

Chemical Pollution arising from Heavy Inorganic Industries in Richards Bay – An Assessment

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By

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ABSTRACT

The industrial port of Richards Bay on the eastern seaboard of KwaZulu-Natal, South Africa has undergone rapid growth over the last 25 years. This industrial growth has inevitably led to an increase in the anthropogenic pollutant inputs in the area. However, the degree of this contamination has not previously been assessed not been accompanied by an awareness of its environmental impacts. This project serves to assess the current environmental situation of the area and provide background levels against which the environmental impacts of further growth in the area can be assessed.

The main pollution point sources in the area were identified as a pulp and paper plant, a sulfuric acid/fertiliser plant and aluminium smelters. The chemical and physical processes involved within these industries were identified and discussed in detail. The common inorganic pollutants emitted by these industries were identified as trace metals, sulfur dioxide, NO_x gases and fluoride. It was these pollutants that therefore became the focus of this study.

Reservoirs within Richards Bay that may become sinks for contamination were identified and water, sediment and soil samples were taken from these reservoirs. The samples were analysed for trace metal contamination, pH, alkalinity and fluoride levels.

Analysis of the acidity and alkalinity of water, sediment and soils samples demonstrated that there is presently no long-term acidification of the environment in Richards Bay. The only samples that showed increased acidity were the soils taken from the roadside sites immediately outside the industries. This lack of overall acidification indicates that, at present, there are no detrimental effects of acidic emissions on the hydrosphere and geosphere.

Only cursory investigations were conducted into the fluoride levels found in water samples. None of the samples analysed demonstrated detectable amounts of fluoride present.

Comprehensive trace metal analyses were performed on the water, sediment and soil samples through the use of ICP-AES. Levels obtained were compared with levels from samples taken from relatively uncontaminated background sites. Trace metal analysis indicated contamination of the freshwater reservoirs when compared with the background, while the soils and saltwater reservoirs remain largely uncontaminated. However, the contaminated areas did not show levels greater than quality guideline concentrations.

Further studies should be conducted with regards to the trace metal contamination of the biosphere and the bioavailability of the contaminants already present in the waters, sediments and soils. More detailed investigations should also be conducted into the levels of atmospheric pollutants and fluoride levels in all reservoirs.

DECLARATION

I hereby certify that this research is a result of my own investigation, which has not been accepted in substance for any degree and is not being submitted in candidature for any other degree.

Signed: ..*Catherine Dyson*.....

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I hereby certify that this statement is correct.

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CHAPTER 1

Industrial Development and Associated Pollution Problems

1.1 Aim of this project

An overseas grant has been obtained to fund projects that focus on assessing the environmental state of the eastern seaboard of South Africa between Richards Bay and Maputo. This means taking into account various pollution point sources and estimating the effect of these on the local and extended environments, historically, presently and in the future. This project, being undertaken with a chemical background and viewpoint, targets the Richards Bay area. (Richards Bay is the most industrialised area along this stretch of the coastline and as such is an obvious source of chemical pollution)

This type of study has not been performed before in Richards Bay and there is, therefore, no indication of the present environmental state of this area. This project aims to provide this indication as well as to predict the likely future of Richards Bay from a chemical and environmental impact point of view.

The first chapter includes a general introduction to industry in South Africa and the Richards Bay area. The main industries within Richards Bay are later discussed in depth, including details of the various chemical processes and the potential of these processes to release contaminants which may pollute the local environment. Chapter one aims to give an idea of the main sources and types of pollution in the study area. The second chapter involves a discussion of what can happen to these potential contaminants after they have been released into the environment. This includes how they move between the various spheres, where they end up and what biological effects they may have. The remaining chapters include the experimental details of the project, the results obtained and the conclusions drawn.

1.2 Introduction

Environmental pollution has become an issue of increasing concern over the past 40 years. Pollution can be defined as the addition of a substance by human activity to the environment which can cause injury to human health or damage to natural ecosystems.¹ Most of the substances that are considered pollutants are actually natural constituents of the environment. An increase in the mobility of these natural constituents, normally by industrial activity, leads to localised concentration of these elements. It is this localised concentration that is of concern as it may lead to the constituents being present at levels at which they may become harmful. These pollutants include heavy metals, oxides of sulfur and nitrogen and ammonia and fluoride containing compounds, which may be released into the environment through mining, smelting and other industrial activity. There are a few pollutants, however, which are entirely synthetic and would not be present in the environment if it were not for human activity.

The number of pollution point sources is constantly rising throughout the world as a consequence of growing industrial development. The driving force behind the increase in pollution is the rapidly growing population of the world and the never-ending quest for an improved economic standard of life. The consequent demand for energy and resources required to feed, clothe and house this increasing population is accompanied by a parallel increase in waste production. The standard of living is also, generally, on the increase, placing additional stress on the environment. Developed countries, which have gone through rapid growth in industrialisation, are now socially (and economically) mature enough to raise environmental concerns to near the top of the political agenda. Economic development in Africa, on the other hand, has been extremely slow over the comparative time scale. The obvious exceptions to this have been the continental 'super-powers', South Africa and Nigeria. However, while economic growth has occurred in these countries it has generally not been accompanied by a growing environmental awareness. Environmental concerns are still, in reality, of secondary concern. Rapid industrialisation is on-going in South Africa and the possibilities of environmental pollution are ever increasing. A country's economic growth is most easily defined in terms of its Gross Domestic Product (GDP). South Africa's economic growth has been substantial between 1946, where a GDP of roughly R100 000 million was

achieved, and 2002 where it was nearly R660 000 million.² This growth is depicted graphically in Figure 1.1.

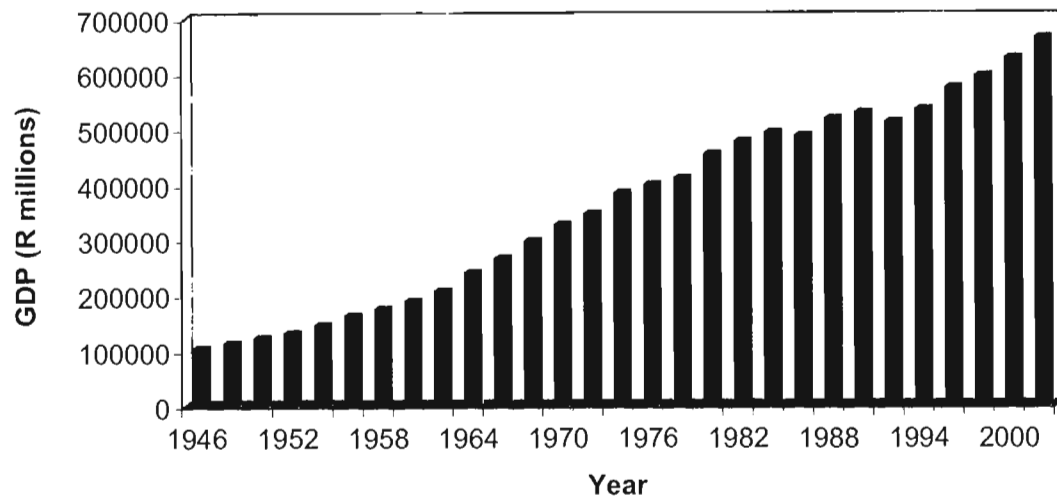


Figure 1.1: Growth of the SA economy in terms of GDP

This economic growth is predicted to continue throughout this millennium² and this growth will be accompanied by an increase in the potential for environmental pollution. This increase in pollution can become a problem if the situation arises where natural processes can no longer cleanse the environment of the pollutants that are generated daily. If this point is reached it means that these pollutants will steadily accumulate in the atmosphere, the hydrosphere and the geosphere and the legacy of present industrial development may have a dramatic effect on future generations.

Consequently, while rapid industrial development is ongoing, the environmental implications of such development should also be investigated. This project centres on the assessment of the environmental impact of the industrial development on the Richards Bay area in KwaZulu-Natal, South Africa. The port at Richards Bay is becomingly increasingly important to South Africa. Many large industries have already invested heavily in this area and many more such investments seem set to follow.³ Surprisingly, there has been little environmental monitoring of this rapid industrial growth. This despite it being the most obvious centre in South Africa where a previously pristine natural environment is obviously at risk from the waste materials generated by a variety of heavy industries.

In this chapter, the heavy industrial centres within South Africa will be located and looked at with reference their growth and their associated potential environmental impacts. In some cases, the environmental impact of these industries has been assessed prior to industrial growth, but in most cases it is only afterwards that the environmental issues become a concern, often too late to be rectified. Our area of interest, Richards Bay, still has the potential for huge industrial growth and as such it could become a centre where environmental monitoring and industrial development can go hand-in-hand.

1.3. Industry in South Africa

1.3.1 South Africa – Setting the scene

South Africa, SA, has the most advanced industrial economy on the African continent.⁴ The country is rich in natural resources and has an economy that can be regarded as reasonably developed. Although officially classified as a developing country by the United Nations,⁵ SA has an economy that is based on a sophisticated financial and physical infrastructure, good telecommunications and energy supply network and one of the top ten stock exchanges in the world. Since the transformation to a representative democracy in 1994, the country's economy has grown rapidly and has been accompanied by sustained economic growth, significant capital inflows, a growing export centre and improved business and consumer confidence.⁴

The most important contributors to the economy are mining, manufacturing and agriculture. Mining is South Africa's largest industrial sector and has been the catalyst for industrial growth in SA. Currently most economic activity occurs in Gauteng, which is the historical centre of the mining industry. A map showing the regions in South Africa where the majority of modern day mining activity takes place is shown in Figure 1.2.

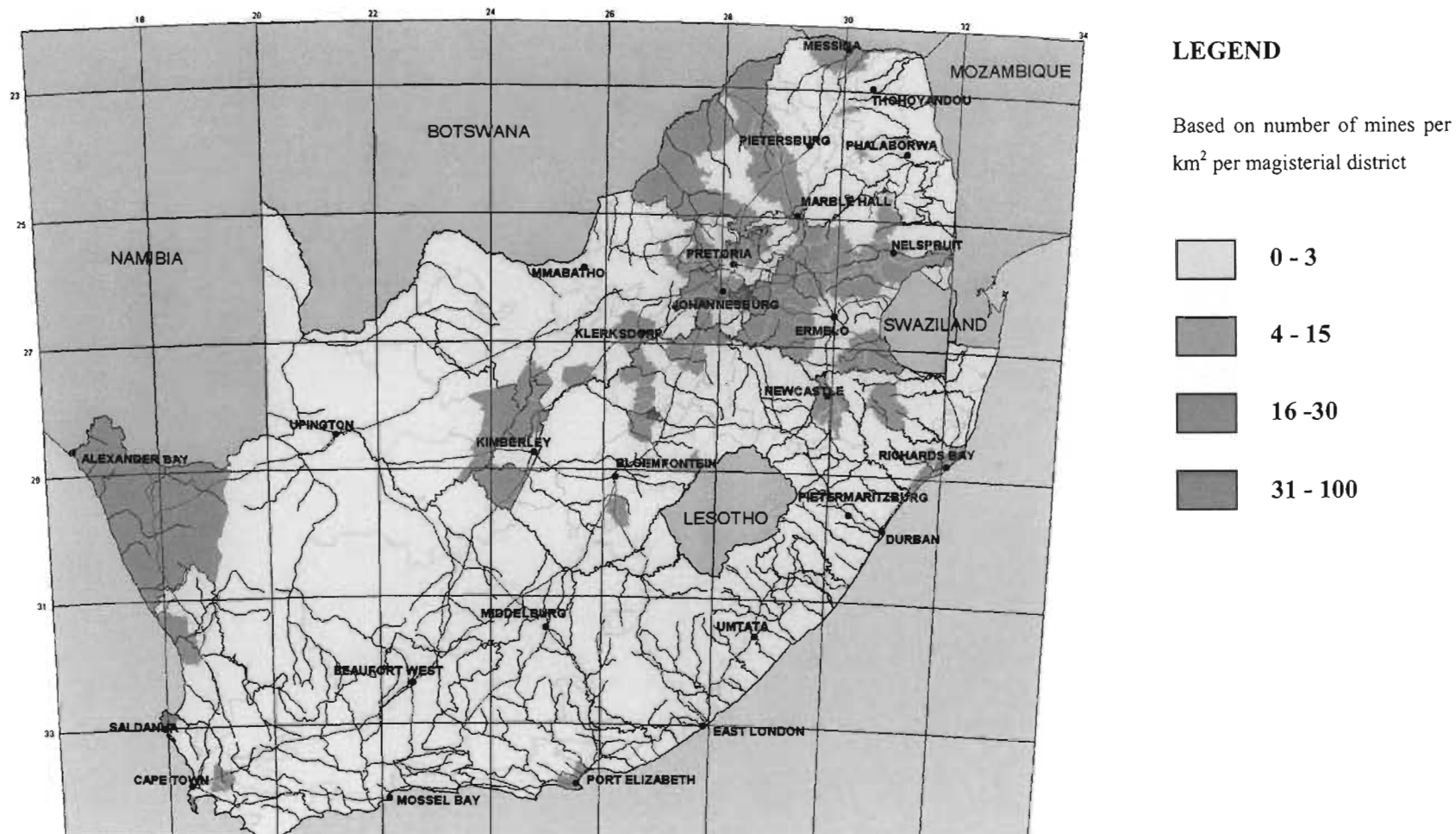


Figure 1.2: Map showing the regional mining intensities in South Africa⁶

South Africa is recognised globally as being a leading supplier of a variety of minerals and mineral products that are exported to as many as 87 countries. Each year approximately 55 different minerals are produced from more than 500 mining facilities, with gold, the platinum group metals and diamonds generating extensive exports and revenue earnings.⁷

The mining industry, probably due to its size and longevity, is one of the few industrial sectors within SA that has generated both internal and external studies into environmental pollution.^{8,9} Mining companies are now forced by law¹⁰ to conduct environmental impact studies for new ventures and to remediate old mining sites. However, much of the remediation has happened only well after the primary sources of pollution have occurred. Consequently, contamination of soils and water tables at relatively large distances from the point sources has been common.¹¹

Another industrial sector that is of substantial, and growing, economic significance to the country is the chemical industry. This sector contributes 5% to the country's GDP and is the largest of its kind in Africa. It is dominated by Sasol Chemical Industries, AECI and Dow Sentrachem and other large companies that are active include Hoechst SA, Afrox, Bayer, Shell Chemicals, BASF, African Products and Engen Petroleum. The industry is highly complex and widely diversified, but can be divided into four broad categories namely base chemicals, intermediate chemicals, chemical end products and specialty end products.⁷

Base chemicals include all the important chemical building blocks sourced from the petrochemical and coal industries. SA's coal industry is the second biggest mining sector after gold and contributes 4% to the country's GDP.⁷ Some intermediate chemicals manufactured in this country are ammonia, waxes, solvents, phenols, tars, plastics, and rubbers.⁷ Chemical end products include processible plastics, paints, explosives, and fertilisers. Specialty chemical end products tend to be lower volume, higher added-value chemical products. Many pharmaceuticals, agro-chemicals, bio-chemicals, food- and fuel- additives fall into this category. Either these products themselves or by-products released through their manufacture may be potentially harmful to the environment.

South Africa is also a key player in the African oil industry. Today the country processes approximately 20 million tonnes per annum of crude oil and consumes 23 million tonnes of liquid fuel products of which 45 % is gasoline and 26% diesel. The oil refineries are a major

contributor to air pollution in South Africa. There are four refineries in the country, the Caltex refinery in Cape Town, the Sapref and Enref refineries in Durban and the Natref refinery in Sasolburg. These refineries contribute to high levels of pollution in the northern suburbs of Cape Town and southern Durban, emitting high levels of sulfur dioxide and several other chemicals known to cause health problems, such as NO_x gases, carbon dioxide, carbon monoxide, methane, dioxins, hydrogen fluoride, chlorine and benzene.¹²

The majority of the industrial centres in South Africa are based in the Gauteng area, specifically in and around Pretoria and Johannesburg. A map depicting these regions of high industrial activity is shown in Figure 1.3.

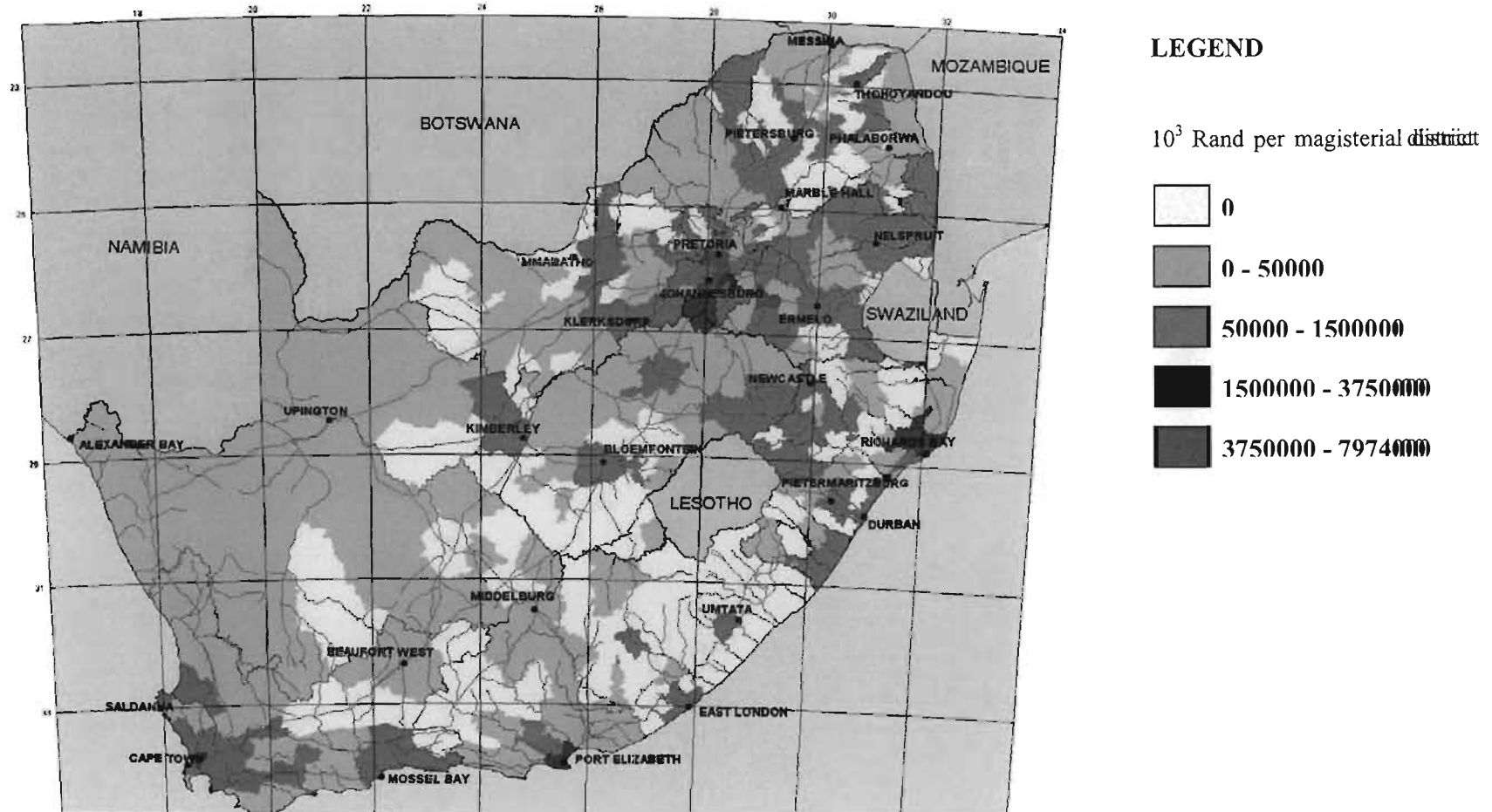


Figure 1.3: Map showing the regional industrial intensities in South Africa

1.4 Richards Bay

Richards Bay is on the east coast of South Africa, roughly 180 km northeast of Durban and 465 km south of Maputo. The growth of Richards Bay from a small fishing village with 200 residents in 1968 to the present thriving town of over 35000 residents was initiated by the decision to develop a deep-water harbour in the area.¹³ The Port of Richards Bay was officially opened on April 1, 1976. Construction of the harbour started in May 1972 after the Minister of Transport had announced back in 1965 that a port was to be built in Richards Bay that would be connected to the Southern Transvaal (now Gauteng) by a new railway line.¹⁴ The town is now growing rapidly and its port is becoming increasingly important in South Africa. The current population of the Mhlathuze Municipality, which includes Richards Bay and the nearby town of Empangeni, is 128000 and is growing at a rate of approximately 2.5% per annum.¹⁵

The port now services the Gauteng and Mpumalanga regions, as well as the harbour-bound industries just outside its borders. It is the biggest deep-water port in South Africa and is currently the country's major port for the handling of bulk freight, handling over 80 million tonnes of cargo per annum, which comprises 56% of the total tonnage handled by all the South African ports. The harbour is primarily used to export bulk goods, although its container handling capacity is growing. Furthermore, currently only 40% of the port's land capacity is being utilised, whereas both the Durban and the Cape Town harbours are working at 90% of their capacity.¹⁵

The Richards Bay region is uniquely placed to access both the commercial and industrial core of South Africa, as well as most international markets. As the closest port to South Africa's industrial heartland, Richards Bay has been able to service the region's growing needs. Currently most of South Africa's coal and steel exports, and a variety of other bulk materials, are routed through Richards Bay. The rail network linking the hinterland of the country to Richards Bay has played a critical role in the industrial development of the region. Rail sidings linked to the main rail network service all industrial areas in Richards Bay. Richards Bay is also linked to Gauteng, Ulundi and Vryheid via the national road network, which is used to transport industrial and manufactured goods and inputs. Richards Bay is also well

suited for investors wanting to access inputs and markets in the rest of the world. Situated as it is, equidistant from all international markets – the Americas, Europe and the East – Richards Bay offers easy access to these markets.¹⁶

The Richards Bay area is rich in mineral resources, including ilmenite, rutile and zircon. The mining of these minerals allows Richards Bay to meet 100% of South Africa's demand for titanium dioxide and zircon and almost the country's entire pig iron requirement. Richards Bay also enjoys a number of other natural advantages. It is, for example, part of the coastal lowlands and thus has a bioclimatic profile that renders it suitable for diverse agricultural production. The region's rich agricultural lands are used mainly for the production of sugarcane and timber. The development of these agricultural crops, in turn, led to the development of the agro-processing industries, some of which are located in the area, e.g. the Mondi Paper Company, the South African Pulp and Paper Industry (SAPPI), the Central Timber Co-operative and Silva-Cel.

Due to the presence of large industries in Richards Bay and its predicted potential for growth, it has become an area of environmental interest. Richards Bay is susceptible to pollution from a number of different sources and newspaper reports of environmental incidents have become commonplace.^{17,18} The heavy marine traffic contributes largely to this pollution, as does the industrial activity in and around the port. No recent studies have been done to determine the extent of, or even the threat of, pollution in this area due to the increasing industrial activity.

Studies of this nature have been limited to the Council for Scientific and Industrial Research (CSIR) reports,^{19,20,21,22} which date from 1975 to 1982. One such study was initiated in 1974, and in view of the huge changes being planned in the area, was followed up in 1975.¹⁹ These studies were limited to looking at the species and numbers of the benthic fauna and zooplankton present. Again in 1976²⁰, it was decided that the harbour area of Richards Bay had been developed to a stage where industrial development made it necessary to survey the area as part of the Marine Pollution Monitoring Programme. The development included the construction of the harbour and the establishment of an aluminium smelter and phosphoric and sulfuric acid plant. This time water, sediment fauna and zooplankton samples were taken and analysed for pesticide and trace metal residues. Industrial and municipal development at

the Richards Bay complex continued at a steady rate and a further survey of the area was done in 1981.²¹ Similar analyses to the 1976 study were performed and it was concluded that there was not a marked increase in pollution levels due to the developments. A specific study was also performed in 1981 in reply to the proposal to build an offshore pipeline to dispose of industrial and municipal wastes. This proposal prompted the need for a detailed baseline study against which any future changes could be judged.²²

1.4.1 Industrial Development in Richards Bay

The establishment of several large industries followed the building of the deepwater port. These large industries are very diverse. At present the major players in the region are:

- i) **Billiton** – The Bayside and Hillside Aluminium smelters combined represent one of the world's leading producers of aluminium.
- ii) **Richards Bay Coal Terminal (RBCT)** - A private coal exporting company exporting over 60 million tonnes of coal per annum.
- iii) **Foskor** - Indian Ocean Fertilisers, owned by Foskor, produces nearly 1 million tonnes of phosphoric acid, powdered fertilisers and fertiliser granules for export annually.
- iv) **Richards Bay Minerals (RBM)** - Produce 28% of the world's titanium dioxide as well as high purity pig iron, rutile and zircon.
- v) **Bell Equipment** - A leading manufacturer of heavy earth-works equipment for local and world markets.
- vi) **Mondi** - The operator of a large pulp mill as well as a wood chipping plant.

The locational decisions of companies are often influenced by their proximity to the market or raw materials, and this is apparent at Richards Bay. The phenomenal growth of the region can be attributed to three factors previously mentioned: the regions strategic location, providing easy access to raw materials and markets in other parts of the country and international markets; the natural resources of the region; and the key infrastructure installed during the 1970's, such as the port and the associated rail links which allow for full exploitation of the region's natural and strategic advantages.²³

The further development of Richards Bay remains dependent on the numerous large industries in the area. These industries, which initially gave the area its growth dynamic, have encouraged the growth of associated support and service industries around their operations. Indications are that the local economy's dependence on these firms is declining, and that a more diverse manufacturing base is beginning to emerge.¹⁶

Several new industrial projects are in the pipeline, which will further expand the industrial infrastructure of Richards Bay. Current project investments, valued at R3.49 billion, include RBM's Zulti North infrastructure mine upgrade and 5th titanium minery plant; Mondi Paper's Kraft Mill upgrade; Foskor's granular fertilizer plant and Blue Circle Cement's cement grinding mill.¹⁶ Hillside Aluminium is in the process of increasing the capacity of its existing smelter through the addition of an extra pot line scheduled for completion around July 2004.

1.5 Processes and Pollution Sources

The present, and potential, industrial development has, and will have, an associated environmental impact. The large industries in the area, Richards Bay Minerals, Indian Ocean Fertilisers, Mondi, Hillside and Bayside Aluminium are the only major industries within the area and as such are the major sources of industrial pollution. Each industry is responsible for releasing process-related pollutants into the air, water and soils. These pollutants may be both organic and inorganic. The inorganic pollutants, which are of particular interest in this project, include metals, metalloids, sulfur compounds, fluoride compounds and a number of simple inorganic species such as phosphate and ammonia, all of which can be problematic in the environment. The main industrial processes and their associated pollutants are outlined in the next section.

1.5.1 Richards Bay Minerals

Richards Bay Minerals is a leading producer of titania slag, high purity pig iron, rutile and zircon. Richards Bay Minerals is the trading name for two registered companies, Tisand (Pty) Ltd and Richards Bay Iron and Titanium (Pty) Ltd, (RBIT). Tisand is responsible for the dune mining and mineral separation operations, and RBIT the smelting and beneficiation processes.²⁴

RBM was formed in 1976 to mine and beneficiate the vast mineral-rich sands in the coastal dunes, which extend 17 kilometres in a 2-kilometre strip from just north of Richards Bay. RBM produces some 1.9 million tonnes of product annually. Of this 95% is exported, yielding a world market share of about 25% of titania slag, rutile, pig iron and zircon.²⁴

RBM uses a dredge mining operation to extract and separate the heavy minerals ilmenite (FeTiO_3), rutile (TiO_2) and zircon (ZrSiO_4) from the sand.²⁵ A large artificial freshwater pond is created in the dunes, on which floats the dredger and concentrator plant. Moving into the mining face of the dune, the dredger advances at a rate of 2-3 metres per day, depending on the height of the dune. As the sand face is undermined it collapses into the pond forming a slurry, which is sucked up and pumped to a floating concentrator. At this point, the heavy minerals are separated from the sand using a gravity process and stockpiled as heavy mineral concentrate (HMC) for transportation to the smelter site.

The heavy mineral concentrate is transported from the mining plants to the mineral separation plant where the material is mixed with water and pumped into the feed preparation circuit. Here the slurry is passed over successive stages of low and high intensity magnets. These remove the ilmenite, which is set aside as feedstock for the smelter. The non-magnetic materials, including zircon and rutile remain, and are further processed in the dry mill. Here they are dried and separated, using an electrostatic process, which takes advantage of the difference in the conductivity of the minerals. At this point the zircon and rutile can be dispatched and sold in their raw form as mineral sands

The ilmenite is then processed to give titania slag and iron. It is first conveyed to a fluid bed calciner where it is roasted. In another process anthracite is heated and dried in a charring plant. The roasted ilmenite and the charred anthracite are then combined and are fed into four electric arc furnaces.²⁵ The furnace feed is melted to reduce most of the iron oxides to metallic iron, thereby producing titanium dioxide-rich slag and high purity iron. The slag and the iron are tapped into moulds and ladles respectively. These furnace products are further upgraded in subsequent processes. The titanium dioxide slag is crushed and classified according to particle size and sold largely to pigment manufacturers. The iron is further purified and alloyed at the iron injection plant where chemical additives, such as fluxing agents, are injected to obtain the grade specifications required by customers.

Titanium slag, which comes from ilmenite, contains 85% TiO_2 (the remaining 25% comprising of unreduced iron oxides) and is RBM's main product, while rutile contains 94% titanium dioxide. Rutile is mainly used in welding rod fluxes. It is also used in the manufacture of titanium metal. RBM's high purity pig iron is used as a raw material in foundries for the production of ductile iron castings.²⁵ Zircon is used in the production of ceramic tiles and sanitary ware. Zircon sand is also used in the foundry industry as moulding sand, as it is resistant to high temperatures.

All these products are then transported to the harbour by rail and subsequently exported all over the world.

Both gaseous and particulate matter is released from various sources at RBM's operations. Particulate emissions comprise metal oxide mineral dusts such as ilmenite, zircon and rutile, and carbon soot. These emissions can be minimized by the installation of various cleaning mechanisms and RBM plans on making improvements to areas of the smelter and iron injection plants.²⁴ When it comes to water pollution, monitoring water quality that returns to the environment via groundwater and surface water systems is essential to ensure that RBM operations do not pollute natural systems. Monitoring is undertaken on a regular basis at over 100 sampling sites within the 280 km² of RBM's operations. One area of concern is the potential leachate from iron residue tailings.²⁴ These tailings deposits may contain sulfides and this combined with exposure to oxygen may cause acid mine drainage (AMD). This AMD will contain elevated levels of metals and when these leachates reach rivers, a wider dispersion of metals both in solution and in particulate form is possible.²⁶

The main source of RBM waste is from the processing of minerals which is disposed of on-site. The three main sources of process waste are bag house dust and clarifier sludge, roaster and mineral separation plant tailings, and iron processing residues. There are also smaller quantities of industrial, domestic and hazardous wastes that are mostly disposed of elsewhere. Where possible, waste material is recycled and retreated by RBM. In the case of iron, an outside contractor collects material for use as scrap metal.

1.5.2 Indian Ocean Fertilisers

Indian Ocean Fertilisers was taken over by Foskor Limited in 1997. The Richards Bay division is a key manufacturer of sulfuric acid, phosphoric acid and granular fertilisers. Foskor is the largest producer of phosphoric acid in the Southern Hemisphere.²⁷

The Richards Bay plant complex includes two Monsanto sulfuric acid plants with a 100% sulfuric acid capacity of 1 650 tonnes per day; one Prayon wet process phosphoric acid plant with a capacity of 450 000 tonnes per year; one DM Weatherly NPK plant with a capacity of 400 000 tonnes of granular products per year; a bulk blending plant; a bagging plant and a bulk loading facility.²⁷

The starting point of phosphate fertilisers is phosphoric acid, which is produced at Foskor by the reaction of concentrated sulfuric acid with phosphate bearing rock.²⁸ A gypsum (calcium sulfate) by-product is separated from the acid by filtration, slurried and sent out to sea via a pipeline.²⁹ The phosphoric acid is then concentrated by vacuum evaporation. This product is sold internationally to fertiliser producers. Sulfuric acid is produced on-site by combusting elemental sulfur with oxygen, to produce sulfur dioxide gas. The sulfur dioxide gas is converted to sulfur trioxide using vanadium pentoxide catalyst, and is absorbed in water to yield the final product.

The phosphate bearing rock is railed some 800 km from Foskor's mine in Phalaborwa and contains fluorapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH})_2]$. Phosphate rock can in fact be any rock with a sufficiently high concentration of some form of the mineral fluorapatite to be of commercial value.³⁰ The production of the fertiliser is a relatively simple process and involves the neutralisation of phosphoric acid with ammonia gas in a reactor. The sludge that is formed is transformed into small, regularly sized spheres in a drum granulator after which it is screened, dried and bagged. The process of granulation is relatively intricate and requires the addition of binding and coating reagents. Special additives are also added during the granulation process to suit the customer's requirements. The whole process of fertiliser production is illustrated in Figure 1.4. The process begins with sulfuric acid production, followed by the production of phosphoric acid and finally the manufacture of the granular fertiliser.

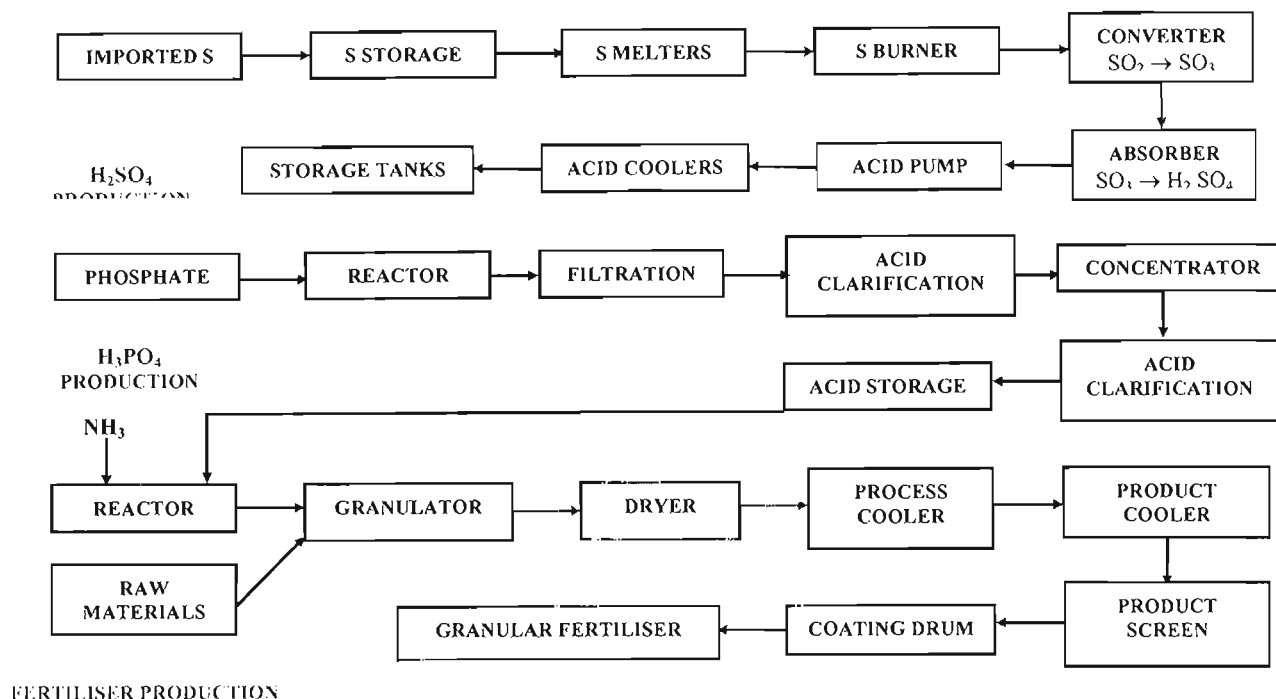


Figure 1.4 Process flow diagram for Indian Ocean Fertilisers

During the production of sulfuric acid, the main pollutant losses occur through the absorber exit gases. The gas composition of this exhaust stream is mainly nitrogen and oxygen. Since there is contact of nitrogen and oxygen with heated metal surfaces in a contact acid plant there is also the potential for the formation and loss of nitrogen oxides (NO_x) in these exit gases.³¹

Sulfuric acid mists can also be emitted and these are harmful to plant life and human populations. This acid mist problem arises from one or more factors. Water vapour in the air feed to the sulfur burner may cause mists because, as the water vapour plus sulfur trioxide steam drops below the dew-point temperature, aerosol formation occurs. If this cooling happens in the absorbers, mist losses can occur. Unconverted sulfur dioxide may also be discharged into the environment.

In the production of phosphoric acid it is the emission of fluoride that must be controlled. Contact of the fluoride present in phosphate rocks with a strong mineral acid mobilises much of the fluoride to hydrofluoric acid (HF) and silicon tetrafluoride (SiF₄). Fluorides are toxic and therefore are easily the most important components requiring control in a wet process

phosphoric acid plant. From an initial 3.8% (by mass) fluoride that may be present in the phosphate rock the fluoride is distributed to virtually all the product streams emanating from the production plant.

Fluoride losses to air occur in dusts raised in phosphate rock grinding and small amounts of dust loss occur from the first digester, as well as fluoride loss, mainly as silicon tetrafluoride vapour, from the whole digestion train.

Gypsum, while a relatively inert by-product of wet process acid production, may pose an environmental problem merely because of the large mass obtained. Early disposal by some facilities was simply into the nearest watercourse via a slurry pipeline, but this has been stopped as these suspended solids can have severe effects on water quality. The search for an alternative use for gypsum is the subject of a specialist study being undertaken for IOF, but at the moment the gypsum is stored in a slimes dam before being slurried in Mondi effluent and sent out to sea via a 'dense' pipeline.²⁹

1.5.3 Mondi Pulp and Paper

The paper mill situated in Richards Bay is a Kraft Mill. It was commissioned in 1984 and is one of the largest single-line operations of its kind in the world and meets the hardwood pulp requirements of the entire Mondi Group, as well as exporting more than half of its annual capacity of 500 000 tonnes.³² Production techniques are employed for a range of products, including Mondi Baycel, a premier grade bleached market pulp. Fourteen batch digesters give the mill the flexibility to produce softwood and hardwood pulp simultaneously, or alternatively. They also allow fibres of different characteristics to be blended to produce linerboard grades with different properties.

Although pulp is produced by both mechanical and chemical processes, the chemical methods produce more than 70% of the pulp used today and the exposures these processes present are much more serious than those of mechanical pulping.³³ The Kraft, or sulfate process, is employed at the Richards Bay site. This process is described in Figure 1.5.

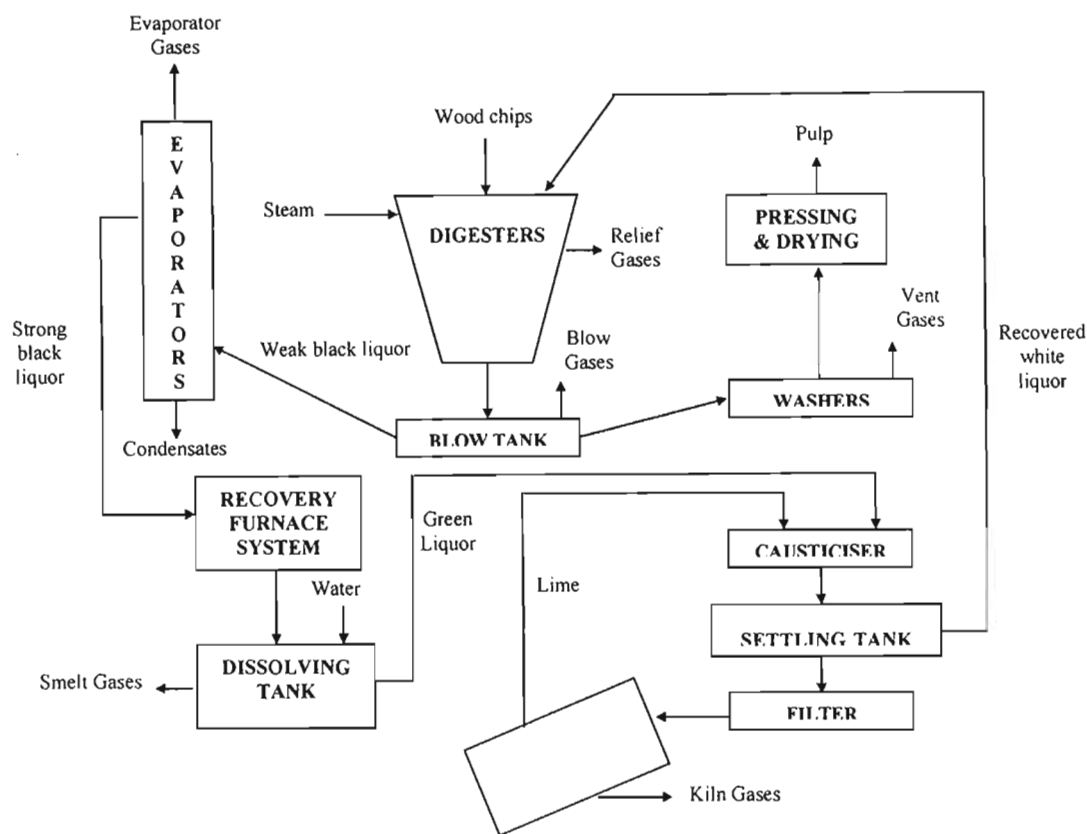


Figure 1.5: Flow diagram of a pulp plant

Chipped wood is digested with steam in tanks using a solution of sodium sulfide and sodium hydroxide (white liquor). Gases are vented periodically from the digester to relieve pressure build-up. When the digestion is complete, the load is dumped to the blow tank and the gases vent from the pulp and digestion liquid. The spent cooking liquid (black liquor) is drained off, and the pulp is washed, screened and bleached. The chemicals are recovered from the spent liquor by concentrating it in multiple-effect evaporators. Salt cake is added and the mixture is sprayed into the recovery furnace; here water is removed, the remaining liquor is burned, and the chemicals are recovered. The chemicals are dissolved in water in the smelt tank, and quicklime is added to convert the sodium carbonate to sodium hydroxide. The calcium carbonate that is formed is converted to calcium oxide in the lime kiln. This product is slaked with water to produce calcium hydroxide for the causticiser. The chemicals, and therefore the possible pollutants, associated with each of these processes are outlined in Table 1.1.

Table 1.1: Kraft Pulp Process

| Process Step | Formula |
|--------------------------------|---|
| White Liquor | $\text{NaS}_2 + \text{NaOH}$ |
| Black Liquor | $\text{NaS}_2 + \text{NaOH} + \text{dissolved lignin} + \text{Na}_2\text{SO}_4$ |
| Combustion of recovery furnace | $\text{NaS}_2 + \text{NaCO}_3$ |
| Green Liquor smelt tank | $\text{NaS}_2 + \text{NaCO}_3 \text{ in } \text{H}_2\text{O}$ |
| Causticiser | $\text{NaS}_2 + \text{NaCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{NaS}_2 + \text{NaOH} + \text{CaCO}_3 \downarrow$ |
| Lime kiln | $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ |

The papermaking process starts with the bleaching of the pulp. Since 2001 the Mondi Kraft Mill at Richards Bay uses an elemental chlorine-free bleaching technique. This involves an oxygen delignification process which allows part of the bleaching to be conducted with oxygen. In the bleach plant the pulp from the oxygen delignification stage is put through a five-stage elemental chlorine-free bleaching process to remove any remaining impurities and to brighten the pulp. This process includes treatment with chemicals such as chlorine dioxide, caustic soda and hydrogen peroxide, under controlled conditions.³² After a series of beating and refining steps, additives are blended with the pulp depending on the paper end-use. The consistency of the pulp is adjusted by adding water and the slurry is pumped to a moving sieve. The water content is then reduced to 5-8%.

Mondi is largely responsible for the air pollution in the Richards Bay area. Air pollution problems centre on control of the formation and discharge of reduced sulfur compounds, which cause severe odour problems and loss of particulates.³¹ Reduced sulfur compounds, such as methyl mercaptan and dimethyl sulfide, arise from the action of hydrosulfide and methyl sulfide anions reacting with the lignin of wood. Escape of the volatile sulfides can occur when excess digester pressure is vented, which occurs at intervals during the digestion. Table 1.2 gives an idea as to the levels of these sulfide emissions in each of the processes and in total.

Table 1.2: Total reduced sulfide emissions of a Kraft Paper Mill³¹

| Source | Total reduced sulfide emissions (kg S / tonne) | |
|---------------------------|---|---------------|
| | No controls | With controls |
| Direct contact evaporator | 7- 10 | 0.05 – 1 |
| Recovery furnace | 0.1 - 1 | 0.05 – 1 |
| Digester and evaporators | 1.0 - 1.5 | 0.0 - 0.3 |
| Black liquor oxidation | 0.05 - 0.2 | 0.05 - 0.2 |
| Pulp washer hoods | 0.05 - 0.2 | 0.05 – 1 |
| Dissolving tank vents | 0.05 - 0.2 | 0.05 – 1 |
| Lime kilns | 0.05 - 1 | 0.05 – 1 |
| Total | 8.3 - 14.1 | 0.03 - 2.8 |

It can be seen that although there are sizeable amounts of sulfide compounds being released into the atmosphere, these can be greatly reduced through the implementation of controls. The mill in Richards Bay was equipped with such controls when it was established in 1984 and thus their emissions can be regarded as being on the lower side of the scale.

Particulate emissions can amount to as much as 0.25 tonne per tonne of pulp produced. Electrostatic precipitators and wet scrubbers can achieve particulate containment of 95% or better. The precipitator catch is returned to the black liquor stream for chemical recovery from the captured inorganic chemicals. Table 1.3 gives an indication of the particulate levels discharged into the atmosphere from a typical Kraft paper mill. The composition of the particulate matter for the different processes is also given.

Table 1.3: Particulate emission loads of a Kraft Paper Mill³¹

| Source | Particulate Composition | Discharge (kg/tonne pulp) | |
|-----------------------|---|---------------------------|-----------------|
| | | No controls | Controls |
| Recovery furnace | Na ₂ SO ₄ , Na ₂ CO ₃ , NaCl | 100 – 200 | 1 - 10 |
| Lime kilns | CaO | 10 – 20 | 0.4-2 |
| Dissolving tank vents | Na ₂ SO ₄ , Na ₂ CO ₃ , NaCl, Na ₂ S | 3 – 4 | 0.4 - 1 |
| Total | | 113 – 224 | 1.8 - 13 |

As with the sulfides, the emission of particulates can be greatly reduced through the implementation of controls. The particulate emission controls are also in place at the Richards Bay mill and the emissions have been minimised.

Kraft process effluents may affect many water quality parameters. Wastewater streams may be high in suspended and dissolved solids, highly acidic or alkaline, and may have a high biological oxygen demand (BOD). Other parameters include intensely coloured streams, which may have a foaming tendency, and streams that are toxic to fish, all effects from dissolved constituents. The toxicity of the effluent may be from sulfides originating from digester relief gases or black liquor evaporation, from unsaturated fatty acids released from wood during pulping, or from chlorinated compounds produced in bleaching steps. The chemical recovery part of Kraft pulping serves to decrease potential effluent loadings of BOD and dissolved inorganic chemicals.

1.5.4 Hillside and Bayside Aluminium

The construction of Hillside Aluminium commenced in June 1993 and it cast its first ingot in June 1995. Hillside Aluminium cost R7.2 billion to build and is a 500 000 tonnes per year Greenfield aluminium smelter. Aluminium is the world's largest metal commodity market with an annual turnover exceeding R1 000 billion.³⁴ The Hillside smelter uses French-based Aluminium Pechiney AP30 technology and is one of the world's cleanest and most efficient smelters.³⁴ The reduction pots are the largest in commercial production worldwide. The 576 pots operate at about 320 000 A and consume less than 13.7 MW/h of electric energy per tonne of aluminium produced. The Hillside smelter was originally designed to produce 466 000 tonnes

per annum (tpa) but with good process control and careful management, this has been increased to around 500 000 tpa without additional equipment or significant cost.

Following an environmental impact assessment and feasibility study conducted by the CSIR to determine the environmental and social acceptability of the proposed expansion³⁵, Hillside Aluminium received approval to increase the capacity of its existing smelter through the addition of an extra pot line of half size. The addition of this third pot line will add a further 25% to Hillside's physical operating capacity and increase total output to 640 000 tpa. The cost of the expansion will be approximately US\$ 442 million.³⁴

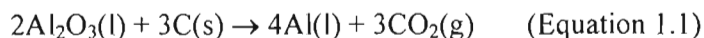
Aluminium is produced by the electrolytic reduction of alumina, which is obtained from bauxite, an ore primarily produced in South America and Australia. Trains deliver alumina to Bayside while Hillside's quota is transferred along a 6.8-km conveyor system to be stored in alumina silos. Approximately 5.3 tonnes of bauxite produce two tonnes of alumina which produce one tonne of aluminium.

Other raw materials used for the production of aluminum are petroleum coke and liquid pitch. When crude oil is refined to produce petrol and diesel, the residual material is used to make petroleum coke. Billiton Aluminium annually imports some 240 000 tonnes of petroleum coke from American and English suppliers. Billiton Aluminium also imports annually some 42 000 tonnes of liquid pitch, which is used for the production of anodes at Hillside. Consignments are shipped in specially converted vessels that keep the pitch at 200 °C. On arrival at the port, the pitch is pumped into the purpose-built storage tanks located at the wharf. Local suppliers deliver liquid pitch in road tankers at 170 °C to the Bayside Smelter for the production of its anodes.

The Hillside and Bayside smelters employ the Hall-Héroult method of aluminium production. This method occurs in large refractory-lined steel containers called pots that are connected in series and housed in long buildings called pot rooms.

The reduction of the alumina takes place in these pots. Each pot consists of a steel shell that is lined with refractory and carbon blocks to serve as the cathode (negative electrode). Suspended above each cathode are several closely arranged carbon blocks that serve as the anode (positive electrode). The anodes are suspended by rods in the bath of molten electrolyte in which the

alumina is dissolved. An electric current of up to 315 000 A enters the pot via the anode blocks and reduces the alumina by electrolysis into aluminium and oxygen. The oxygen is deposited on the carbon anode where it oxidizes the carbon to carbon dioxide. The aluminium, being heavier than the electrolyte, collects at the base of the pot. The equation for the overall reaction is:³⁶



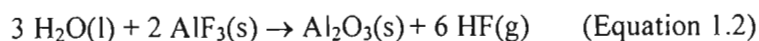
To sustain the electrolytic process, alumina is fed into the pots at regular intervals to maintain a sufficient quantity of dissolved alumina in the bath. The process is controlled by a computer that detects and interprets minute changes in electrical resistance and determines when to feed alumina to the pot. As the carbon anode is gradually consumed, it is periodically lowered to maintain the optimum distance of ± 5 cm between the anode and cathode surfaces.

For each tonne of aluminium produced, about 430 kg of carbon is consumed. A continuous supply of anodes is manufactured at both smelters in dedicated carbon plants that comprise paste plants, carbon bake furnaces and rodding shops. In the paste plants, carefully crushed and graded fractions of calcined petroleum coke and recycled anode butts are heated and mixed with molten pitch. The hot mixture is then compacted into blocks called green (unbaked) anodes. At Hillside, each anode weighs about 836 kg; at Bayside the anodes weigh about 624 kg. Approximately 400 000 anodes are produced each year for both smelters. The green anodes are transferred to the carbon bake furnaces where they are heated in deep brick-lined pits to around 1 100°C over a period of 21 days. This baking process calcines the binding pitch and ensures that the anodes have good thermal and electrical conductivity. Exhaust manifolds collect waste gases and carry them to the fume treatment centre. After baking, aluminium rods are attached to the anodes and sealed with cast iron. The rod suspends the anode in the pot and acts as an electrical conductor. After the rods are attached, the anodes are delivered to the pot rooms for positioning in the pots. Some 27 days later, the remains of the anodes, known as butts, are returned from the pot rooms and recycled. The rods are also reused.

The molten metal is tapped from each pot approximately once per day for transfer in special-purpose hot-metal carriers to holding furnaces in the cast house. The furnaces are heated and maintain the aluminium at the desired casting temperature of 700 °C. After the aluminium is poured into cast house furnaces, elements such as silicon, magnesium, copper, iron, titanium or boron are added to meet requisite alloy specifications. The metal surface is skimmed to remove

the dross. The clean alloy is then cast. Forty-four 22 kg ingots are stacked in a configuration of interlocking bundles. Each weighing one tonne, they are strapped and trucked to the export stockyard at the harbour.

Emission problems of conventional aluminium smelters centre on fluoride losses.³¹ The bulk of this fluoride loss occurs from the operating electrolytic cells, and two thirds, or more of this, is gaseous fluoride. The chief constituents of the fluoride discharge are known to be cryolite (Na_3AlF_6), aluminium fluoride, calcium fluoride, chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$), silicon tetrafluoride, and hydrogen fluoride. Most of these substances are lost as fumes or vapours, except the hydrogen fluoride gas evolution, which results from the reaction of traces of moisture present in alumina added to the cell.



This mode of fluoride loss is the reason that alumina shipment and transfers are conducted with minimum exposure to air, when moisture absorption could occur. In addition to losses of these substances the extremely stable fluorocarbons, carbon tetrafluoride, and hexafluoroethane, which are relatively non-toxic, are also known to form.

While fluoride emissions have undoubtedly been the impact area of greatest concern, a number of other gases are also significant. These include carbon monoxide, sulfur dioxide, hydrogen sulfide, nitrogen oxides (NO and NO_2), carbonyl sulfide (COS), and carbon disulfide.³¹ In some smelters there will also be measurable generation of hydrocarbon vapours and smokes, including polynuclear aromatic hydrocarbons.

There are also some problems dealing with liquid wastes, such as fluoride-contaminated discharge water from wet scrubbers, or drainage of precipitation from areas where spent pot-linings are discarded, since during use the carbon becomes impregnated with the fluoride constituents of the electrolyte. Water used for cooling metal castings or transformers is not contaminated. Disposal of spent pot-linings or discarded pre-baked anodes requires care to minimise problems of the type mentioned above. Of all the pollutants outlined, fluorides represent the aluminium smelter discharge component of greatest hazard to plant life, and also

indirectly to grazing and predatory animals. Since fluoride emission has generally represented the largest mass loss to the atmosphere and it may disperse widely by a variety of ways it has the potential to produce a significant biotic impact.³³

1.6 Determination of Potential Pollutants

As has previously been discussed, the aim of this project was to assess the extent to which the environment around Richards Bay has been affected by industrialisation. The major industries mentioned above are largely responsible for the pollution in the area and each has a variety of process specific pollutants. The range of potential pollutants is huge and it is obviously not possible to assess the effects of all of them. This study is, therefore, limited to the inorganic pollutants that are prevalent in all the industries.

The main focus of this study is on trace metal contamination of the hydrosphere and geosphere. All the industries discussed may be sources of heavy metal pollution, particularly the mining and smelting industries. Metals are released into the atmosphere during any fossil fuel use, but the principle sources of toxic metals in the atmosphere include the high temperature processes, such as coal and oil combustion, gasoline combustion, roasting and smelting of ores and kiln operations.³⁷ Mining activities affect relatively small areas but can have a large local impact on the environment. Release of metals from mining sites occurs primarily through acid mine drainage and erosion of waste dumps and tailing deposits.²⁶

Another inorganic pollutant of interest in this study is SO₂ or rather sulfur in a variety of gaseous forms. The levels of these gases are not measured directly, but indirectly through the monitoring of the pH of the surrounding soils and waters. These pollutants can be linked with all the industries, particularly Mondi, Foskor and to a lesser extent the aluminium industries. High concentrations of sulfur dioxide in the atmosphere can cause severe damage, as well as fostering an overall acidic environment, which may have far reaching consequences. Fluoride levels were also determined.

CHAPTER 2

Fluxes and Reservoirs of Contaminants in the Richards Bay Area

2.1 Introduction

In the previous chapter the main industries within the Richards Bay area were identified and discussed. These industries can be regarded as the point sources of the majority of pollutants in the area. Each industry is responsible for introducing a wide range of process-specific contaminants into the environment. Common contaminants released by all of these industries, to different degrees, are trace metals and it is these contaminants that are of interest in this study. The release of these trace metals into the environment may occur through a variety of means including gaseous emissions or through the disposal of solid or liquid waste. It is important to understand what happens to these contaminants once they enter the environment i.e. do they accumulate in a certain area and become sinks or are they readily transported between the various reservoirs of the environment. In this chapter the general behaviour of contaminants, particularly trace metals, in the environment will be discussed, with specific reference to the different environs within the Richards Bay area.

2.2 General geochemical cycles of contaminants

Geochemical cycles are a tool used to model the movement of an element or chemical species within the different parts of the environment i.e. the geosphere, the hydrosphere and the atmosphere.

Modeling of biogeochemical cycles is becoming increasingly important in understanding and predicting human impacts on the environment, and the possibility of using biogeochemical cycles to solve environmental problems, so-called biogeochemical engineering, has recently been recognized.^{1,38} Cycles are described using reservoirs and transport paths along which material is transferred from one reservoir to another. An example of a geochemical cycle can be seen in Figure 2.1.

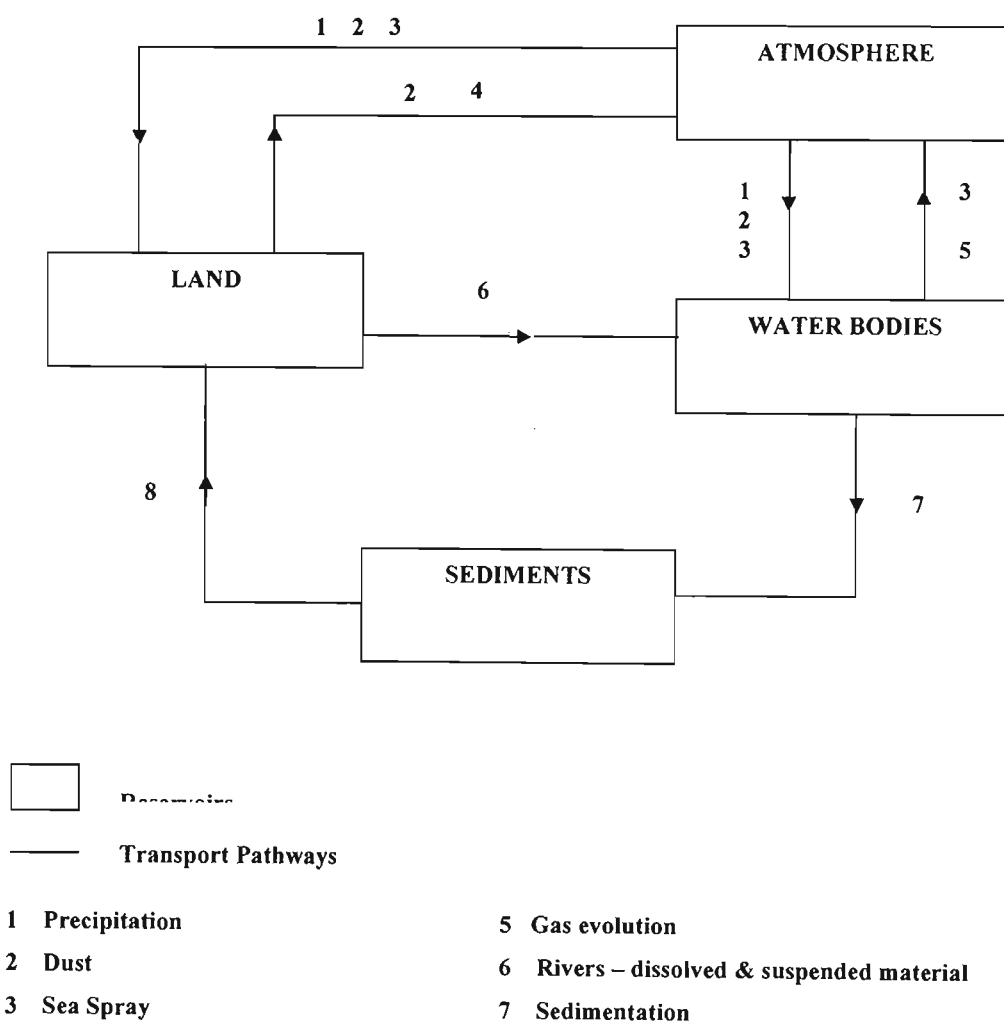


Figure 2.1: A general model of a geochemical cycle³⁹

The movement of substances within this geochemical cycle can be quantified through estimates of the amount of an element in each reservoir and the flux between the reservoirs. The flux is defined as the amount of material passing along a particular transport pathway in a fixed period of time.³⁹ A simpler definition of flux as the rate of input or output through a reservoir allows us

to see how the flux is directly affected by anthropogenic inputs. For example, if the input exceeds the output, there will be an increase in the amount of substance in the reservoir. There are many examples of the build up of pollution in environmental systems since pollutants are often added at rates greater than the rates of natural processes that act to remove them from the system. Another important parameter when evaluating the environmental effects of contaminants is residence time. The amount of an element in each reservoir and its flux can be used to determine the residence times of individual elements in particular reservoirs. The residence time, τ , is defined as:

$$\tau = \text{Amount of substance in the reservoir (mass)} / \text{Flux (mass/time)}^1$$

The residence times can be used to assess how long a contaminant will remain in a reservoir and this is a measure of the potential of a contaminant to become a pollution hazard in that reservoir.

