13577	15635	29212
Goble (East)	1884	3805	4578	10267	10485	20752
Goble (West)	1700	4108	602	6410	5924	12334
Total	9009	32747	8251	50007	50007	

Appendix A5

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Wednesday 18 September 1991 from 06H15 to 18H00 at N3 and Mariannhill road

(Weather : Fine School Holidays: No Comments: TWO WAY COUNT ON N3 AT MARIANNHILL ROAD JGB)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
CARS						
N3 (East)		5602		5602	5296	10898
N3 (West)		5296		5296	5602	10898
Total		10898		10898	10898	
HEAVIES						
N3 (East)		1013		1013	1093	2106
N3 (West)		1093		1093	1013	2106
Total		2106		2106	2106	
BUSES						
N3 (East)		24		24	31	55
N3 (West)		31		31	24	55
Total		55		55		55

Appendix A5 (Continued)

Traffic Volumes System - Total Analysis For All Vehicles

Counted on Wednesday 18 September 1991 from 06H15 to 18H00 at N3 and Mariannhill road

(Weather : Fine School Holidays: No Comments: TWO WAY COUNT ON N3 AT MARIANNHILL ROAD JGB)

ROAD	LEFT	STRAIGHT	RIGHT	APPROACHING	DEPARTING	2 WAY
P.C.U.S.						
N3 (East)		7676		7676	7544	15220
N3 (West)		7544		7544	7676	15220
Total		15220		15220	15220	
ALL VEHICLES						
N3 (East)		6639		6639	6420	13059
N3 (West)		6420		6420	6639	13059
Total		13059		13059	13059	

Appendix B1

AA-1275 Parameters for the analysis of Ni

Working conditions are fixed	
Lamp current	4 mA
Fuel	Acetylene
Support	air
Flame stoichiometry	oxidising
Working conditions are variable	
Wavelength	232.0 nm
Slit width	0.2 nm
Optimum working range	3 - 12 ppm

Appendix B2

AA-1275 Parameters for the analysis of Cu

Working conditions are fixed	
Lamp current	4 mA
Fuel	Acetylene
Support	air
Flame stoichiometry	oxidising
Working conditions are variable	
Wavelength	324.7 nm
Slit width	0.5 nm
Optimum working range	2 - 8 ppm

Appendix C1

GTA-95 Parameters for the analysis of cadmium

Step No.	Temp (^{0}C)	Time (s)	Gas flow (L/min)	Gas Type	Read Command
1	75	5	3	N_2	
2	90	60	3	N_2	
3	300	10	3	N_2	
4	300	2	0		
5	1800	0.9	0		yes
6	1800	2	0		yes
7	1800	1	3	N_2	

AA Instrument parameters	
Lamp current	4 mA
Spectral Bandwidth	0.5 nm
Wavelength	228.0 nm
Background correction	OFF

Appendix C2

GTA-95 Parameters for the analysis of chromium

Step No.	**Temp (^0C)**	**Time (s)**	**Gas flow (L/min)**	**Gas Type**	**Read Command**
1	75	5	3	N_2	
2	90	60	3	N_2	
3	1100	10	3	N_2	
4	1100	2	0		
5	2500	1.2	0		yes
6	2500	2	0		yes
7	2500	1	3	N_2	

AA Instrument parameters	
Lamp current	7 mA
Spectral Bandwidth	0.2 nm
Wavelength	357.9 nm
Background correction	OFF

Appendix C3

GTA-95 Parameters for the analysis of nickel

Step No.	**Temp (^0C)**	**Time (s)**	**Gas flow (L/min)**	**Gas Type**	**Read Command**
1	75	5	3	N_2	
2	90	60	3	N_2	
3	900	10	3	N_2	
4	900	2	0		
5	2400	1.2	0		yes
6	2400	2	0		yes
7	2400	1	3	N_2	

AA Instrument parameters	
Lamp current	4 mA
Spectral Bandwidth	0.2 nm
Wavelength	232.0 nm
Background correction	OFF

Appendix D1

Results on soil samples from Centenary road and the Victiora Bus Rank (First sampling)

Concentrations of Pb on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	162.50	162.96	163.17	162.88	0.34	0.21	162.88 ± 0.85
CTD	227.41	216.35	224.89	222.88	5.80	2.60	222.91 ± 14.40
SAHD	337.97	337.58	335.98	337.18	1.05	0.31	337.18 ± 2.62

Concentrations of Pb on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	71.19	72.45	70.76	71.47	0.88	1.23	71.47 ± 2.18
CTL	91.55	91.77	90.88	91.40	0.46	0.51	91.40 ± 1.15
SAHL	95.54	93.23	94.89	94.55	1.19	1.26	94.55 ± 2.96

Concentrations of Cr on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	81.32	83.00	82.12	82.15	0.84	1.02	82.15 ± 2.09
CTD	65.80	67.23	66.78	66.60	0.73	1.10	66.60 ± 1.82
SAHD	48.61	49.89	48.98	49.16	0.66	1.34	49.16 ± 1.64

Appendix D1 (Continued)

Concentrations of Cr on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	28.44	27.56	27.78	27.93	0.46	1.64	27.93 ± 1.14
CTL	17.36	16.00	16.7	16.69	0.68	4.08	16.69 ± 1.69
SAHL	15.06	17.96	16.67	16.56	1.45	8.77	16.56 ±3.61

Concentrations of Cd on digested samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	9.54	9.08	8.79	9.14	0.38	4.14	9.14 ±0.94
CTD	10.7	9.99	9.91	10.2	0.43	4.26	10.20 ± 1.08
SAHD	9.54	9.08	9.72	9.45	0.33	3.49	9.45 ± 0.82

Concentrations of Cd on leached samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	5.33	5.00	5.67	5.33	0.34	6.28	5.33 ± 0.83
CTL	4.15	3.92	4.08	4.05	0.12	2.91	4.05 ± 0.29
SAHL	5.03	5.89	5.67	5.53	0.45	8.08	5.53 ± 1.11

Concentrations of Ni on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	52.92	52.78	53.04	52.91	0.13	0.25	52.91 ± 0.32
CTD	43	45.78	45.56	44.78	1.55	3.45	44.78 ±3.84
SAHD	47.33	46.33	47.77	47.14	0.74	1.57	47.14 ± 1.83

Appendix D1 (Continued)

Concentrations of Ni on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	6.85	6.95	6.34	6.71	0.33	4.87	6.71 ± 0.81
CTL	6.60	6.67	6.23	6.50	0.24	3.64	6.50 ± 0.59
SAHL	8.30	9.45	8.90	8.88	0.58	6.47	8.88 ± 1.43

Concentrations of Cu on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	43.33	45.00	43.9	44.08	0.85	1.93	44.08 ± 2.11
CTD	36.58	36.87	36.98	36.81	0.21	0.56	36.81 ± 0.51
SAHD	44.56	44.17	45.00	44.58	0.42	0.93	44.58 ± 1.03

Concentrations of Cu on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	15.75	14.65	15.78	15.39	0.64	4.18	15.39 ± 1.60
CTL	31.60	32 .00	31.00	31.53	0.50	1.6	31.53 ± 1.25
SAHL	22.23	23.82	24.09	23.38	1.01	4.3	23.38 ± 2.50

Concentrations of Al on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	20000.00	20033.33	20009.10	20014.15	17.23	0.09	20014.15 ± 42.80
CTD	12667.1	12666.04	12656.10	12663.08	6.05	0.05	12663.08 ± 15.04
SAHD	11248.00	11250.00	11265.10	11254.36	9.35	0.08	11254.36 ± 23.23

Appendix D1 (Continued)

Concentrations of Al on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	3825.00	3800.00	3851.21	3825.40	25.61	0.67	3825.40 ± 63.62
CTL	1985.00	2000.00	1987.98	1990.99	7.94	0.40	1990.99 ± 19.73
SAHL	1065.00	1100.00	1067.00	1077.33	19.66	1.82	1077.33 ± 48.83

Appendix D2

Results on soil samples from Centenary road and the Victiora Bus Rank (Second sampling)

Concentrations of Pb on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	181.48	183.46	181.93	182.29	1.04	0.57	182.29 ± 2.58
CTD	245.67	241.50	242.89	243.35	2.12	0.87	243.35 ± 5.27
SAHD	213.46	210.89	212.89	212.41	1.35	0.64	212.41 ± 3.35

Concentrations of Pb on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	117.92	110.54	111.89	113.45	3.93	3.46	113.45 ± 9.76
CTL	156.11	151.75	153.67	153.84	2.19	1.42	153.84 ± 5.43
SAHL	123.78	121.9	122.67	122.78	0.95	0.77	122.78 ± 2.35

Concentrations of Cr on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	34.43	37.8	35.98	36.07	1.69	4.68	36.07 ± 4.19
CTD	71.49	72.31	72.00	71.93	0.41	0.58	71.93 ± 1.03
SAHD	75.9	77.78	76.54	76.74	0.96	1.25	76.74 ± 2.37

Appendix D2 (Continued)

Concentrations of Cr on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	23.14	20.02	21.98	21.71	1.58	7.26	21.71 ± 3.92
CTL	18.53	17.20	17.67	17.80	0.67	3.79	17.80 ± 1.68
SAHL	20.06	19.45	19.63	19.71	0.31	1.59	19.71 ± 0.78

Concentrations of Cd on digested samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	13.56	12.97	13.64	13.39	0.37	2.73	13.39 ± 0.91
CTD	8.2	6.11	8.1	7.47	1.18	15.78	7.47 ± 2.93
SAHD	9.98	9.23	8.79	9.33	0.60	6.45	9.33 ± 1.49

Concentrations of Cd on leached samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	3.38	3.70	3.67	3.58	0.18	4.93	3.58 ± 0.44
CTL	4.92	3.47	3.92	4.10	0.74	18.09	4.10 ± 1.84
SAHL	4.01	4.09	3.98	4.03	0.06	1.41	4.03 ± 0.14

