

Evaluation of heavy metals in soil: a case study of platinum tailing dam site.

By

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Declaration

I declare that this report titled **“Evaluation of heavy metals in soil: a case study of platinum tailing dam site”** is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

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Date

Dedication

This dissertation is dedicated to my loving and supportive husband Mpho and to my beautiful daughter Nkateko, and all my future offsprings. It is also dedicated to my parents and siblings who have always believed in me.

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I would like to take this opportunity to acknowledge every single contribution made from people and institutions that made the project possible.

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List of abbreviations

UG2----- platiniferous chromitite seam

PGM----- Platinum Group Metals

Al ----- Aluminium

Cu ----- Copper

Fe ----- Iron

Ni ----- Nickel

Pb ----- Lead

Cr----- Chromium

g/t ----- grams per ton

Ha----- Hectors

cm----- centimetres

ICP MS-----Inductive coupled plasma

ICP OES.....Inductive coupled plasma / optical emission spectrometry

CEC-----Cationic Exchange Capacity

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ABSTRACT

Mining industry has been identified as the main sustenance of the South African economy, however the negative impacts of the industry on the ecological systems cannot be over emphasized due to the released waste which is mostly heavy metals into the environment. The study evaluated six heavy metal (Al, Cu, Fe, Ni, Pb and Cr) contents in a tailings dam from a specific mine site. Two sets of samples for the investigation were measured, that is, one in year 2012 and the other in year 2013. In the year 2012, the sample set was only taken at a distance profile of 500 meters from the foot of the dam, whereas the sample set taken in the year 2013 was for the 500 and 1500 meter distance profiles from the foot of the dam. The year 2012 and 2013 sample sets for the 500m distance profile were sampled very similarly to each other. A kilogram of each sample was taken as per grid format. The samples at varied depths were taken at 0-cm depth for the top layer, 20 cm depth for the second layer, and 30cm depth for the third layer. The samples for the surface varied distance were taken at 1 m, 2m, 3m, and 4m away from each 500m and 1500m sampling points. The 2012 samples were analysed using characterization methods namely ICP MS and The 2013 samples were analysed using the ICP OES. The comparison of the field results for the six heavy metals studied (Al, Fe, Pb, Cu, Ni and Cr) was performed using statistical analytical methods, namely ANOVA. The statistical analysis results for heavy metals (Al, Fe, Pb, Cu, Ni and Cr) from 2012 sample and 2013 revealed that the group means are not significantly different from each other which means that there is no significant difference in (Al, Fe, Pb, Cu, Ni and Cr) concentrations with respect to both depth and distance. The observations from both 2012 and 2013 indicate the results of the samples are in agreement. In addition, the comparative average concentrations of the three results obtained reach the same conclusion that the tailing dam probably does not introduce considerable or significant amounts of these metals (Al, Fe, Pb, Cu, Ni and Cr) into the surrounding soils.

CHAPTER ONE

1 INTRODUCTION

1.1 The Context of the Research

Industrialization plays a vital role in sustaining the nation's economy and improving the wellbeing of its citizens. However, industrialization also has a negative impact, particularly in terms of the release by plants of unwanted by-products into the ecological system. Also, the long-term effects of industrial pollution on the environment may be disastrous for not only people but for all living organisms if not carefully controlled. This explains the current awareness among researchers of the need to monitor the activities of process industries, especially those that discharge heavy metals into the environment.

Heavy metals occur naturally in the ecosystem, with large variations in concentration. In modern times, anthropogenic sources of heavy metals, that is, man-made pollution, have also been introduced to the ecosystem. The resultant build-up of heavy metals and sediments in the soil has caused acute concern in environmentalists. The main issues include the potential toxicity to plants and wildlife an overload of heavy metals may cause, and the inherent problems of bio-magnification that may occur at several levels in the biological food chain. This in turn may lead to serious health problems in animals and humans (Suruchi and Pankaj, 2011). Yet another series of problems raised by an excess of heavy metals in soils is that of tropic accumulation and transport, which result in heavy metal contamination of groundwater by leaching, the pollution of waterways, and surface water runoffs that result in erosion. Once a groundwater aquifer has been contaminated, there is little chance that it can be put to use for several lifetimes (Olade *et al.*, 1978).

Heavy metal contamination will always be an issue as long as we have mining operations, beneficiation (metallurgical) plants and chemical industrial sites, all of which are major contributors to the dispersion of heavy metals into our soil. This has given rise to a great deal of research into the topic in the hope of finding methods and technologies that will assist these industries to dispose of their waste more responsibly, and in doing so to minimize the extent to which they contaminate the environment.

In the past, the investigations carried out by soil chemists have focused primarily on plant macronutrients (nitrogen, phosphorus, and potassium). Little work has been done on heavy metals until relatively recently (Alloway, 1998). Although the acutely toxic effects of heavy metals on plants and animals have been recognized for many years, it is only during the last 30 years that the levels of chronic accumulation of many metals in the soil and ecosystems have come under the research spotlight, because they constitute a major environmental problem. Many of the heavy metal elements will persist in polluted soils for hundreds or even thousands of years, according to Alloway (1998). While one objective of the ongoing research is to prevent pollution via heavy metals, another is to manage soils that have already been polluted. In both cases, the researcher requires an understanding of the factors controlling the behaviour and the bioavailability of heavy metals in soil, and also those factors that aid or abate their dispersion. Another prerequisite is the application of equations that are relevant to explaining the dispersion of heavy metals in soil, to enable the researcher to predict the rate at which heavy metals accumulate in it.

Early studies of soil pollution found that cadmium, lead and zinc in soils overlying background and mineralized bedrocks are released through oxidation and leaching during ferralitic weathering. The dominant pathway for their dispersal is aqueous transportation by downward-percolating rainwater, and readjustments in the groundwater table. In mineralized soils, the accumulations of Cd and Pb in the topsoil can reach toxic proportions (Fletcher and Doyle, 1974; Sposito, 1998). Furthermore, concentrations of heavy metals in soils are expected to decrease exponentially with distance from the plant source, mainly owing to dispersion by water and topography (Olorunfemi, 1984). Clarke and Tomlin (1999) showed that the dispersion of metalliferous cations from mineworks is caused by atmospheric processes occurring during the working life of the mine, and by the subsequent sheet and gulley erosion of the spoil heaps remaining, assisted by wind. They also concluded, in agreement with the findings of Olorunfemi, that in general the level of copper, zinc, lead and cadmium contamination dispersal related to the relative distance from the mine workings: the greater the distance, the lower the concentrations of these metals, owing to dry deposition, washout, and rainout processes.

Variations in heavy metal dispersion in soil and in the extent of contamination depend on several factors, including soil texture, temperature and pH. Soil has the ability to immobilise chemicals like heavy metal ions. The results of chemical analyses are likely to indicate that the heavy metals in soils will decrease with distance from the source, but that this is determined mainly by topography and water movement (Myung, 2008). The immobilisation of these metal ions is mainly attributable to the sorption properties of the soil, which are determined by physicochemical factors like the proportion of clay and organic component, pH, water content and temperature, and the properties of the particular metal ion (Alloway, 1998). The dissociation kinetics of the dissolved heavy species and their concentration in the soil are, among others, important causes of toxicity in the environment, as are the dissociation kinetics of the dissolved species (Castilho *et al.*, 1993).

The research described in this dissertation focuses on the evaluation of heavy metal dispersion in soil, using as a case study a tailings dam at Impala platinum mine, which is located to the north of Rustenburg, on the western limb of the Bushveld Complex (Figure 1).

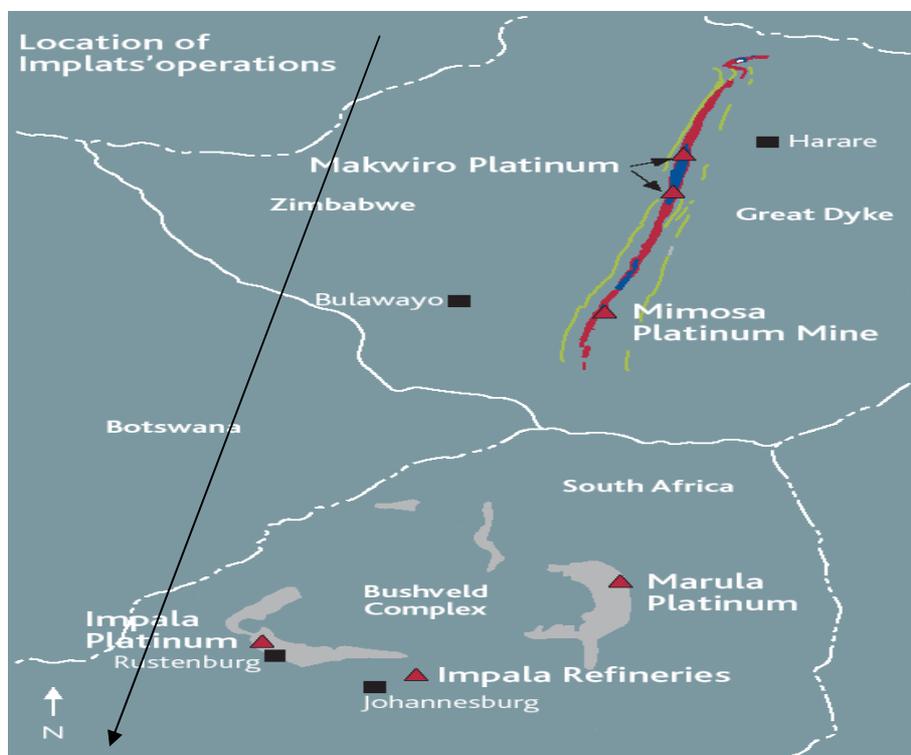


Figure 1: Operations Locations of Impala Platinum Mine

The Bushveld Complex contains two horizons, which are the sites of the Merensky and UG2 reefs, as shown in Figure 1. These two reefs are the host rocks for platinum group metals (PGMs), which are economically exploitable. The mineralogy of the two reefs is very complex. The Merensky consists of feldspathic pyroxenite, which lies between a footwall and hanging wall of anorthosite and norite respectively, with two layers of chromite stringers. The noble metals are usually associated with the two stringers (Lee, 1996).

The UG2 is a platiniferous chromitite seam that lies about 125 m below the Merensky reef, and comprises about 60–90 % of $[(Fe^{2+} \cdot Mg) O(Cr \cdot Fe^{3+} \cdot Al)O_3]$ as shown in Figure 2 (Vermaak, 1950).

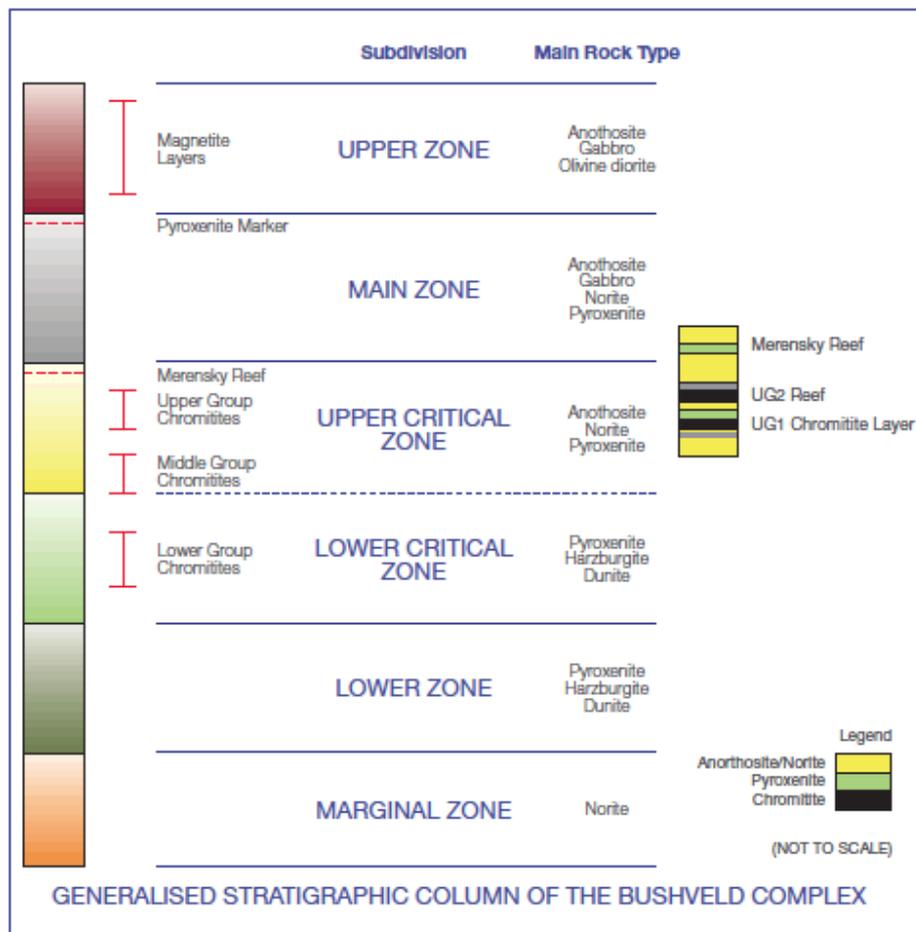


Figure 2: Generalised Stratigraphic Column of the Bushveld Complex (Vermaak, 1950)



Figure 3: Image showing location of PGM Concentrate

The Merensky reef contains pyrrhotite (45%), pentlandite (32%), chalcopyrite (16%), pyrite (4%) and about 3% of base-metal sulphide. The image in Figure 3 shows the layering and location of the chromitite with the PGM concentrate. PGMs are associated with pentlandite, occurring either in pentlandite grains or at the pentlandite-gangue grain boundaries. The constituents of UG2 ore are chromitite (60–90%), orthopyroxene, plagioclase, minor amounts of talc, chlorite, and phlogopite, and small amounts of base-metal and other sulphides and PGMs. The grain sizes supplied for UG2 ore are finer than those yielded by the Merensky reef (Vermaak, 1995).

The conventional route taken to extract PGM from the mined ore is summarized in Figure 4 below. The first step is comminution, either by crushing or grinding. The aim of this step is to increase the concentration of the valuable components in the ore by reducing the bulk of the other products in this raw material. The second step is to separate the desired metals from the gangue by exploiting the density factor (gravity separation). Then the third step introduces the flotation stage, the aim of which is to concentrate the sulphides, after which the flotation concentrate undergoes smelting and converting to produce a PGM-containing nickel-copper matte. The matte is treated by hydrometallurgical processes that separate the base metals from the precious metals. Finally, and fourth, the PGM concentrate is refined to separate the

individual precious metals into their pure forms. As a rough guide, the PGM content during the four stages is ore 0.0005% (5 g/t); flotation concentrate 0.0150% (100–400 g/t); converter matte 0.20%; PGM concentrate 30–65%, refined metals 99.90% for Rh, Os, and 99.95% for Pt, Pd, Au (Roskill ,1994).

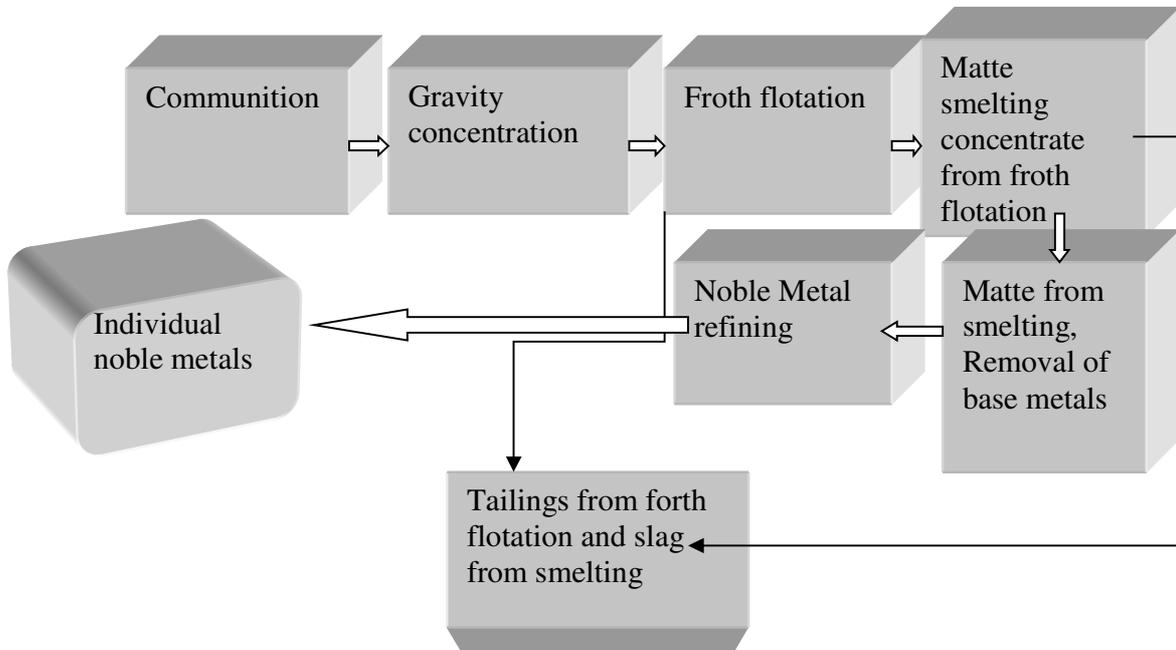


Figure 4: Process Flow Diagram of PGM Extraction

The tailings dam at Impala Platinum mine that was used as a case study for the research has a height of 58 metres and a surface area of 485 ha, as shown in Figure 5. The tailings from both the flotation and smelting processes are discharged into this dam so that the mine can recover some water that can be reused in some of the metallurgical processes.

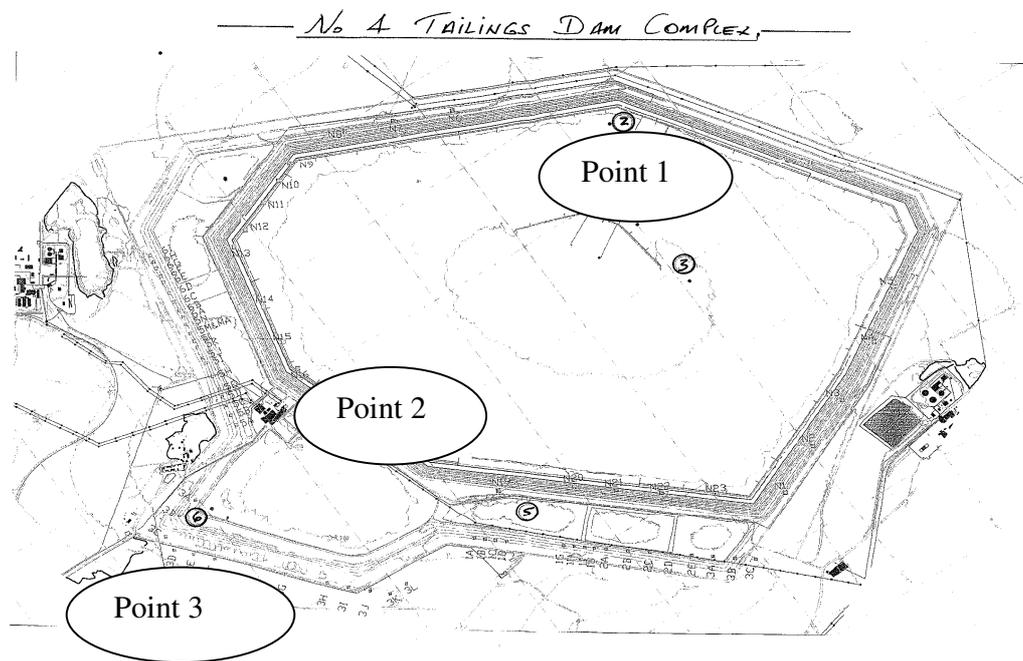


Figure 5: Tailings Dam drawing with sampling points marked

To ensure a proper evaluation of the dispersion of heavy metals in the soil, the researcher carried out soil sampling in a grid pattern both 500 m and 1500 m away from the dam.

1.2 Research Problem

It has been reported that a large amount of heavy metals in soil causes environmental degradation and threatens all life forms because of its toxicity. As a country develops economically, the expansion of industries, the building of new roads and infrastructure, and the increasing population in the cities generates waste that has caused an accumulation of these trace metals in the soil surrounding these sites. It is therefore of the utmost importance to monitor the environment constantly, to prevent disasters arising from the introduction of heavy metals into the soil, particularly by the activities of process industries. Monitoring the levels of heavy metal in the soil will also serve to provide an indication to policy-makers of the pressing need to enforce compliance by various companies and industries with the legislation and regulatory framework already laid down on the control of effluent treatment and discharge.

1.3 Aim and Objectives of the Research

The aim of this study was to evaluate whether or not the platinum tailings dam used as a representative sample plays a significant role in contaminating the soil surrounding it with heavy metals. The aim is expected to be achieved through the following objectives:

- i. Analysis of soil samples collected from the ground adjacent to the tailings dam of the PGM process plant, to determine the concentration of Al, Cu, Fe, Ni, Pb and Cr at various distances both in both vertical and horizontal directions at 500 m and 1500 m from the point of discharge.
- ii. Comparison of the results obtained with the set enrichment factor for each metal as against the global crustal values of the earth's crust for the purpose of determining the level of enrichment in the soil.
- iii. Comparison of the statistical analysis methods such Anova variance to determine whether or not the dam has a significant impact of heavy metal contamination in the soil and the actual field soil samples taken.

1.4 Scope and Limitations of the Study

The scope of this study includes the collection of samples from the PGM process tailings dam, tagging and bagging these samples to prevent contamination, then analyzing these samples to determine the concentration of Al, Cu, Fe, Ni, Pb and Cr, using two different analytical methods, namely Inductively Coupled Mass Spectrometry (ICP MS) and Inductive Coupled Plasma Emission Spectrometer (ICP OES). This study is limited to analysis of the heavy metals Al, Cu, Fe, Ni, Pb and Cr collected at both 500 m and 1500 m distances from the point of discharge.

1.5 Contribution to Knowledge

The findings reported in this dissertation are expected to provide a stimulus for more comprehensive studies of suspected areas of pollution, and to complement further investigations into the chemical behaviour of heavy metals in soils. This subject is of pressing importance, because unless ways of monitoring the activities of heavy metals in soil are found and implemented, the ecological damage they cause will extrapolate.

1.6 Structure of the Dissertation

The dissertation consists of six chapters.

Chapter One introduces the context of the research, which provides a background and a motivation for the study of heavy metal contamination in soil. It further discusses the location and beneficiation processes occurring on the general site on which the sampling site is situated. The objectives of this study are outlined, and the contribution this dissertation can make to work in the field of soil contamination is also discussed.

Chapter Two reviews the existing literature on the factors affecting the mobility of heavy metals in soils, in particular Al, Cu, Fe, Ni, Pb and Cr, by discussing their behaviour in soil and their level of toxicity. The researcher further discusses the properties that determine heavy metal transportation and retention in soil. Soil definition and the processes that take place in soil are exhaustively examined.

Chapter Three discusses in detail the experimental procedures adopted in this study, namely how the field samples were taken, prepared and analyzed. The methods of analyses used were ICP MS and ICP OES characterization techniques, which are fully outlined in this chapter.

Chapter Four focuses on the field results obtained, and compares the behaviour of Al, Cu, Fe, Ni, Pb and Cr in soils. The statistical tool Analysis Of Variance (ANOVA) was used to determine differences in mean concentration attributable to depth and distance for each heavy metal, whether or not the tailings dam was found to introduce significant levels of heavy metal contamination to the surrounding soil areas. The chapter also compares samples measured both in 2012 and 2013. An enrichment factor analysis for each metal was also made to determine whether the existing measured values of heavy metals were the result of anthropogenic or natural causes.

Chapter Five outlines the general conclusions obtained from this study, and makes recommendations for further research in this field.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Introduction

In the previous chapter, the writer provided the reasons for carrying out this research enquiry into heavy metals in soil, and gave details of the stratigraphic levels to be found in the Impala Platinum mine, the processes involved in extracting valuable PGMs, and the location of the adjacent tailings dam. The samples of soil used in this research project were taken from the soil at different distances from the source (the dam), and the different stages of the soil analysis were set out.

In this chapter, the existing published works on soil definition and the processes that take place in soil are discussed in detail, with regard to how these processes affect the behaviour of heavy metals. A further section is devoted to the ways in which heavy metals in soils (or water, or the atmosphere) can affect plant and animal life.

Soil is a complex medium, comprising aqueous and gaseous components as well as mineral and organic solids. The minerals in the soil come from weathered rock particles or secondary clay mineral oxides of Fe, Al, Mn and carbonates. The organic solids consist of living organisms, dead plant material, and colloidal humus generated by microbial activity on the dead plant litter. The particles of organic matter form aggregates that create pores of different sizes, which are interconnected and filled either with air or with water. The organic solids are capable of adsorbing ions, but of course this differs between various materials owing to the influence of the redox conditions, pH and the ion concentration in the soil solution. When carbonates with a pH >7 are present in the soil, they cause an increase in its heavy metal retention capacity. In general, the soil properties that determine heavy metal retention are carbonate content, organic matter, pH and iron oxides (Lafuente and Gonzalez, 2008).

The interaction between heavy metals and soil is also contingent on a number of factors. When metals are introduced to the surface of the soil they sink downward. The extent to which this occurs depends on whether the soil's metal retention capacity is overloaded, and on the

interaction of the metal with the waste matrix, which is associated with accelerated movement. Metal mobility may also increase when changes in the pH, organic waste composition matrix or solution composition occur over time in the soil environment. The extent of metal contamination vertically (downwards) is closely related both to the composition of the soil solution and to the chemistry of the surface of the soil matrix in relation to the heavy metal and organic waste in question. Heavy metals cannot be degraded over time. However, some of them can be oxidized into other states, which greatly reduces their mobility and toxicity.

In soils the mobility of other elements is greater than that of heavy metals. The reason could be that the capacity of soil to adsorb heavy metals is limited.

At this point the writer considers it advisable to supply a definition. The term 'sorption' refers to the process when *adsorption* (the accumulation of ions at the interface between a solid phase and an aqueous phase) and *absorption* (the taking-in of ions to enter a solid phase) take place simultaneously when the metal is removed from the soil solution. Adsorption is different to precipitation because the metal does not form a three-dimensional solid phase, but associates with the existing surfaces of the soil particles.

The role of the soil's organic matter in retaining heavy metals is that water-soluble complexes of heavy metals are formed from the biochemical elements, and this increases metal mobility (Stevenson, 1991). A continuum of reactive sites is required for the binding of heavy metals to organic matter. These range from weak attraction forces to strong formation of chemical bonds. Soil organic matter can therefore become the main source of soil cation exchange. As the organic matter content in the soil decreases with greater soil depth, the mineral content of the soil becomes the surface for sorption (Jenne, 1968).