2.3 Geochemical Cycles of Trace Metals

Accumulation of trace metals due to pollution can become a serious environmental problem for a number of reasons. Unlike the organic pollutants, which can undergo chemical degradation, metals will remain permanently in the environment in one form or another. Anthropogenic sources of heavy metals include mines, smelters and numerous other industrial activities, particularly those industries that use high temperature processes. It is therefore obvious that heavy metal contamination within Richards Bay may be a cause for concern. Emissions of air-pollutants from metal-ore smelting, including heavy metals such as Ni, Co, Cu and Ti, together with SO₂, have been reported as the cause of major damage to many terrestrial and aquatic ecosystems.^{40, 41, 42} Mining activities are responsible for direct trace metal contamination of water and soil systems and, although these affect relatively small areas, they can have a large impact on the local environment.^{26,43,44}

Trace metals may be initially emitted into the atmosphere, but this is not the reservoir in which they generally accumulate. The trace metals are removed from the atmosphere via a number of transport pathways, particularly wet and dry deposition. Wet deposition is defined as the removal

of material from the atmosphere by the combined action of rainout and washout, while dry deposition is the removal of material from the atmosphere by contact with solid surfaces on which the material falls or against which it blows.³⁹ The relative importance of the two depositional processes varies between locations and is primarily a function of the rainfall intensity in the area. Wet deposition accounts for about 80% of the atmospheric removal of elements such as Pb, Cd, Cu, Ni and Zn to the oceans, whereas 40% of the atmospheric removal of Fe and Al occurs through dry deposition.⁴⁵ Deposition of trace metals from the atmosphere is often in the form of insoluble salts and it is therefore rare for water bodies to be sinks for metal contaminants. The contaminants may enter these reservoirs, but are largely removed by transport processes such as sedimentation. Special circumstances, however, may lead to the accumulation of trace metals in water bodies. For example, the solubility of metals increases with a decrease in pH and solubilisation is often aided by the formation of complexes with organic material.⁴⁶ This solubilisation aided by low pH occurs mainly through two pathways, either through the direct reaction of the minerals or by cation exchange. The mechanisms below serve to illustrate how these two processes occur.

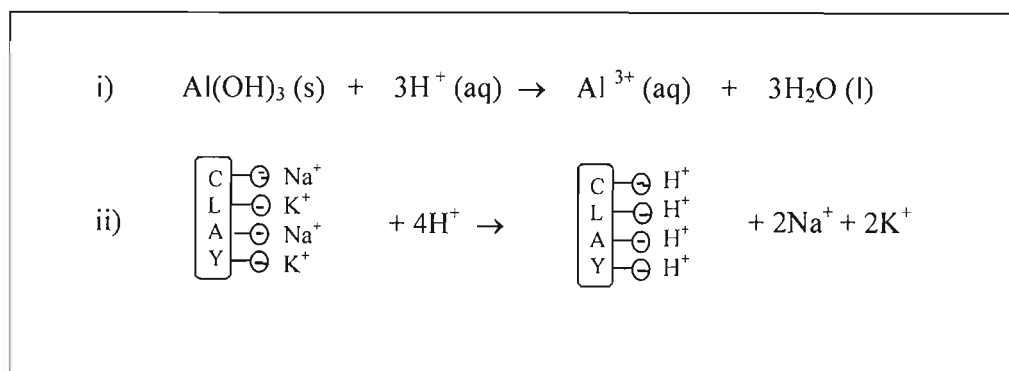


Figure 2.2: Solubilisation of metals at low pH's

Other than through deposition, trace metals may enter water reservoirs through leaching from soils and rocks. The disposal of massive quantities of metal wastes at landfills can lead to metal pollution of ground and surface waters.

It can, however, be seen that although metal contamination of the atmosphere and hydrosphere can occur, it is primarily the sediments and soils that become the reservoirs for trace metals. Atmospheric deposition can provide an input to topsoils of a number of biologically significant

metals and metals may also enter the soil environment through adsorption or absorption from water bodies. Once these metals have entered the soil and water environments, they are capable of undergoing numerous types of chemical and physical changes between the two reservoirs. These include sorption/desorption, complexation and precipitation. It is these reactions that bind the contaminants to the soils and sediments, subsequently making them a sink for trace metal contaminants.

2.3.1 Soils and sediments as a reservoir for trace metal contamination

The main chemical factors that affect the retention of a trace metal in these soil and sediment reservoirs are pH, ionic strength, electron activity and the speciation of the element. When several components (such as organic matter and hydrous oxides) co-exist in soil, the distribution of a trace metal among them will depend on the type and relative quantity of the soil components; how they change with pH, ionic strength etc., and the extent of saturation of absorption sites on soil absorbents. The distribution among these soil components is important for assessing the potential of soil to supply sufficient micronutrients for plant growth or contain toxic quantities of trace metals, and for determining amelioration procedures for soils at risk of causing trace metal contamination of waterways.

The pH of a soil is one of the most frequently measured parameters due to its importance in regulating numerous processes and is arguably the single most diagnostic measurement made on soil.⁴⁷ Acidification is a natural process in many soil environments, agricultural practices and pollution from industrial mining and other human activities have accelerated the process. The main sources of anthropogenic H^+ in soils are strong acids such as H_2SO_4 and HNO_3 in rainwater originating from industrial air pollution.

The availability of different metals depends strongly on pH. The pH of most mineral soils is between 5.5 and 7.5. Soils may become acidic if rainwater leaches out basic cations. Soils with pH values below 5.5 are likely to contain exchangeable aluminium leached from clay minerals. The levels of aluminium and manganese may increase to levels high enough to be biologically toxic at these low pHs. Conversely, soils with a pH of around 7 have a higher availability of the exchangeable cations Mg, Ca and K while the micronutrients Fe, Zn and Cu become less available at high pH. Even more extreme pH values signify the presence of particular minerals or

ions in the soil. A pH of above 8.5 is generally associated with high soluble or exchangeable Na^+ , whereas pH levels less than 3 usually indicate the presence of metal sulfides. The pH of a soil can be viewed as the “master variable” controlling ion-exchange, dissolution/precipitation, reduction/oxidation, adsorption and complexation reactions.⁴⁷

The distribution, mobility and biological availability of chemical elements depends not simply on their concentrations, but critically on the chemical and physical associations that they undergo in natural systems. Changes in environmental conditions, whether natural or anthropogenic, can strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. The existence of an element in different chemical forms in the gaseous, aqueous and solid phases provides the conceptual basis for speciation in soils. Each element has unique speciation tendencies. Soil solutions provide great opportunity for variety in speciation, as they contain organic ligands, the alkaline anions (HCO_3^- , CO_3^{2-} , OH^-), and numerous other anions (Cl^- , NO_3^- , PO_4^{3-}) capable of forming complexes with metal cations.

The speciation of metal cations governs their availability. It can be seen that the amount of a trace metal cation that is in soluble or exchangeable forms can indicate the tendency for uptake of metals by plants or for leaching. Soils containing hydroxy oxides at $\text{pH} > 5$ would have a low risk of contaminating waterways, but may not be able to supply cationic micronutrients for adequate plant growth.⁴⁵ At lower pH values organic matter appears to be the only solid phase component capable of retaining trace metal cations and decreasing soluble and exchangeable forms.⁴⁵

Speciation in solution is considered a major factor in the mobilisation and leaching of metal cations. Complexation increases the total soluble concentration of a metal and hence increases its potential to be leached. Organic ligands are the major complexes involved in this mechanism. Inorganic speciation in solution can also affect the mobility of metal ions. For example, the formation of an ion-pair with Cl^- can more than double the mobility of cadmium. At the same chloride concentration, however, the mobilities of Cu^{2+} and Ni^{2+} are only slightly increased (5-10%), presumably because of weak complexation with chloride.⁴⁵

The existence of an element in soil is transitory because soil is only one “compartment” in the biogeochemical cycling of elements in an ecosystem. The residence time of an element varies considerably depending on the mobility of its predominant species. For example, Al, Fe and Si are the most abundant elements in the soil, but less than 1% of their soil chemical species cycle in one year because most of their chemical forms are extremely immobile.⁴⁵ This slow cycling is fortunate, considering the toxicity of Al to plants and animals, but unfortunate if iron nutrition is thereby limited.

As yet, there are no unequivocal methods of distinguishing between different forms of an element in soil. Table 2.1 is a general indication of the species prevalent in soil solutions, based on the pH of the soils.

Table 2.1: Prevalent species of trace elements in soil solutions

| Cation | pH 3.5 – 6 | pH 6.0 – 8.5 |
|------------------|---|--|
| Al ³⁺ | Al ³⁺ , organic, AlF ²⁺ , Al-OH species | Al(OH) ₄ ⁻ , organic |
| Cd ²⁺ | Cd ²⁺ , CdCl ⁺ , CdSO ₄ | Cd ²⁺ , CdCl ⁺ , CdSO ₄ |
| Cr ³⁺ | Cr ³⁺ , CrOH ²⁺ | Cr(OH) ₄ ⁻ |
| Cu ²⁺ | Organic, Cu ²⁺ | Organic, Cu-OH species, CuCO ₃ |
| Mn ²⁺ | Mn ²⁺ , MnSO ₄ , organic | Mn ²⁺ , MnSO ₄ , MnCO ₃ |
| Fe ²⁺ | Organic, Fe-OH species | Organic, Fe-OH species |
| Ni ²⁺ | Ni ²⁺ , NiSO ₄ , organic | Ni ²⁺ , NiHCO ₃ ⁺ , NiCO ₃ |
| Pb ²⁺ | Pb ²⁺ , organic, PbSO ₄ | Pb – hydroxy's & carbonates |
| Zn ²⁺ | Zn ²⁺ , organic, ZnSO ₄ | Zn ²⁺ , organic, Zn-hydroxy's |

2.3.2 Availability and mobility of elements in soils

The toxicity of the trace metals in soils becomes a problem when these metals move into the plants and waterways. Relative mobility of elements in soils depends on several important factors including the chemical form and nature of the element; the chemical and mineralogical nature of the soil and the physical and biological environment of the soil. With regards to the chemical form and nature of the element, most trace metal cations have low a mobility in soils because they adsorb strongly on minerals and organic matter or form insoluble precipitates.

Some elements that take the form of anions, e.g. boron, are fairly mobile while other anions, such as phosphorus, are considered immobile because they form insoluble precipitates and bond strongly with mineral surfaces. The elements tend to fall naturally into one of four groups and the mobility of the four groups can be described in broad terms:

- i) Soluble weakly hydrating cations – strongly held by clays and humus
- ii) Soluble strongly hydrating cations – exchangeable and somewhat mobile, except strong chemisorbers such as lead and copper
- iii) Easily precipitated amphoteric hydroxides – immobile as insoluble oxides
- iv) Soluble anions – mobile, except strong chemisorbers such as phosphate.

The groups are determined based on relative ionic charge and radius. Figure 2.3 illustrates how the cations fall into these groups.

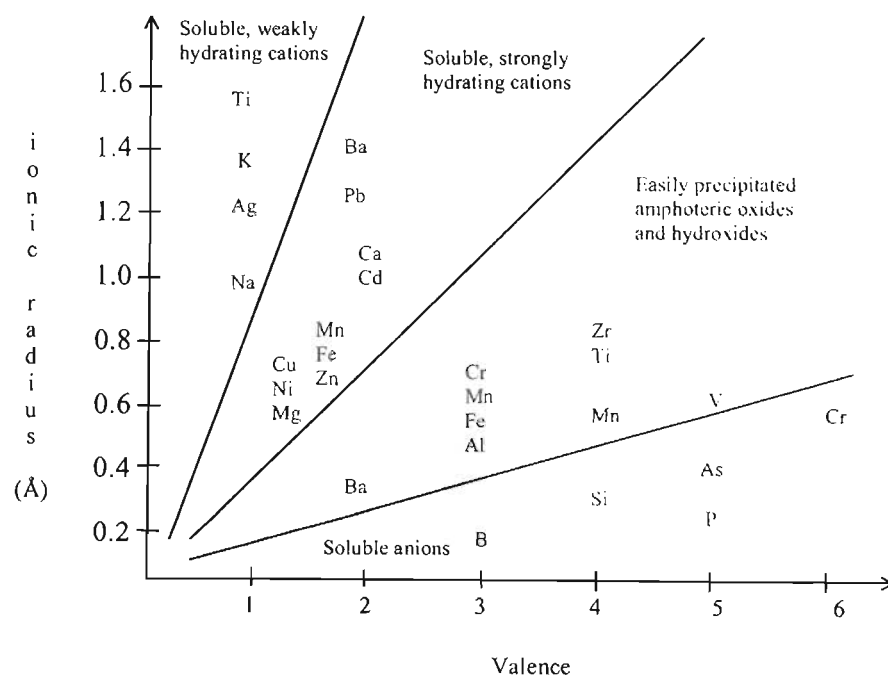


Figure 2.3: Division of elements into 4 groups on the basis of ionic charge and radius

When considering the mineralogical and chemical nature of the soil, elements are less mobile in those soils that provide a large quantity of sorption sites or a chemical environment favourable to

the precipitation of the element. Oxides of Fe, Mn and Al provide chemisorption sites for both cations and anions. Silicate minerals provide exchange sites for cations and a few chemisorption sites for both anions and cations. Soil organic matter is principally involved in metal cation adsorption. Overall, soils high in clays, oxide or humus strongly retain most trace metals. The chemical conditions in the soils can be critical in element retention. For metal cations, high pH favours sorption and precipitation as oxides, hydroxides and carbonates. Alkaline conditions in soils are generally associated with high levels of Na and K. Many anions form soluble compounds with Na and K, and as such soil alkalinity is usually accompanied by a high degree of anion mobility. Alkalinity may mobilise some metal cations as well because it favours the formation of metal organic complexes. Soil redox potential is also critical in controlling elemental mobility. Some elements are much more soluble and mobile in one oxidation state than in another. The elements classified as chalcophiles form insoluble sulfide minerals in reducing environments and their mobility is therefore extremely low.⁴⁷

The physical and biological environment of the soil means that high solubility of elements is not manifested as significant migration unless there is water movement through the soil. Experience with many elements that have found their way into soils as pollutants from agriculture or industry suggests that mobility is so low that the presence of undesired elements is practically permanent. This is certainly true for the strongly sorbing metals such as Pb and Cu. Even in wet climates where leaching is more or less continuous, removal of large portions of these less mobile elements by natural processes could take thousands of years.

Depending on the controlling factors for mobility, the elemental composition of the soils may or may not reflect the composition of the soil's parent material. However, it is generally observed that, all other factors being equal:⁴⁷

- i) Soils high in clay-sized minerals tend to have a higher concentration of trace metals than sandy and gravelly soils
- ii) Soils rich in humus tend to have higher concentrations of most trace elements than soils that are not. This observation applies to comparisons within sites as well as within a single soil profile, as many elements bioaccumulate in the organic-enriched surface horizon.

- iii) Soils of moderate to high pH tend to have higher concentrations of most trace elements than soils that have been acidified naturally (or otherwise) by acid water leaching.

2.3.3 Individual trace metal contaminants of interest

Some of the trace elements found in water and soils are considered as essential micronutrients, where others are potential pollutants. Many trace elements, including all the micronutrients, can reach concentrations in soils that are toxic to plants and microorganisms. Knowledge of a soil's composition in terms of total elemental content is usually not very useful when it comes to understanding the processes and availability, but if elemental concentrations are greatly in excess of those expected for a particular soil type this may be a sign of pollution from human activity or accumulation from natural biogeochemical processes. Table 2.2 is a summary of the biological functions and the relative toxicities of some of the trace elements.

Table 2.2 Biological function and toxicity of some important trace elements

| Element | Biological Function | Phytotoxicity | Mammalian Toxicity |
|---------|---|---------------|--------------------|
| Al | None known | H | H |
| B | Essential to plants | M | L |
| Ba | None known | L | H |
| Cd | None known | MH | H |
| Co | Essential for mammals | MH | M |
| Cr | May be involved in metabolism in mammals | MH | H |
| Cu | Essential to all organisms | MH | M |
| Fe | Essential to all organisms | L | L |
| Mn | Essential to all organisms | LM | M |
| Ni | None known in mammals. May be essential to plants | MH | M |
| Pb | None known | M | H |
| V | Required by green algae | H | H |
| Zn | Essential to all organisms | LM | LM |

(L = Low M = Moderate H = High)

Most studies done on trace metal contamination tend to limit themselves to the elements that have a high mammalian toxicity.⁴⁷ The same approach has been taken here as only toxic elements or elements that may occur at unusually high levels in the study area have been considered. The following section includes a brief discussion of each of these elements and its behaviour within the soil.

Aluminium

Aluminium contamination is of particular concern in the Richards Bay area due to the presence of the two large aluminium smelters. Aluminium is the third most abundant element in the earth's crust and it is a major component of many common minerals.¹ Despite its abundance in soil, only a small fraction is mobile. However, significant quantities of Al may be released in

acidic soils. Increasing inputs of acid, whether due to acid rainfall or to the decaying organic matter, will cause increasing removal of aluminium from soils that have a low buffering capacity.³⁹ Mobile Al has an important influence on soil pH. The effect of acidification of soils is to reduce the concentration of some essential elements and increase the concentration of toxic elements. Al can also be adsorbed onto clay particles and it can contribute to the cation exchange capacity. Some mobile Al is organically bound and may be less toxic than the more soluble inorganic forms. Mobile Al is potentially toxic to plants growing in acidic soils and the leaching of Al from soils into groundwaters could also be a potential concern.

Cadmium

Cadmium is widely used in the manufacture of paints, plastics, batteries and in metal plating.¹ The mobilisation of cadmium by human activities outweighs natural cycling processes.³⁹ Cadmium is a chalcophile. The oxidising conditions of weathering in soils release Cd as the soluble and mobile Cd^{2+} ion. This ion is even more soluble than Zn^{2+} and is said to have medium to high mobility in well-drained acid soils. The high mobility is attributed to the fact that Cd^{2+} adsorbs rather weakly on organic matter, silicate clays and oxides unless the pH is higher than 6. Above pH 7, Cd may precipitate out and mobility and bioavailability of Cd^{2+} in neutral to alkaline soils is low.⁴⁷ The increased quantities of cadmium mobilised are partly related to the demand for cadmium itself, but also to increased use of zinc and phosphate fertilisers.³⁹

Typical soil concentrations of cadmium range from 0.06 to 1.1 mg/l.⁴⁷ Generally, Cd concentrations in soils exceeding 0.5 g/kg are considered to be evidence of soil pollution. These concentrations of Cd have often been measured in soils near to mines and smelters.¹ Nevertheless, natural geochemical processes have been known to concentrate Cd levels in surface soils.⁴⁷ Cd tends to accumulate in peaty soils by precipitation in sulfide minerals, and Cd levels may also be high in poorly drained soils or soils of arid and semi-arid climates.

Cobalt

Cobalt is ordinarily present in plants or animals in concentrations of less than 0.01%, but may be essential to some or all organisms.³⁹ Cobalt levels in soils range from 0.2 to 30 mg/kg.¹ Cobalt occurs in two oxidation states in soil +2 and +3, but +2 is the dominant form in soil solution. This metal associates preferentially with Fe and Mn oxides because of chemisorption and co-

precipitation. It has been discovered that on Mn oxides, Co^{2+} is oxidised and subsequently strongly bound as Co^{3+} . Strongly oxidising conditions in the soil are therefore likely to favour the absorption of cobalt. As the soil pH is raised, Co solubility decreases because of increases chemisorption, complexation by organic matter and possibly precipitation. Cobalt is said to be somewhat mobile in acid soils, but less so as the pH approaches neutrality.⁴⁷

Chromium

Major industrial sources of chromium in the environment are non-ferrous metal plants, paper and pulp production, petrochemicals, electroplating and more. Naturally occurring Cr is ubiquitous in soils and vegetation although concentrations are generally very low.¹ Concentrations of chromium in soils are generally in the range from < 1 to 1000 mg/kg, although at some sites levels as high as 10 000 mg/kg have been reported.¹

Cr in soils potentially occurs in the +3 and the +6 oxidation states. However, soil conditions generally favour the +3 form, a very immobile cation that complexes strongly with organic matter and chemisorbs on oxides and clays, even at quite low pH. The chromic form is very immobile in most soils and generally unavailable to plants, at least if the soil is not exceedingly acidic.

At higher pH, a small fraction of the +3 can be oxidised to the +6, a very toxic form of Cr. Mn oxides promote this oxidation. Chromate absorbs less strongly than Cr^{3+} , and the mobility and bioavailability is consequently higher. Generally, however, if pollutants containing chromate are applied to soils, most or all of the chromate is spontaneously reduced to Cr^{3+} , especially under acidic conditions and if organic matter is present. The soil usually has the ability to detoxify chromate and immobilise the element.

Chromium is rated as an immobile element, most of which is difficult to extract from soils. Toxicity of Cr to plants is occasionally seen in unusually Cr-rich soils under high pH conditions favourable to Cr^{3+} oxidation.⁴⁷

Copper

Copper is an essential element, but may become toxic if present in too high a concentration.³⁹ Copper concentrations in soils are generally < 100 mg/kg, but levels as high as 17 000 mg/kg have been reported, particularly in sludges.¹

Copper exists in soil solids and solutions almost exclusively as Cu^{2+} . Copper is classified as a chalcophile, owing to its tendency to associate with sulfide. In reduced soils, copper has a very low mobility. Most of the colloidal material of soils (oxides of Mn, Al and Fe, silicate clays, and humus) adsorb Cu^{2+} strongly and increasingly so as the pH is raised. For soils with high pH accumulations, precipitation as hydroxides, oxide or carbonates is possible above pH 6.

The trace quantities of Cu found naturally in most soils are probably widely dispersed on sorption sites within oxides and silicates. Because of the high affinity of Cu^{2+} for soil colloids, copper is rated a low-mobility element in near-neutral soils. It builds up in the surface of contaminated soils, showing virtually no downward migration. In more alkaline soils, while free Cu^{2+} solubility is exceedingly low, soluble complexes of Cu^{2+} form and increase the total copper solubility. Consequently, mobility may be significant under pH conditions. Most of the total dissolved copper in surface soils over a fairly wide range of pH, and particularly at higher pH, is the form of Cu^{2+} - organic complexes.⁴⁷

Manganese

Total manganese concentrations in soils are highly variable (< 20 to > 3000 mg/kg), but only some of this is available.¹ Mn has three possible oxidation states in soils, +2, +3, and +4. The most reduced form Mn^{2+} ion is the most stable form in soil solution. Both Mn^{3+} and Mn^{4+} are stable only in the solid phase of soils, where they form insoluble oxide and hydroxide minerals. The Mn^{2+} is released from the soils by spontaneous dissolution or cation exchange, especially under acidic or reducing conditions. Mn solubility is controlled by the redox potential and the pH of the soil. Mn^{2+} ion is a very soluble species on water, forming hydroxide and carbonate precipitates only at high pH (>7). However, as the pH is raised above 6 in soils, Mn^{2+} bonds with organic material, oxides, and silicates and its solubility decreases. Mn solubility within any particular soil can fluctuate tremendously over time, sometimes ranging from deficient to toxic levels.

The mobility of Mn defies classification because it is extremely sensitive to soil conditions. Toxicity to plants is most probably in waterlogged soils or acid soils with low humus content. Deficiency is most often found in soils that are saline and alkaline, coarse textured or acid-leached.⁴⁷

Nickel

Nickel emissions to the atmosphere are mostly anthropogenic, industrial sources account for more than 80% of the total emission. Nickel levels in soils are generally between < 50 and 100 mg/kg, but very high levels may be found in some areas. Concentrations of Ni as high as 5 000 mg/kg have been reported in some soils.¹ Nickel pollution from metal smelting has been reported in Canada, Russia, Australia, Cuba and other countries.¹

The +2 oxidation state is the only stable form of nickel in the soil environments. The Ni^{2+} ion is almost as electronegative as the Cu^{2+} ion; this fact and its electronic structure favour the formation of complexes with organic matter. Bioaccumulation of Ni in humus is pronounced and Ni^{2+} favours bonding to softer organic ligands containing N and S. The Ni^{2+} ion co-precipitates readily into Mn and Fe oxides in soils. Chemisorption on oxides, silicates and clays is favourable above pH 6, but lower pH favours soluble and exchangeable Ni^{2+} . Because solubility decreases markedly at higher pH, mobility of Ni, rated as medium in acid soils, becomes very low in neutral and alkaline soils. Under reducing conditions, Ni^{2+} is incorporated into sulfides that restrict mobility to very low levels.

Toxicity of Ni to plants is found in acid soils. High organic matter in Ni-rich soils can solubilise Ni^{2+} as organic complexes, at least at higher pH. Ni is a strongly phytotoxic element.⁴⁷

Lead

Average concentrations of lead in soil are between 15 and 25 mg/kg. Major anthropogenic sources of Pb include its use as a petrol additive, Pb mining and smelting and the use of pesticides containing lead compounds. Soils in the vicinity of mines and smelters may have concentrations of > 10 000 mg/kg.¹

Lead exists principally in the +2 oxidation state in soils. It is strongly chalcophilic, occurring primarily as PbS and becoming very insoluble in reduced soils. Under oxidising conditions, the Pb^{2+} ion becomes less soluble as the soil pH is raised. Complexation with organic matter, chemisorption on oxides and silicate clays, and precipitation are all favoured at high pH. In alkaline soils, solubility might increase due to the formation of soluble organic and hydroxy-complexes. Lead is the least mobile heavy metal in soils, especially under reducing or non-acid conditions.

As expected by the strong complexation of Pb with organic matter, lead bioaccumulates in the humus-rich surface layer of the soils. Soils polluted at the surface show little indication of lead leaching over many years. Toxic effects of lead on plants have not often been observed, but a hazard to animals exists because of the inherent toxicity of this element to animals. The health concern with lead-polluted soils arises from the contamination of plants from soil particles, and ingestion of soils by humans and grazing animals. The risk of lead movement to edible plants is believed to be low.⁴⁷

Zinc

Zinc is an essential element, but may become toxic if present in too high a concentration. The mobilisation of zinc by human activities outweighs natural cycling processes.³⁹ Anthropogenic sources of zinc in the environment include construction materials, metals, fertilisers, atmospheric deposition and coal combustion. Zinc concentrations in soils typically range from 1 to 2 000 mg/kg, but at some sites levels as high as 10 000 mg/kg have been reported.¹

As a chalcophile, Zn tends to occur as the sulfide mineral, but weathers to the soluble Zn^{2+} ion in the oxidising environment of soils. The +2 oxidation state is the only one possible in the soil. In acid, aerobic soils, Zn has medium mobility, held in exchangeable forms on clays and organic matter. At higher pH, however, chemisorption on oxides and silicates and complexation with humus lower the solubility markedly. Consequently, Zn mobility in neutral soils is very low. If soils are slightly alkaline, Zn organic complexes can become soluble and raise mobility. In strongly alkaline soils, Zn-hydroxy anions may form to increase solubility.⁴⁷

Under acidic, oxidising conditions, Zn^{2+} is one of the most soluble and mobile of the trace elements. It does not complex tightly with organic matter at low pH. Acid-leached soils often have Zn deficiency because of depletion of this element in the surface layer.

Toxicity to plants is most likely to appear in acid soils that have not been subjected to prolonged acid leaching. The rather high potential solubility of Zn in acid soils, and the fact that Zn is typically a high concentration pollutant in industrial wastes, combine to create a significant potential for phytotoxicity. This is in spite of the fact that Zn toxicity to plants is inherently fairly low. Normal zinc levels in plants are 25 – 150 mg/kg, with concentrations above 400 mg/kg being toxic.³⁹

2.4 Geochemical Cycles in Richards Bay

Richards Bay is an area that provides us with a number of obvious pollution point sources and a variety of reservoirs in which the pollutants may accumulate. As previously mentioned, this area is at high risk of trace metal contamination due to the presence of smelters, mining activities and industries that involve high temperature processes. All these activities are reported to be sources of trace metal pollution.^{26, 29, 37, 40, 42, 43} The wide variety of reservoirs within Richards Bay in which these contaminants may accumulate include rivers, a lake, an estuary, a harbour and the general surrounding soils. Figure 2.4 shows a map which illustrates the point sources and the possible reservoirs within the study area.

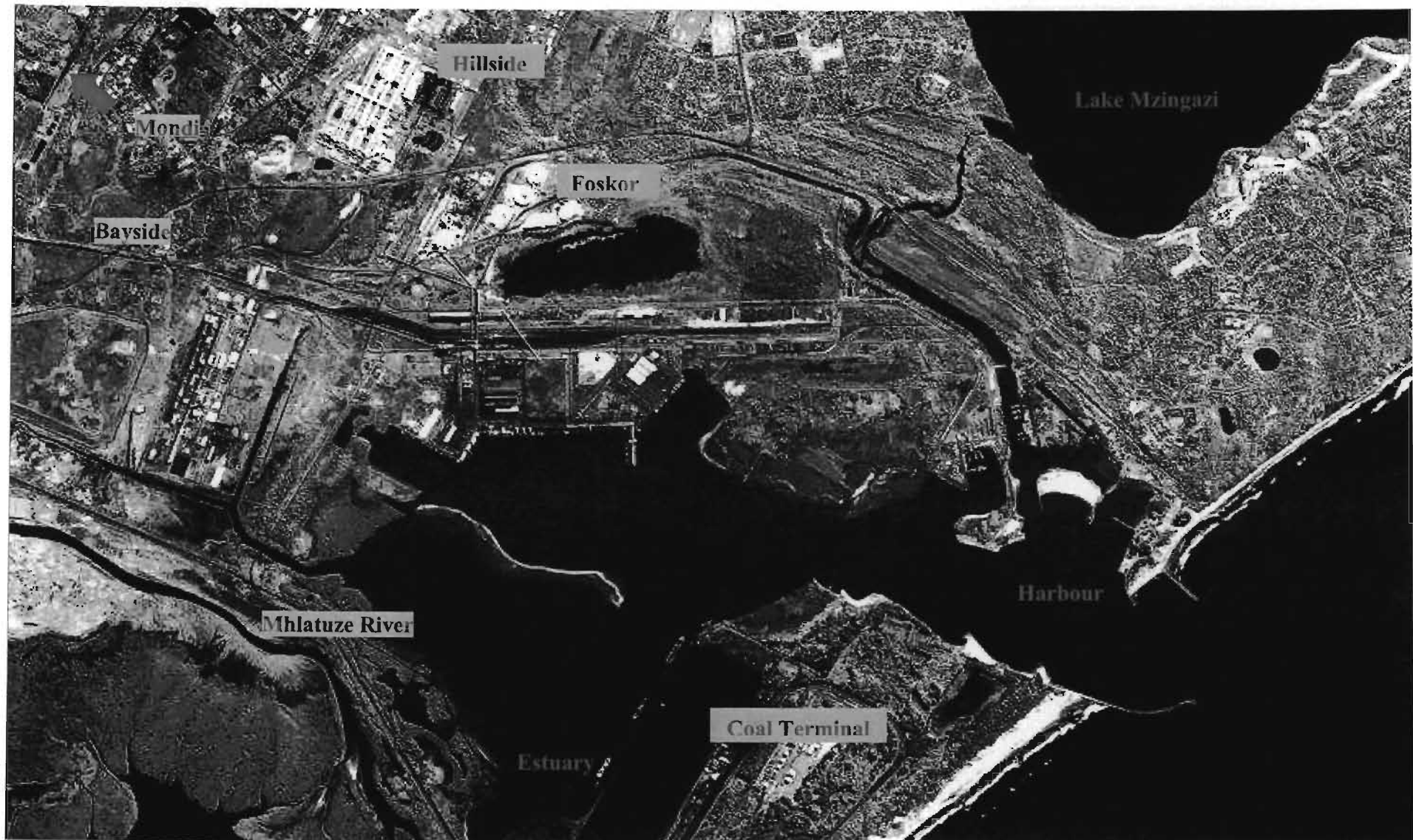


Figure 2.4: Map showing the point sources and reservoirs within the Richards Bay area⁴⁸

Studies have been conducted mainly in Europe and North America to assess the accumulation of trace metal contaminants in these different reservoirs. De Boer *et al.*⁴⁹ have done studies of pollution of harbours by trace metals in Holland, centring on the Amsterdam and Rotterdam harbours. The aim of the study was to contribute data to the understanding of the behaviour and fate of trace metals in harbour areas in a densely populated and highly industrialised area. The metals of interest in this study were arsenic, copper, nickel, lead, cadmium, chromium, mercury and zinc. The concentrations found were compared with concentrations of the same contaminants in sediment from reference locations and with background concentrations. Somewhat elevated concentrations of cadmium and mercury were found in the harbour sediments, whereas for the other trace metals differences between harbour areas and reference locations were generally marginal.

A similar situation is to be found in the Richards Bay. The Richards Bay harbour, covering 1 495 ha of water area⁵⁰, is situated within an industrialised area and, with the prevailing wind in Richards Bay blowing in a north-easterly direction, generally down wind from the pollution sources (see Figure 2.4). As such the harbour may be polluted by deposition of atmospheric pollutants from these point sources. The harbour may also be polluted directly by aqueous effluents from the point sources as well as by the heavy marine traffic.

Studies of estuaries and lakes have been done in the United States, Bulgaria, Russia and France.^{44, 51, 52, 53, 54} Sanger *et al.*⁵³ studied the distribution of trace metals in South Carolina estuaries to determine the levels of sediment trace metal contamination associated with different types and varying levels of human development. The sediment samples were analysed for Al, Fe, Ni, Mn, Cu, Cr, Zn, Sn, As, Pb, Cd, Ag and Se. It was determined that trace metals most commonly associated with urban and industrial sources, including Cu, Cr, Pb, Zn, Cd and Hg, were in significantly higher concentrations in estuaries located in industrial areas compared to the suburban or forested areas.

With regards to lake contamination, a study conducted by Dauvalter⁴⁴ involved assessing the impact of mining and refining on the distribution and accumulation of nickel and other heavy metals in sediments of a lake in Russia. This lake is situated in an industrial area and has a nickel refinery and nickel mines surrounding it. The sediment samples were analysed for Ni, Cu, Co,

Zn, Cd, Pb and Hg and the concentrations found were compared with background concentrations. The background concentrations were represented by those observed in the deepest layers of lake sediments, which exceed 200 years in age and thus precede the industrial development of the region. The sediments were found to be contaminated by nickel, copper, mercury and cobalt.

The studies above are focussed on freshwater bodies within an industrialised region. The local Richards Bay environment contains a large freshwater source in Lake Mzingazi. As in the case of the above studies, Lake Mzingazi is in relatively close proximity to the pollution point sources. The lake has a catchment area of 164 km², a surface area of 1 216 ha, a mean depth of 3.9 m and a maximum depth of 14.2m.⁵⁰ The lake is down-wind from the pollution point sources (see Figure 2.4) and therefore may be contaminated by atmospheric deposition of pollutants. Samples taken from Lake Mzingazi would serve to give an idea of the freshwater contamination in the area.

The majority of studies of this kind are done on trace metal contamination of river sediments that are near areas of considerable industrial activity. For example, Vink *et al.*⁵⁵ and Velinsky *et al.*⁵⁶ were responsible for determining the extent of trace metal pollution, and identifying the nearby point sources, of several rivers flowing through industrialised areas in Europe and North America respectively. These studies took sediment samples and analysed them for Cu, Cr, Cd, Hg, Pb and Zn and compared them with background levels. Both studies concluded that there was contamination of the river sediments taken from within highly industrialised areas when compared with river sediments taken from outside these industrialised areas.

With regards to sediment analysis, the basis of the Richards Bay study is the same as the above studies. The Mhlathuze River in Richards Bay flows directly through the industrialised part of the city. The river may be polluted by atmospheric deposition, as well as directly from aqueous effluents, from the pollution point sources. The sediment samples taken from within the industrialised area can be compared with sediment samples taken from the same river where it flows through an undeveloped, and relatively unpolluted, region.

Even more appropriate to this present work are the extensive studies that have been performed on surface soils near smelters, mines and highly industrialised areas to determine the extent of trace metal contamination.^{26, 40, 41, 42, 43, 44} Surface soils may become reservoirs of trace contamination due to their close proximity to the point sources. Contaminants in the factories' emissions may be deposited directly onto the surface soils or effluent may be discharged directly to the soils. Heavy vehicular traffic may also contribute to the pollution of surface soils. Soils can be used to identify sources of particular contaminants. This is done by sampling soils directly next to a point source and then at varying distances from it. In this way, if the levels of the contaminant decrease as you move away from the point source it can be clearly identified as the specific source of that contaminant. For example, Benim *et al.*⁴⁰, Koptsik *et al.*⁴¹ and Goodarzi *et al.*⁴² all did studies of surface soil contamination in relation to the position of a smelter. These studies were done in Mexico, Russia and Canada respectively and, taking into account the prevailing wind conditions, determined in each case that the levels of trace metal contamination decreased as the distance from the smelter increased.

In this study of the Richards Bay area, point sources are easily identified and surface soils can be analysed for all the trace metals with reference to their distance from these sources. An important issue to take into account when trying to determine levels of contamination in surface soils is the type of soil. Each soil type has a different background trace metal level and also a different affinity for trace metals i.e. some soil types are more susceptible to trace metal contamination. The soil types within the Richards Bay area can be seen in Figure 2.5. It can be seen that the soil types predominantly found in this area are the Ia series (alluvial deposits) and the Hb series (grey sands), specifically Ia74 and Hb75.⁵⁷ These soil types surround the harbour area, covering about 3080 ha in the Richards Bay area. The land type Hb75 consists of deep, grey, medium grained sands to loamy sands with clay contents of 0 to 10%. Land type Ia74 is listed as comprising reclaimed land, and it is difficult to assess the soil characteristics. Alluvial deposits vary in texture from 20% to 60% clay.⁵⁸ The pH values for both the soil types are between 5 and 6. It is this clay content and pH that will have a significant effect on the levels of trace metal contamination of the soils. Theoretically, soils of this type should not be sinks for trace metal contamination as the pH is within the normal range and they have low clay content (soils may have a clay content of up to 90%⁵⁹ and will strongly retain most metals).

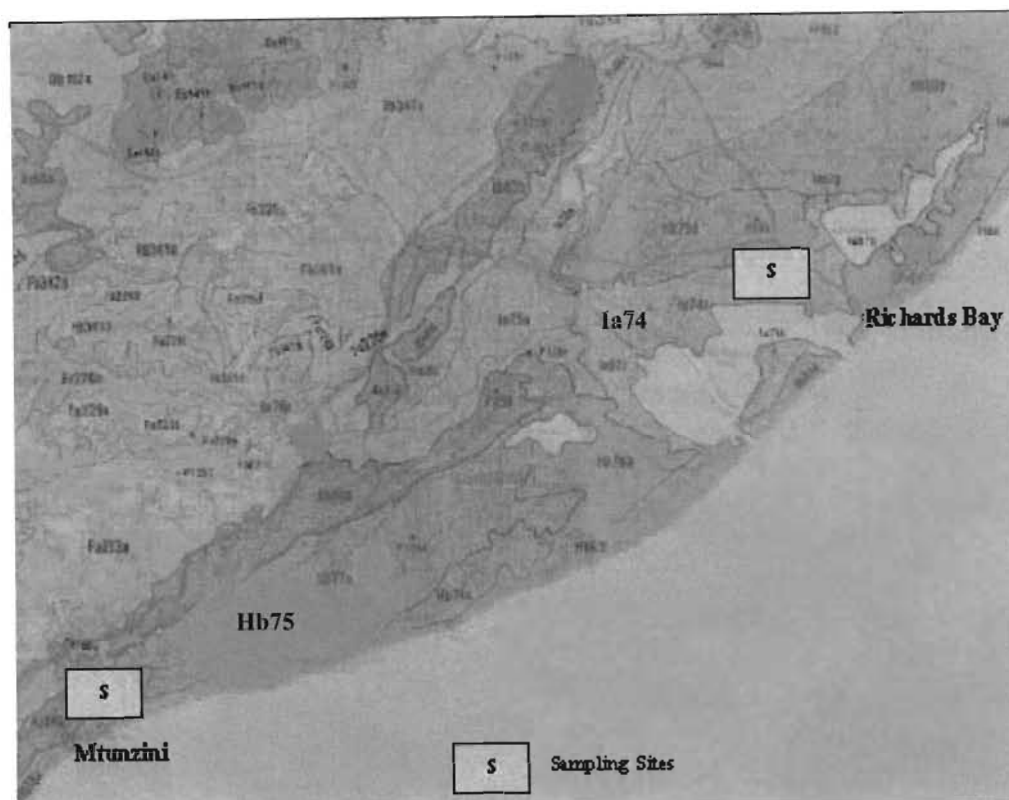


Figure 2.5: Richards Bay land-type map

However, anthropogenically-sourced acidification of the soils in this area may alter the picture. Information on the trace metal levels of uncontaminated soils of this type is unavailable and it is therefore necessary to ensure that when background samples are taken they are taken from an uncontaminated site with the same soil type.

The majority of the studies mentioned in this chapter indicate that it is the sediments of water bodies that generally become the sinks for trace metal contamination and as such they are of particular interest. However, the water bodies themselves should still be monitored, particularly for changes in pH. They are largely affected by these pH changes, which are a reality due to the emission of acids and sulfur dioxide from the local point sources. These emissions can cause an overall acidification of the environment. To determine the full extent of trace metal pollution in the Richards Bay area it is necessary to take water, soil and sediment samples from all the possible reservoirs. The pollution levels in this study are measured in terms of the overall concentrations of contaminants and although this gives a reasonable idea of the contamination it

does **not** take into account the speciation of the contaminants. Speciation is important as it affects the toxicity, mobility and bioavailability of the contaminants within the different reservoirs.

CHAPTER 3

Methodology for Sample Collection and Chemical Analysis

3.1 Background to Sample Collection

The sample is one of the critical elements of the analytical process. The quality of any data produced by any analytical system primarily depends on the sample analysed. Over 50% of all errors in environmental analysis result from incorrect sampling.⁶⁰ A sample must be representative of the whole so that the final result of the chemical analysis represents the entire system that it is intended to represent. Samples collected at a particular time and place are called grab or individual samples. A grab sample is limited to the single time and location of the sample. Representation of the whole sampling area requires taking many grab samples over a period of time, analysis of each sample and the averaging of the results.

A record should be made of every sample collected, and every bottle and bag should be identified. The report should include sufficient information to provide positive identification of the sample at some later date, and should include details such as the date, the time and the exact location, as well as any data which may be needed for future correlations, such as weather conditions. When collecting water samples information such as the temperature and the level of the water body should also be recorded.

The required material and type of sample bottle used and the preservation of the samples may differ depending on the analytical parameter to be measured. Preservatives are used to maintain the chemical integrity of a sample. Most solid samples have only cooling as a preservative. Water samples are subject to a variety of specific preservation techniques depending on the target analytes. Sample holding times before analysis are of critical importance.

Analytes will degrade and be lost from the sample over time, even when correctly preserved and stored. In general, the shorter the time interval between sampling and analysis, the more reliable the analytical results. The laboratory report should state which, if any, preservatives were added and the time elapsed between collection and analysis. An example of the laboratory sheet used in this project can be seen in Appendix 1.1.

3.1.1 Soils and Sediment Samples

Sampling of heterogeneous media such as soils and sediments presents some difficulties and the sampling programme should be carefully planned from the outset if a representative sample is to be obtained. If monitoring is related to a point source then prevailing winds should be taken into account. The depth of the soil sampling depends on the aims of the monitoring. Analysis of the upper layers is relevant in understanding soil interactions with other environmental compartments and the pathways of pollutants between them.¹ Control samples should also be taken at points remote from the area under investigation and an effort should be made to match the control site as closely as possible to the sample site.

Before taking samples leaves, grass and any large external objects should be removed. Surface samples can be collected with corers, spades etc. and stored in either plastic bags or plastic containers. The sample is extruded and homogenised before analysis. Sub-sampling is always a problem with solids, as any agitation tends to separate mixtures according to particle size. Standard methods are well established to overcome this⁶¹; the simplest includes crushing the sample and the ‘cone and quartering’ technique. This process can be repeated successively until the required sub-sample size is produced. It is important to avoid contamination of the samples. When metal determination is to be carried out, metal containers should not be used for collecting, mixing, storing or preparing samples. High-density polyethylene (HDPE) containers should be used instead.

3.1.2 Water Samples

The volume of sample to be collected will depend on the number of analyses that will be carried out. If a comprehensive water analysis is to be done, a 2-litre sample should be collected.¹ If one or a few analytes are to be determined, smaller volumes may be satisfactory depending on the

amounts required for the test. Plastic or glass bottles may be used depending on the analyte of interest; generally plastic should be used for inorganic analytes and glass for organics.

Surface waters are the easiest to collect. Collecting samples at a depth requires special collectors. The empty sample bottles should be rinsed several times with the water to be sampled. The sample bottle should be filled slowly to avoid turbulence and air bubbles. Appropriate preservatives should be added, if necessary, and the sample containers should be completely filled and stored at sub-ambient temperatures until analysis. A temperature of 4 °C is often specified in analytical procedures. This slows down, but does not eliminate, bacterial and chemical reactions. Reaction rates at 4 °C are about a quarter of the rates at 25 °C.¹ Recommended bottle materials, preservatives and storage times are given in Table 3.1. The quoted storage times should be considered as maximum recommended times.

Table 3.1: Recommended storage conditions for some analytes in water samples

| Analyte | Bottle | Preservative | Max storage time |
|--------------|--------------|--------------------------|------------------|
| Calcium | Polyethylene | None | 4 weeks |
| Chloride | Polyethylene | None | 4 weeks |
| Fluoride | Polyethylene | None | 4 weeks |
| Magnesium | Polyethylene | None | 4 weeks |
| Pesticides | Glass | pH 5 - 9 | 6 weeks |
| Phosphate | Polyethylene | None | 2 days |
| Potassium | Polyethylene | None | 4 weeks |
| Sulfate | Polyethylene | None | 4 weeks |
| Trace Metals | Polyethylene | HNO ₃ to pH<2 | 6 months |

3.2 Background to Sample Preparation

Although some samples may be analysed directly, most often the sample has to be prepared for analysis. A variety of sample treatment methods can be used, depending on the type of sample, the analyte to be determined and the kind of analytical method to be used. There are three main

purposes of sample treatment, namely to convert the sample and analyte into a form suitable for analysis by the chosen method, to eliminate interfering substances and, thirdly, to concentrate the sample.⁶⁰ Typical sample treatments include dissolution/digestion⁶², filtration⁶³ and solvent extraction⁶⁴.

3.2.1 Soil and Sediment Samples

In order to determine the amount of trace metals in soils and sediments it is first necessary to bring them into solution. This pre-treatment usually involves the digestion of the samples. Various methods for decomposing and dissolving solid samples are available: acid digestion⁶⁵, ultrasonic digestion⁴³ and microwave digestion.⁴⁹ Such methods are reasonably rapid and inexpensive, and many reports have demonstrated that they provide precision and reproducibility satisfactory for environmental monitoring purposes.⁶⁵ The digestion procedure breaks down organically bound substances and converts the substances to the analysed form by using liquid oxidising agents such as sulfuric acid, nitric acid or hydrofluoric acid. Mineral acids can be obtained in pure forms and do not introduce any major impurities.

Hydrofluoric, sulfuric and perchloric acids are most frequently used for the acid digestion of metals in sediments and soils. Hydrofluoric acid is the only acid that completely dissolves the silicate lattices within the samples and it is therefore used for total metal determination.⁶⁶ The EPA-approved method⁶² for analysing soils and sediments involves acid digestion through the use of 90% nitric acid, 10% hydrochloric acid and 30% hydrogen peroxide. This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become 'environmentally available'.⁶² By design, elements bound in silicate structures, such as aluminium, iron and manganese, are not normally dissolved by this procedure, as they are not usually mobile in the environment. This extraction technique gives results for the weakly held metals (i.e. those which would count towards the cation exchange capacity of the soil), which include those originating from pollution sources.⁶⁶ Due to the fact that this current work is performed as part of an environmental monitoring programme, the extent of this digestion is acceptable and total digestion is not required.

Many studies have been done on the extraction efficiency and accuracy of these acid-digestion methods.^{65,66} In one of these studies⁶⁵ involving an HNO₃/HCl extraction, a reference material

was used to test the accuracy of the acid extraction and very encouraging results were obtained. For Cr, Mn, Ni, Cu, Zn and Pb, recovery appeared to be complete, within the range of analytical precision, while for Fe, Co and Cd modest recoveries of 87, 75 and 80% respectively were observed. This meant that the acid extraction method was accurate (i.e. free of systematic errors in either the preparative or instrumental stages of analysis) for six of the nine elements tested. The same study reported trace metal yields by acid extraction to be highly reproducible with coefficients of variation of below 10% and concluded that monitoring data acquired by the acid extraction method should prove valid for demonstrating changes in environmental quality over a period of time at a particular site.⁶⁵ The acid extraction method approved by the EPA (Method 3050B) reports good recoveries for all the elements tested.⁶² These recoveries are reported in Table 3.2.

Table 3.2: Percent Recovery of Metals for EPA Method 3050B

| Analyte | Recovery (%) |
|---------|--------------|
| Ag | 95 |
| As | 100 |
| Ba | 94 |
| Cd | 94 |
| Co | 94 |
| Cr | 97 |
| Cu | 94 |
| Ni | 98 |
| Pb | 91 |
| V | 93 |
| Zn | 99 |

The two methods discussed differ only in the fact that the EPA method includes a hydrogen peroxide addition in the digestion. From the above discussion it can be noted that acid-extraction methods involving nitric acid and hydrochloric acid demonstrate good recoveries and excellent reproducibility and are suitable for the purpose of environmental monitoring.

3.2.2 Water Samples

Most of the elements that should be analysed in an environmental water sample are usually present at very low concentration levels, so it is often necessary to use a preconcentration treatment before the determination of the elements.⁶⁷ Analysis of seawater, in particular, creates a problem and is currently one of the most important challenges in environmental analytical chemistry.⁶⁸ Analytical inaccuracies arise from the high salt content of seawater and the very low levels of trace metals exacerbate these inaccuracies. Hence, special attention has to be paid to the preconcentration of the analyte and its isolation from the matrix constituents, which might obscure its accurate determination.⁶⁹ The possibility of direct determination⁷⁰ has been investigated with some success, but sample preparation predominates. Sample preparation techniques, which are designed to both preconcentrate the trace elements and separate them from major interfering components prior to analysis, are numerous.^{71,72} These separation-preconcentration procedures most commonly include solvent extraction⁶⁴ and solid-phase extraction.⁷³

A study was done by Sturgeon *et al.*⁷² to check the validity of these methods by comparing the results obtained by the various procedures, in particular ion exchange, chelation-solvent extraction and direct determination by graphite furnace atomic absorption spectrophotometry (GFAAS). Coastal seawater samples were analysed for Cd, Zn, Pb, Fe, Mn, Cu, Ni, Co and Cr and there was good agreement between the results obtained for both of the preconcentration procedures. The precision of replicate determinations between methods for all elements was comparable. However, chelation-solvent extraction was found to be the most useful technique for multi-element determinations when small volumes of seawater were available. If significantly greater preconcentration is required, the more laborious method of ion exchange was recommended. Direct determination by GFAAS is the least favoured method as it is unable to measure Cu, Ni, Pb, Cr and Co because of their inherently low concentrations and pronounced matrix effects. It may be used for determination of the other elements, but it is not a multi-element technique and is distinctly lacking when multi-element determinations must be made on large numbers of samples.

Thus, solvent extraction was decided on as the method of this choice for this study. There are, however, many variations within this method, with the use of different chelating agents, organic solvents⁷⁴ and back-extraction agents.⁶⁴ The premise of solvent extraction involves the mixing of two immiscible liquids and the movement of the analyte of interest between these two phases. One of the phases is usually organic and the other aqueous and the analyte is transferred due to a greater solubility in either one of the phases. Solvent extraction has been widely used for the extractive separation of metal ions as chelates. Many organic chelating agents are weak acids that react with metal ions to give uncharged complexes that are highly soluble in organic solvents. The metal chelates, on the other hand, are usually effectively insoluble in water.⁷⁵ After extraction, the analyte is separated from the sample matrix and an increase in the concentration is accompanied by a decrease in the effect of interfering substances. The analyte of interest is now present in the organic phase and often needs to be returned to an aqueous medium prior to analysis. This can be done by back-extraction or by evaporating off the solvent and redissolving the residue. Figure 3.1. outlines the basic procedure.

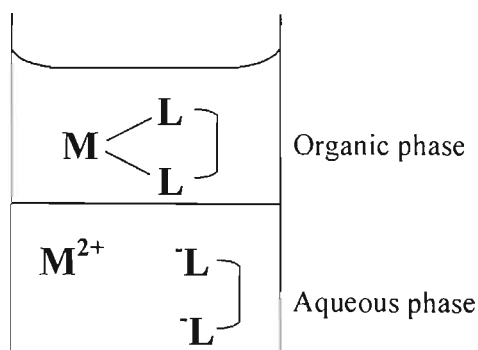
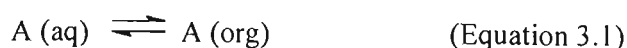


Figure 3.1: The role of a chelating ligand in solvent extraction

The equilibrium, or extraction, constant is a constant that describes the distribution of a solute species between two immiscible solvents. The equilibrium may be described in terms of the concentrations of solute A in the two solvents, i.e.



where (aq) and (org) refer to the aqueous and organic phases. Ideally the ratio of the concentrations of species A in the two phases is constant and independent of the total quantity of A.⁷⁵ That is, at any given temperature

$$K_d = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}} \quad (\text{Equation 3.2})$$

Dithiocarbamate, in varying substituted forms, as the chelating agent is the common factor between many studies of this kind^{71,72}. McLeod *et al.*⁷⁶ studied a method based on dithiocarbamate preconcentration for the simultaneous determination of cadmium, copper, iron, molybdenum, nickel, vanadium and zinc in seawater. The metals were extracted from seawater with a mixture of ammonium pyrrolidine dithiocarbamate (APDC) / diethylammonium diethyl dithiocarbamate (DDDC) in chloroform and back-extracted into nitric acid. The structures of NaDDC and APDC can be seen in Figure 3.2.

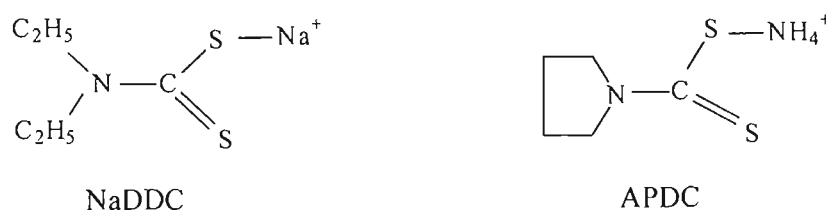


Figure 3.2: Structures of the dithiocarbamate chelating agents

This was found to be a reliable method for the extraction of the metals as when recovery results were tested for a spiked sample element recoveries were essentially 100%.

A combination of APDC and sodium diethyldithiocarbamate (NaDDC) is commonly used in these investigations. Lo *et al.*⁶⁴ studied a two-step preconcentration method, which involved the extraction of metal-dithiocarbamate complexes into chloroform at pH 4.5 followed by back extraction with a dilute Hg(II) solution and determination by AAS. This proved to be an efficient and fast way of preconcentrating a number of trace metals in seawater including cadmium, cobalt, copper, iron, manganese, nickel, lead and zinc in seawater. The back-extraction procedure is based on the fact that the extraction constant of Hg(II) dithiocarbamate is much greater than that of the metals under consideration. This means that when put into solution with other metals, Hg(II) is readily substituted for the other metals in the form of the dithiocarbamate complex. Due to its low atomisation temperature, the presence of a low concentration of Hg(II) in the back-extracted aqueous solution does not cause any noticeable interferences when analysed by AAS. This method was later improved upon and adapted for analysis using inductively coupled

plasma emission spectrometry (ICP-AES) by Lo, Lin and Lin in 1991.⁷⁷ It maintained the use of APDC/NaDDC as the chelating agent and chloroform as the organic solvent, but used a Pd^{2+} solution for the back-extraction. This method was successful in enriching the trace metals and simultaneously removing the matrix interferents. A palladium solution was used as the extraction constant of $\text{Pd}(\text{DTC})_2$ is again much larger than most of the other metal dithiocarbamates. Pd^{2+} is preferred to Hg^{2+} as more metals can be recovered and palladium caused no interference in the determination of trace metals in seawater by ICP-AES. The obvious drawback in the use of this method is the need for large amounts of Pd^{2+} solution, which makes it a very expensive endeavour.

The South African Foundation for Scientific Research has developed a method for the determination of total metals in water samples, which also involves solvent extraction with a dithiocarbamate chelating agent.⁷⁸ It describes a method which involves the use of sodium diethyldithiocarbamate to selectively complex silver, copper, iron, molybdenum, nickel, vanadium, cadmium, cobalt, manganese, lead, chromium and zinc from water. Complexes formed can then be extracted into chloroform. The organic phase is evaporated off leaving a stable, white, inorganic residue. This residue is then redissolved in nitric acid prior to analysis. The method is self-compensating, in that incomplete extraction is corrected for by the similar extraction of the standards. This method is simple, efficient and cost-effective.

3.3 Background to Sample Analysis

The selection of an analytical method is based on the following criteria¹:

- Expected concentration of analyte in the sample.
- Number of samples to be analysed.
- Time that can be devoted to analysis.
- Cost of the analysis.

Instrumental methods in environmental analysis generally involve spectroscopy and chromatography. Spectroscopic methods used in analysis of environmental samples include UV/visible, atomic absorption (AAS) or emission (AES) and infrared (IR). Other advanced

spectroscopic techniques, which may not be generally available in all laboratories, include inductively coupled plasma (ICP) spectroscopy and Fourier-transform infrared spectroscopy (FTIR). A variety of electrochemical techniques can also be used for environmental analysis, including ion selective electrodes and voltammetry.⁶⁰

3.3.1 Sample Analysis

Due to the fact that the metals from the soil and sediment samples are extracted into an aqueous medium, the same analytical procedure can be used for both water and soil samples. The determination of trace metals in both media is usually done by atomic absorption spectroscopy (AAS) (both flame⁵¹ and flameless⁴⁴) and inductively coupled plasma atomic emission spectrometry (ICP-AES),³⁷ after acid digestion of the soil samples and preconcentration of the water samples. Some lesser-used methods used include anodic stripping voltammetry (ASV),⁷⁹ X-ray fluorescence (XRF),⁸⁰ and neutron activation analysis (NAA).⁷⁰ Direct comparisons of different methods via determinations done on the same samples are rarely found in the literature since most laboratories specialise in just one method.⁸¹

One such comparative study by Sturgeon *et al.*⁷² involved the analysis of coastal seawater for various trace metals using isotope dilution spark source mass spectrometry (IDSSMS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma emission spectrometry (ICP-AES). It was found that IDSSMS offers the advantages of multi-element capability coupled with high sensitivity. Replicate multi-element determinations on many samples can therefore be rapidly achieved. Unfortunately, the method requires a large capital outlay and can only process relatively few samples per day, making routine use unfeasible. GFAAS is a fast, accurate method for the determination of trace metals. Problems arise as although commercial GFAAS remains relatively inexpensive, it is not a multi-element technique and is distinctly lacking when multi-element determinations must be made on a large number of samples. However, GFAAS, in conjunction with a preconcentration technique, remains the most common method of seawater analysis for trace metals. ICP-AES is a multi-element technique, but its inferior detection limits necessitate the processing of large volumes of seawater.

AAS is a low temperature method that uses a flame to atomise elements up to 2000 °C.⁶⁰ This is a very good technique for easily atomised metals such as the alkali and alkaline-earth metals.

Graphite furnace AAS uses a small graphite tube with electrothermal heating to atomise the metals. Detection limits are 100 to 10000 times lower than with flame AA due to the elimination of the flame as a background interferent.

Electrochemical methods are suitable for the determination of trace metals in both water and soil samples and voltammetry is the most common method used. Anodic stripping voltammetry (ASV) is often a preferred technique for water analysis as no separate preconcentration techniques are required as this concentration is done electrochemically. ASV is a two-part electrochemical process.⁶⁰ The first part is an electrolysis that serves to reduce the metal ions and deposit them as an amalgam on the mercury cathode. This serves a concentration function by removing the analyte ions from solution and placing them within the confines of the electrode. The polarity of the cell is then reversed so the mercury electrode becomes the anode. The potential of the cell is then scanned and the current monitored. A spike in the current will occur at the dissolution potential for each of the analytes in the mercury electrode. The size of the spike is related to the original concentration of the analyte. Achterberg and Braungardt⁷⁹ studied the use of voltammetry in trace metal determinations and concluded the selectivity, extremely low detection limits for more than 20 elements, high accuracy, modest cost and suitability to flow analysis have made stripping voltammetry an important technique for total dissolved trace metal studies and metal speciation analysis. However, ASV is a slow technique and is therefore unsuitable for large-scale routine work.⁷¹

ICP-AES is a powerful tool for the determination of metals in a variety of different sample matrices, particularly environmental and biological ones.⁷⁷ The analytical performance of this technique is competitive with most other inorganic analysis techniques especially with regards to throughput and sensitivity.⁸² Compared to these other techniques, ICP-AES enjoys a higher atomisation temperature, a more inert environment and the ability to provide simultaneous determination for up to 70 elements. The ability to identify and quantify elements from a large set of emission lines offers improved accuracy in analysis.⁶⁰ In cases where sample volume is not limited, ICP-AES provides detection limits as low as, or lower than its best competitor for all but a few elements. The ICP technique lacks the sensitivity of GFAAS but provided relatively high preconcentration factors are achieved, the sensitivity limitation can be circumvented and the

analytical advantages of the ICP technique such as a simultaneous multi-element capability, a relative absence of matrix interference and a wide dynamic range, can be realised for analysis.⁷⁶

The development of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of trace elements in water at sub-parts per billion levels has already had a considerable impact on the field of water analysis, and it appears that ICP-MS will revolutionise this field. ICP-MS is capable of rapid, accurate, multi-element analysis.⁸³

In general, ICP-AES has the required sensitivity for the analysis of trace metals in soils and has the distinct advantage of being the most 'time-efficient' technique, according to the number of samples to be analysed and the time that could be devoted to analysis.

3.4 Sampling

As previously mentioned sampling is one of the most important elements in the analytical process and choices of the sampling sites can be the most critical decision. The Richards Bay area provides a wide variety of possible sampling sites.

3.4.1 Selection of Sampling Sites

The area of interest in this project is Richards Bay. Richards Bay is susceptible to pollution from a number of different sources as outlined in Chapter 1. As previously stated the main aim of this project is to assess the environmental impact of the heavy industries in this area and, as such, sampling sites were chosen with respect to the position of these industries. The industries of particular interest were Hillside Aluminium, Bayside Aluminium, Foskor and the Richards Bay Coal Terminal. A sampling area was chosen to include the sites of these industries and any nearby water bodies that may be affected by them. The overall sampling area covered a square area with the following co-ordinates: NW 28°45" (latitude) and 32°00" (longitude) and SE 28°50" and 32°10". An aerial map of the overall sampling area can be seen in Figure 3.3.