Concentrations of Ni on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	63.75	60.54	61.87	62.05	1.61	2.6	62.05 ± 4.01
CTD	40.32	41.13	40.76	40.74	0.41	1.00	40.74 ± 1.01
SAHD	36.09	36.97	36.45	36.5	0.44	1.21	36.50 ± 1.10

Appendix D2 (Continued)

Concentrations of Ni on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	7.20	7.11	7.24	7.18	0.07	0.93	7.18 ± 0.17
CTL	5.45	5.13	5.28	5.29	0.16	3.03	5.29 ± 0.40
SAHL	6.50	6.71	6.45	6.55	0.14	2.11	6.55 ± 0.34

Concentrations of Cu on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	31.25	32.13	32.04	31.81	0.48	1.52	31.81 ± 1.20
CTD	45.83	41.50	43.21	43.51	2.18	5.01	43.51 ± 5.42
SAHD	41.78	42.00	41.56	41.78	0.22	0.53	41.78 ± 0.55

Concentrations of Cu on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	16.87	16.88	17.01	16.92	0.08	0.46	16.92 ± 0.19
CTL	24.35	22.4	22.56	23.10	1.08	4.69	23.10 ± 2.69
SAHL	22.75	22.12	22.13	22.33	0.36	1.62	22.33 ± 0.90

Concentrations of Al on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRD	12500	12509	12511.1	12506.7	5.89	0.05	12506.70 ± 14.64
CTD	16251.9	16250	16211.1	16237.66	23.03	0.14	16237.66 ± 57.21
SAHD	15208.3	15211	15231.8	15217.03	12.83	0.08	15217.03 ± 31.86

Appendix D2 (Continued)

Concentrations of Al on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BRL	1100.00	1087.98	1098.60	1095.53	6.57	0.60	1095.53 ± 16.33
CTL	2275.00	2276.02	2274.98	2275.33	0.59	0.03	2275.33 ± 1.48
SAHL	2734.09	2700	2756.98	2730.36	28.67	1.05	2730.36 ± 71.23

Appendix D3

Results on dust particles samples from the Victoria Bus rank

Concentrations of Pb on digested samples analyzed by the ICP - AES

Sample	**Concentration(ppm)**			**Average**	**SD**	**% RSD**	**95% CL**
p1	180.17	185.38	183.88	183.14	2.68	1.46	183.14 ± 6.66
p2	151.04	160.29	160.83	157.39	5.50	3.50	157.39 ± 13.67
p3	207.46	210.42	210.58	209.49	1.76	0.84	209.49 ± 4.37
p4	260.04	244.63	248.04	250.9	8.10	3.23	250.90 ± 20.12
p5	121.04	113.04	112.79	115.63	4.69	4.06	115.63 ± 11.66

Concentrations of Pb on leached samples analyzed by the ICP - AES

Sample	**Concentration(ppm)**			**Average**	**SD**	**% RSD**	**95% CL**
p1	3.56	1.88	2.12	2.52	0.91	36.13	2.52 ± 0.26
p2	2.02	2.02	2.34	2.12	0.18	8.63	2.12 ± 0.46
p3	2.33	2.33	2.18	2.28	0.09	3.87	2.28 ± 0.22
p4	2.34	2.27	2.26	2.29	0.05	1.98	2.29 ± 0.11
p5	2.11	2.17	2.3	2.19	0.10	4.44	2.19 ± 0.24

Concentrations of Cr on digested samples analyzed by the ICP - AES

Sample	**Concentration(ppm)**			**Average**	**SD**	**% RSD**	**95% CL**
p1	24.67	24.54	23.83	24.39	0.48	1.97	24.39 ± 1.20
p2	22.17	21.25	21.33	21.89	0.48	2.20	21.89 ± 1.20
p3	33.50	32.86	33.38	33.46	0.07	0.22	33.46 ± 0.18
p4	44.08	40.58	42.13	43.43	1.13	2.60	43.43 ± 2.81
p5	19.21	17.46	16.54	18.32	1.54	8.4	18.32 ± 3.82

Appendix D3 (Continued)

Concentrations of Cr on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	0.67	0.58	0.52	0.59	0.08	13.32	0.59 ± 0.19
p2	0.61	0.33	0.37	0.43	0.15	35.08	0.43 ± 0.38
p3	0.51	0.36	0.38	0.42	0.08	19.55	0.42 ± 0.20
p4	4.57	4.91	4.48	4.65	0.23	4.91	4.65 ± 0.57
p5	0.52	0.39	0.39	0.43	0.08	17.73	0.43 ± 0.19

Concentrations of Cd on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	0.28	0.18	0.14	0.20	0.07	36.06	0.20 ± 0.18
p2	0.14	0.16	0.16	0.15	0.01	7.53	0.15 ± 0.03
p3	0.14	0.16	0.15	0.15	0.01	6.67	0.15 ± 0.02
p4	0.15	0.13	0.14	0.14	0.01	7.14	0.14 ± 0.02
p5	0.14	0.15	0.15	0.15	0.01	3.94	0.15 ± 0.01

Concentrations of Cd on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	%RSD	95% CL
p1	ND						
p2	ND						
p3	ND						
p4	ND						
p5	ND						

ND = NOT DETECTED

Appendix D3(Continued)

Concentrations of Ni on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	58.29	61.29	59.21	59.60	1.54	2.58	59.60 ± 3.82
p2	60.58	57.17	62.92	60.22	2.89	4.8 0	60.22 ± 7.18
p3	82.25	82.38	86.79	83.81	2.59	3.09	83.81 ± 6.43
p4	104.63	94.67	96.71	98.67	5.26	5.33	98.67 ± 2.11
p5	47.25	48.50	46.88	47.54	0.85	1.79	47.54 ± 1.67

Concentrations of Ni on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	1.58	0.59	0.71	0.96	0.54	56.57	0.96 ± 0.34
p2	0.77	0.66	0.7	0.71	0.05	7.57	0.71 ± 0.13
p3	0.79	0.76	0.81	0.79	0.03	3.20	0.79 ± 0.06
p4	1.18	1.16	1.09	1.14	0.04	3.78	1.14 ± 0.11
p5	0.72	0.77	0.88	0.79	0.08	10.14	0.79 ± 0.20

Concentrations of Cu on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	33.92	33.58	33.38	33.63	0.27	0.81	33.63 ± 0.68
p2	23.75	23.17	23.00	23.31	0.39	1.69	23.31 ± 0.98
p3	49.88	50.46	52.00	50.78	1.10	2.16	50.78 ± 2.73
p4	85.25	79.83	82.17	72.42	19.62	27.09	72.42 ± 8.74
p5	27.42	28.71	26.21	27.44	1.25	4.56	27.44 ± 3.11

Appendix D3(Continued)

Concentrations of Cu on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	1.08	0.99	0.98	1.02	0.06	5.55	1.02 ± 0.14
p2	0.24	0.26	0.24	0.24	0.01	4.78	0.24 ± 0.03
p3	0.67	0.65	0.65	0.66	0.01	1.32	0.66 ± 0.02
p4	1.14	1.16	1.11	1.14	0.02	2.14	1.14 ± 0.06
p5	2.38	2.44	2.33	2.38	0.06	2.31	2.38 ± 0.14

Concentrations of Al on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	2241.25	2207.50	2187.50	2212.08	27.17	1.23	2212.08 ± 67.49
p2	2870.42	2793.33	2795.00	2819.58	44.03	1.56	2819.58 ± 109.39
p3	2707.08	2795.00	2872.92	2791.67	82.97	2.97	2791.67 ± 206.12
p4	3288.33	2690.00	3112.83	3030.14	307.47	10.15	3030.14 ± 763.86
p5	1857.08	1792.92	1813.33	1821.11	32.78	1.80	1821.11 ± 81.44

Concentrations of Al on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
p1	3.75	4.25	4.35	4.12	0.32	7.81	4.12 ± 0.80
p2	4.10	4.15	4.25	4.17	0.08	1.83	4.17 ± 0.19
p3	4.85	5.00	5.10	4.98	0.13	2.53	4.98 ± 0.31
p4	5.06	5.3	5.25	5.2	0.13	2.47	5.20 ± 0.32
p5	3.95	4.10	4.00	4.02	0.08	1.9.00	4.02 ± 0.19

Appendix E1

Results on soil samples from the Botanic Garden (First sampling)

Concentrations of Pb on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	92.77	92.12	93.45	92.78	0.67	0.72	92.78 ± 1.65
BGPD	89.04	88.83	88.98	88.95	0.11	0.12	88.95 ± 0.27

Concentrations of Pb on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	39.25	33.2	35.12	35.86	3.09	8.62	35.86 ± 7.68
BGPL	48.95	41.65	45.67	45.42	3.66	8.05	45.42 ± 9.08

Concentrations of Cr on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	37.58	38.98	37.76	38.11	0.76	2.00	38.11 ± 1.89
BGPD	45.14	44.78	44.36	44.76	0.39	0.87	44.76 ± 0.97

Concentrations of Cr on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	4.34	4.56	5.00	4.63	0.34	7.25	4.63 ± 0.83
BGPL	3.38	4.12	4.19	3.90	0.45	11.52	3.90 ± 1.12

Appendix E1(Continued)

Concentrations of Cd on digested samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	4.07	4.48	4.35	4.30	0.21	4.87	4.30 ± 0.52
BGPD	5.03	5.06	4.78	4.96	0.15	3.10	4.96 ± 0.38

Concentrations of Cd on leached samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	2.09	2.35	2.98	2.47	0.46	18.5	2.47 ± 1.14
BGPL	2.45	3	2.67	2.71	0.28	10.23	2.71 ± 0.69