The movement of heavy metal in soil depends on its amount, its behavioural interaction with other solid phases it encounters, environmental factors and soil components. The sorption surfaces include clay particles, Fe, Al and Mn (hydro) oxides and organic matter (Jalali and Khanlari, 2008).

Heavy metals in the soil introduced by anthropogenic activities fall into several types of pools: those associated with insoluble soil organic matter, precipitated as pure or mixed solids; those occupying exchange sites on inorganic soil constituents; those dissolved in the soil solution; and specifically those adsorbed on inorganic soil constituents (Shuman, 1991). In the soil the heavy metals can be associated with mobile organic or inorganic colloidal material. They are also present in the form of either free (uncomplexed) ions (for example $\text{Cd}^{2+}\text{Zn}^{2+}$), or in more than one soluble complex (organic or inorganic) ligand like ZnCl or CdSO_4 . (A complex is defined as an atom or ion bonded to an array of molecules or anions in a geometric pattern.) Adsorption, sorption and precipitation processes, including metal organic complex formations, all depend on the pH value of the soil matrix. Under conditions in which the soil is neutral and basic, the mobility of heavy metals is minimal (Hlavay *et al.*, 2004).

The precipitation of heavy metals in soil may occur to form a three-dimensional solid phase. These may be either pure or mixed. The latter is formed when different elements co-precipitate. An example of a pure solid is CdCO_3 , $\text{Pb}(\text{OH})_2$, while an instance of a mixed soil is $(\text{Fe}_x\text{Cr}_{1-x})(\text{OH})_3$. Co-precipitation is found in three forms — inclusion, solid solution formation and adsorption, depending on the association between the host mineral and the trace element(s) (Sposito, 1989). Solid solution formation takes place when the trace metal and the mineral host element are compatible. The trace metal can replace the host element in the mineral uniformly, as occurs when Ca is replaced by Cd in calcium carbonate. (Ca and Cd have almost identical ionic radii).

Heavy metal binding affinity differs between organic material and soil mineral constituencies. Table 1 below shows that the competitive sorption nature of heavy metal also depends on the soil's mineralogical composition (Dube *et al.*, 2001).

Table 1: Relative Affinity of Metals for soil and soil constituents (Dube et al, 2001)

Soil or Soil type	Relative Order of Sorption	Reference
Goethite	Cu>Pb>Zn>Co>Cd	Forbes et al., 1976
Fe oxides	Pb>Cu>Zn>Cd	Benjamin and Leckie, 1981
montmorillonite	Cd=Zn>Ni	Puls and Bohn, 1988
Kaolinite	Cd>Zn>Ni	Puls and Bohn, 1988
soils	Cu>Zn>Cd>Ni	Biddappa et al., 1981
soils	Zn>Ni>Cd	Tiller et al., 1984
mineral soils	Pb>Cu>Zn>Cd	Elliott et al., 1986
organic soils	Pb>Cu>Cd>Zn	Elliott et al., 1986
soil	Pb>Cu>Zn>Ni	Harter, 1983

The capacity for adsorption in soil, whether specific or exchange, is determined by the number of sites available. Metal cation adsorption, which is similar to that of sorption, is affected by the calcium carbonate, clay, organic matter, pH and redox potential contained in the soil, whereas the metal anion adsorption is influenced by the redox potential, Mn oxide, pH and Fe oxide. All these interactions depend on how the heavy metal, together with the solvent, is added to the soil. As discussed above, how metals are sorped in soil is particular to that specific metal. The range (in ascending order) of heavy metal adsorption onto soil is Ni< Cu < Cr< Pb, whereas Cu and Pb are regarded as of low mobility (Rikers, 1999). Further, published studies have shown that the adsorption tendency of components for Pb to Cd decrease in the order Mn- oxides > Fe- oxides > organic matter.

Table 2 shows the different affinities found for heavy metal adsorption in the soil compounds. The reader will observe that nickel has a low affinity for oxides and organic matter, and is more mobile than other heavy metals like lead, copper and zinc.

Table 2: Affinity Order of heavy metal ion for oxides and organic matter

Affinity of heavy metal ions for oxides and Organic matter Order	Mn-oxides	Amorphous Fe- oxides	Amorphous Fe- oxides	Organic matter
High affinity	Cu	Pb	Pb	Ni- Cu
	Co	Cu	Cu	Co- Ni
	Mn	Zn	Zn	Pb -Co
	Zn	Ni	Ni	Cu- Pb
	Ni	Cd	Cd	Zn -Ca
	Ba	Co	Co	Mn -Zn
	Se	Sr	Sr	Ca- Mn
Low affinity	Ca	Mg	Mg	Mg -Mg

The concentration of heavy metals retained in soils varies widely. These differences are brought about by the surrounding geological environment, and by the anthropogenic and natural activities taking place in that area. Heavy metals transport is mainly dependent on the physical and chemical properties of soil: the pH, mineralogical composition, and the clay and organic content. Because the soil matrix is very complex, it is difficult to chart the interaction of a specific metal with other elements and to assess its contribution to adsorption. This in turn makes the development of accurate soil models for the prediction of metal transport problematic (Prusinkiewicz, 1992).

The binding forces between heavy metals and soil fractions are dependent on pH and ion properties like charge and ionic radius. The forces that bind metal ions to soil decrease as the pH rises. Another important factor is that affinity for binding heavy metals varies when there are differences in soil mineral constituencies and organic material.

Table 3: Range of Affinities of metal ions to soil sorbents (Benedetti, 1995)

Soil Adsorbents	$\text{Ca}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$
Montmorillonite	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$
Illite	$\text{Pb}^{2+} > \text{Ca}^{2+} > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$
Kaoline	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$
Hydrous oxides of Fe humic	$\text{Fe}^{3+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+} = \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}$

Prusinkiewicz (1992) described a study of soil conducted in Barcelona that aimed to standardize extraction procedures by assessing three extraction methods for heavy metals. His research focused on Cd, Zn, Cu and Pb. The final assessment was that the relative mobility of trace metals was $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb}$ in the soils studied. These findings are in agreement with those obtained from another study undertaken in London by Diatta and Polish (1998), in which the objective was to measure heavy metal migration rates in low-permeability soil. In the latter, centrifuge infiltration tests with three different gravities were used. The findings were later extrapolated into a gravity of 1, which indicated the field conditions. The predictions made by Diatta and Polish, based on analysis of the tests, were that when the rates of migration of Cu, Ni and Zn were compared, the mobility of Ni is more significant than that of Cu and Zn, and that Zn is more mobile than Cu.

The retention mechanism for heavy metals normally occurs via the precipitation of metal ions with either carbonates or hydroxides (Griffin *et al.* 1977). However, when the pH solution is >4 , the retainers are carbonates and hydroxide. The presence of carbonates in a soil contributes significantly to the retention capability of the soil (Yong and Phandunchewit, 1993).

2.1.1 Soil properties affecting heavy metal mobility

Organic matter: All soil types contain organic matter, but the variation in the amount and type of the organic component results in marked differences in the chemistry of the soil. The colloidal organic matter can be categorized into humic and non-humic substances. The non-humic category consists of carbohydrates, organic acids, waxes and fats, whilst the humic category comprises acidic polyelectrolytes, which are yellow to black in colour. The soil humus consists predominantly of humic substances and biochemicals, which are bound to the humic polymers (Alloway, 1995).

Soil pH: Reactions taking place in the soil are the most important factor affecting the chemical behaviour of heavy metals. Because of the soil's complex heterogeneity, the pH concept, which applies to the concentration of the hydrogen ion (H^+) present in solution in the soil pores, cannot be determined precisely. The hydrogen ion (H^+), which has the ability to replace other cations, is in dynamic equilibrium with the negatively-charged soil particles. Soil pH is also affected by changes in redox reactions, which mean that under reducing conditions a pH increases and under oxidizing conditions it decreases. Heavy metals are generally most mobile under acid polymer conditions (Alloway, 1995).

Clay minerals: These minerals, which are the products of rock weathering, affect both the physical and chemical properties of soil. Clay minerals have a large surface area and a permanent surface negative charge. Their mobility is greater than that of heavy metals in soils. The reason could be that the adsorption capacity of heavy metal is limited, and that its mobility depends on behavioural interaction with other solid phases. The amount of heavy metal introduced, environmental factors and other soil components affect how heavy metals are sorped in the soil. Some of the sorption surfaces are clay particles, Fe, Al and Mn (hydro) oxides and organic matter (Jalali and Khanlari, 2008).

Oxides of iron, manganese and aluminium: The oxides and hydrous oxides of Fe, Mn, Al have marked effects on the chemical behaviour of metals in soils and on soil colour. Each of these three oxides displays a colour different to the others in soil, which is why the colours serve as indicators of the soil formation. The factors that affect these oxides are temperature, moisture,

parent material, Eh and pH. They can be found mixed with clays and with no ordered structure, and in soils that are drained as they precipitate and form coatings on soil particles. They can also occur as fillings in pores and concentric nodules (Alloway, 1995). The hydrous oxides can also adsorb cations, which include Cr, Cu and Ni from soil solutions, which is why they are referred to as efficient sorbents and sinks for cations such as Al, Cu, Pb, V, Co, Cr, and Ni. Oxides and hydroxides in soil are characterized as having a high cation exchange capacity because of the dissociation of protons from $-OH_2$ and $-OH$ groups of the hydroxides (Miller, 1981).

Oxidation and reduction in soils: Oxidation and reduction conditions in soil are subject to variations that affect the elements it contains, Fe and Mn in particular, although Cr, Cu and Pb are also influenced. The equilibrium position is dependent on the value of Pe , the negative logarithm of an electron activity, which occurs locally for a given redox couple. The redox status of soil is described conceptually by using the aqueous electron.

The equation below expresses the oxidizability of the soil, in terms of which electron-poor oxidizing species are favoured by large Pe values, whereas the opposite (low Pe values) are achieved by reducing species rich in electrons:

$$pe = -\log(e^-)$$

Figure 6 shows an example of the range in the redox potential of soils, and the location in the redox range where the various electron acceptors are active (modified from R. W. Miller, 1981).

Example Of The Range In Redox Potentials In Waterlogged Soils And The Location In The Redox Range Where The Various Electron Acceptors Are Active

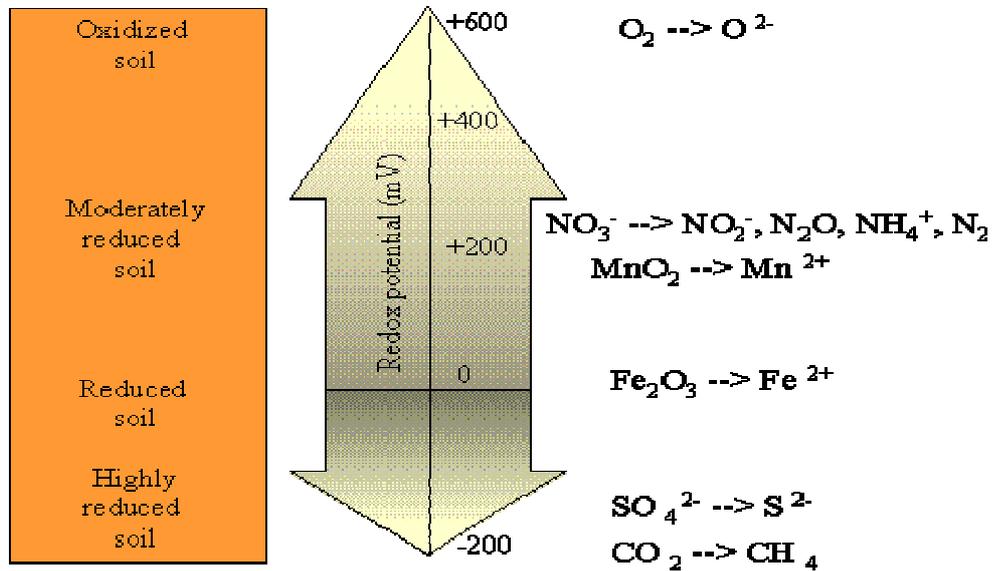


Figure 6: Range in redox potential in waterlogged soils

Interpretation of the figure above indicates that when the redox potential value is high, the environmental conditions in the soil are well aerated. On the other hand, when the redox potential value is low, the environmental conditions are saturated, which means that there is no oxygen in the soil, causing other electron acceptors to begin functioning. When flooding occurs, the order of reduction is nitrate>manganese>iron>sulphate>carbon dioxide (Miller, 1981).

2.1.2 Behaviour of Al, Cu, Fe, Ni, Pb and Cr in Soil

Many factors come into play when the researcher investigates heavy metal cations with soil associations. A study carried out by Al-Barrak concluded that heavy metals can be ranged according to their soil affinity (K_d), in the sequence $Pb > Cr > Cu > Cd$, which is similar to the sequences established by Al-Barrak (1990) for intact soil — $Pb > Cu > Zn > Co > Cd$. It is also fairly close to the sequence for organic matter observed by Rikers (1999) — $Pb > Zn = Cd > Ca > Cu = Ag$.

Parameters such as iron oxides are just as important as organic content to soil analysis. In the case of Cr and Pb they are adsorbed in soils with a high organic matter content. Cu, on the other hand, is particularly sensitive to the minerals in soil that contains calcite and dolomite (Cave and Talens-Alesson, 2005).

Every heavy metal has a different adsorbent selectivity, based on the metal ions it contains. Research undertaken by chemists (for example Gome, 2001) showed that both the ionic radius and the ionization potential determine whether or not metals will form covalent bonds. The metal cations can create strong complexes (Pb>Cd>Cu>Ni>Zn). When more than one heavy metal is introduced into the soil, competition for sorption sites is unavoidable. Competition between heavy metals will cause mobility, toxicity, leachability and potential bioavailability (Rabi and Usman, 2008).

Copper (Cu): Copper is an element essential to both plants and animals. It is reddish, with a bright metallic lustre in its metal state, and it is used to produce wire and brass alloys. Copper metal is associated with soil silicate clays and soil organic matter. Copper in the soil can be categorised in terms of six pools: Cu adsorbed by hydrous oxides of Mn, Fe and Al; soluble ions; inorganic and organic complexes in soil solution; exchangeable Cu; stable organic complexes in humus and Cu adsorbed on the clay humus — colloidal complex (Adediran and Kramer, 1987).

The chemistry of copper in soil is that it is specifically adsorbed. The organic matter plays an important role in retaining copper in soil, as shown in the sequence organics>Fe/Mn oxides>>>clay minerals (Harter, 1986). Mn oxides and organic matter in the soil are likely to bind copper in a non-exchangeable form (Bradl, 2004). As indicated in Table 2 above, copper has strong affinity for soil organic matter. Sorption isotherms indicate that adsorption of Cu onto soil organic matter associated with the clay fraction of the soil may occur, but its adsorption is clearly shown by the Langmuir isotherm (a commonly-used phase diagram).

Nickel (Ni): The most solid phase that is likely to precipitate in soils is Ni ferrite. Ni sulphides control the concentration of nickel in a soil solution in an acidic and reducing environment (Sadiq, 1984). In comparison with the other transition elements, Ni is the least sorbed by clay and Fe oxides. PH is an important factor that determines the distribution of Ni between the solid and solution states, and therefore mobility in the soil increases as the pH decreases (Willaert and Verloo, 1988). The retention and precipitation of nickel in soil is encouraged by competitive adsorption with other metals. The factors affecting competitive adsorption are non-particular,

and may include changes in ionic strength, pH, the concentration of Ca^{2+} , and complexation reactions with inorganic and organic ligands in the solution phase.

Table 2 above shows that Ni has a high affinity with dissolved organic matter. One can therefore deduce that the organic matter content and pH are the most significant factors in Ni binding (Ponizovsky and Thakali, 2008).

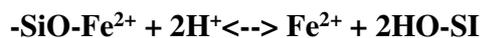
Lead (Pb): Lead is an element that is toxic to both plants and animals. When it is exposed to the environment lead has a long residence time as a pollutant, owing to its low solubility and freedom to microbial degradation. All these factors make it bio-available. A study conducted by Korte *et al.*, (1976) on 11 different soil samples spiked with lead and other trace metals found that lead was immobile in all the soils. The reason is that lead tends to adsorb specifically to other solid phases, which renders it the least mobile heavy metal in soil. Lead precipitates as a highly stable compound, and it also forms complexes or chelates that result from interaction with soil organic matter (Bradl, 2004). As with copper, lead adsorption onto soils and clay minerals is accurately described by the Langmuir isotherm over a wide range of concentrations. The presence of Mn and Fe oxides and organic matter also play an important role in Pb adsorption. Another interesting fact is that carbonate content in a soil affects the behaviour of lead, for example when a pH increase forms PbCO_3 in a calcareous soil.

Chromium (Cr): Various factors affect the adsorption and precipitation of chromium in soil, leading to its retention: competing ions, complexing agents, redox potential and pH (Bradl, 2004). The most critical of these factors are the hydrolysis of Cr (III) and Cr (VI), the redox reactions Cr (III) and Cr(VI), and adsorption/desorption and precipitation of Cr (VI) (Bradl, 2004). This heavy metal occurs in a number of oxidation states, the most stable of which are Cr (III) and Cr (VI). Cr (III) is less mobile and adheres strongly to soil aggregates. At a pH above six there is complete precipitation. Cr (III) is the most common form of chromium to be found in soils (Smith *et al.*, 1989).

Cr (VI) is an anion and the most toxic form of chromium, because it is readily removed from soil and is more stable than Cr (III). Cr (VI) is readily reduced to Cr (III) in acid soils with soil organic matter, although the reduction is slower in alkaline soils (Carry *et al.*, 1977).

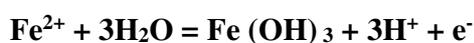
Aluminium (Al): Aluminium is the most common metal in the earth's crust, and can be found in various primary silicate minerals (Sposito, 1989). Hydrolysis of the aluminium in soil causes soil acidity. During weathering these minerals are leached downwards through the soil profile as secondary minerals, especially as alumina silicates. If further weathering occurs, these secondary minerals lose silicon more rapidly than aluminium, and precipitate as hydroxides and oxides. In advanced stages of weathering, soils like ferrosols in the tropics are generally very rich in aluminium oxides. Part of the Al released during the dissolution and weathering processes may also become complexed with soil organic matter and exert a strong influence on heavy metal sorption through competitive effects. In contaminated soil the behaviour of Al will affect the binding and leaching of heavy metal (Gustafsson *et al.*, 2001).

Iron (Fe): Iron is a common constituent in soils and groundwater. It participates readily in subsurface redox reactions, and under some conditions can cause problems in groundwater remediation systems. Not only is iron prevalent, but it is also reactive in that it reflects changes in surrounding Eh/pH conditions. Owing to protonation ($\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$) and oxidation, ions such as Al^{3+} and Fe^{2+} are released. This may be broken down as follows:



(Fe^{2+} silicate \leftrightarrow Fe^{2+} oxide)

If the environmental conditions are aerobic (oxygenated), the Fe^{2+} liberated may be oxidized, migrate to another anaerobic zone, or remain in a reduced state (Schwertmann, 1985). The oxidation (release of electrons) may occur as follows:



Iron has a tendency to hydrolyze because of its high affinity for the OH ligand. From the above equation it can be seen that it hydrolyzes when it comes into contact with H₂O. The iron hydroxides that result have a low solubility, and in the pH range > 3 are quite stable. However, iron hydroxides are easily transformed in response to an increase in reducing conditions:



Reduced species are very mobile (Schwertmann, 1985). Figure 7 shows the Eh/pH stability diagram of iron.

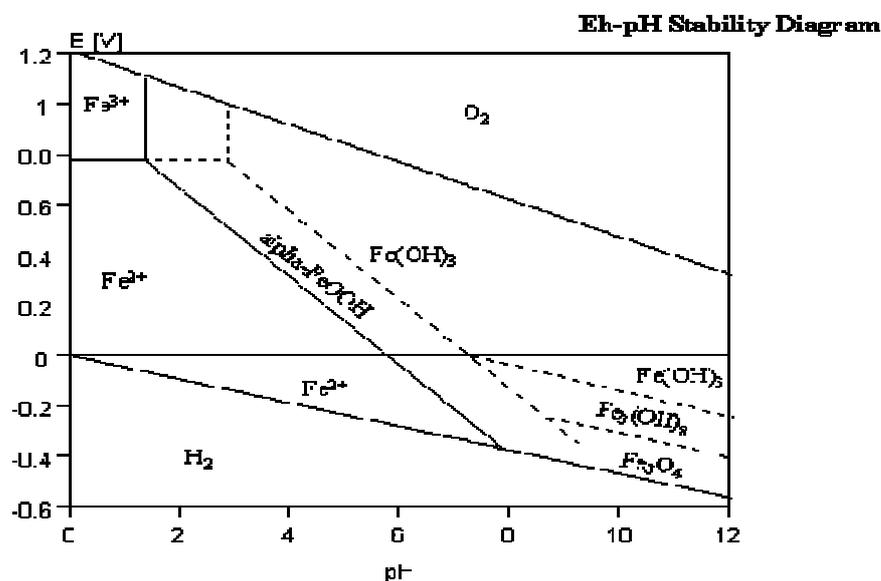


Figure 7: Eh-pH Stability Diagram

2.1.3 Toxicity of Al, Cu, Fe, Ni, Pb and Cr in Soil

Copper: This metal is essential to both plants and animals. Copper improves the metabolism of plants. It also assists the DNA disease resistance mechanism in humans. A deficiency of copper, on the other hand, inhibits growth in mammals (Anderson, 1995), resulting in cardiovascular lesions and myelination of the spinal cord, and defects in pigmentation, bone and connective tissue formation, and reproduction (Buck, 1978). In animals a deficiency of copper results in adverse effects on the central nervous system, skin enzymes, kidney, liver and blood vessels.

Excess copper is life-threatening to both man and animals because it reduces enzyme activity, and if released suddenly from hepatic storage into the blood-stream may cause icterus, anaemia and hemolysis. Copper also affects other biological substances like aldolase, alkaline phosphodiesterase, pepsin, lipase adenosine triphosphate, and aminoacyl tRNA (Owen, 1981). According to Howell and Gawthorne (1987), the primary effects of copper overload on humans are damage to the liver and organs.

A concentration of heavy metal in soil and groundwater threatens agricultural production in a number of ways. An unacceptable level of accumulation of metals in plants causes phytotoxicity, and these plants, especially cauliflower and potatoes, are toxic to the humans and animals that consume them. Wildlife, aquatic life and human health can be at risk if the concentration of copper in either foodstuffs or water is above natural background levels (Borg, 1989). The levels that have been shown to be toxic in aquatic environments are 19–21 mg/l for plants (Owen, 1981). The same researcher reported that the aquatic organisms found to be sensitive to copper are snails, fish and oysters (Owen, 1981).

Copper metal was found to be the fifth most toxic metal (behind silver, mercury, chromium and cadmium) in a ranking of 17 other metals that are harmful to soil bacteria, fungi and actinomycetes (Owen, 1981). In general the toxic forms of copper are free ions and some inorganic complexes, whereas the organic and sorbed complex forms are harmless. Different factors decrease the toxicity of these heavy metals. For example, complexation and humic acid can improve the availability of Cu (II) to plants and other microorganisms and at the same time reduce the toxic effects of free Cu (II) (Stevenson and Chen, 1991).

Aluminium: Aluminium is a very reactive metal, and occurs naturally in combination with other elements. It is the most abundant metal in the earth's crust, representing 8% of the total mineral components. Natural water aluminum is found in its ionic form in the tissues of most animals and plants (Jiang HX *et al.*, 2008). Dietary aluminum in small quantities poses no threat to persons with normal renal elimination capacity. This element is also used in water treatment plants, so that traces of aluminum are common in municipal water supplies. Some of the

processes of water purification remove the organic compounds that bind to the aluminium, leaving it in its free state, which increases the concentration of aluminum in the water.

Aluminium has some known physiological effects. Because of its atomic size and electric charge (0.051 nm and 3⁺ respectively), it sometimes acts as a competitive inhibitor of other important elements in the human body, like calcium (0.099 nm, 2⁺), iron (0.064 nm, 3⁺) and magnesium (0.066 nm, 2⁺). When aluminium is taken orally, only 0.3% of it is absorbed by the gastrointestinal (GI) tract. The remainder is discharged via the kidneys. If however the aluminium bypasses the GI, it may accumulate in the human body (Brown *et al.*, 2008), which might cause dysfunction and toxicity in both tissues and organs (Verstraeten *et al.*, 2008). Aluminum is absorbed as aluminium hydroxide, which acts as a phosphate binding agent in the GI tract. Aluminium could be absorbed via the urinary mucosa through bladder irrigation, via immunization, and transdermally via antiperspirants. Lactate, citrate, dialysis or total parenteral nutrition (TPN) contamination and ascorbate all facilitate GI absorption. If a large amount of aluminium is excreted, the excess is accumulated in various tissues as well as in the brain, liver, heart, spleen and muscles. These result in morbidity and mortality through various mechanisms. Furthermore, toxicity caused by aluminum in humans may cause dementia and osteomalacia or metabolic bone disease in dialysis (Suarez-Fernandez *et al.*, 1999) which could be controlled by controlling aluminum levels in the dialysis fluids (Mazzafarro *et al.*, 1997). Children, especially preterm infants, are also at risk of Al-induced neurotoxicity when exposed to parenteral nutrition containing this element (Coffey *et al.*, 1994).

Aluminum inhalation may be associated with an increased incidence of asthma, especially in people living or working in an industrial environment (Sorgdrager *et al.*, 1998). The research undertaken by Garruto *et al.*, (1989) in the field of animal studies to assess the toxicity of aluminium found that excess aluminium caused neurological disease in monkeys similar to amyotrophic lateral sclerosis and Parkinsonism in humans. A similar study of the effects of aluminium on rats showed a rise in mortality when 0.5 ppm of AlF₃ complexes were put in their drinking water (Varner *et al.*, 1994).

Aluminium toxicity in the roots of plants is largely attributable to monomeric cationic aluminium in solution. Anionic Al species in solution are not toxic.

Iron: The fourth most abundant metal in the earth's crust, after oxygen, silicon and aluminum, is Fe. Because plants require small amounts of iron to thrive, a 2.5% concentration of iron in soil is classified as a micronutrient. Examples of the effects on plants when the iron in the soil reaches toxic levels are the bronzing of rice and sugar cane (Foy *et al.*, 1978).