Soil, sediment, fresh- and salt-water samples were collected from a variety of sampling sites. The sampling sites were divided into three distinct categories:

- i) Soil samples taken from the roadsides immediately outside the industries.
- ii) Water and sediment samples taken from fresh- and saltwater bodies.
- iii) Samples taken from specifically chosen background sites.



Figure 3.3: Aerial view of the overall sampling area

The roadside samples were taken from the grass verges alongside the roads directly outside the respective industries. These samples would serve as an indication of the extent of local pollution from these sources. A schematic of these roadside sampling sites can be seen in Figure 3.4.

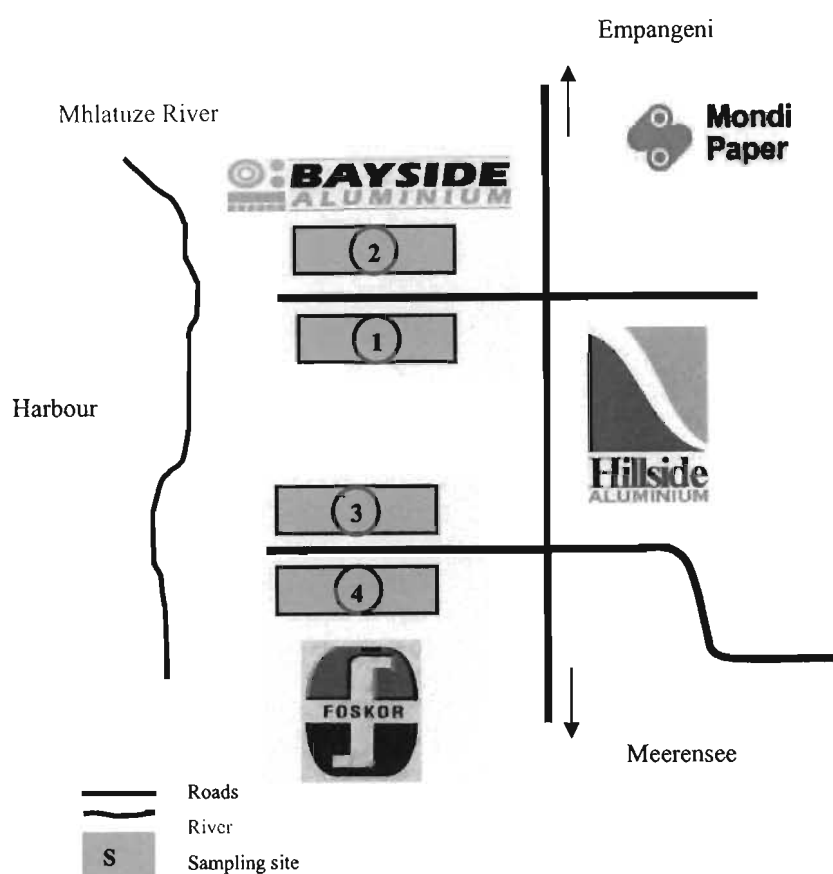


Figure 3.4: Map of sites for the sampling of roadside soils

These roadside soils may give an indication of the industry specific pollutants present in the surrounding soils. For example, the main pollutants produced by Foskor are sulfur and nitrogen gases. These gases can cause increased acidity in the adjacent soils and subsequently harm the surrounding plant life. The potentially harmful pollutants emitted from Hillside and Bayside include fluoride emissions, SO_2 , H_2S , NO_x , CO_2 and CS_2 .

The second distinct set of samples was mainly water and sediment samples taken from water bodies that are situated around the industrial sites. These sites may encounter pollution from the industrial point sources or from the heavy marine traffic within the harbour. Pollutants from the point sources enter these water bodies by atmospheric deposition, either wet or dry.

The harbour inlet (site 5) alongside the coal terminal is one of these water bodies of interest. This inlet provided a salt-water sampling site within the industrial area of interest. Samples were taken from the Mhlatuze River (site 6) as it flows through the industrial area, providing a freshwater sampling site. Two ponds (sites 10 and 11) situated alongside the railway line between Hillside and Bayside provided further sampling sites. These ponds were stagnant and as such can give us a good idea of the pollution caused by deposition and leaching. A schematic of these sampling sites can be seen in Figure 3.5.

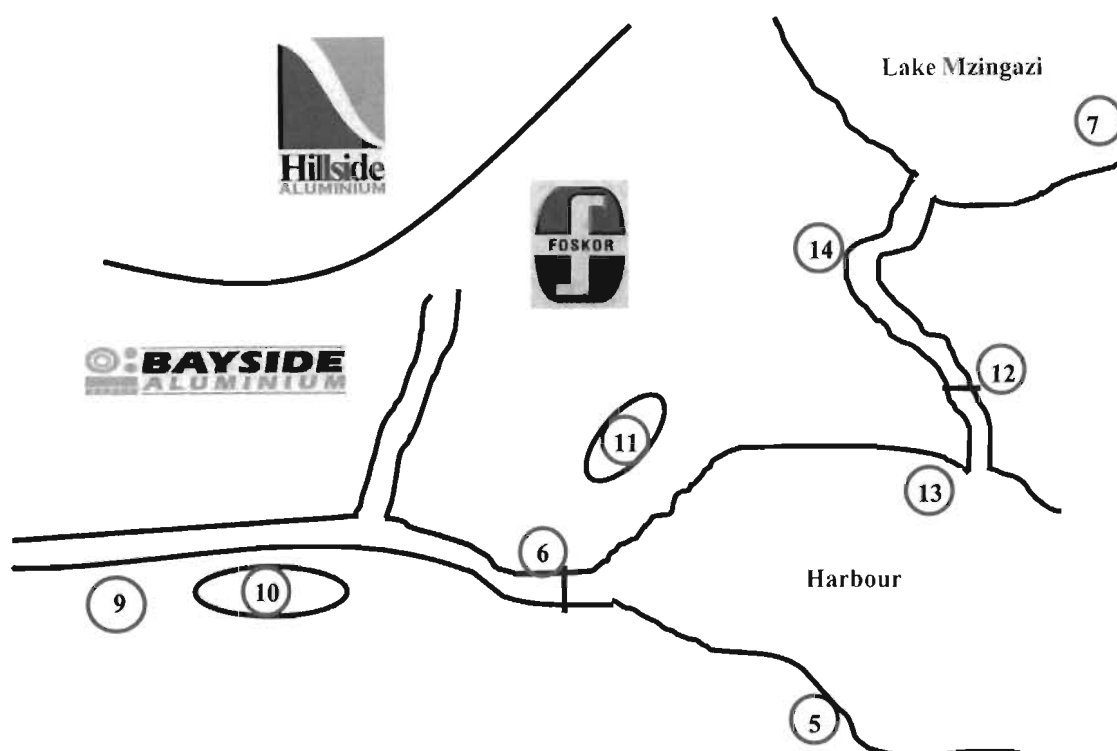


Figure 3.5: Schematic representing the water sampling sites

Further water samples were taken from within the harbour itself. These samples may give an indication of pollution caused by marine traffic. Samples were also taken from Lake Mzingazi and the Mzingazi Canal. Both of these water bodies are outside of the immediate industrial area and can be used to assess the geographical extent of any possible pollution.

No conclusions can be drawn from the analysis of the samples from identified “problem” sites without comparing them with background samples. A background sampling site can be regarded as an uncontaminated, adjacent area with the same soil type and healthy vegetation suitable for attaining background levels. Using areas of the same soil type is important as it

means that the soil samples will have the same background mineral levels. Two sampling sites were used to obtain background samples. A site 10km outside of Richards Bay alongside the Mhlatuze River, upwind from the prevailing wind direction, was chosen as the first background site. It maintains the Ia-type soil profile, has healthy vegetation and allows us to take uncontaminated soil, sediment and water samples. The map below illustrates the position of this background sampling site relative to the other sites. The site was used mainly in the comparison of soil samples.

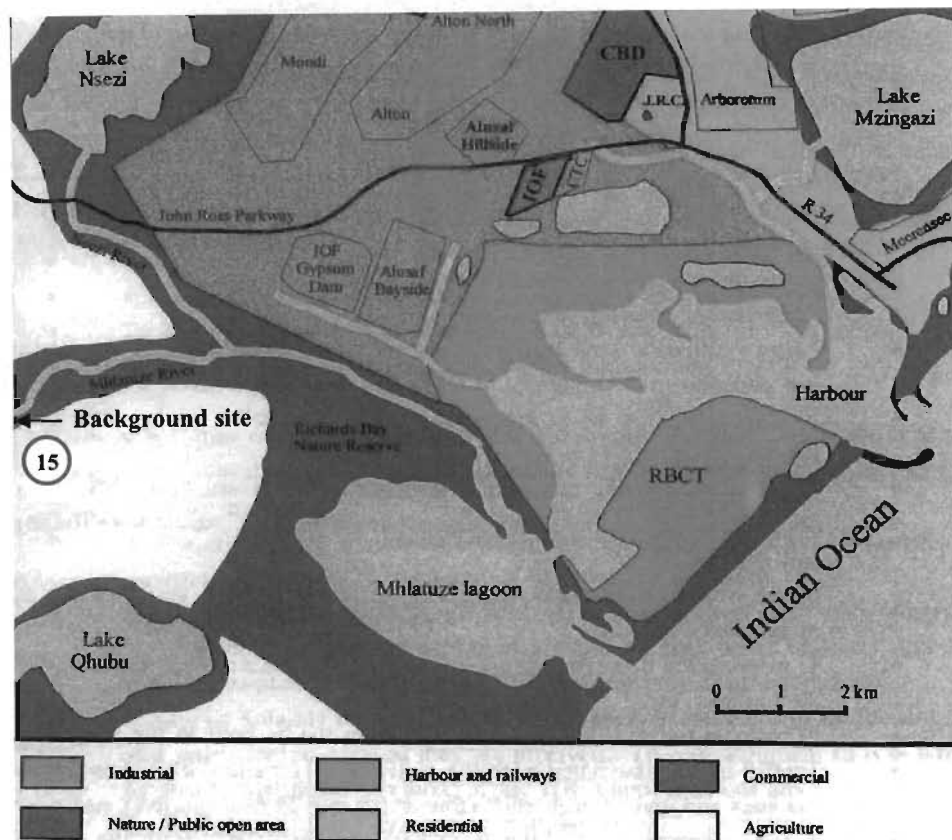


Figure 3.6: Position of background site relative to other sampling sites⁸⁴

The Mtunzini area was also used as a background site. Mtunzini is a small coastal town about 50 kilometres outside of Richards Bay. This area is geographically similar to Richards Bay, but it is industrially undeveloped and therefore remains a relatively pristine environment. Soil, water and sediment samples were taken from various sites within the area, including the lagoon and the Mtunzini River. These sites were mainly used as background concentrations for the water samples and some sediment samples. A mangrove area similar to that found alongside the Mhlatuze River in Richards Bay surrounds the lagoon. The sediment samples from this region are of interest as the mangrove mud is an obvious sink for trace metal

contamination due to its high clay content. Soil samples from this region are not suitable to attain background levels as they have a different soil profile to the original sampling area. This difference in soil type, as well as the position of Mtunzini relative to Richards Bay, can be seen in Figure 2.5. A schematic diagram of the sampling areas within Mtunzini can be seen in Figure 3.7.

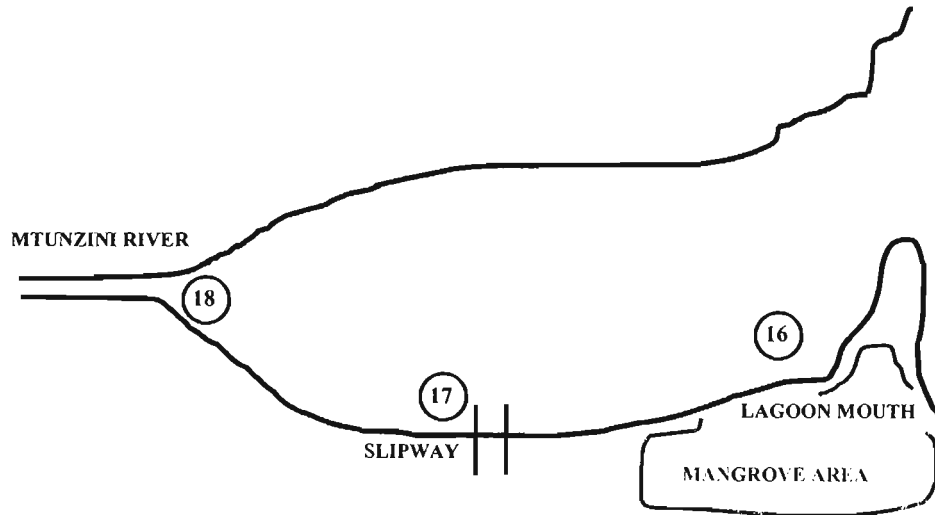


Figure 3.7: Schematic diagram representing Mtunzini background sampling sites

The overall sampling sites are listed and described in Table. 3.3.

Table 3.3: List and description of the sampling sites

| Site | Site Name | Description | GPS Position | Samples |
|------|----------------|---|---|----------------------------|
| ① | Roadside 1 | Roadside between Hillside and Bayside on Hillside side of the rd. | S 28°46'43" E 32°01'14" (within 6m) | Soils |
| ② | Roadside 2 | Roadside between Hillside and Bayside on Bayside side of the rd. | S 28°46'43" E 32°01'16" (within 6m) | Soils |
| ③ | Roadside 3 | Roadside between Foskor and Bayside on Bayside side of the rd. | S 28°46'27" E 32°02'24" (within 6m) | Soils |
| ④ | Roadside 4 | Roadside between Foskor and Hillside on both sides of the rd. | S 28°46'03" E 32°02'11" (within 6m) | Soils |
| ⑤ | Harbour inlet | Off the Coal Terminal Rd alongside the railway line | S 28°49'49" E 32°02'24" (within 7m) | Water Soils Sediment |
| ⑥ | Mhlatuze River | Off the Coal Terminal Rd, under a bridge, 100m from mouth | S 28°48'00" E 32°01'08" (within 4m) | Water Soils Sediment |
| ⑦ | Lake Mzingazi | Edge of the lake alongside the Country Club | S 28°46'12" E 32°06'04" (within 6m) | Water Sediment |
| ⑧ | Harbour 1 | North West area alongside mangroves in slack water | S 28°47'52" E 32°01'48" (within 6m) | Water |
| ⑨ | Mhlatuze River | Running alongside pond between Hillside and Bayside | S 28°48'07" E 32°00'50" (within 4m) | Water Sediment |
| ⑩ | Pond 1 | Groundwater pond btw Hillside and Bayside next to railway line | S 28°48'07" E 32°00'50" (within 4m) | Water Soils Sediment |
| ⑪ | Pond 2 | Groundwater pond on Coal Terminal rd. | S 28°47'24" E 32°01'48" (within 5m) | Water Sediment |

Table 3.3 (contd.): List and description of the sampling sites

| | | | | |
|----|-----------------|-------------------------------|--|-----------------------------|
| 12 | Mzingazi Canal | North side | S 28°47'13" E 32°04'59" (within 5m) | Water Soils Sediments |
| 13 | Harbour inlet | North side | S 28°59'56" E 32°04'48" (within 12m) | Water Soils Sediments |
| 14 | Mzingazi River | Next to the Croc Sanctuary | S 28°46'26" E 32°04'23" (within 6m) | Water |
| 15 | Mhlatuze River | 10kms outside of Richards Bay | S 28°48'00" E 31°57'40" (within 11m) | Water Soils Sediments |
| 16 | Mtunzini Inlet | Mouth of the lagoon | S 28°57'18" E 31°46'30" (within 11m) | Water Sediment |
| 17 | Mtunzini Lagoon | | S 28°57'00" E 31°46'30" (within 5m) | Water Sediment |
| 18 | Mtunzini River | | S 28°56'46" E 31°46'59" (within 11m) | Water Sediment |

3.5 Chosen Methods of Analysis and Preparation

In the first part of this chapter, the possibilities of a variety of analytical methods are discussed with reference to the determination of trace metals in water, sediment and soil samples. Many factors govern the decision of which analytical method to employ. Primarily the availability of equipment and time is taken into consideration, as well as the required sensitivity of the analytical technique.

As was previously discussed, the most commonly used instrumental technique for trace metal determination in various matrices is spectroscopy, either atomic absorption or inductively-coupled plasma emission. Both of these instruments were available for use in this project. The AAS, while having better detection limits for most of the elements of interest, is a single

element technique and is therefore is not suitable for large-scale analysis of this type. A total of approximately 130 water samples, 800 sediment samples and 540 soil samples were analysed for trace metals and it was therefore necessary to employ a multi-element technique such as ICP-AES.

The sensitivity of the ICP-AES is not a point of concern during the analysis of the soil and sediment samples as the expected trace metal levels in the samples are generally greater than the detection limits of the instrument. For example, the average trace metal levels in sediments determined by the CSIR in the study region,²⁰ are compared with the ICP-AES detection limits in Table 3.4 and it can be seen that they are all higher and sensitivity does not therefore pose a problem.

Table 3.4: CSIR measured sediment levels compared with detection limits

| | Measured Level (g/kg) ²⁰ | Detection Limit (g/kg) |
|-----------------|-------------------------------------|------------------------|
| Copper | 0.023 | 0.002 |
| Cadmium | 0.002 | 0.002 |
| Lead | 0.016 | 0.014 |
| Zinc | 0.091 | 0.0009 |
| Iron | 6.00 | 0.0015 |
| Chromium | 0.092 | 0.010 |
| Cobalt | 0.015 | 0.005 |
| Nickel | 0.030 | 0.006 |

It is in the analysis of the water samples that the sensitivity becomes an issue due to the low concentrations of the analytes. This sensitivity problem can, however, be overcome with the use of a preconcentration technique as previously discussed. It is just the degree of preconcentration that needs to be established. The mitigating factor in preconcentration involving ICP-AES analysis is sample volume. The fact that a sample volume of approximately 20 ml is required for this analysis inhibits the possible concentration. For example, with the use of GFAAS a sample volume of just 1 ml is required and a hundred-fold preconcentration is possible through the processing of small sample volumes.⁷² For 100-fold preconcentrations to be attained using ICP-AES, sample volumes of up to 2 litres must be used. This processing of relatively large volumes of seawater can be cumbersome, so a lesser

preconcentration is favoured. A 25-fold preconcentration allows for easily manageable sample volumes and is sufficient to bring most trace metal analytes to levels above the ICP-AES detection limits.^{72,77}

With the analytical technique to be used, and the degree of preconcentration required, determined, it is necessary to investigate the best methods for sample preparation.

3.6 Sample Preparation

Decisions made regarding the sample preparation techniques used in this study were largely governed by the availability of equipment and time.

3.6.1 Preparation of soil and sediment samples

As previously discussed the sample preparation necessary for the soil and sediment samples is extraction. This extraction moves the analytes from solid to aqueous phase, thus making analysis easier. Acid digestion was chosen as the method of choice in this study due to equipment availability. This method involves only rudimentary equipment, such as a steam bath.

Hydrofluoric acid is commonly used for these digestions, but was not employed in this case due to the safety hazards and was replaced by nitric and hydrochloric acids. As previously explained, these acids provide sufficient digestion for analysis of this kind.

The specific method chosen for use in this study was the EPA approved method⁶² as it is stated to be appropriate for most environmental monitoring studies. This method was also chosen due to the fact that it has demonstrated good recoveries for all the elements tested.

3.6.2 Preparation of water samples

In the process of method development, various preconcentration methods were investigated. The first set of investigations included solid-phase extraction (SPE) with various chelating agents, eluents and buffers.

Isolute C18 (EC) solid phase cartridges and NaDDC were used, as the stationary phase and chelating agent respectively, in all the solid phase extractions. The eluents, buffers and flow

rates were varied according to a number of different methods.^{73, 85,86,88} Poor recoveries were obtained for all solid phase extractions. These recoveries can be seen in Table 3.5.

Table 3.5: Recoveries of various solid phase extraction techniques

| Method | Buffer | Eluent | Recovery (%) | | |
|--------|--------|------------------------------|--------------|-----|-----|
| | | | Fe | Cu | Zn |
| 1 | None | 1M HNO ₃ /Acetone | 0 | 0 | 0 |
| 2 | pH 6 | 1M HNO ₃ /Acetone | 68 | 54 | 58 |
| 3 | TISAB | 1M HNO ₃ /Acetone | 40 | 14 | 20 |
| 4 | pH 6 | Acetone / Hexane | 1.7 | 2.8 | 9.4 |
| 5 | pH 6 | 5M HNO ₃ | 63 | 4 | 72 |

Due to the low recoveries obtained by SPE, investigations moved onto the use of solvent extraction. Chelation and solvent extraction has been established as an efficient, and widely used, means of obtaining the necessary preconcentration for the analysis of water samples. Solvent extraction with use of a dithiocarbamate chelate was the method of choice in this study. This method has been widely used and is well documented.^{87,64,77,78}

In the preparation of these water samples, a method combining elements of the methods outlined by Watling⁷⁸ and Lo *et al.*⁷⁷ was used. Chelation solvent extraction was used, employing a mixture of sodium diethyldithiocarbamate (NaDDC) and ammonium tetramethylenedithiocarbamate (APDC) as the chelating agent and chloroform as the organic solvent. The structures of these chelating agents can be seen in Figure 3.8

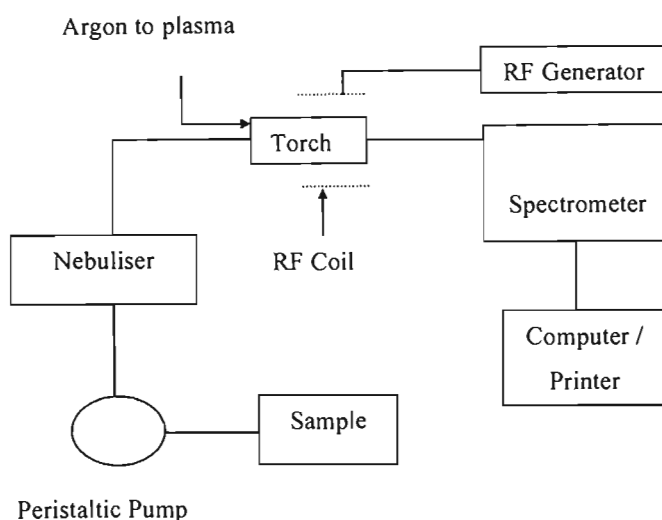


Figure 3.10: Typical Components of an ICP-AES⁸⁹

On introduction, the sample is aspirated via a peristaltic pump to a nebuliser. The role of the nebuliser is to convert the sample solution into an aerosol. There are many different nebulisers that can be used, but only two were used during the course of this study namely a pneumatic nebuliser for the soil samples and an ultrasonic nebuliser for the water samples. The differences between the nebulisers lie in the transport efficiency of the nebulisers, the ultrasonic being far more efficient than the pneumatic, resulting in much greater intensities for respective concentrations on the ultrasonic nebuliser.⁸⁹ The pneumatic nebuliser is sufficient for the analysis of the soil samples due to the higher concentrations of the analytes, furthermore the high concentrations of some of the analytes in the soil samples may prove problematic if the ultrasonic nebuliser is employed.

The analyte, in aerosol form, is then transported from the nebuliser by an inert carrier gas, in this case argon, and introduced into the plasma. The plasma can be defined as a conducting gaseous mixture of electrons and cations⁷⁵, and is sparked by a Tesla coil. The plasma is sustained through ohmic resistance resulting from the interaction of cations and electrons with the fluctuating magnetic field supplied to the coil by the Radio Frequency (RF) generator. The plasma is contained in a quartz torch. The torch is also cooled by argon as it can reach temperatures of up to 10 000 K.⁷⁵ These high temperatures mean that the analyte species in the sample become excited to the point of emission and this subsequent emission can be monitored by the spectrometer.

An atomic or ionic spectrum is emitted and two pieces of information can be gleaned from this spectrum. Firstly, the wavelength at which emission occurs is used to identify which element is emitting and secondly, the intensity of the emission can be directly related to concentration of the analyte. The spectrometer is usually composed of a monochromator to monitor the emission wavelength, a photomultiplier to boost the signal and a photodetector for detection of the radiation.

As previously discussed ICP-AES is not the most sensitive of all the analytical techniques, but the advantages of its use far outweigh the disadvantages, i.e. the lack of sensitivity can be circumvented and it remains one of the most cost and time effective techniques.

CHAPTER 4

Experimental

4.1 Sample Collection

Water, soil and sediment samples were collected over a period of 18 months on five separate sampling trips. These trips were in July 2002, September 2002, April 2003, July 2003 and December 2003.

4.1.1 Collection of soil and sediment samples

An auger was used for the collection of the soil samples. An auger consists of a sharpened spiral blade attached to a central metal rod, which can be screwed into the soil. The sampler is screwed into the soil to a depth of about 20cm and the sample withdrawn. The samples were then placed in polyethylene bags.

Random sampling was employed in that there were a random number of sampling points spatially distributed over the site area.¹ However, a degree of composite sampling was also used as when taking a sample from a specific point, five samples were taken over 1m² and combined in one bag. This sampling technique is illustrated in Figure 4.1.

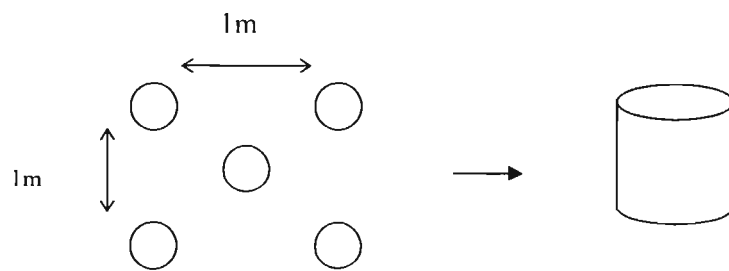


Figure 4.1: Composite sampling technique employed for soil samples

The polyethylene sample bags were sealed and labelled with a number corresponding to the sampling site.

Sediment samples were collected from the edges of the respective water bodies and it was therefore sufficient to just sample by hand without the need for depth samplers. Surface and near-surface sediment samples, about 1kg in size, were taken by hand and placed in polyethylene bags. Once again random sampling was employed with a random number of sampling points evenly distributed over the sampling area. The sample bags were sealed and labelled with an appropriate number.

4.1.2 Collection of water samples

Water samples were collected in 500 ml pre-cleaned polyethylene bottles. Before the sampling trip these bottles had been rinsed first with dilute nitric acid followed by distilled water. When sampling, the bottles were first rinsed several times with the water to be collected and were then filled up. The bottle was filled slowly to avoid turbulence and bubbles and the bottle was filled right up to the top in order to avoid reaction of the water sample with the air above it during storage. Analytical grade concentrated nitric acid (approx. 2 ml) was added to half of the samples collected at each site. This is the recommended preservative for determination of trace metals in water as it decreases the chances of analyte loss by adsorption or precipitation.⁶⁰ The sample bottles were finally sealed and labelled according to the sampling site. Once at the laboratory the samples were refrigerated at 4 °C prior to analysis.

The pH, temperature and conductivity of the water samples were tested on site using a handheld pH meter (Yellow Springs Instrument Model No. 63/10FT). The meter was calibrated between each sampling session with Merck buffer solutions of pH 4.00, 7.02 and 10.02.

4.2 Sample Preparation

The analytical technique chosen for the trace metal determination of both the soil and water samples was ICP-AES. Before the samples could be analysed by this technique they had to undergo various sample preparations. The analytes in the soil samples had to be brought into solution and the water samples had to be concentrated and cleared of sample matrix effects before analysis.

4.2.1. Soil and sediment samples

The soil and sediment samples, about 1-2 kg in size, were emptied from their bags and spread out in cardboard boxes (30 x 45 cm) that had been lined with waxed paper. All foreign matter, including vegetation and stones, was removed from the samples. The boxes were then placed in *Gallenkamp* drying ovens and the samples were oven-dried at 40°C over-night. This has been reported to be the recommended temperature for drying with the purpose of trace metal determination.¹ Drying serves to eliminate water (the moisture content of the samples was approximately 2%) from the sample thereby terminating all possible microbial activity within the sample. After drying, the approximately 1kg soil samples were crushed using a porcelain mortar and pestle, to pass through a stainless steel 425µm sieve. The grinding and sieving of the samples allows for a homogenous sample to be obtained. Each soil sample was mixed well and a sampling method, known as coning and quartering, was employed to obtain a representative sample of suitable size for the determination. Coning and quartering first involves forming a cone with the entire sample, flattening the cone to form a circular layer of sample, dividing the circular material into four parts and discarding two opposite corners. The two retained quarters are combined and the cone and quartering process is repeated until the required sample size had been obtained.¹ In this way, the sample size can be reduced without any bias – each particle in the sample has the same chance of being accepted or rejected. This technique is illustrated in Figure 4.2.

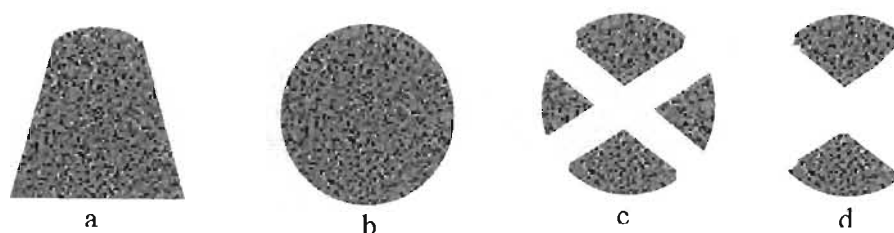


Figure 4.2: Coning and quartering - a) form sample into a cone, b) flatten the cone, c) quarter the sample, d) discard two opposite corners¹

Through coning and quartering four representative sub-samples were obtained from each of the original 1kg samples. Samples (approximately 1g) from each of the four sub-samples were weighed into polytop vials, transferred to the digestion vessels and were acid digested in order to prepare them for trace metal analysis. The acid-digestion method recommended by the EPA was followed.⁶² The digestion was carried out in 100 ml beakers that had been

modified. The modification involved putting a glass “ledge” around the vessel, about halfway up the walls. This “ledge” meant that the vessel could be immersed in a standard steam bath, through a ring roughly 6 cm in diameter. This is illustrated in Figure 4.3.

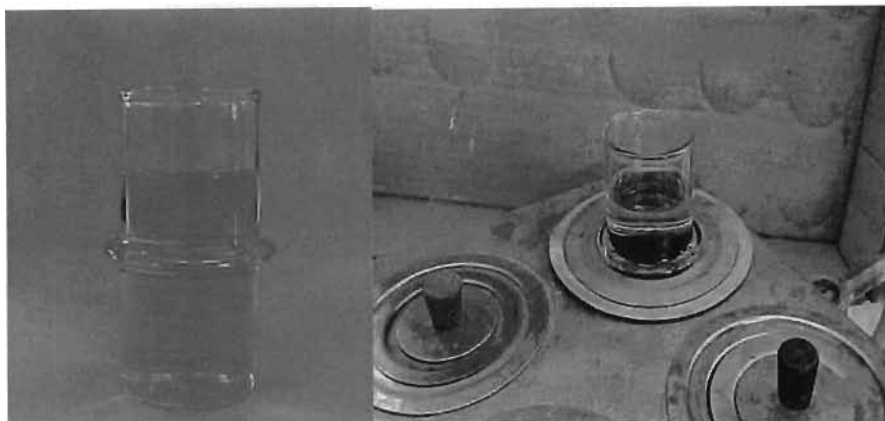


Figure 4.3: Specially designed digestion vessels

For each digestion procedure, a 1 g sample (dry weight) was weighed to the nearest 0.001g and placed in a digestion vessel. AR grade 1:1 HNO_3 (10 ml) was added to the vessel, the slurry was mixed with a glass rod, and the vessel covered with a watch glass. The sample was heated on a steam bath at 95°C for 10 to 15 minutes. The sample was then allowed to cool, and AR grade concentrated HNO_3 (5 ml) was added. The cover was replaced and the sample refluxed for a further 30 minutes. The sample was then covered with a watch glass and heated on the steam bath, without boiling, for two hours.

The sample was cooled and ultrapure water (2 ml) and AR grade, 30% H_2O_2 (3 ml) was added. The vessel was covered with a watch glass and returned to the heat source for warming in order to start the peroxide reaction, i.e. the hydrogen peroxide acts as an oxidizing agent converting all the trace metals present into their ionic forms. The vessel was heated until effervescence subsided and then cooled. Once cooled, 30% H_2O_2 in 1-ml aliquots was added continuously with warming until the effervescence was minimal or until the general sample appearance appeared unchanged.

The sample was then covered with a watch glass and the acid-peroxide digestate was heated on the steam bath for two hours. Concentrated HCl (10 ml) was added to the digestate and

refluxed for 15 minutes. After cooling, the sample was filtered through Whatman No.1 filter paper and the digestate was then diluted to 100 ml with water in a volumetric flask.

Reagent grade chemicals were used throughout the procedure and all references to water in the method refer to ultrapure water. Details of the reagents used can be seen in Appendix 1.2.1.

4.2.2 Water samples

The dithiocarbamate buffer was prepared by dissolving a mixture of NaDDC and APDC (1g each) in 100 ml of water. The buffer solution was then stirred and shaken well with chloroform (10 ml) and the organic phase was discarded. This process was repeated twice. This solvent extraction serves to remove any impurities, particularly trace metals ions, which may be present in any of the reagents and lead to inaccurate results. The aqueous solution, referred to as the purified extracting agent, was used in subsequent work. The buffer (pH 6) has been reported to be only stable for one week⁷⁸ and as such a new buffer solution was prepared for each set of extractions.

The water sample (500 ml) was placed in a separating funnel with 10 ml of the purified extracting agent and the funnel was shaken vigorously for 5 minutes. Chloroform (30 ml) was then added and the mixture was shaken on a mechanical shaker for 30 minutes. After waiting ten minutes to allow the phases to separate, the organic layer was drawn off. Concentrated HNO₃ was added to the chloroform extract, which was then evaporated to dryness at low heat on a hot plate. The white inorganic residue was then redissolved in 5% HNO₃ (20.00 ml) prior to analysis.

Reagent specifications can be seen in Appendix 1.2.2.

4.3 Sample Analysis

While trace metal determination was the focus for both the soil and water samples, additional analyses were also performed on the samples. The water samples were analysed for pH, alkalinity, major anions and trace metals, and the soil and sediment samples for pH and trace metals.

4.3.1 Trace element determination using the ICP-AES

The use of ICP-AES to determine trace element levels for both the water and soil samples can be discussed together due to the fact that they may be treated much the same after they have undergone their respective preparation procedures. A Varian Liberty 150 AX Turbo ICP-AES was used and the general operating specifications used in this study are shown in Table 4.1.

Table 4.1: Operating conditions and specifications for the ICP-AES

| | |
|-------------------------|--|
| Instrument | Liberty 150 AX Turbo (Varian) |
| Torch mounting | Axial, low flow |
| Nebuliser (1) | Ultrasonic (Cetac U-5000 AT ⁺) |
| Nebuliser (2) | Pneumatic (concentric) |
| RF Power supply | 40.68 MHz |
| Operating power | 1.00 kW |
| Nebuliser pressure | (1) 200 kPa (2) 240 kPa |
| Photomultiplier voltage | 800 V |
| Plasma argon flow | 1.50 l/min |
| Auxiliary argon flow | 1.50 l/min |
| Pump speed | 12 rpm |

Before bulk analysis of the samples could be done, various preliminary investigations had to be performed. The trace metals present at detectable levels in both water and soil samples had to be identified, a rough estimate of their concentrations had to be obtained in order to make appropriate standards and the optimum wavelength for each detectable element had to be determined. A wavelength scan was performed on both a water and a soil sample. This wavelength scan allows us to determine which elements are present at detectable concentrations and by simultaneously scanning a standard solution a rough estimation of the concentration of these elements can be obtained. Once the detectable elements had been identified, samples spiked with known amounts of these metal standards were then analysed in order to determine the optimum wavelength for each metal. The metals identified in the respective samples and their optimum wavelengths are reported in Tables 4.2 and 4.3.

Table 4.2: Trace elements detected in the water samples and their associated wavelengths

| Element | Wavelength (nm) | Detection Limit (mg/l) |
|---------|-----------------|------------------------|
| Cu | 327.39 | 0.020 |
| Mn | 259.37 | 0.003 |
| Fe | 259.94 | 0.015 |
| Zn | 213.86 | 0.009 |
| Co | 228.63 | 0.050 |
| Cd | 226.50 | 0.015 |
| Pb | 220.35 | 0.14 |

Although the wave scan of the water sample indicated that there were more elements present at detectable levels, it is only these metals that demonstrated suitably high recoveries in the sample preparation procedure. Thus the water analysis was limited to these metals.

Table 4.3: Trace elements detected in the soil samples and their associated wavelengths

| Element | Wavelength (nm) | Element | Wavelength (nm) |
|---------|-----------------|---------|-----------------|
| Cu | 327.39 | Mg | 280.27 |
| Ti | 334.94 | V | 292.40 |
| Zr | 343.82 | Na | 589.59 |
| Al | 396.15 | Ca | 317.93 |
| Sr | 407.77 | Zn | 213.86 |
| Ni | 231.60 | P | 214.91 |
| Ba | 493.41 | Cd | 226.50 |
| B | 249.77 | Co | 228.62 |
| Mn | 259.37 | K | 766.49 |
| Fe | 259.94 | Pb | 220.35 |
| Cr | 267.2 | | |

4.3.1.1 Calibration curves for trace element determination

Standard solutions were made for all the analytes of interest and two separate sets of standards were made for the soil and water analyses respectively. Before embarking on the standards a set of stock solutions was made up. For the elements, except Ti, Pd, Zr and Y, the stock solutions were made up from Fluka Chemica spectroscopy standard concentrates. These

Fluka solutions came in ampoules containing an exact mass of the analyte (usually 1.000 g). Predominantly 1000 mg/l stocks were made up by diluting the 1.000 g solutions to exactly 1 litre using ultra-pure water. For Ti, Pd, Zr and Y, Fluka Chemica standard solutions were used as stock solutions. These are previously mixed 1000 mg/l stocks. Details of these standard solutions can be seen in Appendix 1.2.3.

Three sets of standard solutions were made up for the analysis of the soil and sediment samples. A mixed set for the elements present at lower concentrations, a mixed set for the three elements (i.e. Al, Fe and Ca) present at higher concentrations and a separate set for chromium. A separate set of standards was necessary for chromium as when combined with the other elements it precipitated out. For all the sets the appropriate volume of stock solution was placed in the volumetric flask with AR grade nitric acid (5.00 ml) before being diluted to 100 ml with ultra pure water. The nitric acid was necessary to ensure that the standards have the same sample matrix as the samples. The digestates that form the sample in this instance are known to have a sample matrix of 5% acid. A 5% acid solution was used as a blank for the procedure. The elements of interest and their respective standard concentrations used to calibrate the spectrometer for soil analyses can be seen in Table 4.4.

The standards were run on the ICP-AE spectrometer and it constructs its own calibration curve for each element. For some of the elements, such as aluminium, iron and calcium, the calibration curves may not be linear due to the range of the standards and the high concentrations that may be reached. In this case, the maximum curve coefficient is set at 2 and a non-linear calibration graph may be used. The instrument was calibrated each time before use as it may be subject to a certain amount of instrumental drift. Examples of the calibration curves obtained can be seen in Appendix 1.3.

Table 4.4: Standard solutions (in mg/l) to calibrate the ICP-AES for soil analyses

| Analyte | Std. | | | | | | | | | |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Cu | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Ti | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Zr | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Sr | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Ni | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Ba | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| B | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Mn | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| V | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Zn | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Cd | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Co | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Pb | | | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Cr | | | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | | | |
| Mg | | | | | | 1.000 | 2.000 | 10.00 | 25.00 | 50.00 |
| Na | | | | | | 1.000 | 2.000 | 10.00 | 25.00 | 50.00 |
| P | | | | | | 1.000 | 2.000 | 10.00 | 25.00 | 50.00 |
| K | | | | | | 1.000 | 2.000 | 10.00 | 25.00 | 50.00 |
| Al | 1.000 | 2.000 | 5.000 | 10.00 | 25.00 | 50.00 | 100.0 | 150.0 | 200.0 | 300.0 |
| Fe | 1.000 | 2.000 | 5.000 | 10.00 | 25.00 | 50.00 | 100.0 | 150.0 | 200.0 | 300.0 |
| Ca | 1.000 | 2.000 | 5.000 | 10.00 | 25.00 | 50.00 | 100.0 | 150.0 | 200.0 | 300.0 |

The standard solutions for the water analysis were initially made up from the same stock solutions and diluted to the required volume with ultra pure water. However, before using these standard solutions to calibrate the spectrometer, they were required to undergo the same extraction method as the samples. The procedure also included a blank correction using water as the blank. This not only ensures that the samples and standards have the same sample matrix, but also means that the extraction method is self-compensating in that incomplete extraction of the samples is corrected for by similar extraction of the standards. After extraction these standards were used to calibrate the instrument and the concentrations of these standards can be seen in Table 4.5.

Table 4.5: Standard solutions (in mg/l) used to calibrate the ICP-AES for water analyses

| Analyte | Std 1 | Std 2 | Std 3 | Std 4 | Std 5 | Std 6 | Std 7 | Std 8 |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cu | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | 5.000 |
| Mn | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | 5.000 |
| Fe | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | 5.000 |
| Zn | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | 5.000 |
| Pb | | | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | 5.000 |
| Co | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | 5.000 |
| Cd | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 | 2.000 | 5.000 |

The instrument was calibrated before each use and examples of the calibration curves obtained for the water analyses can be found in Appendix 1.4. Due to the low concentrations and the narrow range of concentrations for all elements all the calibration curves were linear and it was not necessary to adjust the curve coefficient. The calibration curve was rejected if the correlation coefficient was found to be less than 0.995.

4.3.2 pH tests on soil and sediment samples

The pH of soils and sediments is one of the most frequently measured parameters due to the importance of pH in regulating numerous processes. The pH gives an indication of the acidity or alkalinity and this makes it valuable for soil characterisation.

pH tests were conducted by weighing out approximately 20 g of dry soil and placing it in a 100 ml beaker. 50 ml of distilled water was added and the slurry was stirred vigorously. The solution was left to stand and equilibrate for a couple of hours.¹ The pH was then measured with a Crison bench-top pH meter and a Crison glass pH electrode (Catalogue No. 52-03). Before each set of measurements the pH meter was calibrated with a three-point calibration process including Merck buffer solutions of pH 4.00; 7.02 and 10.02

4.3.3 Alkalinity titrations of water samples

Alkalinity is used to measure the buffering capacity of natural waters and is determined by titrating a measured volume of sample with H_2SO_4 . Samples had a pH of less than 8.3 and as such they are titrated to a single end-point to determine the total alkalinity. This titration can be done with the use of an indicator, such as methyl orange, or it can be done potentiometrically. This is done by measuring the pH with a glass membrane electrode and plotting the titration curve. This potentiometric titration was the method of choice in this study.

100 ml of the sample was measured out and a combination pH electrode was inserted into the solution. The pH of the sample was monitored while adding 0.01M H_2SO_4 from a burette. The volume of acid required to reach pH 4.5 was recorded. The pH meter used in this determination was the Crison bench-top meter (Catalogue No. 52-03) and it was calibrated before each use using Merck buffer solutions of pH 4.00; 7.02 and 10.02.

The details of all reagents used can be seen in Appendix 1.2.4.

4.3.4 Determination of major anions by ion-selective electrode

The anions that were determined in this study were chloride, fluoride and nitrate. The levels of all three anions were measured using a Crison bench-top meter (Catalogue No. 52-03) with the appropriate ion-selective electrode. The specifications of the electrodes used can be seen in Appendix 1.2.5. The samples were all filtered through Whatman No. 41 filter paper prior to analysis. For the determination of fluoride and chloride it was necessary to use an ionic strength adjustment buffer in order to ensure that the ionic strength of all standards and samples were the same. Total ionic strength adjustment buffer (TISAB) was used for fluoride determination and NaNO_3 (1M) was used for chloride determination. (Although NaNO_3 is not classified as a buffer, it also adjusts all the solutions to the same ionic strength.)

Three sets of standards were prepared from analytical grade sodium salts i.e. sodium fluoride, sodium chloride and sodium nitrate. Details of these reagents can be seen in Appendix 1.2.5. These sets of standards were made with the same concentration range, i.e. 1, 10, 100 and 1000 ppm. The potential of the standards was plotted against the logarithm of the standard concentrations and a linear calibration curve was obtained.

The detection limits for the three ion-selective electrodes in Table 4.6.

Table 4.6: Detection limits for the ion-selective electrodes

| Detection Limits (ppm) | | |
|-------------------------------|-----------------|-----------------|
| Nitrate | Chloride | Fluoride |
| 0.43 | 1 | 1 |

This analysis was not pursued in detail due to the fact that the ion-selective electrodes are limited by their high detection limits. Determinations were done on the initial water samples taken, but the analysis was not continued.

CHAPTER 5

Results

5.1 Sampling sites

It is necessary to link the sampling sites with their respective results. Water, sediment and soil samples were taken from a wide variety of sampling sites within the sampling area. All these sampling sites, except for the background sites, can be seen in Figure 5.1. The site numbers illustrated on this figure are related to all the site numbers quoted in Table 3.3 in Chapter 3.

5.2 Water Results

Water analysis included pH measurements, alkalinity titrations, anion determinations with ion selective electrodes and trace metal determination through the use of ICP-AES.

5.2.1 pH Measurements

The pH and temperature of the water body were measured and recorded simultaneously. The pH of the various water sampling sites was measured on each sampling trip, which spread over the period of 18 months. The range of pH and temperature readings over the four sampling trips and are recorded in Table 5.1.

Table 5.1: pH and temperature measurements for water samples

| Site | Temp (°C) | pH |
|---------------------|-------------|-------------|
| 5. Harbour Inlet | 17.6 – 24.4 | 7.40 – 7.80 |
| 6. Mhlatuze River | 18.0 – 20.5 | 7.38 – 7.65 |
| 7. Lake Mzingazi | 17.1 – 25.4 | 7.30 – 8.20 |
| 9. Mhlatuze River | 19.5 – 21.9 | 7.19 – 7.42 |
| 10. Railway Pond | 20.2 – 26.4 | 7.30 – 7.99 |
| 11. Harbour Pond | 22.1 – 24.2 | 7.38 – 7.54 |
| 12. Mzingazi Canal | 17.9 - 22.6 | 7.50 - 7.95 |
| 13. Harbour Inlet | 18.0 - 21.2 | 7.95 – 8.20 |
| 14. Mzingazi River | 15.8 – 25.7 | 7.21 – 7.51 |
| 15. Mhlatuze River | 21.2 – 23.4 | 7.80 - 7.85 |
| 16. Mtunzini Inlet | 21.3 | 7.52 |
| 17. Mtunzini Lagoon | 20.5 | 7.48 |
| 18. Mtunzini River | 21.2 | 7.45 |



Figure 5.1: Sampling site map

5.2.2 Alkalinity Titrations

Alkalinity titrations were performed on the water samples that were not acidified on collection. The alkalinity of a water sample reflects its capacity to neutralise acids. These titrations were only performed on samples taken from five of the sampling sites, namely the Mhlatuze River (Point 6), Lake Mzingazi (Point 7), the Mzingazi River (Point 14) and the background-sampling sites on the Mhlatuze River (Point 15) and the Mtunzini River (Point 18). These five sampling sites were chosen as they are all freshwater bodies. The results of these alkalinity titrations can be seen in Table 5.2. Details of these alkalinity titrations can be seen in Appendix 2.1.

Table 5.2: Results of the alkalinity titrations

| | Alkalinity (mg CaCO ₃ / litre) | | | | |
|---------|---|-------------------|---------------------|---------------------|---------------------|
| | Mhlatuze River (6) | Lake Mzingazi (7) | Mzingazi River (14) | Mhlatuze River (15) | Mtunzini River (18) |
| n | 6 | 6 | 5 | 6 | 6 |
| avg. | 124 | 38 | 48 | 108 | 118 |
| sd. | 2 | 0.6 | 1 | 3 | 2 |
| RSD (%) | 2 | 2 | 3 | 3 | 2 |

5.2.3 Ion selective electrode results

Ion selective electrodes were used on un-nitrified, filtered water samples to determine the levels of chloride, fluoride and nitrate in the water samples. The sampling sites involved in this analysis were the harbour inlet (site 5), the Mhlatuze River (site 6), Lake Mzingazi (site 7) and the pond (site 10). The results of this analysis are reflected in Table 5.3. The calibration graphs for nitrate and chloride can be seen in Appendix 2.2. No fluoride is detectable given the detection limit of the fluoride electrode as 1 ppm.

Table 5.3: Results of determinations via ion selective electrodes

| Sampling Site | Concentration (ppm) | | |
|--------------------|------------------------------|---------------------|----------------|
| | NO ₃ ⁻ | Cl ⁻ | F ⁻ |
| 5. Harbour inlet | < dl | 1.7x10 ³ | < dl |
| 6. Mhlathuze River | 3.8 | 2.0x10 ² | <dl |
| 7. Lake Mzingazi | < dl | 44 | <dl |
| 10. Pond | 2.9 | 1.4x10 ³ | <dl |

5.2.4 Trace element determination of water samples

All water samples were preconcentrated by solvent extraction and then analysed by ICP-AES. There were seven metals of interest in this study, namely copper, manganese, iron, zinc, cobalt, cadmium and lead. A summary of the concentration levels of these elements over a variety of sampling sites is presented in Table 5.4. The raw data associated with the summaries can be seen in Appendix 2.3, while the calibration curves can be seen in Appendix 1.4.

Table 5.4: Trace metal concentrations in water samples

| Sampling site | COPPER | | | | MANGANESE | | | | IRON | | | |
|---------------------|------------------------------|------------------------------|-------------|------------|------------------------------|------------------------------|-------------|------------|------------------------------|------------------------------|-------------|------------|
| | Conc. ^a (mg/l) | Conc. ^b (mg/l) | Std dev. | RSD (%) | Conc. ^a (mg/l) | Conc. ^b (mg/l) | Std dev. | RSD (%) | Conc. ^a (mg/l) | Conc. ^b (mg/l) | Std dev. | RSD (%) |
| 5. Harbour inlet | 0.007 | 0.17 | 0.04 | 25.6 | 0.001 | 0.033 | 0.009 | 26.9 | 0.584 | 14.6 | 3.7 | 25.1 |
| 6. Mhlatuze River | 0.007 | 0.17 | 0.03 | 18.4 | 0.002 | 0.045 | 0.007 | 15.8 | 1.116 | 27.9 | 6.6 | 23.7 |
| 7. Lake Mzingazi | 0.004 | 0.09 | 0.01 | 14.7 | 0.0005 | 0.012 | 0.002 | 18.8 | 0.060 | 1.5 | 0.3 | 22.3 |
| 9. Mhlatuze River | 0.005 | 0.132 | 0.009 | 6.7 | 0.004 | 0.09 | 0.020 | 21.7 | 0.516 | 12.9 | 2.6 | 20.5 |
| 10. Railway Pond | 0.006 | 0.15 | 0.03 | 19.7 | 0.002 | 0.06 | 0.014 | 25.6 | 0.328 | 8.2 | 1.8 | 21.4 |
| 11. Harbour Pond | 0.005 | 0.12 | 0.01 | 12.1 | 0.001 | 0.021 | 0.003 | 12.2 | 0.188 | 4.7 | 0.8 | 16.2 |
| 12. Mzingazi Canal | 0.006 | 0.15 | 0.02 | 11.8 | 0.001 | 0.034 | 0.009 | 28.2 | 0.108 | 2.7 | 0.6 | 22.8 |
| 13. Harbour inlet | 0.005 | 0.12 | 0.01 | 8.2 | 0.002 | 0.045 | 0.009 | 19.3 | 0.132 | 3.3 | 0.3 | 10.5 |
| 14. Mzingazi River | 0.004 | 0.11 | 0.02 | 18.8 | 0.001 | 0.025 | 0.007 | 26.5 | 0.124 | 3.1 | 0.5 | 14.8 |
| 15. Mhlatuze River | 0.003 | 0.08 | 0.01 | 13.8 | 0.03 | 0.71 | 0.02 | 21.3 | 1.216 | 30.4 | 4.6 | 15.0 |
| 16. Mtunzini Inlet | 0.006 | 0.15 | 0.04 | 25.6 | 0.0008 | 0.019 | 0.006 | 30.1 | 0.20 | 5.0 | 1.3 | 26.6 |
| 17. Mtunzini Lagoon | 0.004 | 0.11 | 0.02 | 15.6 | 0.0008 | 0.019 | 0.006 | 29.9 | 0.28 | 7.0 | 2.4 | 31.3 |
| 18. Mtunzini River | 0.002 | 0.05 | 0.004 | 8.6 | 0.0004 | 0.009 | 0.002 | 22.7 | 0.128 | 3.2 | 0.9 | 28.8 |

Table 5.4 (contd.): Trace metal concentrations in water samples

| Sampling site | ZINC | | | | COBALT | | | | CADMIUM | | | |
|---------------------|------------------------------|------------------------------|------------|------------|------------------------------|------------------------------|------------|------------|------------------------------|------------------------------|------------|------------|
| | Conc. ^a (mg/l) | Conc. ^b (mg/l) | Std dev | RSD (%) | Conc. ^a (mg/l) | Conc. ^b (mg/l) | Std dev | RSD (%) | Conc. ^a (mg/l) | Conc. ^b (mg/l) | Std dev | RSD (%) |
| 5. Harbour inlet | 0.016 | 0.40 | 0.1 | 30.4 | < dl | < dl | - | - | < dl | < dl | - | - |
| 6. Mhlatuze River | 0.013 | 0.32 | 0.07 | 21.7 | < dl | < dl | - | - | < dl | < dl | - | - |
| 7. Lake Mzingazi | 0.010 | 0.24 | 0.06 | 25.4 | < dl | < dl | - | - | < dl | < dl | - | - |
| 9. Mhlatuze River | 0.016 | 0.41 | 0.03 | 8.0 | < dl | < dl | - | - | < dl | < dl | - | - |
| 10. Railway Pond | 0.024 | 0.60 | 0.13 | 23.4 | < dl | < dl | - | - | < dl | < dl | - | - |
| 11. Harbour Pond | 0.005 | 0.12 | 0.02 | 15.7 | < dl | < dl | - | - | < dl | < dl | - | - |
| 12. Mzingazi Canal | 0.011 | 0.28 | 0.05 | 19.3 | < dl | < dl | - | - | < dl | < dl | - | - |
| 13. Harbour inlet | 0.010 | 0.25 | 0.04 | 14.9 | < dl | < dl | - | - | < dl | < dl | - | - |
| 14. Mzingazi River | 0.011 | 0.28 | 0.04 | 13.8 | < dl | < dl | - | - | < dl | < dl | - | - |
| 15. Mhlatuze River | 0.009 | 0.22 | 0.02 | 7.2 | < dl | < dl | - | - | < dl | < dl | - | - |
| 16. Mtunzini Inlet | 0.015 | 0.38 | 0.12 | 31.3 | < dl | < dl | - | - | < dl | < dl | - | - |
| 17. Mtunzini Lagoon | 0.014 | 0.36 | 0.05 | 15.0 | < dl | < dl | - | - | < dl | < dl | - | - |
| 18. Mtunzini River | 0.007 | 0.17 | 0.05 | 30.8 | < dl | < dl | - | - | < dl | < dl | - | - |

Table 5.4 (contd.): Trace metal concentrations in water samples

| Sampling site | LEAD | | | |
|---------------------|------------------------------|------------------------------|------------|------------|
| | Conc. ^a (mg/l) | Conc. ^b (mg/l) | Std dev | RSD (%) |
| 5. Harbour inlet | 0.007 | 0.18 | 0.03 | 18.2 |
| 6. Mhlatuze River | 0.026 | 0.65 | 0.09 | 13.3 |
| 7. Lake Mzingazi | < dl | < dl | - | - |
| 9. Mhlatuze River | < dl | < dl | - | - |
| 10. Railway Pond | < dl | < dl | - | - |
| 11. Harbour Pond | < dl | < dl | - | - |
| 12. Mzingazi Canal | 0.019 | 0.47 | 0.09 | 18.3 |
| 13. Harbour inlet | < dl | < dl | - | - |
| 14. Mzingazi River | < dl | < dl | - | - |
| 15. Mhlatuze River | < dl | < dl | - | - |
| 16. Mtunzini Inlet | < dl | < dl | - | - |
| 17. Mtunzini Lagoon | < dl | < dl | - | - |
| 18. Mtunzini River | < dl | < dl | - | - |

a Concentration of the original water sample, without concentration (mg/l), calculated from concentrated sample, **b**.

b Concentration of the water sample after preconcentration (mg/l)

5.3 Sediment Results

Sediment analysis involved pH measurement and the determination of trace metals by ICP-AES.

5.3.1 pH measurements

The pH's of the sediment samples from each sampling trip, which spread over the period of 18 months, were measured. The ranges of pH readings over the four sampling trips are recorded in Table 5.5.

Table 5.5: pH measurements for sediment samples

| Site | pH |
|--------------------|-------------|
| 5. Harbour Inlet | 7.34 – 7.85 |
| 6. Mhlatuze River | 7.63 – 8.09 |
| 7. Lake Mzingazi | 5.99 – 7.00 |
| 10. Railway Pond | 7.30 – 7.51 |
| 11. Harbour Pond | 7.54 – 8.06 |
| 12. Mzingazi Canal | 7.65 – 7.65 |
| 13. Harbour Inlet | 7.00 – 7.45 |
| 14. Mzingazi River | 7.27 – 7.27 |

5.3.2 Trace element determination of sediment samples

Sediment samples were initially acid-digested, in order to bring the elements into solution, and then analysed by ICP-AES. There were twenty-one elements of interest in this study, namely Cu, Al, Sr, Ni, Zr, Ba, B, Mn, Ca, Fe, Zn, Mg, P, V, Cd, Na, Co, K, Cr and Pb. A summary of the concentration levels of these elements over a variety of sampling sites is presented in Table 5.6. The raw data associated with the summaries can be seen in Appendix 2.4, while the calibration curves can be seen in Appendix 1.3. For each element at a specific wavelength there is an associated ICP-AES detection limit, these limits are also recorded in Appendix 2.4.

An example calculation of how the concentrations reflected in these tables were obtained is illustrated below.

Sediment sample 909 was taken from sampling site 5 in April 2003. The sample was divided into four sub-samples and the replicates were analysed. If we look at the copper levels determined in this sample:

909A – 0.368 mg/l

909B – 0.362 mg/l

909C – 0.402 mg/l

909D – 0.380 mg/l

In the case of sediment and soil samples it is necessary to convert these concentrations into g/kg:

$$\begin{aligned} 909A &= (0.368 \text{ mg/l} \times 0.100 \text{ l}) / 1.2492 \text{ g} \\ &= 0.0295 \text{ mg/g} \\ &= 0.0295 \text{ g/kg} \end{aligned}$$

$$\begin{aligned} 909B &= (0.362 \text{ mg/l} \times 0.100 \text{ l}) / 1.2275 \text{ g} \\ &= 0.0295 \text{ mg/g} \\ &= 0.0295 \text{ g/kg} \end{aligned}$$

$$\begin{aligned} 909C &= (0.402 \text{ mg/l} \times 0.100 \text{ l}) / 1.3905 \text{ g} \\ &= 0.0289 \text{ mg/g} \\ &= 0.0289 \text{ g/kg} \end{aligned}$$

$$\begin{aligned} 909D &= (0.380 \text{ mg/l} \times 0.100 \text{ l}) / 1.3475 \text{ g} \\ &= 0.0282 \text{ mg/g} \\ &= 0.0282 \text{ g/kg} \end{aligned}$$

The average, standard deviation and relative standard deviation of these replicates were then calculated to determine if there were any outliers:

Average – 0.0290 g/kg

Std. Dev. – 0.0006 g/kg

RSD – 2.1 %

This average was then combined with all the other sediment samples taken from Site 5 and reported in Table 2.16 in Appendix 2.4.2. (This value is highlighted in the Appendix) Once combined, some of these averages were excluded as outliers. For the remaining averages the average, standard deviations and relative standard deviations were calculated and these were reported in the following tables.

In the tables below; < dl indicates levels below the detection limit and ND indicates that the levels were not determined.