Concentrations of Ni on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	97.85	102.42	100.89	100.39	2.33	2.32	100.39 ± 5.78
BGPD	97.85	95.38	97.13	96.79	1.27	1.31	96.79 ± 3.16

Concentrations of Ni on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	38.83	36.63	36.90	37.45	1.20	3.20	37.45 ± 2.98
BGPL	39.77	41.95	40.45	40.72	1.12	2.74	40.72 ± 2.77

Appendix E1 (Continued)

Concentrations of Cu on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	10.70	10.29	10.76	10.58	0.26	2.42	10.58 ± 0.64
BGPD	9.80	8.21	8.27	8.76	0.90	10.29	8.76 ± 2.24

Concentrations of Cu on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	5.07	4.28	4.34	4.56	0.44	9.64	4.56 ± 1.09
BGPL	3.45	3.10	3.13	3.23	0.19	6.01	3.23 ± 0.48

Concentrations of Al on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	9999.98	9996.14	10009.1	10001.70	6.66	0.07	10001.74 ± 16.55
BGPD	9978.78	9967.78	9981.76	9976.11	7.36	0.07	9976.11 ± 18.29

Concentrations of Al on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	994.98	989.45	991.78	992.07	2.78	0.28	992.07 ± 6.90
BGPL	1006.79	1018.01	1011.65	1012.15	5.63	0.56	1012.15 ± 13.98

Appendix E2

Results on soil samples from the Botanic Garden (Second sampling)

Concentrations of Pb on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	91.37	92.12	93.45	92.23	0.5	0.54	93.23 ± 1.24
BGPD	89.04	88.83	88.21	88.69	0.43	0.49	88.69 ± 1.07

Concentrations of Pb on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	39.55	38.98	39.68	39.30	0.35	0.90	39.30 ± 0.88
BGPL	48.23	46.65	45.98	47.19	1.56	3.30	47.19 ± 3.87

Concentrations of Cr on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	49.98	47.11	47.98	48.36	1.47	3.04	48.36 ± 3.66
BGPD	37.79	37.24	37.33	37.45	0.30	0.79	37.45 ± 0.73

Concentrations of Cr on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	11.89	12.00	11.34	11.74	0.35	3.01	11.74 ± 0.88
BGPL	13.23	12.00	13.09	12.77	0.67	5.27	12.77 ± 1.67

Appendix E2(Continued)

Concentrations of Cd on digested samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	0.30	0.41	0.40	0.37	0.06	16.44	0.37 ± 0.15
BGPD	1.21	1.13	1.18	1.17	0.04	3.44	1.17 ± 0.10

Concentrations of Cd on leached samples analyzed by the GF - AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	0.13	0.11	0.14	0.13	0.02	12.06	0.13 ± 0.04
BGPL	0.22	0.32	0.23	0.26	0.06	21.46	0.26 ± 0.14

Concentrations of Ni on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	38.90	37.86	38.12	38.29	0.54	1.41	38.29 ± 1.34
BGPD	35.98	35.78	34.00	35.25	1.09	3.09	35.25 ± 2.71

Concentrations of Ni on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	9.87	9.86	9.56	9.76	0.18	1.8	9.76 ± 0.89
BGPL	8.09	7.54	7.67	7.77	0.29	3.7	7.77 ± 1.56

Appendix E2(Continued)

Concentrations of Cu on digested samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	10.7	10.29	10.76	10.58	0.26	2.42	10.58 ± 0.64
BGPD	9.80	8.21	8.51	8.84	0.84	9.56	8.84 ± 2.10

Concentrations of Cu on leached samples analyzed by the AAS

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	5.07	4.28	4.75	4.70	0.40	8.45	4.70 ± 0.99
BGPL	3.45	3.1	3.87	3.47	0.39	11.10	3.47 ± 0.96

Concentrations of Al on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGED	10000.00	10009.80	10001.20	10003.7	5.33	0.05	10003.67 ± 13.23
BGPD	14583.3	14534.00	14524.00	14547.1	31.77	0.22	14547.11 ± 78.92

Concentrations of Al on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
BGEL	900.00	912.09	911.98	908.02	6.95	0.77	908.02 ± 17.26
BGPL	867.98	865.12	865.12	866.92	1.56	0.18	866.92 ± 3.89

Appendix F

Results on soil samples from Umgeni road next Goble road intersection

Concentrations of Pb on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	193.55	195.02	193.92	194.16	0.76	0.88	194.16 ± 1.90
ISLAND	201.87	200.98	198.98	200.61	1.48	1.46	200.61 ± 3.68
4.6 m	177.71	178.09	176.98	177.59	0.56	0.77	177.59 ± 1.40
10 m	247.11	248	245.98	247.03	1.01	1.24	247.03 ± 2.52
13 m	269.14	267.09	267.76	268.00	1.05	0.98	268.00 ± 2.60
Umgudluli	596.34	596.87	595.62	596.28	0.63	0.84	596.28 ± 1.56

Concentrations of Pb on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	100.89	99.98	102.66	101.18	1.36	1.58	101.18 ± 3.39
ISLAND	100.00	100.76	101.21	100.66	0.61	0.68	100.66 ± 1.52
4.6 m	100.98	97 .00	98.34	98.77	2.03	1.64	98.77 ± 5.03
10 m	149.76	150.98	152.01	150.92	1.13	1.08	150.92 ± 2.80
13 m	149.99	149.11	151.09	150.06	0.99	1.22	150.06 ± 2.46
Umgudluli	279.43	280	269.98	276.47	5.63	5.49	276.47 ± 13.98

Appendix F(Continued)

Concentrations of Cr on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	24.80	24.98	23.00	24.26	1.09	1.27	24.26 ± 2.72
ISLAND	5.56	5.65	5.52	5.58	0.07	0.19	5.58 ± 0.17
4.6 m	29.13	29.56	27.99	28.89	0.81	1.02	28.89 ± 2.02
10 m	22.64	23.00	25.76	23.8	1.71	1.76	23.80 ± 4.24
13 m	38.32	38.98	35.00	37.43	2.13	2.29	37.43 ± 5.30
Umgudluli	39.11	39.09	36.54	38.25	1.48	1.60	38.25 ± 3.67

Concentrations of Cr on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	2.6	2.74	1.99	2.44	0.40	0.59	2.44 ± 0.99
ISLAND	2.30	2.3	1.98	2.19	0.18	0.35	2.19 ± 0.46
4.6 m	2.00	1.89	1.76	1.88	0.12	0.26	1.88 ± 0.30
10 m	2.50	2.98	3.01	2.83	0.29	0.41	2.83 ± 0.71
13 m	2.27	2.89	3 .00	2.72	0.39	0.5	2.72 ± 0.98
Umgudluli	3.17	2.89	3.57	3.21	0.34	0.54	3.21 ± 0.85

Appendix F(Continued)

Concentrations of Cd on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	2.15	1.67	1.56	1.79	0.31	0.44	1.79 ± 0.78
ISLAND	2.82	2.98	3.11	2.97	0.15	0.29	2.97 ± 0.36
4.6 m	2.46	2.45	2.23	2.38	0.13	0.28	2.38 ± 0.32
10 m	2.18	2.12	2.34	2.21	0.11	0.26	2.21 ± 0.28
13 m	2.62	2.45	2.61	2.56	0.10	0.23	2.56 ± 0.24
Umgudluli	1.11	1.11	1.12	1.11	0.01	0.05	1.11 ± 0.01

Concentrations of Cd on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	1.06	1.09	1.2	1.12	0.07	0.2	1.12 ± 0.18
ISLAND	1.08	1.09	1.23	1.13	0.08	0.22	1.13 ± 0.21
4.6 m	1.00	1.89	0.98	1.29	0.52	0.70	1.29 ± 0.29
10 m	0.87	0.98	0.79	0.88	0.10	0.24	0.88 ± 0.24
13 m	1.02	1.09	0.96	1.02	0.07	0.19	1.02 ± 0.16
Umgudluli	0.61	0.63	0.69	0.64	0.04	0.15	0.64 ± 0.10

Appendix F(Continued)

Concentrations of Ni on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	108.3	104.98	105.9	106.39	1.71	1.41	106.39 ± 4.26
ISLAND	75	69.74	70.23	71.66	2.91	2.08	71.66 ± 7.22
4.6 m	104.77	102.23	107.00	104.67	2.39	2.62	104.67 ± 5.93
10 m	108.3	109.87	109.00	109.06	0.79	0.85	109.06 ± 1.95
13 m	112.57	110.98	115.09	112.88	2.07	2.30	112.88 ± 5.15
Umgudluli	85.45	90.00	87.94	87.8 0	2.28	1.89	87.80 ± 5.66

Concentrations of Ni on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	51.00	47.90	49.09	49.33	1.56	1.35	49.33 ± 3.89
ISLAND	56 .00	55.67	56.78	56.15	0.57	0.77	56.15 ± 1.42
4.6 m	45.02	40.89	46.11	44.01	2.75	2.91	44.01 ± 6.84
10 m	45.00	45.09	47.98	46.02	1.70	1.79	46.02 ± 4.21
13 m	55.66	54.98	53.00	54.55	1.38	1.41	54.55 ± 3.43
Umgudluli	29.16	30.98	28.65	29.60	1.22	1.42	29.60 ± 3.04

Appendix F(Continued)

Concentrations of Cu on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	31.09	31.23	33.09	31.8	1.12	1.25	31.80 ± 2.77
ISLAND	49.66	49.09	48.00	48.92	0.84	0.93	48.92 ± 2.10
4.6 m	26.33	26.98	27.98	27.10	0.83	0.9	27.10 ± 2.06
10 m	38.04	38.87	36	37.64	1.48	1.68	37.64 ± 3.67
13 m	28.26	28.54	27.98	28.26	0.28	0.47	28.26 ± 0.70
Umgudluli	15.08	14.33	14.87	14.76	0.39	0.54	14.76 ± 0.96