Iron is also required by most living organisms, including humans, animals and bacterial species, and is to be found in a large variety of food sources. Iron in a living organism has unusual flexibility, because it can serve as both a donor and an acceptor. If iron is free within the cell it catalyzes the conversion of hydrogen peroxide into free radicals that can ultimately kill the cell by damaging its structure (Bartlett, 1999). To prevent cell damage, iron is bound to proteins, which allow the cell to balance its use of iron. Heme molecules are a group of iron-binding proteins that carry out the redox reactions and electron transport processes required for oxidative phosphorylation, which is the principal source of energy for human cells. The hemoglobin of red blood cells iron transports oxygen to the tissues from the lungs, and moves carbon dioxide back to the lungs (Pietrangelo, 1999).

Nickel: Nickel is a silvery-white metal and the 24th most abundant element in the environment. It is used for making stainless steel, but also has properties suitable for making alloys, for example with iron, copper, chromium, and zinc. These alloys make a variety of products that include heat exchangers, jewellery and coins. Nickel compounds are used to make some types of battery, coatings to colour ceramics, and catalysts for chemical reactions.

Most of the information available on health hazards caused by nickel is based on animal studies, which show that ingesting excessive amounts of nickel causes lung disease and consequently death in dogs (ASTDR, 2005). Nickel can cause allergic reactions in humans, and in extreme cases result in degenerative respiratory disease that proves fatal. The most obvious example of those most at risk is workers in metallurgical plants that process nickel, who have inhaled nickel dust over a long period. Exposure to nickel is now regulated (it should not exceed 0.05 mg/cm³

in nickel equivalents per 40-hour work-week). Nickel dust and various other nickel compounds are also believed to be carcinogenic (ASTDR, 2005).

Lead: Lead poisoning may be caused by prolonged and intense exposure to this metal, and may result in strokes, heart attacks, hypertension and kidney disease. Some studies have established the harmful effects on the blood pressure of adults of even low-level exposure to lead in communities where the drinking water is carried by lead piping. (New England Journal of Medicine, 1979). These studies also claim proof of a direct relationship between water consumption and a rise in lead levels in the blood.

Chromium: Chromium, which is hard and grey in colour, is the sixth most abundant element in the earth's crust. It is highly resistant to oxidation, even at high temperatures, but when it occurs, the range of oxidation states is from -2 to +6 valence. When it is combined with iron and oxygen then this metal is referred to as chromite ore. The important states for chromite ore are 0 and +3 (trivalent) and +6 (hexavalent). The toxicity of chromium is related to the valence of the metal states. The trivalent and hexavalent compounds are thought to be the most biologically significant (Dayan and Paine, 2001). Chromium compounds are respiratory tract irritants and can cause pulmonary sensitization when inhaled. Excessive amounts may increase the risk of lung and sinus cancer. Cr (VI) compounds can also cause mild to severe liver abnormalities.

2.2 Conclusion

This chapter illustrates the various processes involving heavy metals that take place in the complex medium of soil. Among the processes mentioned are factors such as sorption, adsorption and organic matter contents, which affect the mobility of heavy metals and their behaviour in different types of soil quite extensively. The author supplies further detail on the differences in affinity of each individual metal as compared with those of other metals. Most researchers have found that the range of heavy metal adsorption onto soil (in increasing order) is $Ni < Cu < Cr < Pb$, whereas Cu and Pb are regarded as having low mobility. Fe and Al are easily retained in topsoil. The final section of this chapter is devoted to an outline of the toxic effects these metals can have, mostly as they occur in soils but also in water and the air.

CHAPTER THREE

3. METHODOLOGY

3.1 Investigation procedure

3.1.1 Collection of Samples

To initiate her investigation of soil contaminated by heavy metals, the author collected sludge from the effluent pipe feeding waste into the dam, and two samples of soil from two locations on the tailings dam: one in a central position and one at the edge. These locations are marked as points 1, 2 and 3 in Figure 8 . The results of an analysis of these three samples by the ICP OES, carried out according to the procedures outlined below in Section 3.2, were used to provide a basic comparison of the occurrence of heavy metals in these three locations. They also served as points of reference for the assessment of the results obtained from sampling on sites at a distance from the tailings dam, so that the extent of soil contamination in the area surrounding the tailings dam could be determined.

In the chapters that follow, a distinction is made between the preliminary tests at the source of contamination and the field tests described below, which aimed to establish whether, and if so to what extent, the soil surrounding the tailings dam had been affected by the heavy metals in it.

For the field tests, the researcher collected two sets of ‘distance’ soil samples, the first in 2012 and the other in 2013. In the former year, the samples were obtained only at a distance of 500 meters from the foot (outer edge) of the dam, whereas the set taken in 2013 comprised samples collected at distances from the dam of 500 and 1500m (designated in the Figure as points 3 and 4).

Figure 8 shows the tailings dam and marks all but one of the sampling points. Point 4 (for samples collected in 2013) is not included in the Figure, for two reasons: it was much further away from the dam than the points shown in the drawing; and no map of the surrounding area was provided to the author.

Point 1: Pipeline connected to the metallurgical plant discharging tails into the dam.

Point 2: The dam basin.

Point 3: Location 500 m away from the edge of the dam.

Point 4: Location 1500 m away from the edge of the dam.

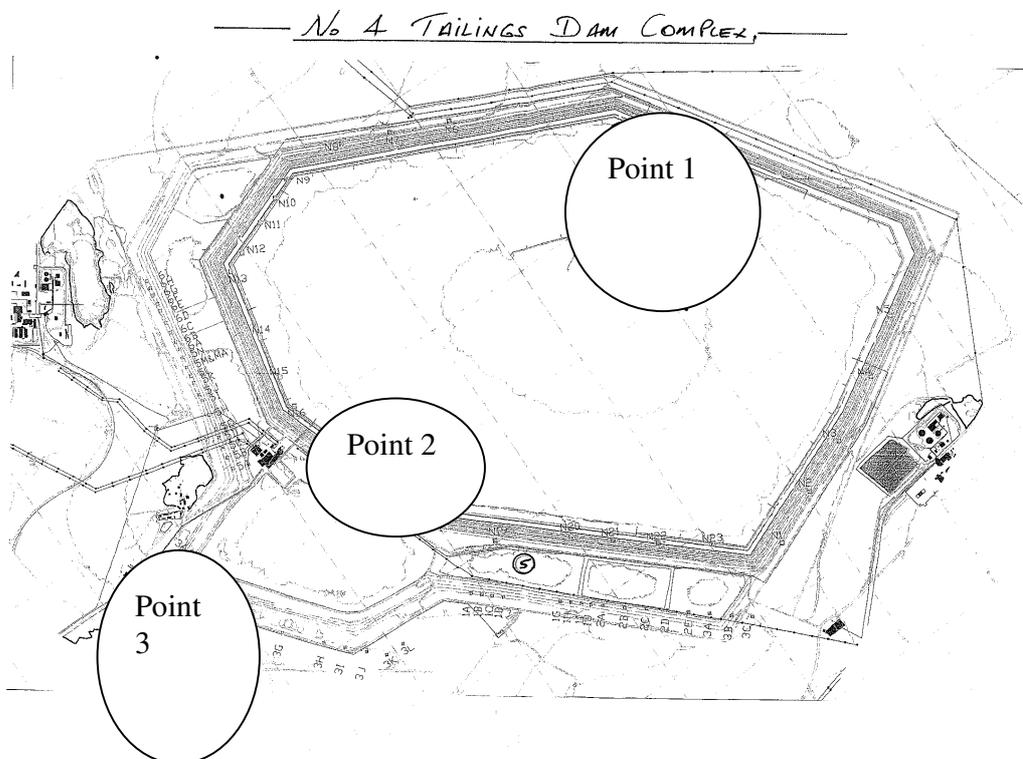


Figure 8: Illustration of sampling locations near the Tailings Dam

Before taking the soil samples in locations away from the dam, the author measured a distance of 500 m from the outer edge of the dam in a straight line (point 3) in the direction of the water run off near the foot of the dam, and then measured a further 1000 m in a straight line to arrive at the 1500 m sampling point (point 4). Both points were marked and the surface of the soil scraped to

remove any plant residue, as a preliminary to marking out a sampling grid in which three soil samples were taken spaced one metre apart, and at three levels of depth, as shown in Figure 9 .

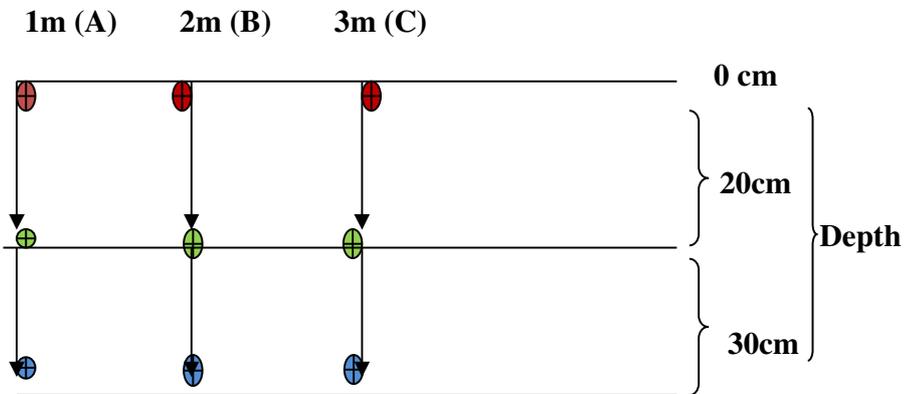


Figure 9: Drawing showing the soil sampling pattern approximately 500m (similarly at 1500 m) from the Tailings Dam

- Sampling point topsoil 0 cm= 
- Sampling point 20 cm depth = 
- Sampling point 30 cm depth = 

The researcher took 18 one-kilogram samples from the locations marked 500 m and 1500 m away from the tailings dam. Broken down according to the grid, nine samples were taken at 500 m and nine at 1500 m. In each case, three sampling sites were designated on the surface at one-metre intervals: therefore 1 m, 2 m and 3 m away from the marked point. These were identified as A, B and C respectively. Samples were taken from these sites at three different depths: 0cm for the surface layer, 20 cm for the second, and 30cm for the third (thus, A at 1 m included the surface sample and the two layers below at 20 and 30 cm; B at 2 m refers to the same three layers and so on).

The samples were tagged and bagged on site in clean colourless polyethylene bags to avoid contamination, and were then taken to the laboratory for analysis.

3.2 Sample Preparation

In the laboratory, the samples were dried, ground in a 4mm jaw crusher, and split on a rotary splitter. They were then pulverized for six minutes. Sub-samples of 12 g each were removed from the well-mixed composite obtained from each sampling point, and these were each mixed with 3 g wax micro powder for binding. The mixture was then put into an Intelli-mixer at 99 rpm to ensure adequate blending.

The homogenized powder samples collected in 2012 were then prepared for analysis by an Inductively Coupled Mass Spectrometer (ICP MS). First, each sample was subjected to a sequence of digestion procedures carried out in open vessels on a hot-plate. All samples were placed in digestion tubes in a block heater which was set at a temperature of 130°C. The heating continued for the duration of 14 hours. Then the samples were cooled for about 7 minutes. 30% hydrogen peroxide was added to each sample at a ratio of 1 mL per sample and the tubes were placed back onto the block heater for further heating which was between 20 and 30 minutes. The tubes were then taken off from the block heater and then cooled and 30% of hydrogen peroxide was then added and digested by reheating for another for another 20- 30 minutes. Then the tubes were taken off from the block heater and 50 mL of water was added to each tube and this samples had to rest for 30 minutes or more. This process of digestion with different acids is to dissolve most of the silicate minerals and liberate most of the analyte. The resultant liquids was pipetted into the argon plasma of the ICP MS and analyzed.

The flow diagram in Figure 10 summarises the procedures followed in preparation for the sample analysis.

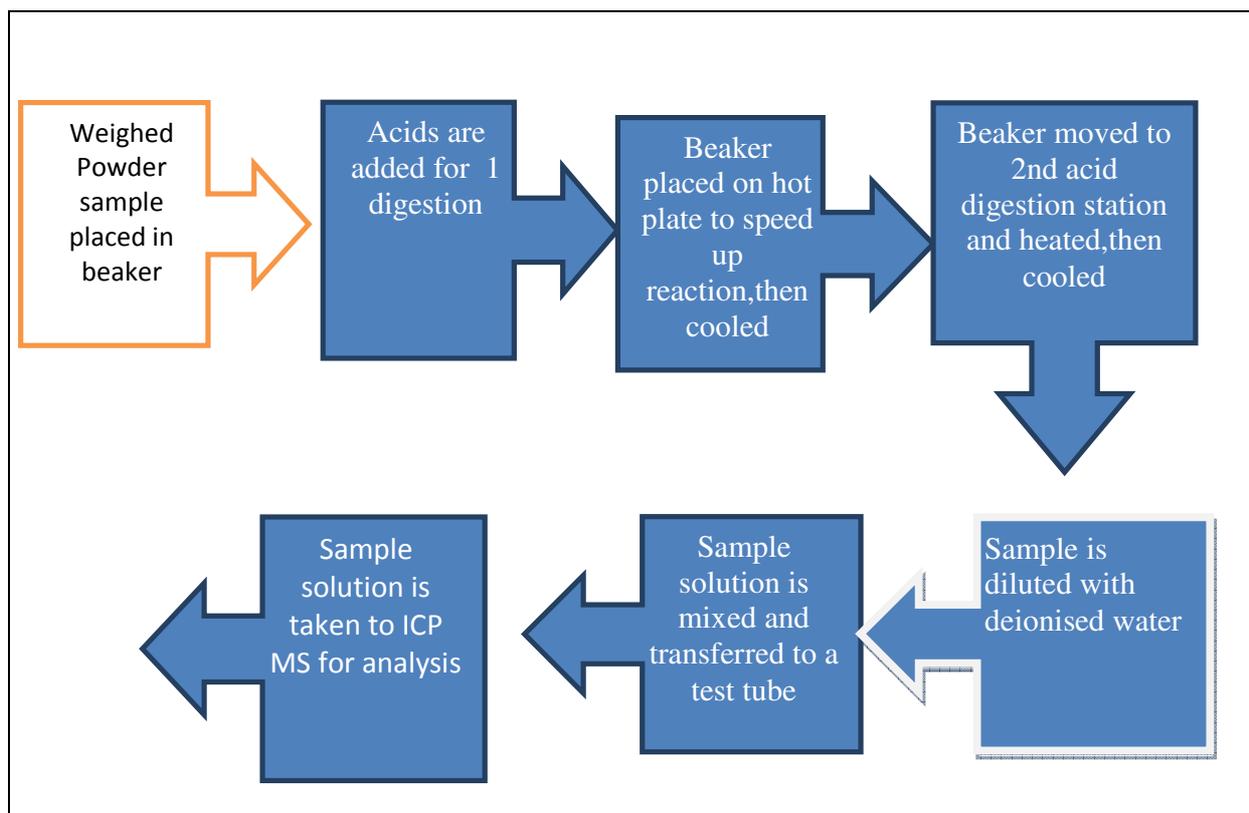


Figure 10: Sample Preparation Flow Diagram

The ICP MS is most commonly used to measure the individual isotopes of each element, but it also has the capability to measure the ratio between two isotopes of an element. The samples are decomposed to neutral elements in high-temperature argon plasma and analyzed according to their mass-to-charge ratios. The flow process of an ICP-MS procedure includes sample introduction and aerosol generation, ionization by an argon plasma source, mass discrimination, and the detection system.

The 2013 samples, on the other hand, underwent the same initial processing as the 2012 set, but in this case each blended sample was placed in an aluminium cup. These were pressed at 10 tons mpa in a laboratory pressing machine to form pellets, which were then taken to an Inductively Coupled Plasma Emission Spectrometer (ICP OES) for elemental analysis of heavy metals. The ICP OES is a powerful instrument for trace element analysis, using a technique based upon “the spontaneous emission of photons from atoms and ions that have been excited in a RF discharge” (Hou and Jones, 2000).

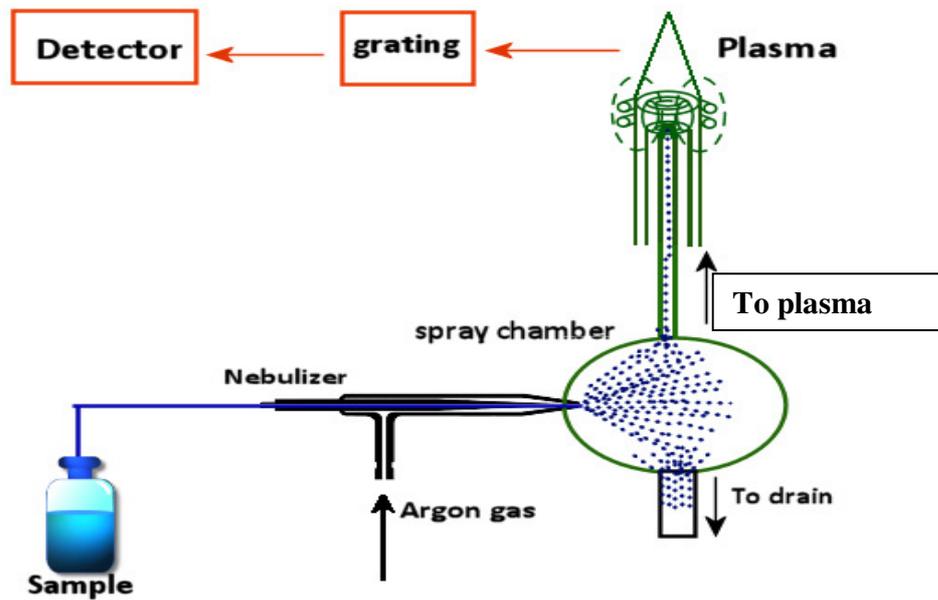


Figure 11: Schematic Diagram of the process of introducing a sample for analysis in the ICP OES (<http://www.chemicalsoft.com/chemd/node/52>)

The results of the analyses carried out on the soil samples taken in the field form the subject of the chapter four.

CHAPTER FOUR

4. ANALYSIS AND DISCUSSION OF RESULTS ON HEAVY METALS

4.1 Field results

The soil samples taken in 2013 were analysed to determine the amounts of the six heavy metals studied (Al, Fe, Pb, Cu, Ni and Cr) they contained. The results are presented both graphically and in table format.

4.2 Statistical analysis

The researcher applied the F-test (named after Sir Roger Fisher) to the findings on heavy metal concentration levels relative to the various distances and depths at which the samples had been taken for each of the six types under consideration. The F-test is a statistical tool by means of which a scientist can establish whether the data obtained are significant to his or her enquiry. The data obtained from the test were used to plot graphs of heavy metal concentration for each separate metal, which were compared in terms of both distance and depth. Both bar-type and line-type graph formats were used in order to establish trends that could be followed up in discussion. The statistical analysis tool ANOVA (analysis of variance) was then used to compare the results for the occurrence of each heavy metal.

The researcher calculated the means, standard of deviation and variance for both distance at 500 m and at 1500 m and at three different depth levels. The mean and standard of deviation of the differences obtained from these calculations using MS Excel were then used to calculate the 95% limits of agreement and the associated confidence limits for each metal. ANOVA was used to determine differences in mean concentration attributable to depth and distance.

The conditions of the test and equations used were as follows.

- **The null hypothesis, H_0** , is that the means of all members of the group are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$. (In other words, the mean concentrations at varying distances are equal.)
- **The alternative hypothesis, H_1** , is that at least two of the group means are different.
- **The significance level of 5% is $\alpha = 0.05$ (95% probability):**

$$\bar{x} = \frac{\sum x}{n} \dots\dots\dots\text{equation 1 (Good,1983)}$$

$$\text{s.d.} = \sqrt{\frac{\sum (x - \bar{x})^2}{n}} \dots\dots\dots\text{equation 2 (Good,1983).}$$

where; sd = standard deviation, x = sample, \bar{x} = sample mean

\sum =summation, n= sample size

The Anova table shows the general format of an analysis of variance table.

Table 4: ANOVA Table (for k groups, total sample size,.....N)

Source	S.S	Degrees of freedom	M.S.S.	F
Between groups	S SG	k - 1	$\frac{SSG}{k - 1} = MSG$	$\frac{MSG}{MSE} = F$
Errors	SSE	(N-1) - (k-1)	$\frac{SSE}{N - k} = MSE$	
Total	SST	N - 1		

Total variance = between systems variance + variance due to errors

- **SST**- Total sum of squares between systems
- **SSSys**- Sum of squares between systems or groups (SSG)
- **SSE**- Sum of squares of errors.
- **SSE = SST - SSSys**

In this table the test statistic is the F-value calculated from the ANOVA table, which is then compared with the critical value read from the F-tables, $F_{\alpha}(v_1, v_2)$, with the given two degrees of freedom for the groups (v_1) and the errors(v_2).The two F values are then compared. The result of this process leads to either acceptance of the null hypothesis or its rejection.

4.3 Analysis of Results (All raw data analysis figures for each metal refer to the year 2013)

4.3.1 Cr – Chromium

4.3.1.1 Raw data analysis – Cr

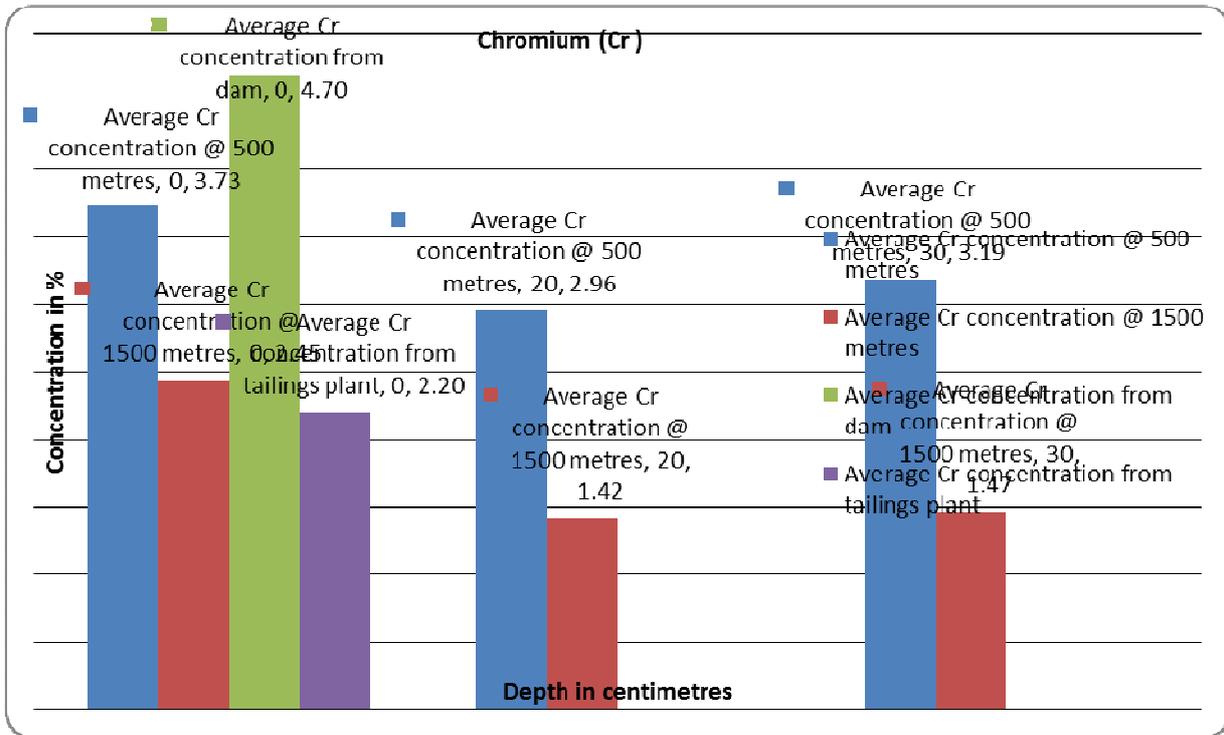


Figure 12: Comparison of average chromium concentration at four different sampling points and at three different sampling depths

The four different sampling points were 1) the centre of the tailings dam, 2) the outflow pipe from the plant, 3) 500 metres from the edge of the dam, and 4) 1500 metres from the dam. As shown in Figure 12, the most significant proportion of contamination is limited to the upper 0 cm (or the surface) of the soil. In other words, the chromium concentration decreased slightly from the surface downwards. The proportion of Cr contamination observed remained at an average of 3.29% for all three soil layer samples, and less than 3.29% for a distance of 500 metres.

However, this was not the case when the chromium concentration was measured in relation to greater distance. The average concentration of chromium at the furthest point from the dam,

1500 metres, was 1.80%, lower than that obtained at 500 metres, which was higher by 1.49%. This confirmed the assumption that the nearer the sampling point was to the source of contamination (the dam), the higher the concentration of contaminant in the soil.

The fluctuation in concentration of Cr at 1500m could be attributed to some level of contamination, although there is agreement between the two points of distance sampling that most of the chromium is situated in the topsoil. In decreasing order of concentration levels, As per Figure 12, was observed as follows, Cr at 0 cm > Cr at 20 cm > Cr at 30 cm and the concentration of Cr at 500 metres > Cr at 1500 metres.

Previously published reports on this subject support a decreasing order in chromium concentration, both vertically and horizontally. Chromium most stable states are Cr (III) and Cr (VI), since the heavy metal exists in a number of oxidation forms. Cr (III) is the most prevalent form of chromium in most soils because it precipitates easily in soil aggregates, especially when the pH is greater than 6, and it is considered less mobile than other chromium states as it adheres strongly to soil aggregates (Smith *et al.*, 1989).

Figure 12 also shows that the difference in concentration between the plant discharge and the dam contents is due to a greater degree of accumulation of these heavy metals in the dam. The heavy metals have been building up over time. Although the Figure 12 illustrates the prevalence of chromium behaviour in soil at various distances and depths comprehensively, Figures 13 and 14 indicate the different profiles of chromium behaviour in soil at various depths and distances for, first, the 500 metre samples, and second, for those collected at 1500 metres.