Table 5.6: Trace element concentrations in sediment samples

| Site | COPPER | | | TITANIUM | | | ZIRCONIUM | | |
|---------------------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 5. Harbour inlet | 0.040 | 0.008 | 20.5 | 0.27 | 0.08 | 31.2 | 0.010 | 0.002 | 18.9 |
| 6. Mhlatuze River | 0.013 | 0.005 | 35.0 | 0.12 | 0.01 | 11.3 | 0.0026 | 0.0005 | 21.0 |
| 7. Lake Mzingazi | 0.0019 | 0.0006 | 30.7 | 0.020 | 0.006 | 31.3 | 0.0024 | 0.0005 | 22.6 |
| 9. Mhlatuze River | 0.06 | 0.01 | 23.3 | 0.47 | 0.09 | 19.7 | 0.0016 | 0.0004 | 27.1 |
| 10. Railway Pond | 0.03 | 0.01 | 37.0 | 0.27 | 0.08 | 28.7 | 0.0037 | 0.0008 | 20.4 |
| 11. Harbour Pond | 0.0095 | 0.0007 | 7.2 | 0.148 | 0.009 | 6.3 | 0.0040 | 0.0005 | 11.4 |
| 12. Mzingazi Canal | 0.004 | 0.001 | 37.2 | 0.09 | 0.01 | 12.8 | 0.0017 | 0.0005 | 27.1 |
| 13. Harbour inlet | 0.007 | 0.002 | 23.8 | 0.109 | 0.009 | 8.5 | 0.004 | 0.001 | 29.4 |
| 15. Mhlatuze River | 0.005 | 0.001 | 20.2 | 0.13 | 0.02 | 11.5 | 0.0016 | 0.0002 | 13.3 |
| 16.^a Mzingazi Inlet | 0.014 | 0.003 | 19.5 | 0.26 | 0.01 | 5.0 | 0.0078 | 0.0011 | 14.0 |
| 16.^b Mzingazi Inlet | 0.024 | 0.005 | 20.8 | 0.31 | 0.02 | 7.7 | 0.0082 | 0.0011 | 13.6 |
| 17. Mzingazi Lagoon | 0.008 | 0.002 | 22.2 | 0.25 | 0.06 | 25.7 | 0.0042 | 0.0010 | 24.3 |
| 18. Mzingazi River | 0.012 | 0.002 | 18.5 | 0.213 | 0.003 | 16.0 | 0.0050 | 0.0007 | 13.6 |

^a Sediment samples from the inlet^b Mud from the mangrove area of the inlet

Table 5.6 (contd.): Trace element concentrations in sediment samples

| Site | ALUMINIUM | | | STRONTIUM | | | NICKEL | | |
|---------------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 5. Harbour inlet | 27.0 | 5.3 | 19.6 | 0.036 | 0.006 | 15.4 | 0.020 | 0.007 | 33.6 |
| 6. Mhlatuze River | 3.2 | 0.6 | 18.2 | 0.020 | 0.007 | 35.8 | < dl | - | - |
| 7. Lake Mzingazi | 0.9 | 0.1 | 13.7 | 0.0024 | 0.0008 | 31.1 | 0.03 | 0.01 | 33.3 |
| 9. Mhlatuze River | 23.1 | 5.1 | 22.1 | 0.07 | 0.01 | 21.4 | < dl | - | - |
| 10. Railway Pond | 15.6 | 4.5 | 29.1 | 0.06 | 0.02 | 34.3 | 0.099 | 0.003 | 29.3 |
| 11. Harbour Pond | 3.1 | 0.4 | 12.5 | 0.09 | 0.01 | 13.6 | < dl | - | - |
| 12. Mzingazi Canal | 1.4 | 0.2 | 15.4 | 0.005 | 0.001 | 19.6 | 0.016 | 0.002 | 11.2 |
| 13. Harbour inlet | 2.1 | 0.2 | 8.6 | 0.012 | 0.001 | 9.7 | 0.028 | 0.009 | 35.5 |
| 15. Mhlatuze River | 2.1 | 0.2 | 9.4 | 0.0035 | 0.0006 | 17.4 | 0.017 | 0.004 | 22.6 |
| 16. ^c Mzingazi Inlet | 3.8 | 0.4 | 9.3 | 0.021 | 0.001 | 5.2 | < dl | - | - |
| 16. ^d Mzingazi Inlet | 17.0 | 4.2 | 24.6 | 0.022 | 0.006 | 28.8 | < dl | - | - |
| 17. Mzingazi Lagoon | 1.5 | 0.2 | 12.8 | 0.006 | 0.001 | 19.2 | < dl | - | - |
| 18. Mzingazi River | 6.6 | 0.2 | 3.1 | 0.009 | 0.001 | 16.6 | < dl | - | - |

^c Sediment samples from the inlet^d Mud from the mangrove area of the inlet

Table 5.6 (contd.): Trace element concentrations in sediment samples

| Site | BARIUM | | | BORON | | | MANGANESE | | | IRON | | |
|---------------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 5. Harbour inlet | 0.06 | 0.01 | 19.1 | 0.085 | 0.002 | 18.4 | 0.6 | 0.2 | 24.1 | 29.1 | 5.9 | 20.3 |
| 6. Mhlatuze River | 0.008 | 0.002 | 26.5 | 0.016 | 0.003 | 22.7 | 0.070 | 0.009 | 13.6 | 5.5 | 0.9 | 16.4 |
| 7. Lake Mzingazi | 0.0023 | 0.0006 | 25.6 | 0.005 | 0.001 | 19.8 | 0.019 | 0.004 | 18.9 | 1.1 | 0.1 | 13.1 |
| 9. Mhlatuze River | 0.12 | 0.03 | 22.2 | 0.007 | 0.001 | 19.6 | 0.9 | 0.2 | 23.2 | 31.2 | 2.7 | 8.6 |
| 10. Railway Pond | 0.015 | 0.004 | 24.4 | 0.020 | 0.005 | 23.6 | 0.13 | 0.04 | 30.9 | 17.8 | 2.9 | 16.6 |
| 11. Harbour Pond | 0.0060 | 0.0007 | 10.9 | 0.015 | 0.003 | 17.7 | 0.063 | 0.006 | 9.3 | 6.3 | 0.6 | 9.9 |
| 12. Mzingazi Canal | 0.0023 | 0.0005 | 21.1 | 0.007 | 0.001 | 19.7 | 0.048 | 0.005 | 10.2 | 4.1 | 0.5 | 12.9 |
| 13. Harbour inlet | 0.0044 | 0.0005 | 11.3 | < dl | - | - | 0.060 | 0.005 | 7.5 | 4.0 | 0.3 | 7.4 |
| 15. Mhlatuze River | 0.012 | 0.001 | 11.2 | 0.013 | 0.001 | 9.7 | 0.112 | 0.014 | 12.8 | 5.2 | 0.4 | 9.1 |
| 16. ^e Mzingazi Inlet | 0.0062 | 0.0005 | 7.3 | 0.020 | 0.001 | 5.4 | 0.060 | 0.002 | 3.7 | 9.4 | 0.4 | 4.1 |
| 16. ^f Mzingazi Inlet | 0.022 | 0.005 | 23.0 | 0.058 | 0.014 | 24.7 | 0.109 | 0.008 | 7.1 | 25.3 | 5.3 | 21.0 |
| 17. Mzingazi Lagoon | 0.006 | 0.001 | 23.0 | 0.008 | 0.002 | 24.9 | 0.051 | 0.011 | 22.2 | 4.0 | 0.5 | 11.7 |
| 18. Mzingazi River | 0.0147 | 0.0003 | 1.8 | 0.019 | 0.001 | 7.2 | 0.045 | 0.007 | 14.7 | 9.9 | 0.5 | 5.5 |

^e Sediment samples from the inlet^f Mud from the mangrove area of the inlet

Table 5.6 (contd.): Trace element concentrations in sediment samples

| Site | MAGNESIUM | | | VANADIUM | | | SODIUM | | | CALCIUM | | |
|---------------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 5. Harbour inlet | 3.4 | 0.4 | 12.1 | 0.09 | 0.02 | 19.1 | 6.2 | 1.4 | 23.4 | 2.1 | 0.4 | 19.6 |
| 6. Mhlatuze River | 1.1 | 0.1 | 13.8 | 0.018 | 0.003 | 16.5 | 1.8 | 0.3 | 14.9 | 2.8 | 0.6 | 20.3 |
| 7. Lake Mzingazi | 0.06 | 0.01 | 23.7 | 0.012 | 0.002 | 14.3 | 0.32 | 0.08 | 24.5 | 0.32 | 0.05 | 17.0 |
| 9. Mhlatuze River | 6.5 | 0.8 | 12.6 | 0.008 | 0.002 | 22.1 | 0.32 | 0.05 | 15.5 | 1.7 | 0.4 | 23.7 |
| 10. Railway Pond | 7.5 | 1.3 | 17.9 | 0.010 | 0.002 | 19.7 | 5.8 | 0.8 | 14.7 | 4.5 | 1.3 | 28.3 |
| 11. Harbour Pond | 1.6 | 0.2 | 12.5 | 0.017 | 0.003 | 18.9 | 2.9 | 0.6 | 19.1 | 19.1 | 3.8 | 19.7 |
| 12. Mzingazi Canal | 0.72 | 0.07 | 9.5 | 0.0057 | 0.0005 | 9.0 | 2.3 | 0.5 | 22.3 | 0.6 | 0.1 | 21.6 |
| 13. Harbour inlet | 1.3 | 0.1 | 9.9 | 0.013 | 0.001 | 9.8 | 2.7 | 0.5 | 19.0 | 19.9 | 2.3 | 11.6 |
| 15. Mhlatuze River | 0.53 | 0.07 | 13.6 | < dl | - | - | 0.4 | 0.1 | 25.2 | 0.42 | 0.07 | 16.3 |
| 16. ^g Mzingazi Inlet | 1.67 | 0.05 | 3.1 | 0.010 | 0.002 | 15.3 | 2.9 | 0.2 | 8.4 | 5.5 | 0.1 | 2.4 |
| 16. ^h Mzingazi Inlet | 3.7 | 0.6 | 17.5 | 0.019 | 0.004 | 21.9 | 5.4 | 0.4 | 7.6 | 2.1 | 0.3 | 14.4 |
| 17. Mzingazi Lagoon | 0.78 | 0.11 | 13.8 | 0.005 | 0.001 | 25.7 | 2.8 | 0.4 | 15.5 | 0.8 | 0.1 | 12.4 |
| 18. Mzingazi River | 1.5 | 0.3 | 22.8 | 0.0094 | 0.0006 | 6.8 | 3.3 | 0.3 | 10.3 | 0.88 | 0.07 | 8.3 |

^g Sediment samples from the inlet^h Mud from the mangrove area of the inlet

Table 5.6 (contd.): Trace element concentrations in sediment samples

| Site | ZINC | | | PHOSPHORUS | | | CADMIUM | | |
|---------------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 5. Harbour inlet | 0.07 | 0.02 | 24.0 | 0.17 | 0.03 | 18.2 | 0.009 | 0.002 | 24.1 |
| 6. Mhlatuze River | 0.018 | 0.004 | 22.7 | 0.39 | 0.08 | 19.3 | 0.0015 | 0.0002 | 16.4 |
| 7. Lake Mzingazi | 0.011 | 0.002 | 21.3 | 0.45 | 0.08 | 18.2 | < dl | - | - |
| 9. Mhlatuze River | 0.010 | 0.002 | 15.1 | 2.7 | 0.5 | 19.0 | < dl | - | - |
| 10. Railway Pond | 0.07 | 0.02 | 22.9 | 1.9 | 0.3 | 13.9 | < dl | - | - |
| 11. Harbour Pond | 0.017 | 0.003 | 17.7 | 0.90 | 0.06 | 6.4 | 0.0018 | 0.0002 | 8.8 |
| 12. Mzingazi Canal | 0.018 | 0.004 | 21.1 | 0.57 | 0.06 | 10.5 | < dl | - | - |
| 13. Harbour inlet | 0.020 | 0.003 | 17.4 | 0.73 | 0.09 | 11.8 | < dl | - | - |
| 15. Mhlatuze River | 0.019 | 0.004 | 21.7 | 0.44 | 0.06 | 13.3 | 0.0019 | 0.0002 | 12.2 |
| 16. ⁱ Mzingazi Inlet | 0.019 | 0.002 | 9.9 | ND | - | - | < dl | - | - |
| 16. ^j Mzingazi Inlet | 0.036 | 0.002 | 4.5 | ND | - | - | < dl | - | - |
| 17. Mzingazi Lagoon | 0.015 | 0.002 | 11.5 | ND | - | - | < dl | - | - |
| 18. Mzingazi River | 0.017 | 0.003 | 18.5 | ND | - | - | < dl | - | - |

ⁱ Sediment samples from the inlet^j Mud from the mangrove area of the inlet

Table 5.6 (contd.): Trace element concentrations in sediment samples

| Site | LEAD | | | CHROMIUM | | | COBALT | | |
|---------------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 5. Harbour inlet | 0.022 | 0.006 | 24.9 | 0.16 | 0.04 | 26.8 | 0.011 | 0.003 | 21.8 |
| 6. Mhlatuze River | < dl | - | - | 0.05 | 0.01 | 21.1 | < dl | - | - |
| 7. Lake Mzingazi | < dl | - | - | 0.020 | 0.003 | 16.8 | < dl | - | - |
| 9. Mhlatuze River | < dl | - | - | 0.13 | 0.02 | 16.3 | < dl | - | - |
| 10. Railway Pond | < dl | - | - | 0.085 | 0.008 | 9.1 | < dl | - | - |
| 11. Harbour Pond | < dl | - | - | 0.052 | 0.009 | 18.8 | < dl | - | - |
| 12. Mzingazi Canal | < dl | - | - | 0.04 | 0.01 | 25.7 | < dl | - | - |
| 13. Harbour inlet | < dl | - | - | 0.04 | 0.01 | 26.9 | < dl | - | - |
| 15. Mhlatuze River | < dl | - | - | 0.025 | 0.006 | 21.6 | < dl | - | - |
| 16. ^k Mzingazi Inlet | < dl | - | - | 0.018 | 0.005 | 27.4 | < dl | - | - |
| 16. ^l Mzingazi Inlet | 0.026 | 0.003 | 10.9 | 0.012 | 0.001 | 9.7 | 0.0087 | 0.0006 | 7.2 |
| 17. Mzingazi Lagoon | < dl | - | - | 0.007 | 0.001 | 15.7 | < dl | - | - |
| 18. Mzingazi River | < dl | - | - | 0.025 | 0.004 | 16.2 | < dl | - | - |

^k Sediment samples from the inlet^l Mud from the mangrove area of the inlet

5.4 Soil Results

Soil analysis involved determining pH levels and trace element concentrations. Pollutants such as heavy metals can accumulate in soils and subsequently enter the food chain or seep into the ground water. Maintaining good soil quality and minimising soil pollution is therefore of fundamental importance.

5.4.1 pH measurements

The pH's of the soil samples from each sampling trip, which spread over the period of 18 months, were measured. The range of pH readings over the four sampling trips and are recorded in Table 5.7.

Table 5.7: pH measurements for soil samples

| Sampling site | pH |
|--------------------|-------------|
| 1. Roadside | 5.38 – 5.65 |
| 2. Roadside | 5.08 – 5.72 |
| 3. Roadside | 5.36 – 5.36 |
| 4. Roadside | 5.18 – 5.60 |
| 5. Harbour inlet | 8.03 – 8.17 |
| 6. Mhlatuze River. | 7.24 – 8.04 |
| 7. Lake Mzingazi | 6.10 – 6.50 |
| 10. Railway Pond | 8.09 – 8.17 |
| 15. Mhlatuze River | 6.16 – 7.25 |

5.4.2 Trace element determination of soil samples

Soil samples were initially acid-digested, in order to bring the metal ions into solution, and then analysed by ICP-AES. There were twenty-one elements of interest in this study, namely Cu, Al, Sr, Ni, Zr, Ba, B, Mn, Ca, Fe, Zn, Mg, P, V, Cd, Na, Co, K, Cr and Pb. A summary of the concentration levels of these elements over a variety of sampling sites is presented in Table 5.8. The raw data associated with the summaries can be seen in Appendix A-2.5., while the calibration curves can be seen in Appendix 1.3. For each element at a specific wavelength

there is an associated ICP-AES detection limit, these limits are also recorded in Appendix 2.5.

Table 5.8: Trace element concentrations in soil samples

| Site | COPPER | | | TITANIUM | | | ZIRCONIUM | | |
|---------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 1. Roadside soils | 0.019 | 0.003 | 14.8 | 0.11 | 0.02 | 21.6 | 0.012 | 0.001 | 8.8 |
| 2. Roadside soils | < dl | - | - | 0.05 | 0.01 | 24.8 | 0.004 | 0.001 | 23.1 |
| 3. Roadside soils | < dl | - | - | 0.05 | 0.01 | 24.7 | < dl | - | - |
| 4. Roadside soils | 0.007 | 0.002 | 33.8 | 0.05 | 0.01 | 27.9 | 0.003 | 0.001 | 27.3 |
| 5. Harbour inlet | < dl | - | - | ND | - | - | ND | - | - |
| 6. Mhlatuze River | 0.016 | 0.003 | 19.7 | 0.0012 | 0.0003 | 23.2 | 0.007 | 0.001 | 14.1 |
| 7. Lake Mzingazi | 0.015 | 0.002 | 12.8 | ND | - | - | ND | - | - |
| 10. Railway Pond | < dl | - | - | 0.09 | 0.02 | 18.4 | < dl | - | - |
| 15. Mhlatuze River | 0.013 | 0.005 | 35.2 | 0.22 | 0.05 | 25.7 | 0.002 | 0.0008 | 34.4 |

Table 5.8 (contd.): Trace element concentrations in soil samples

| Site | ALUMINIUM | | | STRONTIUM | | | NICKEL | | |
|---------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std Dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 1. Roadside soils | 4.6 | 1.1 | 23.2 | 0.005 | 0.002 | 33.7 | 0.03 | 0.01 | 32.6 |
| 2. Roadside soils | 3.0 | 0.8 | 28.3 | 0.003 | 0.001 | 21.0 | 0.033 | 0.006 | 18.9 |
| 3. Roadside soils | 1.3 | 0.3 | 19.7 | 0.002 | 0.001 | 30.3 | < dl | - | - |
| 4. Roadside soils | 1.7 | 0.5 | 9.6 | 0.004 | 0.001 | 27.2 | < dl | - | - |
| 5. Harbour inlet | 2.5 | 0.6 | 22.6 | 0.19 | 0.02 | 9.9 | ND | - | - |
| 6. Mhlatuze River | 3.4 | 0.8 | 22.8 | 0.025 | 0.006 | 25.6 | 0.021 | 0.003 | 13.6 |
| 7. Lake Mzingazi | 2.2 | 1.2 | 56.5 | < dl | - | - | ND | - | - |
| 10. Railway Pond | 1.5 | 0.15 | 10.5 | 0.027 | 0.009 | 33.5 | < dl | - | - |
| 15. Mhlatuze River | 4.3 | 1.3 | 30.1 | 0.006 | 0.002 | 33.3 | 0.025 | 0.007 | 29.2 |

Table 5.8 (contd.): Trace element concentrations in soil samples

| Site | BARIUM | | | BORON | | | MANGANESE | | | IRON | | |
|---------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std Dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 1. Roadside soils | 0.011 | 0.003 | 32.0 | 0.037 | 0.007 | 18.5 | 0.09 | 0.04 | 35.0 | 6.0 | 1.5 | 24.4 |
| 2. Roadside soils | 0.006 | 0.002 | 26.1 | 0.032 | 0.009 | 28.5 | 0.014 | 0.004 | 26.2 | 2.3 | 0.3 | 14.6 |
| 3. Roadside soils | < dl | - | - | < dl | - | - | < dl | - | - | 1.8 | 0.5 | 25.1 |
| 4. Roadside soils | < dl | - | - | < dl | - | - | 0.021 | 0.006 | 31.0 | 1.7 | 0.5 | 31.5 |
| 5. Harbour inlet | 0.015 | 0.003 | 19.0 | 0.034 | 0.005 | 14.8 | 0.042 | 0.009 | 21.9 | 6.6 | 1.2 | 18.1 |
| 6. Mhlatuze River | 0.011 | 0.003 | 27.5 | 0.029 | 0.007 | 23.3 | < dl | - | - | 4.8 | 1.4 | 29.3 |
| 7. Lake Mzingazi | < dl | - | - | 0.013 | 0.002 | 16.5 | < dl | - | - | 1.1 | 0.3 | 26.7 |
| 10. Railway Pond | 0.006 | 0.001 | 18.6 | 0.014 | 0.002 | 12.5 | 0.021 | 0.006 | 20.8 | 2.3 | 0.4 | 17.4 |
| 15. Mhlatuze River | 0.029 | 0.008 | 28.8 | 0.020 | 0.006 | 29.2 | 0.17 | 0.06 | 34.3 | 7.9 | 2.2 | 28.1 |

Table 5.8 (contd.): Trace element concentrations in soil samples

| Site | MAGNESIUM | | | VANADIUM | | | SODIUM | | | CALCIUM | | |
|--------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std Dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 1. Roadside soils | 0.6 | 0.1 | 21.2 | 0.030 | 0.008 | 26.6 | 0.54 | 0.07 | 13.0 | 0.7 | 0.2 | 20.9 |
| 2. Roadside soils | 0.09 | 0.02 | 22.2 | 0.026 | 0.005 | 20.6 | 0.28 | 0.09 | 32.4 | 0.20 | 0.05 | 26.7 |
| 3. Roadside soils | 0.13 | 0.04 | 29.5 | 0.016 | 0.003 | 16.0 | 0.37 | 0.04 | 11.7 | 0.24 | 0.06 | 24.2 |
| 4. Roadside soils | 0.10 | 0.03 | 24.7 | < dl | - | - | 0.52 | 0.09 | 18.3 | 0.6 | 0.2 | 29.0 |
| 5. Harbour inlet | 1.4 | 0.1 | 8.4 | 0.04 | 0.01 | 32.3 | 0.5 | 0.1 | 22.5 | 3.6 | 0.6 | 16.7 |
| 6. Mhlatuze River | 1.4 | 0.1 | 9.0 | 0.018 | 0.003 | 16.5 | 0.20 | 0.01 | 7.1 | 2.6 | 0.3 | 13.0 |
| 7. Lake Mzingazi | 0.15 | 0.02 | 13.4 | 0.008 | 0.002 | 22.3 | 0.19 | 0.03 | 17.1 | 0.59 | 0.09 | 16.3 |
| 10. Railway Pond | 0.36 | 0.08 | 23.3 | 0.013 | 0.003 | 25.6 | 0.36 | 0.07 | 19.6 | 2.5 | 0.4 | 15.6 |
| 15. Mhlatuze River | 0.8 | 0.2 | 31.0 | 0.014 | 0.005 | 34.7 | 0.5 | 0.1 | 21.9 | 0.9 | 0.3 | 33.3 |

Table 5.8 (contd.): Trace element concentrations in soil samples

| Site | ZINC | | | PHOSPHORUS | | | CADMIUM | | | COBALT | | |
|--------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std Dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 1. Roadside soils | 0.024 | 0.006 | 24.6 | 1.6 | 0.2 | 12.8 | 0.015 | 0.003 | 16.9 | 0.019 | 0.006 | 31.8 |
| 2. Roadside soils | 0.016 | 0.002 | 14.4 | 1.2 | 0.2 | 12.2 | 0.008 | 0.001 | 6.8 | 0.017 | 0.003 | 16.8 |
| 3. Roadside soils | 0.015 | 0.004 | 26.4 | 1.5 | 0.3 | 16.8 | 0.006 | 0.001 | 12.4 | < dl | - | - |
| 4. Roadside soils | 0.018 | 0.003 | 18.6 | 1.7 | 0.3 | 15.2 | 0.009 | 0.001 | 13.0 | < dl | - | - |
| 5. Harbour inlet | 0.03 | 0.01 | 33.2 | ND | - | - | ND | - | - | ND | - | - |
| 6. Mhlatuze River | 0.019 | 0.005 | 23.6 | ND | - | - | ND | - | - | ND | - | - |
| 7. Lake Mzingazi | 0.023 | 0.006 | 28.3 | ND | - | - | ND | - | - | ND | - | - |
| 10. Railway Pond | 0.028 | 0.006 | 22.4 | 0.6 | 0.1 | 16.9 | < dl | - | - | < dl | - | - |
| 15. Mhlatuze River | 0.029 | 0.010 | 35.0 | 0.9 | 0.1 | 15.3 | < dl | - | - | 0.006 | 0.001 | 15.3 |

Table 5.8 (contd.): Trace element concentrations in soil samples

| Site | POTASSIUM | | | LEAD | | | CHROMIUM | | |
|---------------------------|-----------------|------------|------------|-----------------|------------|------------|-----------------|------------|------------|
| | Conc. (g/kg) | Std dev | RSD (%) | Conc. (g/kg) | Std Dev | RSD (%) | Conc. (g/kg) | Std dev | RSD (%) |
| 1. Roadside soils | 0.31 | 0.06 | 17.4 | 0.024 | 0.005 | 19.4 | 0.021 | 0.006 | 28.8 |
| 2. Roadside soils | 0.14 | 0.03 | 18.8 | 0.021 | 0.004 | 19.3 | < dl | - | - |
| 3. Roadside soils | 0.08 | 0.01 | 16.5 | 0.017 | 0.003 | 18.2 | < dl | - | - |
| 4. Roadside soils | 0.05 | 0.01 | 28.1 | 0.016 | 0.002 | 10.2 | < dl | - | - |
| 5. Harbour inlet | 0.45 | 0.04 | 8.73 | < dl | - | - | 0.013 | 0.004 | 27.1 |
| 6. Mhlatuze River | 0.18 | 0.04 | 20.1 | < dl | - | - | 0.015 | 0.001 | 8.6 |
| 7. Lake Mzingazi | 0.15 | 0.02 | 11.2 | 0.016 | 0.002 | 10.0 | 0.017 | 0.005 | 26.0 |
| 10. Railway Pond | 0.15 | 0.02 | 14.2 | < dl | - | - | < dl | - | - |
| 15. Mhlatuze River | 0.6 | 0.2 | 33.5 | < dl | - | - | < dl | - | - |

CHAPTER 6

Statistical Analysis of Results

Most analytical projects produce large amounts of data, which need to be presented, analysed and interpreted in respect of the chemical phenomena being studied. For such data and related analysis to have any validity, it is necessary to utilise methods that can produce the required interpretational information. Statistics provides such methods so that data can be turned into useful and meaningful scientific knowledge.⁹⁰ A statistical analysis of the results obtained in this study is necessary in order to be able to formulate any conclusions about pollution levels in the waters, sediments and soils. Elementary statistical calculations were performed to obtain the averages, standard deviations and various other statistical parameters, which can be used to estimate if there is a statistical difference between the elemental levels found at the various sampling sites when compared with the background sites. These statistical parameters will be discussed in general terms.

Three basic parameters were calculated initially for each element at each sampling site; the mean, standard deviation and confidence intervals. The mean is defined as the arithmetic average of a set of experimental measurements, the standard deviation is defined as a magnitude-dependent measure of the absolute precision of replicate experimental data, and the confidence interval as an interval or range of values which contains the experimental effect being estimated with a given level of probability.⁹⁰

These parameters and others were used in the first step of the statistical analysis employed in this project, which was an analysis of variance (ANOVA). In analysis of variance, the basic idea is to express a measure of the total variation of a set of data as a sum of terms, which can be attributed to specific sources or causes of variation.⁹¹ Typically, ANOVA is used to determine whether the mean dependent variable scores, in this case elemental concentrations, obtained in the experimental conditions differ significantly.

This is achieved by determining how much variation in the scores is attributable to differences between the scores obtained in the different experimental conditions, and comparing this with the error term, which is attributable to variation in the scores within each of the experimental conditions.⁹² The experimental conditions in this case can be regarded as the different sampling sites. Thus, this statistical tool allows us to see if there are significant differences in concentrations between all the different sampling sites within the distinct categories e.g. freshwater, saltwater, sediments and soils. If there was no obvious difference in concentration between the 16 different sampling sites, a conclusion could be drawn that there was little or no pollution in the area due to anthropogenic sources.

ANOVA involves measuring the total variation of a data set, i.e. the variation among the sample means and the variation within the samples.⁹¹ In this case the two terms are the variations in concentrations of an element found within one site and the variations in concentrations of that element between sites. These two terms are compared by means of an F statistic, which is a ratio of the mean squares of the two terms. The F statistic is then compared with a tabulated F_{critical} statistic and if $F < F_{\text{critical}}$, it can be concluded that there is no statistical difference between the data sets for that particular measured parameter. The tables presented below are examples of ANOVA calculations.

Table 6.1: ANOVA calculation for analysis of saltwater copper levels

| <i>Groups</i> | <i>Count</i> | <i>Sum</i> | <i>Average</i> | <i>Variance</i> |
|---------------|--------------|------------|----------------|-----------------|
| Site 5 | 9 | 1.530 | 0.170 | 0.0021 |
| Site 12 | 9 | 1.110 | 0.123 | 0.0001 |
| Site 13 | 9 | 1.360 | 0.151 | 0.0003 |
| Site 16 | 6 | 0.900 | 0.150 | 0.0015 |
| Site 17 | 6 | 0.690 | 0.115 | 0.0003 |

| <i>Source of Variation</i> | <i>SS</i> | <i>df</i> | <i>MS</i> | <i>F</i> | <i>P-value</i> | <i>F crit</i> |
|----------------------------|-----------|-----------|-----------|----------|----------------|---------------|
| Between Groups | 0.0156 | 4 | 0.0039 | 4.482 | 0.0051 | 2.650 |
| Within Groups | 0.0296 | 34 | 0.0009 | | | |
| Total | 0.0453 | 38 | | | | |

Table 6.2: ANOVA calculation for analysis of saltwater zinc levels

| <i>Groups</i> | <i>Count</i> | <i>Sum</i> | <i>Average</i> | <i>Variance</i> |
|---------------|--------------|------------|----------------|-----------------|
| Site 5 | 10 | 3.31 | 0.331 | 0.023 |
| Site 12 | 9 | 2.27 | 0.252 | 0.002 |
| Site 13 | 9 | 2.51 | 0.279 | 0.003 |
| Site 16 | 6 | 2.30 | 0.383 | 0.014 |
| Site 17 | 7 | 2.52 | 0.360 | 0.003 |

| <i>Source of Variation</i> | <i>SS</i> | <i>df</i> | <i>MS</i> | <i>F</i> | <i>P-value</i> | <i>F crit</i> |
|----------------------------|-----------|-----------|-----------|----------|----------------|---------------|
| Between Groups | 0.092 | 4 | 0.023 | 2.471 | 0.0619 | 2.634 |
| Within Groups | 0.335 | 36 | 0.009 | | | |
| Total | 0.427 | 40 | | | | |

The first of the ANOVA tables lists the number of groups involved in the analysis. In this case, the groups are the different saltwater sampling sites, i.e. sampling sites 5, 12, 13, 16 and 17. The count is the number of samples taken from that site. Also recorded are the sum, average and variance of these samples.

The second of the ANOVA table illustrates how the variances are calculated between groups and within groups and how they may be compared through the F-statistic. In the case of the saltwater copper, $F > F_{crit}$ and from this information we are able to deduce that there is a significant difference in the levels of copper between sampling sites. For saltwater zinc, $F < F_{crit}$ and as such the levels of zinc do not differ appreciably between sites. This illustrates that there may be copper contamination of the saltwater bodies, but they remain uncontaminated by zinc.

The analysis of variance allows a broad view of whether or not there is pollution present in the area. It does not, however, provide any information as to the extent of the pollution, the areas of concern or the elements of concern. Another statistical method was employed to identify these issues. The method used was a graphical one as a visual display of information – whether in the raw data, effects, residuals, comparisons, or relationships among variables – helps discovery, understanding and effective communication.⁹³ In this case, confidence intervals were calculated

for all the sampling sites and these were represented graphically for each element. A population mean (μ) for a population data can never be determined because such a determination requires an infinite number of measurements to be made. Therefore, statistical theory allows limits to be set around an experimentally determined average within which the population mean lies with a given degree of probability. These limits are called confidence limits, and the interval they define is known as the confidence interval.⁷⁵ The size of the confidence interval is mainly dependent on the standard deviations.

The confidence intervals were represented graphically in the form of floating bar graphs. Individual graphs were plotted for each element and the confidence intervals (90%), in terms of concentration, were plotted against sampling site. Each graph then clearly illustrates the concentration range at each sampling site. From the graph we are then able to determine if the concentrations for each site are significantly different from the background concentrations, i.e. if the confidence levels overlap there is no significant difference between that site and the background site. An example of these graphs can be seen below.

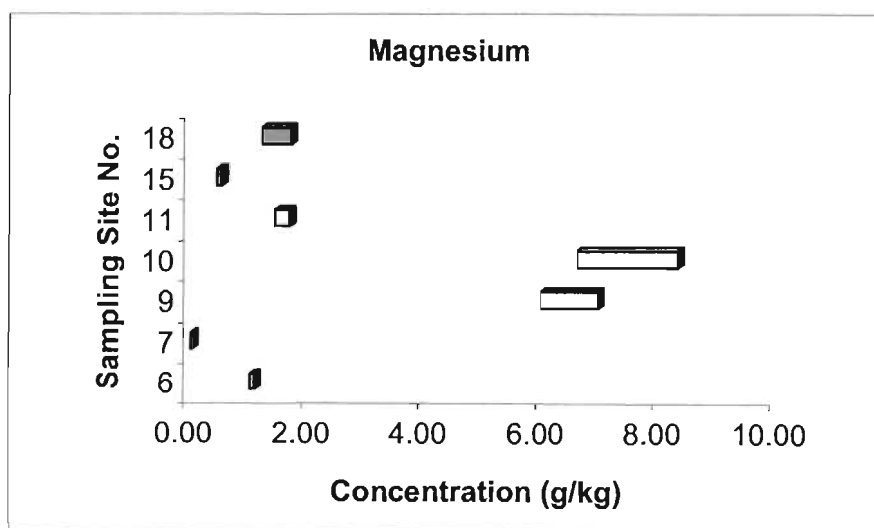


Figure 6.1: Example of a floating bar graph for magnesium in freshwater sediments

The graph immediately gives an idea of the range of concentrations of magnesium between all the sampling sites. In this instance, sites 15 and 18 provide the background levels and from the graph we are able to see that only the levels at sites 9 and 10 differ significantly from them. The

bars for sites 6, 7 and 11 overlap the background bars and it can therefore be assumed that there is no significant difference in the levels of magnesium between these sites.

The floating bar graphs allow us to determine which are the areas of concern with regards to relatively high amounts of contamination as well as to determine which of the elements are present at elevated levels.

It can therefore be seen that although the ANOVA calculations are useful when determining if there is overall contamination, they do not provide any information as to which are the contaminated sites and to what extent these sites are contaminated. As such, ANOVA calculations were performed on all the water, sediment and soil samples, but it was the graphical representations that became the focus of the statistical analysis as they provide more detailed information.

6.1 Water Results

The water results obtained were first divided into fresh and saltwater samples before any sort of statistical analysis could take place. This is because freshwater samples must be compared with a freshwater background site and in turn, saltwater samples with a saltwater background. Only five elements were present at detectable levels in both the salt and freshwater samples. The levels of each element present at each of the sampling sites, fresh and saltwater sites separately, were compared graphically using the method previously discussed.

6.1.1 Freshwater

There were eight sampling sites that were identified as freshwater sites. These sites included two sites that were to provide background levels. The sites are identified in Table 6.3.

Table 6.3: Identification of the freshwater sampling sites

| | Site | Site Name | Description | GPS Position |
|----|------|----------------|--|----------------------------|
| 6 | | Mhlatuze River | Off the Coal Terminal Rd, under a bridge, 100m from mouth | S 28°48'00" E 32°01'08" |
| 7 | | Lake Mzingazi | Edge of the lake alongside the Country Club | S 28°46'12" E 32°06'04" |
| 9 | | Mhlatuze River | Running alongside pond between Hillside and Bayside | S 28°48'07" E 32°00'50" |
| 10 | | Pond 1 | Groundwater pond btw Hillside and Bayside next to railway line | S 28°48'07" E 32°00'50" |
| 11 | | Pond 2 | Groundwater pond on Coal Terminal rd. | S 28°47'24" E 32°01'48" |
| 14 | | Mzingazi River | Next to the Croc Sanctuary | S 28°46'26" E 32°04'23" |
| 15 | | Mhlatuze River | 10km outside of Richards Bay | S 28°48'00" E 31°57'40" |
| 18 | | Mtunzini River | 50km outside Richards Bay | S 28°56'46" E 31°46'59" |

Sites 15 and 18 are used as the background for the freshwater samples.

The statistical graphs allow us to see which sampling sites are polluted with which elements and by how much the levels differ from the background levels. These graphs can be seen in Appendix 3.1.1. When looking at the graphs for the freshwaters it can be seen that for most sampling sites there are elevated levels of all the elements when compared with the background sites. All the elements show a consistent trend with regards to the levels at the various sampling sites, i.e. sites 6, 9 and 10 are consistently the most polluted, sites 11 and 14 have levels only marginally above those reported for the background, while the levels for site 7 consistently overlap with the background levels. Lead is only detectable at site 6. An example of the graphs obtained for the freshwater samples can be seen in Figure 6.2.

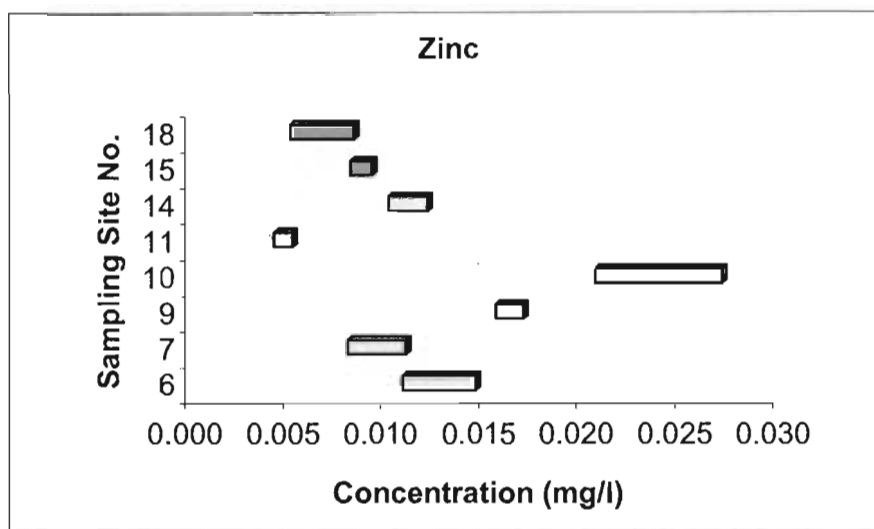


Figure 6.2: Example of a floating bar graph for zinc in freshwater

6.1.2 Saltwater

There were five sampling sites that were classified as saltwater sites. These included two background sites. Descriptions of these sites can be seen in Table 6.4. There were only four elements that were present at detectable levels in the saltwater samples. Lead, found at detectable levels in freshwater, was found to be present at levels below the detection limit in the saltwater samples.

Table 6.4: Description of the saltwater sampling sites

| | Site | Site Name | Description | GPS Position |
|----|------|-----------------|---|----------------------------|
| 5 | | Harbour inlet | Off the Coal Terminal Rd alongside the railway line | S 28°49'49" E 32°02'24" |
| 12 | | Mzingazi Canal | North side | S 28°47'13" E 32°04'59" |
| 13 | | Harbour inlet | North side | S 28°59'56" E 32°04'48" |
| 16 | | Mtunzini Inlet | Mouth of the lagoon 50 km outside Richards Bay | S 28°57'18" E 31°46'30" |
| 17 | | Mtunzini Lagoon | 50 km outside Richards Bay | S 28°57'00" E 31°46'30" |

The background sites used for saltwater analysis were site 16 and 17, as the Mtunzini area is regarded as a relatively pristine environment.

When looking at the saltwater graphs it can be seen that there is predominantly little difference between the sampling sites and the background sites. The graphs can be seen in Appendix 3.1.2. For copper and zinc all the sites overlap with the back ground levels, while for iron it is only site 5 that is seen to deviate significantly from the background. For manganese, all the sites show marginal elevation (i.e. 0.0004-0.0006 mg/l) compared to the background. Lead is only detectable at sites 5 and 12. Figure 6.3 provides an example of the graphs obtained for the saltwater samples.

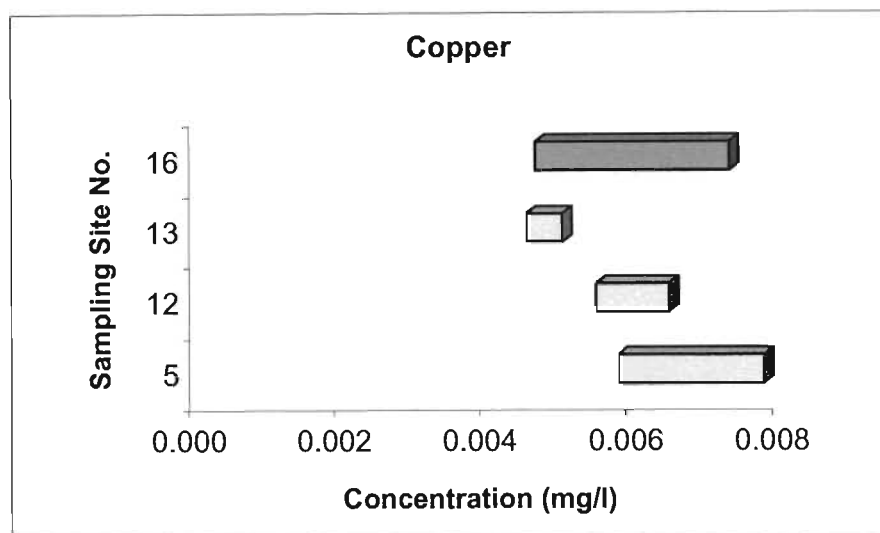


Figure 6.3: Example of a floating bar graph for copper in saltwater

6.2 Sediment Results

As for the water samples, the sediment samples had to be divided into freshwater and saltwater samples. In addition, the samples that were taken from mangrove areas were treated independently. This is because muds taken from the mangrove areas have very different physical properties from the other sediments and therefore a different affinity for contaminants. For example, the mangrove muds have higher clay contents and would therefore retain trace metal contaminants to a greater degree than the sediments.

Freshwater sediment samples were compared with a freshwater sediment background site, saltwater sediment samples with a saltwater sediment background and mangrove mud samples were compared with background mangrove mud samples. Twenty elements were present at detectable levels in all the sediment samples. The levels of each element present at each of the sampling sites (mangrove, fresh and saltwater sites independently) were compared graphically.

6.2.1 Mangrove Sediments

There were only two sites where the samples were taken from mangrove areas. One of the sites was a background site. Descriptions of the two sites can be seen in Table 6.5.

Table 6.5: Identification of the mangrove sampling sites

| Site | Site Name | Description | GPS Position |
|------|----------------|---|----------------------------|
| 5 | Harbour inlet | Off the Coal Terminal Rd alongside the railway line | S 28°49'49" E 32°02'24" |
| 16 | Mtunzini Inlet | Mouth of the lagoon 50km outside Richards Bay | S 28°57'18" E 31°46'30" |

The samples from the Mtunzini Inlet were used as the background samples as this area is regarded as relatively unpolluted.

When looking at the graphical plots, when the bar from site 5 overlaps with the background bar these elements may be disregarded as contaminants. The ANOVA calculations allowed us to disregard titanium, zirconium, iron, magnesium, sodium, calcium and the graphical method allows us to add two more elements, namely cobalt and lead, to this list.

According to the graphs, which can be seen in Appendix 3.2.1, the levels of chromium, potassium, cadmium, zinc, vanadium, manganese, boron, barium, strontium, aluminium and copper all exist at levels higher than those of the background. An example of these graphs can be seen in Figure 6.4.

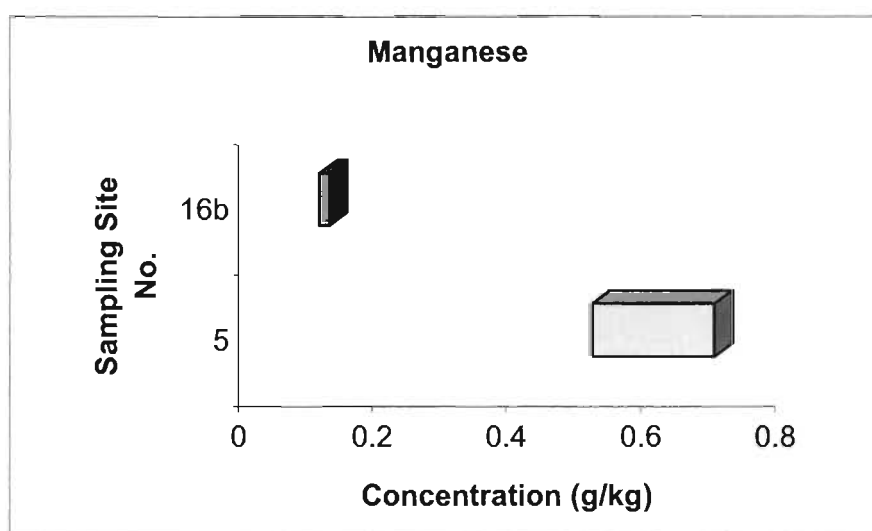


Figure 6.4: Example of a floating bar graph for manganese in mangrove mud

6.2.2 Freshwater Sediments

There were seven sampling sites that were identified as freshwater sediment sites. These sites included two sites that were to provide background levels. The sites are identified below.

Table 6.6: Identification of the freshwater sediment sampling sites

| | Site | Site Name | Description | GPS Position |
|----|------|----------------|--|----------------------------|
| 6 | | Mhlatuze River | Off the Coal Terminal Rd, under a bridge, 100m from mouth | S 28°48'00" E 32°01'08" |
| 7 | | Lake Mzingazi | Edge of the lake alongside the Country Club | S 28°46'12" E 32°06'04" |
| 9 | | Mhlatuze River | Running alongside pond between Hillside and Bayside | S 28°48'07" E 32°00'50" |
| 10 | | Pond 1 | Groundwater pond btw Hillside and Bayside next to railway line | S 28°48'07" E 32°00'50" |
| 11 | | Pond 2 | Groundwater pond on Coal Terminal rd. | S 28°47'24" E 32°01'48" |
| 15 | | Mhlatuze River | 10km outside of Richards Bay | S 28°48'00" E 31°57'40" |
| 18 | | Mtunzini River | 50km outside Richards Bay | S 28°56'46" E 31°46'59" |

Sites 15 and 18 are used as the background for the freshwater sediment samples. Site 15 provides samples from the same river as the other river sampling sites, but from outside the industrialised area. Site 18 provides samples from another river, but from one that flows through an area that is regarded as uncontaminated. All the sediment samples were taken from the edge of the water bodies at a depth of about 50 cm.

The graphs allow us to disregard elements as contaminants. In the case of the freshwater sediments the elements that can be disregarded are boron, zirconium, cadmium and sodium. The rest of the elements show a degree of contamination at certain sites and seem to follow the same trends. Sites 9, 10 and 11 are generally the most contaminated with regards to all the elements. Site 9 is contaminated with copper, strontium, barium, manganese, iron, magnesium, potassium and chromium, while site 10 is contaminated with copper, strontium, iron, magnesium, sodium, calcium, zinc, potassium and chromium and finally site 11 is contaminated with strontium, manganese, vanadium, calcium and chromium. Sites 6 and 7 remain largely uncontaminated, i.e. their levels overlap with those found at the background sites, except for vanadium and chromium

at site 6. All the graphs can be seen in Appendix 3.2.2, while an example can be seen in Figure 6.5.

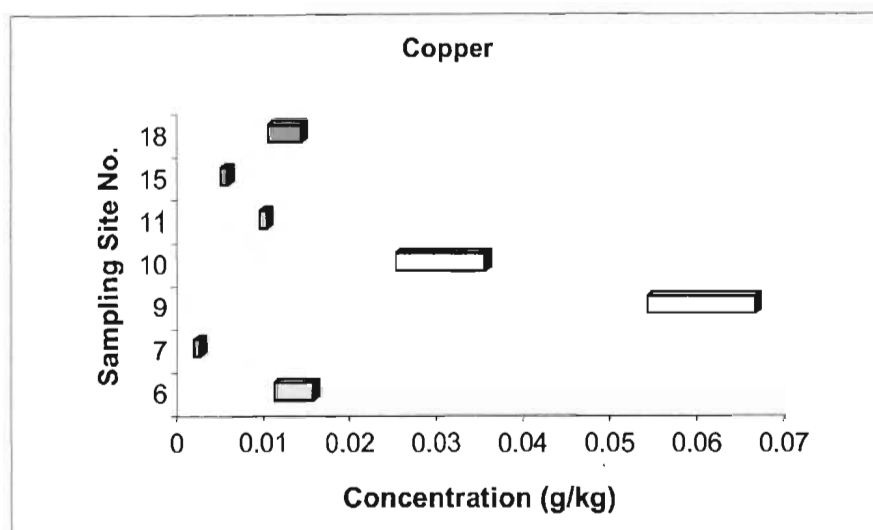


Figure 6.5: Example of a bar graph for copper in freshwater sediments

6.2.3 Saltwater Sediments

Saltwater sediment samples were only taken from 4 sites, two of which were background sites. The sites are described in Table 6.7.

Table 6.7: Description of the saltwater sediment sampling sites

| Site | Site Name | Description | GPS Position |
|------|-----------------|---|----------------------------|
| 12 | Mzingazi Canal | North side | S 28°47'13" E 32°04'59" |
| 13 | Harbour inlet | North side | S 28°59'56" E 32°04'48" |
| 16 | Mtunzini Inlet | Mouth of the lagoon 50 km outside Richards Bay | S 28°57'18" E 31°46'30" |
| 17 | Mtunzini Lagoon | 50 km outside Richards Bay | S 28°57'00" E 31°46'30" |

Sites 16 and 17 were used as the background sites. All sediment samples were taken at a depth of approximately 50 cm.

From comparison of the F statistics, ANOVA calculations revealed that there was no significant difference in the levels of boron, iron, sodium, zinc, potassium and chromium between sites.

The graphs further demonstrated that the saltwater sediments showed little evidence of contamination. For all the sites the levels of virtually all the elements overlap with the background levels. Chromium is the only element that seems to contaminate both sites 12 and 13. Site 13 also has elevated levels of calcium and vanadium. Figure 6.6 provides an example of the graphs obtained, while the remainder of the graphs are presented in Appendix 3.2.3

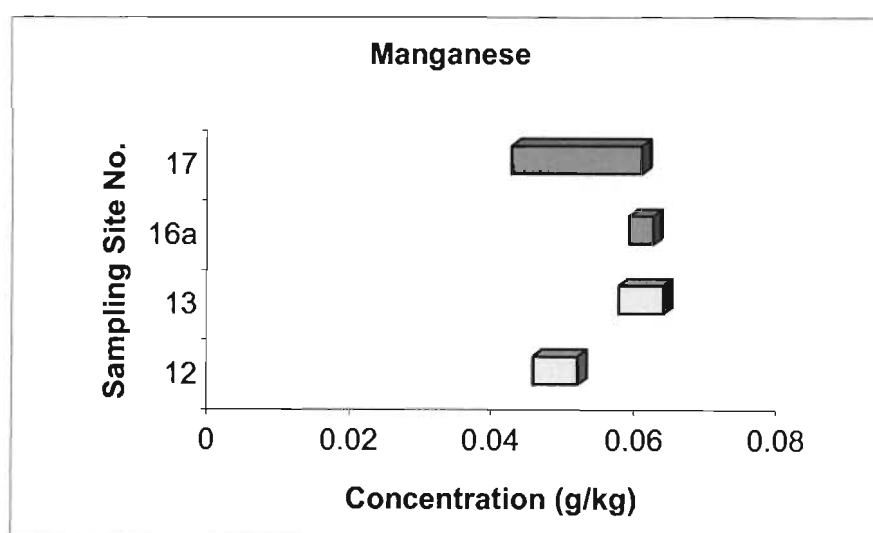


Figure 6.6: Example of a bar graph for manganese in saltwater sediments

6.3 Soil Results

Soil samples were taken from 9 sampling sites, including one background site. Descriptions of the sampling sites can be seen in Table 6.8. Site 15 was used as the background site as it has the same soil type as the other sampling sites and is from a relatively unpolluted area.

Table 6.8: Description of the soil sampling sites

| | Site | Site Name | Description | GPS Position |
|----|------|----------------|---|----------------------------|
| 1 | | Roadside 1 | Roadside between Hillside and Bayside on Hillside side of the rd. | S 28°46'43" E 32°01'14" |
| 2 | | Roadside 2 | Roadside between Hillside and Bayside on Bayside side of the rd. | S 28°46'43" E 32°01'16" |
| 3 | | Roadside 3 | Roadside between Foskor and Bayside on Bayside side of the rd. | S 28°46'27" E 32°02'24" |
| 4 | | Roadside 4 | Roadside between Foskor and Hillside on both sides of the rd. | S 28°46'03" E 32°02'11" |
| 5 | | Harbour inlet | Off the Coal Terminal Rd alongside the railway line | S 28°49'49" E 32°02'24" |
| 6 | | Mhlatuze River | Off the Coal Terminal Rd, under a bridge, 100m from mouth | S 28°48'00" E 32°01'08" |
| 7 | | Lake Mzingazi | Edge of the lake alongside the Country Club | S 28°46'12" E 32°06'04" |
| 10 | | Pond 1 | Groundwater pond btw Hillside and Bayside next to railway line | S 28°48'07" E 32°00'50" |
| 15 | | Mhlatuze River | 10km outside of Richards Bay | S 28°48'00" E 31°57'40" |

From the graphs it can be concluded that the soils remain generally uncontaminated. From the graphs, none of the sites are contaminated with copper, titanium, aluminium, nickel, barium, manganese, iron, sodium, zinc and potassium. The contamination of the sites by the other elements does not seem to follow any trend, some areas are contaminated by certain elements while other sites demonstrate elevated levels of other elements, i.e. no one site is consistently contaminated by a range of elements. For example, site 5 has fairly elevated levels of chromium, vanadium and boron, but undetectable amounts of cadmium, cobalt and lead. Sites 1 and 2 have higher levels of zirconium, vanadium, phosphorus, cadmium, cobalt and lead and appear to be the most contaminated sites. Sites 7 and 10 remain largely uncontaminated. Figure 6.7 is an example of the graphs obtained for the soil samples. The remainder of the graphs are presented in Appendix 3.3.

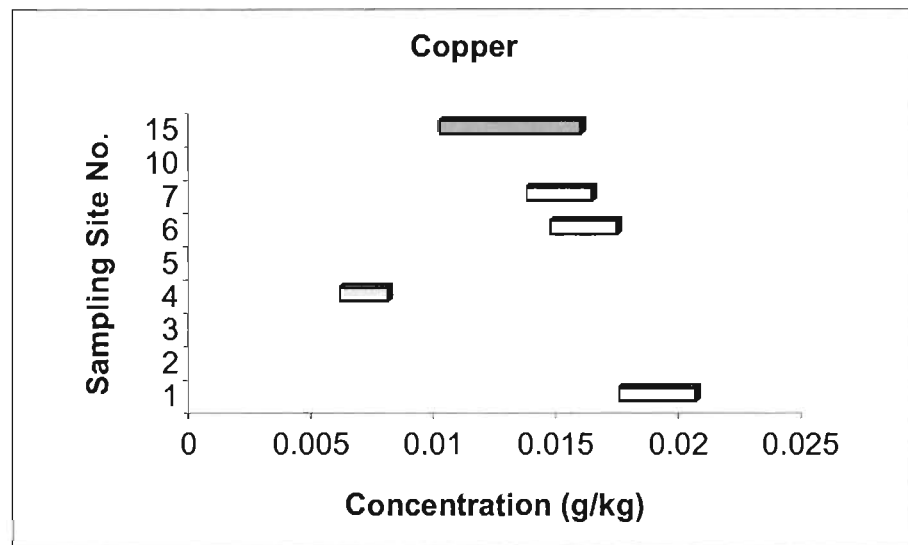


Figure 6.7: Example of a bar graph for copper in soils

CHAPTER 7

Discussion

Ideally, the results obtained from this study should be compared with results obtained from similar studies done in the same area in the past. This is not entirely possible, as similar studies have not been done in this area since the 1970's. A series of reports were published by the CSIR in the 1970's and it is only these reports that provide any means for the comparison of contamination levels. However, these reports are far from comprehensive, making contextualisation a difficult task.

In 1976, a research team from the CSIR conducted an estuarine survey on the Richards Bay harbour and sanctuary.¹⁹ This study was undertaken due to the extensive changes that were being planned for the harbour area. The main focus of this study was the collection and classification of the benthic fauna and zooplankton found in the harbour waters. Only a few chemical analyses were done on the water and sediments of the harbour area. These samples were analysed for chlorinated pesticide and trace metal residues. With regards to the trace metal analysis, samples of the water, sediments and various marine organisms were taken and analysed for mercury, copper, lead, zinc, iron, chromium, cobalt and nickel.

In the CSIR study results were obtained for ten sampling stations within the harbour area. The exact locations of these sampling sites are given, but no record is made of the nature of the samples or the number of samples taken from each site. In addition, there is no record of the analytical techniques used for either the water or soil analysis and it is therefore difficult to assess the limits of detection. Also adding to the problem of contextualisation is the lack of standard deviations in the recording of the results. Overall, the report provides rather a weak set of data making comparison difficult. However, if the results are directly compared with the levels of harbour contamination found in this present study, the 1976 trace metal levels in both the water and sediment samples are considerably lower. This is expected due to the very different stages in the harbour development between 1976 and 2002.

The CSIR followed up on this study in 1981²⁰ after the industrial and municipal development in the Richards Bay area had been continuing at a steady rate since 1976. This survey included the same analyses of samples from the same stations as the 1976 study. Once again no mention is made of the sampling or analytical techniques and the associated detection limits. The results are recorded without the number of samples analysed and without standard deviations for the analysis making comparison of results difficult. The 1981 report concluded that there was no indication of a marked increase in the pollution levels in the Richards Bay harbour and sanctuary since 1976.

Another survey was undertaken between June 1981 and June 1982 in connection with a proposed offshore pipeline.²² The proposal to build an offshore pipeline to dispose of industrial and municipal wastes in Richards Bay prompted the need for a detailed baseline study against which any future changes could be judged. The exact sampling locations were given in the report and the samples were analysed for trace metals and chlorinated hydrocarbons. Yet again no detail is given with regards to the number of samples taken, the analytical methods employed and the standard deviation of the results. The report concluded that the results for both the water and sediment samples were generally low and consistent with normal background levels for KwaZulu-Natal.

It can therefore be seen that contextualisation for this study remains a problem. Not only were these studies conducted more than twenty years ago, but also the reports are missing important information and therefore provide data which cannot be directly compared with data from the current study. Thus, the results from this study cannot be viewed against results obtained from similar studies performed in the same area and an alternative means of comparison and contextualisation must be found. This contextualisation can be accomplished by the comparison of the levels obtained within the study area with levels obtained from a background area, which is geographically similar but remains relatively unpolluted.

Two background sites were chosen for this comparison and water, sediment and soil samples were taken from both sites. The first site chosen was about 10 kilometres outside of Richards Bay and consisted of the Mhlatuze River and associated sediments and soils. This site was chosen as it is the same river that passes directly through Richards Bay, but at a point upstream (and upwind) from any pollution point sources. It is also possible at this site to compare the sediment and soil samples as they have the same soil profile that exists in the

Richards Bay area. This means that they will have the same trace metal background levels and any increases in concentration found can be attributed to anthropogenic sources.

The other site used to obtain background levels was the Mtunzini area. Mtunzini is a small coastal town about 50 kilometres from Richards Bay with a small population and no industrial development. It was chosen as a background site due to the absence of any obvious pollution point sources and its geographical similarity to Richards Bay. It has a natural lagoon, skirted by a mangrove area and the Mtunzini River emptying into it. Water, soil and sediment samples were taken from the lagoon and the river, but it is the water samples and those sediment samples taken from the mangrove areas that are of particular interest. The water samples can be used to obtain good background concentrations due to the relatively pristine condition of the sampling area. The sediments from the mangrove area can be used in comparison with mangrove sediments obtained from Richards Bay. The mangrove areas in Richards Bay are of particular interest as they may form a sink for trace metal contamination due to their high adsorption and desorption capacities. Comparison of soil samples taken from this background site is not, however, ideal as the soils in this area have a different soil profile to those found in the Richards Bay area. This means that background trace metal levels could be vastly different and comparison of these levels could lead to false conclusions being drawn about the levels of contamination.

Statistical analysis of trace metal concentrations of samples taken from the study area and from the background area can provide an indication of the level of trace metal contamination in the study area. Due to the lack of previous studies no conclusions can be drawn as to the rate of contamination in response to the industrial development of the area and consequently the results of this study may have to form baseline levels against which the extent of future pollution can be assessed.

The pollutants of interest in this study were identified in Chapter 2 as sulfur dioxide, and other acidic gaseous emissions, fluorine and trace metals. Each of the heavy industries identified as pollution point sources in this area is responsible for releasing all of these contaminants into the environment. The aim of this study was to determine if there had been an accumulation of these contaminants in the reservoirs of Richards Bay.

As mentioned previously sulfur and nitrogen oxides are released into the environment by all the heavy industries in the area. As extensive atmospheric monitoring was not part of this study, the accumulation of these gaseous emissions in the various reservoirs is judged by the changes in the pH of the reservoirs. The pH results obtained illustrate that as far as the waters and sediments are concerned there is no measurable increased acidity and therefore no local effect of these emissions. This lack of local contamination may be due to the relatively slow deposition velocities of these gases. For example, depending upon the amount of moisture in the atmosphere, 20 – 80% of the sulfur dioxide emitted into the air is oxidized to sulfate whilst the remainder is removed by dry deposition. Sulfate has a dry depositional velocity of 873.55 kg/km²/yr and a wet deposition velocity of 1182.2 kg/km²/yr³⁷ and as such most of it is removed by wet deposition.³⁹ The sulfur dioxide and sulfate mixture has an average lifetime of two to six days in the atmosphere during which time it may travel up to 4 000 km from its source.³⁹ With the prevailing wind conditions in Richards Bay the gaseous emissions would be taken out to sea and therefore not contaminate the local environment.

This pH monitoring gives an idea of the long-term contamination of the reservoirs. Short-term contaminations cannot be monitored in this way, but do frequently occur. The gas leak experienced by Foskor in July 2002 ^{17,18, 94} for example, would certainly have led to short-term acidification of the local environment. The gas leak was actually a regular emission of SO₂ and SO₃, which instead of being blown away by the wind as usual, descended to the ground. The effects of this are no longer obvious, but would have been had pH levels been monitored immediately before and after the emission.

Another reason for the lack of local acidification of the environment may also be the buffering capacity of the surrounding waters and sediments. If the contamination has not gone beyond the natural buffering capacity of the reservoirs there would be no obvious acidification of the local environment. The natural buffering capacity means that the reservoirs can maintain a reasonably constant pH even when relatively large amounts of acid are added. The buffering capacity of the water bodies can be estimated by the alkalinity of the water, which is defined as the capacity of natural water to neutralise acid. In this study alkalinity titrations were performed on samples from some of the freshwater sampling sites and it can be seen that the majority of the sites have high alkalinities, ranging from 108 to 124 mg CaCO₃/l, and therefore relatively large buffering capacities. Lake Mzingazi, and its outlet the Mzingazi River, have low alkalinities (38 and 48 mg CaCO₃/l respectively) and are

therefore not buffered to the same extent. This is often the case with freshwater lakes and means that their pH's may change rapidly with the addition of acid.³⁹ However, the size of, and large volume of water in, the lake may delay this acidification. Therefore it can be seen that the natural buffering capacities of the reservoirs may also account for the lack of local, long term acidification. The problem with this is that these reservoirs cannot act as buffers indefinitely and eventually there will be a marked change in pH when the buffering capacity is exhausted and acidic inputs into the reservoirs continues.