Concentrations of Cu on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	12.9	12.09	11.00	12 .00	0.95	0.99	12.00 ± 2.37
ISLAND	10.98	11 .00	11.83	11.27	0.49	0.66	11.27 ± 1.21
4.6 m	10.86	10.76	9.91	10.51	0.52	0.69	10.51 ± 1.30
10 m	10 .00	9.89	11.11	10.33	0.67	0.86	10.33 ± 1.68
13 m	10.23	11.99	11.03	11.08	0.88	0.92	11.08 ± 2.19
Umgudluli	2.63	1.78	2.09	2.17	0.43	0.54	2.17 ± 1.07

Appendix F(Continued)

Concentrations of Al on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	13333.32	13334.00	13345.00	13337.40	6.56	6.15	13337.44 ± 16.29
ISLAND	9375.09	9354.09	9393.09	9374.09	19.52	19.75	9374.09 ± 48.49
4.6 m	16350.98	16357.00	16345.00	16351.00	5.99	6.23	16350.99 ± 14.88
10 m	13958.90	13900.00	13911.00	13923.30	31.32	19.05	13923.29 ± 77.82
13 m	13650.00	13667.50	13655.90	13657.80	8.88	7.28	13657.77 ± 22.06
Umgudluli	12856.87	12876.1	12859.60	12864.20	10.41	9.32	12864.17 ± 25.86

Concentrations of Al on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
7 m (across)	1050.1	1109	1087	1082.03	29.77	19.77	1082.03 ± 73.95
ISLAND	1300	1278.8	1288.09	1288.96	10.63	7.57	1288.96 ± 26.40
4.6 m	998.5	967.09	976.43	980.67	16.13	10.46	980.67 ± 40.07
10 m	1006.2	1004.09	1012.9	1007.73	4.6	4.72	1007.73 ± 11.43
13 m	1200	1211.33	1232.54	1214.62	16.52	13.2	1214.62 ± 41.04
Umgudluli	1550	1554.89	1554.99	1553.29	2.85	2.03	1553.29 ± 7.09

Appendix G1

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Pb on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	789.88	769.5	729.5	762.96	30.71	4.03	762.96 ± 76.30
2m - A	187.67	179.5	178.21	181.79	5.13	2.82	181.79 ± 12.74
4m - A	190.42	194.71	188.17	191.1	3.32	1.74	191.10 ± 8.25
8m - A	106.79	103	99.67	103.15	3.56	3.46	103.15 ± 8.85
12m - A	160.75	166	162.92	163.22	2.64	1.62	163.22 ± 6.55
1m - B	828.1	872.25	849.65	850	22.08	2.6	850.00 ± 54.85
2m - B	296.17	296.17	293.63	295.32	1.47	0.5	295.32 ± 3.65
4m - B	191.33	203.88	201.58	198.93	6.68	3.36	198.93 ± 16.59
8m - B	116.42	122.96	120.88	120.08	3.34	2.78	120.08 ± 8.30
12m - B	145.5	146.46	147.46	146.47	0.98	0.67	146.47 ± 2.43
1m - C	943.21	941.08	885.63	923.31	32.65	3.54	923.31 ± 81.11
2m - C	683.17	675.21	666.58	674.99	8.29	1.23	674.99 ± 20.60
4m - C	191.88	202.63	185.58	193.36	8.62	4.46	193.36 ± 21.41
8m - C	172.58	170.08	173	171.89	1.58	0.92	171.89 ± 3.92
12m - C	158.92	163.7	165.65	162.71	3.4	2.09	162.71 ± 8.46
1m - D	409.92	401.38	412.17	407.82	5.69	1.4	407.82 ± 14.14
2m - D	163.5	156.08	156.13	158.57	4.27	2.69	158.57 ± 10.61
4m - D	194.63	198.17	191.92	194.9	3.13	1.61	194.90 ± 7.79
8m - D	152.25	146.67	150.5	149.81	2.86	1.91	149.81 ± 7.09
12m - D	140.21	141.33	149.04	143.53	4.81	3.35	143.53 ± 11.95

Appendix G2

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Pb on leached samples analyzed by the ICP - AES

Sample	**Concentration(ppm)**			**Average**	**SD**	**% RSD**	**95% CL**
1m - A	1.54	1.69	1.56	1.59	0.08	5	1.59 ± 0.20
2m - A	1.71	1.86	1.85	1.8	0.09	4.72	1.80 ± 0.21
4m - A	1.35	1.36	1.65	1.45	0.17	11.66	1.45 ± 0.42
8m - A	1.99	2.15	1.86	2	0.15	7.39	2.00 ± 0.37
12m - A	2.2	1.94	2.04	2.06	0.13	6.36	2.06 ± 0.33
1m - B	2.96	2.84	2.97	2.92	0.07	2.48	2.92 ± 0.18
2m - B	2.86	2.78	2.97	2.87	0.1	3.34	2.87 ± 0.24
4m - B	2.75	2.77	3.2	2.91	0.25	8.75	2.91 ± 0.63
8m - B	3.25	3.11	3.1	3.15	0.08	2.52	3.15 ± 0.20
12m - B	3.12	3.3	3.78	3.4	0.34	10.1	3.40 ± 0.85
1m - C	4.9	4.79	5.21	4.97	0.21	4.31	4.97 ± 0.53
2m - C	3.65	3.32	3.35	3.44	0.18	5.36	3.44 ± 0.46
4m - C	4.22	4.1	4.22	4.18	0.07	1.69	4.18 ± 0.18
8m - C	3.61	3.74	3.67	3.67	0.07	1.84	3.67 ± 0.17
12m - C	3.78	3.64	3.86	3.76	0.11	2.9	3.76 ± 0.27
1m - D	3.62	3.48	3.54	3.55	0.07	1.89	3.55 ± 0.17
2m - D	3.81	3.75	3.98	3.84	0.12	3.11	3.84 ± 0.30
4m - D	3.78	3.56	3.57	3.63	0.12	3.38	3.63 ± 0.31
8m - D	3.57	3.5	3.69	3.58	0.1	2.68	3.58 ± 0.24
12m - D	3.51	3.45	3.46	3.47	0.03	0.98	3.47 ± 0.08

Appendix G3

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Cr on digested samples analyzed by the ICP -AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	78.04	74.79	84.2	79.01	4.78	6.05	79.01 ± 11.88
2m - A	69.42	69.42	70.42	69.75	4.78	0.83	69.75 ± 1.43
4m - A	74	71.38	71	72.13	0.58	2.27	72.13 ± 4.06
8m - A	46	42.08	39.21	42.46	1.63	7.94	42.46 ± 8.37
12m - A	60.79	60.25	61.21	60.75	3.37	0.79	60.75 ± 1.19
1m - B	78.65	74.55	75.75	76.32	2.11	2.76	76.32 ± 5.24
2m - B	52.21	52.58	54.88	53.22	1.44	2.71	53.22 ± 3.59
4m - B	75.42	72.13	72.92	73.49	1.72	2.34	73.49 ± 4.27
8m - B	57.33	50.54	50.58	52.82	3.91	7.4	52.82 ± 9.71
12m - B	62.79	58.96	60.71	60.82	1.92	3.16	60.82 ± 4.77
1m - C	82.33	80.42	75.79	79.51	3.36	4.23	79.51 ± 8.35
2m - C	55.58	56.92	54.79	55.76	1.07	1.93	55.76 ± 2.67
4m - C	65.45	68.54	68	67.33	1.65	2.44	67.33 ± 4.09
8m - C	71.25	68.25	74.4	71.3	3.08	4.32	71.30 ± 7.65
12m - C	52.5	53.58	52.08	52.72	0.77	1.47	52.72 ± 1.92
1m - D	45.92	45.38	45.58	45.63	0.27	0.6	45.63 ± 0.68
2m - D	30.46	27.83	27.7	28.67	1.55	5.42	28.67 ± 3.86
4m - D	61.67	62.92	60.29	61.63	1.31	2.13	61.63 ± 3.26
8m - D	70.88	69.42	66.58	68.96	2.18	3.16	68.96 ± 5.42
12m - D	58.38	62.63	58	59.67	2.57	4.31	59.67 ± 6.38

Appendix G4

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Cr on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	0.27	0.28	0.29	0.28	0.01	3.76	0.28 ± 0.03
2m - A	0.33	0.32	0.4	0.35	0.04	12.87	0.35 ± 0.11
4m - A	0.28	0.3	0.3	0.29	0.01	3.57	0.29 ± 0.03
8m - A	0.37	0.33	0.33	0.34	0.02	5.91	0.34 ± 0.05
12m - A	0.42	0.33	0.37	0.37	0.04	11.44	0.37 ± 0.11
1m - B	0.54	0.47	0.44	0.48	0.05	10.82	0.48 ± 0.13
2m - B	0.43	0.45	0.42	0.43	0.02	3.57	0.43 ± 0.04
4m - B	0.54	0.4	0.39	0.44	0.08	18.92	0.44 ± 0.21
8m - B	0.5	0.41	0.42	0.44	0.05	11.86	0.44 ± 0.13
12m - B	0.55	0.44	0.41	0.47	0.08	16.27	0.47 ± 0.19
1m - C	0.66	0.66	0.66	0.66	0	0.61	0.66 ± 0.01
2m - C	0.5	0.44	0.47	0.47	0.03	5.9	0.47 ± 0.07
4m - C	0.59	0.52	0.54	0.55	0.03	6.23	0.55 ± 0.08
8m - C	0.56	0.47	0.51	0.51	0.05	8.87	0.51 ± 0.11
12m - C	0.54	0.48	0.52	0.51	0.03	5.56	0.51 ± 0.07
1m - D	0.51	0.45	0.45	0.47	0.03	6.66	0.47 ± 0.08
2m - D	0.51	0.49	0.52	0.51	0.01	2.97	0.51 ± 0.04
4m - D	0.46	0.52	0.51	0.49	0.03	6.75	0.49 ± 0.08
8m - D	0.5	0.48	0.55	0.51	0.04	7	0.51 ± 0.09
12m - D	0.56	0.54	0.46	0.52	0.05	10.34	0.52 ± 0.13