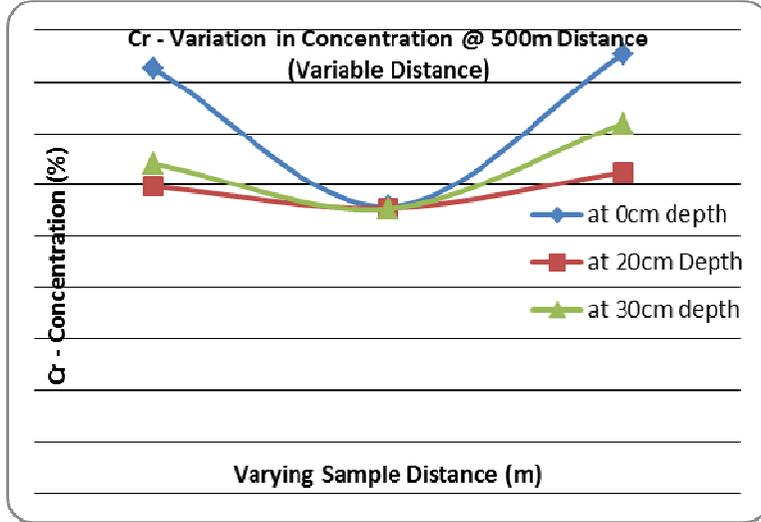
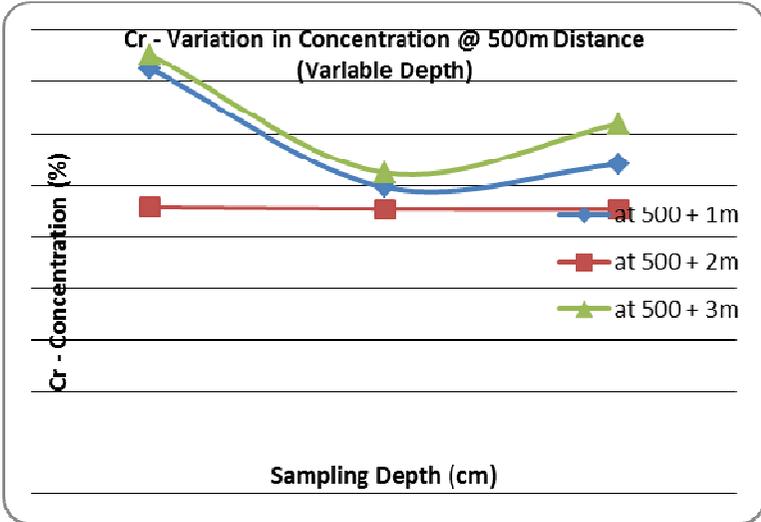


Figure 13: Cr - Samples at 500m

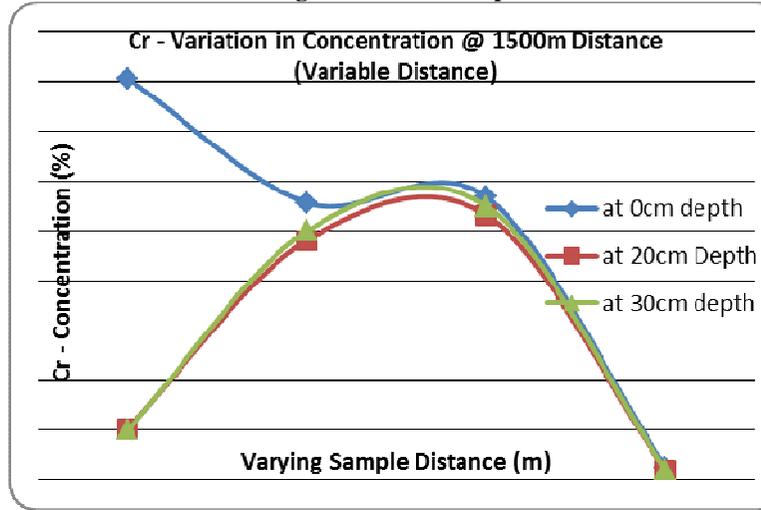
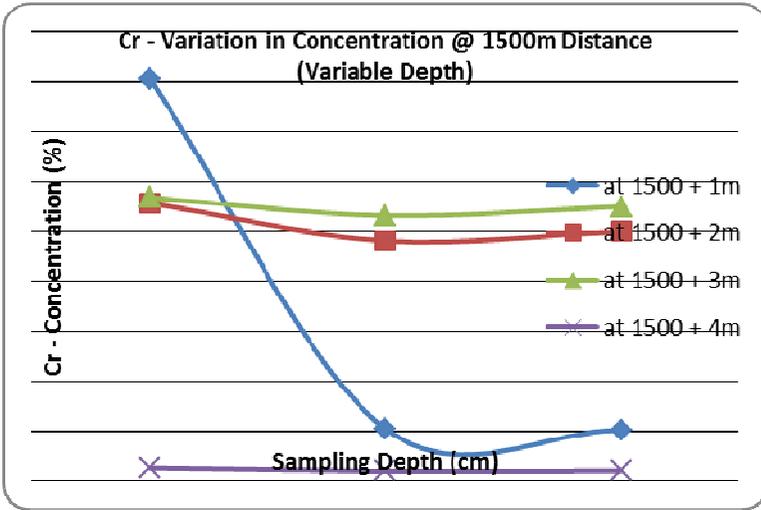


Figure 14: Cr - Profile at 1500m

4.3.1.2 Statistical analysis – Cr

Table 5: Cr - ANOVA - F-test (Variation by depth and distance) from 2013 Sample

Chromium		
variation by depth		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.225785674	0.103426447
F-table (Ftab)	5.14	4.26
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.
variation by distance		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.315321446	0.644326561
F-table (Ftab)	5.14	4.07
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.

Although Figures 13 indicates that there is a slight difference in chromium concentration with respect to depth, the ANOVA test in Table 5 confirms that the difference is insignificant and can therefore be ignored. The F-calculated value for variation both in distance and depth at 500 m and 1500 m is less than the F value obtained from the F- table (Appendix A), which confirms the null hypothesis H_0 . This means that there was no significant difference between the group means.

The insignificant differences in the group concentration means suggest that the tailing dam does not introduce considerable or significant amounts of chromium into the surrounding soils.

Both the statistical analysis in Table 5 and the raw data analysis in Figures 12, 13 and 14 concur that the concentration does not vary significantly. The latter indicates that chromium contamination averaged 3.29% in all three sampled soil layers for the vertical direction and 3.293% for the horizontal direction.

Table 6: Cr - ANOVA - F-test (Variation by depth and distance) from 2012 Sample Chromium

Chromium	
variation by depth	
Distance	500 m
F-calculated (Fcal)	0.010823236
F-table (Ftab)	5.14
Statement	$F_{cal} < F_{tab}$
Conclusion	Accept H_0 there is no significant difference between the group means.
variation by distance	
Distance	500 m
F-calculated (Fcal)	0.026905271
F-Table (Ftab)	5.14
Statement	$F_{cal} < F_{tab}$
Conclusion	Accept H_0 there is no significant difference between the group means.

The statistical analysis results for chromium from sample one, taken in 2012, revealed that the group means are not significantly different from each other (Table 6), which suggests there is no significant difference in chromium concentration with respect to both depth and distance. The findings from both the chromium concentration from raw data and chromium concentration from sample two (2013) are in agreement. The comparative average concentrations of the three results obtained also concur, so the researcher concludes that the tailing dam does not introduce significant amounts of chromium into the soils surrounding the dam.

4.3.2 Cu – Copper

4.3.2.1 Raw data analysis – Cu

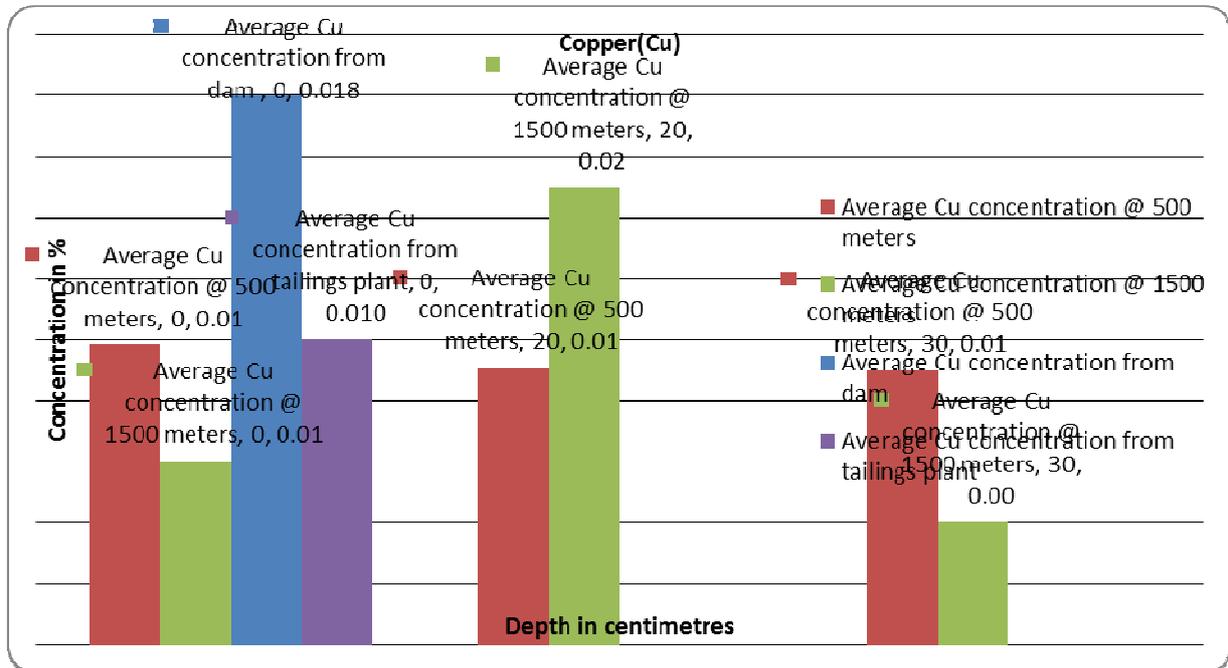


Figure 15: Average Copper concentration at four sampling points and three sampling depths

Figure 15 shows that the most significant part of the contamination is limited to the upper 0 cm or the surface of the soil. Cu contamination averaged 0.01% in both all three sampled soil layers (the vertical direction) and in the horizontal direction.

The average concentration of copper at the furthest point from the dam, 1500 m, was observed to be lower than at 500 m at a concentration of 0.0084%, but the difference was very slight.

Previous studies have shown that when soluble Cu is added to soil it reacts with phosphates, clays and organic matter, which reduces its solubility considerably and results in greater retention of copper in the soil. The graph above also shows that Cu is abundant in the topsoil and is least concentrated in the 30cm layer. Butkus and Grasso (1999) explain this in terms of drying, which hinders Cu mobility. Because the topsoil is dryer than the subsoil, the copper is concentrated in the top layer of the soil.

In terms of increasing concentration, Cu at 500 metres is greater than Cu at 1500 metres. The fluctuation content with the concentration of Cu at 1500 variable depth could be an indication of contamination of the sample. The concentration profile trend for Figure 4.3 shows that the order is decreasing as follows: Cu at 0 cm > Cu at 20 cm > Cu at 30 cm and Cu 500 metres > Cu 1500 metres.

Figure 15 also shows that the concentrations of Cu in the plant tails are lower than those in the dam basin. This, like the findings on chromium, can be attributed to the accumulation of heavy metal contamination in the dam, whereas it is diluted in the plant tails. Although the Figure provides an accurate overview of the extent of copper in the soil at various distances and depths on the same graph, Figures 16 and 17 give simplified profiles of copper prevalence in the soil at various distances and depths.

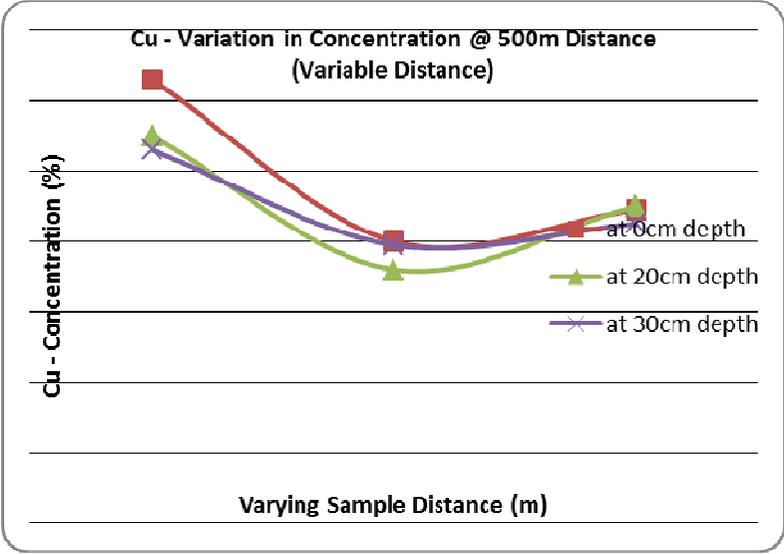
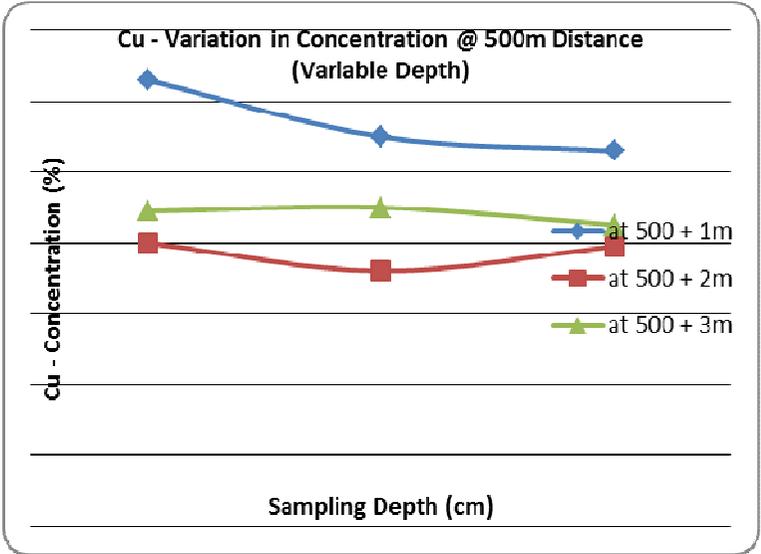


Figure 16: Cu - Profile at 500m

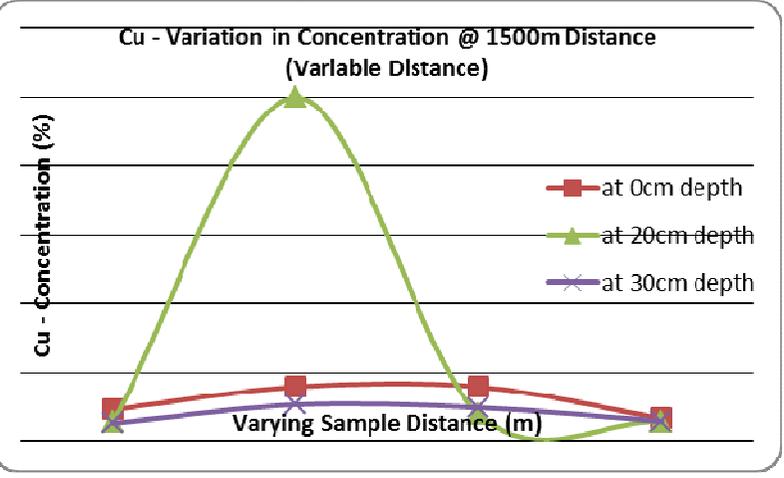
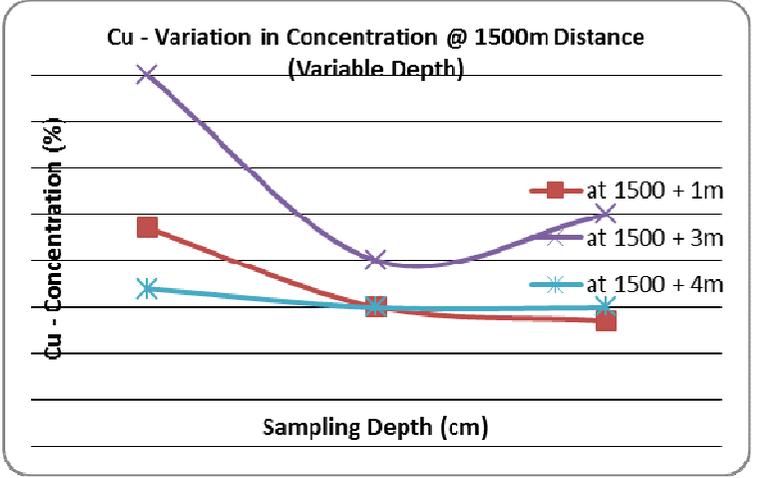


Figure 17: Cu - Profile at 1500m

4.3.2.2 Statistical analysis – Cu

Table 7: Cu - ANOVA - F-test (variation by depth) from 2013 Samples

Copper		
variation by depth		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.100840336	0.093932801
F-table (Ftab)	5.14	4.26
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.
variation by distance		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.617647059	0.258723281
F-table (Ftab)	5.14	4.07
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.

Although Figure 16 indicates that there is a slight variation in copper concentration with respect to different depths, the ANOVA test table for 2013 sample above confirms that the dissimilarity is insignificant and can be ignored. The F-calculated value for variations in both distance and depth at 500 m and 1500 m is lower than the F-value obtained from the F-table (Appendix A). The researcher therefore accepted the null hypothesis H_0 , that there was no significant difference between the group means. The insignificant differences in the group concentration means imply that the tailing dam does not introduce significant amounts of copper into the surrounding soils. The data contained in all of the Figures and the Table in this subsection lead to the conclusion that the concentration of copper in the samples at different depths does not vary significantly.

Figure 17 indicates that copper contamination remained at an average of 0.01% in all three sampled soil layers in the vertical direction, and at an average of 0.0084% in the horizontal direction.

Table 8: Cu - ANOVA - F-test (Variation by depth and distance) from 2012 samples

Copper	
variation by depth	
Distance	500 m
F-calculated (Fcal)	0.546352241
F-table (Ftab)	5.14
Statement	$F_{cal} < F_{tab}$
Conclusion	Accept H_0 there is no significant difference between the group means.
variation by distance	
Distance	500 m
F-calculated (Fcal)	0.073265083
F-table (Ftab)	5.14
Statement	$F_{cal} < F_{tab}$
Conclusion	Accept H_0 there is no significant difference between the group means.

The F-calculated value for variation in both distance and depth at 500 m is lower than that obtained from the F-table (Appendix A), which indicates the acceptability of the null hypothesis H_0 . The ANOVA test table for the 2012 samples shown above also confirms that the difference is insignificant and thus can be ignored.

The statistical analysis results for copper from sample one, taken in 2012, revealed that the group means do not vary significantly (Table 8), so there is no significant difference in copper concentration with respect to either depth or distance. The findings on the copper concentration from both the raw data and from sample two (2013) are in agreement. The comparative average

concentrations of the three results obtained allow the researcher to conclude that the tailing dam probably does not introduce considerable amounts of copper into the surrounding soils.

4.3.3 Ni – Nickel

4.3.3.1 Raw data analysis – Ni

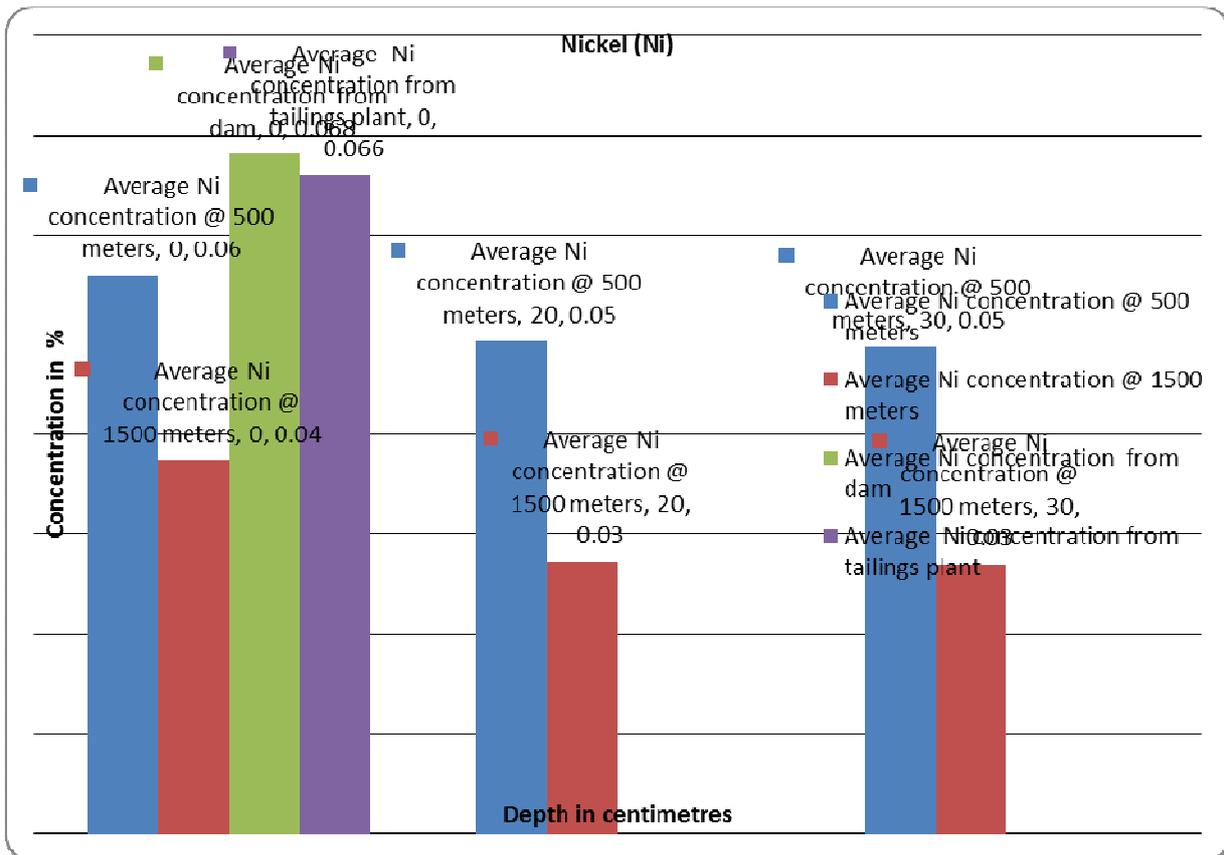


Figure 18: Average nickel concentration at four different sampling points and three sampling

The concentration of nickel declined from the surface downward at both 500 and 1500 m, as can be seen in Figure 18 . The most significant contamination was limited to the upper 0 cm, the soil surface, as was the case with chromium and copper.

The concentration of nickel was slightly higher in samples taken at 500 m from the dam, at an average of 0.0533%, than those collected at 1500 m (0.031%). The difference of 0.022% could be attributed to the precept that the nearer the sampling points to the source of contamination, the

higher the concentration of the contaminant, although the mean average appears to be the same in the vertical direction. Because the horizontal concentration of nickel proved similar also, the researcher concluded that there was not much variation in concentration in samples taken at one metre apart.

Figure 18 also shows that the concentration of nickel in the plant tails is lower than that in the dam basin, for reasons already given with respect to chromium and copper. The comprehensive depiction of the copper concentration in all the samples taken in the different locations in the figure 18 is broken down in the Figures that follow, 19 and 20, which chart the profiles of nickel behaviour in soil at various distances and depths.

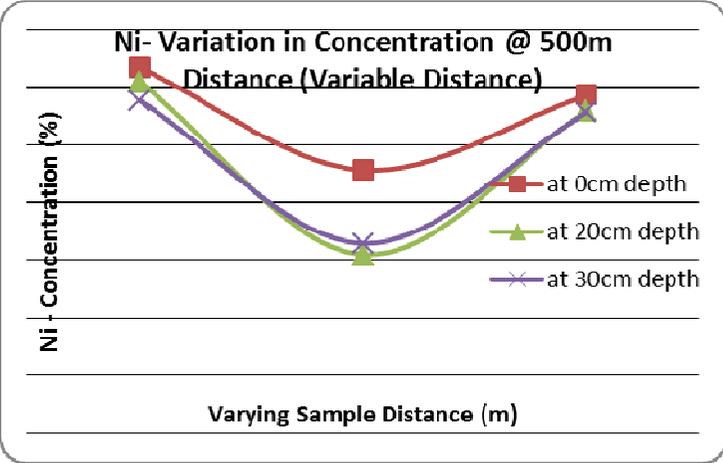
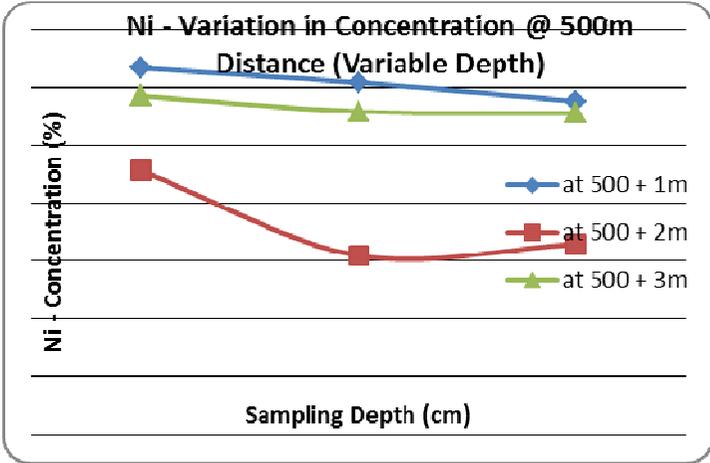


Figure 19: Ni - Profile at 500m

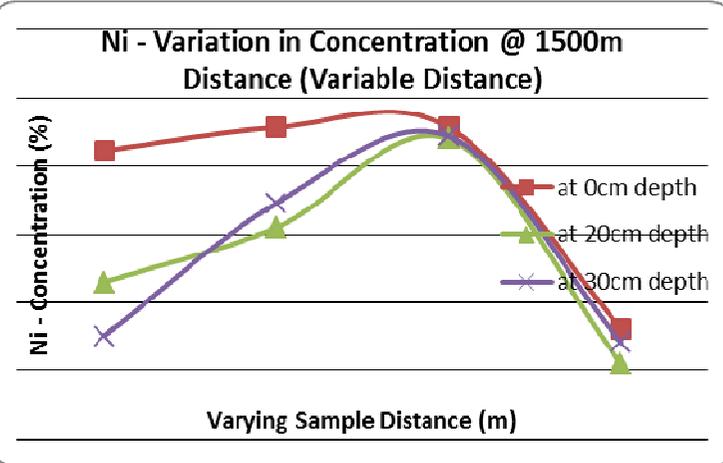
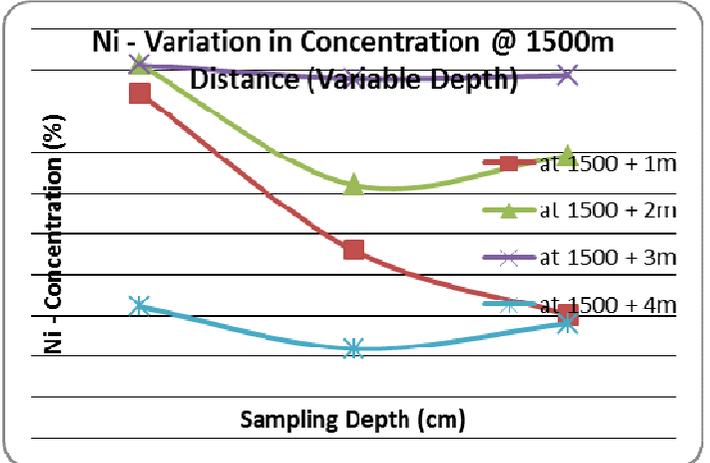


Figure 20: Ni - Profile at 1500m

4.3.3.2 Statistical analysis – Ni

Table 9: Ni - ANOVA - F-test (variation by depth and distance) from 2013 samples

Nickel		
variation by depth		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.079929625	0.132388481
F-table (Ftab)	5.14	4.26
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.
variation by distance		
Distance	500 m	1 500 m
F-calculated (Fcal)	1.142062146	0.16989139
F-table (Ftab)	5.14	4.07
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.