The only samples that demonstrated any increased acidity were those taken from the roadsides directly outside the industries. The pH of these samples ranged between 5.08 and 5.72 and there is therefore acidification when compared with the other surrounding soils, which have an average pH of 7.38. The pH of most mineral soils is between 5.5 and 7.5.¹ This acidification may be due to the heavy road traffic along these roads as well as atmospheric deposition from the industries. The atmospheric depositions would still contaminate these areas despite their high residence times as this is where the concentrations of the atmospheric pollutants will be at their highest. The contamination of soils within the industrial sites due to solid or liquid effluents produced, stored or dumped on site may also contribute to the acidification of the soils directly outside these sites.

Another main inorganic pollutant identified in the initial chapters is fluorine. Indian Ocean Fertilisers and the Alusaf smelters release large amounts of fluoride into the atmosphere. In this study, water samples from the various reservoirs were analysed for fluoride, but it was never present in detectable amounts. This may be due to the fact that the fluoride ion-selective electrode is not particularly sensitive with a detection limit of 1 ppm. However, the fact that water is not an obvious sink for fluoride contamination may also explain the low levels present. It is in fact plants that are particularly susceptible to the gaseous effects of fluorides.⁶¹ Fluorides from the atmosphere appear to enter the leaf tissue through the stomata, where it acts as a cumulative poison.

When looking at trace metal contamination, it is necessary to examine each of the sample types separately, i.e. water, sediment and soil contamination should be assessed individually. The water and sediment samples were further divided into fresh and saltwater sub-categories.

The water samples, both fresh- and saltwater, indicated that there was in fact trace metal contamination of some of the water bodies within the Richards Bay area. The freshwater statistics may, however, be slightly misleading as they involve the comparison of lakes, rivers and ponds. It is difficult to combine and compare these different water reservoirs as they may not have the same water quality naturally regardless of any anthropogenic influences. The statistics do, however give a general idea of the relative degree of contamination of the water bodies.

The results from the freshwater trace metal determination revealed that there was contamination at all the freshwater sampling sites by all the elements that were analysed for (viz. Cu, Mn, Fe, Zn and Pb). As discussed in Chapter 6, these elements showed a consistent trend with regards to the levels at the various sampling sites, i.e. sites 6, 9 and 10 were consistently the most polluted, sites 11 and 14 had levels only marginally above those reported for the background, while the levels for site 7 consistently overlapped with the background levels. Lead was only found to be detectable at site 6. Sites 6 and 9 were sites on the Mhlathuze River downstream of the large industries and site 10 is a pond situated in the midst of the industries. The contamination of these sites is not surprising as they are all in close proximity to the large industries and may be polluted by deposition or directly by aqueous effluents. The deposition velocities of particulates are much greater than those of the gases such as SO₂ and as such the contaminants may be deposited close to their sources. The pond, in particular, is most likely to accumulate contaminants as it is not very big and has no outlet. Site 7, Lake Mzingazi, remains relatively uncontaminated. Lake Mzingazi, of course, does have an outlet, the Mzingazi River.

The fact that some of the freshwater bodies in the area are contaminated has been established, but it is necessary to determine if these levels are elevated to such an extent that they may become hazardous. This can be done by comparing the levels with water quality criteria for heavy metals established by the EPA. These criteria are established with reference to the effect of the aquatic life and are defined in terms of criteria maximum concentrations (CMC) and criterion continuous concentration (CCC). The CMC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect. The CCC is an estimate of the highest concentration of a material in surface water to which aquatic life can be exposed indefinitely

without resulting in an unacceptable effect.⁹⁵ Table 7.1 lists these EPA criteria as well as the highest levels detected in this study.

Table 7.1: Water quality criteria and levels detected for freshwater

| Element | EPA Quality Criteria ⁹⁵ (mg/l) | | Current Study (mg/l) |
|-----------|--|-------|-------------------------|
| | CMC | CCC | Max. Conc. |
| Copper | 0.013 | 0.009 | 0.008 |
| Manganese | 0.100 | 0.050 | 0.006 |
| Iron | - | - | 1.6 |
| Zinc | 0.120 | 0.120 | 0.032 |
| Lead | 0.065 | - | 0.032 |

Table 7.1 illustrates that the levels obtained from the most contaminated sites in this study are still generally below the water quality guidelines established by the EPA. However, the levels of freshwater copper, especially, and lead are becoming dangerously close to those guidelines.

The results from the saltwater analysis demonstrated that there is little or no contamination of the saltwater sites. Copper and zinc levels for all the sites overlap with the background levels, manganese shows only a slight elevation (0.0004 – 0.0006 mg/l) from the background site and lead is largely undetectable. The saltwater sampling sites consisted of two harbour inlets and the Mzingazi Canal which branches off from the harbour. This means that these water bodies are tidal and directly linked to the ocean. This means that any contaminants initially deposited in the water of these reservoirs would not remain in them for a long period of time. This movement of contaminants between reservoirs, and low residence times, may explain the lack of contamination of the three saltwater sites investigated. The EPA quality criteria and the maximum concentrations found at the three saltwater sampling sites can be seen in Table 7.2.

Table 7.2: Water quality criteria and levels detected for saltwater

| Element | EPA Quality Criteria ⁹⁵ (mg/l) | | Current Study (mg/l) |
|-----------|--|-------|-------------------------|
| | CMC | CCC | Max. Conc. |
| Copper | 0.005 | 0.003 | 0.007 |
| Manganese | 0.100 | 0.050 | 0.002 |
| Iron | - | - | 0.584 |
| Zinc | 0.090 | 0.081 | 0.016 |
| Lead | 0.210 | - | 0.019 |

From the table it can be seen that the levels obtained in this study are below the quality criteria with the exception of copper. The copper level is over the guideline but, as can be seen by the statistical analysis of the saltwater levels in Chapter 6, still overlaps with the area background of copper and is therefore is not of serious concern.

The sediment samples were split into three groups; mangrove muds, freshwater sediments and saltwater sediments. As previously mentioned the samples from the mangrove areas must be treated independently as the mud has very different physical properties from the other sediments. The mangrove mud samples taken within the Richards Bay area were from the harbour inlet (site 5). Due to the fact that there was only one sampling site it was possible to compare it directly with the background and it was discovered that the muds at site 5 were contaminated with a host of metals. The mangrove muds within the industrial area are predictably contaminated due to the high percentage of clay in the muds. The increased clay content in the mud means that trace metals are readily, and strongly adsorbed, and the mangrove areas thereby become a sink for trace metal contamination. The contaminating metals previously established as the metals of concern are chromium, cadmium, manganese, aluminium and copper. These maximum concentrations of these metals were compared with the EPA sediment quality guidelines. These guidelines are defined in terms of sediment quality guidelines (SQG) and probable effect levels (PEL). The SQG's are an estimate of general sediment quality while the PEL's reflect levels where the elements may become hazardous to aquatic life. A comparison of these guidelines and the maximum concentrations obtained in this study can be seen in Table 7.3.

Table 7.3: Sediment quality criteria and levels detected for saltwater sediments

| Element | EPA Quality Criteria (g/kg) | | Current Study (g/kg) |
|-----------|--------------------------------|-------|-------------------------|
| | SQG | PEL | Max. Conc. |
| Chromium | 0.05 | 0.16 | 0.16 |
| Cadmium | 0.001 | 0.004 | 0.009 |
| Manganese | - | - | 0.6 |
| Aluminium | - | - | 27.0 |
| Copper | 0.019 | 0.108 | 0.040 |

For the elements where sediment quality guidelines are available, the levels detected in the mangrove muds are always higher than the SQG and sometimes even greater than the PEL. This means that chromium, cadmium and cobalt are present at levels of concern within the mangrove muds. However, this comparison may be misleading as these guidelines do not stipulate the nature of the sediments. As previously discussed the mangrove muds have a higher clay content than most sediments and therefore may accumulate contaminants. Furthermore, these elevated levels may not be of huge concern as, due to the physical nature of the muds, these metals are strongly absorbed and therefore are not easily bioavailable. The bioavailability is also decreased by the pH of the surrounding environment. Neither the waters nor the sediments at site 5 are acidified and therefore leaching of the metals should not be a problem at present.

The sandy sediment samples were divided into fresh- and saltwater samples. As discussed in chapter 6 the freshwater sediments demonstrated a degree of contamination at certain sites from a range of metals. The metals of concern that were present at elevated levels are copper, manganese, chromium, vanadium and zinc. The contamination followed a trend in that sites 9, 10 and 11 were consistently the most contaminated while for the most part sites 6 and 7 remained largely uncontaminated. Sites 9, 10 and 11 are the two groundwater ponds and the Mhlathuze River where it runs alongside these ponds respectively. These groundwater ponds naturally become a sink for contamination as they are stagnant and are in close proximity to the industries. Site 6 is the Mhlathuze River as it flows into the harbour and site 7 is Lake Mzingazi. As with the mangrove sediments, these freshwater sediments can be compared with sediment quality guidelines to ascertain if the metals are present at levels of concern.

Table 7.4 compares the maximum levels obtained from the freshwater sediments in this study with the EPA quality criteria.

Table 7.4: Sediment quality criteria and levels detected for freshwater sediments

| Element | EPA Quality Criteria ⁹⁵ (g/kg) | | Current Study (g/kg) |
|-----------|--|-------|-------------------------|
| | SQG | PEL | Max. Conc. |
| Chromium | 0.04 | 0.09 | 0.05 |
| Manganese | - | - | 0.13 |
| Copper | 0.036 | 0.197 | 0.06 |
| Zinc | 0.123 | 0.315 | 0.07 |
| Vanadium | - | - | 0.018 |

None of the metals are present at greater concentrations than the probable effects level and as such there should be no detrimental effects from these metals despite the fact that they are elevated with respect to the background levels.

When analysed the sediments from the saltwater sampling sites showed little evidence of contamination. Chromium was the only element that was found at elevated concentrations when compared with the background levels. As discussed for the saltwater samples, the sites involved here are tidal and directly linked to the ocean. Consequently, there is a lot of movement within the saltwater sediment reservoir and contaminants may not remain in the same reservoir for long. This increase in flux and decrease in residence time may explain how the saltwater sediments remain largely uncontaminated. The sediments are also sandy in nature and will not therefore have a great tendency to adsorb metals.

Like the saltwater sediments, the soils within the Richards Bay area appear to remain relatively uncontaminated. Elevated levels of some elements at some sites were recorded, but no site appears generally contaminated and none particularly pristine. Chromium, cadmium, cobalt and lead were found to be present at slightly elevated levels at some of the sites and as such the maximum concentrations were compared with quality guidelines. The quality criteria stipulate that it is soil from an industrial area.

Table 7.5: Soil quality criteria and levels detected for Richards Bay soils

| | QC ⁹⁶ | Current Study |
|----------|------------------|---------------|
| Element | g/kg | g/kg |
| Chromium | 0.087 | 0.021 |
| Cadmium | 0.022 | 0.015 |
| Cobalt | 0.300 | 0.019 |
| Lead | 0.600 | 0.024 |

Even the elevated levels found in the soil samples remain below the soil quality criteria and the soils remain relatively unpolluted. The elevated levels of these metals occurred mainly at the roadside sampling sites and this contamination can therefore be largely attributed to the heavy traffic through the area. The fact that there is not more severe contamination of lead and cadmium at these roadside sites is interesting. Many studies conducted throughout the world,^{37,40, 41, 80, 97} have indicated that roadside soils show marked accumulation of lead and cadmium. The general lack of accumulation of contaminants in the soils is probably due to the physical nature of the soils to be found in the Richards Bay area. The surrounding soils are sandy and have a low clay content. These soil properties mean that trace metals will not be readily and strongly adsorbed onto the soil. The lack of cadmium and lead contamination from the traffic is a sure sign of the non-adsorptive properties of the local soils.

Thus, it can be seen that the freshwater and mangrove sites are contaminated while the saltwater site and soil samples remain largely uncontaminated. These relative contaminations have previously been explained with reference to the physical properties of the sampling sites themselves and the nature of the samples taken from them, i.e. the stagnant nature of the freshwater ponds compared with the tidal waters of the harbour inlet and the high clay content of the mangrove muds compared with the sandy saltwater sediments. Similar studies on trace metal contamination have offered other such explanations. For example, Forstner *et al.*⁹⁸ studied heavy metal accumulation in water sediments and discovered that freshwater sediments were considerably more contaminated than saltwater sediments despite similar locations with reference to pollution point sources. In particular, copper, chromium and zinc concentrations demonstrated a distinct decrease under marine influences. This is seen to be the case in this study and the same effect has also been observed by de Groot *et al.*⁹⁹ These studies have offered two possible explanations for these observations. One explanation

assumed that the depletion occurred in a state where the future sediment particles were still in suspension, while the other accounted for the depletion by the partial desorption of heavy metals by competing cations, especially sodium, from seawater.

Clay content is the only physical property of the solid samples that has been used to explain their relative contamination in this study. Another physical property that has been investigated in detail by other studies is particle size. Park and Presley⁵¹ and Murray *et al.*¹⁰⁰ linked particle size to trace metal contamination and concluded that trace metal concentrations generally increase with decreasing particle size. Although particle size was not investigated in this study, the conclusions drawn by Park and Murray can be loosely confirmed. The samples from the mangrove area were seen to be very finely grained, while the sediments from the saltwater sampling sites were sandy with a relatively large grain size.

Therefore, for a number of varying reasons the water and sediments from the freshwater sampling sites appear to demonstrate trace metal contamination by the growth of the heavy inorganic industry over the last 25 years. However, when compared with quality guidelines for both water and sediments the metals do not seem to be present at dangerous levels as yet. It cannot be estimated in any detail for how long these contaminants will stay below the level at which they will start demonstrating adverse environmental effects. How soon the levels will be considered problematic can be roughly estimated by assuming a linear extrapolation of pollution from this point on. This assumption is far from ideal as it does not take factors like pH and buffer capacity into account and assumes a constant flux in and out of each reservoir. It can, however, give a general idea of the timescale upon which pollution levels might become problematic. Due to the fact that no comprehensive studies have been conducted in this area, there are no levels with which we may compare the present day levels. Consequently, a less than satisfactory two-point plot makes up the linear forecast. The levels obtained from the background areas are assumed to represent the uncontaminated concentrations of 25 years ago, and the present day results indicate the increase in contamination levels 25 years on. Figure 7.1 is an example of such a linear forecast.

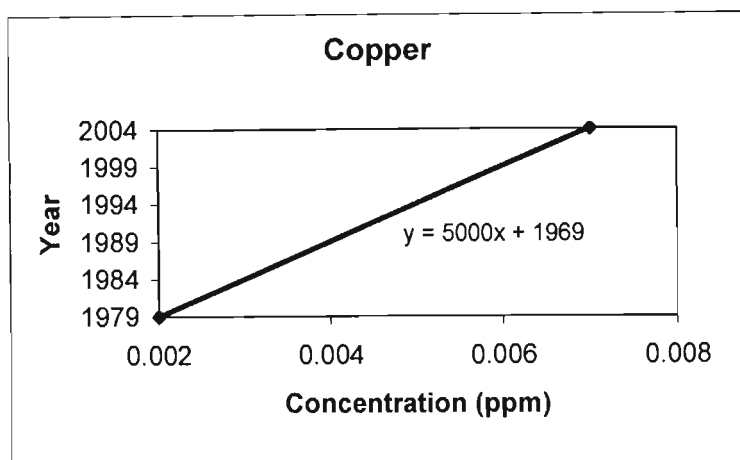


Figure 7.1: Prediction of future copper concentrations in freshwater

Over the last 25 years, from 1979 to 2004, the copper concentrations have increased from the background levels of 0.002 mg/l to today's level of 0.007 mg/l. If this rate of pollution continues in 25 years in 2029, the levels of copper in the water will be above the quality control guideline of 0.013 mg/l. It should be reinforced that this is a two-point straight line and therefore the figure should not be over-analysed.

A similar timescale can be predicted for the contamination of the sediments. Chromium levels in freshwater sediment, for example, are currently below the probable effects level of 0.09 mg/l. By employing a similar linear forecast it can be seen that by the year 2044 the chromium levels will be above the probable effects levels.

As previously mentioned these linear forecasts are not a true reflection of the situation in the environment, but they serve to demonstrate the fact that although the contaminants are not yet present at hazardous levels, this is not going to be the case indefinitely. At present, heavy metals present in the sediments present no direct danger as long as they are tightly bound to the sediment. The potential danger, however, lies in the possibility that, under certain circumstances, e.g. changes in pH and the redox potential of the sediments, dissolution or desorption might lead to a release of the metals into the water. This leaching of the metals into the water may detrimentally affect the aquatic life.

It has been discussed that by changing various parameters such as pH and the redox potential of the surrounding environment, the contaminants may become more bioavailable. Many other factors, however affect this bioavailability and even what effect the contaminants will

have if, in fact, they do become available. Luoma¹⁰¹ suggests that the biological impacts of trace metal contamination are poorly understood due to the fact that the bioavailability of metals in sediments appears to be altered by variations in sediment geochemistry. Luoma discovered through extensive analysis of sediment, water and biotic tissues that bioaccumulation in plants and animals may vary considerably from one environment to another, independent of the concentration in the sediments or water. Luoma further suggested that no methods exist yet that can convincingly approximate the availability of sediment-bound metals as they occur in nature.

A step toward assessing the bioavailability of these metals, however, may be to determine the chemical forms in which the contaminants exist. As long as very little is known about the different states of bonding of metals on a sediment (adsorbed, complexed, organically or inorganically bonded etc.), it is difficult to predict the behaviour of a certain heavy metal under changed conditions.⁹⁸ The chemical forms of elements greatly differ in their transfer ability and bioavailability in the ecosystem. For example, dissolved or weakly adsorbed metals may be easily available to plants and aquatic organisms, while metals bound in the crystalline structural lattice of primary and secondary minerals are not available to biota, unless the minerals undergo geochemical weathering.¹⁰² During the last decade the major objective of research on metal-polluted waters have changed from the initial surveys of sources and pathways to more detailed investigations of the mechanisms controlling the mobility and bioavailability of particular metal species.¹⁰⁰ Unfortunately, many studies rely on total metal concentration. The use of total metal concentration as a criterion to assess the effects of sediment contamination on aquatic biota implies that all forms of a given metal have an equal impact on the ecosystem. Such an assumption is suspect.

This study indicates that there is trace metal contamination of certain reservoirs within the Richards Bay area, but these conclusions are based on total metal concentrations. No investigations were done on the form and speciation of the contaminants and as such we have no idea of their bioavailability.

As previously mentioned, the results of this study may not be directly compared with results obtained from similar studies in this area. They can, however, be compared with similar studies performed in other parts of the world. For example, Kopstik *et al.*⁴¹ conducted a study in Russia which centred around heavy metals in soils near a nickel smelter. This study

concluded that despite the high SO₂ emissions (150 000 tpa) there was no significant acidification of the topsoils surrounding the smelter and the average trace metal concentrations in soil samples were 0.756 g/kg Al, 0.179 g/kg Mg, 1.624 g/kg Fe, 0.062 g/kg Mn, 0.667 g/kg Ni, 1.030 g/kg Cu and 0.016 g/kg Zn. This study illustrated that the surrounding soils were contaminated only with nickel and copper. When compared with the results from our study, the lack of acidification was common to both studies and the trace metal concentrations were also within the same ranges, except for nickel and copper. The average soil concentrations obtained in this study were 2.72 g/kg Al, 0.115 g/kg Mg, 3.8 g/kg Fe, 0.038 g/kg Mn, 0.028 g/kg Ni, 0.014 g/kg Cu and 0.022 g/kg Zn.

A study by Bogner *et al.*¹⁰³ looked at trace metal contamination of sediments from a saltwater bay in Croatia. The coastal strip surrounding the bay was densely populated and industrially developed. The sediments from this bay demonstrated trace metal levels that were found to be primarily from natural origin with negligible anthropogenic influence. The levels of 0.020 g/kg Zn and 0.015 g/kg copper obtained are comparable with those found in the present study which were 0.036 g/kg Zn and 0.017 g/kg Cu. The lack of general contamination of the saltwater sediments was common to both studies.

Similar studies have also been conducted on freshwater sediments. Grosser *et al.*⁴³ analysed heavy metals in stream sediments near a gold mining area in Columbia, South America. This study found Zn, Cd, Ni and Cr levels to be twice the background levels, but below the threshold levels. The levels found by Grosser were 0.083 g/kg Cr, 0.043 g/kg Ni, 0.046 g/kg Zn and 0.015 g/kg Cd. These results are similar to those found in the present study where levels in the freshwater sediments were above the background levels, but below the threshold values. The concentrations determined in the present study were 0.010 g/kg Ni, 0.014 g/kg Zn, 0.002 g/kg Cd and 0.067 g/kg Cr, which are all below the concentrations determined by Grosser, but roughly of the same order of magnitude.

Devaulter⁴⁴ studied freshwater sediments contaminated by trace metals. He focused on the impact of mining and refining on the distribution and accumulation of heavy metals in the sediments of a lake in Russia. The levels in the lake were found to be one and a half times greater than levels from similar lakes. The study, therefore, concluded that sixty years of mining and smelting had led to local contamination of the area. The concentrations in the lake were determined to be 0.09 g/kg Ni, 0.067 g/kg Cu, 0.024g/kg Co, 0.135 g/kg Zn and

0.013 g/kg Pb, which are comparable with the freshwater sediment levels obtained in our study. Dauvalter also looked at water samples from the lake and found levels of 0.005 mg/l Cu, 0.005 mg/l Zn, 0.0003 – 0.0008 mg/l Co, Cd and Pb, which were greater than background levels. The present study also found elevated levels in the freshwaters at concentrations of 0.006 mg/l Cu, 0.010 mg/l Zn, but undetectable levels of Co, Cd and Pb. All very similar to the results obtained by Dauvalter.

Finally, de Boer *et al.*⁴⁹ looked at trace metal contamination of harbour sediments in The Netherlands. The levels recorded were 0.003 g/kg Cd, 0.110 g/kg Cr, 0.129 g/kg Cu, 0.050 g/kg Ni, 0.292 g/kg Pb and 0.719 g/kg Zn. All these levels are elevated in comparison to the levels obtained in the present study; 0.009 g/kg Cd, 0.008 g/kg Cr, 0.017 g/kg Cu, 0.036 g/kg Zn, 0.020 g/kg Ni and 0.022 g/kg Pb. De Boer, however, concluded that the harbours were not contaminated with trace metals as there was little difference in the concentrations obtained between the harbour areas and the reference locations. This is also found to be the case for the Richards Bay harbour area.

The results from the studies discussed above cannot be directly compared with the results obtained from this study. Each area of study has a different degree of industrial growth, different types of industries, different reservoirs available for contamination, different background levels and a variety of other properties specific to that region. This means, for example, that the concentrations found in freshwater sediments in Russia are not directly comparable with the levels found in freshwater sediments in Richards Bay. The studies above, however, do give an indication as to whether similar conclusions are being drawn about trace metal contamination in different parts of the world. In the limited studies discussed here, it can be seen that the conclusions drawn do, in fact, concur with those that can be drawn from the study of the various reservoirs within Richards Bay. Studies of saltwater reservoirs and soils seem to point to a general lack of contamination, while freshwater reservoirs show varying degrees of contamination. This is seen to be the case in Richards Bay.

CHAPTER 8

Conclusions and Recommendations

Richards Bay was identified as an area that has undergone rapid industrial growth over the last 25 years, and has the potential for substantial future growth. The initial growth of the area was not accompanied by an environmental monitoring of the area. This project served to assess the current environmental situation of the area and provide background levels against which environmental impacts of further growth in the area can be assessed.

The major sources of pollution within the study area were identified as Mondi Pulp and Paper, Indian Ocean Fertilisers, Hillside and Bayside Aluminium and Richards Bay Minerals. The processes involved in these four large industries were discussed. Each of these industries has process specific potential pollutants and these pollutants were identified. Although, these industries release both organic and inorganic pollutants, this study was limited to the determination of inorganic pollutants. The inorganic pollutants that were common to most of these industries were inorganic gaseous emissions, such as SO₂, NO_x and fluoride, and trace metals. It was these contaminants that became the focus of this study.

After the pollution point sources and possible contaminants had been identified it was necessary to explore the reservoirs within the Richards Bay area in which the contaminants could be deposited and accumulate. The range of reservoirs within the study area included a freshwater lake, a harbour, a river and general surrounding soils. Water, sediment and soil samples were taken from within, and around, these reservoirs. Predominantly, sediment and soil samples were taken as it was these solid phase samples that were identified as possible sinks for trace metal contamination.

The effects of the atmospheric emissions from the point sources were identified through pH changes within the reservoirs. There was no evidence of acidification of the local environment. This is not to say that there were little or no acidic emissions, but rather that they had little or no effect on the local environment. The high residence times of the contaminants mean that, with the prevailing wind conditions in Richards Bay, they are carried over the ocean and presumably deposited there.

The high buffering capacity of the area may also account for the fact that there is no as yet any overall acidification of the surrounding area.

Cursory investigations were conducted into the fluoride levels found in water samples. None of the samples analysed demonstrated detectable amounts of fluoride being present.

Analysis for trace metal contamination revealed that the freshwater sampling sites showed elevated concentrations in comparison with background levels. The saltwater sampling sites, however, remained relatively uncontaminated. The soil samples taken from within the industrial area also remained relatively uncontaminated. Although the freshwater water and sediment sample demonstrated elevated levels, the metals are not present as levels of concern. This was concluded as the elemental levels remain below the quality criteria laid down by the Environmental Protection Agency.

Samples taken from the mangrove area within the Richards Bay harbour demonstrated the highest levels of trace metal contamination. This was most probably due to the high clay content and small grain size of the mangrove muds. The levels present in these samples were greater than the levels designated by the EPA as sediment quality guidelines.

Future work should perhaps involve more detailed investigations into the physical properties of the soil and sediment samples. For example, the sediments should be classified according to grain size and clay content. This would ensure that samples are compared with background samples with identical physical properties, thereby decreasing the chance of false conclusions being drawn.

The overall picture painted by this study is that, to date, there is no immediate danger presented by any of these inorganic contaminants. However, there is, a potential danger as elevated levels presently bound onto sediments may become available due to changes in environmental conditions such as pH and redox potential.

With regards to gaseous emissions, and the subsequent acidification of the local environment, future studies should involve more detailed atmospheric analysis. Although fairly difficult and expensive to do, atmospheric analyses would give a more accurate account of the local effect of emissions than simply monitoring pH changes. Measuring depositions of these

atmospheric pollutants would serve to confirm if they are indeed swept out over the ocean and deposited there or if they are deposited in the local environment, but their effects are masked by the buffering capacity of the local environment. These buffering capacities of the various reservoirs should also be investigated in more detail.

Future work should also involve greater focus on fluoride emissions. The release of fluoride into the environment remains one of the larger pollution problems for both Indian Ocean Fertilisers and the two Billiton smelters. Fluoride is known to accumulate in plants and has a cumulative toxic effect. Its presence in plants means that it can readily enter the food chain, thereby becoming a problem for many organisms, humans included. This study limited fluoride determination to water samples where it is not present at detectable levels. Further studies should involve the determination of fluoride levels in soils, plants and even organisms to determine the actual effects of the fluoride emissions from the industries.

It was trace metal analysis that was the main focus of this study. The analysis in this case involved measuring total metal concentrations in various samples. This analysis, while giving an idea of relative contamination, has its shortfalls as it gives no idea of bioavailability of the contaminants. This bioavailability determines if elevated levels of contaminants will actually have any adverse effects on the local environment. It is recommended that in future studies the form and speciation of the metal contaminants be determined and taken into account as it is these factors that determine the mobility and availability of the contaminant within the environment.

This identification of contaminant speciation within samples may prove to be difficult. An easier way to assess the bioavailability of the contaminants would be to extend the investigations into the biosphere. Future work should involve trace metal determination of plant and animal tissues. These samples will reflect whether the contaminants are actually moving into the biosphere with detrimental effect.

In conclusion, this study may be used as a reference for all future investigations into the environmental situation within Richards Bay. The levels measured here represent a baseline against which all future contamination may be measured.

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APPENDIX ONE

A-1.1 Example of a sampling form

Location: River

Date: 27-09

| Sample No. | Sampling Point | Time | Observations |
|------------|----------------|------|---|
| 1 | 2 | 7:30 | 1st bridge on Coal Terminal Rd (opposite Urania Rd) |
| 2 | | | 100m up river from the bridge and 3 m from vegetation |
| 4 | | | pH 7.30 |
| 13 | | | Conductivity 46.05 mS |
| 14 | | | Temp 21.8°C |
| 24* | | | * = Samples not nitrified with nitric acid |
| 22* | | | |
| SOILS | | | |
| 601 | | | Samples from waters edge (open area) |
| 602 | | | |
| 603 | | | |
| 604 | | | Samples from shallow waters |
| 605 | | | |

A-1.2 Reagents

1.2.1. Reagents used in the preparation of soil and sediment samples

1. Fluka Chemica Nitric Acid 65%, Catalogue No. 84378
2. Riedel-de Haën Hydrochloric Acid min 32% (Cat. No. 30720), Analytical Reagent
3. Associated Chemical Enterprises Hydrogen Peroxide 30% (100vols), AR
4. Modulab Continental Water Systems – Ultrapure water

1.2.2. Reagents used in the preparation of water samples

1. NaDDC - Aldrich *N,N*-diethyldithiocarbamic acid, sodium salt trihydrate 99+%, ACS Reagent (Catalogue No. 22,868-0)
2. APDC - Aldrich 1-pyrrolidinecarbodithioic acid, ammonium salt 97% (Catalogue No. 14,269-7)
3. Set Point Instruments chloroform, Chemically Pure Reagent, (Cat No. 307000)

1.2.3. Reagents used in the preparation of ICP-AES standards

1. Fluka Chemica Atomic Spectroscopy Standard Concentrates
2. Fluka Chemica Atomic Spectroscopy Standard Solution
3. Fluka Chemica ICP Standard Solution
4. Aldrich titanium AA/ICP Calibration Standard for Environmental Analysis

1.2.4. Reagents used pH determinations and alkalinity titrations

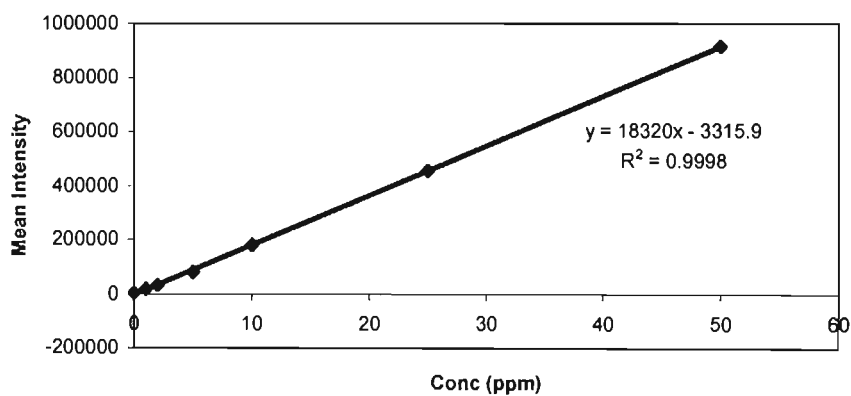
1. Merck Buffers, pH 4.00, 7.02 and 10.02
2. Merck Pro-Analysi sulfuric acid 95-97%

1.2.5. Reagents and electrodes used in the ISE analysis

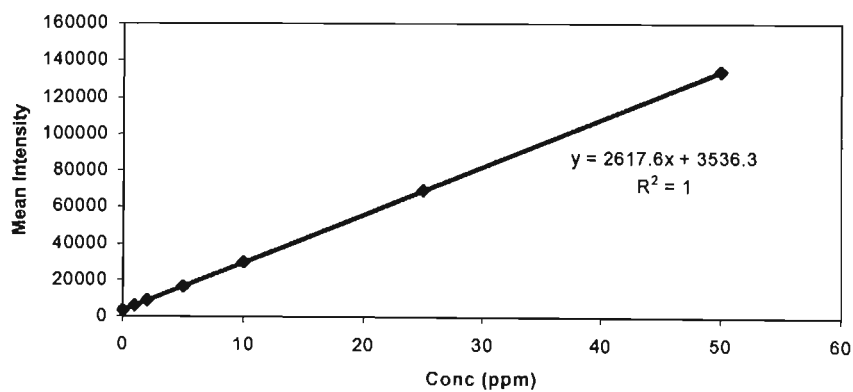
1. Jenway Nitrate Combination Ion Selective Electrode (924-300)
2. Jenway Fluoride Combination Ion Selective Electrode (924-305)
3. Jenway Chloride Combination Ion Selective Electrode (924-304)
4. Saarchem UnivAR sodium nitrate, Min 99%
5. Saarchem UniLAB sodium fluoride, Min 99%
6. Merck Chemically Pure sodium chloride, 99.5%

A-1.3 Calibration curves for the ICP-OES determination of trace elements in sediment and soil samples

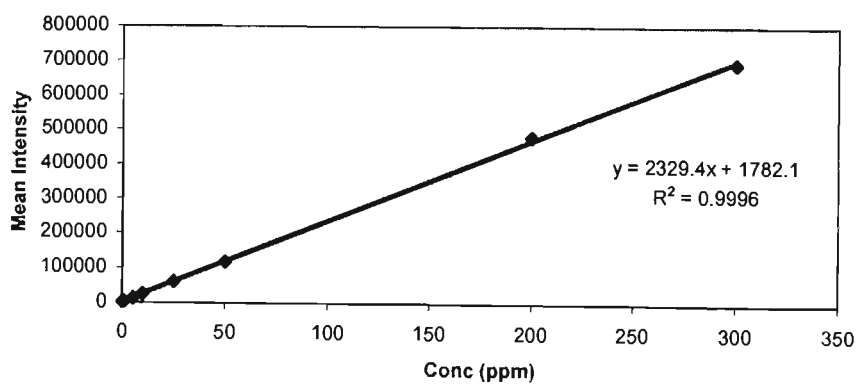
(1) Potassium



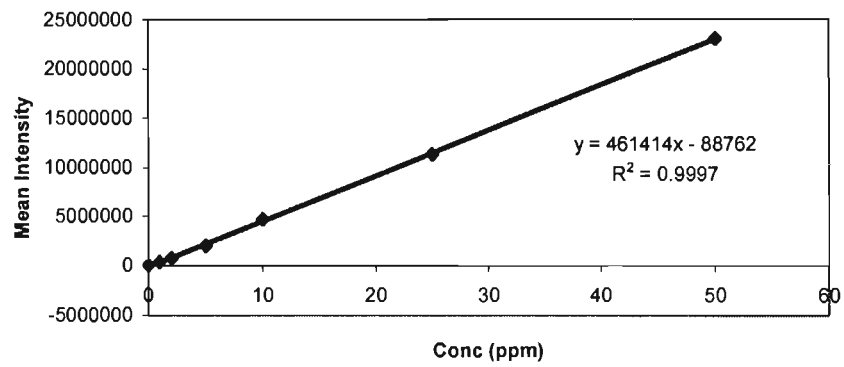
(2) Phosphorus



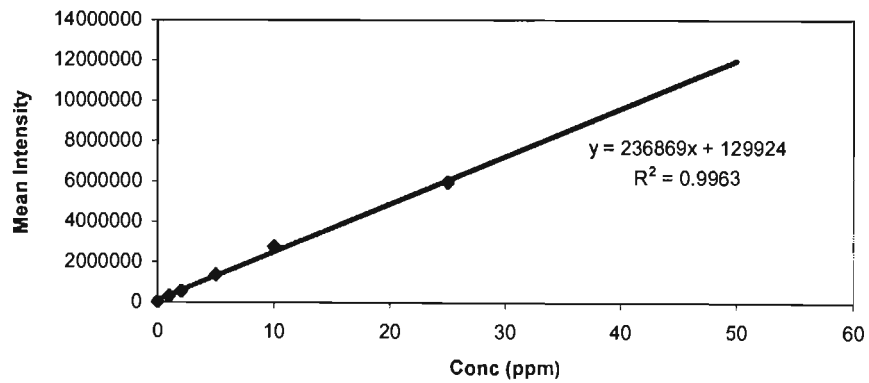
(3) Calcium



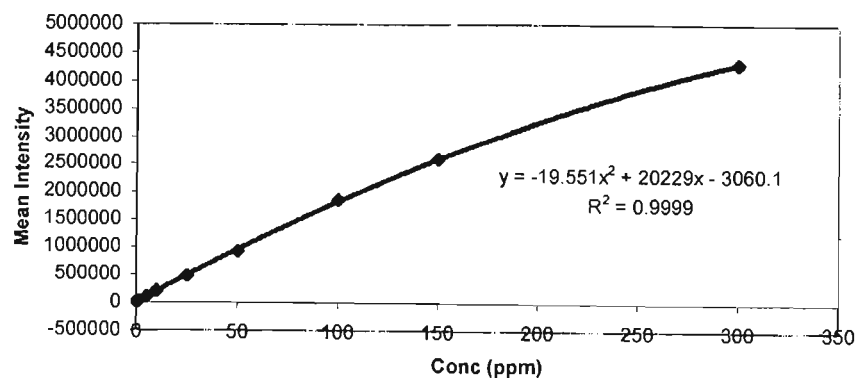
(4) Sodium



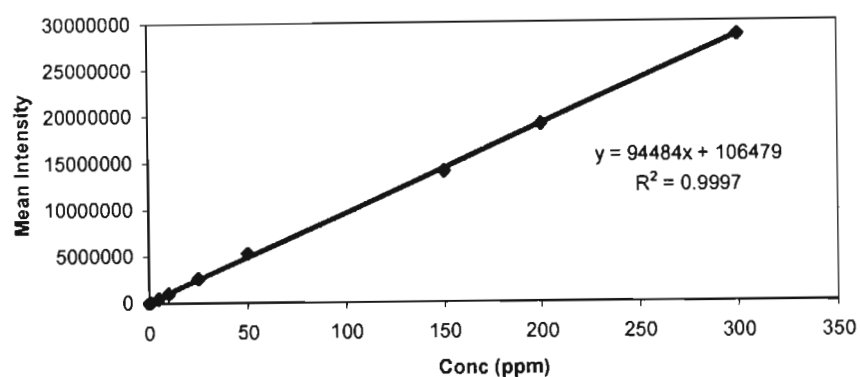
(5) Magnesium



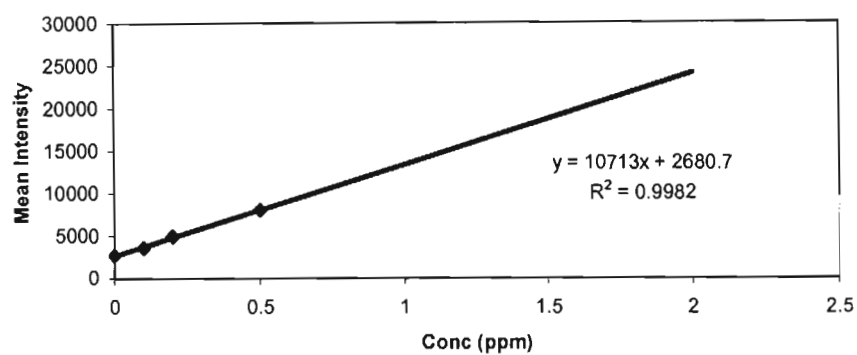
(6) Iron



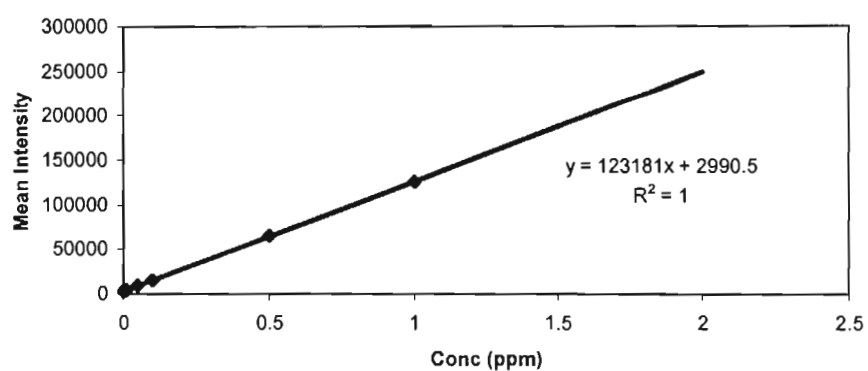
(7) Aluminium



(8) Lead

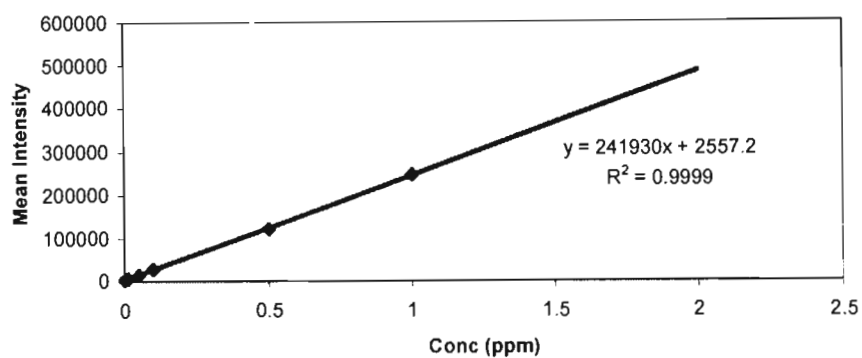


(9) Cobalt

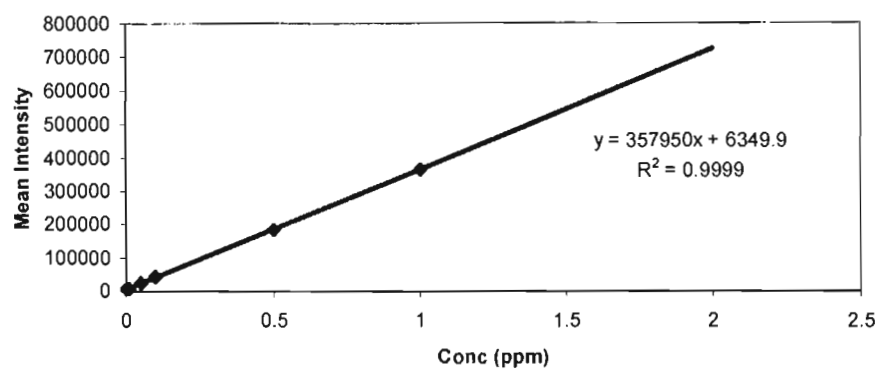


Appendix One

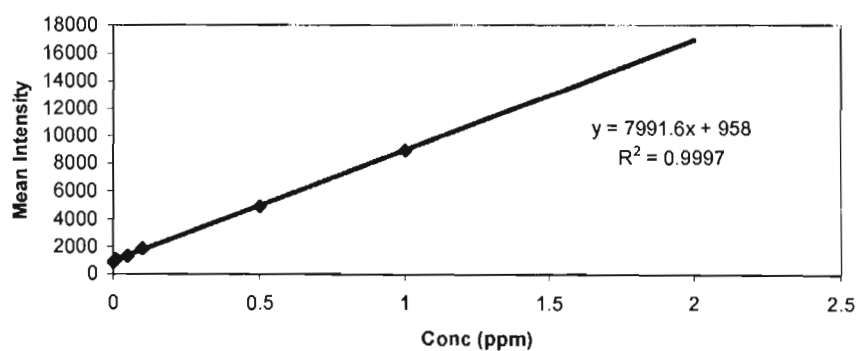
(10) Cadmium



(11) Zinc

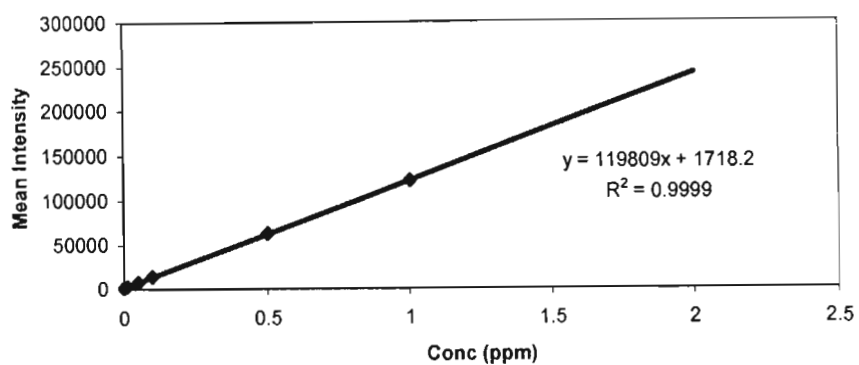


(12) Vanadium

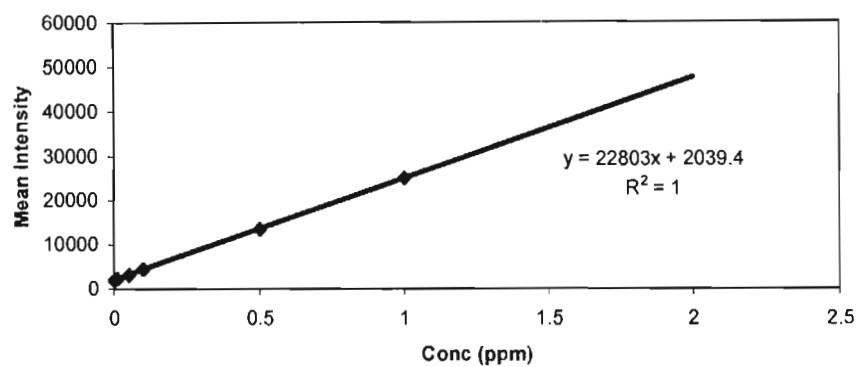


Appendix One

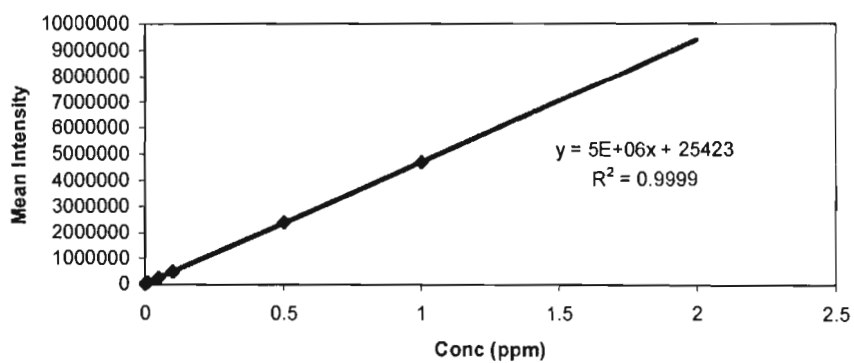
(13) Manganese



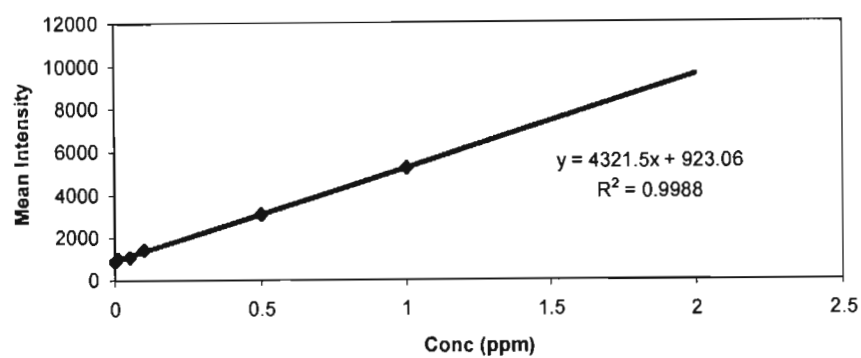
(14) Boron



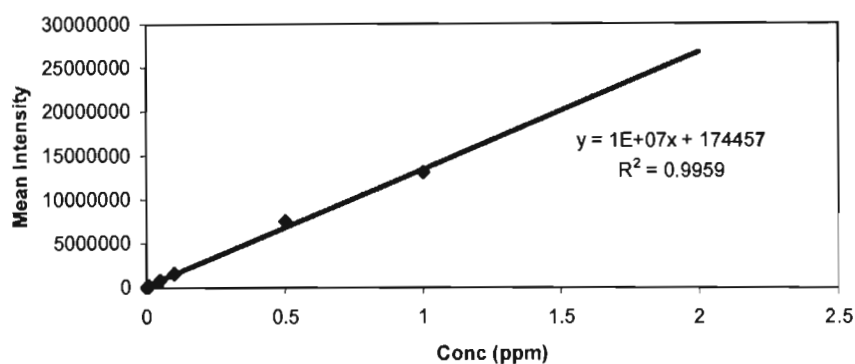
(15) Barium



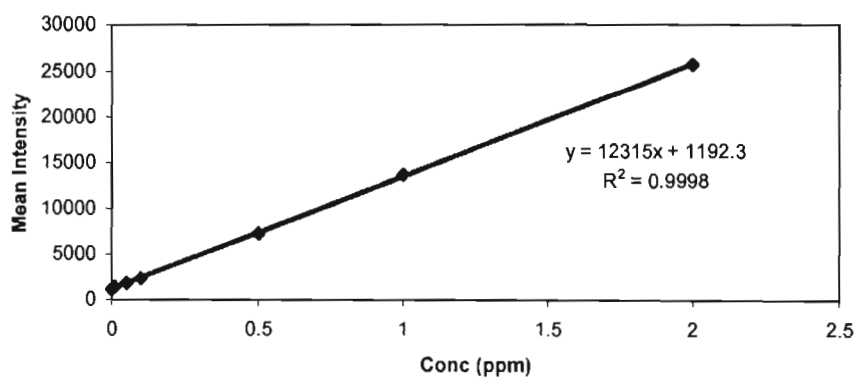
(16) Nickel



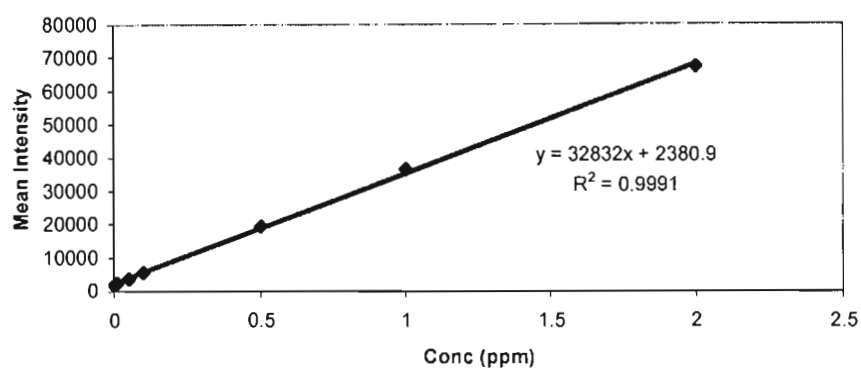
(17) Strontium



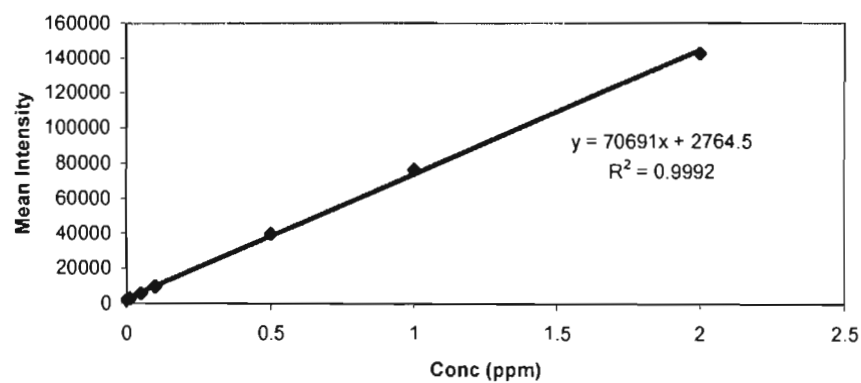
(18) Chromium



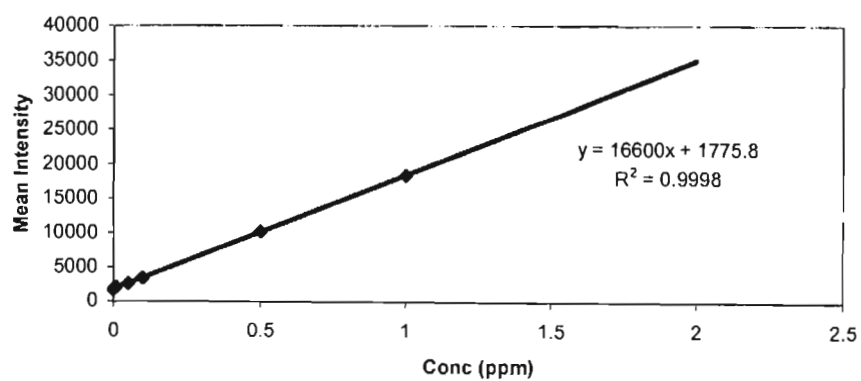
(19) Zirconium



(20) Titanium

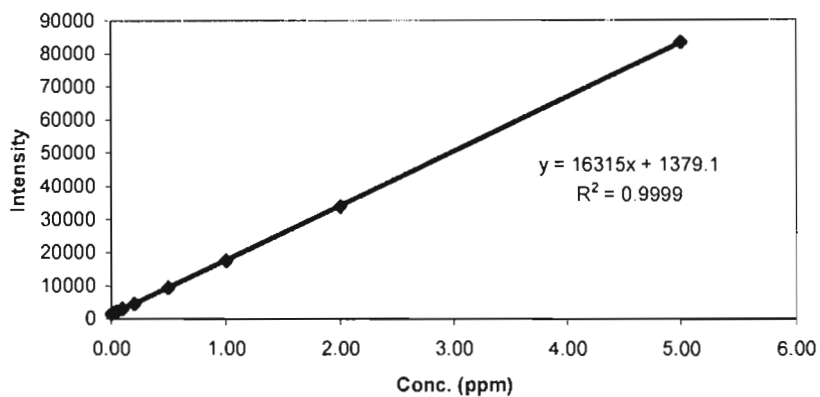


(21) Copper

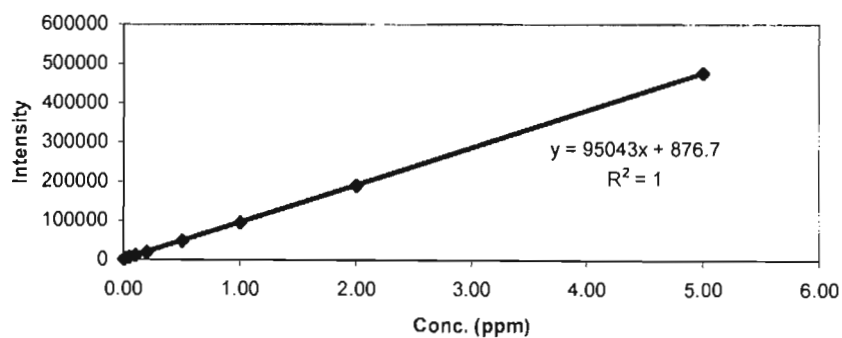


A-1.4 Calibration curves for the ICP-OES determination of trace elements in water samples

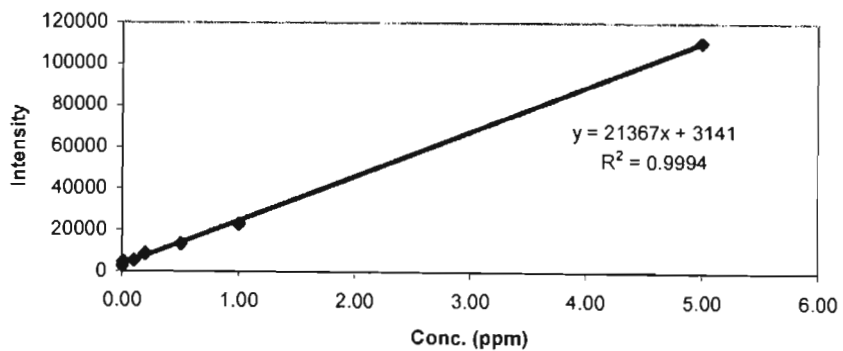
(1) Copper



(2) Manganese

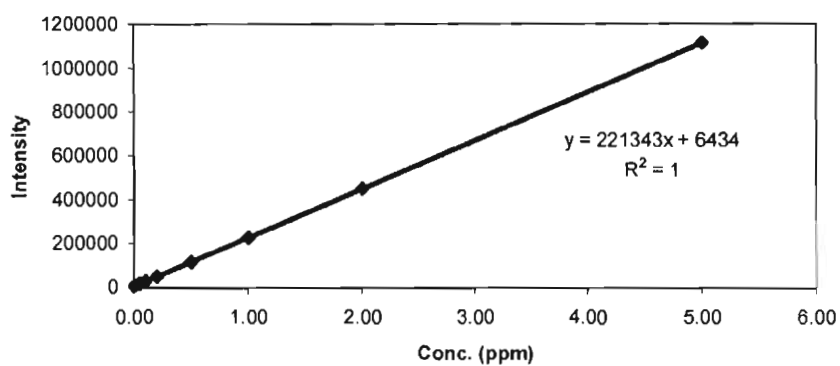


(3) Iron

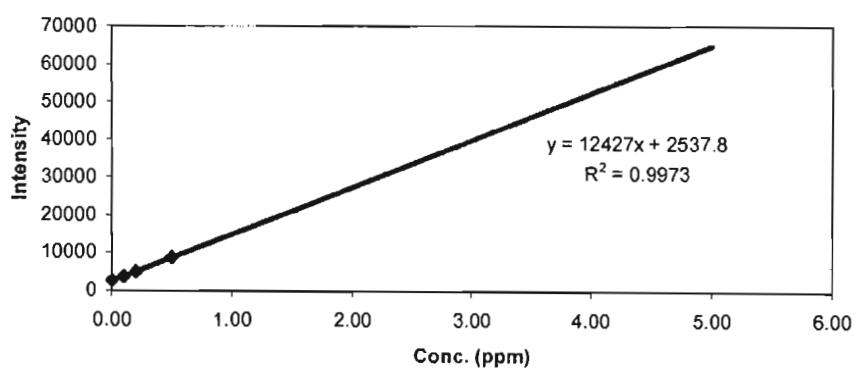


Appendix One

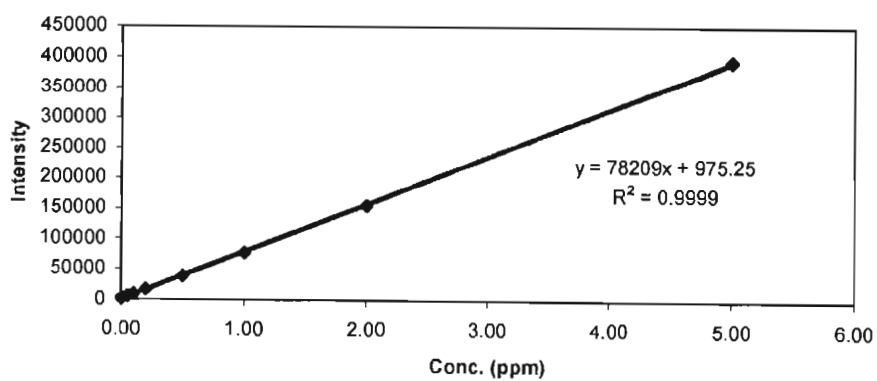
(4) Zinc



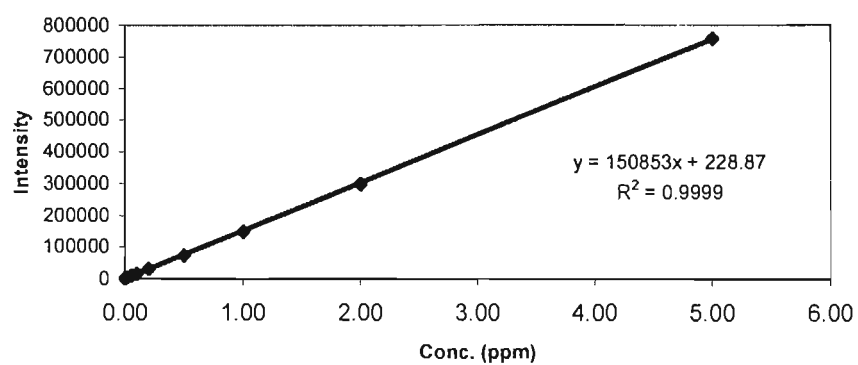
(5) Lead



(6) Cobalt



(7) Cadmium



APPENDIX TWO

A-2.1 Alkalinity titration results

2.1.1 Results from sampling point 6 – Mhlatuze River

The results for the potentiometric titrations for this sampling site are recorded in Table 2.1 and an example of the titration curves obtained can be seen in Figure. 2.1

Table 2.1: Data obtained from potentiometric titrations for site 6

| H ₂ SO ₄ (ml) | pH | | | | | |
|-------------------------------------|------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 0.00 | 6.97 | 7.06 | 6.98 | 7.08 | 7.23 | 6.89 |
| 3.00 | 6.91 | 7.07 | 6.94 | 7.00 | 6.81 | 7.12 |
| 6.00 | 6.53 | 6.46 | 6.39 | 6.50 | 6.34 | 6.42 |
| 9.00 | 6.16 | 6.03 | 5.95 | 6.05 | 5.84 | 5.99 |
| 13.00 | 5.17 | 5.09 | 5.09 | 4.91 | 4.88 | 5.07 |
| 13.50 | 4.71 | 4.64 | 4.70 | 1.41 | 4.50 | 4.66 |
| 13.80 | 4.61 | 4.27 | 4.46 | 4.01 | 4.11 | 4.30 |
| 14.00 | 4.42 | 4.00 | 4.16 | 3.80 | 3.87 | 4.04 |
| 14.50 | 3.84 | 3.64 | 3.73 | 3.47 | 3.55 | 3.64 |
| 15.00 | 3.51 | 3.39 | 3.45 | 3.31 | 3.36 | 3.42 |
| 17.00 | 3.00 | 2.97 | 2.96 | 2.95 | 2.97 | 2.97 |
| 19.00 | 2.76 | 2.75 | 2.74 | 2.75 | 2.77 | 2.74 |

The graph below is an example of the curves obtained for this set of titrations. It corresponds with the data from sample number 5.