Appendix G5

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Cd on digested samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	6.54	5.46	9.04	7.01	1.84	26.2	7.01 ± 0.57
2m - A	18.2	18.21	17.49	17.96	0.43	2.41	17.96 ± 1.08
4m - A	19.79	18.17	16.58	18.18	1.60	8.82	18.18 ± 3.99
8m - A	10.67	9.58	9.79	10.01	0.57	5.74	10.01 ± 1.43
12m - A	14.96	14.79	14.63	14.79	0.17	1.13	14.79 ± 0.41
1m - B	4.10	4.25	4.20	4.18	0.08	1.83	4.18 ± 0.19
2m - B	10.83	10.83	11.04	10.90	0.12	1.10	10.90 ± 0.30
4m - B	19.83	19.08	19.75	19.56	0.41	2.10	19.56 ± 1.02
8m - B	12.88	11.88	12.13	12.29	0.52	4.23	12.29 ± 1.29
12m - B	14.92	14.58	14.2	14.57	0.35	2.43	14.57 ± 0.88
1m - C	6.42	6.38	6.17	6.32	0.13	2.12	6.32 ± 0.33
2m - C	11.92	11.04	10.92	11.29	0.54	4.83	11.29 ± 1.35
4m - C	13.67	12.92	12.42	13.00	0.63	4.84	13.00 ± 1.56
8m - C	18.17	17.04	18.38	17.86	0.72	4.02	17.86 ± 1.78
12m - C	12.54	11.71	12.21	12.15	0.42	3.45	12.15 ± 1.04
1m - D	4.80	4.88	4.58	4.75	0.15	3.20	4.75 ± 0.38
2m - D	6.29	5.79	6.39	6.16	0.32	5.21	6.16 ± 0.80
4m - D	16.04	15.58	15.75	15.79	0.23	1.47	15.79 ± 0.58
8m - D	16.17	16.13	16.13	16.17	0.05	0.33	16.17 ± 0.13
12m - D	14.54	13.49	14.63	14.39	0.35	2.40	14.39 ± 0.86

Appendix G6

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Cd on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	0.12	0.13	0.13	0.12	0.01	6.19	0.12 ± 0.02
2m - A	0.13	0.13	0.12	0.12	0.00	2.34	0.12 ± 0.01
4m - A	0.10	0.10	0.09	0.11	0.03	8.36	0.11 ± 0.08
8m - A	0.11	0.13	0.13	0.12	0.01	7.22	0.12 ± 0.02
12m - A	0.13	0.12	0.12	0.12	0.01	4.68	0.12 ± 0.01
1m - B	0.20	0.19	0.18	0.19	0.01	4.82	0.19 ± 0.02
2m - B	0.14	0.15	0.26	0.18	0.06	35.07	0.18 ± 0.16
4m - B	0.23	0.21	0.24	0.23	0.02	8.01	0.23 ± 0.04
8m - B	0.22	0.22	0.28	0.24	0.03	14.07	0.24 ± 0.08
12m - B	0.25	0.26	0.26	0.26	0.01	1.96	0.26 ± 0.01
1m - C	0.37	0.37	0.37	0.37	0.00	0.00	0.37 ± 0.00
2m - C	0.27	0.28	0.28	0.28	0.01	3.15	0.28 ± 0.02
4m - C	0.28	0.3	0.29	0.29	0.01	4.36	0.29 ± 0.03
8m - C	0.27	0.26	0.28	0.27	0.01	3.88	0.27 ± 0.03
12m - C	0.29	0.25	0.28	0.27	0.02	7.62	0.27 ± 0.05
1m - D	0.24	0.25	0.24	0.24	0.01	4.10	0.24 ± 0.02
2m - D	0.27	0.30	0.29	0.28	0.02	5.42	0.28 ± 0.04
4m - D	0.28	0.30	0.29	0.29	0.01	3.51	0.29 ± 0.02
8m - D	0.28	0.26	0.29	0.27	0.01	4.60	0.27 ± 0.03
12m - D	0.27	0.28	0.28	0.27	0.01	2.13	0.27 ± 0.01

Appendix G7

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Ni on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	153.33	144.58	147.38	148.43	4.47	3.01	148.43 ± 11.10
2m - A	247.5	250.21	250.96	249.56	1.82	0.73	249.56 ± 4.52
4m - A	241.83	235.88	251.79	243.17	8.04	3.31	243.17 ± 19.98
8m - A	152.96	146.00	160.13	153.03	7.06	4.62	153.03 ±17.55
12m - A	223.75	218.08	225.5	222.44	3.88	1.74	222.44 ± 9.63
1m - B	132.50	131.20	113.90	125.87	10.38	8.25	125.87 ± 25.80
2m - B	180.21	189.67	184.54	184.81	4.73	2.56	184.81 ± 11.76
4m - B	261.63	274.67	274.63	270.31	7.52	2.78	270.31 ± 18.68
8m - B	197.54	202.08	194.21	197.94	3.95	2.00	197.94 ± 9.82
12m - B	234.58	220.79	221.00	225.46	7.90	3.51	225.46 ± 19.63
1m - C	168.79	166.21	166.63	167.21	1.39	0.83	167.21 ± 3.45
2m - C	192.42	206.75	199.00	199.39	7.17	3.60	199.39 ± 17.82
4m - C	212.46	224.00	219.29	218.58	5.80	2.65	218.58 ± 14.42
8m - C	247.29	249.83	250.42	249.18	1.66	0.67	249.18 ± 4.13
12m - C	196.08	194.25	198.08	196.14	1.92	0.98	196.14 ± 4.76
1m - D	129.71	125.04	127.13	127.29	2.34	1.84	127.29 ± 5.81
2m - D	96.25	88.92	90.63	91.93	3.84	4.17	91.93 ± 9.53
4m - D	223.71	219.75	206.79	216.75	8.85	4.08	216.75 ± 21.98
8m - D	248.21	253.38	244.58	248.72	4.42	1.78	248.72 ± 10.98
12m - D	218.88	216.42	229.46	221.58	6.93	3.13	221.58 ± 17.22

Appendix G8

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Ni on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95%CL
1m - A	1.13	1.25	1.12	1.17	0.07	6.32	1.17 ± 0.18
2m - A	1.28	1.25	1.18	1.23	0.05	4.22	1.23 ± 0.13
4m - A	1.06	0.97	1.07	1.03	0.06	5.62	1.03 ± 0.14
8m - A	1.19	1.23	1.33	1.25	0.07	5.77	1.25 ± 0.18
12m - A	1.23	0.63	0.77	0.88	0.32	36.1	0.88 ± 0.78
1m - B	1.18	1.15	1.07	1.14	0.06	4.90	1.14 ± 0.14
2m - B	1.02	0.96	1.22	1.06	0.14	13.07	1.06 ± 0.35
4m - B	1.28	1.29	1.40	1.32	0.07	4.95	1.32 ± 0.16
8m - B	1.32	1.44	1.48	1.41	0.08	5.85	1.41 ± 0.20
12m - B	1.44	1.42	1.55	1.47	0.07	4.89	1.47 ± 0.18
1m - C	2.21	2.33	2.28	2.27	0.06	2.75	2.27 ± 0.16
2m - C	1.55	1.50	1.64	1.56	0.07	4.69	1.56 ± 0.18
4m - C	1.6	1.76	1.68	1.68	0.08	4.78	1.68 ± 0.20
8m - C	1.56	1.57	1.62	1.58	0.03	2.04	1.58 ± 0.08
12m - C	1.69	1.61	1.59	1.63	0.05	3.08	1.63 ± 0.12
1m - D	1.43	1.42	1.44	1.43	0.01	0.76	1.43 ± 0.03
2m - D	1.55	1.70	1.53	1.59	0.09	5.85	1.59 ± 0.23
4m - D	1.58	1.56	1.65	1.59	0.05	2.92	1.59 ± 0.12
8m - D	1.52	1.52	1.55	1.53	0.02	1.00	1.53 ± 0.04
12m - D	1.56	1.64	1.63	1.61	0.05	2.82	1.61 ± 0.11

Appendix G9

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Cu on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	36.08	33.17	36.04	35.1	1.67	4.76	35.10 ± 4.15
2m - A	17.08	17.04	16.29	16.81	0.45	2.65	16.81 ± 1.11
4m - A	16.25	16.00	15.29	15.85	0.50	3.14	15.85 ± 1.23
8m - A	8.46	8.46	7.42	8.11	0.60	7.41	8.11 ± 1.49
12m - A	12.38	12.46	11.67	12.17	0.44	3.58	12.17 ± 1.08
1m - B	40.85	41	42.4	41.42	0.85	2.06	41.42 ± 2.12
2m - B	11.96	12.13	12.13	12.07	0.10	0.80	12.07 ± 0.24
4m - B	13.19	12.71	13.83	13.24	0.57	4.27	13.24 ± 1.41
8m - B	6.79	6.33	6.54	6.56	0.23	3.50	6.56 ± 0.57
12m - B	9.67	9.00	9.38	9.35	0.33	3.58	9.35 ± 0.83
1m - C	47.63	40.88	44.21	44.24	3.38	7.63	44.24 ± 8.38
2m - C	10.79	11.08	10.67	10.85	0.21	1.97	10.85 ± 0.53
4m - C	22.67	21.92	19.71	21.43	1.54	7.18	21.43 ± 3.82
8m - C	8.04	8.67	8.04	8.25	0.36	4.37	8.25 ± 0.90
12m - C	7.50	7.83	7.88	7.74	0.21	2.66	7.74 ± 0.51
1m - D	11.38	12.04	11.71	11.71	0.33	2.85	11.71 ± 0.83
2m - D	2.96	3.25	3.08	3.10	0.15	4.72	3.10 ± 0.36
4m - D	9.79	9.13	9.04	9.32	0.41	4.41	9.32 ± 1.02
8m - D	8.25	8.71	7.63	8.19	0.54	6.64	8.19 ± 1.35
12m - D	6.29	6.79	6.71	6.60	0.27	4.06	6.60 ± 0.67