Although Figure 19 shows that there is a slight difference in nickel concentration with respect to depth, the ANOVA test table for the 2013 samples confirms that the difference is insignificant and thus can be ignored. Because the F-calculated value for variation by both distance and depth at 500 m and 1500 m is less than the F-value obtained from the F-table (Appendix A), the researcher accepted the null hypothesis H_0 that there was no significant difference between the group means.

The negligible differences in the group concentration averages indicate that the tailing dam does not introduce large amounts of nickel into the surrounding soils.

The statistical analysis from the 2013 sample in Table 19 and the raw data analysis in Figure 20 both confirm that there are no significant variations in the concentration of nickel. The latter also showed that nickel contamination remained at an average of 0.0533% in all three sampled soil layers.

Table 10: Ni - ANOVA - F-test (Variation by depth and distance) from 2012 samples

Nickel	
variation by depth	
Distance	500 m
F-calculated (Fcal)	0.777796257
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.
variation by distance	
Distance	500 m
F-calculated (Fcal)	0.010510029
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.

The F-calculated value for variations caused by both distance and depth at 500 m is less than the F-value obtained from the F-table (Appendix A), which confirmed the null hypothesis H_0 , and the test table for the 2012 samples above proved that any differences are insignificant. This in turn indicates that the tailing dam does not contaminate the soils adjacent to the dam to any significant extent.

The statistical analysis of the amounts of nickel found in sample one, taken in 2012, revealed that the group means are not significantly different from each other (Table 10), which means there is no significant difference in nickel concentration with respect to either depth or distance. The findings on the concentration of nickel from both the raw data analysis from 2012 and sample two (2013) are in agreement. The comparative average concentrations of the three results obtained suggest the same conclusion: that the tailings dam is not a source of serious nickel contamination in the soil surrounding it.

4.3.4 Pb - Lead

4.3.4.1 Raw data analysis – Pb

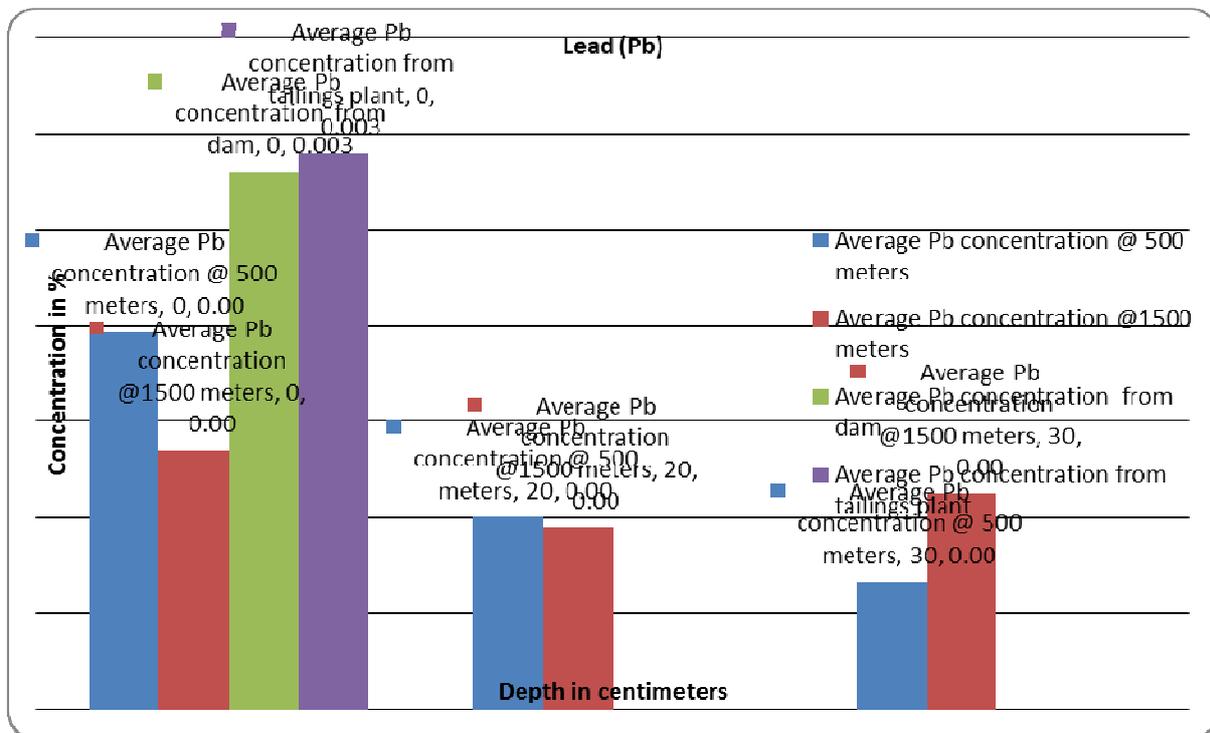


Figure 21: Average Lead concentration at four different sampling points and at three sampling depths

As the Figure 21 shows, the lead (Pb) concentration declined slightly from the surface downward: in other words, the most significant contamination was limited to the surface of the soil. According to Figure 21, the concentration of Pb is slightly higher at 500 m from the dam, probably because of its closer proximity to it as the source of contamination. Nevertheless, the

mean average of lead appears to be the same in both the vertical and horizontal directions, at 0.00% concentration.

The agreement between the Tables and the graphs in the Figures between all trends of Pb concentration distribution in all three depths (0 cm, 20 cm and 30 cm) reveal that lead concentration is very low and that Pb is largely retained in the upper surface layer of 0 cm.

The published reports of similar studies have shown that when soluble Pb is added to soil it is largely retained by soil. Lead reacts with phosphates, clays and organic matter, which greatly reduces its solubility. In terms of the profile trend for Figure 21 above, the lead concentration decreases as follows: Pb at 0 cm > Pb at 20 cm > Pb at 30 cm and Pb 500 metres > Pb 1500 metres. The vertical Pb concentration distribution seen in Figures 4.11 and 4.12 below is the same at both 500 meters and 1500 m, and the mean average is 0.00% in both the vertical and the horizontal directions.

Figure 21 shows that the concentrations of lead in the plant tails is almost the same as those found in the soil samples. Figures 22 and 23 give more detailed information on the presence of lead in the soil at various distances and depths.

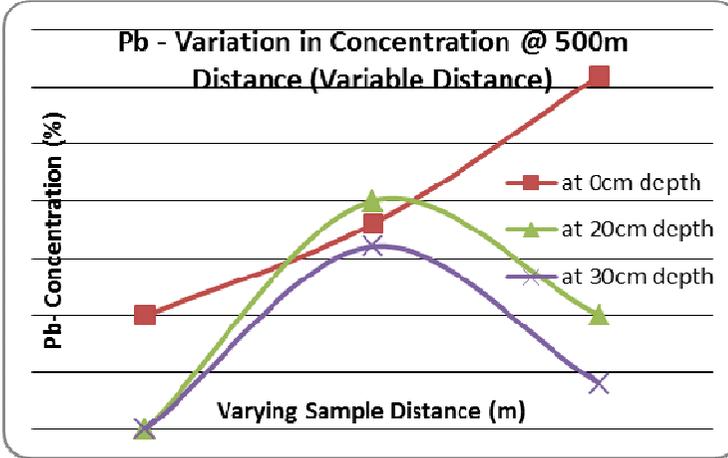
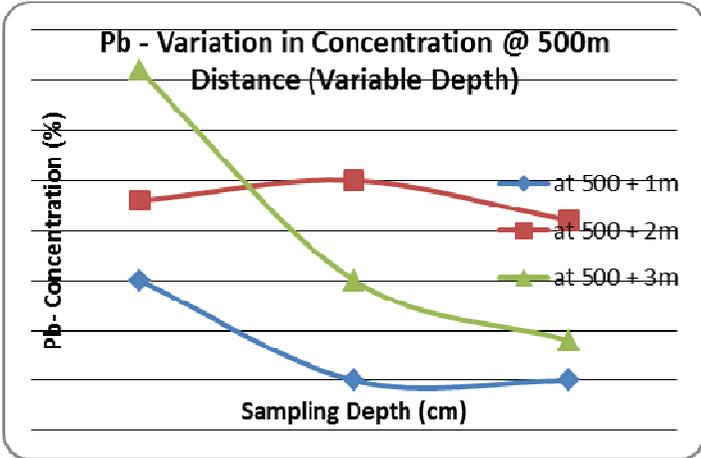


Figure 22: Pb - Profile at 500m

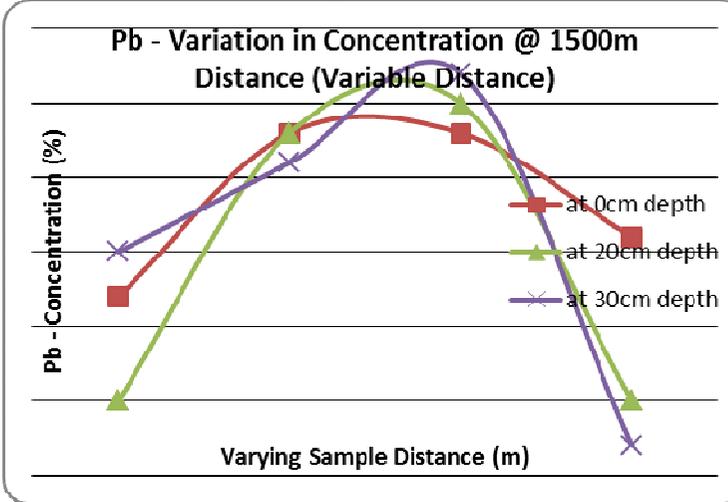
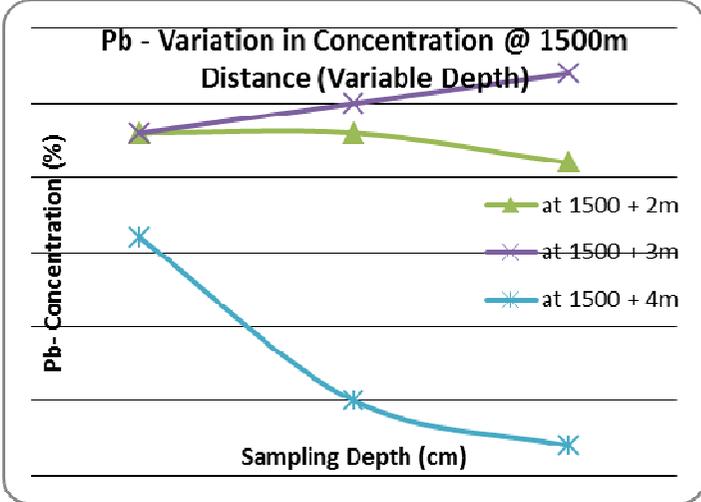


Figure 23: Pb - Profile at 1500m

4.3.4.2 Statistical analysis – Pb

Table 11: Pb - ANOVA - F-test (Variation by depth and distance) from 2013 Sample

Lead		
variation by depth		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.181064915	0.050084628
F-table (Ftab)	5.14	4.26
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.
variation by distance		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.243077077	1.156036735
F-table (Ftab)	5.14	4.26
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.

Although Figure 22 indicates that there is a slight difference in lead concentration with respect to depth, the ANOVA test table for the 2013 samples confirms that the difference is insignificant and thus can be ignored. The F-calculated value for variations in both distance and depth at 500 m and 1500 m is lower than the F-value obtained from the F-table (Appendix A), thus the null hypothesis H_0 is confirmed.

The negligible differences in the group concentration means indicate that the tailing dam does not cause the release of considerable amounts of lead into the adjacent soil.

Both the statistical analysis and the raw data analysis of the 2013 samples confirm that the concentration of lead does not vary significantly. Lead contamination remained at an average of 0.00% % in all three sampled soil layers.

Table 12: Pb – ANOVA – F-test (Variation by depth and distance) from 2012 samples

Lead	
variation by depth	
Distance	500 m
F-calculated (Fcal)	0.34125
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.
variation by distance	
Distance	500 m
F-calculated (Fcal)	0.174584323
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.

Since the F-calculated value for variation by both distance and depth at 500 m is lower than the F-value obtained from the F-table (Appendix A), the researcher accepted the null hypothesis H_0 . The ANOVA test table for the 2012 samples confirms that any differences are insignificant and therefore need not be taken into account.

The statistical analysis results for lead from sample set one taken in 2012 revealed that the group means do not differ significantly (Table 4.8). This means there is no significant variation in lead concentration with respect to both depth and distance. The findings from both the lead concentration from raw data and lead concentration from sample two (2013) agreed. The comparative average concentrations of the three results led to the same conclusion that the tailings dam probably does not contaminate the soil around it with excessive amounts of lead.

4.3.5 Fe - Iron

4.3.5.1 Raw data analysis – Fe

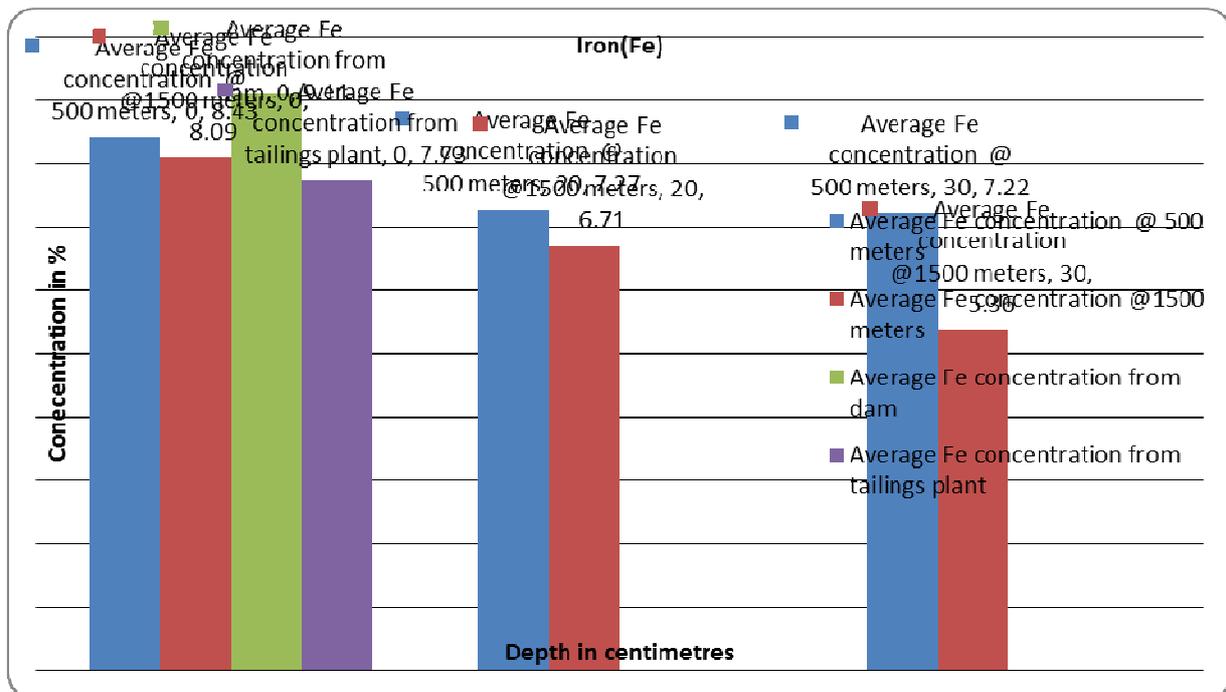


Figure 24: Average iron concentration at four different sampling points and three sampling depths

Iron is a common constituent of soils and groundwater. It participates readily in subsurface redox reactions, and under some conditions can cause problems in groundwater remediation systems. Iron occurs in higher concentrations in the effluent from the tailings plant, and is already present in the soil, so it is unsurprising that the analysis showed an average concentration of 7.46%.

Nonetheless an increasing order of agreement was found between the three sampled layers: most of the iron was found at the surface (0 cm).

According to Figure 4.13, the concentration of Fe is slightly higher nearer the dam at 500 m than at 1500 m, which has a value of 6.72%. The reason for the former is that it is closer to the source of contamination.

In terms of the profile trend, in Figure 4.13 the iron concentration decreases as follows, Fe at 0 cm > Fe at 20 cm > Fe at 30 cm and Fe 500 m > Fe 1500 m.

The Figure also shows that the concentration of iron in the plant tails is lower than that in the dam basin, probably as the result of accumulation in the latter. The mean average concentration values of iron at 7.46% and 6.72% are not markedly dissimilar. This supports the statement made that iron is a common constituent in soils. In fact the iron concentrations in the samples are very similar to those of the dam and plant tails. Figures 4.14 and 4.15 present the different profiles of iron behaviour in soil at various distances and depths.

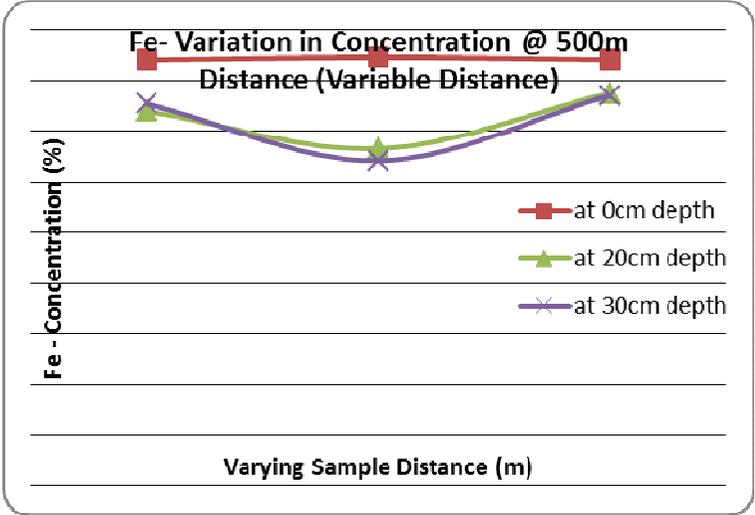
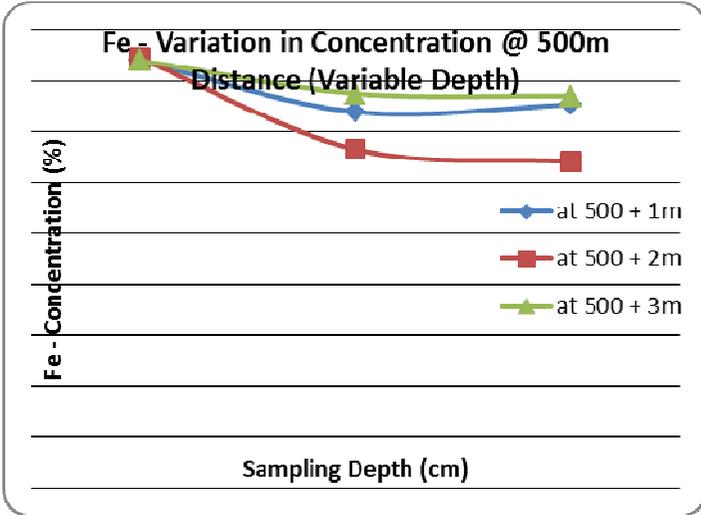


Figure 25: Fe - Profile at 500m

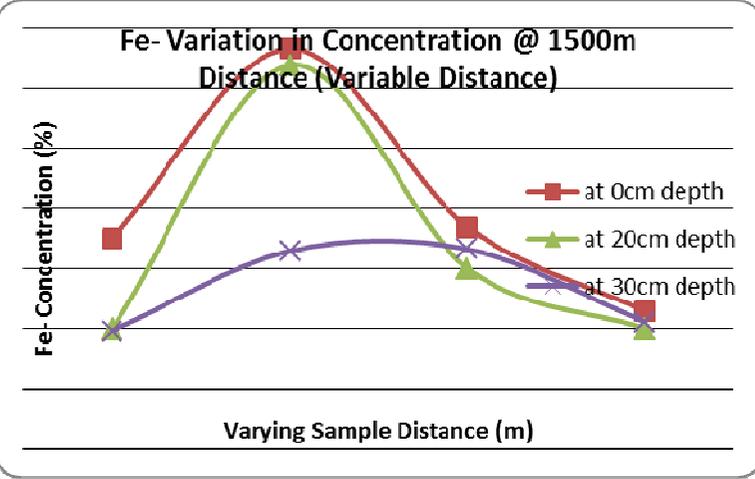
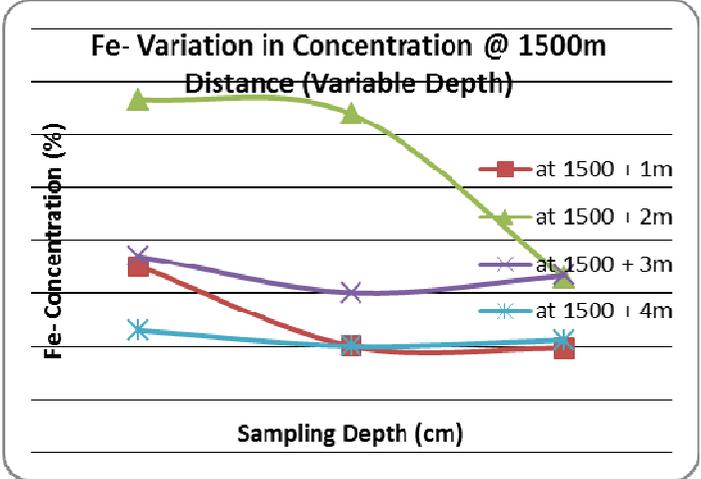


Figure 26: Fe - Profile at 1500m

4.3.5.2 Raw data analysis – Fe

Table 13: Fe - ANOVA - F-test (variation by depth and distance) from 2013 samples

Iron		
variation by depth		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.608090426	0.117238596
F-table (Ftab)	5.14	4.26
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.
variation by distance		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.194792925	0.843531662
F-table (Ftab)	5.14	4.07
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.

Although Figure 4.13 shows that there is a slight difference in iron concentration with respect to depth, the ANOVA test table for the 2013 samples confirms that the difference is insignificant. The F-calculated value for both variation in distance and depth at 500 m and 1500 m is lower than the F-value obtained from the F-table (Appendix A), which justifies acceptance of the null hypothesis H_0 that there was no significant difference between the group means. It also implies that the tailing dam does not introduce large amounts of iron into the surrounding soil.

Both Figure and Table lead the researcher to conclude that the concentration does not vary significantly. As the former demonstrated, the major iron contamination remained at an average of 7.01 % % in all three sampled soil layers.

Table 14: Fe - ANOVA - F-test (variation by depth and distance) from 2012 samples

Iron	
variation by depth	
Distance	500 m
F-calculated (Fcal)	0.17775104
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.
variation by distance	
Distance	500 m
F-calculated (Fcal)	0.096262953
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.

The F-calculated value for both variation by distance and depth at 500 m is lower than the F-value obtained from the F-table (Appendix A), thus the null hypothesis H_0 was accepted. The ANOVA test table for 2012 sample confirmed that the difference was insignificant and could be ignored.

The statistical analysis results for iron from sample one, taken in 2012, revealed that the group means are not significantly different from each other (Table 4.10), which indicates there is no significant difference in iron concentration with respect to either depth or distance. The findings

on sample two (2013) showed that the results are in agreement. The comparative average concentrations of the three results obtained led to the same conclusion: that in all probability the tailing dam does not introduce excessive amounts of iron into the soils around the dam.

4.3.6 Al₂O₃–Aluminium oxide

4.3.6.1 Raw data analysis – Al₂O₃

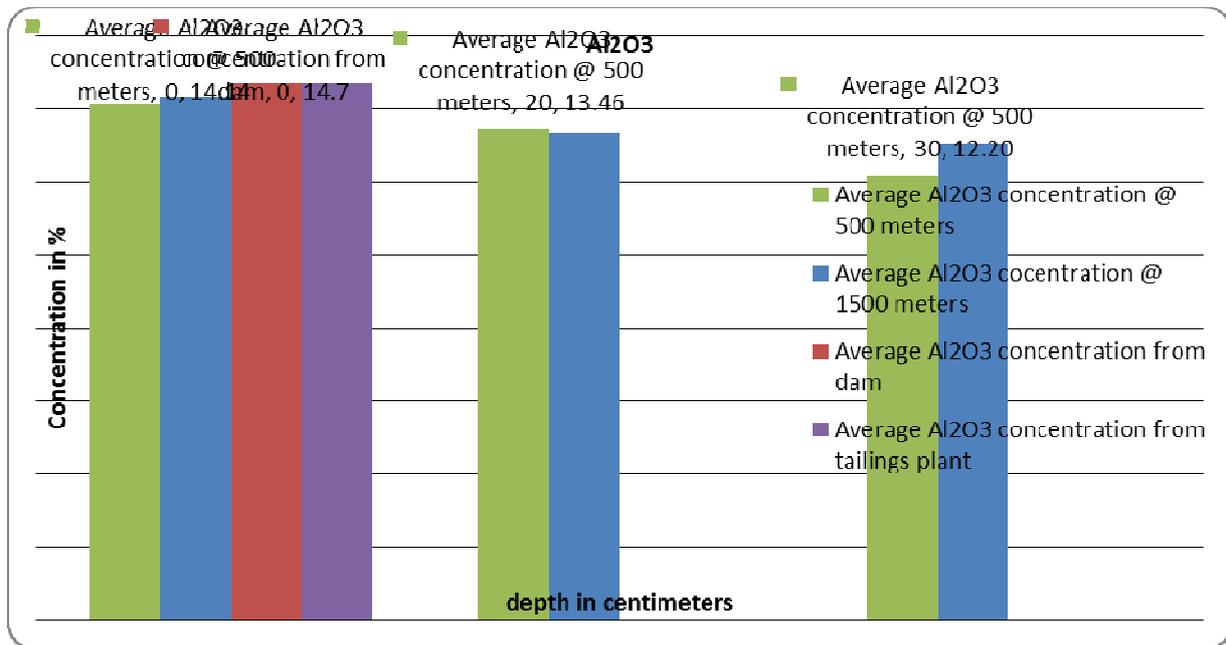


Figure 27: Average Al₂O₃ concentration at four different sampling points and three sampling depths

Aluminium is strongly complexed in soils and most commonly occurs as Al₂O₃, which exerts a strong influence on the sorption of heavy metals through competitive effects. According to Table 4.12, the concentration of Al₂O₃ at 13.26% is slightly lower at 500 m than the mean average at 1500 m (13.58%), although the former is closer to the tailings dam than the latter. The reasons for this discrepancy could be that an error was made in the analyses or that the sample was contaminated.