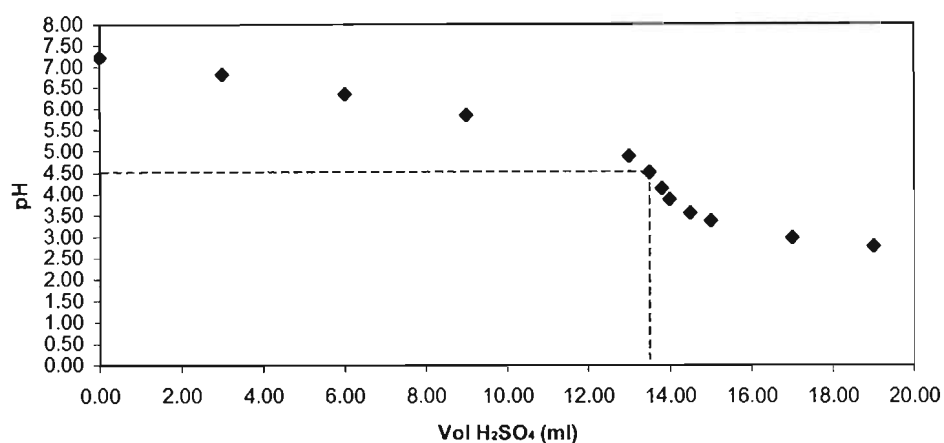


Figure 2.1: Example of a potentiometric titration curve obtained for site 6

2.1.2 Results from sampling point 7 – Lake Mzingazi

The results for the potentiometric titrations for this sampling site are recorded in Table 2.2 and an example of the titration curves obtained can be seen in Figure. 2.2

Table 2.2: Data obtained from potentiometric titration for site 7

| H ₂ SO ₄ (ml) | pH | | | | | |
|-------------------------------------|------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 0.00 | 6.46 | 6.58 | 6.57 | 6.29 | 6.35 | 6.94 |
| 1.00 | 6.41 | 6.48 | 6.47 | 6.19 | 6.28 | 6.90 |
| 2.00 | 6.32 | 6.43 | 6.35 | 5.99 | 6.02 | 6.84 |
| 3.00 | 6.21 | 6.22 | 6.24 | 5.91 | 5.87 | 6.00 |
| 3.50 | 5.52 | 5.56 | 5.70 | 5.51 | 5.62 | 5.67 |
| 4.00 | 4.94 | 4.97 | 5.21 | 5.09 | 5.05 | 4.86 |
| 4.10 | 4.69 | 4.72 | 4.86 | 4.79 | 4.75 | 4.47 |
| 4.30 | 4.23 | 4.35 | 4.46 | 4.36 | 4.38 | 4.04 |
| 4.50 | 3.93 | 3.91 | 4.02 | 3.99 | 3.94 | 3.79 |
| 5.00 | 3.52 | 3.53 | 3.52 | 3.58 | 3.55 | 3.48 |
| 7.00 | 3.02 | 2.99 | 2.99 | 3.02 | 3.01 | 3.00 |
| 9.00 | 2.79 | 2.76 | 2.78 | 2.79 | 2.79 | 2.79 |

The graph below is an example of the curves obtained for this set of titrations. It corresponds with the data from sample number 6.

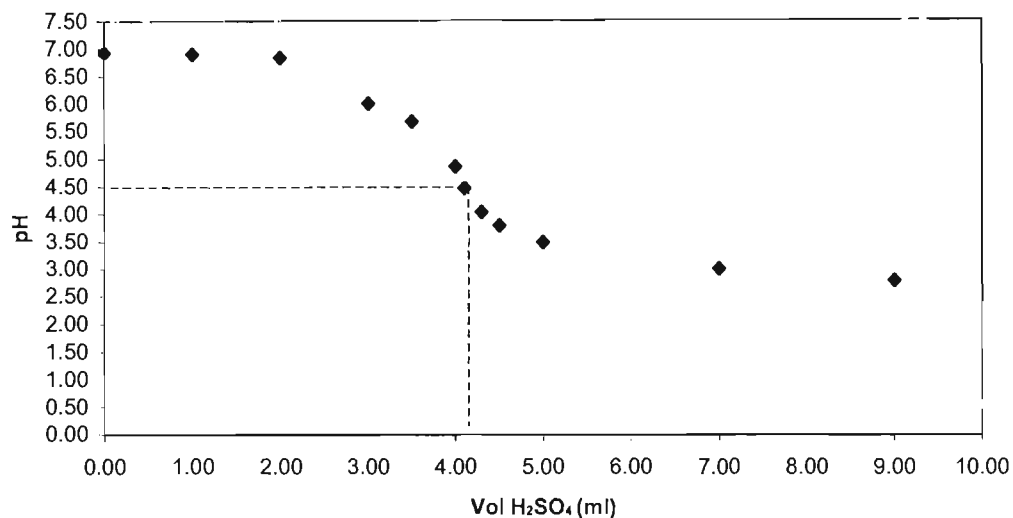


Figure 2.2: Example of a potentiometric titration curve obtained for site 7

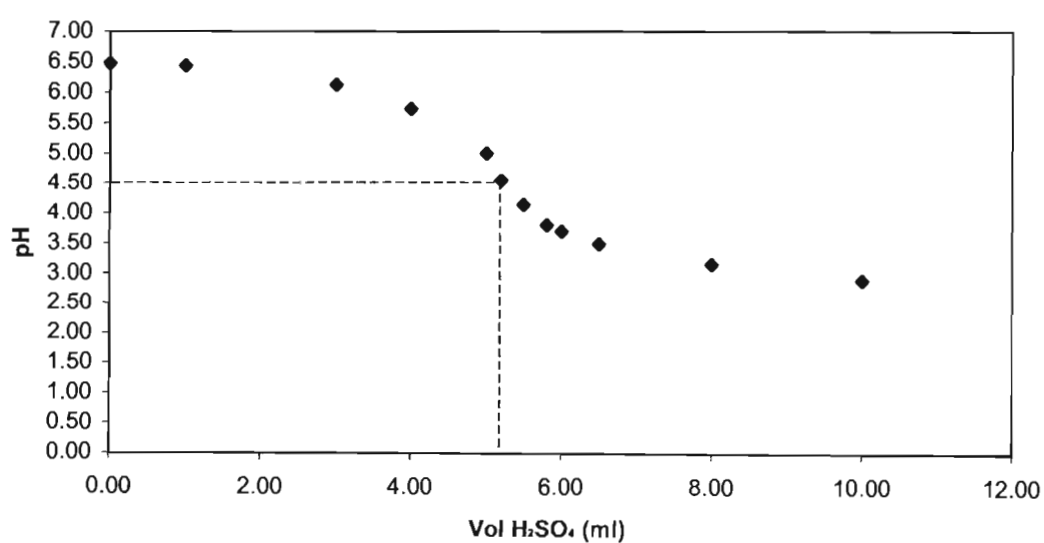
2.1.3 Results from sampling point 14 – Mzingazi River

The results for the potentiometric titrations for this sampling site are recorded in Table 2.3 and an example of the titration curves obtained can be seen in Figure. 2.3

Table 2.3: Data obtained for potentiometric titration from site 14

| H ₂ SO ₄ (ml) | pH | | | | |
|-------------------------------------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 |
| 0.00 | 6.41 | 6.44 | 6.43 | 6.48 | 6.56 |
| 1.00 | 6.58 | 6.43 | 6.39 | 6.44 | 6.55 |
| 3.00 | 6.25 | 6.12 | 6.09 | 6.12 | 6.29 |
| 4.00 | 6.04 | 5.74 | 5.73 | 5.73 | 5.73 |
| 5.00 | 5.30 | 4.96 | 4.96 | 5.01 | 4.83 |
| 5.20 | 5.04 | 4.56 | 4.60 | 4.55 | 4.40 |
| 5.50 | 4.57 | 4.09 | 4.20 | 4.14 | 4.04 |
| 5.80 | 4.13 | 3.77 | 3.88 | 3.81 | 3.80 |
| 6.00 | 3.90 | 3.66 | 3.74 | 3.70 | 3.64 |
| 6.50 | 3.61 | 3.47 | 3.50 | 3.49 | 3.46 |
| 8.00 | 3.19 | 3.13 | 3.15 | 3.15 | 3.14 |
| 10.00 | 2.92 | 2.89 | 2.89 | 2.89 | 2.91 |

The graph below is an example of the curves obtained for this set of titrations. It corresponds with the data from sample number 4.

**Figure 2.3: Example of a potentiometric titration curve obtained for site 14**

2.1.4 Results from sampling point 15 – Mhlatuze River

The results for the potentiometric titrations for this sampling site are recorded in Table 2.4 and an example of the titration curves obtained can be seen in Figure. 2.4

Table 2.4: Data obtained for potentiometric titration from site 15

| H ₂ SO ₄ (ml) | pH | | | | | |
|-------------------------------------|------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 0.00 | 7.37 | 7.37 | 7.39 | 7.45 | 7.38 | 7.55 |
| 1.00 | 7.11 | 7.09 | 7.05 | 7.09 | 7.14 | 7.12 |
| 3.00 | 6.65 | 6.67 | 6.63 | 6.65 | 6.70 | 6.67 |
| 5.00 | 6.35 | 6.34 | 6.31 | 6.32 | 6.39 | 6.34 |
| 10.00 | 5.47 | 5.51 | 5.35 | 5.46 | 5.61 | 5.52 |
| 11.00 | 5.16 | 5.14 | 4.88 | 5.05 | 5.36 | 5.00 |
| 11.50 | 4.87 | 4.83 | 4.45 | 4.75 | 5.20 | 4.59 |
| 11.80 | 4.65 | 4.54 | 4.12 | 4.37 | 5.07 | 4.18 |
| 12.00 | 4.40 | 4.37 | 3.86 | 4.12 | 4.96 | 3.92 |
| 13.00 | 3.49 | 3.51 | 3.33 | 3.41 | 4.13 | 3.36 |
| 15.00 | 3.00 | 3.00 | 2.94 | 2.99 | 3.18 | 2.96 |
| 17.00 | 2.79 | 2.87 | 2.75 | 2.78 | 2.90 | 2.76 |

The graph below is an example of the curves obtained for this set of titrations. It corresponds with the data from sample number 1.

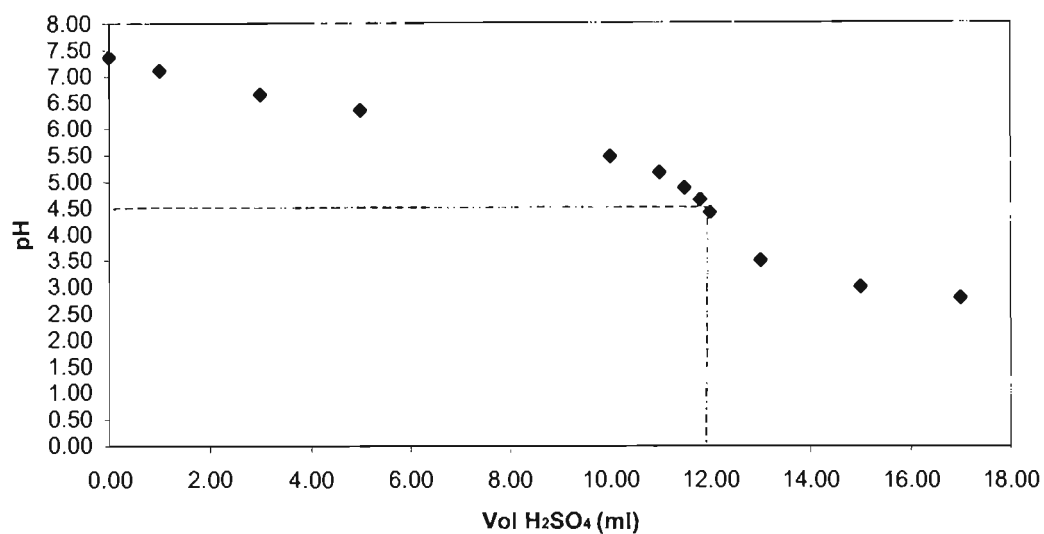


Figure 2.4: Example of a potentiometric titration curve obtained for site 15

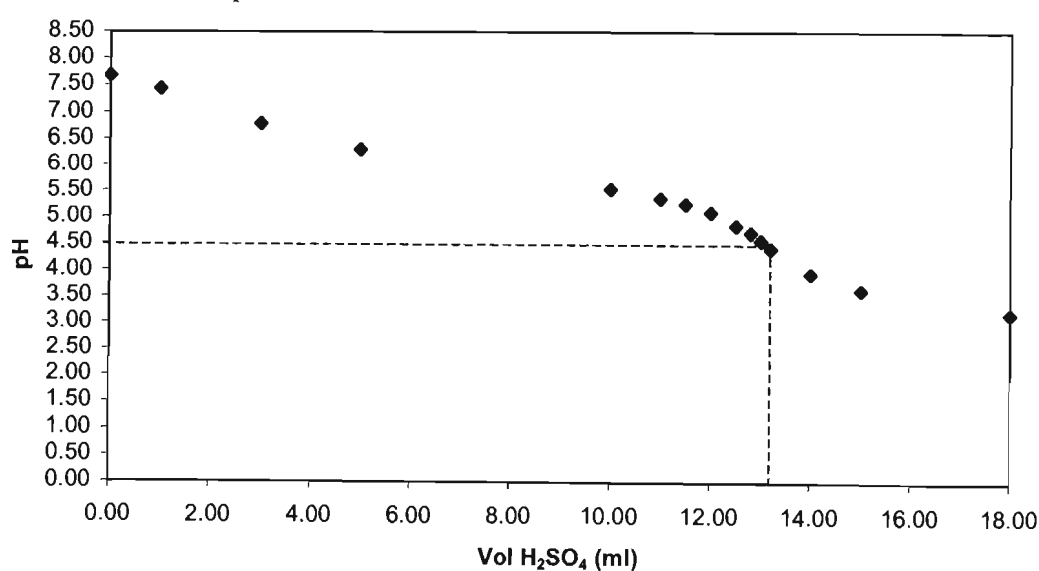
2.1.5 Results from sampling point 18 – Mtunzini River

The results for the potentiometric titrations for this sampling site are recorded in Table 2.5 and an example of the titration curves obtained can be seen in Figure. 2.5

Table 2.5: Data obtained for potentiometric titration from site 18

| H ₂ SO ₄ (ml) | pH | | | | | |
|-------------------------------------|------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 0.00 | 7.42 | 7.63 | 7.66 | 7.57 | 7.68 | 7.70 |
| 1.00 | 7.45 | 7.60 | 7.47 | 7.43 | 7.43 | 7.40 |
| 3.00 | 6.91 | 6.88 | 6.84 | 6.85 | 6.79 | 6.80 |
| 5.00 | 6.54 | 6.66 | 6.47 | 6.49 | 6.30 | 6.44 |
| 10.00 | 5.75 | 5.73 | 5.67 | 5.69 | 5.54 | 5.58 |
| 11.00 | 5.50 | 5.47 | 5.49 | 5.44 | 5.36 | 5.30 |
| 11.50 | 5.36 | 5.34 | 5.29 | 5.21 | 5.26 | 5.11 |
| 12.00 | 5.19 | 5.15 | 5.11 | 5.06 | 5.09 | 4.87 |
| 12.50 | 4.92 | 4.88 | 4.85 | 4.83 | 4.84 | 4.46 |
| 12.80 | 4.70 | 4.68 | 4.62 | 4.58 | 4.71 | 4.24 |
| 13.00 | 4.57 | 4.43 | 4.49 | 4.43 | 4.56 | 4.10 |
| 13.20 | 4.40 | 4.31 | 4.35 | 4.27 | 4.41 | 4.01 |
| 14.00 | 3.90 | 3.86 | 3.88 | 3.86 | 3.94 | 3.69 |
| 15.00 | 3.58 | 3.55 | 3.59 | 3.57 | 3.62 | 3.49 |
| 18.00 | 3.15 | 3.15 | 3.18 | 3.18 | 3.19 | 3.12 |

The graph below is an example of the curves obtained for this set of titrations. It corresponds with the data from sample number 4.

**Figure 2.5: Example of a potentiometric titration curve obtained for site 18**

2.1.5: Alkalinity Calculations

$$\text{Alkalinity (mg CaCO}_3\text{/l)} = 1000 \times V_t \times M/V_s$$

where,

V_t = volume of standard acid used

M = mass (mg) of CaCO_3 equivalent to 1ml of titrant

V_s = volume of sample used

$$\begin{aligned} \square \quad [\text{H}_2\text{SO}_4] &= 0.009150 \text{ mol/dm}^3 \\ \text{mol H}_2\text{SO}_4 &= 9.150 \times 10^{-6} \text{ mol} \\ \text{mol CaCO}_3 &= 9.150 \times 10^{-6} \text{ mol} \end{aligned}$$

$$\begin{aligned} m(\text{CaCO}_3) &= 9.150 \times 10^{-6} \text{ mol} \times 100.09 \text{ g/mol} \\ &= 9.158 \times 10^{-4} \text{ g} \end{aligned}$$

$$\therefore M = 0.9158 \text{ mg}$$

$$\square \quad V_s = 100.00 \text{ ml}$$

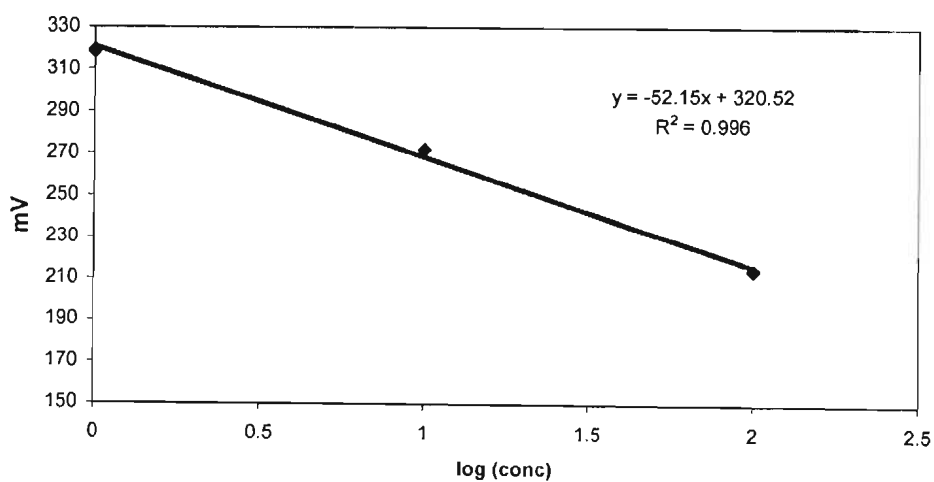
Table 2.6: Results from the alkalinity titrations

| | Mhlatauze River (point 6) | | Lake Mzingazi (point 7) | | Mzingazi River (point 14) | | Mhlatauze River (point 15) | |
|---------|------------------------------|--|----------------------------|--|------------------------------|--|-------------------------------|--|
| Sample | V_t (ml) | Alkalinity (mgCaCO ₃ /l) | V_t (ml) | Alkalinity (mgCaCO ₃ /l) | V_t (ml) | Alkalinity (mgCaCO ₃ /l) | V_t (ml) | Alkalinity (mgCaCO ₃ /l) |
| 1 | 13.95 | 127.75 | 4.15 | 38.01 | 5.50 | 50.37 | 11.95 | 109.44 |
| 2 | 13.52 | 123.82 | 4.15 | 38.01 | 5.20 | 47.62 | 11.85 | 108.52 |
| 3 | 13.75 | 125.92 | 4.30 | 39.38 | 5.25 | 48.08 | 11.55 | 105.77 |
| 4 | 13.45 | 123.18 | 4.20 | 38.46 | 5.20 | 47.62 | 11.70 | 107.15 |
| 5 | 13.30 | 121.80 | 4.20 | 38.46 | 5.15 | 47.16 | 12.50 | 114.48 |
| 6 | 13.55 | 124.09 | 4.10 | 37.55 | | | 11.60 | 106.23 |
| Average | 13.59 | 124.43 | 4.18 | 38.31 | 5.26 | 48.17 | 11.86 | 108.60 |

Table 2.6 (contd.): Results from alkalinity titrations

| Mtunzini River (point 18) | | |
|------------------------------|------------|--|
| Sample | Vt (ml) | Alkalinity (mgCaCO ₃ /l) |
| 1 | 13.05 | 119.51 |
| 2 | 13.06 | 119.60 |
| 3 | 12.98 | 118.87 |
| 4 | 12.91 | 118.23 |
| 5 | 13.08 | 119.27 |
| 6 | 12.45 | 114.02 |
| Average | 12.92 | 118.34 |

A-2.2 Calibration curves for ion selective electrode determinations

**Figure 2.6. Calibration curve for nitrate determination via ISE**

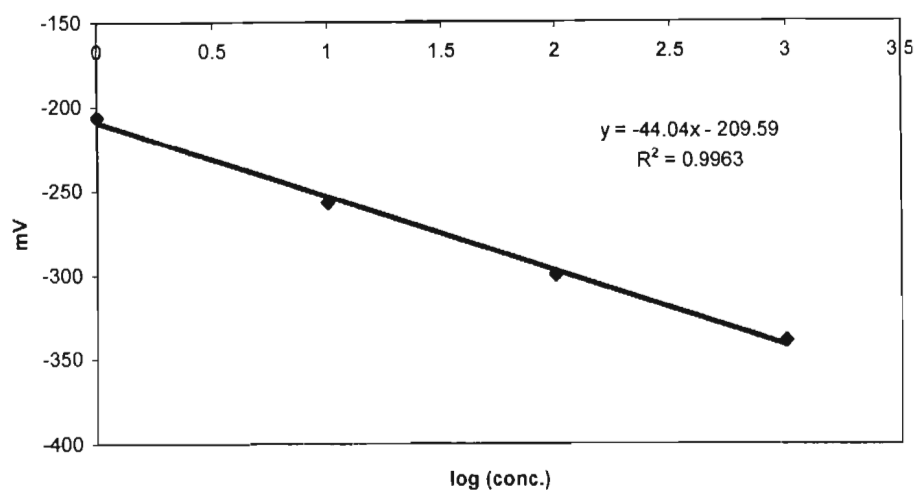


Figure 2.7. Calibration curve for chloride determination via ISE

A-2.3 Trace metal analysis of water samples

2.3.1. ICP-OES detection limits for the elements of interest

For each element at a particular wavelength there is an associated detection limit. These detection limits are recorded in Table 2.7.

Table 2.7: Wavelengths and detection limits

| Element | Wavelength (nm) | Detection limit (ppm) |
|-----------|-----------------|-----------------------|
| Copper | 327.39 | 0.020 |
| Manganese | 259.37 | 0.003 |
| Iron | 259.94 | 0.015 |
| Zinc | 213.86 | 0.009 |
| Cobalt | 228.62 | 0.050 |
| Cadmium | 226.50 | 0.015 |
| Lead | 220.35 | 0.140 |

2.3.2. ICP-OES results of trace metal determination

The concentrations reflected in the following tables are a combination of the results found over the five sampling trips and the sampling site numbers correspond to those found in Table 3.3 in Chapter 3. The concentrations reported are those of the concentrated samples and as such are 25 times more concentrated than the actual samples. The results are sorted by element. The numbers represented in bold type were regarded as outliers and discarded.

Table 2.8: Results of copper determination

| Site | Concentration in extract (ppm) (= 25 x concentration in sample) | | | | | | | | | | | | |
|------|---|-------------|------|-------|-------------|-------------|-------------|-------------|------|------|-------------|-------------|--------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | 0.22 | 0.13 | 0.09 | 0.133 | 0.11 | 0.11 | 0.14 | 0.10 | 0.08 | 0.07 | 0.22 | 0.22 | 0.049 |
| 2 | 0.14 | 0.14 | 0.08 | 0.138 | 0.16 | 0.11 | 0.15 | 0.13 | 0.09 | 0.09 | 0.34 | 0.34 | 0.040 |
| 3 | 0.09 | 0.16 | 0.10 | 0.124 | 0.21 | 0.15 | 0.19 | 0.12 | 0.13 | 0.10 | 0.11 | 0.14 | 0.050 |
| 4 | 0.11 | 0.22 | 0.08 | 0.130 | 0.11 | 0.11 | 0.15 | 0.14 | 0.10 | 0.08 | 0.15 | 0.10 | 0.050 |
| 5 | 0.12 | 0.21 | 0.11 | 0.153 | 0.19 | 0.12 | 0.16 | 0.12 | 0.11 | 0.07 | 0.12 | 0.09 | 0.110 |
| 6 | 0.22 | 0.19 | 0.09 | 0.125 | 0.19 | 0.25 | 0.13 | 0.13 | 0.12 | 0.09 | 0.15 | 0.11 | 0.109 |
| 7 | 0.17 | 0.20 | 0.10 | 0.124 | 0.18 | 0.12 | 0.02 | 0.12 | 0.10 | 0.10 | 0.15 | 0.12 | 0.050 |
| 8 | 0.22 | 0.30 | 0.10 | 0.131 | 0.15 | 0.14 | 0.16 | 0.06 | 0.13 | 0.08 | 1.16 | 0.13 | 0.045 |
| 9 | 0.13 | 0.17 | 0.12 | 0.130 | 0.18 | 0.10 | 0.14 | 0.13 | 0.13 | 0.06 | | | |
| 10 | 0.20 | 0.14 | 0.08 | 0.277 | 0.12 | 0.12 | 0.14 | 0.12 | 0.15 | 0.08 | | | |
| Avg | 0.17 | 0.17 | 0.09 | 0.132 | 0.15 | 0.12 | 0.15 | 0.12 | 0.11 | 0.08 | 0.15 | 0.12 | 0.047 |
| sd | 0.04 | 0.03 | 0.01 | 0.009 | 0.03 | 0.01 | 0.02 | 0.01 | 0.02 | 0.01 | 0.04 | 0.02 | 0.004 |
| %RSD | 25.6 | 18.4 | 14.7 | 6.6 | 19.7 | 12.1 | 11.7 | 8.2 | 18.7 | 13.7 | 25.6 | 15.6 | 8.6 |

Table 2.9: Results of manganese determination

| Site | Concentration in extract (ppm) (= 25 x concentration in sample) | | | | | | | | | | | | |
|------|---|--------------|--------------|------|-------------|--------------|--------------|-------|--------------|------|--------------|--------------|--------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | 0.029 | 0.042 | 0.011 | 0.10 | 0.03 | 0.024 | 0.031 | 0.044 | 0.017 | 0.05 | 0.017 | 0.016 | 0.009 |
| 2 | 0.022 | 0.047 | 0.010 | 0.07 | 0.04 | 0.018 | 0.056 | 0.042 | 0.043 | 0.07 | 0.199 | 0.126 | 0.005 |
| 3 | 0.040 | 0.035 | 0.012 | 0.11 | 0.07 | 0.022 | 0.034 | 0.035 | 0.021 | 0.07 | 0.011 | 0.014 | 0.008 |
| 4 | 0.016 | 0.053 | 0.014 | 0.11 | 0.06 | 0.024 | 0.072 | 0.031 | 0.040 | 0.10 | 0.020 | 0.017 | 0.010 |
| 5 | 0.030 | 0.056 | 0.014 | 0.06 | 0.04 | 0.023 | 0.029 | 0.050 | 0.037 | 0.10 | 0.015 | 0.015 | 0.024 |
| 6 | 0.024 | 0.038 | 0.010 | 0.10 | 0.08 | 0.021 | 0.039 | 0.053 | 0.027 | 0.06 | 0.027 | 0.029 | 0.022 |
| 7 | 0.041 | 0.116 | 0.013 | 0.08 | 0.06 | 0.048 | 0.033 | 0.052 | 0.022 | 0.07 | 0.024 | 0.024 | 0.010 |
| 8 | 0.048 | 0.050 | 0.027 | 0.07 | 0.05 | 0.020 | 0.027 | 0.042 | 0.031 | 0.07 | 0.902 | 0.015 | 0.010 |
| 9 | 0.032 | 0.048 | 0.017 | 0.08 | 0.06 | 0.017 | 0.026 | 0.043 | 0.025 | 0.06 | | | |
| 10 | 0.027 | 0.040 | 0.100 | 0.12 | 0.04 | 0.019 | 0.084 | 0.060 | 0.019 | 0.06 | | | |
| Avg | 0.033 | 0.045 | 0.012 | 0.09 | 0.06 | 0.021 | 0.034 | 0.045 | 0.025 | 0.07 | 0.019 | 0.019 | 0.009 |
| sd | 0.009 | 0.007 | 0.002 | 0.02 | 0.01 | 0.003 | 0.009 | 0.009 | 0.007 | 0.02 | 0.006 | 0.006 | 0.002 |
| %RSD | 26.9 | 15.8 | 18.8 | 21.6 | 25.5 | 12.1 | 28.1 | 19.2 | 26.5 | 21.2 | 30.14 | 29.9 | 22.7 |

Table 2.10: Results of iron determination

| | Concentration in extract (ppm) (= 25 x concentration in sample) | | | | | | | | | | | | |
|------|---|-------------|------------|------------|-------------|------|------------|------------|------|-------------|-------------|------------|-------------|
| Site | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | 14.3 | 26.8 | 2.0 | 16.4 | 5.4 | 4.5 | 2.0 | 3.3 | 3.9 | 35.7 | 3.4 | 7.9 | 2.9 |
| 2 | 21.2 | 16.6 | 1.7 | 7.6 | 13.7 | 4.2 | 2.7 | 3.4 | 3.2 | 24.4 | 11.1 | 9.8 | 2.9 |
| 3 | 13.5 | 35.0 | 1.1 | 12.7 | 10.6 | 5.2 | 3.4 | 3.9 | 2.7 | 30.9 | 5.0 | 4.5 | 3.1 |
| 4 | 30.0 | 19.1 | 1.0 | 11.4 | 6.2 | 6.0 | 1.6 | 2.9 | 3.1 | 31.9 | 1.9 | 3.7 | 3.2 |
| 5 | 9.5 | 33.0 | 1.9 | 4.0 | 9.0 | 3.2 | 2.2 | 1.5 | 2.3 | 38.3 | 7.4 | 6.4 | 0.7 |
| 6 | 14.9 | 36.3 | 1.8 | 12.9 | 15.5 | 5.2 | 3.0 | 1.3 | 3.7 | 19.6 | 4.7 | 10.2 | 12.2 |
| 7 | 9.4 | 24.2 | 1.6 | 12.1 | 10.1 | 5.0 | 2.4 | 3.2 | 3.7 | 30.3 | 4.3 | 8.3 | 2.2 |
| 8 | 16.3 | 18.0 | 1.2 | 14.2 | 8.5 | 5.0 | 2.0 | 2.8 | 2.8 | 29.4 | 4.3 | 5.2 | 4.9 |
| 9 | 17.0 | 27.3 | 1.5 | 16.2 | 8.2 | 4.1 | 3.2 | 3.5 | 3.0 | 27.1 | | | |
| 10 | 15.2 | 31.3 | 2.1 | 12.5 | 8.0 | 5.0 | 3.7 | 2.9 | 3.0 | 25.4 | | | |
| Avg | 14.6 | 27.9 | 1.5 | 12.9 | 8.2 | 4.7 | 2.7 | 3.3 | 3.1 | 30.4 | 5.0 | 7.0 | 3.2 |
| sd | 3.7 | 6.6 | 0.3 | 2.6 | 1.8 | 0.8 | 0.6 | 0.3 | 0.5 | 4.6 | 1.3 | 2.2 | 0.9 |
| %RSD | 25.1 | 23.7 | 22.3 | 20.5 | 21.4 | 16.2 | 22.8 | 10.5 | 14.8 | 15.0 | 26.6 | 31.3 | 28.8 |

Table 2.11: Results of zinc determination

| Site | Concentration in extract (ppm) (= 25 x concentration in sample) | | | | | | | | | | | | |
|------|---|-------------|--------------|------|-------------|------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | 0.50 | 0.29 | 0.259 | 0.40 | 0.97 | 0.13 | 0.24 | 0.22 | 0.46 | 0.46 | 0.33 | 0.43 | 0.14 |
| 2 | 0.49 | 0.30 | 0.210 | 0.42 | 0.43 | 0.15 | 0.29 | 0.21 | 0.26 | 0.43 | 0.28 | 0.33 | 0.23 |
| 3 | 0.47 | 0.39 | 0.161 | 0.47 | 0.39 | 0.11 | 0.21 | 0.30 | 0.24 | 0.24 | 0.37 | 1.31 | 0.03 |
| 4 | 0.47 | 0.39 | 0.323 | 0.40 | 0.64 | 0.11 | 0.22 | 0.21 | 0.26 | 0.22 | 0.05 | 0.43 | 0.09 |
| 5 | 0.36 | 0.18 | 0.156 | 0.41 | 0.37 | 0.09 | 0.29 | 0.27 | 0.36 | 0.21 | 0.54 | 0.35 | 0.11 |
| 6 | 0.34 | 0.19 | 0.412 | 0.34 | 0.76 | 0.11 | 0.34 | 0.36 | 0.27 | 0.22 | 0.26 | 0.37 | 0.24 |
| 7 | 0.20 | 0.43 | 0.309 | 0.43 | 0.56 | 0.14 | 0.31 | 0.21 | 0.28 | 0.25 | 0.52 | 0.32 | 0.17 |
| 8 | 0.25 | 0.24 | 0.298 | 0.43 | 0.61 | 0.12 | 0.15 | 0.30 | 0.32 | 0.23 | 1.10 | 0.29 | 0.13 |
| 9 | 0.12 | 0.25 | 0.215 | 0.39 | 0.65 | 0.11 | 0.36 | 0.29 | 0.25 | 0.20 | | | |
| 10 | 0.11 | 0.12 | 0.246 | 0.42 | 0.57 | 0.14 | 0.25 | 0.26 | 0.29 | 0.22 | | | |
| Avg | 0.38 | 0.32 | 0.242 | 0.41 | 0.55 | 0.12 | 0.28 | 0.25 | 0.28 | 0.22 | 0.38 | 0.36 | 0.17 |
| sd | 0.12 | 0.07 | 0.061 | 0.03 | 0.13 | 0.02 | 0.05 | 0.04 | 0.04 | 0.02 | 0.12 | 0.05 | 0.05 |
| %RSD | 30.7 | 21.7 | 25.40 | 8.0 | 23.4 | 15.7 | 19.3 | 14.9 | 13.8 | 7.2 | 31.3 | 15.0 | 30.8 |

Table 2.12: Results of cobalt determination

| Site | Concentration in extract (ppm) (= 25 x concentration in sample) | | | | | | | | | | | | |
|------|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------------|-----|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl |
| 2 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl |
| 3 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | 0.06 | <dl |
| 4 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | 0.05 | <dl |
| 5 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl |
| 6 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl |
| 7 | <dl | <dl | <dl | <dl | <dl | <dl | <d | <dl | <dl | <dl | <dl | <dl | <dl |
| 8 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl |
| 9 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | | | |
| 11 | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | | | |
| Avg | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl | <dl |
| sd | - | - | - | - | - | - | - | - | - | - | - | - | - |
| %RS | - | - | - | - | - | - | - | - | - | - | - | - | - |
| D | | | | | | | | | | | | | |

Table 2.13: Results of cadmium determination

| Site | Concentration in extract (ppm) (= 25 x concentration in sample) | | | | | | | | | | | | |
|------|---|------|------|------|------|------|------|------|------|------|------|-------------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| 2 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.07 | < dl |
| 3 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| 4 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| 5 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| 6 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| 7 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| 8 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| 9 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | |
| 10 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | |
| Avg | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl |
| sd | - | - | - | - | - | - | - | - | - | - | - | - | - |
| %RSD | - | - | - | - | - | - | - | - | - | - | - | - | - |

Table 2.14: Results of lead determination

| Site | Concentration in extract (ppm) (= 25 x concentration in sample) | | | | | | | | | | | | |
|------|---|------|------|------|------|------|-------------|------|------|------|-------------|------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | 0.14 | 0.71 | < dl | < dl | < dl | < dl | 0.32 | < dl | < dl | < dl | < dl | < dl | < dl |
| 2 | < dl | 0.62 | < dl | < dl | < dl | < dl | 0.66 | < dl | < dl | < dl | 0.15 | < dl | < dl |
| 3 | < dl | 0.84 | < dl | < dl | < dl | < dl | 0.49 | < dl | < dl | < dl | < dl | < dl | < dl |
| 4 | < dl | 0.58 | < dl | < dl | < dl | < dl | 0.59 | < dl | < dl | < dl | < dl | < dl | < dl |
| 5 | 0.23 | 0.57 | < dl | < dl | 0.15 | 0.15 | 0.51 | < dl | < dl | < dl | < dl | < dl | < dl |
| 6 | 0.21 | 0.56 | < dl | < dl | < dl | < dl | 0.75 | < dl | < dl | < dl | < dl | < dl | < dl |
| 7 | 0.15 | 0.66 | < dl | < dl | < dl | < dl | 0.51 | < dl | < dl | < dl | < dl | < dl | < dl |
| 8 | 0.17 | 0.63 | < dl | < dl | < dl | < dl | 0.49 | < dl | < dl | < dl | 0.26 | < dl | < dl |
| 9 | 0.18 | 0.70 | < dl | < dl | < dl | < dl | 0.46 | < dl | < dl | < dl | | | |
| 10 | 0.18 | 0.58 | < dl | < dl | < dl | < dl | 0.38 | < dl | < dl | < dl | | | |
| Avg | 0.18 | 0.65 | < dl | < dl | < dl | < dl | 0.47 | < dl | < dl | < dl | < dl | < dl | < dl |
| sd | 0.03 | 0.09 | - | - | - | - | 0.09 | - | - | - | - | - | - |
| %RSD | 18.2 | 13.3 | - | - | - | - | 18.3 | - | - | - | - | - | - |

A-2.4 Trace element determination of sediment samples

2.4.1. ICP-OES detection limits for the elements of interest

For each element at a particular wavelength there is an associated detection limit. These detection limits are recorded in Table 2.15.

Table 2.15: Wavelengths and detection limits

| Element | Wavelength (nm) | Detection limit (g/kg) |
|------------|-----------------|------------------------|
| Copper | 327.39 | 0.0020 |
| Manganese | 259.37 | 0.0003 |
| Iron | 259.94 | 0.0015 |
| Zinc | 213.86 | 0.0009 |
| Cobalt | 228.62 | 0.0050 |
| Cadmium | 226.50 | 0.0015 |
| Lead | 220.35 | 0.0140 |
| Aluminium | 396.15 | 0.0040 |
| Titanium | 334.94 | 0.0006 |
| Zirconium | 343.82 | 0.0015 |
| Phosphorus | 214.91 | 0.0190 |
| Boron | 249.77 | 0.0060 |
| Calcium | 317.93 | 0.00006 |
| Potassium | 766.49 | 0.0100 |
| Strontium | 407.77 | 0.00002 |
| Nickel | 231.60 | 0.0060 |
| Barium | 493.41 | 0.00007 |
| Magnesium | 280.27 | 0.0001 |
| Vanadium | 292.40 | 0.0020 |
| Sodium | 589.59 | 0.0010 |
| Chromium | 267.72 | 0.0100 |

2.4.2. ICP-OES results of trace element determination

The concentrations reflected in the following tables are a combination of the results found over the five sampling trips and the sampling site numbers correspond to those found in Table 3.3 in Chapter 3. The results are sorted by element. The numbers represented in bold type were regarded as outliers and discarded.

Table 2.16: Results for copper determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------------|---------------|-------------|-------------|--------|--------------|-------|-------|--------|--------|--------|---------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.007 | 0.010 | 0.0048 | 0.07 | 0.04 | 0.0094 | 0.005 | 0.008 | 0.005 | 0.0105 | 0.0253 | 0.0052 | 0.0043 |
| 2 | 0.007 | 0.007 | 0.0017 | 0.04 | 0.03 | 0.0091 | 0.005 | 0.009 | 0.004 | 0.0151 | 0.0321 | 0.0073 | 0.0102 |
| 3 | 0.024 | 0.008 | 0.0054 | 0.07 | 0.01 | 0.0097 | 0.002 | 0.008 | 0.004 | 0.0164 | 0.0219 | 0.0085 | 0.0155 |
| 4 | 0.029 | 0.007 | 0.0054 | 0.07 | 0.05 | 0.0089 | 0.002 | 0.009 | 0.007 | 0.0183 | 0.0186 | 0.0064 | 0.0101 |
| 5 | 0.036 | 0.005 | 0.0047 | 0.06 | 0.02 | 0.0095 | 0.001 | 0.007 | 0.006 | 0.0125 | 0.0240 | 0.0100 | 0.0118 |
| 6 | 0.029 | 0.005 | 0.0060 | 0.05 | 0.02 | 0.0112 | 0.004 | 0.005 | 0.007 | 0.0135 | 0.0195 | 0.0076 | 0.0115 |
| 7 | 0.045 | 0.007 | 0.0028 | 0.07 | 0.02 | 0.0096 | 0.004 | 0.006 | 0.006 | | | | |
| 8 | 0.049 | 0.006 | 0.0027 | 0.05 | 0.02 | 0.0087 | 0.002 | 0.005 | 0.006 | | | | |
| 9 | 0.041 | 0.010 | 0.0013 | 0.04 | 0.05 | 0.0093 | 0.002 | 0.005 | 0.004 | | | | |
| 10 | 0.043 | 0.011 | 0.0015 | 0.03 | 0.01 | 0.0096 | 0.004 | 0.007 | 0.005 | | | | |
| 11 | 0.041 | 0.014 | 0.0014 | | 0.03 | | | | 0.006 | | | | |
| 12 | 0.049 | 0.015 | 0.0014 | | 0.02 | | | | 0.006 | | | | |
| 13 | 0.047 | 0.016 | 0.0012 | | 0.03 | | | | 0.005 | | | | |
| 14 | 0.046 | 0.017 | 0.0016 | | 0.04 | | | | 0.005 | | | | |
| 15 | 0.047 | 0.019 | 0.0020 | | | | | | 0.004 | | | | |
| 16 | 0.049 | 0.017 | 0.0025 | | | | | | 0.005 | | | | |
| 17 | 0.052 | 0.021 | 0.0026 | | | | | | 0.006 | | | | |
| 18 | 0.034 | 0.017 | 0.0017 | | | | | | 0.006 | | | | |
| Avg. | 0.040 | 0.013 | 0.0019 | 0.06 | 0.03 | 0.0095 | 0.004 | 0.007 | 0.005 | 0.0144 | 0.0236 | 0.0075 | 0.0118 |
| sd | 0.008 | 0.005 | 0.0006 | 0.01 | 0.01 | 0.0007 | 0.001 | 0.002 | 0.001 | 0.0028 | 0.0049 | 0.0017 | 0.0022 |
| %RSD | 20.5 | 35.0 | 30.7 | 23.3 | 37.0 | 7.2 | 37.2 | 23.8 | 20.2 | 19.5 | 20.8 | 22.2 | 18.5 |

Table 2.17: Results for titanium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|-------------|-------|-------------|------|-------|------|-------|-------------|-------|--------|--------|---------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.14 | 0.12 | 0.018 | 0.63 | 0.37 | 0.144 | 0.10 | 0.096 | 0.13 | 0.253 | 0.2891 | 0.2383 | 0.3719 |
| 2 | 0.20 | 0.13 | 0.028 | 0.46 | 0.28 | 0.150 | 0.10 | 0.117 | 0.16 | 0.278 | 0.3515 | 0.2924 | 0.2172 |
| 3 | 0.19 | 0.10 | 0.027 | 0.44 | 0.13 | 0.148 | 0.08 | 0.106 | 0.13 | 0.245 | 0.2861 | 0.2721 | 0.2136 |
| 4 | 0.19 | 0.10 | 0.036 | 0.45 | 0.30 | 0.149 | 0.10 | 0.122 | 0.13 | 0.248 | 0.3153 | 0.1656 | 0.2083 |
| 5 | 0.17 | 0.11 | 0.018 | 0.35 | 0.24 | 0.162 | 0.08 | 0.112 | 0.12 | 0.267 | 0.3100 | 0.3407 | 0.2115 |
| 6 | 0.30 | 0.11 | 0.029 | 0.34 | 0.29 | 0.155 | 0.10 | 0.103 | 0.15 | 0.250 | 0.3000 | 0.1957 | 0.2150 |
| 7 | 0.29 | 0.14 | 0.021 | 0.94 | 0.26 | 0.149 | 0.08 | 0.104 | 0.09 | | | | |
| 8 | 0.32 | 0.12 | 0.012 | 0.53 | 0.38 | 0.127 | 0.08 | 0.114 | 0.11 | | | | |
| 9 | 0.38 | 0.18 | 0.012 | 0.55 | 0.51 | 0.143 | 0.08 | 0.098 | 0.13 | | | | |
| 10 | 0.39 | 0.13 | 0.017 | 0.43 | 0.21 | 0.155 | 0.10 | 0.121 | 0.11 | | | | |
| Avg. | 0.27 | 0.12 | 0.020 | 0.47 | 0.27 | 0.148 | 0.09 | 0.109 | 0.13 | 0.257 | 0.3087 | 0.2508 | 0.2131 |
| sd | 0.08 | 0.01 | 0.006 | 0.09 | 0.08 | 0.009 | 0.01 | 0.009 | 0.02 | 0.013 | 0.0239 | 0.0644 | 0.0034 |
| %RSD | 32.2 | 11.3 | 31.3 | 19.7 | 28.7 | 6.3 | 12.8 | 8.5 | 11.5 | 5.0 | 7.7 | 25.7 | 16.0 |

Table 2.18: Results for aluminium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------------|------|------|------------|------|------|------------|------------|-----|------|------------|------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 18.9 | 3.6 | 0.8 | 25.5 | 23.4 | 3.4 | 1.9 | 1.7 | 2.3 | 3.6 | 16.4 | 1.5 | 1.4 |
| 2 | 27.4 | 3.1 | 1.0 | 16.7 | 13.3 | 3.6 | 1.7 | 1.9 | 1.9 | 3.6 | 25.0 | 1.4 | 6.8 |
| 3 | 13.1 | 3.1 | 1.0 | 27.6 | 4.4 | 3.5 | 1.4 | 1.9 | 1.9 | 3.6 | 13.3 | 1.8 | 6.5 |
| 4 | 14.5 | 3.2 | 1.0 | 27.7 | 19.2 | 3.1 | 1.5 | 2.2 | 2.4 | 4.5 | 14.7 | 3.8 | 6.4 |
| 5 | 16.8 | 2.6 | 0.8 | 22.2 | 16.6 | 3.3 | 1.2 | 2.9 | 3.1 | 3.8 | 15.0 | 1.6 | 6.9 |
| 6 | 13.1 | 3.1 | 1.3 | 22.8 | 11.4 | 3.2 | 1.5 | 2.1 | 1.7 | 3.7 | 17.5 | 1.3 | 6.6 |
| 7 | 21.7 | 4.1 | 0.9 | 31.9 | 12.0 | 3.3 | 1.2 | 2.2 | 2.1 | | | | |
| 8 | 21.1 | 3.8 | 0.9 | 20.8 | 10.6 | 2.3 | 1.1 | 2.2 | 2.3 | | | | |
| 9 | 23.2 | 6.9 | 0.9 | 19.1 | 18.4 | 2.7 | 1.5 | 2.2 | 1.8 | | | | |
| 10 | 29.1 | 4.4 | 0.7 | 16.4 | 4.5 | 3.0 | 1.5 | 2.1 | 2.3 | | | | |
| 11 | 31.1 | 3.7 | 1.0 | | | | | | 2.1 | | | | |
| 12 | 30.9 | 2.2 | 1.0 | | | | | | 1.9 | | | | |
| 13 | 30.6 | 3.2 | 1.2 | | | | | | 2.3 | | | | |
| 14 | 31.0 | 2.6 | 1.0 | | | | | | 2.0 | | | | |
| 15 | 28.1 | 3.1 | 0.9 | | | | | | 2.0 | | | | |
| 16 | 29.1 | 1.8 | 1.0 | | | | | | 1.9 | | | | |
| 17 | 33.8 | 2.6 | 0.9 | | | | | | 2.2 | | | | |
| 18 | 31.8 | 3.6 | 0.8 | | | | | | 2.0 | | | | |
| Avg. | 27.0 | 3.2 | 0.9 | 23.1 | 15.6 | 3.1 | 1.4 | 2.1 | 2.1 | 3.8 | 17.0 | 1.5 | 6.6 |
| sd | 5.3 | 0.6 | 0.1 | 5.1 | 4.5 | 0.4 | 0.2 | 0.2 | 0.2 | 0.4 | 4.2 | 0.2 | 0.2 |
| %RSD | 19.6 | 18.2 | 13.7 | 22.1 | 29.1 | 12.5 | 15.4 | 8.7 | 9.4 | 9.3 | 24.6 | 12.8 | 3.1 |

Table 2.19: Results for zirconium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------|--------|---------------|---------------|--------|---------------|-------|--------|--------|--------|--------|--------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.012 | 0.0029 | 0.0023 | < dl | 0.0097 | 0.0044 | 0.0042 | 0.002 | 0.0017 | 0.0062 | 0.0073 | 0.0047 | 0.0038 |
| 2 | 0.003 | 0.0029 | 0.0027 | 0.0021 | 0.0067 | 0.0046 | 0.0040 | 0.002 | < dl | 0.0071 | 0.0103 | 0.0030 | 0.0047 |
| 3 | 0.008 | 0.0030 | 0.0026 | 0.0022 | 0.0025 | 0.0039 | 0.0021 | 0.002 | 0.0015 | 0.0079 | 0.0077 | 0.0039 | 0.0051 |
| 4 | 0.008 | 0.0022 | 0.0027 | < dl | 0.0080 | 0.0042 | 0.0023 | 0.006 | 0.0033 | 0.0092 | 0.0074 | 0.0036 | 0.0052 |
| 5 | 0.008 | 0.0019 | 0.0024 | < dl | 0.0046 | 0.0044 | 0.0020 | 0.006 | 0.0016 | 0.0087 | 0.0080 | 0.0059 | 0.0057 |
| 6 | 0.008 | 0.0019 | 0.0029 | 0.0034 | 0.0033 | 0.0040 | 0.0016 | 0.004 | 0.0020 | 0.0075 | 0.0085 | 0.0039 | 0.0055 |
| 7 | 0.011 | 0.0024 | 0.0021 | < dl | 0.0038 | 0.0041 | < dl | 0.004 | 0.0017 | | | | |
| 8 | 0.010 | 0.0020 | < dl | 0.0016 | 0.0032 | 0.0032 | < dl | 0.004 | 0.0016 | | | | |
| 9 | 0.012 | 0.0034 | < dl | < dl | 0.0040 | 0.0033 | 0.0018 | 0.005 | 0.0018 | | | | |
| 10 | 0.012 | 0.0029 | < dl | 0.0021 | 0.0045 | 0.0042 | 0.0015 | 0.004 | 0.0016 | | | | |
| Avg. | 0.010 | 0.0026 | 0.0024 | 0.0016 | 0.0037 | 0.0040 | 0.0017 | 0.004 | 0.0016 | 0.0078 | 0.0082 | 0.0042 | 0.0050 |
| sd | 0.002 | 0.0005 | 0.0005 | 0.0005 | 0.0008 | 0.0005 | 0.0005 | 0.001 | 0.0002 | 0.0011 | 0.0011 | 0.0010 | 0.0007 |
| %RSD | 18.9 | 21.0 | 22.6 | 27.1 | 20.4 | 11.4 | 27.1 | 29.4 | 13.3 | 14.0 | 13.6 | 24.3 | 13.6 |

Table 2.36: Results for chromium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|-------------|--------------|------|-------|-------|-------------|-------------|--------------|--------|--------|---------------|---------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.14 | 0.05 | 0.017 | 0.13 | 0.099 | 0.066 | 0.05 | 0.20 | 0.019 | 0.0192 | 0.0100 | 0.0187 | 0.0071 |
| 2 | 0.16 | 0.07 | 0.015 | 0.16 | 0.078 | 0.065 | 0.04 | 0.04 | 0.017 | 0.0172 | 0.0131 | 0.0058 | 0.0275 |
| 3 | 0.16 | 0.12 | 0.025 | 0.11 | 0.083 | 0.047 | 0.04 | 0.02 | 0.029 | 0.0218 | 0.0132 | 0.0071 | 0.0261 |
| 4 | 0.15 | 0.06 | 0.067 | 0.12 | 0.091 | 0.055 | 0.04 | 0.06 | 0.034 | 0.0226 | 0.0124 | 0.0065 | 0.0180 |
| 5 | 0.21 | 0.06 | 0.095 | 0.12 | 0.080 | 0.057 | 0.03 | 0.07 | 0.106 | 0.0096 | 0.0125 | 0.0087 | 0.0279 |
| 6 | 0.22 | 0.06 | 0.015 | 0.14 | 0.075 | 0.048 | 0.04 | 0.03 | 0.027 | 0.0150 | 0.0118 | 0.0078 | 0.0250 |
| 7 | 0.19 | 0.04 | 0.018 | 0.11 | 0.093 | 0.039 | 0.06 | 0.04 | 0.024 | | | | |
| 8 | 0.22 | 0.03 | 0.023 | 0.17 | 0.085 | 0.038 | 0.07 | 0.05 | 0.028 | | | | |
| 9 | 0.22 | 0.04 | 0.022 | 0.12 | 0.085 | 0.055 | 0.04 | 0.04 | 0.078 | | | | |
| 10 | 0.19 | 0.05 | 0.024 | 0.12 | 0.077 | 0.046 | 0.10 | 0.05 | 0.025 | | | | |
| 11 | 0.11 | 0.03 | 0.021 | | | | | | | | | | |
| 12 | 0.11 | 0.05 | 0.020 | | | | | | | | | | |
| 13 | 0.16 | 0.04 | 0.016 | | | | | | | | | | |
| 14 | 0.11 | 0.05 | 0.021 | | | | | | | | | | |
| 15 | 0.12 | 0.05 | 0.022 | | | | | | | | | | |
| 16 | 0.12 | 0.05 | 0.017 | | | | | | | | | | |
| 17 | 0.12 | 0.04 | 0.024 | | | | | | | | | | |
| 18 | 0.12 | 0.05 | 0.020 | | | | | | | | | | |
| Avg. | 0.16 | 0.05 | 0.020 | 0.13 | 0.085 | 0.052 | 0.04 | 0.04 | 0.025 | 0.0176 | 0.0122 | 0.0072 | 0.0249 |
| Sd | 0.04 | 0.01 | 0.003 | 0.02 | 0.008 | 0.009 | 0.01 | 0.01 | 0.006 | 0.0048 | 0.0012 | 0.0011 | 0.0040 |
| %RSD | 26.8 | 21.2 | 16.8 | 16.3 | 9.1 | 18.8 | 25.7 | 26.9 | 21.6 | 27.4 | 9.7 | 15.7 | 16.2 |

Table 2.20: Results for barium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------------|---------------|-------------|--------------|--------|--------|--------|-------|--------|--------|---------------|---------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.03 | 0.006 | 0.0031 | 0.07 | 0.015 | 0.0062 | 0.0029 | 0.0035 | 0.012 | 0.0061 | 0.0216 | 0.0048 | 0.0060 |
| 2 | 0.03 | 0.005 | 0.0023 | 0.12 | 0.017 | 0.0065 | 0.0031 | 0.0046 | 0.012 | 0.0059 | 0.0313 | 0.0071 | 0.0147 |
| 3 | 0.04 | 0.007 | 0.0025 | 0.11 | 0.006 | 0.0061 | 0.0024 | 0.0039 | 0.010 | 0.0058 | 0.0185 | 0.0069 | 0.0146 |
| 4 | 0.03 | 0.007 | 0.0020 | 0.14 | 0.021 | 0.0064 | 0.0021 | 0.0045 | 0.012 | 0.0070 | 0.0182 | 0.0129 | 0.0144 |
| 5 | 0.05 | 0.005 | 0.0019 | 0.08 | 0.014 | 0.0067 | 0.0023 | 0.0048 | 0.016 | 0.0060 | 0.0195 | 0.0046 | 0.0151 |
| 6 | 0.05 | 0.006 | 0.0034 | 0.17 | 0.013 | 0.0061 | 0.0016 | 0.0041 | 0.011 | 0.0065 | 0.0200 | 0.0044 | 0.0148 |
| 7 | 0.05 | 0.009 | 0.0028 | 0.13 | 0.013 | 0.0064 | 0.0016 | 0.0051 | 0.012 | | | | |
| 8 | 0.06 | 0.011 | 0.0024 | 0.15 | 0.018 | 0.0046 | 0.0021 | 0.0047 | 0.014 | | | | |
| 9 | 0.06 | 0.015 | 0.0017 | 0.12 | 0.041 | 0.0052 | 0.0023 | 0.0045 | 0.012 | | | | |
| 10 | 0.06 | 0.011 | 0.0021 | 0.14 | 0.010 | 0.0057 | 0.0025 | 0.0039 | 0.012 | | | | |
| 11 | 0.07 | 0.010 | 0.0020 | | | | | | 0.012 | | | | |
| 12 | 0.06 | 0.012 | 0.0040 | | | | | | 0.012 | | | | |
| 13 | 0.06 | 0.009 | 0.0010 | | | | | | 0.010 | | | | |
| 14 | 0.06 | 0.010 | 0.0025 | | | | | | 0.013 | | | | |
| 15 | 0.06 | 0.008 | 0.0018 | | | | | | 0.012 | | | | |
| 16 | 0.06 | 0.008 | 0.0022 | | | | | | 0.012 | | | | |
| 17 | 0.06 | 0.007 | 0.0030 | | | | | | 0.012 | | | | |
| 18 | 0.09 | 0.010 | 0.0020 | | | | | | 0.013 | | | | |
| Avg. | 0.06 | 0.008 | 0.0023 | 0.12 | 0.015 | 0.0060 | 0.0023 | 0.0044 | 0.012 | 0.0062 | 0.0215 | 0.0056 | 0.0147 |
| sd | 0.01 | 0.002 | 0.0006 | 0.03 | 0.004 | 0.0007 | 0.0005 | 0.0005 | 0.001 | 0.0005 | 0.0049 | 0.0013 | 0.0003 |
| %RSD | 19.1 | 26.5 | 25.6 | 22.2 | 24.4 | 10.9 | 21.1 | 11.3 | 11.2 | 7.3 | 23.0 | 23.8 | 1.8 |

Table 2.21: Results for boron determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------------|--------------|-------|--------------|-------|-------|-------|-------|--------|--------|---------------|---------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.050 | 0.014 | 0.007 | 0.006 | 0.012 | 0.016 | 0.007 | < dl | 0.011 | 0.0178 | 0.0542 | 0.0071 | 0.0066 |
| 2 | 0.056 | 0.014 | 0.006 | 0.013 | 0.017 | 0.018 | 0.008 | 0.005 | 0.011 | 0.0197 | 0.0860 | 0.0069 | 0.0195 |
| 3 | 0.069 | 0.012 | 0.006 | 0.010 | 0.011 | 0.017 | <dl | < dl | 0.014 | 0.0203 | 0.0460 | 0.0098 | 0.0178 |
| 4 | 0.052 | 0.010 | 0.006 | 0.013 | 0.023 | 0.016 | < dl | 0.007 | 0.014 | 0.0206 | 0.0545 | 0.0142 | 0.0184 |
| 5 | 0.082 | 0.011 | 0.006 | 0.005 | 0.021 | 0.016 | 0.005 | 0.006 | 0.015 | 0.0207 | 0.0500 | 0.0100 | 0.0214 |
| 6 | 0.079 | 0.012 | 0.009 | 0.008 | 0.019 | 0.015 | 0.009 | < dl | 0.012 | 0.0195 | 0.0560 | 0.0055 | 0.0190 |
| 7 | 0.088 | 0.017 | 0.004 | 0.009 | 0.017 | 0.014 | 0.007 | < dl | 0.012 | | | | |
| 8 | 0.104 | 0.016 | 0.004 | 0.008 | 0.027 | 0.010 | 0.007 | < dl | 0.014 | | | | |
| 9 | 0.100 | 0.030 | 0.004 | 0.006 | 0.017 | 0.011 | < dl | 0.006 | 0.012 | | | | |
| 10 | 0.096 | 0.020 | 0.002 | 0.007 | 0.025 | 0.016 | 0.008 | < dl | 0.014 | | | | |
| 11 | 0.089 | 0.021 | 0.005 | | | | | | 0.012 | | | | |
| 12 | 0.091 | 0.019 | 0.005 | | | | | | 0.014 | | | | |
| 13 | 0.074 | 0.017 | 0.005 | | | | | | 0.013 | | | | |
| 14 | 0.089 | 0.014 | 0.006 | | | | | | 0.013 | | | | |
| 15 | 0.094 | 0.019 | 0.006 | | | | | | 0.012 | | | | |
| 16 | 0.110 | 0.018 | 0.004 | | | | | | 0.015 | | | | |
| 17 | 0.080 | 0.020 | 0.007 | | | | | | 0.013 | | | | |
| 18 | 0.089 | 0.021 | 0.005 | | | | | | 0.014 | | | | |
| Avg. | 0.085 | 0.016 | 0.005 | 0.007 | 0.020 | 0.015 | 0.007 | < dl | 0.013 | 0.0198 | 0.0578 | 0.0079 | 0.0192 |
| Sd | 0.002 | 0.003 | 0.001 | 0.001 | 0.005 | 0.003 | 0.001 | - | 0.001 | 0.0011 | 0.0143 | 0.0020 | 0.0014 |
| %RSD | 18.4 | 22.7 | 19.8 | 19.6 | 23.6 | 17.7 | 19.7 | - | 9.7 | 5.4 | 24.7 | 24.9 | 7.2 |