Appendix G10

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Cu on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	0.43	0.39	0.40	0.40	0.02	5.18	0.40 ± 0.05
2m - A	0.18	0.21	0.21	0.20	0.01	7.34	0.20 ± 0.04
4m - A	0.16	0.18	0.18	0.17	0.01	7.78	0.17 ± 0.03
8m - A	0.17	0.17	0.17	0.17	0.00	1.73	0.17 ± 0.01
12m - A	0.15	0.21	0.24	0.20	0.05	22.88	0.20 ± 0.11
1m - B	0.63	0.7	0.68	0.67	0.03	5.15	0.67 ± 0.09
2m - B	0.31	0.33	0.41	0.35	0.05	15.01	0.35 ± 0.13
4m - B	0.37	0.40	0.41	0.39	0.02	5.36	0.39 ± 0.05
8m - B	0.41	0.43	0.42	0.42	0.01	2.41	0.42 ± 0.02
12m - B	0.44	0.4	0.43	0.42	0.02	4.92	0.42 ± 0.05
1m - C	0.81	0.82	0.84	0.83	0.01	1.74	0.83 ± 0.04
2m - C	0.45	0.43	0.46	0.44	0.02	3.46	0.44 ± 0.04
4m - C	0.50	0.49	0.52	0.5	0.01	2.65	0.50 ± 0.03
8m - C	0.42	0.40	0.42	0.41	0.01	2.79	0.41 ± 0.03
12m - C	0.46	0.43	0.43	0.43	0.02	4.12	0.43 ± 0.04
1m - D	0.46	0.46	0.46	0.46	0.00	0.00	0.46 ± 0.00
2m - D	0.44	0.43	0.44	0.44	0.01	1.74	0.44 ± 0.02
4m - D	0.42	0.39	0.42	0.40	0.02	4.33	0.40 ± 0.04
8m - D	0.41	0.41	0.41	0.40	0.00	0.72	0.40 ± 0.01
12m - D	0.37	0.38	0.37	0.38	0.01	2.31	0.38 ± 0.02

Appendix G11

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Al on digested samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	5971.67	5748.75	5889.17	5869.86	112.71	1.92	5869.86 ± 280.00
2m - A	30181.25	30165.42	30335.42	30227.36	93.91	0.31	30227.36 ± 233.31
4m - A	37613.33	37669.17	37460.83	37581.11	107.84	0.29	37581.11 ± 267.91
8m - A	22616.25	21725.42	21727.48	22022.92	513.84	2.33	22022.92 ± 1276.56
12m - A	32525.42	33831.67	31826.67	32727.92	1017.72	3.11	32727.92 ± 2528.37
1m - B	7073.5	7016	7148	7079.17	66.18	0.93	7079.17 ± 164.42
2m - B	25090.42	25880	26500	25823.47	706.49	2.74	25823.47 ± 1755.16
4m - B	37590.83	37924.17	37616.25	37710.42	185.55	0.49	37710.42 ± 460.97
8m - B	29647.08	28347.33	28714.58	28903.33	669.63	2.32	28903.33 ± 1663.59
12m - B	35557.5	32825.42	32825.42	34087.5	1377.86	4.04	34087.50 ± 3423.06

Appendix G11(Continued)

Sample	**Concentration(ppm)**			**Average**	**SD**	**% RSD**	**95% CL**
1m - C	14337.92	14051.25	14612.5	14333.89	280.65	1.96	14333.89 ± 697.22
2m - C	27354.58	28230.42	27551.27	27712.08	459.53	1.66	27712.08 ± 1141.64
4m - C	31242.08	31829.17	30066.67	31045.97	897.47	2.89	31045.97 ± 2229.61
8m - C	37678.33	37781.67	37561.67	37673.89	110.07	0.29	37673.89 ± 273.44
12m - C	37561.67	29470.83	29234.58	32089.03	4740.92	14.77	32089.03 ± 11778.04
1m - D	13915.83	14327.92	14341.67	14195.14	241.98	1.70	14195.14 ± 601.17
2m - D	16950.00	16205.42	16565	16573.47	372.36	2.25	16573.47 ± 925.08
4m - D	375950	37417.08	37552.92	37521.67	92.98	0.25	37521.67 ± 231.00
8m - D	37897.5	37605.83	36960	37487.78	479.77	1.28	37487.78 ± 1191.91
12m - D	37504.17	36636.67	37516.67	37219.17	504.5	1.36	37219.17 ± 1253.34

Appendix G12

Results on soil samples from the N3 freeway next to Shongweni off-ramp

Concentrations of Al on leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
1m - A	7.05	15.5	150	12.52	4.74	37.88	12.52 ± 1.78
2m - A	11.4	11.2	11.55	11.38	0.18	1.54	11.38 ± 0.44
4m - A	11.8	6.70	7.05	8.52	2.85	33.45	8.52 ± 7.08
8m - A	5.15	5.50	5.4	5.35	0.18	3.37	5.35 ± 0.45
12m - A	8.80	6.65	6.90	7.45	1.18	15.78	7.45 ± 2.92
1m - B	3.28	3.46	3.52	3.42	0.13	3.70	3.42 ± 0.31
2m - B	11.7	12.15	12.45	12.1	0.38	3.12	12.10 ± 0.94
4m - B	6.65	6.9.00	7.35	6.97	0.35	5.09	6.97 ± 0.88
8m - B	10.55	10.6	10.85	10.67	0.16	1.51	10.67 ± 0.40
12m - B	9.2	8.9	9.05	9.05	0.15	1.66	9.05 ± 0.37
1m - C	5.79	6.00	6.21	6.00	0.21	3.45	6.00 ± 0.51
2m - C	8.00	8.3	8.4	8.23	0.21	2.53	8.23 ± 0.52
4m - C	12.75	12.35	12.75	12.62	0.23	1.83	12.62 ± 0.57
8m - C	9.35	9.15	8.95	9.15	0.2	2.19	9.15 ± 0.50
12m - C	8.45	8.7	8.7	8.62	0.14	1.68	8.62 ± 0.36
1m - D	6.78	7.22	9.94	7.98	1.71	21.43	7.98 ± 4.25
2m - D	6.5	6.75	6.75	6.65	0.13	1.99	6.65 ± 0.33
4m - D	8.55	8.90	8.90	8.70	0.18	2.07	8.70 ± 0.45
8m - D	4.65	4.40	4.40	4.47	0.16	3.60	4.47 ± 0.40
12m - D	7.85	7.85	7.85	7.85	0.00	0.00	7.85 ± 0.00

Appendix H1

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Pb on digested samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	1043.80	1084.54	1047.25	1058.53	22.59	2.13	1058.53 ± 56.13
A 10 - 15	198.17	208.67	197.92	201.58	6.14	3.04	201.58 ± 15.24
A 20 - 25	161.38	173.75	175.92	170.35	7.85	4.61	170.35 ± 19.49
B - TOP	1316.3	1325.25	1316.21	1319.24	5.21	0.39	1319.24 ± 12.94
B 10 - 15	1090.3	1243.17	1277.29	1203.57	99.61	8.28	1203.57 ± 247.46
B 20 - 25	156.46	166.92	154.83	159.4	6.56	4.11	159.40 ± 16.29
C - TOP	1160	1159.21	1180.25	1166.49	11.93	1.02	1166.49 ±29.63
C 10 - 15	76.58	77.42	69.54	74.51	4.33	5.81	74.51 ± 10.75
C 20 - 25	77.63	77.96	71.00	75.53	3.92	5.20	75.53 ± 9.75
C 30 - 35	22.88	23.46	22.46	22.93	0.50	2.19	22.93 ± 1.25
D - TOP	1836.5	1857.79	1878.29	1857.53	20.9	1.12	1857.53 ± 51.92
D 10 - 15	64.37	63.50	69.29	65.72	3.12	4.75	65.72 ± 7.76
D 20 - 25	44.38	40.25	42.75	42.46	2.08	4.89	42.46 ± 5.16
E - TOP	1461.21	1427.54	1458.54	1449.1	18.72	1.29	1449.10 ± 46.49
E 10 - 15	303.08	292	289.71	294.93	7.15	2.43	294.93 ± 17.77
E 20 - 25	28.33	23.83	26.38	26.18	2.26	8.62	26.18 ± 5.61

Appendix H2

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Pb on pH 4 leached samples analysed by the ICP -AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	2.93	2.8	3.18	2.97	0.2	6.6	2.97 ± 0.49
A 10 - 15	3.60	3.72	3.87	3.73	0.13	3.56	3.73 ± 0.33
A 20 - 25	4.09	4.28	4.66	4.34	0.29	6.68	4.34 ± 0.72
B - TOP	5.06	5.42	5.59	5.36	0.27	5.01	5.36 ± 0.67
B 10 - 15	4.93	5.02	5.22	5.06	0.15	2.94	5.06 ± 0.37
B 20 - 25	5.5	5.46	5.57	5.51	0.10	1.01	5.51 ± 0.14
C - TOP	7.74	7.74	8.57	8.01	0.48	5.98	8.01 ± 1.19
C 10 - 15	5.65	5.69	5.81	5.72	0.10	1.47	5.72 ± 0.21
C 20 - 25	5.54	5.78	5.47	5.60	0.16	2.94	5.60 ± 0.41
C 30 - 35	5.33	5.24	5.10	5.22	0.12	2.22	5.22 ± 0.29
D - TOP	5.59	5.44	5.65	5.56	0.11	1.93	5.56 ± 0.27
D 10 - 15	5.23	5.21	5.09	5.18	0.10	1.52	5.18 ± 0.20
D 20 - 25	5.36	5.32	5.10	5.26	0.14	2.61	5.26 ± 0.34
E - TOP	8.55	9.04	8.75	8.78	0.25	2.87	8.78 ± 0.63
E 10 - 15	5.45	5.09	5.09	5.21	0.21	3.96	5.21 ± 0.51
E 20 - 25	4.92	5.18	5.17	5.09	0.15	2.89	5.09 ± 0.37