Figure 4.16 also shows that the concentration of aluminium oxide in the plant tails is equivalent to that in the dam basin at 14.7%. The mean average concentration values of Al₂O₃ of 13.26% (at

1500 m) and 13.58% (at 500 m) are fairly similar, which confirms the researcher's earlier statement that Al_2O_3 is a common constituent of soils. The concentrations in the samples are very similar to those in the dam and plant tails. Figures 4.17 and 4.18 show the profiles of Al_2O_3 occurrence in soil at various distances and depths.

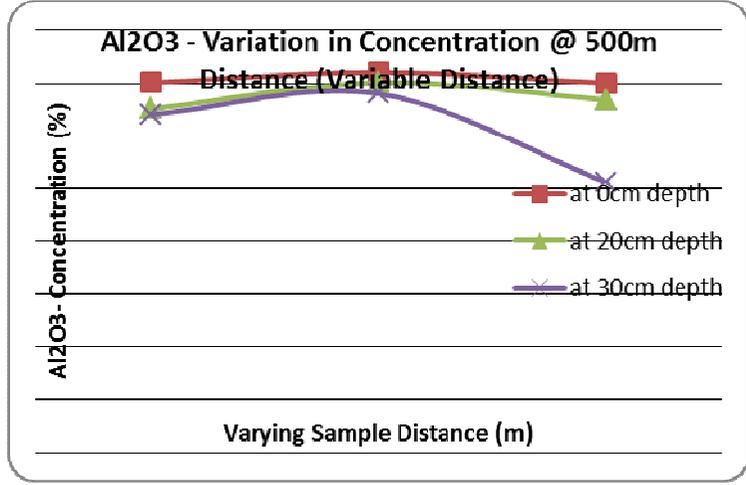
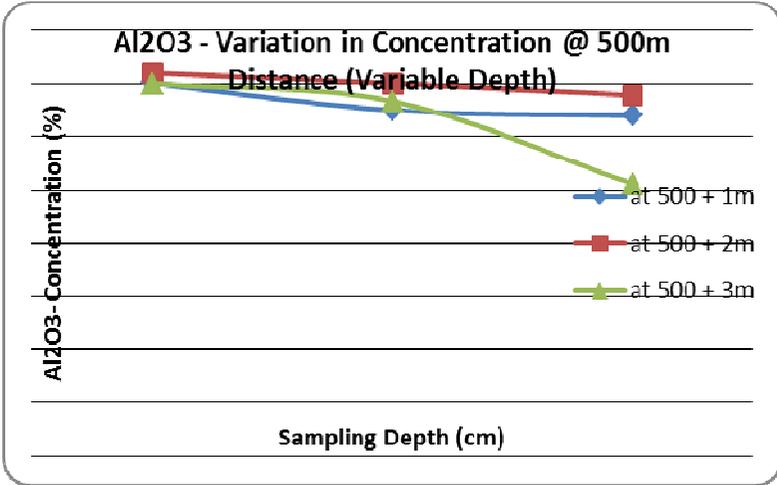


Figure 28: Al₂O₃ - Profile at 500m

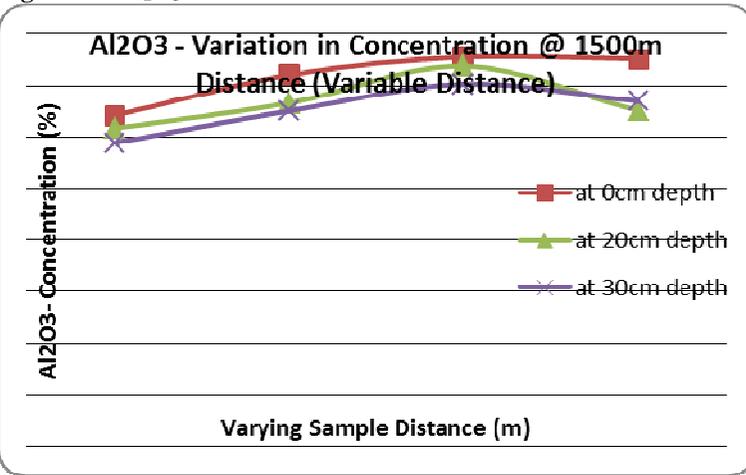
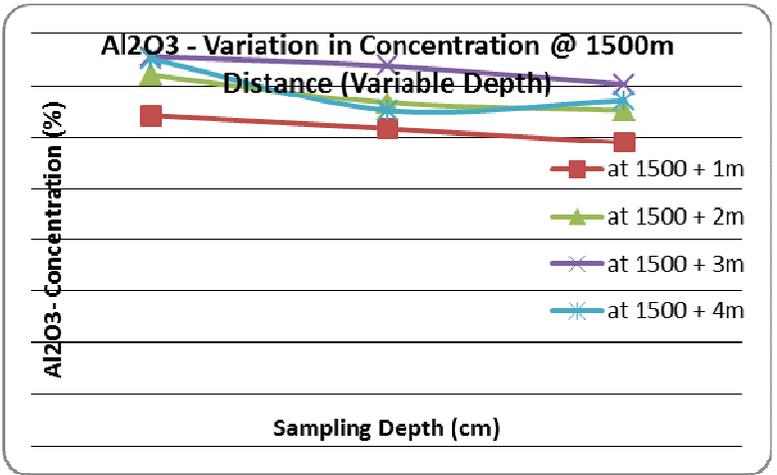


Figure 29: Al₂O₃ - Profile at 1500m

4.3.6.2 Statistical analysis – Al₂O₃

Table 15: Al₂O₃ - ANOVA - F-test (variation by depth and distance) from 2013 samples

Al ₂ O ₃		
variation by depth		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.291724717	0.11537013
F-table (Ftab)	5.14	4.26
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.
variation by distance		
Distance	500 m	1 500 m
F-calculated (Fcal)	0.156675975	1.136318278
F-table (Ftab)	5.14	4.07
Statement	Fcal<Ftab	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.	Accept Ho there is no significant difference between the group means.

Although Figure 4.15 shows that there is a slight difference in iron concentration with respect to depth, the ANOVA test table for the 2013 samples above confirms that the difference is insignificant and thus can be ignored. The F-calculated value for both variation by distance and depth at 500 m and 1500 m is less than the F value obtained from the F-table (Appendix A), which justifies acceptance of the null hypothesis Ho and agrees with the mean average concentration values of Al₂O₃, which are 13.26% and 13.58% at 1500 m and 500 m respectively. Although different, these means are quite similar, which supports the conclusion derived from the statistical analysis.

The insignificant differences in the group concentration means indicate that the tailings dam does not introduce marked amounts of aluminium into the surrounding soil.

The statistical analysis from the 2013 sample, Table 4.11 and Figure 4.15 (raw data analysis) are in agreement that the concentration does not vary significantly .

Table 16: Al₂O₃ - ANOVA - F-test (variation by depth and distance) from 2012 samples

Aluminium	
variation by depth	
Distance	500 m
F-calculated (Fcal)	0.010823236
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.
variation by distance	
Distance	500 m
F-calculated (Fcal)	0.026905271
F-table (Ftab)	5.14
Statement	Fcal<Ftab
Conclusion	Accept Ho there is no significant difference between the group means.

The F-calculated value for variation both by distance and depth at 500 m is lower than the F-value obtained from the F-table (see Appendix A), thus the null hypothesis Ho was accepted. The ANOVA test table 16 confirms that the difference is negligible and can be disregarded.

The statistical analysis results for aluminium from the first sample set taken in 2012 revealed that the group means are not significantly different from each other, which means that there is little variation in aluminium concentration with respect to both depth and distance. The findings on aluminium concentration from both the raw data and the second set of samples (2013) are in

agreement. The comparative average concentrations of the three results obtained lead to the same conclusion: that the tailings dam does not introduce aluminium contamination into the soil surrounding it.

4.4 Comparison of all six metals in the 2013 samples

A comparison of the field results for all six metals (Al, Fe, Pb, Cu, Ni and Cr) is graphically represented in Figure 4.18, which confirms that heavy metals occur in the soil in both the horizontal and vertical directions. It can also be seen that there is no discernible pattern for the behaviour of each of these metals in soil. The ICP OES results of the initial samples taken from the pipe carrying effluent from the plant tails to the dam gave the concentration of heavy metals feeding the tailings dam as follows: Al at 14.7 %, Fe at 7.73%, Cr at 2.2%, Ni at 0.068%, Cu at 0.018% and (the lowest concentration) Pb at 0.003%.

The Figures show the following trends in terms of concentration percentage values for all metals in samples collected at points A, B and C at distances of both 500 m and 1500 m. As explained in Chapter Three, each point relates to three levels of and depth (0, 20 and 30 cm). The sequence from highest to lowest was Al>Fe>Cr>Ni>Cu>Pb.

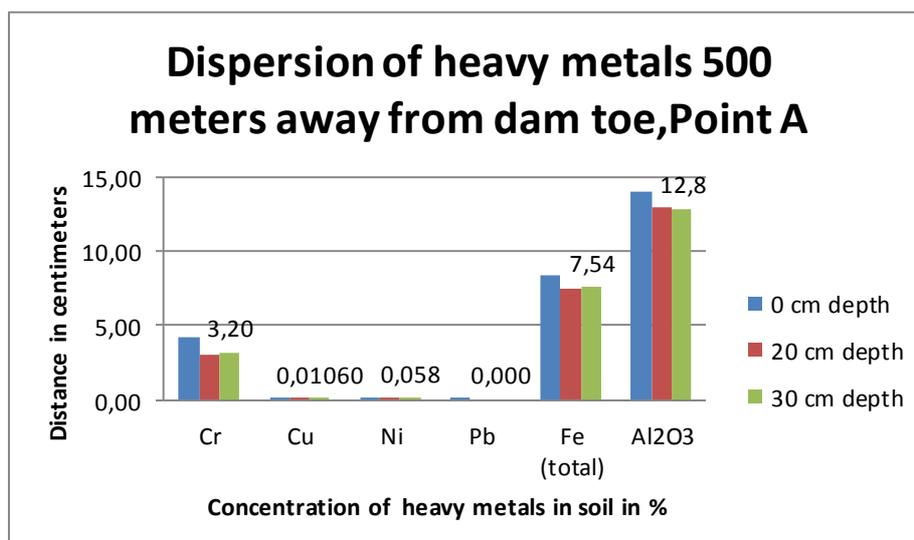


Figure 30: Point A - Profile at 500m

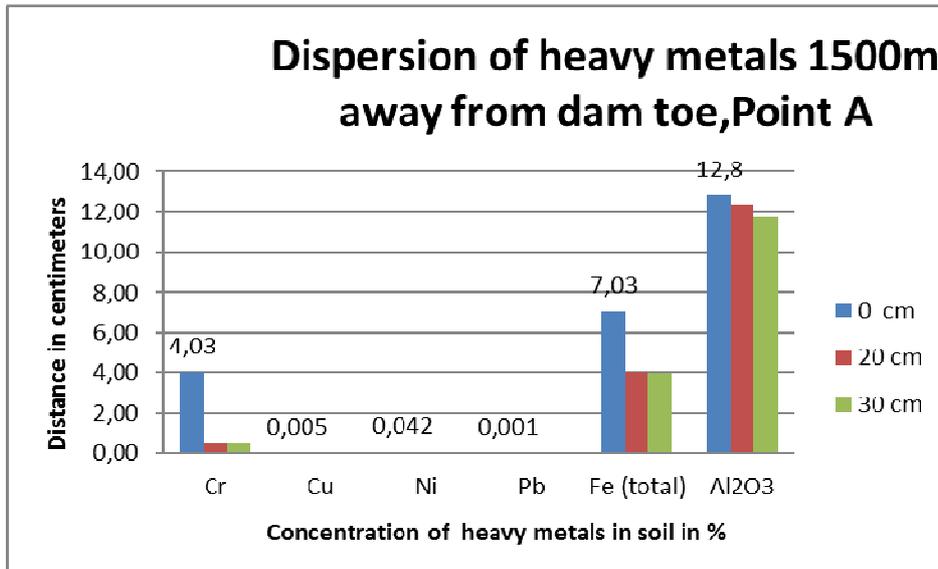


Figure 31: Point A - Profile at 1500m

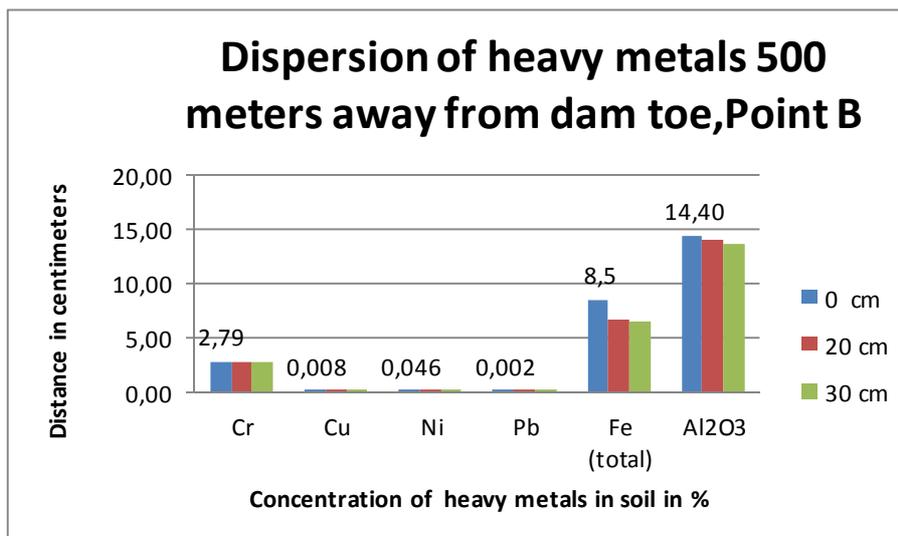


Figure 32: Point B - Profile at 500m

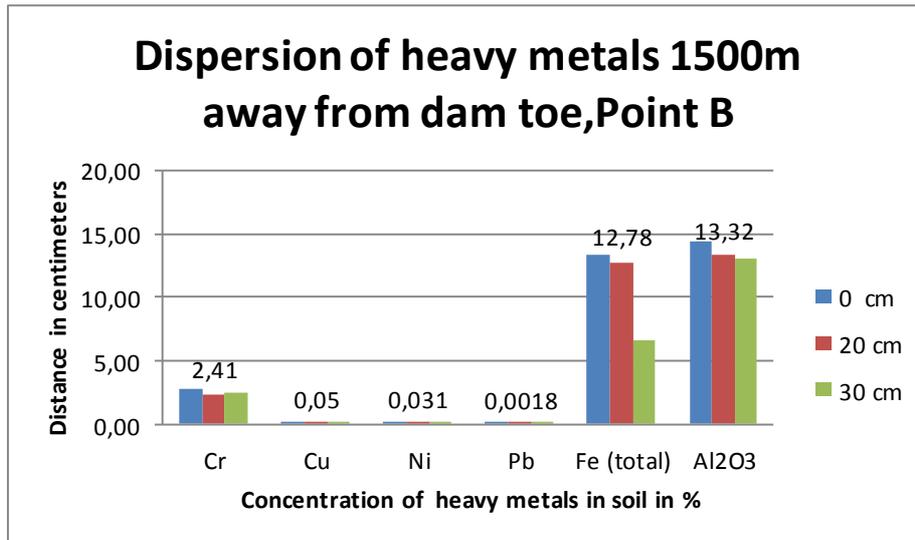


Figure 33: Point B - Profile at 1500m

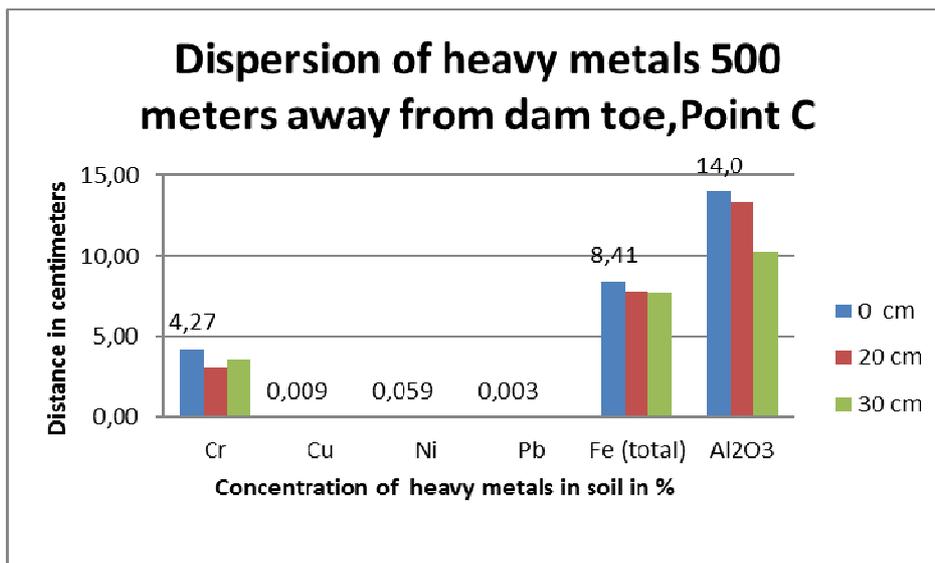


Figure 34: Point C - Profile at 500m

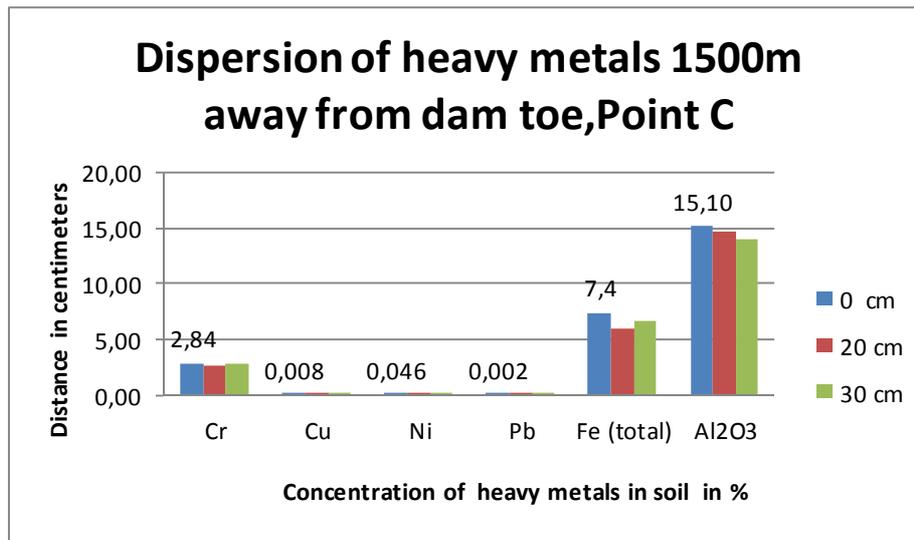


Figure 35: Point C - Profile at 1500m

4.4.1 Heavy metal enrichment analysis

The statistical analysis showed that there is less mobility in these heavy metals both at 500 m and 1500m. This would indicate that the levels of contamination with heavy metals are saturated. This is probably attributable to the character of the soil samples studied, which had a high clay content. The retention capacity of these metals is quite high, which results in poor aeration and low permeability in the soil. This would also explain both why the mobility of the six metals in this particular area at depths of 30 cm was so limited, and why the saturation levels of these metals in the soil around the dam at both 500 m and 1500 m were low.

Previous research has shown that over 95% of the earth's crust is made up of the following major elements; oxygen, hydrogen, iron, aluminium, calcium, sodium, potassium, magnesium and titanium. If these metals occur in soil in excessive quantities, they present a toxic threat to wild life, plants and human beings. Very little research has been done to assess whether the levels of the heavy metals occurring in the soil surrounding the dam are the result of the tailings it contains or the natural environment. Accordingly, the researcher used an enrichment factor (EF) calculation to determine the degree of enrichment of each metal (Loska *et al.*, 2004).

The method of calculation was as follows:

$$EF = [(C_x / C_{al}) / (C_{x \text{ crust}} / C_{al \text{ crust}})]$$

where C_x = Concentration of the measured heavy metal

C_{al} = Concentration of the reference metal and in this case its aluminium

$C_{x \text{ crust}}$ = Concentration of the average crustal value of the heavy metal in the earth's crust.

$C_{al \text{ crust}}$ = Concentration of the average crustal value of aluminium in the earth's crust.

The reference sample chosen for the calculation was aluminium, since the ferric-luvisol soil near the dam has a high clay content and aluminium is associated with clay minerals, making it suitable to use as a reference indicator (Sommer and Pyzik, 1974).

The calculated enrichment values were scaled according to the standards below .

- If the calculated EF (enrichment factor) IS < 2 it means minimal enrichment.
- If the calculated EF (enrichment factor) IS $2 < x < 5$ it means moderate enrichment.
- If the calculated EF (enrichment factor) IS $5 < x < 20$ it means a significant level of enrichment.
- If the calculated EF (enrichment factor) IS $20 < x < 40$ it means very high levels of enrichment.
- If the calculated EF (enrichment factor) IS > 40 it means extremely high levels of enrichment.

The tabulated results for both the 2012 and 2013 data reveal that iron, lead and copper have enrichment values less than 2; therefore they contributed minimal enrichment. The chromium EF value exceeded 5, which indicates moderate chromium enrichment. These results suggest that the dam has minimal impact in terms of soil contamination with lead, copper and iron, and only moderate impact from chromium and nickel contamination.

Table 17: Comparative enrichment values for both 2012 and 2013 data

Heavy Metal compared	Global crustal averages (ppm) ^{Note 1}	2012 data	2013 data	Enrichment Factor 2012	Enrichment Factor 2013
		averages (ppm)	averages (ppm)		
Aluminium	81 300	114 642	109900	1	1
Iron	50 000	60 977	63125	0.86485408	0.9339513
Chromium	200	1482	1008	5.25490658	3.7284076
Nickel	80	249	212	2.20727351	1.9603731
Lead	16	8	5	0.35458209	0.2311761
Copper	70	89	74	0.9016516	0.7820356

Note 1: Data taken from Data of Geochemistry sixth edition Chapter D. Composition of the Earth's Crust geological survey professional paper 440-d,pg d15 table 20

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The results obtained by the researcher after the soil samples had been collected and analysed indicated that regardless of the manner in which heavy metals are introduced into the soil, the soil will generally act like a sieve and retain these metals. Migration of the heavy metals into groundwater or the atmosphere is normally not expected to occur as long as the retention capacity of the soil is not exceeded.

In the soil, the extent of heavy metal movement in the y-direction (that is, horizontal to the surface) was found to be closely related to the chemical properties specific to each metal and solution on the surface.

The results also showed that there was no particular descriptive pattern showing the behaviour of each of these metals in soil.

The analytical results obtained for each metal in the 2013 samples were compared with those obtained for the 2012 samples. The findings all agreed with the same conclusion: that the group means did not differ significantly. The inference to be drawn is that the tailings dam does not introduce considerable amounts of the heavy metals and there is no concentration profile for these heavy metals (Al, Fe, Pb, Cu, Ni and Cr) into the soils surrounding it.

The most important findings are listed below.

1. The results of this research study showed that when the concentrations of the six heavy metals at the Impala tailings dam site were compared, their prevalence followed the order Al>Fe>Cr>Ni>Cu>Pb.
2. For samples taken at both 500 m and 1500 m, the Anova tests confirmed that the difference between the group concentration means for each metal with respect to depth (0 cm, 20 cm and 30 cm) was not significant. This was in agreement with the raw data analysis, which

provided a concentration profile for each metal and led to the conclusion that the average means were very similar.

3. For both sets of samples (at 500 m and 1500 m), the Anova tests confirmed that the difference between the group concentration means for each metal with respect to distance (1 m, 2 m, and 3 m) was insignificant, and this finding agreed with the raw data analysis, which examined the concentration profile of each separate metal and showed that the average means were very similar.
4. The statistical analysis results for heavy metals (Al, Fe, Pb, Cu, Ni and Cr) obtained from sample set one, taken in 2012, revealed that the group means do not differ significantly from each other, which implies that there is no marked variation in the concentration of the six metals with respect to both depth and distance. The findings of the raw data analyses of the concentration of these metals from both the 2012 and 2013 sets of samples were in agreement. The comparative average concentrations obtained by the three analyses provided the same overall result, confirming the conclusion that the soil surrounding the tailings dam is probably not affected by excessive amounts of Al, Fe, Pb, Cu, Ni and Cr.
5. A great deal of soil contamination by heavy metals is caused by mining activities and metallurgical process plants, because in both cases the waste material created by these processes is dumped in tailings dams. However, in this study the results of the samples taken revealed that the dam has not significantly contaminated the surrounding soil. This could be attributed to two factors: the tails are treated before being sent to the dam; and the dam has been designed relatively recently and incorporates new technology, following the failures of the mine dams used in the past.
6. The findings obtained from this study showed that the levels of contamination by heavy metals appeared to be saturated hence the concentration profiles of the metals at the measured depth and distance were not significant. The main reason is the character of the soil that was analysed, which showed a high clay content. This in turn causes poor aeration and permeability in the soil, and suggests why there is less mobility of these metals in the areas sampled at 30 cm below the surface. On the other hand, the retention capacity of the six

metals is quite high, which explains their saturation levels in the soil around the dam at both 500 m and 1500 m.

7. The results of the enrichment factor calculations for the 2012 and 2013 data revealed that iron, lead and copper have enrichment values less than 2 (and therefore minimal enrichment). The chromium EF value exceeds 5 (which indicates moderate chromium enrichment). These findings also suggest that the dam has minimal impact in terms of contaminating the soil with lead, copper and iron, and moderate impact from chromium and nickel.

5.2 Recommendations

If this research were to be taken further, the assessment of heavy metal contamination in the soil would profit from an extended distance profile. For example, the researcher should collect more than 10 samples around the dam at a radius of 500 m, 2000 m and 3000 m with respect to distance, and at a depth of up to 2 m, with the following sequence of layers: 0 cm, 30 cm, 60 cm, 1 m, 1.5 m and 2 m.