Table 2.22: Results for strontium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------------|---------------|------|-------------|-------------|--------------|------|--------|--------|--------|--------|--------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.028 | 0.033 | 0.0051 | 0.07 | 0.08 | 0.10 | 0.007 | 0.11 | 0.0046 | 0.0223 | 0.0244 | 0.0047 | 0.0063 |
| 2 | 0.033 | 0.035 | 0.0036 | 0.06 | 0.08 | 0.10 | 0.005 | 0.11 | 0.0032 | 0.0202 | 0.0347 | 0.0071 | 0.0098 |
| 3 | 0.033 | 0.022 | 0.0017 | 0.08 | 0.01 | 0.07 | 0.005 | 0.13 | 0.0030 | 0.0203 | 0.0187 | 0.0064 | 0.0100 |
| 4 | 0.033 | 0.023 | 0.0016 | 0.07 | 0.06 | 0.09 | 0.010 | 0.11 | 0.0039 | 0.0200 | 0.0177 | 0.0069 | 0.0090 |
| 5 | 0.035 | 0.014 | 0.0012 | 0.05 | 0.04 | 0.10 | 0.005 | 0.11 | 0.0043 | 0.0225 | 0.0190 | 0.0064 | 0.0100 |
| 6 | 0.022 | 0.020 | 0.0069 | 0.05 | 0.04 | 0.08 | 0.006 | 0.10 | 0.0025 | 0.0210 | 0.0200 | 0.0044 | 0.0080 |
| 7 | 0.033 | 0.012 | 0.0027 | 0.11 | 0.04 | 0.11 | 0.004 | 0.13 | 0.0034 | | | | |
| 8 | 0.036 | 0.013 | 0.0052 | 0.06 | 0.05 | 0.08 | 0.005 | 0.13 | 0.0041 | | | | |
| 9 | 0.039 | 0.015 | 0.0024 | 0.09 | 0.09 | 0.06 | 0.007 | 0.11 | 0.0030 | | | | |
| 10 | 0.046 | 0.010 | 0.0021 | 0.07 | 0.04 | 0.10 | 0.006 | 0.13 | 0.0035 | | | | |
| 11 | 0.039 | 0.019 | 0.0018 | | | | | | 0.0032 | | | | |
| 12 | 0.037 | 0.018 | 0.0023 | | | | | | 0.0028 | | | | |
| 13 | 0.038 | 0.037 | 0.0032 | | | | | | 0.0027 | | | | |
| 14 | 0.039 | 0.020 | 0.0037 | | | | | | 0.0041 | | | | |
| 15 | 0.046 | 0.029 | 0.0022 | | | | | | 0.0040 | | | | |
| 16 | 0.039 | 0.019 | 0.0028 | | | | | | 0.0036 | | | | |
| 17 | 0.034 | 0.006 | 0.0032 | | | | | | 0.0029 | | | | |
| 18 | 0.038 | 0.024 | 0.0019 | | | | | | 0.0035 | | | | |
| Avg. | 0.036 | 0.020 | 0.0024 | 0.07 | 0.06 | 0.09 | 0.005 | 0.12 | 0.0035 | 0.021 | 0.0224 | 0.0060 | 0.0089 |
| sd | 0.006 | 0.007 | 0.0008 | 0.01 | 0.02 | 0.01 | 0.001 | 0.01 | 0.0006 | 0.0011 | 0.0065 | 0.0011 | 0.0015 |
| %RSD | 15.4 | 35.8 | 31.1 | 21.4 | 34.3 | 13.6 | 19.6 | 9.7 | 17.4 | 5.2 | 28.8 | 19.2 | 16.6 |

Table 2.23: Results for nickel determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------|--------------|------|--------------|------|--------------|--------------|--------------|------|------|------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.007 | < dl | 0.05 | < dl | 0.020 | < dl | 0.017 | 0.060 | 0.010 | < dl | < dl | < dl | < dl |
| 2 | 0.009 | < dl | 0.03 | < dl | 0.013 | < dl | 0.015 | 0.088 | 0.023 | < dl | < dl | < dl | < dl |
| 3 | 0.017 | < dl | 0.03 | < dl | 0.024 | < dl | 0.004 | 0.045 | 0.017 | < dl | < dl | < dl | < dl |
| 4 | 0.011 | < dl | 0.04 | < dl | 0.015 | < dl | 0.017 | 0.024 | 0.019 | < dl | < dl | < dl | < dl |
| 5 | 0.021 | < dl | 0.04 | < dl | 0.008 | < dl | 0.014 | 0.023 | 0.016 | < dl | < dl | < dl | < dl |
| 6 | 0.021 | < dl | 0.05 | < dl | 0.009 | < dl | 0.019 | 0.001 | 0.018 | < dl | < dl | < dl | < dl |
| 7 | 0.022 | < dl | 0.03 | < dl | 0.006 | < dl | 0.036 | 0.003 | 0.091 | | | | |
| 8 | 0.033 | < dl | 0.02 | < dl | 0.001 | < dl | 0.018 | 0.018 | 0.036 | | | | |
| 9 | 0.015 | < dl | 0.01 | < dl | 0.010 | < dl | 0.015 | 0.023 | 0.057 | | | | |
| 10 | 0.017 | < dl | 0.001 | < dl | 0.010 | < dl | 0.015 | 0.035 | 0.021 | | | | |
| Avg. | 0.020 | < dl | 0.03 | < dl | 0.010 | < dl | 0.016 | 0.028 | 0.018 | < dl | < dl | < dl | < dl |
| sd | 0.007 | - | 0.01 | - | 0.003 | - | 0.002 | 0.009 | 0.004 | - | - | - | - |
| %RSD | 33.6 | - | 33.3 | - | 29.3 | - | 11.2 | 35.5 | 22.6 | - | - | - | - |

Table 2.24: Results for manganese determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------------|--------------|-------------|-------------|--------------|--------------|--------------|-------------|--------|---------------|--------|--------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.14 | 0.081 | 0.028 | 1.16 | 0.20 | 0.066 | 0.051 | 0.059 | 0.11 | 0.0567 | 0.1181 | 0.0555 | 0.0344 |
| 2 | 0.17 | 0.062 | 0.020 | 0.99 | 0.15 | 0.072 | 0.053 | 0.077 | 0.13 | 0.0624 | 0.2156 | 0.0573 | 0.0494 |
| 3 | 0.35 | 0.065 | 0.020 | 1.17 | 0.03 | 0.060 | 0.048 | 0.064 | 0.08 | 0.0590 | 0.1008 | 0.0380 | 0.0515 |
| 4 | 0.3 | 0.067 | 0.017 | 0.78 | 0.17 | 0.063 | 0.049 | 0.063 | 0.11 | 0.0593 | 0.1132 | 0.0666 | 0.0402 |
| 5 | 0.64 | 0.058 | 0.014 | 0.66 | 0.09 | 0.062 | 0.042 | 0.061 | 0.13 | 0.0624 | 0.1120 | 0.0386 | 0.0497 |
| 6 | 0.70 | 0.068 | 0.029 | 0.72 | 0.10 | 0.057 | 0.044 | 0.061 | 0.14 | 0.0610 | 0.1010 | 0.0479 | 0.0452 |
| 7 | 0.75 | 0.088 | 0.019 | 2.27 | 0.12 | 0.069 | 0.038 | 0.063 | 0.13 | | | | |
| 8 | 0.90 | 0.082 | 0.019 | 0.68 | 0.16 | 0.042 | 0.042 | 0.065 | 0.10 | | | | |
| 9 | 0.58 | 0.147 | 0.011 | 1.14 | 0.26 | 0.054 | 0.044 | 0.054 | 0.09 | | | | |
| 10 | 0.63 | 0.084 | 0.014 | 0.98 | 0.08 | 0.061 | 0.055 | 0.051 | 0.10 | | | | |
| 11 | 0.58 | 0.058 | 0.015 | | | | | | 0.11 | | | | |
| 12 | 0.60 | 0.066 | 0.018 | | | | | | 0.13 | | | | |
| 13 | 0.59 | 0.075 | 0.022 | | | | | | 0.12 | | | | |
| 14 | 0.78 | 0.069 | 0.019 | | | | | | 0.10 | | | | |
| 15 | 0.79 | 0.084 | 0.021 | | | | | | 0.13 | | | | |
| 16 | 0.67 | 0.059 | 0.016 | | | | | | 0.12 | | | | |
| 17 | 0.72 | 0.064 | 0.017 | | | | | | 0.11 | | | | |
| 18 | 0.98 | 0.082 | 0.018 | | | | | | 0.13 | | | | |
| Avg. | 0.64 | 0.070 | 0.019 | 0.92 | 0.13 | 0.063 | 0.048 | 0.060 | 0.11 | 0.060 | 0.1090 | 0.0507 | 0.0451 |
| Sd | 0.15 | 0.009 | 0.004 | 0.21 | 0.04 | 0.006 | 0.005 | 0.005 | 0.01 | 0.0022 | 0.0078 | 0.0113 | 0.0066 |
| %RSD | 24.1 | 13.6 | 18.9 | 23.2 | 30.9 | 9.3 | 10.2 | 7.5 | 12.8 | 3.7 | 7.1 | 22.2 | 14.7 |

Table 2.25: Results for cadmium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|---------------|------|------|------|---------------|------|------|--------|------|------|------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.007 | 0.0016 | < dl | < dl | < dl | 0.0018 | < dl | < dl | 0.0016 | < dl | < dl | < dl | < dl |
| 2 | 0.007 | 0.0015 | < dl | < dl | < dl | 0.0019 | < dl | < dl | 0.0017 | < dl | < dl | < dl | < dl |
| 3 | 0.008 | 0.0015 | < dl | < dl | < dl | 0.0018 | < dl | < dl | 0.0018 | < dl | < dl | < dl | < dl |
| 4 | 0.007 | 0.0015 | < dl | < dl | < dl | 0.0018 | < dl | < dl | 0.0019 | < dl | < dl | < dl | < dl |
| 5 | 0.011 | 0.0020 | < dl | < dl | < dl | 0.0020 | < dl | < dl | 0.0024 | < dl | < dl | < dl | < dl |
| 6 | 0.011 | 0.0017 | < dl | < dl | < dl | 0.0017 | < dl | < dl | 0.0019 | < dl | < dl | < dl | < dl |
| 7 | 0.012 | 0.0034 | < dl | < dl | < dl | 0.0019 | < dl | < dl | 0.0018 | | | | |
| 8 | 0.010 | < dl | < dl | < dl | < dl | 0.0125 | < dl | < dl | 0.0021 | | | | |
| 9 | 0.010 | < dl | < dl | < dl | < dl | 0.0015 | < dl | < dl | 0.0018 | | | | |
| 10 | 0.006 | < dl | < dl | < dl | < dl | 0.0016 | < dl | < dl | 0.0021 | | | | |
| Avg. | 0.009 | 0.0015 | < dl | < dl | < dl | 0.0018 | < dl | < dl | 0.0019 | < dl | < dl | < dl | < dl |
| sd | 0.002 | 0.0002 | - | - | - | 0.0002 | - | - | 0.0002 | - | - | - | - |
| %RSD | 24.1 | 16.4 | - | - | - | 8.8 | - | - | 12.2 | - | - | - | - |

Table 2.26: Results for iron determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------|------|-------------|-------------|------------|------|-----|-----|-----|------|------------|------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 18.8 | 5.7 | 1.5 | 33.2 | 20.9 | 6.7 | 4.7 | 3.9 | 5.7 | 9.1 | 25.4 | 3.7 | 4.4 |
| 2 | 19.3 | 5.2 | 1.0 | 19.8 | 15.7 | 7.1 | 4.7 | 4.5 | 5.6 | 9.9 | 35.7 | 4.2 | 10.2 |
| 3 | 20.1 | 4.9 | 1.1 | 30.5 | 18.9 | 6.7 | 4.7 | 4.2 | 4.5 | 9.7 | 21.5 | 4.6 | 9.3 |
| 4 | 17.7 | 5.0 | 1.1 | 34.3 | 21.7 | 6.6 | 3.9 | 3.9 | 5.1 | 9.6 | 22.2 | 6.9 | 9.6 |
| 5 | 22.3 | 4.9 | 1.0 | 18.2 | 17.7 | 6.6 | 3.4 | 4.0 | 6.3 | 8.9 | 24.3 | 4.2 | 10.7 |
| 6 | 21.9 | 5.3 | 1.8 | 28.5 | 10.1 | 5.9 | 4.2 | 3.9 | 4.6 | 9.2 | 22.5 | 3.4 | 9.8 |
| 7 | 23.8 | 7.6 | 1.1 | 34.5 | 12.5 | 6.6 | 3.3 | 3.8 | 4.9 | | | | |
| 8 | 36.9 | 7.1 | 1.0 | 30.3 | 11.3 | 4.1 | 3.7 | 4.3 | 5.6 | | | | |
| 9 | 34.0 | 13.0 | 1.0 | 31.2 | 18.1 | 5.1 | 4.3 | 3.6 | 4.8 | | | | |
| 10 | 20.1 | 8.7 | 0.9 | 27.1 | 16.7 | 5.6 | 4.0 | 3.8 | 5.4 | | | | |
| 11 | 32.2 | 5.3 | 1.2 | | | | | | 5.3 | | | | |
| 12 | 31.8 | 5.5 | 1.0 | | | | | | 5.1 | | | | |
| 13 | 34.6 | 5.3 | 1.1 | | | | | | 5.0 | | | | |
| 14 | 31.4 | 6.1 | 1.0 | | | | | | 4.7 | | | | |
| 15 | 36.9 | 4.1 | 1.1 | | | | | | 5.1 | | | | |
| 16 | 31.0 | 6.7 | 1.0 | | | | | | 4.8 | | | | |
| 17 | 28.9 | 4.7 | 1.1 | | | | | | 4.6 | | | | |
| 18 | 30.7 | 5.3 | 1.0 | | | | | | 5.1 | | | | |
| Avg. | 29.1 | 5.5 | 1.1 | 31.2 | 17.8 | 6.3 | 4.1 | 4.0 | 5.2 | 9.4 | 25.3 | 4.0 | 9.9 |
| Sd | 5.9 | 0.9 | 0.1 | 2.7 | 2.9 | 0.6 | 0.5 | 0.3 | 0.4 | 0.4 | 5.3 | 0.5 | 0.5 |
| %RSD | 20.3 | 16.4 | 13.1 | 8.6 | 16.6 | 9.9 | 12.9 | 7.4 | 9.1 | 4.1 | 21.0 | 11.7 | 5.5 |

Table 2.27: Results for cobalt determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------|------|------|------|------|------|------|------|------|--------|------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.009 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.0078 | < dl | < dl |
| 2 | 0.010 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.0095 | < dl | < dl |
| 3 | 0.012 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.0086 | < dl | < dl |
| 4 | 0.010 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.0091 | < dl | < dl |
| 5 | 0.011 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.0082 | < dl | < dl |
| 6 | 0.019 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.0090 | < dl | < dl |
| 7 | 0.020 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| 8 | 0.013 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| 9 | 0.017 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| 10 | 0.011 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| Avg. | 0.011 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.0087 | < dl | < dl |
| Sd | 0.003 | - | - | - | - | - | - | - | - | - | 0.0006 | - | - |
| %RSD | 21.8 | - | - | - | - | - | - | - | - | - | 7.2 | - | - |

Table 2.28: Results for magnesium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------|------|------|------|------|------|-----|------|------|------|------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 3.0 | 1.3 | 0.06 | 6.3 | 9.2 | 1.7 | 0.79 | 1.0 | 0.59 | 1.63 | 3.8 | 0.69 | 0.77 |
| 2 | 3.0 | 1.2 | 0.06 | 5.3 | 7.6 | 1.7 | 0.73 | 1.2 | 0.51 | 1.63 | 4.9 | 0.70 | 1.54 |
| 3 | 3.5 | 1.2 | 0.06 | 7.3 | 1.1 | 1.7 | 0.58 | 1.3 | 0.45 | 1.74 | 3.5 | 0.88 | 1.55 |
| 4 | 2.6 | 1.2 | 0.05 | 7.8 | 8.8 | 1.7 | 0.82 | 1.2 | 0.55 | 1.73 | 3.2 | 0.94 | 1.43 |
| 5 | 3.7 | 0.8 | 0.06 | 6.4 | 3.1 | 1.7 | 0.65 | 1.4 | 0.67 | 1.64 | 3.1 | 0.78 | 1.66 |
| 6 | 3.9 | 0.9 | 0.08 | 6.4 | 5.4 | 1.5 | 0.64 | 1.2 | 0.37 | 1.65 | 3.7 | 0.69 | 1.50 |
| 7 | 4.1 | 1.1 | 0.07 | 8.6 | 7.2 | 1.8 | 0.66 | 1.5 | 0.45 | | | | |
| 8 | 7.3 | 1.0 | 0.11 | 6.4 | 6.2 | 1.1 | 0.67 | 1.6 | 0.56 | | | | |
| 9 | 6.4 | 1.9 | 0.04 | 6.8 | 6.8 | 1.3 | 0.72 | 1.2 | 0.48 | | | | |
| 10 | 3.4 | 1.2 | 0.03 | 5.4 | 8.7 | 1.3 | 0.79 | 1.3 | 0.56 | | | | |
| 11 | 3.1 | 0.9 | 0.09 | | | | | | | | | | |
| 12 | 3.0 | 0.9 | 0.11 | | | | | | | | | | |
| 13 | 3.7 | 1.0 | 0.12 | | | | | | | | | | |
| 14 | 3.1 | 1.0 | 0.08 | | | | | | | | | | |
| 15 | 3.6 | 1.1 | 0.06 | | | | | | | | | | |
| 16 | 3.9 | 0.9 | 0.07 | | | | | | | | | | |
| 17 | 3.8 | 1.1 | 0.06 | | | | | | | | | | |
| 18 | 3.5 | 1.1 | 0.07 | | | | | | | | | | |
| Avg. | 3.4 | 1.1 | 0.06 | 6.5 | 7.5 | 1.6 | 0.71 | 1.3 | 0.53 | 1.67 | 3.7 | 0.78 | 1.4 |
| Sd | 0.4 | 0.1 | 0.01 | 0.8 | 1.3 | 0.2 | 0.08 | 0.1 | 0.07 | 0.05 | 0.7 | 0.11 | 0.3 |
| %RSD | 12.1 | 13.8 | 23.7 | 12.6 | 17.9 | 12.5 | 9.5 | 9.9 | 13.6 | 3.1 | 17.5 | 13.8 | 22.8 |

Table 2.29: Results for vanadium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|--------------|-------|---------------|--------------|------|--------|--------|--------|---------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.06 | 0.021 | 0.013 | 0.008 | 0.008 | 0.013 | 0.0183 | 0.012 | < dl | 0.0095 | 0.0215 | 0.0067 | 0.0048 |
| 2 | 0.06 | 0.021 | 0.014 | 0.012 | 0.016 | 0.014 | 0.0066 | 0.013 | < dl | 0.0110 | 0.0235 | 0.0031 | 0.0101 |
| 3 | 0.07 | 0.020 | 0.013 | 0.010 | 0.009 | 0.015 | 0.0059 | 0.011 | < dl | 0.0116 | 0.0208 | 0.0044 | 0.0095 |
| 4 | 0.06 | 0.015 | 0.015 | 0.006 | 0.013 | 0.013 | 0.0059 | 0.014 | < dl | 0.0113 | 0.0125 | 0.0052 | 0.0086 |
| 5 | 0.09 | 0.014 | 0.013 | 0.006 | 0.007 | 0.021 | 0.0057 | 0.014 | < dl | 0.0078 | 0.0210 | 0.0064 | 0.0100 |
| 6 | 0.08 | 0.014 | 0.016 | 0.013 | 0.009 | 0.019 | 0.0183 | 0.014 | < dl | 0.0088 | 0.0155 | 0.0051 | 0.009 |
| 7 | 0.09 | 0.019 | 0.012 | 0.008 | 0.011 | 0.020 | 0.0054 | 0.003 | < dl | | | | |
| 8 | 0.04 | 0.017 | 0.010 | 0.009 | 0.008 | 0.016 | 0.0051 | 0.003 | < dl | | | | |
| 9 | 0.03 | 0.025 | 0.007 | 0.007 | 0.012 | 0.019 | 0.0050 | 0.011 | < dl | | | | |
| 10 | 0.08 | 0.022 | 0.004 | 0.007 | 0.009 | 0.021 | 0.0058 | 0.012 | < dl | | | | |
| 11 | 0.10 | 0.025 | 0.010 | | | | | | < dl | | | | |
| 12 | 0.10 | 0.018 | 0.010 | | | | | | < dl | | | | |
| 13 | 0.11 | 0.021 | 0.011 | | | | | | < dl | | | | |
| 14 | 0.10 | 0.020 | 0.011 | | | | | | < dl | | | | |
| 15 | 0.10 | 0.017 | 0.013 | | | | | | < dl | | | | |
| 16 | 0.11 | 0.014 | 0.012 | | | | | | < dl | | | | |
| 17 | 0.11 | 0.014 | 0.013 | | | | | | < dl | | | | |
| 18 | 0.09 | 0.015 | 0.014 | | | | | | < dl | | | | |
| Avg. | 0.09 | 0.018 | 0.012 | 0.008 | 0.010 | 0.017 | 0.0057 | 0.013 | < dl | 0.0100 | 0.0191 | 0.0052 | 0.0094 |
| Sd | 0.02 | 0.003 | 0.002 | 0.002 | 0.002 | 0.003 | 0.0005 | 0.001 | - | 0.0015 | 0.0042 | 0.0013 | 0.0006 |
| %RSD | 19.1 | 16.5 | 14.3 | 22.1 | 19.7 | 18.9 | 9.0 | 9.8 | - | 15.3 | 21.9 | 25.7 | 6.8 |

Table 2.30: Results for sodium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------|------|------|------|------|------|------|------|-----|-----|------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 6.7 | 1.4 | 0.21 | 0.32 | 10.9 | 2.7 | 2.4 | 1.6 | 0.6 | 2.8 | 5.0 | 2.3 | 2.8 |
| 2 | 6.1 | 1.6 | 0.43 | 0.35 | 6.5 | 2.4 | 1.6 | 2.4 | 0.3 | 2.5 | 6.0 | 2.7 | 3.2 |
| 3 | 8.1 | 1.7 | 0.28 | 0.37 | 5.2 | 3.1 | 1.6 | 3.2 | 0.3 | 3.1 | 5.6 | 3.2 | 3.4 |
| 4 | 5.2 | 1.6 | 0.31 | 0.29 | 6.9 | 3.5 | 3.1 | 1.6 | 0.3 | 3.1 | 5.0 | 0.8 | 3.1 |
| 5 | 7.2 | 1.8 | 0.45 | 1.30 | 5.4 | 3.0 | 2.2 | 2.5 | 0.7 | 3.0 | 5.2 | 3.2 | 3.8 |
| 6 | 8.1 | 1.9 | 0.67 | 2.13 | 5.3 | 3.3 | 1.9 | 2.2 | 0.3 | 2.7 | 5.7 | 2.4 | 3.4 |
| 7 | 7.8 | 1.8 | 0.43 | 0.33 | 5.2 | 3.8 | 1.9 | 3.2 | 0.4 | | | | |
| 8 | 10.5 | 1.7 | 0.71 | 0.21 | 6.8 | 1.9 | 2.3 | 3.4 | 0.3 | | | | |
| 9 | 7.1 | 2.8 | 0.24 | 0.33 | 9.0 | 2.5 | 2.5 | 2.2 | 0.3 | | | | |
| 10 | 5.6 | 1.8 | 0.27 | 0.36 | 4.7 | 3.0 | 2.8 | 2.3 | 0.6 | | | | |
| 11 | 7.7 | 2.7 | 0.29 | | | | | | 0.4 | | | | |
| 12 | 7.7 | 1.7 | 0.29 | | | | | | 0.4 | | | | |
| 13 | 5.4 | 3.3 | 0.22 | | | | | | 0.4 | | | | |
| 14 | 5.5 | 2.2 | 0.35 | | | | | | 0.7 | | | | |
| 15 | 4.0 | 2.4 | 0.32 | | | | | | 0.6 | | | | |
| 16 | 4.1 | 1.5 | 0.29 | | | | | | 0.5 | | | | |
| 17 | 4.6 | 1.6 | 0.43 | | | | | | 0.4 | | | | |
| 18 | 4.5 | 1.6 | 0.33 | | | | | | 0.4 | | | | |
| Avg. | 6.2 | 1.8 | 0.32 | 0.32 | 5.8 | 2.9 | 2.3 | 2.7 | 0.4 | 2.9 | 5.4 | 2.8 | 3.3 |
| Sd | 1.4 | 0.3 | 0.08 | 0.05 | 0.8 | 0.6 | 0.5 | 0.5 | 0.1 | 0.2 | 0.4 | 0.4 | 0.3 |
| %RSD | 23.4 | 14.9 | 24.5 | 15.5 | 14.7 | 19.1 | 22.3 | 19.0 | 25.2 | 8.4 | 7.6 | 15.5 | 10.3 |

Table 2.31: Results for calcium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------------|-------------|------------|-------------|------|------------|------|-------------|-----|------|------------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 3.5 | 7.1 | 0.38 | 1.2 | 12.5 | 19.2 | 0.7 | 16.1 | 0.52 | 5.5 | 1.9 | 0.71 | 0.81 |
| 2 | 2.5 | 7.4 | 0.28 | 1.3 | 10.0 | 19.4 | 0.7 | 18.4 | 0.42 | 5.3 | 2.6 | 0.84 | 0.87 |
| 3 | 1.9 | 3.4 | 0.40 | 1.4 | 4.9 | 14.5 | 0.5 | 20.9 | 0.35 | 5.5 | 2.1 | 0.91 | 1.00 |
| 4 | 1.4 | 3.4 | 0.31 | 1.6 | 6.7 | 16.9 | 1.1 | 20.5 | 0.39 | 5.7 | 2.0 | 1.4 | 0.82 |
| 5 | 2.2 | 2.1 | 0.32 | 1.9 | 3.6 | 24.9 | 0.4 | 20.4 | 0.49 | 5.5 | 1.8 | 0.91 | 0.93 |
| 6 | 2.3 | 3.3 | 0.25 | 4.4 | 2.8 | 21.0 | 0.8 | 17.9 | 0.28 | 5.6 | 2.4 | 0.71 | 0.85 |
| 7 | 3.0 | 2.5 | 0.81 | 2.4 | 4.5 | 25.4 | 0.5 | 23.6 | 0.39 | | | | |
| 8 | 3.5 | 3.3 | 0.33 | 5.1 | 4.2 | 16.5 | 0.5 | 22.9 | 0.45 | | | | |
| 9 | 3.5 | 0.9 | 0.60 | 1.6 | 5.9 | 15.0 | 0.7 | 18.4 | 0.33 | | | | |
| 10 | 2.5 | 3.4 | 0.27 | 2.0 | 3.8 | 18.4 | 0.6 | 19.5 | 0.37 | | | | |
| 11 | 1.8 | 2.3 | | | | | | | 0.36 | | | | |
| 12 | 1.9 | 2.8 | | | | | | | 0.29 | | | | |
| 13 | 1.8 | 2.2 | | | | | | | 0.50 | | | | |
| 14 | 1.5 | 2.6 | | | | | | | 0.47 | | | | |
| 15 | 1.9 | 2.1 | | | | | | | 0.33 | | | | |
| 16 | 1.9 | 2.1 | | | | | | | 0.51 | | | | |
| 17 | 2.2 | 3.5 | | | | | | | 0.48 | | | | |
| 18 | 2.2 | 2.4 | | | | | | | 0.36 | | | | |
| Avg. | 2.1 | 2.8 | 0.32 | 1.7 | 4.5 | 19.1 | 0.6 | 19.9 | 0.42 | 5.5 | 2.1 | 0.82 | 0.88 |
| Sd | 0.4 | 0.6 | 0.05 | 0.4 | 1.3 | 3.8 | 0.1 | 2.3 | 0.07 | 0.1 | 0.3 | 0.10 | 0.07 |
| %RSD | 19.6 | 20.3 | 17.0 | 23.7 | 28.3 | 19.7 | 21.6 | 11.6 | 16.3 | 2.4 | 14.4 | 12.4 | 8.3 |

Table 2.32: Results for zinc determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|-------------|--------------|--------------|--------------|--------------|--------|--------|---------------|--------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.04 | 0.018 | 0.010 | 0.010 | 0.09 | 0.020 | 0.028 | 0.022 | 0.038 | 0.0218 | 0.0386 | 0.0131 | 0.0114 |
| 2 | 0.04 | 0.018 | 0.013 | 0.011 | 0.06 | 0.060 | 0.022 | 0.025 | 0.031 | 0.0195 | 0.0372 | 0.0179 | 0.0185 |
| 3 | 0.04 | 0.014 | 0.018 | 0.011 | 0.03 | 0.015 | 0.013 | 0.023 | 0.012 | 0.0186 | 0.0376 | 0.0155 | 0.0162 |
| 4 | 0.03 | 0.013 | 0.013 | 0.010 | 0.07 | 0.016 | 0.015 | 0.045 | 0.015 | 0.0206 | 0.0343 | 0.0217 | 0.0173 |
| 5 | 0.06 | 0.015 | 0.011 | 0.012 | 0.09 | 0.016 | 0.014 | 0.016 | 0.022 | 0.0165 | 0.0350 | 0.0146 | 0.0208 |
| 6 | 0.06 | 0.019 | 0.010 | 0.017 | 0.05 | 0.017 | 0.017 | 0.016 | 0.027 | 0.0180 | 0.0362 | 0.0150 | 0.0170 |
| 7 | 0.06 | 0.021 | 0.009 | 0.009 | 0.06 | 0.023 | 0.035 | 0.021 | 0.020 | | | | |
| 8 | 0.07 | 0.019 | 0.008 | 0.007 | 0.07 | 0.013 | 0.023 | 0.022 | 0.026 | | | | |
| 9 | 0.07 | 0.030 | 0.008 | 0.009 | 0.01 | 0.017 | 0.021 | 0.017 | 0.017 | | | | |
| 10 | 0.05 | 0.018 | 0.017 | 0.010 | 0.04 | 0.016 | 0.017 | 0.018 | 0.025 | | | | |
| 11 | 0.09 | 0.031 | 0.013 | | | | | | 0.018 | | | | |
| 12 | 0.09 | 0.019 | 0.010 | | | | | | 0.016 | | | | |
| 13 | 0.08 | 0.019 | 0.011 | | | | | | 0.021 | | | | |
| 14 | 0.09 | 0.030 | 0.010 | | | | | | 0.021 | | | | |
| 15 | 0.07 | 0.024 | 0.009 | | | | | | 0.018 | | | | |
| 16 | 0.07 | 0.017 | 0.011 | | | | | | 0.021 | | | | |
| 17 | 0.08 | 0.015 | 0.009 | | | | | | 0.019 | | | | |
| 18 | 0.07 | 0.015 | 0.011 | | | | | | 0.015 | | | | |
| Avg. | 0.07 | 0.018 | 0.011 | 0.010 | 0.07 | 0.017 | 0.018 | 0.020 | 0.019 | 0.0192 | 0.0365 | 0.0152 | 0.0169 |
| sd | 0.02 | 0.004 | 0.002 | 0.002 | 0.02 | 0.003 | 0.004 | 0.004 | 0.004 | 0.0019 | 0.0016 | 0.0017 | 0.0031 |
| %RSD | 24.0 | 22.7 | 21.3 | 15.1 | 22.9 | 17.7 | 21.1 | 17.4 | 21.7 | 9.9 | 4.5 | 11.5 | 18.5 |

Table 2.33: Results for phosphorus determination of sediment samples

| | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------------|------|------------|------------|------|------|-------------|------|
| Site | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 |
| 1 | 0.15 | 0.45 | 0.32 | 2.0 | 4.6 | 0.89 | 0.66 | 0.68 | 0.56 |
| 2 | 0.13 | 0.45 | 0.44 | 3.1 | 1.6 | 0.98 | 0.63 | 0.85 | 0.49 |
| 3 | 0.12 | 0.39 | 0.43 | 2.9 | 1.8 | 0.90 | 0.48 | 0.86 | 0.39 |
| 4 | 0.11 | 0.30 | 0.50 | 2.3 | 1.9 | 1.00 | 0.58 | 0.77 | 0.44 |
| 5 | 0.19 | 0.29 | 0.51 | 3.3 | 2.8 | 0.85 | 0.51 | 0.75 | 0.49 |
| 6 | 0.19 | 0.39 | 0.57 | 3.4 | 1.90 | 0.85 | 0.63 | 0.65 | 0.39 |
| 7 | 0.21 | 0.48 | 0.56 | 4.0 | 2.1 | 0.85 | 0.54 | 0.71 | 0.39 |
| 8 | 0.18 | 0.33 | 0.38 | 2.5 | 2.1 | 0.93 | 0.52 | 0.79 | 0.40 |
| 9 | 0.16 | 0.58 | 0.37 | 2.5 | 3.2 | 0.84 | 0.59 | 0.60 | 0.40 |
| 10 | 0.19 | 0.49 | 0.44 | 2.3 | 1.4 | 0.94 | 0.59 | 0.69 | 0.46 |
| Avg. | 0.17 | 0.39 | 0.45 | 2.7 | 1.9 | 0.90 | 0.57 | 0.73 | 0.44 |
| sd | 0.03 | 0.07 | 0.08 | 0.5 | 0.3 | 0.06 | 0.06 | 0.09 | 0.06 |
| %RSD | 18.2 | 19.3 | 18.2 | 19.0 | 13.9 | 6.4 | 10.5 | 11.8 | 13.3 |

Table 2.34: Results for potassium determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------------|--------------|------------|------------|------|-------------|------|-------------|------|-----|------|-------------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 2.7 | 0.6 | 0.037 | 3.5 | 4.2 | 0.8 | 0.46 | 0.3 | 0.01 | 0.62 | 2.5 | 0.34 | 0.40 |
| 2 | 2.6 | 0.5 | 0.041 | 2.4 | 2.1 | 0.8 | 0.43 | 0.3 | 0.02 | 0.55 | 2.7 | 0.41 | 0.98 |
| 3 | 3.0 | 0.6 | 0.052 | 3.3 | 3.4 | 0.8 | 0.33 | 0.4 | 0.01 | 0.64 | 2.3 | 0.52 | 0.98 |
| 4 | 2.3 | 0.6 | 0.041 | 3.3 | 1.0 | 0.7 | 0.38 | 0.4 | 0.01 | 0.62 | 2.4 | 0.53 | 0.91 |
| 5 | 3.2 | 0.5 | 0.041 | 3.9 | 3.2 | 0.8 | 0.29 | 0.5 | 0.01 | 0.71 | 2.5 | 0.48 | 1.10 |
| 6 | 3.3 | 0.5 | 0.059 | 4.2 | 3.0 | 0.7 | 0.21 | 0.4 | 0.02 | 0.65 | 2.6 | 0.40 | 0.95 |
| 7 | 3.4 | 0.7 | 0.057 | 4.6 | 3.0 | 0.8 | 0.26 | 0.5 | < dl | | | | |
| 8 | 4.9 | 0.6 | 0.083 | 5.2 | 3.2 | 0.4 | 0.30 | 0.5 | < dl | | | | |
| 9 | 4.4 | 1.3 | 0.026 | 3.5 | 4.0 | 0.5 | 0.32 | 0.7 | 0.01 | | | | |
| 10 | 3.6 | 0.9 | 0.028 | 3.4 | 3.0 | 0.6 | 0.36 | 0.4 | 0.01 | | | | |
| 11 | 5.0 | 0.7 | 0.036 | | | | | | 0.01 | | | | |
| 12 | 4.5 | 0.5 | 0.032 | | | | | | 0.01 | | | | |
| 13 | 4.6 | 0.6 | 0.040 | | | | | | 0.01 | | | | |
| 14 | 4.4 | 0.4 | 0.030 | | | | | | 0.01 | | | | |
| 15 | 4.6 | 0.3 | 0.032 | | | | | | 0.01 | | | | |
| 16 | 4.7 | 0.3 | 0.043 | | | | | | 0.01 | | | | |
| 17 | 4.6 | 0.7 | 0.045 | | | | | | < dl | | | | |
| 18 | 4.8 | 0.5 | 0.032 | | | | | | 0.01 | | | | |
| Avg. | 4.2 | 0.5 | 0.039 | 3.6 | 3.2 | 0.7 | 0.35 | 0.5 | 0.010 | 0.63 | 2.5 | 0.45 | 0.98 |
| sd | 0.7 | 0.1 | 0.009 | 0.6 | 0.6 | 0.1 | 0.07 | 0.1 | 0.002 | 0.05 | 0.1 | 0.08 | 0.07 |
| %RSD | 16.2 | 24.4 | 24.6 | 17.3 | 19.1 | 18.3 | 19.3 | 23.6 | 18.4 | 8.2 | 5.7 | 16.9 | 7.2 |

Table 2.35: Results for lead determination of sediment samples

| Site | Concentration (g/kg) | | | | | | | | | | | | |
|------|----------------------|------|-------|------|------|------|-------|------|------|------|-------|------|------|
| | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 | 15 | 16a | 16b | 17 | 18 |
| 1 | 0.017 | < dl | 0.017 | < dl | < dl | < dl | 0.016 | < dl | < dl | < dl | 0.022 | < dl | < dl |
| 2 | 0.018 | < dl | 0.017 | < dl | < dl | < dl | 0.015 | < dl | < dl | < dl | 0.029 | < dl | < dl |
| 3 | 0.019 | < dl | 0.015 | < dl | < dl | < dl | 0.016 | < dl | < dl | < dl | 0.027 | < dl | < dl |
| 4 | 0.016 | < dl | 0.018 | < dl | < dl | < dl | 0.016 | < dl | < dl | < dl | 0.028 | < dl | < dl |
| 5 | 0.021 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.023 | < dl | < dl |
| 6 | 0.026 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.025 | < dl | < dl |
| 7 | 0.027 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| 8 | 0.037 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| 9 | 0.033 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| 10 | 0.023 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | | | | |
| Avg. | 0.022 | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | < dl | 0.026 | < dl | < dl |
| sd | 0.006 | - | - | - | - | - | - | - | - | - | 0.003 | - | - |
| %RSD | 24.9 | - | - | - | - | - | - | - | - | | 10.9 | | |

A-2.5 Trace element determination of soil samples

2.5.1. ICP-OES results of trace element determination

The concentrations reflected in the following tables are a combination of the results found over the five sampling trips and the sampling site numbers correspond to those found in Table 3.3 in Chapter 3. The results are sorted by element. The numbers represented in bold type were regarded as outliers and discarded.

Table 2.37: Results for copper determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------|--------------|--------------|------|-------|-------|-------|--------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.016 | < dl | < dl | 0.005 | < dl | 0.019 | 0.012 | 0.002 | 0.005 |
| 2 | 0.019 | < dl | 0.010 | 0.004 | < dl | 0.017 | 0.014 | 0.001 | 0.004 |
| 3 | 0.017 | < dl | 8 | 0.004 | < dl | 0.021 | 0.015 | 0.002 | 0.004 |
| 4 | 0.009 | < dl | < dl | 0.007 | < dl | 0.017 | 0.015 | 0.003 | 0.010 |
| 5 | 0.008 | < dl | < dl | 0.010 | < dl | 0.014 | 0.017 | < dl | 0.014 |
| 6 | 0.015 | < dl | < dl | 0.010 | < dl | 0.014 | 0.048 | < dl | 0.015 |
| 7 | 0.023 | < dl | < dl | 0.008 | < dl | 0.015 | 0.016 | < dl | 0.017 |
| 8 | 0.016 | < dl | 0.014 | 0.010 | < dl | 0.015 | 0.016 | < dl | 0.012 |
| 9 | 0.018 | < dl | 3 | 0.008 | < dl | 0.018 | | < dl | 0.008 |
| 10 | 0.017 | < dl | < dl | 0.005 | < dl | 0.017 | | < dl | 0.011 |
| 11 | 0.020 | 0.002 | < dl | 0.007 | < dl | 0.011 | | < dl | 0.121 |
| 12 | 0.023 | 0.002 | < dl | 0.009 | < dl | 0.009 | | < dl | 0.008 |
| 13 | 0.022 | 0.002 | < dl | 0.061 | < dl | 0.011 | | 0.004 | 0.009 |
| 14 | 0.019 | 0.003 | < dl | 0.037 | < dl | 0.009 | | < dl | 0.005 |
| 15 | | 0.003 | < dl | 0.010 | < dl | 0.016 | | < dl | 0.020 |
| | | | < dl | | | | | | |
| | | | < dl | | | | | | |
| Avg. | 0.019 | < dl | < dl | 0.007 | < dl | 0.016 | 0.015 | < dl | 0.013 |
| sd | 0.003 | - | - | 0.002 | - | 0.003 | 0.002 | - | 0.005 |
| %RSD | 14.8 | - | - | 33.8 | - | 19.7 | 12.8 | - | 35.22 |

Table 2.38: Results for titanium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------------|-------------|-------------|---|--------|---|-------------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.12 | 0.08 | 0.04 | 0.05 | - | 0.0014 | - | 0.12 | 0.19 |
| 2 | 0.14 | 0.06 | 0.04 | 0.06 | - | 0.0012 | - | 0.09 | 0.17 |
| 3 | 0.11 | 0.06 | 0.08 | 0.05 | - | 0.0018 | - | 0.08 | 0.15 |
| 4 | 0.10 | 0.04 | 0.08 | 0.06 | - | 0.0011 | - | 0.10 | 0.28 |
| 5 | 0.08 | 0.05 | 0.05 | 0.05 | - | 0.0009 | - | 0.09 | 0.25 |
| 6 | 0.10 | 0.04 | 0.04 | 0.07 | - | 0.0009 | - | 0.08 | 0.23 |
| 7 | 0.06 | 0.04 | 0.04 | 0.04 | - | 0.0010 | - | 0.11 | 0.28 |
| 8 | 0.11 | 0.04 | 0.07 | 0.05 | - | 0.0014 | - | 0.06 | 0.23 |
| 9 | 0.10 | 0.04 | 0.06 | 0.02 | - | 0.0012 | - | 0.07 | 0.19 |
| 10 | 0.12 | | | 0.03 | - | | - | 0.08 | 0.20 |
| 11 | 0.15 | | | 0.08 | - | | - | 0.10 | 0.17 |
| 12 | 0.18 | | | 0.60 | - | | - | 0.08 | 0.28 |
| 13 | 0.21 | | | 0.29 | - | | - | 0.22 | 0.30 |
| 14 | 0.13 | | | 0.05 | - | | - | 0.22 | 0.12 |
| Avg. | 0.11 | 0.05 | 0.05 | 0.05 | - | 0.0012 | - | 0.09 | 0.22 |
| sd | 0.02 | 0.01 | 0.01 | 0.01 | - | 0.0003 | - | 0.02 | 0.05 |
| %RSD | 21.6 | 24.8 | 24.7 | 27.9 | - | 23.2 | - | 18.4 | 25.2 |

Table 2.39: Results for zirconium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|---|-------|---|------|---------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.004 | 0.006 | < dl | 0.002 | - | 0.007 | - | < dl | 0.0017 |
| 2 | 0.004 | 0.005 | < dl | 0.002 | - | 0.006 | - | < dl | 0.0016 |
| 3 | 0.011 | 0.004 | < dl | 0.002 | - | 0.008 | - | < dl | 0.0014 |
| 4 | 0.012 | 0.004 | < dl | 0.003 | - | 0.008 | - | < dl | 0.0025 |
| 5 | 0.012 | 0.003 | < dl | 0.003 | - | 0.006 | - | < dl | 0.0036 |
| 6 | 0.013 | 0.003 | < dl | 0.003 | - | 0.005 | - | < dl | 0.0026 |
| 7 | 0.014 | 0.003 | < dl | 0.003 | - | 0.007 | - | < dl | 0.0040 |
| 8 | 0.011 | < dl | 0.009 | 0.003 | - | 0.005 | - | < dl | 0.0020 |
| 9 | 0.011 | 0.011 | 0.012 | 0.003 | - | 0.007 | - | < dl | 0.0018 |
| 10 | 0.012 | | | 0.004 | - | | - | < dl | 0.0025 |
| 11 | 0.012 | | | 0.004 | - | | - | < dl | 0.0017 |
| 12 | 0.012 | | | 0.007 | - | | - | < dl | 0.0048 |
| 13 | 0.012 | | | 0.005 | - | | - | < dl | 0.0046 |
| 14 | 0.013 | | | 0.004 | - | | - | < dl | 0.0050 |
| Avg. | 0.012 | 0.004 | < dl | 0.003 | - | 0.007 | - | < dl | 0.0022 |
| sd | 0.001 | 0.001 | - | 0.001 | - | 0.001 | - | - | 0.0008 |
| %RSD | 8.8 | 23.1 | - | 27.3 | - | 14.1 | - | - | 34.42 |

Table 2.40: Results for aluminium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------------|------------|-------------|------------|------------|-------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 6.6 | 19.2 | 0.9 | 2.1 | 2.9 | 3.7 | 1.0 | 1.3 | 2.9 |
| 2 | 5.8 | 5.8 | 1.4 | 1.9 | 0.9 | 2.6 | 0.9 | 1.7 | 2.2 |
| 3 | 4.4 | 4.3 | 2.1 | 1.3 | 1.2 | 3.1 | 1.2 | 1.4 | 2.2 |
| 4 | 4.9 | 3.9 | 1.7 | 2.0 | 2.7 | 1.8 | 1.0 | 1.4 | 5.1 |
| 5 | 3.7 | 3.1 | 1.5 | 1.4 | 2.7 | 1.6 | 3.2 | 1.4 | 4.2 |
| 6 | 5.3 | 1.3 | 1.6 | 2.6 | 2.7 | 1.6 | 3.4 | 1.4 | 5.2 |
| 7 | 16.9 | 2.1 | 1.3 | 1.6 | 2.5 | 4.2 | 3.3 | 1.7 | 5.1 |
| 8 | 3.1 | 1.8 | 1.2 | 1.5 | 2.6 | 4.3 | 3.4 | 1.4 | 5.2 |
| 9 | 8.0 | 3.3 | 1.1 | 1.0 | | 4.2 | | 1.4 | 3.6 |
| 10 | 10.1 | 3.4 | | 1.4 | | 4.1 | | 1.4 | 3.7 |
| 11 | 3.9 | 3.3 | | 2.6 | | 2.3 | | 1.5 | 6.6 |
| 12 | 3.4 | 3.4 | | 10.7 | | 2.2 | | 1.4 | 4.0 |
| 13 | 4.2 | 1.9 | | 8.0 | | 3.4 | | 1.8 | 4.8 |
| 14 | 5.2 | 2.2 | | 1.3 | | 3.3 | | 1.3 | 5.9 |
| Avg. | 4.6 | 3.0 | 1.3 | 1.7 | 2.5 | 3.4 | 2.175 | 1.5 | 4.3 |
| sd | 1.1 | 0.8 | 0.3 | 0.5 | 0.6 | 0.8 | 1.228 | 0.2 | 1.3 |
| %RSD | 23.2 | 28.3 | 19.7 | 29.6 | 22.6 | 22.8 | 56.5 | 10.5 | 30.7 |

Table 2.41: Results for strontium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|------|--------------|------|--------------|---------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.004 | 0.004 | < dl | 0.004 | 0.21 | 0.037 | < dl | 0.013 | 0.0035 |
| 2 | 0.005 | 0.002 | 0.006 | 0.003 | < dl | 0.020 | < dl | 0.022 | 0.0032 |
| 3 | 0.003 | 0.001 | 0.003 | 0.004 | < dl | 0.029 | < dl | 0.025 | 0.0033 |
| 4 | 0.004 | 0.001 | 0.001 | 0.007 | < dl | 0.019 | < dl | 0.029 | 0.0069 |
| 5 | 0.004 | 0.003 | 0.002 | 0.005 | 0.19 | 0.006 | < dl | 0.024 | 0.0071 |
| 6 | 0.004 | 0.003 | 0.003 | 0.008 | 0.17 | 0.024 | < dl | 0.024 | 0.0052 |
| 7 | 0.008 | 0.003 | 0.002 | 0.003 | 0.17 | 0.032 | < dl | 0.038 | 0.0053 |
| 8 | 0.001 | 0.003 | 0.001 | 0.005 | 0.20 | 0.030 | < dl | 0.026 | 0.0075 |
| 9 | 0.002 | 0.003 | 0.002 | 0.002 | | 0.030 | < dl | 0.046 | 0.0078 |
| 10 | 0.003 | 0.003 | | 0.001 | | 0.027 | | 0.035 | 0.0054 |
| 11 | 0.004 | 0.004 | | 0.004 | | 0.018 | | 0.057 | 0.0088 |
| 12 | 0.008 | 0.003 | | 0.003 | | 0.019 | | 0.053 | 0.0081 |
| 13 | 0.007 | 0.003 | | 0.003 | | 0.018 | | 0.053 | 0.0092 |
| 14 | 0.007 | 0.004 | | 0.001 | | 0.020 | | 0.020 | 0.0178 |
| Avg. | 0.005 | 0.003 | 0.002 | 0.004 | 0.19 | 0.025 | < dl | 0.027 | 0.0063 |
| sd | 0.002 | 0.001 | 0.001 | 0.001 | 0.02 | 0.006 | - | 0.009 | 0.002 |
| %RSD | 33.7 | 21.0 | 30.3 | 27.1 | 9.9 | 25.6 | - | 33.5 | 33.3 |

Table 2.42: Results for nickel determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|---|-------|---|------|--------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.04 | 0.043 | < dl | < dl | - | 0.025 | - | < dl | 0.017 |
| 2 | 0.05 | 0.036 | < dl | < dl | - | 0.021 | - | < dl | 0.020 |
| 3 | 0.03 | 0.029 | < dl | < dl | - | 0.024 | - | < dl | 0.018 |
| 4 | 0.02 | 0.035 | < dl | < dl | - | 0.022 | - | < dl | 0.043 |
| 5 | 0.02 | 0.035 | < dl | < dl | - | 0.019 | - | < dl | 0.034 |
| 6 | 0.02 | 0.030 | < dl | < dl | - | 0.016 | - | < dl | 0.035 |
| 7 | 0.02 | 0.006 | < dl | < dl | - | 0.017 | - | < dl | 0.026 |
| 8 | 0.02 | 0.023 | 0.011 | < dl | - | 0.020 | - | < dl | 0.024 |
| 9 | 0.03 | 0.012 | 0.024 | < dl | - | 0.021 | - | < dl | 0.009 |
| 10 | 0.02 | | | < dl | - | | - | < dl | |
| 11 | 0.03 | | | 0.015 | - | | - | < dl | |
| 12 | 0.06 | | | 0.072 | - | | - | < dl | |
| 13 | 0.05 | | | 0.023 | - | | - | < dl | |
| 14 | 0.04 | | | 0.013 | - | | - | < dl | |
| Avg. | 0.03 | 0.033 | < dl | < dl | - | 0.021 | - | < dl | 0.025 |
| sd | 0.01 | 0.006 | - | - | - | 0.003 | - | - | 0.007 |
| %RSD | 32.9 | 18.9 | - | - | - | 13.6 | - | - | 29.2 |

Table 2.43: Results for barium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|-------|--------------|--------------|--------------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.009 | 0.002 | < dl | < dl | 0.021 | 0.009 | < dl | 0.005 | 0.020 |
| 2 | 0.010 | 0.009 | < dl | < dl | 0.015 | 0.004 | < dl | 0.005 | 0.015 |
| 3 | 0.007 | 0.009 | < dl | 0.003 | 0.017 | 0.011 | < dl | 0.006 | 0.015 |
| 4 | 0.007 | < dl | 0.003 | < dl | 0.018 | 0.015 | < dl | 0.006 | 0.036 |
| 5 | 0.007 | 0.006 | 0.001 | 0.002 | 0.012 | 0.011 | 0.002 | 0.006 | 0.033 |
| 6 | 0.011 | 0.004 | < dl | < dl | 0.013 | 0.011 | < dl | 0.005 | 0.032 |
| 7 | 0.013 | 0.006 | < dl | 0.001 | 0.013 | 0.008 | 0.018 | 0.006 | 0.037 |
| 8 | 0.006 | 0.006 | < dl | < dl | 0.015 | 0.008 | < dl | 0.005 | 0.037 |
| 9 | 0.009 | 0.005 | < dl | < dl | 0.015 | 0.017 | 0.001 | 0.005 | 0.024 |
| 10 | 0.012 | 0.007 | | 0.002 | | 0.007 | | 0.005 | 0.026 |
| 11 | 0.016 | 0.001 | | < dl | | | | 0.007 | 0.026 |
| 12 | 0.020 | 0.006 | | < dl | | | | 0.008 | 0.033 |
| 13 | 0.015 | 0.004 | | < dl | | | | 0.014 | 0.037 |
| 14 | 0.015 | 0.007 | | < dl | | | | 0.009 | 0.039 |
| Avg. | 0.011 | 0.006 | < dl | < dl | 0.015 | 0.011 | < dl | 0.006 | 0.029 |
| sd | 0.003 | 0.002 | - | - | 0.003 | 0.003 | - | 0.001 | 0.008 |
| %RSD | 32.0 | 26.1 | - | - | 19.0 | 27.5 | - | 18.6 | 28.8 |

Table 2.44: Results for boron determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.040 | 0.046 | 0.010 | < dl | 0.041 | 0.039 | 0.011 | 0.013 | 0.012 |
| 2 | 0.035 | 0.040 | < dl | < dl | 0.010 | 0.033 | 0.014 | 0.010 | 0.013 |
| 3 | 0.031 | 0.027 | < dl | < dl | 0.007 | 0.034 | 0.011 | 0.014 | 0.010 |
| 4 | < dl | 0.026 | < dl | < dl | 0.033 | 0.028 | 0.012 | 0.012 | 0.023 |
| 5 | < dl | 0.021 | < dl | < dl | 0.028 | 0.021 | 0.016 | 0.014 | 0.021 |
| 6 | 0.039 | 0.027 | < dl | < dl | 0.039 | 0.011 | 0.014 | 0.015 | 0.023 |
| 7 | 0.038 | 0.007 | 0.030 | < dl | 0.035 | 0.030 | 0.013 | 0.012 | 0.028 |
| 8 | 0.034 | 0.009 | 0.029 | < dl | 0.030 | 0.029 | 0.017 | 0.016 | 0.023 |
| 9 | 0.054 | 0.038 | < dl | < dl | 0.028 | 0.034 | 0.013 | 0.014 | 0.015 |
| 10 | 0.042 | | | 0.039 | | 0.030 | | 0.017 | |
| 11 | 0.032 | | | 0.039 | | 0.020 | | 0.013 | |
| 12 | 0.036 | | | 0.039 | | 0.015 | | 0.013 | |
| 13 | 0.042 | | | 0.004 | | 0.018 | | 0.013 | |
| 14 | 0.027 | | | < dl | | 0.014 | | 0.014 | |
| Avg. | 0.037 | 0.032 | < dl | < dl | 0.034 | 0.029 | 0.013 | 0.014 | 0.020 |
| sd | 0.007 | 0.009 | - | - | 0.005 | 0.007 | 0.002 | 0.002 | 0.006 |
| %RSD | 18.5 | 28.5 | - | - | 14.8 | 23.3 | 16.5 | 12.5 | 29.2 |

Table 2.45: Results for manganese determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|--------------|--------------|------|--------------|-------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.07 | 0.019 | < dl | 0.026 | 0.074 | 0.084 | < dl | 0.022 | 0.11 |
| 2 | 0.14 | 0.018 | < dl | 0.017 | 0.045 | 0.045 | < dl | 0.025 | 0.08 |
| 3 | 0.10 | 0.012 | 0.016 | 0.012 | 0.035 | 0.059 | < dl | 0.026 | 0.08 |
| 4 | 0.06 | 0.016 | 0.013 | 0.022 | 0.050 | 0.013 | < dl | 0.028 | 0.22 |
| 5 | 0.05 | 0.027 | < dl | 0.021 | 0.057 | 0.023 | < dl | 0.025 | 0.18 |
| 6 | 0.09 | 0.008 | < dl | 0.028 | 0.037 | < dl | < dl | 0.022 | 0.24 |
| 7 | 0.08 | 0.013 | < dl | 0.022 | 0.031 | < dl | < dl | 0.027 | 0.23 |
| 8 | 0.06 | 0.011 | < dl | 0.032 | 0.039 | < dl | < dl | 0.023 | 0.29 |
| 9 | 0.003 | 0.017 | < dl | 0.011 | | < dl | < dl | 0.027 | 0.14 |
| 10 | 0.04 | | | 0.018 | | < dl | | 0.024 | 0.10 |
| 11 | 0.14 | | | 0.043 | | < dl | | 0.029 | 0.17 |
| 12 | 0.13 | | | 0.371 | | < dl | | 0.032 | 0.10 |
| 13 | 0.10 | | | 0.171 | | < dl | | 0.057 | 0.13 |
| 14 | 0.10 | | | 0.020 | | < dl | | 0.043 | 0.26 |
| Avg. | 0.09 | 0.014 | < dl | 0.021 | 0.042 | < dl | < dl | 0.027 | 0.17 |
| sd | 0.04 | 0.004 | - | 0.006 | 0.009 | - | - | 0.006 | 0.06 |
| %RSD | 35.0 | 26.2 | - | 31.0 | 21.9 | - | - | 20.8 | 34.3 |

Table 2.46: Results for iron determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|------------|------|-------------|-------------|------------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 7.3 | 4.4 | 1.2 | 1.9 | 11.0 | 6.7 | 0.8 | 3.5 | 7.0 |
| 2 | 7.8 | 4.2 | 1.3 | 1.7 | 4.9 | 4.7 | 0.8 | 2.4 | 7.2 |
| 3 | 4.7 | 2.3 | 2.3 | 1.0 | 5.4 | 5.3 | 1.0 | 2.0 | 5.8 |
| 4 | 4.9 | 2.8 | 2.4 | 1.7 | 2.9 | 3.6 | 1.0 | 2.2 | 11.8 |
| 5 | 4.1 | 2.7 | 1.6 | 1.4 | 7.7 | 3.1 | 1.6 | 2.2 | 8.3 |
| 6 | 6.0 | 1.9 | 1.9 | 2.5 | 7.8 | 9.0 | 1.0 | 2.0 | 8.9 |
| 7 | 7.9 | 2.5 | 1.4 | 1.8 | 7.1 | 6.3 | 1.4 | 2.3 | 10.5 |
| 8 | 4.7 | 2.7 | 2.2 | 1.6 | 6.6 | 6.3 | 1.2 | 2.0 | 10.5 |
| 9 | 4.1 | 2.1 | 2.0 | 1.0 | | 3.5 | | 2.1 | 7.0 |
| 10 | 6.2 | 2.0 | | 1.3 | | 5.9 | | 2.0 | 10.4 |
| 11 | 7.8 | 2.2 | | 2.7 | | 3.2 | | 2.5 | 4.8 |
| 12 | 9.3 | 2.4 | | 17.9 | | 3.6 | | 2.3 | 8.2 |
| 13 | 10.5 | 1.8 | | 13.1 | | 4.3 | | 2.0 | 4.8 |
| 14 | 6.4 | 2.6 | | 1.3 | | 3.2 | | 2.3 | 6.1 |
| Avg. | 6.0 | 2.3 | 1.8 | 1.7 | 6.6 | 4.8 | 1.1 | 2.3 | 8.0 |
| sd | 1.5 | 0.3 | 0.5 | 0.5 | 1.2 | 1.4 | 0.30 | 0.4 | 2.2 |
| %RSD | 24.4 | 14.6 | 25.1 | 31.5 | 18.1 | 29.3 | 26.7 | 17.4 | 28.1 |

Table 2.47: Results for magnesium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------------|-------------|-------------|------------|-----|-------------|------|------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.6 | 0.09 | 0.12 | 0.14 | 1.5 | 1.2 | 0.03 | 0.23 | 0.6 |
| 2 | 0.8 | 0.19 | 0.09 | 0.10 | 0.1 | 1.3 | 0.02 | 0.45 | 0.4 |
| 3 | 0.5 | 0.10 | 0.27 | 0.11 | 1.4 | 1.3 | 0.04 | 0.33 | 0.4 |
| 4 | 0.6 | 0.12 | 0.30 | 0.11 | 0.1 | 1.3 | 0.14 | 0.38 | 1.1 |
| 5 | 0.4 | 0.18 | 0.13 | 0.12 | 1.2 | 1.5 | 0.13 | 0.33 | 0.8 |
| 6 | 0.5 | 0.06 | 0.11 | 0.12 | 1.3 | 1.5 | 0.16 | 0.28 | 0.7 |
| 7 | 0.5 | 0.07 | 0.09 | 0.08 | 1.4 | 1.5 | 0.13 | 0.51 | 0.9 |
| 8 | 0.5 | 0.06 | 0.20 | 0.09 | 1.3 | 1.5 | 0.16 | 0.27 | 0.9 |
| 9 | 0.3 | 0.08 | 0.16 | 0.06 | | | 0.18 | 0.35 | 0.7 |
| 10 | 0.6 | 0.10 | | 0.10 | | | | 0.48 | 1.0 |
| 11 | 0.7 | 0.01 | | 0.45 | | | | 0.34 | 1.1 |
| 12 | 0.9 | 0.09 | | 2.41 | | | | 0.31 | 1.7 |
| 13 | 0.8 | 0.09 | | 1.29 | | | | 0.35 | 1.8 |
| 14 | 0.6 | 0.11 | | 0.08 | | | | 0.36 | 1.0 |
| Avg. | 0.6 | 0.09 | 0.13 | 0.10 | 1.4 | 1.4 | 0.15 | 0.36 | 0.8 |
| sd | 0.1 | 0.02 | 0.04 | 0.03 | 0.1 | 0.1 | 0.02 | 0.08 | 0.2 |
| %RSD | 21.2 | 22.2 | 29.5 | 24.7 | 8.4 | 9.0 | 13.4 | 22.3 | 31.0 |