Appendix H3

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Cr on digested samples analysed by the ICP - AES

Sample	**Concentration(ppm)**			**Average**	**SD**	**% RSD**	**95% CL**
A - TOP	76.58	75.00	73.75	75.11	1.42	1.89	75.11 ± 3.53
A 10 - 15	85.83	89.17	86.67	87.22	1.73	1.99	87.22 ± 4.31
A 20 - 25	45.83	47.92	48.33	47.36	1.34	2.83	47.36 ± 3.33
B - TOP	78.33	96.25	102.92	92.50	12.71	13.74	92.50 ± 31.58
B 10 - 15	103.8	105.8	103.75	104.44	1.20	1.15	104.44 ± 2.99
B 20 - 25	80.42	76.25	76.67	77.78	2.29	2.95	77.78 ± 5.70
C - TOP	114.17	115.83	118.75	116.25	2.32	2.00	116.25 ± 5.76
C 10 - 15	36.25	36.67	35.83	36.25	0.42	1.15	36.25 ± 1.04
C 20 - 25	33.75	37.92	37.92	36.53	2.41	6.59	36.53 ± 5.98
C 30 - 35	9.17	8.75	10.00	9.31	0.64	6.84	9.31 ± 1.58
D - TOP	123.8	122.9	126.7	124.44	1.97	1.58	124.44 ± 4.89
D 10 - 15	31.67	29.58	31.25	30.83	1.10	3.58	30.83 ± 2.74
D 20 - 25	25.83	24.17	25.42	25.14	0.87	3.45	25.14 ± 2.15
E - TOP	132.08	128.33	127.08	129.17	2.60	2.01	129.17 ± 6.46
E 10 - 15	114.58	116.25	114.17	115.00	1.10	0.96	115.00 ± 2.74
E 20 - 25	13.33	10.83	9.58	11.25	1.91	16.97	11.25 ± 4.74

Appendix H4

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Cr on pH 4 leached samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	0.60	0.55	0.55	0.57	0.03	5.09	0.57 ± 0.07
A 10 - 15	0.70	0.70	0.70	0.70	0.00	0 .00	0.70 ± 0.00
A 20 - 25	0.80	0.80	0.80	0.8 0	0.00	0 .00	0.80 ± 0.00
B - TOP	1.00	0.95	0.95	0.97	0.03	2.99	0.97 ± 0.07
B 10 - 15	0.69	0.67	0.72	0.69	0.02	3.32	0.69 ± 0.06
B 20 - 25	0.9	0.95	1.00	0.95	0.05	5.26	0.95 ± 0.12
C - TOP	1.05	1.05	1.05	1.05	0.00	0.00	1.05 ± 0.00
C 10 - 15	1.05	1.00	1.00	1.02	0.03	2.84	1.02 ± 0.07
C 20 - 25	1.00	1.00	1.05	1.02	0.03	2.84	1.02 ± 0.07
C 30 - 35	0.95	0.95	0.95	0.95	0.00	0.00	0.95 ± 0.00
D - TOP	1.00	1.05	1.00	1.02	0.03	2.84	1.02 ± 0.07
D 10 - 15	0.95	0.95	0.9	0.93	0.03	3.09	0.93 ± 0.07
D 20 - 25	0.95	0.95	0.95	0.95	0.00	0.00	0.95 ± 0.00
E - TOP	1.25	1.25	1.25	1.25	0.00	0.00	1.25 ± 0.00
E 10 - 15	1.00	1.00	0.95	0.98	0.03	2.94	0.98 ± 0.07
E 20 - 25	1.00	0.95	0.95	0.97	0.03	2.99	0.97 ± 0.07

Appendix H5

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Cd on digested samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	3.42	3.33	3.33	3.36	0.05	1.43	3.36 ± 0.12
A 10 - 15	7.08	6.67	6.67	6.81	0.24	3.53	6.81 ± 0.60
A 20 - 25	3.33	3.75	3.33	3.47	0.24	6.93	3.47 ± 0.60
B - TOP	1.67	1.67	2.5	1.94	0.48	24.74	1.94 ± 1.20
B 10 - 15	3.33	3.75	4.17	3.75	0.42	11.11	3.75 ± 1.04
B 20 - 25	4.17	4.58	4.17	4.31	0.24	5.59	4.31 ± 0.60
C - TOP	5.83	6.25	5.83	5.97	0.24	4.03	5.97 ± 0.60
C 10 - 15	1.67	2.08	1.67	1.81	0.24	13.32	1.81 ± 0.60
C 20 - 25	2.08	2.08	2.08	2.08	0.00	0.00	2.08 ± 0.00
C 30 - 35	0.42	0.42	0.42	0.42	0.00	0 .00	0.42 ± 0.00
D - TOP	5.00	5.00	5.83	5.28	0.48	9.12	5.28 ± 1.20
D 10 - 15	1.67	1.67	2.08	1.81	0.24	13.32	1.81 ± 0.60
D 20 - 25	1.25	1.25	1.67	1.39	0.24	17.32	1.39 ± 0.60
E - TOP	6.25	6.25	6.25	6.25	0.00	0.00	6.25 ± 0.00
E 10 - 15	7.92	7.08	7.50	7.50	0.42	5.56	7.50 ± 1.04
E 20 - 25	0.83	0.42	0.42	0.56	0.24	43.3	0.56 ± 0.60

Appendix H6

Results of soil samples from the N3 freeway next to Eshongweni off-ramp

Vertical distribution of Cd on pH 4 leached samples analyzed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	0.15	0.20	0.20	0.18	0.03	15.75	0.18 ± 0.07
A 10 - 15	0.25	0.25	0.25	0.25	0.00	0.00	0.25 ± 0.00
A 20 - 25	0.30	0.30	0.30	0.30	0.00	0.00	0.30 ± 0.00
B - TOP	0.30	0.30	0.30	0.30	0.00	0.00	0.30 ± 0.00
B 10 - 15	0.30	0.30	0.30	0.30	0.00	0.00	0.30 ± 0.00
B 20 - 25	0.40	0.30	0.30	0.33	0.06	17.32	0.33 ± 0.14
C - TOP	0.35	0.35	0.35	0.35	0.00	0.00	0.35 ± 0.00
C 10 - 15	0.35	0.35	0.35	0.35	0.00	0.00	0.35 ± 0.00
C 20 - 25	0.35	0.35	0.35	0.35	0.00	0.00	0.35 ± 0.00
C 30 - 35	0.30	0.30	0.30	0.30	0.00	0.00	0.30 ± 0.00
D - TOP	0.35	0.30	0.30	0.32	0.03	9.12	0.32 ± 0.07
D 10 - 15	0.30	0.30	0.25	0.28	0.03	10.19	0.28 ± 0.07
D 20 - 25	0.30	0.30	0.30	0.03	0.00	0.00	0.30 ± 0.00
E - TOP	0.45	0.45	0.50	0.47	0.03	6.19	0.47 ± 0.07
E 10 - 15	0.30	0.3 0	0.30	0.30	0.00	0.00	0.30 ± 0.00
E 20 - 25	0.30	0.25	0.30	0.28	0.03	10.19	0.28 ± 0.07

Appendix H7

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Ni on digested samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	135.08	139.00	134.58	136.21	2.39	1.76	136.21 ± 5.95
A 10 - 15	302.10	300.90	300.9	301.29	0.69	0.23	301.29 ± 1.70
A 20 - 25	154.40	162.20	167.20	161.26	6.44	4.00	161.26 ± 16.01
B - TOP	190.60	215.70	237.30	214.54	23.36	10.89	214.54 ± 58.02
B 10 - 15	244.6	246.60	244.17	245.13	1.32	0.54	245.13 ± 3.27
B 20 - 25	250.3	260.70	248.50	253.19	6.57	2.59	253.19± 16.32
C - TOP	316.4	307.70	297.00	307.03	9.68	3.15	307.03 ± 24.05
C 10 - 15	120.2	113.70	112.00	115.31	4.29	3.72	115.31± 10.66
C 20 - 25	109.8	118.30	120.7	116.24	5.74	4.94	116.24 ± 14.26
C 30 - 35	36.54	38 .00	37.92	37.49	0.82	2.18	37.49 ± 2.03
D - TOP	261.7	256.2	267.8	261.88	5.82	2.22	261.88 ± 14.45
D 10 - 15	95.71	90.00	97.29	94.33	3.84	4.07	94.33 ± 9.53
D 20 - 25	83.08	83.92	88.5	85.17	2.92	3.42	85.17 ± 7.25

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E - TOP	312.54	307.58	312.25	310.79	2.78	0.9	310.79 ± 6.91
E 10 - 15	360.88	364.00	363.42	362.76	1.66	0.46	362.76 ± 4.13
E 20 - 25	41.54	39.04	37.96	39.51	1.84	4.65	39.51 ± 4.57