REFERENCES

- Adediran, S. and Kramer, J., 1987. *Applied Geochemistry*, 2, pp. 213-216.
- Al-Barrak, S., 1990. Characteristics of some soils under Date palm in AL-Hassa eastern oasis, Saudi Arabia. *J. King Saud University*, 2, pp. 115-130.
- Alloway, B., 1995. *Soil Processes and the behavior of Metals*. In: *Heavy Metals in Soil*. Edited by: B.J. Alloway, Blackie Academic & Professional, London.
- Alloway, B., 1998. The mobilization of trace elements in soil, in Prost, R. (ed.), contaminated soils. *Les colloques*, 85, pp. 133-145.
- ATSDR, 2005. *Toxicological profile for nickel*. Atlanta, GA: Agency for Toxic Substances and Disease Registry.
- Anderson, M., 1997. *Long Term Copper Availability and Adsorption in a Sludge-Amended Davidson Clay Loam*. Dissertation, April 1997, Blacksburg, VA.
- Bartlett, A., Hoffbrand, A., and Kontoghiorghes, G. 1990. Long-term trial with the oral iron chelator 1,2-dimethyl-3-hydroxypyrid-4-one (L1). II. Clinical observations. *Haematol*, 76, pp.301-4.
- Bear, J., 1972. *Dynamics of fluids in porous media*. Dover publications, Inc., NY
- Benedetti, M. F., 1995. *Environmental Science Technology*, 29, p 446.
- Borg, H. and Johansson, K., 1989. Metal Fluxes Swedish Forest Lakes Water, Air and Soil Pollution, 47, pp.427-440.
- Bradl, H., 2004. Adsorption of heavy metals ions on soils and soil constituents. *Colloid and Interface Science*, 277, pp. 1-18.
- Brown, R., Morgan, L., Bhattacharya, S., Johnson, P., Minard, G. and Dickerson, R., 2008. Potential aluminum exposure from parenteral nutrition in patients with acute kidney injury. *Ann Pharmacother*, 42(10), pp.1410-5.
- Buck, W., 1978. *Copper/Molybdenum Toxicity in Animals: Toxicity of Heavy Metals in the Environment*, Part I, edited by F.W. Oehme, Marcel Dekker, Inc. New York and Basel.
- Butkus, M. and Grasso, D., 1999. *Environmental Engineering Science*, 16, p.117.
- Cary, E., Alloway, W. and Olson, O., 1977. Control of chromium concentration in food plants. II. Chemistry of chromium in soils and its availability to plants. *Agric. Food Chem*, 25, pp.305-309.

- Clarke, A.G. and Tomlin, A.S., 1999. Understanding Our Environment. *Royal Society for Chemistry*, pp. 9-70.3.
- Cave, K. and Talens- Alesson, F., 2005. Comparative effects of Mn(II) and Fe(III) as activators and inhibitors of the adsorption of other heavy metals on Calcite. *Colloids and surface*, 268, pp. 19-23.
- Dayan, A. D. and Paine, A. J., 2001. Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. *Human & Experimental Toxicology*,20(9), pp. 439-51.
- Del-Castilho, P., Chardon W., and Salomons, W., 1993. Influence of cattle-manure slurry application on the solubility of cadmium, copper and zinc in a manured acidic, loamy and soil. *Environmental Quality*, 22, pp. 689-697.
- Diatta, J., 1998. Polish J. Environ. Stud, 8, p. 195.
- Dube, A. Zbytniewski, R. Kowalski, T., Cukrowska, E. and Buszeski, B., 2001. Adsorption and migration of heavy metals in soil. *Environmental Studies*,10,pp.1-10.
- Fletcher, K. and Doyle, P., 1974. Regional geochemical reconnaissance and the molybdenum content of bedrock, soils and vegetation from the Eastern Yukon in Hemphill. *Trace Substances in Environmental Health*,pp. 369-373.
- Foy, C.D., Chaney R.L. and White, M.C, 1978. The physiology of metal toxicity in plants. *Ann.Rev. Plant Physiol*, 29, pp. 511-566.
- Garruto, R. M., Shankar, S. K., Yanagihara, R., Salazar, A. M., Amyx, H. L. and Gajdusek, D. C., 1989. Low-calcium, high-aluminum diet-induced motor neuron pathology in cynomolgus monkeys. *Acta Neuropathol (Berl)*, 78(2), pp.210-219.
- Gomes, P. and Fontes -Mauricio, P., 2001. Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. *Soil Sci. Soc. AM*, 65.
- Griffin, R. and Au, A., 1977. Lead adsorption by montmorillonite using a competitive Langmuir equation. *Soil Sci. Soc. Am. J*, 41, pp. 880-882.
- Gustafsson, J., Lumsdon, D. and Simonsson, M., 1998. Aluminium solubility characteristics of spodic B horizons containing imogolite-type materials. *Clay Minerals*, 33, pp. 77-86.
- Harter, R., 1986. Adsorption phenomena. edited

- Hawkins, N. M., Coffey, S., Lawson, M. S. and Delves, H.T., 1994. Potential aluminium toxicity in infants fed special infant formula. *Pediatr. Gastroenterol. Nutr*, 19 (4), pp. 377-381.
- Hlavay, J., Prohaska, T., Weisz, M., Wenzel, W. and Stingeder, J., 2004. Determination of trace elements bound to soils and sediment fractions. *Pure Applied Chemistry*, 76, pp. 415-442
- Hou, X., and Jones, B., 2000. Inductively Coupled Plasma/Optical Emission Spectrometry. *Encyclopedia of Analytical Chemistry*. R.A. Meyers (Ed.) pp. 9468–9485, John Wiley & Sons Ltd, Chichester.
- Howell, J. and Gawthorne, J., 1987. *Copper in Animals and Man*. Volume II. CRC Press, Inc. Boca Raton, Florida.
- Jalali, M. and Khanlari, Z., 2008. Environmental contamination of Zn, Cd, Ni, Cu, and Pb from industrial areas in Hamadan Province, Western Iran. *Environmental Geology*, 55, pp. 1537-1543.
- Jenne, E., 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In *Trace Elements in Water, Adv. in Chemistry, Ser. 73*.
- Jenne, E., 1968. Control of Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water—the dominant role of hydrous manganese and iron oxides. *Adv. in Chem*, 7, pp. 337-387.
- Korte, N., Skopp, J., Fuller, W., Niebla, E. and Aleshii, B.J., 1976. Trace element movement in soils: influence of soil physical and chemical properties. *Soil Sci*, 122, pp. 350-359.
- Lafuente, A. and Gonzalez, C. 2008. Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region. *Geoderma*, 145, pp. 238-244.
- Lasaga, A., 1998. *Kinetic theory in the earth sciences*. Princeton University Press, NJ.
- Lee, C., 1996. A review of mineralization in the Bushveld complex and some other layered intrusions. *Elsevier*, pp. 103-145.
- Loska, K., Wiechula, D. and Korus, I., 2004. Metal contamination of farming soils affected by industry. *Environmental*, 30, pp. 159-165.
- Mason, B., 1952. *Principles of Geochemistry*. London: John Wiley.

- Mathews, J. H. and Kurtis, K., 2004. Numerical Methods Using Matlab, 4th Edition, Prentice-Hall Inc.
- Mazzaferro, S., Perruzza, I., Constantini, S., Pasquali, M., Onorato, L., Sardella, D., Giordano, R., Ciaralli, L., Ballanti, P., B Gonucci, E., Cinotti, G. A. and Coen, G., 1997. Relative roles of intestinal absorption and dialysis fluid-related exposure of aluminium in haemodialysis patients. *Nephrol. Dial. Transplant*, 12 (12), pp. 2679-2682.
- Miller, W., Martens, D. and Zelazny, L., 1986. Effect of sequence in extraction of trace metals from soils. *Soil Sci. Soc. Am*, 50, pp.598-601.
- Myung, J., 2008. Heavy Metal Concentrations in Soils and Factors Affecting Metal Uptake by Plants in the Vicinity of a Korean Cu-W Mine. *Department of Earth and Environmental Sciences, College of Natural Sciences, Sejong University, Seoul, pp. 143-747.
- New England Journal of Medicine, 1979: Volume 300, Page 689; Lancet, 1976, Volume 2, Pages 1-3.
- Olade, M., Van de Kraats, A. and Ukpong, E., 1978. Effects of environmental parameters on metal dispersion patterns in stream sediments from the lead-zinc belt. *Geologie en Mijnb*, 58, pp. 341-351.
- Olorunfemi, B., 1984. Factors influencing the geochemistry of lateritic soils in the green-schist-amphibolite meta-tectonic belt, S. W. Nigeria. *Chem. Geo.* 42, pp. 261-275.
- Owens, C., 1981. *Copper Deficiency and Toxicity*. Noyes Publications, Park Ridge, New Jersey, USA.
- Ponizovsky, A. and Thakali, S., 2008. Nickel partitioning in acid soils at low moisture content. *Geoderma*, 145, pp. 69-75.
- Prusinkiewicz, Z., 1999. *Floia Forestalia Polonica*, 34, pp. 34,49.
- Rabi, A. and Usman, A., 2008. The relative selectivities of Pb, Cu, Zn, Cd and Cd by soil developed on shale in New Vally, Egypt. *Geoderma*, 144, pp. 334-343.
- Rikers, R., 1999. Characterization of heavy metals in soils, using magnetic separation. Proefschrift.
- Roskill 1994. Platinum: Market update, analysis & outlook. Roskill Information Services, London, p.5.
- Sadiq, M. and Enfield, C., 1984. *Soil Science*, 138, pp. 335-340.

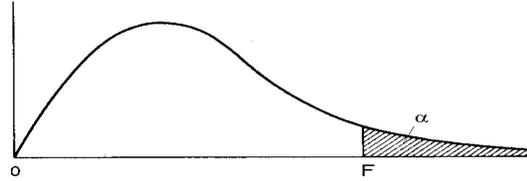
- Schwertmann, U., 1985. *The Effect of Pedogenic Environments on Iron Oxides Minerals*. In: *Advances in Soil Science*, 1, Springer-Verlag, New York, Inc.
- Shuman, L., 1991. Chemical forms of micronutrients in soils. In J. J. Mortvedt (ed.). *Micronutrients in agriculture*. Soil Soc. Soc. Amer. Book Series #4. Soil Sci. Soc. Amer., Inc., Madison, WI.
- Smith, S., Peterson, P. and Kwan, K.J., 1989. Toxicology. *Environmental Chemistry*, 24, pp.241-251.
- Sommer, S., and Pyzik, A., 1974. Geochemistry of middle Chesapeake bay sediments from upper cretaceous to present: *Chesapeake sci*, 15, pp. 839-844.
- Sorgdrager, B., de Loeff, A. J., de Monchy, J. G., Pal, T. M., Dubois, A. E. and Rijcken, B., 1998. Occurrence of occupational asthma in aluminum potroom workers in relation to preventative measures. *Int. Arch. Occup. Environ. Health*, 71(1), pp. 53-59.
- Sposito, G., 1989. *The chemistry of soils*. Oxford University Press, New York. p.277.
- Stevenson, F., 1991. Organic matter-micronutrient reactions in soil. In J. J. Mortvedt (ed.). *Micronutrients in agriculture*. Soil Soc. Soc. Amer. Book Series #4. Soil Sci. Soc. Amer., Inc., Madison, WI.
- Stevenson, F. and Chen, Y., 1991. Stability Constant of Copper (II) Humate Complexes Determined by Modified Potentiometric Titration. *Soil Sci. Soc. Am. J*, 55, pp. 1586-1591.
- Suárez-Fernández, M., Soldado, A., Sanz-Medel, A., Vega, J., Novelli, A., Fernández-Sánchez, M., 1999. Aluminum-induced degeneration of astrocytes occurs via apoptosis and results in neuronal death, 835, pp. 125-36.
- Suruchi and Pankaj, 2011. Assessment of Heavy Metal Contamination in Different Vegetables Grown in and Around Urban Areas. *Environmental Toxicology*, 5, pp.162-179.
- Varner, J. A., Horvath, W. J., Huie, C. W., Naslund, H. R. and Isaacson, R. L., 1994. Chronic aluminum fluoride administration. I. Behavioral observations. *Behav. Neural Biol*, 61 (3), pp. 233-241.
- Vermaak, C. and Hendriks, L., 1976. A review of the geology of the Merensky reef, with specific reference to new data on the precious metal mineralogy. *Economic Geology*, 71, pp. 1244-1269.

- Vermaak, C., 1995. The platinum-group metals: a global perspective. Mintek Randburg, pp.86-87.
- Verstraeten, S., Aimo, L. and Oteiza, P., 2008. Aluminium and lead: molecular mechanisms of brain toxicity. *Arch Toxicol*, 82(11),pp.789-802.
- Vince de Capio., 2003. Lead Sorption on Goethite Coated Silica Sand Columns, *Environmental Engineering Science*, pp. 3-13.
- Willaert, G. and Verloo, M., 1988. Plant and Soil, 138, pp. 285-292.
- Yahya, M. D and Abdulfatai, J., 2007. Mathematical Modelling and Simulation of Mobility of Heavy Metals in Soil Contaminated With Sewage Sludge. Leonardo Electronic Journal of Practices and Technologies, 6 (10), pp. 157-168.
- Yong, R. and Phandunchewit, Y., 1993. PH Influence on Selectivity and Retention of Heavy Metals in Some Clay Soils. *Can. Geotech*, 30, pp .821-833.

APPENDICES

Appendix A -F-table

Table 4 **PERCENTAGE POINTS OF THE F DISTRIBUTION** **$\alpha = 5\%$**



		Numerator degrees of freedom									
		v_1									
Denominator degrees of freedom	v_2		1	2	3	4	5	6	7	8	9
		1		161.40	199.50	215.70	224.60	230.20	234.00	236.80	238.90
	2		18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38
	3		10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81
	4		7.71	6.94	6.56	6.39	6.26	6.16	6.09	6.04	6.00
	5		6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77
	6		5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10
	7		5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68
	8		5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39
	9		5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18
	10		4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02
	11		4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90
	12		4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80
	13		4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71
	14		4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65
	15		4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59
	16		4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54
	17		4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49
	18		4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46
	19		4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42
	20		4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39
	21		4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37
	22		4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34
	23		4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32
	24		4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30
	25		4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28
	26		4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27
	27		4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25
	28		4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24
	29		4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22
	30		4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21
	40		4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12
	60		4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04
	120		3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96
	∞		3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88

Appendix B – 2012 ICP-MS RESULTS

2012 ICP-MS results in mg/l, as analysed in dried material.						
Samples	Al (27)ppm	Pb (208)ppm	Fe (57)ppm	Ni (60)ppm	Cu (63)ppm	Cr (52)ppm
1 Point A 20cm - 0m	107 484	7	55 751	260	83	2118
2 Point A 30cm - 0m	118 612	8	58 624	284	98	1894
3 Point B 30cm - 1m	96 406	7	48 196	199	79	762
4 Point B 20cm - 1m	115 273	9	58 309	298	107	1773
5 Point C 20cm - 2m	124 128	9	65 365	296	95	2153
6 Point C 30cm - 2m	129 817	9	64 427	249	91	965

Appendix C – Analytical Results

ANALYTICAL REPORT: UNISA

No unauthorised copies may be made of this report.

To:	UNISA	Date of Request	27.08.2013
Attention Ref:	Molebogeng Nkobane COD		
Tel:	+27 11 471 2156		
Fax:			
			UIS Analytical Services Analytical Chemistry Laboratories 4, 6 Tel: (012) 665 4291 Fax: (012) 665 4294

Certificate of analysis: 8275

LIMS ID	Sample ID	Note: all results in percentage (%) unless specified otherwise																	
		SiO2	Al2O3	Fe (total)	Fe2O3	TiO2	CaO	MgO	K2O	MnO	P	Ba	Cr	Cu	Ni	Sr	V	Pb	Zn
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
8275 - 356564	DAM/TOE/A/30CM/DOWN	44.1	14.2	7.54	10.8	0.354	7.05	11.6	0.238	0.183	0.021	0.009	3.20	0.011	0.058	0.015	0.033	0.002	0.023
8275 - 356565	B-1.5KM/AWAY/FROM/DAM/0CM	45.0	13.3	13.3	8.36	0.628	7.56	5.72	0.302	0.178	0.015	0.016	2.50	0.005	0.035	0.011	0.030	0.002	0.015
8275 - 356566	TAILINGS/SAMPLE/FROM/PLANT	45.7	14.7	7.73	11.1	0.326	8.43	13.8	0.275	0.158	0.012	0.009	2.20	0.018	0.066	0.019	0.027	0.003	0.017
8275 - 356567	DAM/TOE/B=30CM/DOWN	45.1	15.6	8.56	12.2	0.319	8.75	11.7	0.192	0.162	0.008	0.008	2.77	0.018	0.066	0.017	0.030	0.003	0.016
8275 - 356568	DAM/TOE/B/2M/0CM	41.5	14.4	6.63	9.48	0.476	8.31	8.85	0.241	0.160	0.017	0.009	2.79	0.008	0.046	0.014	0.031	0.002	0.015
8275 - 356569	C/1.5KM/AWAY/FROM/DAM/30CM	44.8	13.0	5.13	7.34	0.598	6.75	4.07	0.234	0.229	0.016	0.029	1.73	0.004	0.026	0.008	0.024	<0.001	0.010
8275 - 356570	D/1.5KM/AWAY/FROM/DAM/0CM	56.3	15.0	4.59	6.56	0.828	7.10	2.96	0.432	0.207	0.027	0.026	0.13	0.003	0.016	0.010	0.014	0.001	0.005
8275 - 356571	C/1.5KM/AWAY/FROM/DAM/0CM	48.4	15.1	7.40	10.6	0.710	7.29	7.01	0.298	0.191	0.011	0.016	3.94	0.005	0.044	0.011	0.040	0.002	0.020
8275 - 356572	B-1.5KM/AWAY/FROM/DAM/30CM	47.6	13.5	4.48	6.41	0.629	8.33	3.57	0.328	0.155	0.013	0.019	0.819	0.003	0.019	0.010	0.017	<0.001	0.007
8275 - 356573	TAILINGS/DAM/SAMPLE/INSIDE/THE/BASIN	40.8	13.3	9.11	13.0	0.374	6.58	13.6	0.204	0.173	0.012	0.007	4.70	0.010	0.068	0.015	0.046	0.003	0.023
8275 - 356574	A/1.5KM/AWAY/FROM/DAM/30CM	41.5	11.8	3.94	5.64	0.594	13.3	3.24	0.201	0.196	0.011	0.022	0.508	0.003	0.015	0.013	0.016	<0.001	0.004
8275 - 356575	DAM/TOE/C=30CM	43.0	14.0	7.76	11.1	0.410	5.72	10.0	0.210	0.177	0.019	0.010	3.59	0.009	0.056	0.013	0.036	0.000	0.018
8275 - 356576	T3/CREST/NEXT/TO/THE/WALL/TAILINGS/DAM/I	40.9	12.1	9.03	12.9	0.314	6.37	13.7	0.169	0.168	0.010	0.007	3.71	0.018	0.079	0.013	0.037	0.002	0.021
8275 - 356577	D/1.5KM/AWAY/FROM/DAM/30CM	50.9	13.4	4.23	6.05	0.663	6.38	2.69	0.367	0.222	0.010	0.023	0.103	0.003	0.014	0.008	0.012	0.000	0.003
8275 - 356578	DAM/TOE/A/0CM/0M	39.9	12.8	8.41	12.0	0.335	6.57	12.2	0.209	0.162	0.029	0.007	4.13	0.013	0.064	0.014	0.039	0.000	0.021
8275 - 356579	A/1.5KM/AWAY/FROM/DAM/0CM	40.0	12.8	7.03	10.1	0.545	9.28	6.90	0.237	0.218	0.014	0.017	4.03	0.005	0.042	0.012	0.040	0.001	0.017
8275 - 356580	DAM/TOE/C/4M/0C/0.2M/DOWN=20CM/DOWN	39.4	12.8	8.41	12.0	0.410	5.77	10.5	0.154	0.175	0.015	0.008	4.27	0.009	0.059	0.009	0.040	0.003	0.020
8275 - 356581	T2/TAILING/DAM/INSIDE/BASIN/2ND/700M/APA	40.1	13.2	8.90	12.7	0.355	6.85	13.0	0.183	0.161	0.010	0.007	4.62	0.009	0.066	0.013	0.045	0.002	0.021
8275 - 356573qc	duplicate	41.1	13.2	9.13	13.1	0.373	6.60	13.7	0.209	0.176	0.010	0.007	4.74	0.011	0.069	0.014	0.048	0.003	0.023
8275 - 356581qc	duplicate	40.6	13.4	8.88	12.7	0.353	6.95	13.2	0.221	0.163	0.011	0.007	4.54	0.010	0.066	0.014	0.044	0.002	0.022

Chemical elements:	Si, Al, Fe, Ti, Ca, Mg, K, Mn, P, Ba, Cr, Cu, Ni, Sr, V, Pb, Zn
Instrument:	ICP-OES
Date:	04.10.2013
Authorised:	JJ Oberholzer

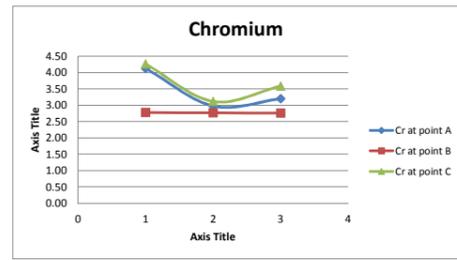
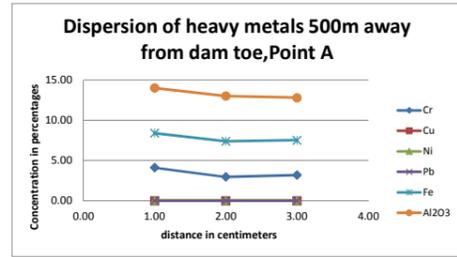
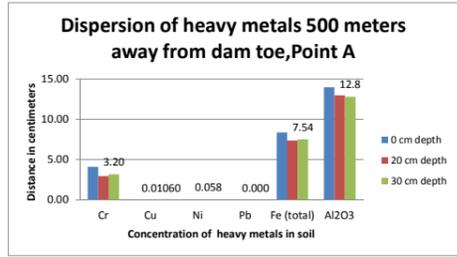
Date: 03.10.2013
Analysed by: Walter Masoga

Appendix D – FIELD RESULTS

SAMPLE | **DEPTH** | Note: all results in percentage (%) unless specified otherwise

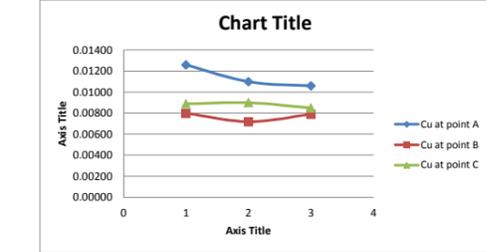
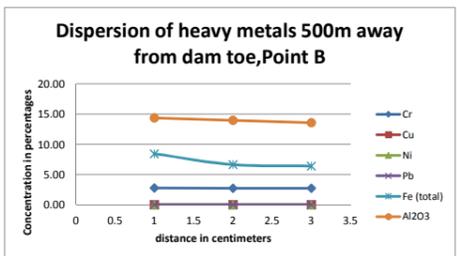
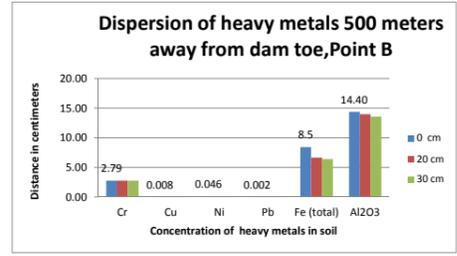
500 METERS AWAY FROM DAM(Dam Toe) point A,1 meter

Depth	Cr	Cu	Ni	Pb	Fe (total)	Al2O3
0 cm	4.13	0.01260	0.064	0.001	8.41	14.0
20 cm	2.98	0.01100	0.061	0	7.4	13.01
30 cm	3.20	0.01060	0.058	0.000	7.54	12.8



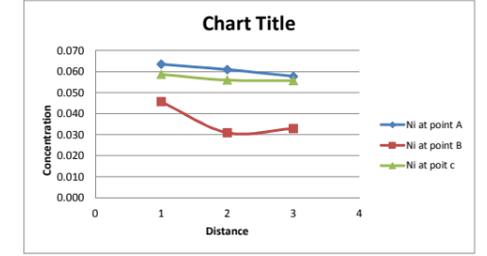
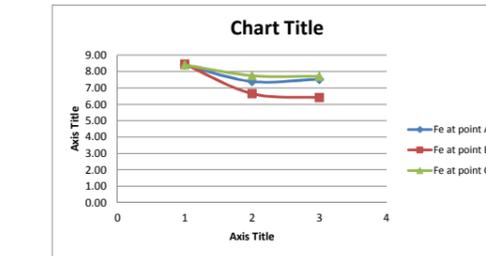
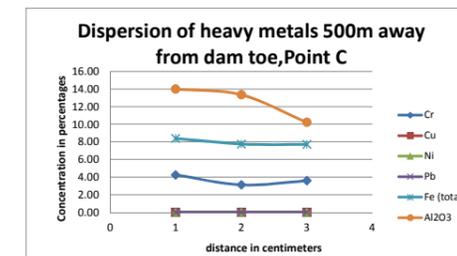
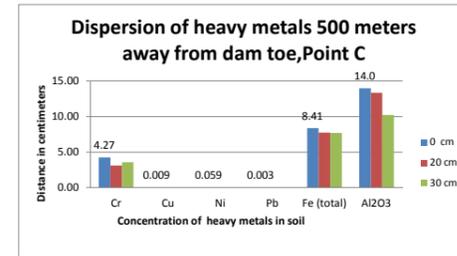
500 METERS AWAY FROM DAM(Dam Toe) point B,2 meters

Depth	Cr	Cu	Ni	Pb	Fe (total)	Al2O3
0 cm	2.79	0.008	0.046	0.002	8.5	14.40
20 cm	2.77	0.0072	0.031	0.002	6.66	14.01
30 cm	2.77	0.008	0.033	0.002	6.42	13.6