Table 2.48: Results for vanadium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|-------|--------------|-------------|--------------|-------|--------------|--------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.043 | 0.035 | 0.014 | < dl | 0.05 | 0.020 | 0.004 | 0.005 | 0.015 |
| 2 | 0.039 | 0.031 | 0.017 | < dl | 0.05 | 0.020 | < dl | 0.009 | 0.015 |
| 3 | 0.025 | 0.025 | 0.020 | < dl | 0.05 | 0.020 | < dl | 0.010 | 0.013 |
| 4 | 0.020 | 0.026 | 0.018 | < dl | 0.01 | 0.018 | < dl | 0.009 | 0.025 |
| 5 | 0.016 | 0.026 | 0.017 | < dl | 0.03 | 0.009 | 0.008 | 0.012 | 0.020 |
| 6 | 0.026 | 0.021 | 0.017 | 0.009 | 0.03 | 0.013 | 0.008 | 0.010 | 0.023 |
| 7 | 0.084 | 0.072 | 0.014 | < dl | 0.02 | 0.015 | 0.008 | 0.005 | 0.029 |
| 8 | 0.022 | 0.019 | 0.012 | 0.005 | 0.02 | 0.017 | 0.009 | 0.012 | 0.016 |
| 9 | 0.027 | 0.014 | 0.020 | 0.005 | | | 0.009 | 0.012 | 0.009 |
| 10 | 0.036 | | | 0.006 | | | | 0.010 | 0.018 |
| 11 | 0.029 | | | 0.011 | | | | 0.018 | 0.007 |
| 12 | 0.033 | | | 0.005 | | | | 0.014 | 0.015 |
| 13 | 0.033 | | | < dl | | | | 0.015 | 0.008 |
| 14 | 0.035 | | | < dl | | | | 0.018 | 0.011 |
| Avg. | 0.030 | 0.026 | 0.016 | < dl | 0.04 | 0.018 | 0.008 | 0.013 | 0.014 |
| sd | 0.008 | 0.005 | 0.003 | - | 0.01 | 0.003 | 0.002 | 0.003 | 0.005 |
| %RSD | 26.5 | 20.6 | 16.0 | - | 32.3 | 16.5 | 22.3 | 25.6 | 34.7 |

Table 2.49: Results for sodium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------------|------|-------------|------------|------|-------------|-------------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.46 | 0.39 | 0.34 | 0.46 | 0.5 | 0.19 | 0.15 | 0.20 | 0.4 |
| 2 | 0.57 | 0.21 | 0.42 | 0.53 | 0.2 | 0.20 | 0.18 | 0.69 | 0.3 |
| 3 | 0.50 | 0.18 | 0.37 | 0.62 | 0.2 | 0.20 | 0.17 | 0.46 | 0.5 |
| 4 | 0.57 | 0.15 | 0.43 | 0.42 | 0.3 | 0.19 | 0.16 | 0.45 | 0.7 |
| 5 | 0.62 | 0.21 | 0.32 | 0.56 | 0.4 | 0.21 | 0.23 | 0.30 | 0.5 |
| 6 | 0.53 | 0.09 | 0.40 | 0.59 | 0.5 | 0.17 | 0.32 | 0.23 | 0.4 |
| 7 | 0.62 | 0.10 | 0.33 | 0.53 | 0.5 | 0.21 | 0.22 | 0.52 | 0.4 |
| 8 | 0.40 | 0.10 | 0.32 | 0.50 | 0.5 | 0.22 | 0.22 | 0.41 | 0.6 |
| 9 | 0.62 | 0.41 | 0.40 | 0.35 | | | | 0.40 | 0.5 |
| 10 | 0.62 | 0.27 | | 0.46 | | | | 0.31 | 0.4 |
| 11 | 0.51 | 0.31 | | 0.44 | | | | 0.31 | 0.3 |
| 12 | 0.46 | 0.33 | | 0.86 | | | | 0.37 | 0.6 |
| 13 | 0.51 | 0.25 | | 0.70 | | | | 0.38 | 0.4 |
| 14 | 0.52 | 0.38 | | 0.58 | | | | 0.38 | 0.5 |
| Avg. | 0.54 | 0.28 | 0.37 | 0.52 | 0.5 | 0.20 | 0.19 | 0.36 | 0.5 |
| sd | 0.07 | 0.09 | 0.04 | 0.09 | 0.1 | 0.01 | 0.03 | 0.07 | 0.1 |
| %RSD | 13.0 | 32.4 | 11.7 | 18.3 | 22.5 | 7.1 | 17.1 | 19.6 | 21.9 |

Table 2.50: Results for calcium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------------|-------------|------------|------------|------|-------------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.7 | 0.34 | 0.19 | 0.6 | 3.6 | 2.5 | 0.70 | 2.3 | 0.5 |
| 2 | 1.0 | 0.25 | 0.22 | 0.5 | 3.2 | 2.6 | 0.53 | 2.6 | 0.5 |
| 3 | 0.7 | 0.27 | 0.58 | 0.5 | 4.1 | 3.2 | 0.72 | 3.4 | 0.5 |
| 4 | 0.8 | 0.17 | 0.37 | 0.8 | 0.1 | 2.9 | 0.10 | 2.9 | 1.1 |
| 5 | 0.7 | 0.23 | 0.26 | 0.6 | 2.6 | 2.8 | 0.49 | 2.4 | 0.8 |
| 6 | 0.7 | 0.16 | 0.49 | 0.8 | 4.3 | 2.2 | 0.63 | 3.0 | 0.6 |
| 7 | 0.8 | 0.15 | 0.24 | 0.4 | 4.2 | 2.7 | 0.48 | 1.9 | 0.6 |
| 8 | 0.5 | 0.16 | 0.21 | 0.6 | 3.4 | 2.2 | 0.60 | 2.2 | 0.8 |
| 9 | 0.4 | 0.12 | 0.21 | 0.5 | | | | 2.2 | 1.0 |
| 10 | 0.5 | 0.17 | | 0.3 | | | | 2.7 | 1.2 |
| 11 | 0.5 | 0.24 | | 0.6 | | | | 2.4 | 0.9 |
| 12 | 1.0 | 0.18 | | 2.9 | | | | 2.0 | 1.5 |
| 13 | 0.9 | 0.28 | | 2.5 | | | | 2.4 | 1.2 |
| 14 | 0.6 | 0.33 | | 0.3 | | | | 2.5 | 1.1 |
| Avg. | 0.7 | 0.20 | 0.24 | 0.6 | 3.6 | 2.6 | 0.59 | 2.5 | 0.9 |
| sd | 0.2 | 0.05 | 0.06 | 0.2 | 0.6 | 0.3 | 0.09 | 0.4 | 0.3 |
| %RSD | 20.9 | 26.7 | 24.5 | 29.0 | 16.7 | 13.0 | 16.3 | 15.6 | 33.3 |

Table 2.51: Results for zinc determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------|--------------|--------------|-------------|--------------|--------------|-------|--------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.018 | 0.014 | 0.007 | 0.018 | 0.03 | 0.018 | 0.011 | 0.023 | 0.028 |
| 2 | 0.054 | 0.017 | 0.013 | 0.017 | 0.01 | 0.018 | 0.025 | 0.034 | 0.023 |
| 3 | 0.018 | 0.015 | 0.014 | 0.017 | 0.04 | 0.026 | 0.014 | 0.027 | 0.022 |
| 4 | 0.015 | 0.017 | 0.025 | 0.017 | 0.01 | 0.022 | 0.015 | 0.034 | 0.062 |
| 5 | 0.016 | 0.020 | 0.013 | 0.023 | 0.02 | 0.013 | 0.028 | 0.034 | 0.273 |
| 6 | 0.019 | 0.019 | 0.010 | 0.022 | 0.04 | 0.009 | 0.104 | 0.032 | 0.040 |
| 7 | 0.031 | 0.013 | 0.014 | 0.019 | 0.03 | 0.019 | 0.025 | 0.030 | 0.035 |
| 8 | 0.029 | 0.013 | 0.021 | 0.019 | 0.04 | 0.009 | 0.029 | 0.034 | 0.032 |
| 9 | 0.027 | 0.014 | 0.020 | 0.010 | | | | 0.033 | 0.033 |
| 10 | 0.026 | 0.016 | | 0.016 | | | | 0.035 | 0.047 |
| 11 | 0.027 | 0.015 | | 0.019 | | | | 0.018 | 0.030 |
| 12 | 0.023 | 0.016 | | 0.107 | | | | 0.018 | 0.019 |
| 13 | 0.030 | 0.014 | | 0.105 | | | | 0.021 | 0.017 |
| 14 | 0.030 | 0.016 | | 0.015 | | | | 0.024 | 0.014 |
| Avg. | 0.024 | 0.016 | 0.015 | 0.018 | 0.03 | 0.019 | 0.023 | 0.028 | 0.029 |
| sd | 0.006 | 0.002 | 0.004 | 0.003 | 0.01 | 0.005 | 0.006 | 0.006 | 0.010 |
| %RSD | 24.6 | 14.4 | 26.4 | 18.6 | 33.2 | 23.6 | 28.3 | 22.4 | 35.03 |

Table 2.52: Results for phosphorus determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|------|------------|------------|---|---|---|------------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 1.4 | 1.2 | 1.2 | 1.6 | - | - | - | 0.9 | 0.7 |
| 2 | 1.7 | 1.4 | 2.4 | 1.7 | - | - | - | 0.6 | 0.7 |
| 3 | 1.4 | 1.4 | 1.6 | 1.4 | - | - | - | 0.5 | 0.7 |
| 4 | 1.6 | 1.2 | 1.8 | 1.7 | - | - | - | 0.6 | 1.0 |
| 5 | 1.5 | 1.4 | 1.6 | 1.6 | - | - | - | 0.6 | 1.0 |
| 6 | 1.6 | 1.4 | 1.9 | 2.1 | - | - | - | 0.5 | 0.9 |
| 7 | 1.4 | 1.1 | 1.3 | 1.8 | - | - | - | 0.6 | 0.9 |
| 8 | 1.2 | 1.1 | 1.3 | 2.0 | - | - | - | 0.5 | 1.1 |
| 9 | 1.9 | 1.0 | 1.7 | 1.2 | - | - | - | 0.5 | 0.9 |
| 10 | 1.9 | | | 1.6 | - | - | - | 0.5 | |
| 11 | 1.6 | | | 1.8 | - | - | - | 0.6 | |
| 12 | 1.4 | | | 5.9 | - | - | - | 0.6 | |
| 13 | 1.5 | | | 4.5 | - | - | - | 0.3 | |
| 14 | 1.7 | | | 1.7 | - | - | - | 0.8 | |
| Avg. | 1.6 | 1.2 | 1.5 | 1.7 | - | - | - | 0.6 | 0.9 |
| sd | 0.2 | 0.2 | 0.3 | 0.3 | - | - | - | 0.1 | 0.1 |
| %RSD | 12.8 | 12.2 | 16.8 | 15.2 | - | - | - | 16.9 | 15.3 |

Table 2.53: Results for cadmium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|--------------|-------|---|---|---|------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.006 | 0.007 | 0.005 | 0.009 | - | - | - | < dl | 0.002 |
| 2 | 0.007 | 0.008 | 0.008 | 0.010 | - | - | - | < dl | 0.002 |
| 3 | 0.010 | 0.007 | 0.006 | 0.010 | - | - | - | < dl | 0.002 |
| 4 | 0.006 | 0.008 | 0.007 | 0.008 | - | - | - | < dl | 0.003 |
| 5 | 0.007 | 0.008 | 0.006 | 0.009 | - | - | - | < dl | 0.003 |
| 6 | 0.012 | 0.008 | 0.006 | 0.009 | - | - | - | < dl | 0.003 |
| 7 | 0.014 | 0.007 | 0.006 | 0.009 | - | - | - | < dl | 0.003 |
| 8 | 0.017 | 0.008 | 0.011 | 0.008 | - | - | - | < dl | 0.003 |
| 9 | 0.015 | 0.014 | 0.014 | 0.006 | - | - | - | < dl | 0.002 |
| 10 | 0.015 | | | 0.008 | - | - | - | < dl | |
| 11 | 0.018 | | | 0.009 | - | - | - | < dl | |
| 12 | 0.017 | | | 0.012 | - | - | - | < dl | |
| 13 | 0.016 | | | 0.009 | - | - | - | < dl | |
| 14 | 0.018 | | | 0.010 | - | - | - | < dl | |
| Avg. | 0.015 | 0.008 | 0.006 | 0.009 | - | - | - | < dl | 0.003 |
| sd | 0.003 | 0.001 | 0.001 | 0.001 | - | - | - | - | 0.001 |
| %RSD | 16.9 | 6.8 | 12.4 | 13.0 | - | - | - | - | 24.8 |

Table 2.54: Results for cobalt determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|--------------|--------------|---|---|---|------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.023 | 0.021 | < dl | < dl | - | - | - | < dl | < dl |
| 2 | 0.027 | 0.020 | < dl | < dl | - | - | - | < dl | < dl |
| 3 | 0.016 | 0.015 | < dl | < dl | - | - | - | < dl | < dl |
| 4 | 0.010 | 0.018 | < dl | < dl | - | - | - | < dl | 0.006 |
| 5 | 0.008 | 0.019 | < dl | < dl | - | - | - | < dl | 0.006 |
| 6 | 0.015 | 0.015 | < dl | < dl | - | - | - | < dl | 0.007 |
| 7 | 0.019 | 0.006 | < dl | < dl | - | - | - | < dl | 0.007 |
| 8 | 0.013 | 0.013 | 0.007 | < dl | - | - | - | < dl | 0.006 |
| 9 | 0.012 | 0.008 | 0.015 | < dl | - | - | - | < dl | 0.004 |
| 10 | 0.015 | | | < dl | - | - | - | < dl | 0.006 |
| 11 | 0.018 | | | 0.007 | - | - | - | < dl | 0.007 |
| 12 | 0.027 | | | 0.049 | - | - | - | < dl | < dl |
| 13 | 0.028 | | | 0.023 | - | - | - | < dl | < dl |
| 14 | 0.023 | | | 0.007 | - | - | - | < dl | < dl |
| Avg. | 0.019 | 0.017 | < dl | < dl | - | - | - | < dl | 0.006 |
| sd | 0.006 | 0.003 | - | - | - | - | - | - | 0.001 |
| %RSD | 31.8 | 16.8 | - | - | - | - | - | - | 15.3 |

Table 2.55: Results for potassium determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------------|-------------|-------------|-------------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.30 | 0.29 | 0.07 | 0.07 | 0.51 | 0.22 | 0.15 | 0.14 | 0.5 |
| 2 | 0.35 | 0.14 | 0.09 | 0.04 | 0.08 | 0.16 | 0.16 | 0.12 | 0.7 |
| 3 | 0.25 | 0.13 | 0.17 | 0.06 | 0.06 | 0.10 | 0.16 | 0.14 | 0.4 |
| 4 | 0.33 | 0.13 | 0.15 | 0.07 | 0.12 | 0.17 | 0.16 | 0.13 | 0.7 |
| 5 | 0.29 | 0.15 | 0.08 | 0.04 | 0.46 | 0.19 | 0.13 | 0.13 | 0.7 |
| 6 | 0.29 | 0.10 | 0.09 | 0.07 | 0.42 | 0.19 | 0.15 | 0.11 | 0.7 |
| 7 | 0.42 | 0.09 | 0.07 | 0.03 | 0.42 | 0.20 | 0.12 | 0.13 | 0.8 |
| 8 | 0.23 | 0.11 | 0.11 | 0.05 | 0.42 | 0.19 | 0.13 | 0.13 | 0.5 |
| 9 | 0.25 | 0.16 | 0.08 | 0.03 | | | | 0.17 | 0.4 |
| 10 | 0.38 | 0.29 | | 0.05 | | | | 0.16 | 1.0 |
| 11 | 0.28 | 0.12 | | 0.14 | | | | 0.16 | 1.0 |
| 12 | 0.30 | 0.14 | | 1.13 | | | | 0.16 | 0.4 |
| 13 | 0.37 | 0.26 | | 0.59 | | | | 0.18 | 0.8 |
| 14 | 0.34 | 0.19 | | 0.03 | | | | 0.17 | 0.6 |
| Avg. | 0.31 | 0.14 | 0.08 | 0.05 | 0.45 | 0.18 | 0.15 | 0.15 | 0.6 |
| sd | 0.06 | 0.03 | 0.01 | 0.01 | 0.04 | 0.04 | 0.02 | 0.02 | 0.2 |
| %RSD | 17.4 | 18.8 | 16.5 | 28.1 | 8.7 | 20.1 | 11.2 | 14.2 | 33.5 |

Table 2.56: Results for lead determination of soil samples

| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|-------|-------|--------------|------|--------------|--------------|--------------|--------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.024 | 0.029 | < dl | 0.015 | < dl | 0.015 | < dl | < dl | < dl |
| 2 | 0.028 | 0.024 | 0.014 | 0.014 | < dl | 0.015 | 0.014 | < dl | < dl |
| 3 | 0.022 | 0.021 | 0.017 | < dl | < dl | 0.018 | 0.015 | 0.024 | < dl |
| 4 | 0.015 | 0.020 | 0.021 | 0.016 | < dl | 0.017 | 0.015 | < dl | < dl |
| 5 | 0.015 | 0.023 | 0.014 | 0.016 | < dl | < dl | 0.017 | < dl | 0.014 |
| 6 | 0.021 | 0.020 | < dl | 0.018 | < dl | < dl | 0.048 | < dl | 0.018 |
| 7 | 0.031 | 0.016 | < dl | 0.014 | < dl | < dl | 0.016 | < dl | < dl |
| 8 | 0.021 | 0.016 | 0.015 | 0.016 | < dl | < dl | 0.018 | < dl | < dl |
| 9 | 0.026 | 0.017 | 0.021 | < dl | | | | 0.014 | < dl |
| 10 | 0.027 | | | < dl | | | | < dl | < dl |
| 11 | 0.024 | | | 0.018 | | | | < dl | < dl |
| 12 | 0.025 | | | 0.240 | | | | < dl | 0.015 |
| 13 | 0.025 | | | 0.144 | | | | 0.014 | < dl |
| 14 | 0.028 | | | 0.019 | | | | < dl | < dl |
| Avg. | 0.024 | 0.021 | 0.017 | 0.016 | < dl | < dl | 0.016 | < dl | < dl |
| sd | 0.005 | 0.004 | 0.003 | 0.002 | - | - | 0.002 | - | - |
| %RSD | 19.4 | 19.3 | 18.2 | 10.2 | - | - | 10.0 | - | - |

Table 2.57: Results for chromium determination of soil samples

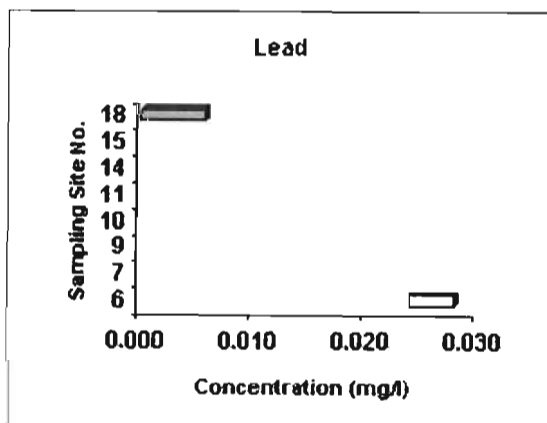
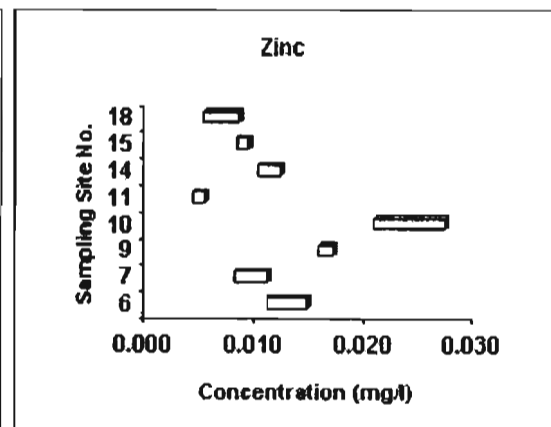
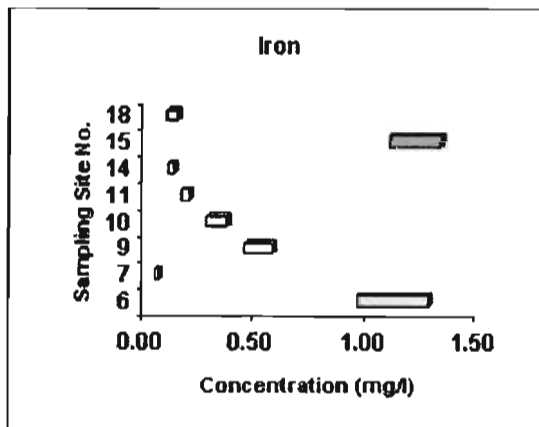
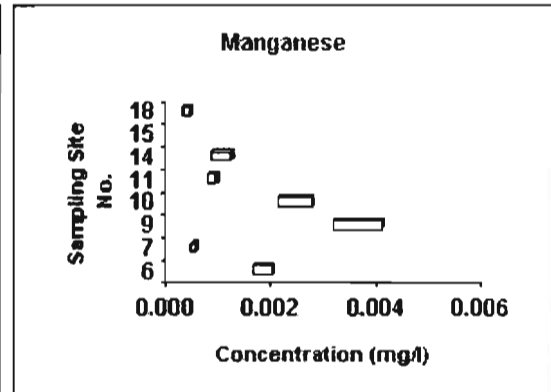
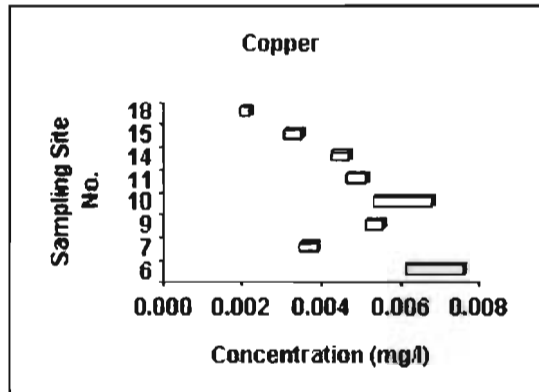
| Site | Concentration (g/kg) | | | | | | | | |
|------|----------------------|--------------|------|--------------|-------|-------|-------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 | 15 |
| 1 | 0.015 | 0.019 | < dl | < dl | 0.020 | 0.016 | < dl | < dl | < dl |
| 2 | 0.011 | < dl | < dl | < dl | < dl | 0.015 | < dl | < dl | < dl |
| 3 | 0.024 | < dl | < dl | < dl | < dl | 0.014 | < dl | < dl | < dl |
| 4 | < dl | < dl | < dl | 0.010 | 0.010 | 0.014 | 0.015 | < dl | < dl |
| 5 | < dl | < dl | < dl | < dl | 0.015 | < dl | 0.019 | < dl | < dl |
| 6 | 0.013 | < dl | < dl | 0.014 | 0.011 | < dl | 0.028 | < dl | < dl |
| 7 | 0.027 | < dl | < dl | 0.011 | 0.013 | < dl | 0.017 | < dl | < dl |
| 8 | 0.013 | < dl | < dl | < dl | 0.012 | < dl | 0.018 | < dl | < dl |
| 9 | 0.040 | < dl | | < dl | | | | | |
| 10 | 0.030 | < dl | | < dl | | | | | |
| 11 | 0.020 | < dl | | < dl | | | | | |
| 12 | 0.022 | < dl | | 0.051 | | | | | |
| 13 | 0.025 | < dl | | 0.067 | | | | | |
| 14 | 0.018 | < dl | | 0.012 | | | | | |
| Avg. | 0.021 | < dl | < dl | < dl | 0.013 | 0.015 | 0.017 | < dl | < dl |
| sd | 0.006 | - | - | - | 0.004 | 0.001 | 0.005 | - | - |
| %RSD | 28.8 | - | - | - | 27.1 | 8.6 | 26.0 | - | - |

APPENDIX THREE

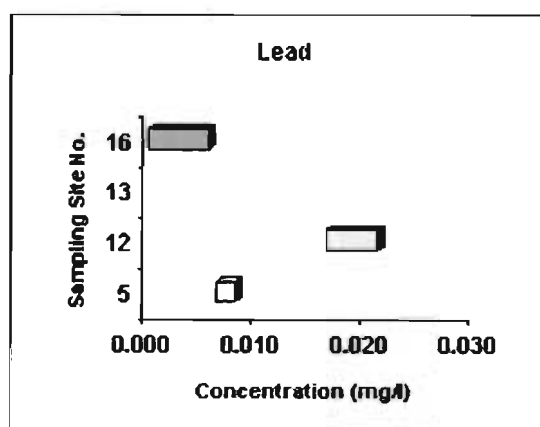
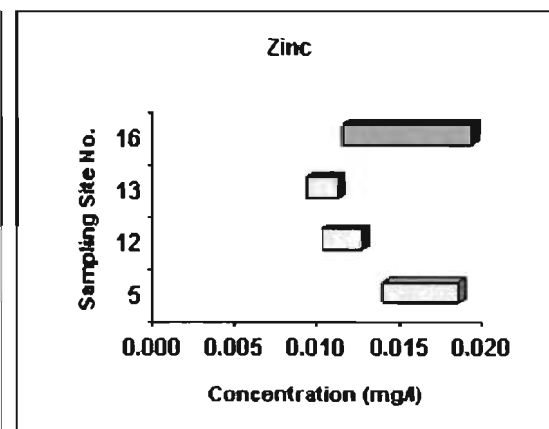
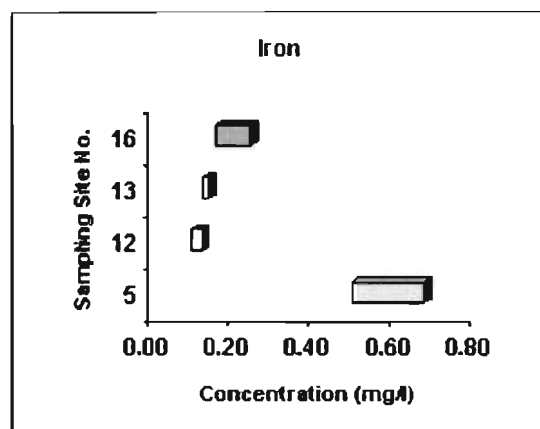
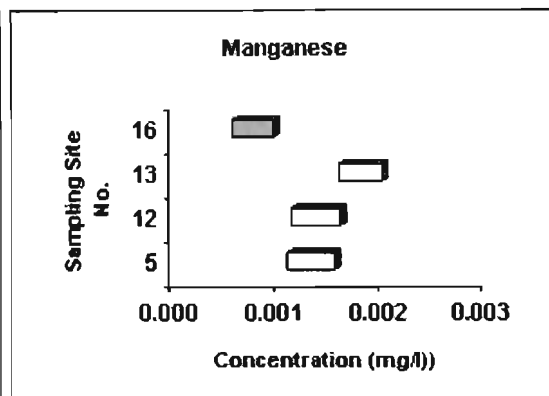
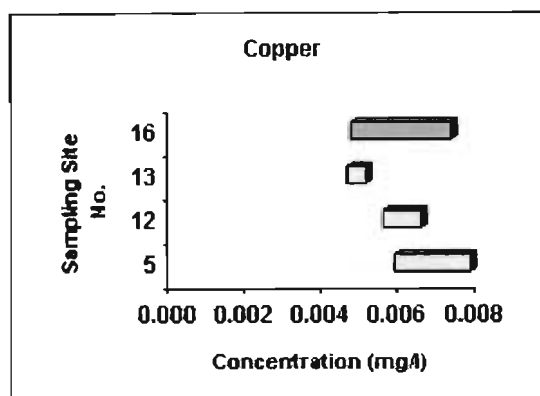
A-3.1 Confidence Interval Graphs for Water Samples

The shaded bars on the graphs below indicate the background sites.

3.1.1 Freshwater Samples

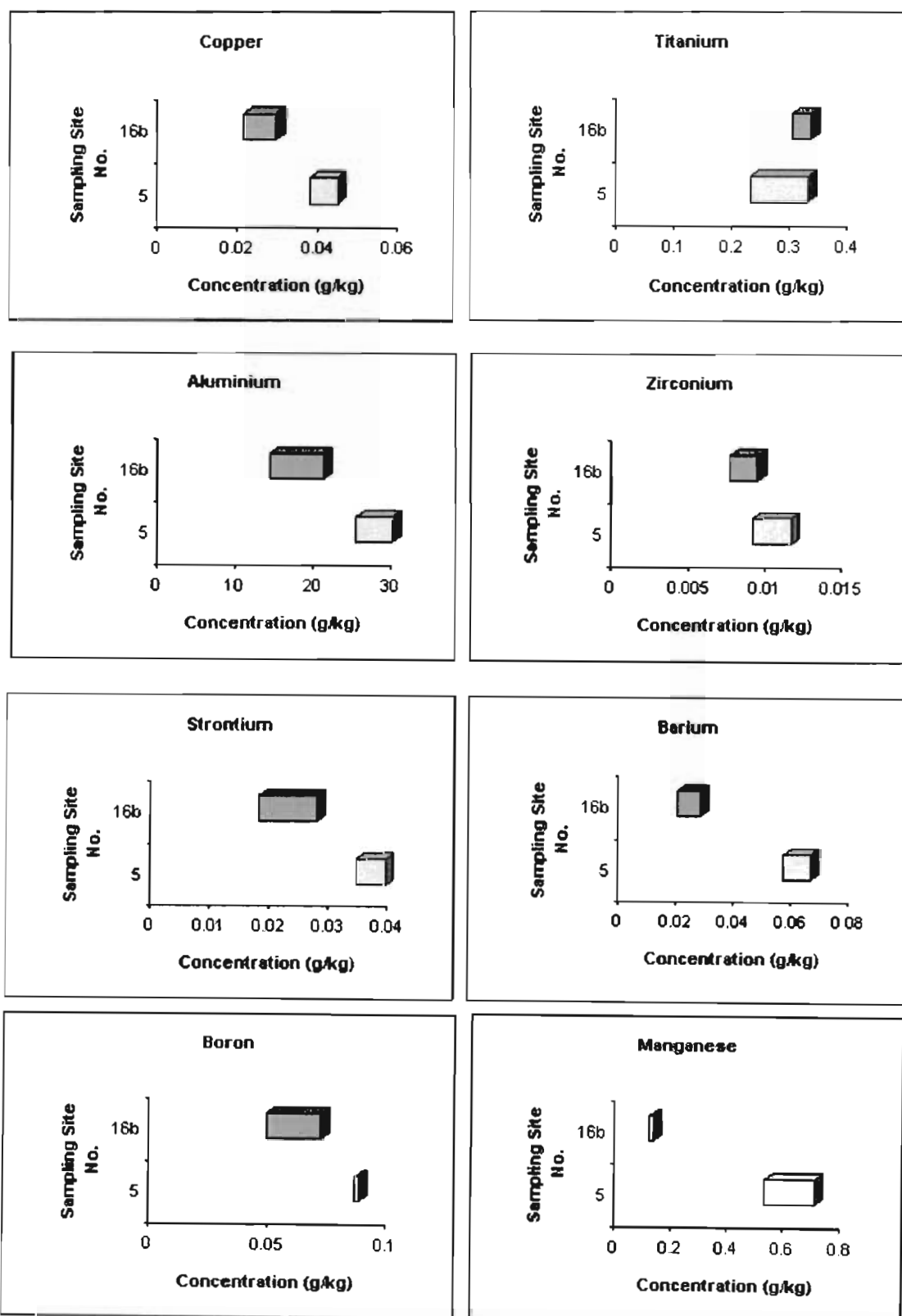


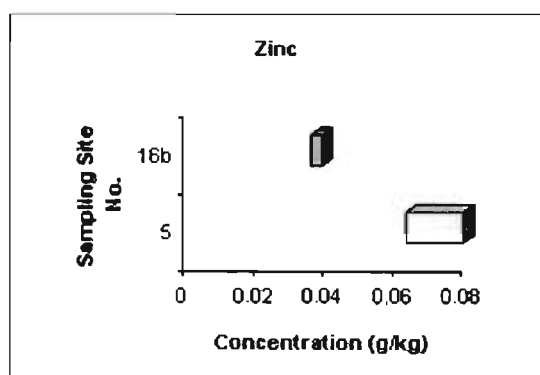
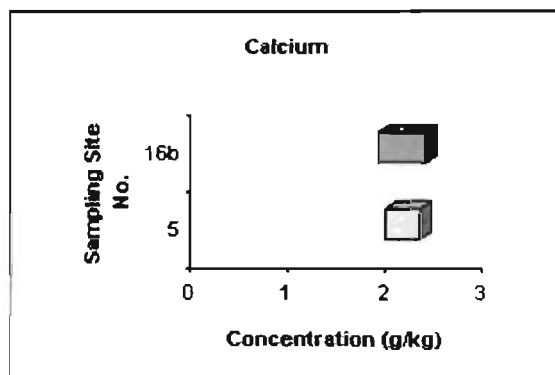
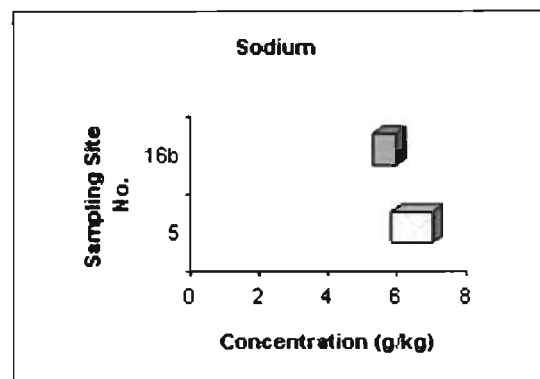
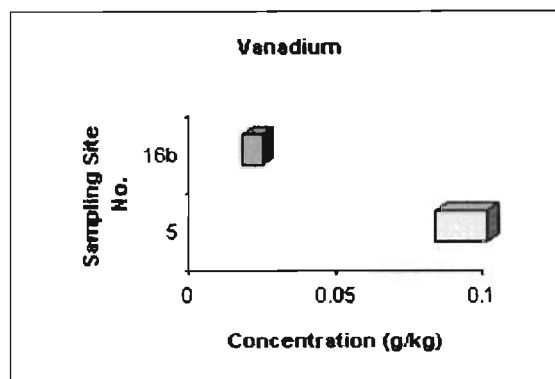
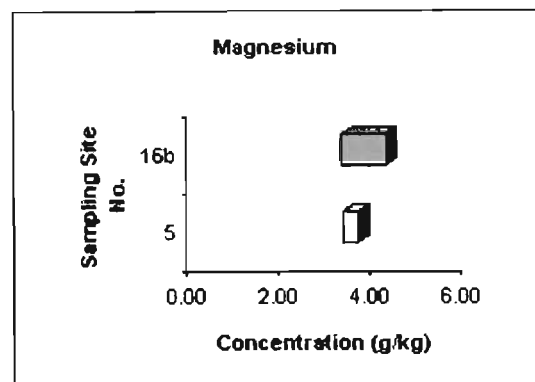
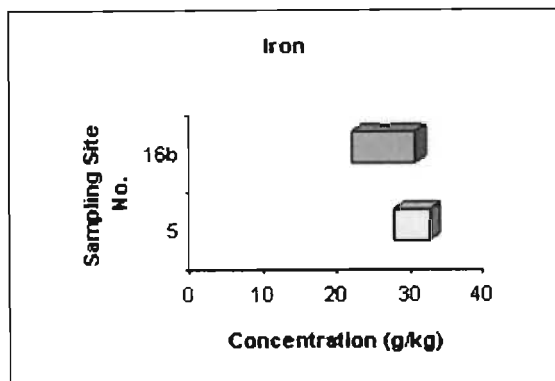
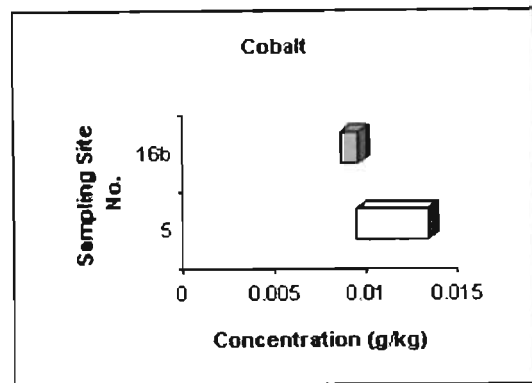
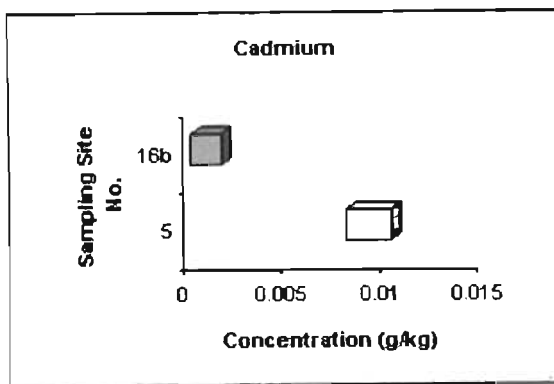
3.1.2 Saltwater Samples

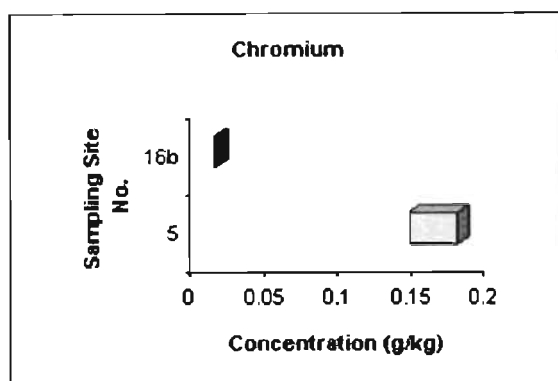
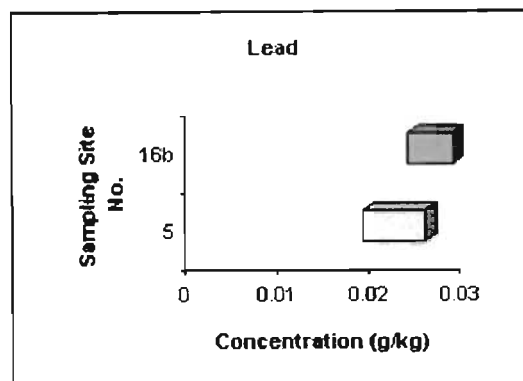
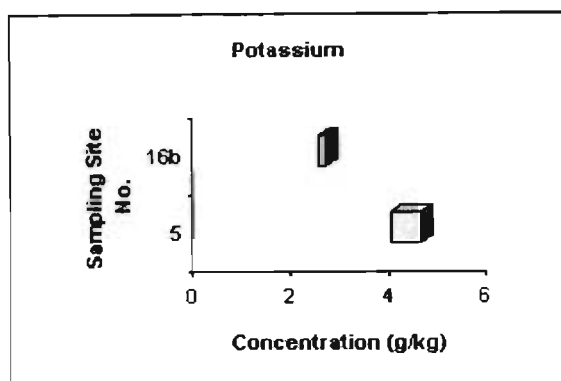


A-3.2 Confidence Interval Graphs for Sediment Samples

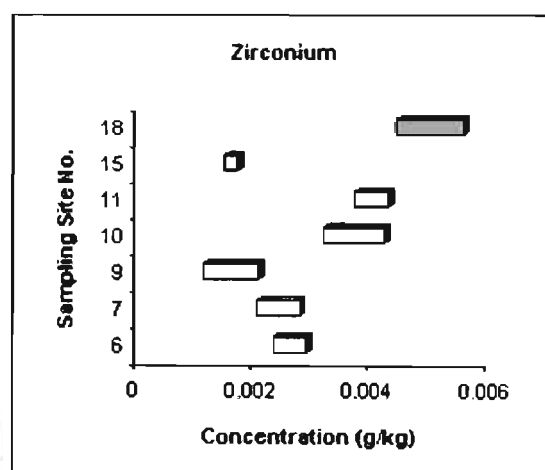
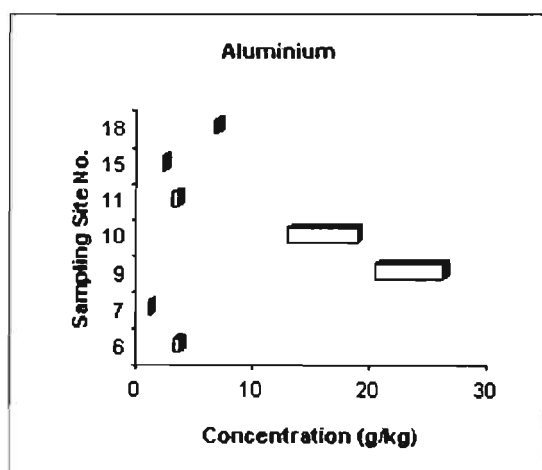
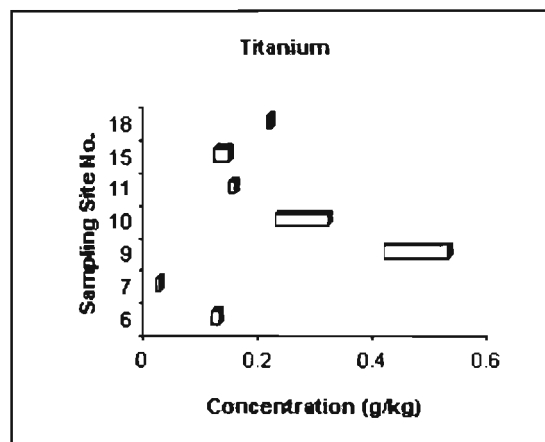
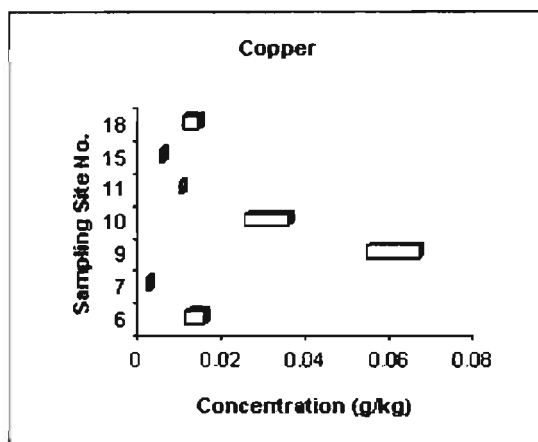
3.2.1 Mangrove Sediment Samples

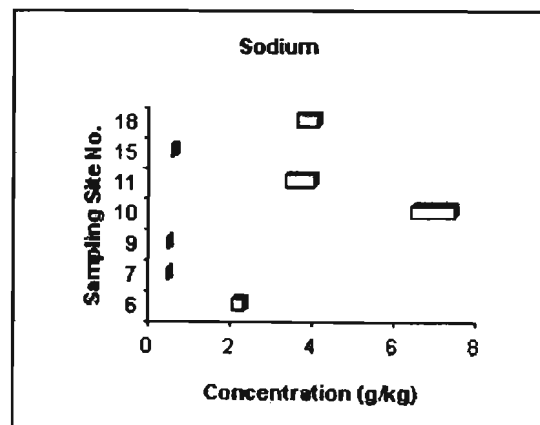
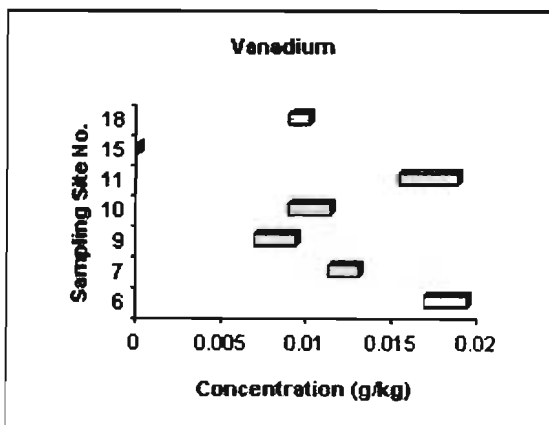
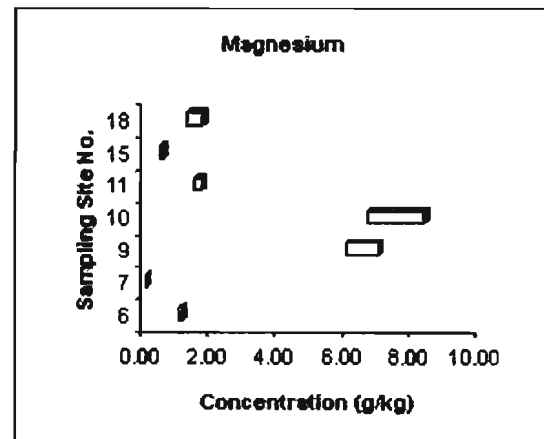
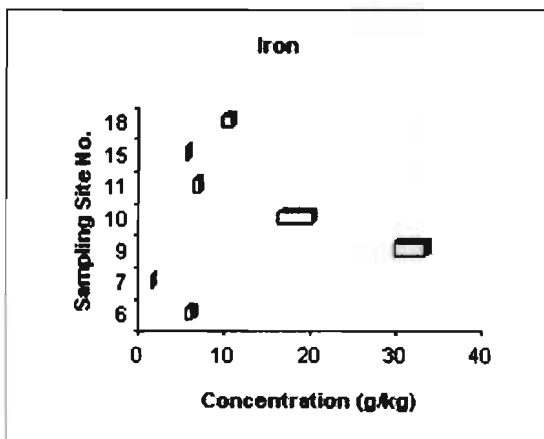
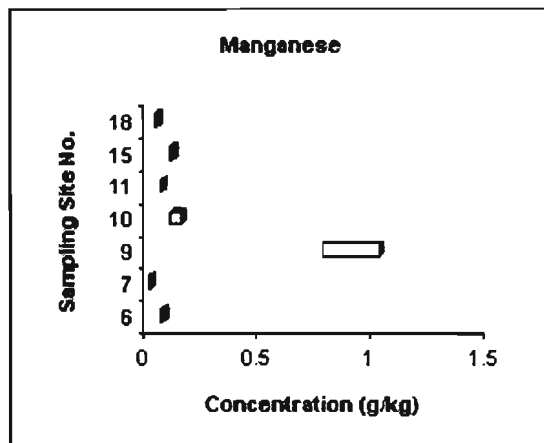
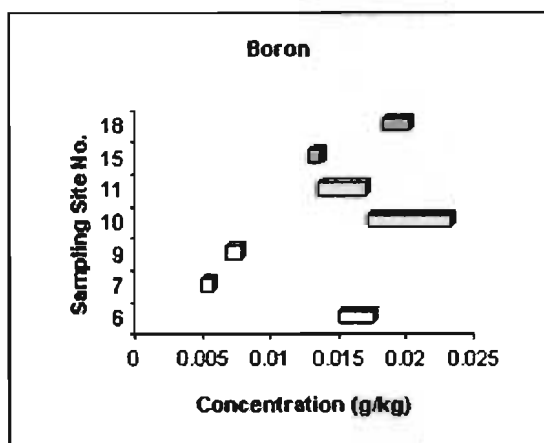
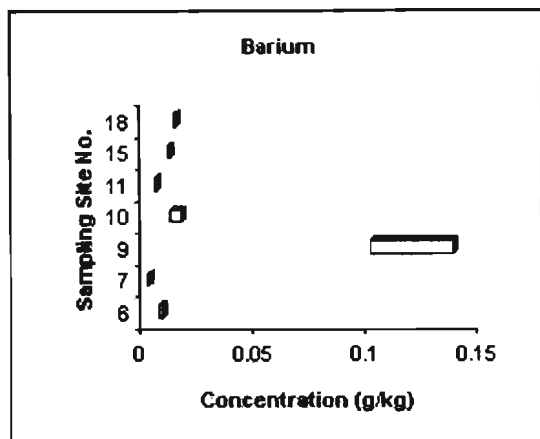
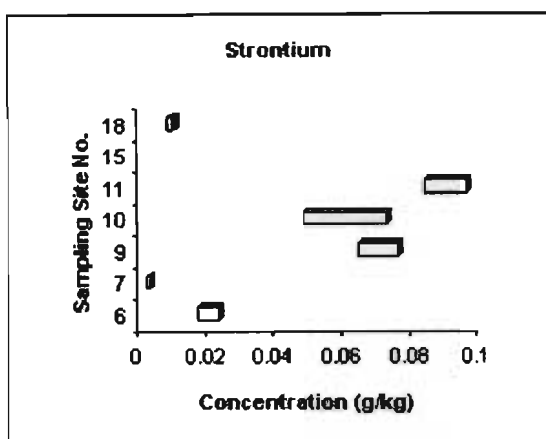


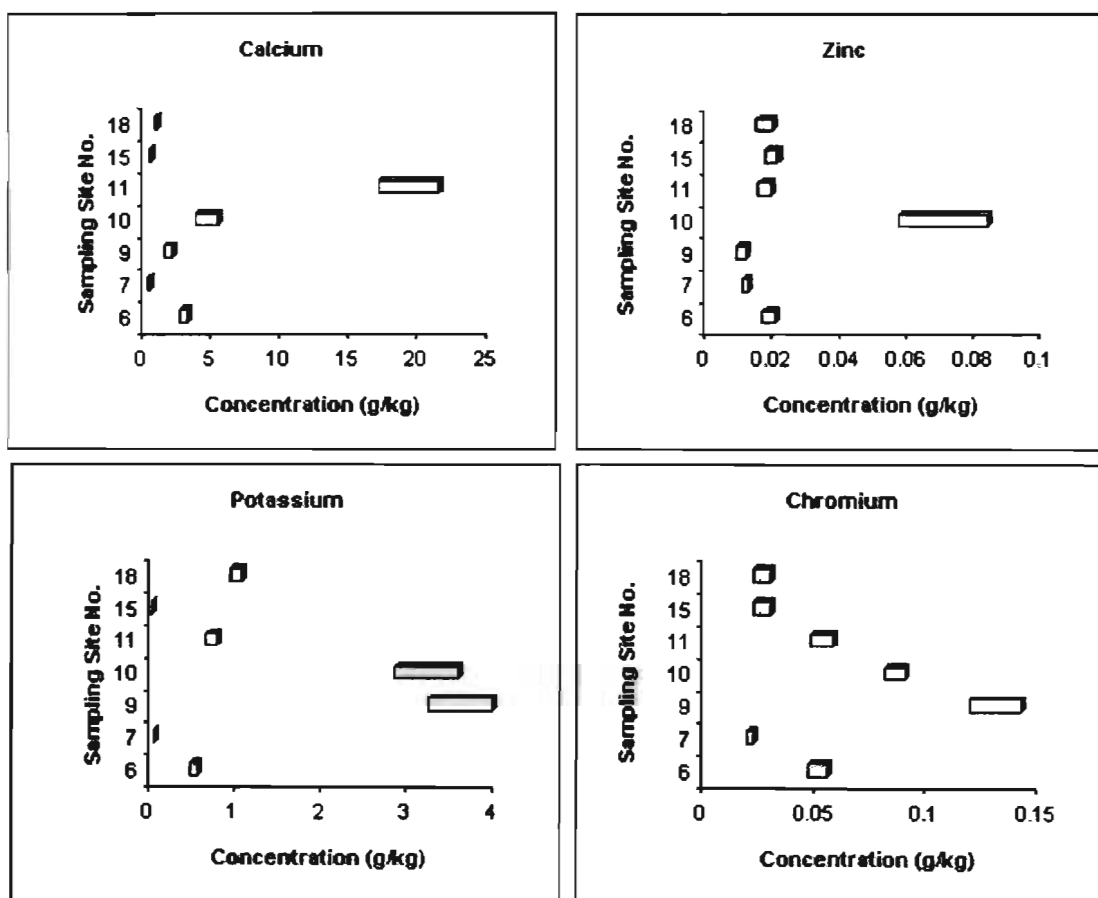




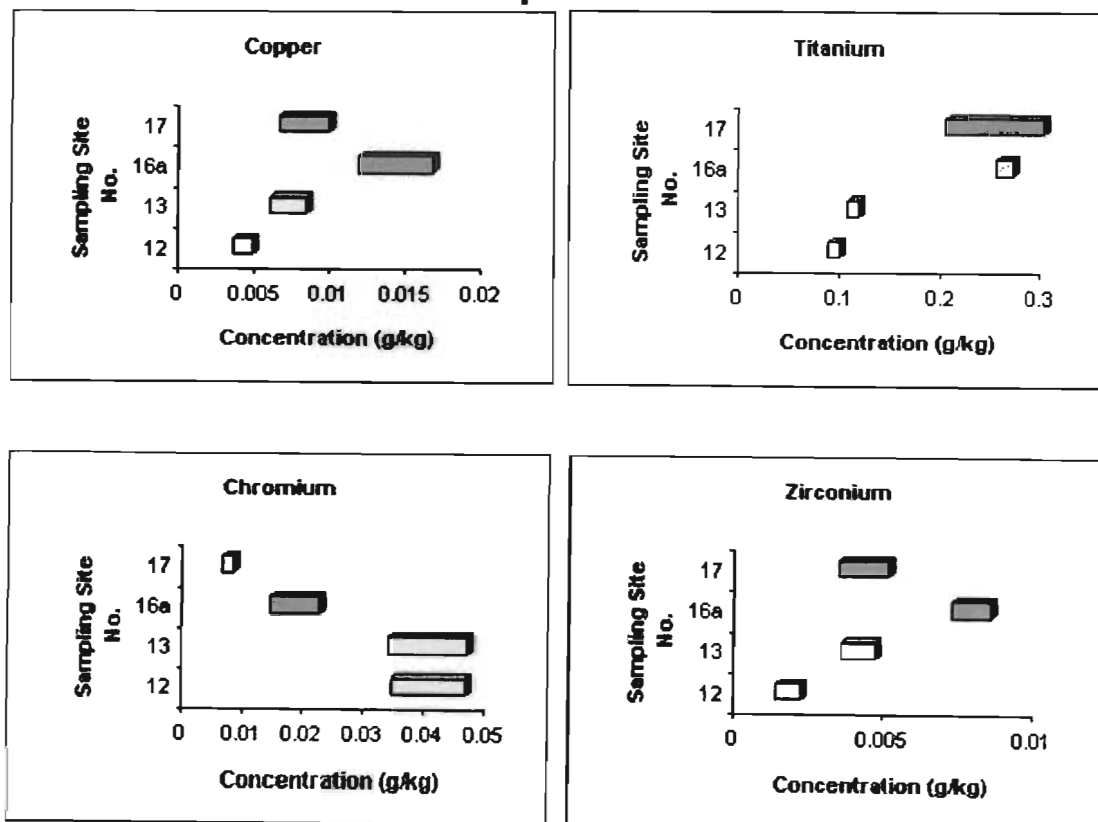
3.2.2 Freshwater Sediment Samples

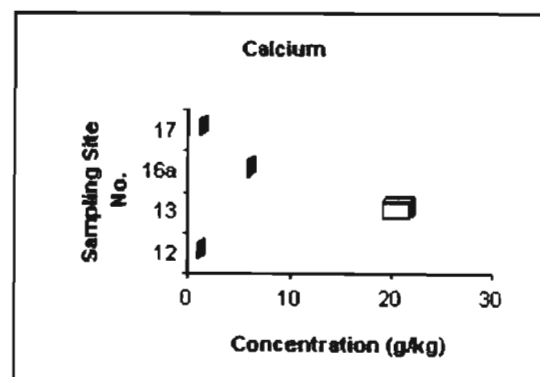
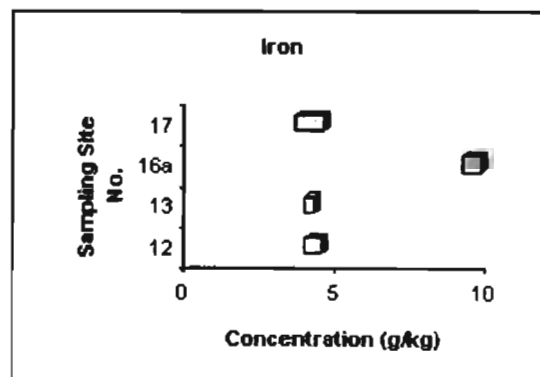
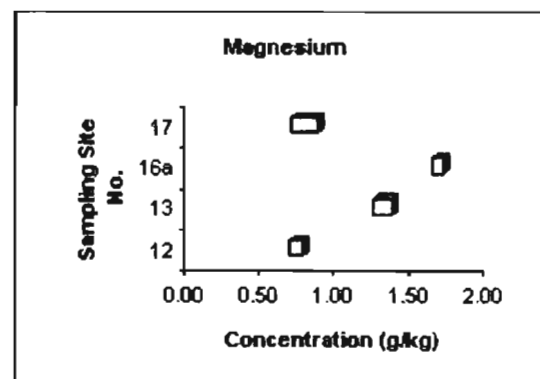
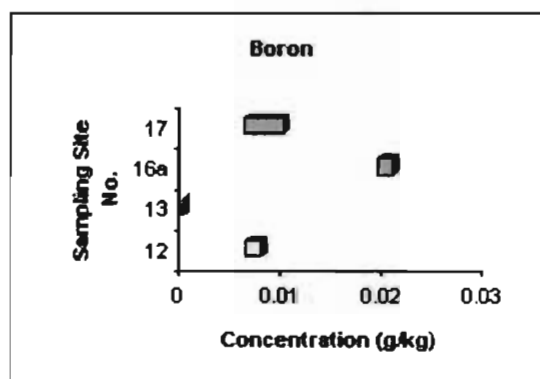
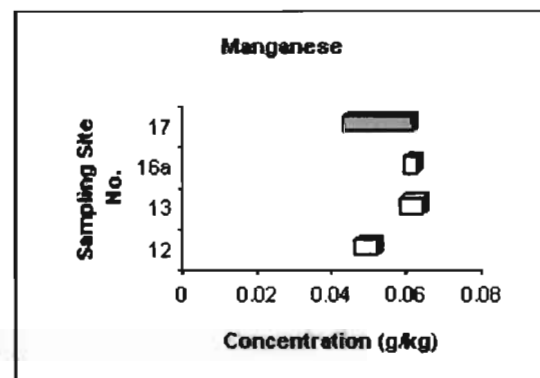
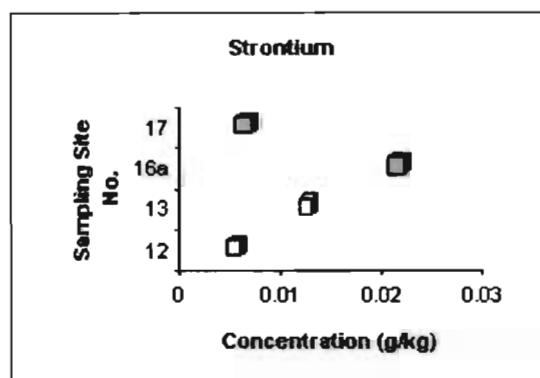
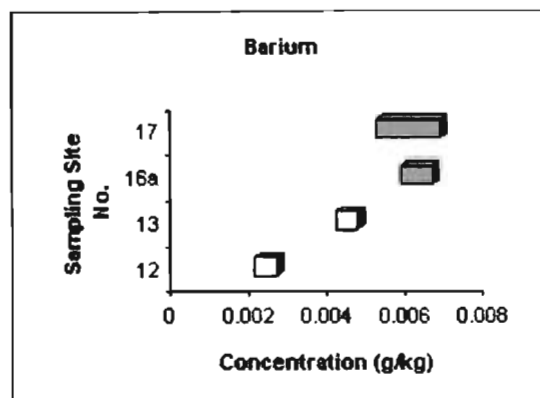
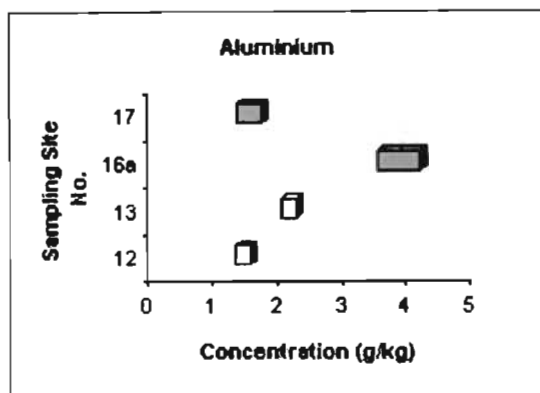


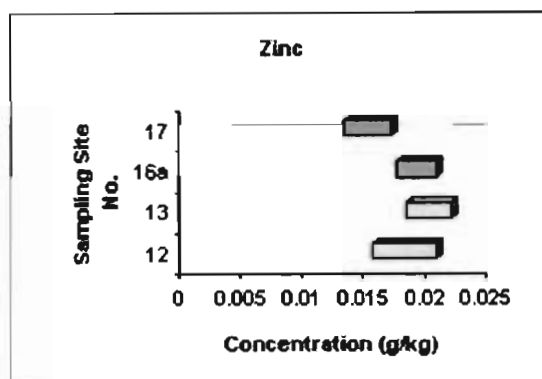
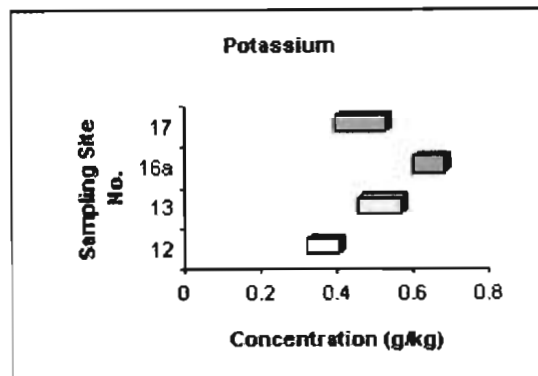
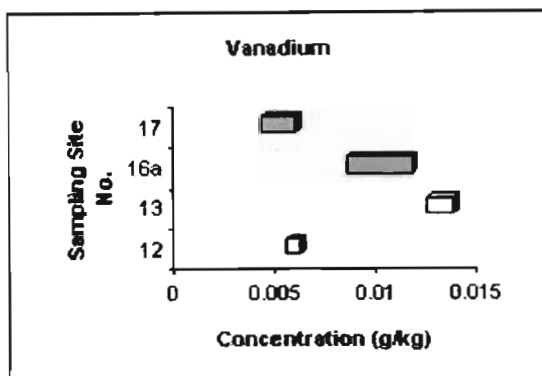




3.2.3 Saltwater Sediment Samples







A-3.3 Confidence Interval Graphs for Soil Samples