Appendix H8

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Ni on pH 4 leached samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	1.31	1.27	1.37	1.32	0.05	3.63	1.32 ± 0.12
A 10 - 15	1.65	1.72	1.76	1.71	0.06	3.29	1.71 ± 0.14
A 20 - 25	1.98	2.01	2.14	2.04	0.08	4.08	2.04 ± 0.21
B - TOP	2.19	2.33	2.4	2.31	0.11	4.64	2.31 ± 0.27
B 10 - 15	2.45	2.34	2.43	2.41	0.06	2.36	2.41 ± 0.14
B 20 - 25	2.52	2.55	2.52	2.53	0.02	0.80	2.53 ± 0.05
C - TOP	2.70	2.69	2.67	2.68	0.00	0.6	2.68 ± 0.04
C 10 - 15	2.62	2.64	2.71	2.66	0.00	1.67	2.66 ± 0.11
C 20 - 25	2.65	2.69	2.6	2.64	0.00	1.61	2.64 ± 0.11
C 30 - 35	2.40	2.39	2.57	2.45	0.10	4.12	2.45 ± 0.25
D - TOP	2.55	2.63	2.68	2.62	0.10	2.4	2.62 ± 0.16
D 10 - 15	2.42	2.56	2.35	2.44	0.11	4.38	2.44 ± 0.27
D 20 - 25	2.46	2.36	2.31	2.37	0.10	3.22	2.37 ± 0.19
E - TOP	3.18	3.27	3.15	3.20	0.06	1.89	3.20 ± 0.15
E 10 - 15	2.40	2.39	2.47	2.42	0.04	1.80	2.42 ± 0.11
E 20 - 25	2.33	2.31	2.31	2.32	0.01	0.57	2.32 ± 0.03

Appendix H9

Results of soil samples from the N3 freeway next to Eshongweni off-ramp

Vertical distribution of Cu on digested samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	141.40	143.40	147.5	144.10	3.12	2.16	144.10 ± 7.75
A 10 - 15	18.08	17.33	16.96	17.46	0.57	3.28	17.46 ± 1.42
A 20 - 25	16.08	17.25	18.96	17.43	1.45	8.30	17.43 ± 3.59

B - TOP	50.13	59.38	63.46	57.65	6.83	11.85	57.65 ± 16.97
B 10 - 15	65.71	63.29	65.08	64.69	1.25	1.94	64.69 ± 3.12
B 20 - 25	10.25	10.58	10.54	10.46	0.18	1.74	10.46 ± 0.45

C - TOP	40.25	39.12	38.92	39.43	0.72	1.82	39.43 ± 1.78
C 10 - 15	8.29	8.42	8.71	8.47	0.21	2.52	8.47 ± 0.53
C 20 - 25	8.33	9.75	9.38	9.15	0.73	8.02	9.15 ± 1.82
C 30 - 35	1.08	1.08	1.29	1.15	0.12	10.43	1.15 ± 0.30

D - TOP	78.17	82.25	82.29	80.9	2.37	2.93	80.90 ± 5.89
D 10 - 15	5.46	4.50	5.83	5.26	0.69	13.06	5.26 ± 1.71
D 20 - 25	4.58	3.58	4.38	4.18	0.53	12.62	4.18 ± 1.31

E - TOP	95.92	94.25	95.13	95.10	0.83	0.88	95.10 ± 2.07
E 10 - 15	20.79	20.29	21.96	21.01	0.86	4.07	21.01 ± 2.12
E 20 - 25	1.79	1.25	0.92	1.32	0.44	33.47	1.32 ± 1.10

Appendix H10

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Cu on pH 4 leached samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	0.86	0.86	0.84	0.85	0.02	1.88	0.85 ± 0.04
A 10 - 15	0.43	0.44	0.49	0.45	0.03	6.49	0.45 ± 0.07
A 20 - 25	0.55	0.56	0.57	0.56	0.01	2.25	0.56 ± 0.03
B - TOP	0.69	0.67	0.72	0.69	0.02	3.32	0.69 ± 0.06
B 10 - 15	0.68	0.67	0.68	0.68	0.01	0.74	0.68 ± 0.01
B 20 - 25	0.66	0.66	0.67	0.66	0.01	1.15	0.66 ± 0.02
C - TOP	0.88	0.86	0.88	0.87	0.01	0.87	0.87 ± 0.02
C 10 - 15	0.66	0.66	0.65	0.66	0	0.76	0.66 ± 0.01
C 20 - 25	0.73	0.73	0.76	0.74	0.02	2.74	0.74 ± 0.05
C 30 - 35	0.60	0.59	0.58	0.59	0.01	2.14	0.59 ± 0.03
D - TOP	1.18	1.16	1.14	1.16	0.02	1.73	1.16 ± 0.05
D 10 - 15	0.71	0.69	0.68	0.69	0.01	1.92	0.69 ± 0.03
D 20 - 25	0.59	0.58	0.6	0.59	0.01	1.69	0.59 ± 0.02
E - TOP	1.45	1.45	1.42	1.44	0.02	1.32	1.44 ± 0.05
E 10 - 15	0.56	0.58	0.61	0.58	0.03	4.31	0.58 ± 0.06
E 20 - 25	0.63	0.62	0.6	0.62	0.01	2.15	0.62 ± 0.03

Appendix H11

Results of soil samples from the N3 freeway next to Eshongweni off-ramp

Vertical distribution of Al on digested samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	6644.17	6573.33	6363.33	6526.94	146.05	2.24	6526.94 ± 362.84
A 10 - 15	52814.20	52316.70	51344.58	52158.47	747.45	1.43	52158.47 ± 1856.93
A 20 - 25	22306.30	22735.00	28193.75	24411.67	3282.40	13.45	24411.67 ± 8154.56
B - TOP	32529.20	33366.70	33560.00	33151.94	547.94	1.65	33151.94 ± 1361.26
B 10 - 15	34002.90	34404.20	33548.75	33985.28	427.98	1.26	33985.28 ± 1063.25
B 20 - 25	48151.70	48336.30	47805.83	48097.92	269.26	0.56	48097.92 ± 668.94
C - TOP	49635.40	49092.50	49956.67	49561.53	436.8	0.88	49561.53 ± 1085.15
C 10 - 15	22018.30	22317.92	22558.33	22298.19	270.54	1.21	22298.19 ± 672.11
C 20 - 25	22068.80	22977.90	22412.08	22486.25	459.1	2.04	22486.25 ± 1140.56
C 30 - 35	4885.83	5020.420	5017.50	4974.58	76.87	1.55	4974.58 ± 190.98

Appendix H11(Continued)

Vertical distribution of Al on digested samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
D - TOP	32719.2	32798.3	32351.67	32623.06	238.34	0.73	32623.06 ± 592.12
D 10 - 15	18103.8	18367.50	17739.17	18070.14	315.51	1.75	18070.14 ± 783.84
D 20 - 25	11400	11545.8	11540.42	11495.42	82.68	0.72	11495.42 ± 205.40
E - TOP	42963.33	43135	41802.08	42633.47	725.1	1.70	42633.47 ± 1801.40
E 10 - 15	75842.5	75784.58	76625.42	76084.17	469.63	0.62	76084.17 ± 1166.72
E 20 - 25	5255.83	5212.92	5357.50	5275.42	74.25	1.41	5275.42 ± 184.47

Appendix H12

Results of soil samples from the N3 freeway next to Shongweni off-ramp

Vertical distribution of Al on pH 4 leached samples analysed by the ICP - AES

Sample	Concentration(ppm)			Average	SD	% RSD	95% CL
A - TOP	3.75	3.85	3.85	3.82	0.06	1.51	3.82 ± 0.14
A 10 - 15	5.10	5.00	5.2	5.10	0.10	1.96	5.10 ± 0.25
A 20 - 25	3.85	5.10	4.00	4.32	0.68	15.81	4.32 ± 1.70
B - TOP	8.85	9.00	8.95	8.93	0.08	0.85	8.93 ± 0.19
B 10 - 15	8.65	8.65	8.85	8.72	0.12	1.32	8.72 ± 0.29
B 20 - 25	4.55	4.75	4.60	4.63	0.10	2.25	4.63 ± 0.26
C - TOP	26.45	26.35	27.15	26.65	0.44	1.64	26.65 ± 1.08
C 10 - 15	4.75	4.75	4.95	4.82	0.12	2.4	4.82 ± 0.29
C 20 - 25	4.95	4.60	5.15	4.90	0.28	5.68	4.90 ± 0.69
C 30 - 35	4.50	4.45	4.35	4.43	0.08	1.72	4.43 ± 0.19
D - TOP	7.40	7.45	7.80	7.55	0.22	2.89	7.55 ± 0.54
D 10 - 15	4.35	4.50	4.45	4.43	0.08	1.72	4.43 ± 0.19
D 20 - 25	4.40	4.25	4.30	4.32	0.08	1.77	4.32 ± 0.19
E - TOP	51.00	51.45	50.95	51.13	0.28	0.54	51.13 ± 0.68
E 10 - 15	4.85	4.95	4.90	4.90	0.05	1.02	4.90 ± 0.12
E 20 - 25	4.20	4.35	4.27	4.27	0.08	1.79	4.27 ± 0.19

Appendix I

$$\text{Mean } (x) = (x_1 + x_2 + \dots + x_n) / n$$

where $x_1 + x_2 + \dots + x_n = x_i$ are measured values and n is the number of measured values.

$$\text{Standard deviation } (s) = \sqrt{\left(\left(\sum_{i=1\dots n} | x_i - x |^2\right) / (n - 1)\right)}$$

$$\text{Relative standard deviation } (\%RSD) = (s / x) \times 100$$

$$\text{Confidence limits } (\mu) = x \pm (ts / \sqrt{n})$$

the quantity t is called student's t

$$\text{Degrees of freedom} = n - 1$$

Table of values of student's t

Degrees of freedom	Probability levels	
n - 1	95%	99%
2	4.303	9.925
3	3.182	5.841
4	2.776	4.601
5	2.571	4.302
6	2.447	3.707
7	2.365	3.5
8	2.306	3.355
9	2.262	3.25
10	2.228	3.169