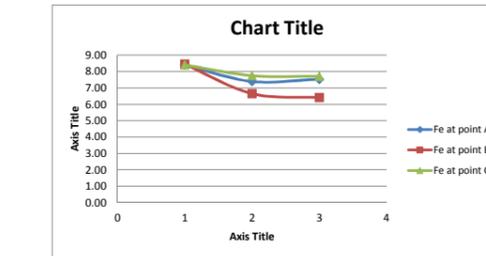
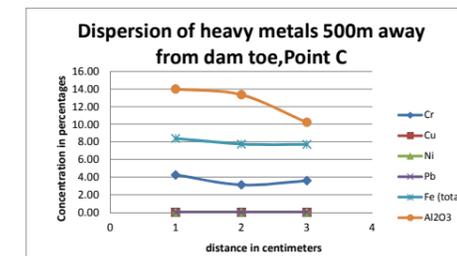
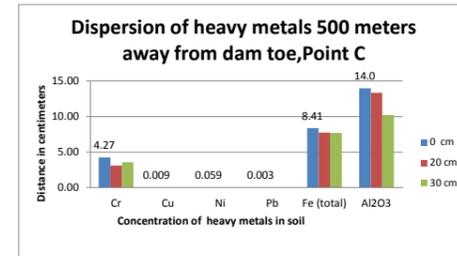
500 METERS AWAY FROM DAM(Dam Toe) point C,3 meters

Depth	Cr	Cu	Ni	Pb	Fe (total)	Al2O3
0 cm	4.27	0.009	0.059	0.003	8.41	14.0
20 cm	3.12	0.009	0.056	0.001	7.76	13.35
30 cm	3.59	0.009	0.056	0.000	7.71	10.2



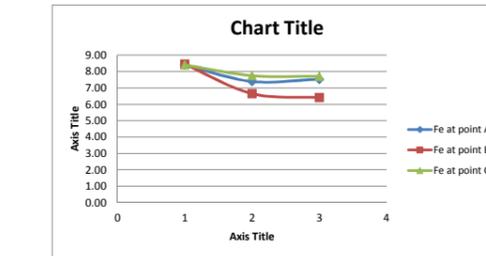
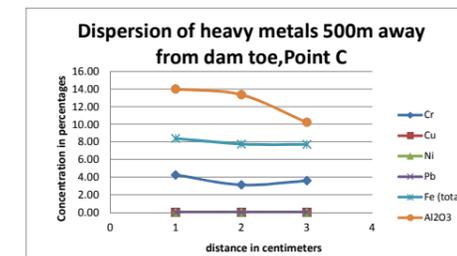
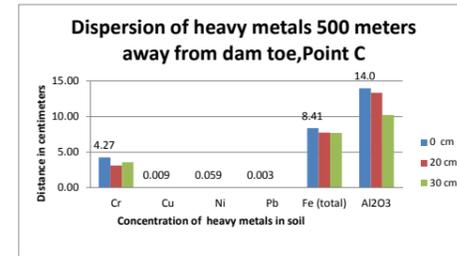
1500 METERS AWAY FROM DAM point A,1 meters

Depth	Cr	Cu	Ni	Pb	Fe (total)	Al2O3
0 cm	4.03	0.005	0.042	0.001	7.03	12.8
20 cm	0.522	0.003	0.023	0	4.012	12.3
30 cm	0.508	0.003	0.015	0.001	3.94	11.8



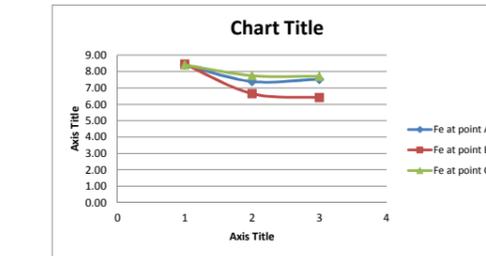
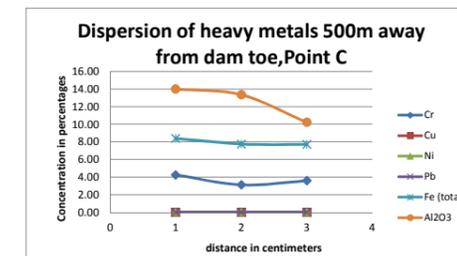
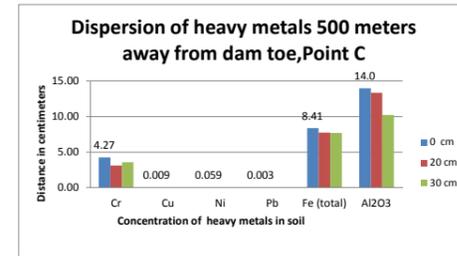
1500 METERS AWAY FROM DAM. point B , 2 meters

Depth	Cr	Cu	Ni	Pb	Fe (total)	Al2O3
0 cm	2.79	0.008	0.046	0.002	13.3	14.40
20 cm	2.41	0.05	0.031	0.0018	12.78	13.32
30 cm	2.50	0.005	0.035	0.002	6.6	13.0



1500 METERS AWAY FROM DAM. point C , 3 meters

Depth	Cr	Cu	Ni	Pb	Fe (total)	Al2O3
0 cm	2.84	0.008	0.046	0.002	7.4	15.10
20 cm	2.66	0.004	0.044	0.002	6.02	14.74
30 cm	2.75	0.005	0.044	0.002	6.66	14.1

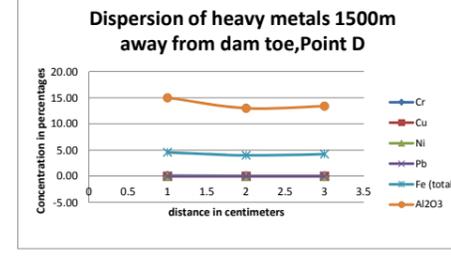
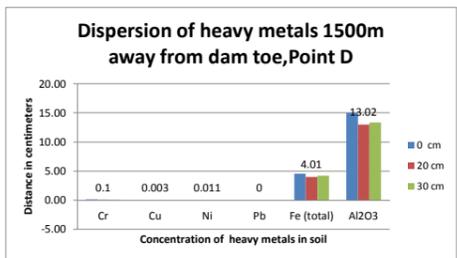
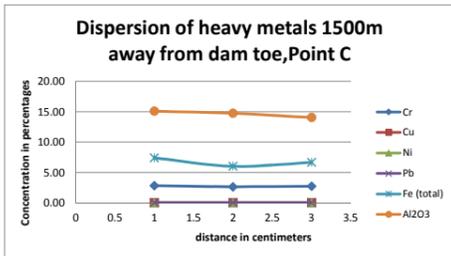
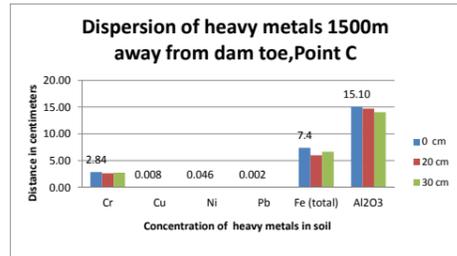
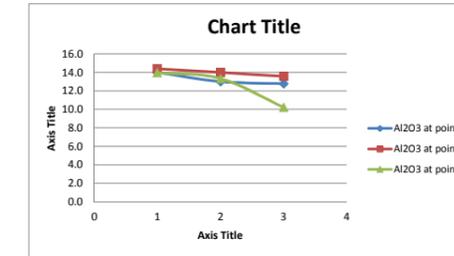
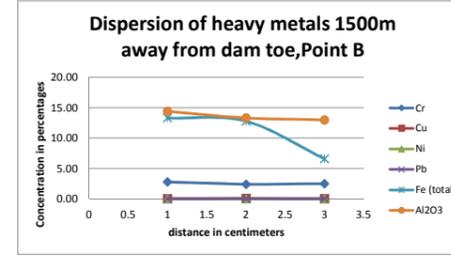
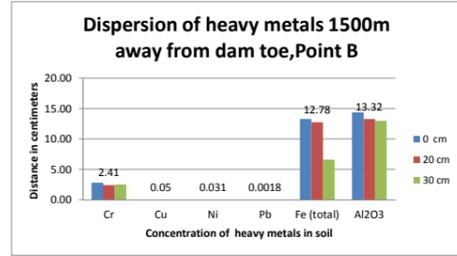
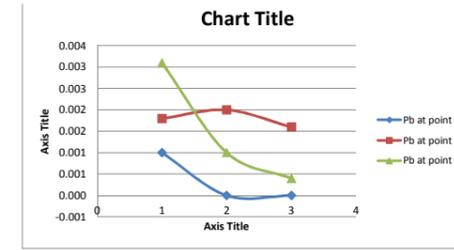
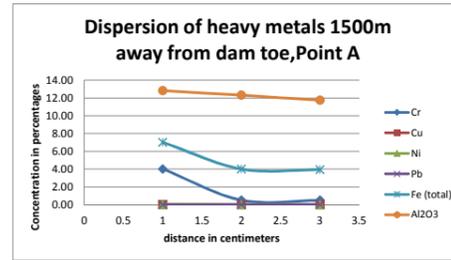
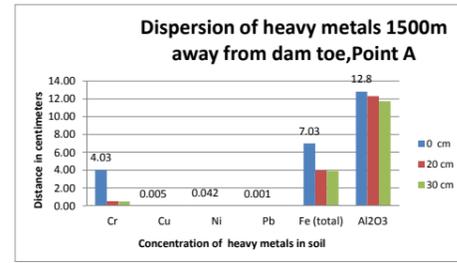
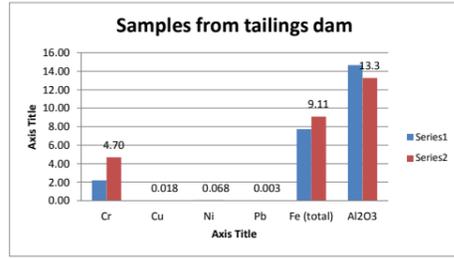


1500 METERS AWAY FROM DAM, point D , 4 meters

Depth	Cr	Cu	Ni	Pb	Fe (total)	Al2O3
0 cm	0.13	0.003	0.016	0.001	4.58	15.0
20 cm	0.1	0.003	0.011	0	4.01	13.02
30 cm	0.103	0.003	0.014	0.000	4.23	13.4

Tailing sample from plant sample inside tailing dam basin

Cr	Cu	Ni	Pb	Fe (total)	Al2O3
2.20	0.010	0.066	0.003	7.73	14.7
4.70	0.018	0.068	0.003	9.11	13.3



Appendix E.1 – STATISTICAL ANALYSIS – Cr

Analysis A: Fixed Distance vs Variable Depth

1. Metal Type

Cr
 Sample Distance = 500 meters i.e. from Tailings Dam
 n = sample size = 3
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)			Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 500 ± 1m	at 500 ± 2m	at 500 ± 3m			
Depth Below Ground (cm)	501	502	503			
0	4.13	2.79	4.27	3.73	0.448	0.669
20	2.98	2.77	3.12	2.96	0.021	0.144
30	3.20	2.77	3.59	3.19	0.115	0.338
Mean	3.44	2.77	3.86			
Variance	0.28073	0.02027	0.28727			
Standard Deviation (S.D)	0.530	0.142	0.536			

$$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$$

$$\bar{x} = \frac{\sum x}{n}$$

$$\text{s.d.} = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 3.29089
 Total Mean = \bar{X} = 1.494
 Variance for entire samples = 13.4462 σ^2
 Total SS = 13.4462 σ^2

Step 2: SSSys = 0.94115
 SSE is found by difference SSE = 12.5051244
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	0.94115089	2	0.470575444	0.225785674
Errors	12.5050124	6	2.084168741	
Total	13.4461633	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5%.

Degrees of Freedom = ν_1
 $\alpha = 0.05$ (95% probability)
 Error = ν_2
 From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 3.29089
 Total Mean = \bar{X} = 1.494
 Variance for entire samples = 13.4462 σ^2
 Total SS = 13.4462 σ^2

Step 2: SSSys = 1.27887
 SSE is found by difference SSE = 12.16729378
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	1.27886956	2	0.639434778	0.315321446
Errors	12.1672938	6	2.027882296	
Total	13.4461633	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5%.

Degrees of Freedom = ν_1
 $\alpha = 0.05$ (95% probability)
 Error = ν_2
 From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**

1. Metal Type

Cr
 Sample Distance = 1500 meters i.e. from Tailings Dam
 n = sample size = 3
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)				Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 1500 ± 1m	at 1500 ± 2m	at 1500 ± 3m	at 1500 ± 4m			
Depth Below Ground (cm)	1501	1502	1503	1504			
0	4.03	2.79	2.84	0.13	2.45	2.037	1.427
20	0.52	2.41	2.66	0.1	1.42	1.267	1.126
30	0.51	2.50	2.75	0.1033	1.47	1.375	1.173
Mean	1.6871	2.5660	2.7500	0.1110			
Variance	2.7470	0.0254	0.0054	0.0002			
Standard Deviation (S.D)	1.657	0.159	0.073	0.014			

$$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$$

$$\bar{x} = \frac{\sum x}{n}$$

$$\text{s.d.} = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 1.77853
 Total Mean = \bar{X} = 7.456
 Variance for entire samples = 89.4723 σ^2
 Total SS = 89.4723 σ^2

Step 2: SSSys = 2.0102
 SSE is found by difference SSE = 87.4621442
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	2.01019973	2	1.005099864	0.103426447
Errors	87.4621442	9	9.718016023	
Total	89.4723439	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5%.

Degrees of Freedom = ν_1
 $\alpha = 0.05$ (95% probability)
 Error = ν_2
 From F-Distribution Table = F = 4.28

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 1.77853
 Total Mean = \bar{X} = 7.456
 Variance for entire samples = 89.4723 σ^2
 Total SS = 89.4723 σ^2

Step 2: SSSys = 17.4115
 SSE is found by difference SSE = 72.0608291
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

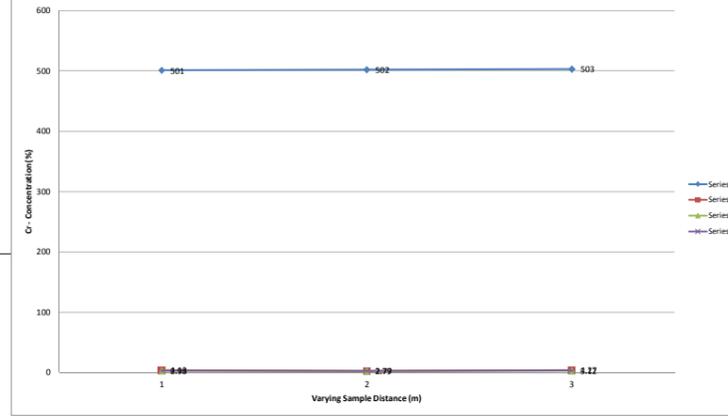
Source	S.S	d.f.	M.S.S.	F
Between groups	17.4115148	3	5.803838277	0.644326561
Errors	72.0608291	8	9.007603638	
Total	89.4723439	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5%.

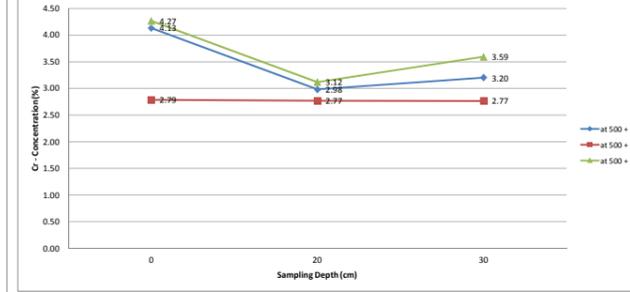
Degrees of Freedom = ν_1
 $\alpha = 0.05$ (95% probability)
 Error = ν_2
 From F-Distribution Table = F = 4.07

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**

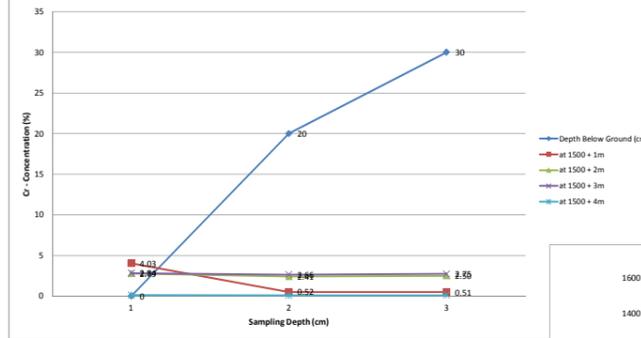
Cr - Variation in Concentration @ 500m Distance (Variable Distance)



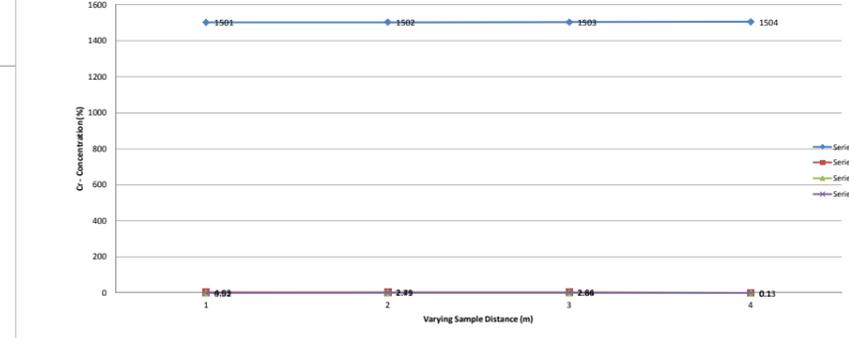
Cr - Variation in Concentration @ 500m Distance (Variable Depth)



Cr - Variation in Concentration @ 1500m Distance (Variable Depth)



Cr - Variation in Concentration @ 1500m Distance (Variable Distance)



Appendix E.2 – STATISTICAL ANALYSIS – Cu

Analysis A: Fixed Distance vs Variable Depth

1. Metal Type

Sample Distance = 500 meters i.e. from Tailings Dam
 n = sample size = 3
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)			Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 500 ± 1m	at 500 ± 2m	at 500 ± 3m			
Depth Below Ground (cm)	501	502	503			
0	0.01	0.01	0.01	0.01	0.000	0.000
20	0.01	0.01	0.01	0.01	0.000	0.000
30	0.01	0.01	0.01	0.01	0.000	0.000
Mean	0.01	0.01	0.01			
Variance	0.0000	0.0000	0.0000			
Standard Deviation (S.D)	0.000	0.000	0.000			

$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$
 $\bar{x} = \frac{\sum x}{n}$
 $\text{s.d.} = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 0.01047
 Total Mean = \bar{X} = 0.000
 Variance for entire samples = 2.3E-05
 Total SS = 0.01047

Step 2: SSSys = 7.5E-07
 SSE is found by difference SSE = 2.22133E-05
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	7.4667E-07	2	3.73333E-07	0.100840336
Errors	2.2213E-05	6	3.70222E-06	
Total	0.00002296	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$

The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 0.01047
 Total Mean = \bar{X} = 0.000
 Variance for entire samples = 2.3E-05
 Total SS = 0.01047

Step 2: SSSys = 3.9E-06
 SSE is found by difference SSE = 0.00001904
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	0.0000392	2	0.0000196	0.617647059
Errors	0.00001904	6	3.17333E-06	
Total	0.00002296	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)

The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**

1. Metal Type

Sample Distance = 1500 meters i.e. from Tailings Dam
 n = sample size = 3
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)				Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 1500 ± 1m	at 1500 ± 2m	at 1500 ± 3m	at 1500 ± 4m			
Depth Below Ground (cm)	1501	1502	1503	1504			
0	0.00	0.01	0.01	0.00	0.01	0.000	0.000
20	0.00	0.05	0.00	0.003	0.02	0.000	0.000
30	0.00	0.01	0.01	0.003	0.00	0.000	0.000
Mean	0.0035	0.0211	0.0057	0.0031			
Variance	0.0000	0.0004	0.0000	0.0000			
Standard Deviation (S.D)	0.000	0.020	0.000	0.000			

$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$
 $\bar{x} = \frac{\sum x}{n}$
 $\text{s.d.} = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 0.00835
 Total Mean = \bar{X} = 0.001
 Variance for entire samples = 0.01003
 Total SS = 0.00835

Step 2: SSSys = 0.00021
 SSE is found by difference SSE = 0.00982091
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	0.000205	2	0.000102501	0.093932801
Errors	0.00982091	9	0.001091212	
Total	0.01002591	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$

The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 4.28

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 0.00835
 Total Mean = \bar{X} = 0.001
 Variance for entire samples = 0.01003
 Total SS = 0.00835

Step 2: SSSys = 0.00089
 SSE is found by difference SSE = 0.009139214
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	0.0008867	3	0.000295566	0.258723281
Errors	0.00913921	8	0.001142402	
Total	0.01002591	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)

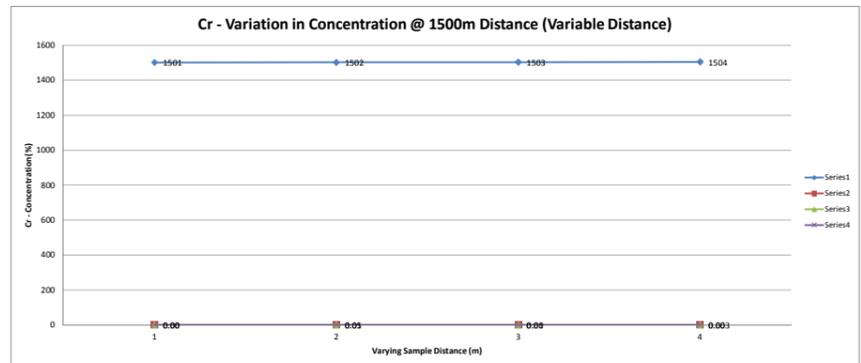
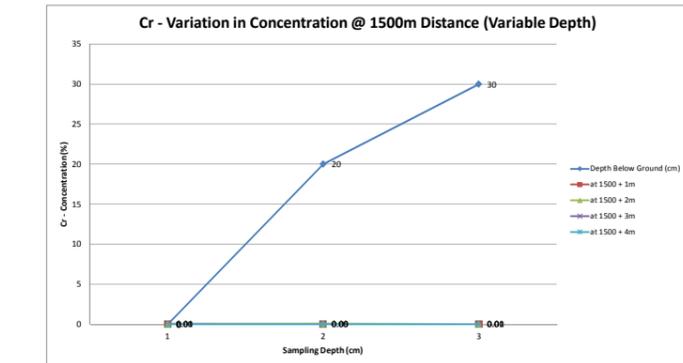
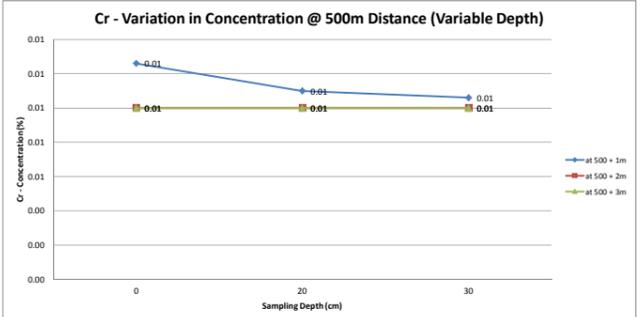
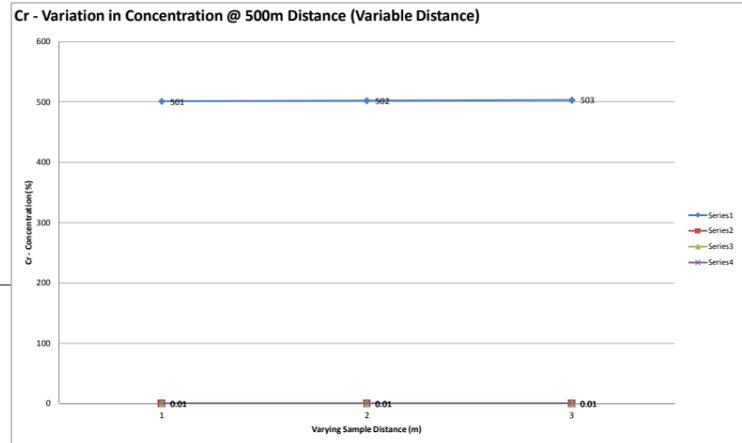
The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 4.07

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**



Appendix E.3 – STATISTICAL ANALYSIS – Ni

Analysis A: Fixed Distance vs Variable Depth

1. Metal Type **Cr**
 Sample Distance = **500** meters i.e. from Tailings Dam
 n = sample size = **3**
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)			Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 500 + 1m	at 500 + 2m	at 500 + 3m			
Depth Below Ground (cm)	501	502	503			
0	0.06	0.05	0.06	0.06	0.000	0.000
20	0.06	0.03	0.06	0.05	0.000	0.000
30	0.06	0.03	0.06	0.05	0.000	0.000
Mean	0.06	0.04	0.06			
Variance	0.0000	0.0004	0.0000			
Standard Deviation (S.D)	0.000	0.020	0.000			

variance = $\frac{\sum(x-\bar{x})^2}{n}$ $\bar{x} = \frac{\sum x}{n}$ s.d. = $\sqrt{\frac{\sum(x-\bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS
 Total Mean = $\bar{Xbar} = 0.05138$
 Variance for entire samples = 0.000
 Total SS = 0.00367 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 0.003570724 SSSys = $0.5E-05$

ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	9.5136E-05	2	4.75678E-05	0.079929625
Errors	0.00357072	6	0.000595121	
Total	0.00366586	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$

The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS
 Total Mean = $\bar{Xbar} = 0.05138$
 Variance for entire samples = 0.000
 Total SS = 0.00367 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 0.002655098 SSSys = 0.00101

ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	0.00101076	2	0.000505381	1.142062146
Errors	0.0026551	6	0.000442516	
Total	0.00366586	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)

The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**

1. Metal Type **Cr**
 Sample Distance = **1500** meters i.e. from Tailings Dam
 n = sample size = **3** N = **4** population size
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)				Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 1500 + 1m	at 1500 + 2m	at 1500 + 3m	at 1500 + 4m			
Depth Below Ground (cm)	1501	1502	1503	1504			
0	0.42	0.05	0.05	0.02	0.13	0.028	0.170
20	0.02	0.03	0.04	0.011	0.03	0.000	0.017
30	0.02	0.03	0.04	0.0141	0.03	0.000	0.017
Mean	0.1537	0.0371	0.0447	0.0137			
Variance	0.0363	0.0000	0.0000	0.0000			
Standard Deviation (S.D)	0.190	0.000	0.000	0.000			

variance = $\frac{\sum(x-\bar{x})^2}{n}$ $\bar{x} = \frac{\sum x}{n}$ s.d. = $\sqrt{\frac{\sum(x-\bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS
 Total Mean = $\bar{Xbar} = 0.06231$
 Variance for entire samples = 0.065
 Total SS = 0.77855 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 0.756297298 SSSys = 0.02225

ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	0.02225001	2	0.011125006	0.132388481
Errors	0.7562973	9	0.084033033	
Total	0.77854731	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$

The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 4.28

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS
 Total Mean = $\bar{Xbar} = 0.06231$
 Variance for entire samples = 0.065
 Total SS = 0.77855 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 0.731917386 SSSys = 0.04663

ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	0.04662992	3	0.015543308	0.16989139
Errors	0.73191729	8	0.091489673	
Total	0.77854731	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)

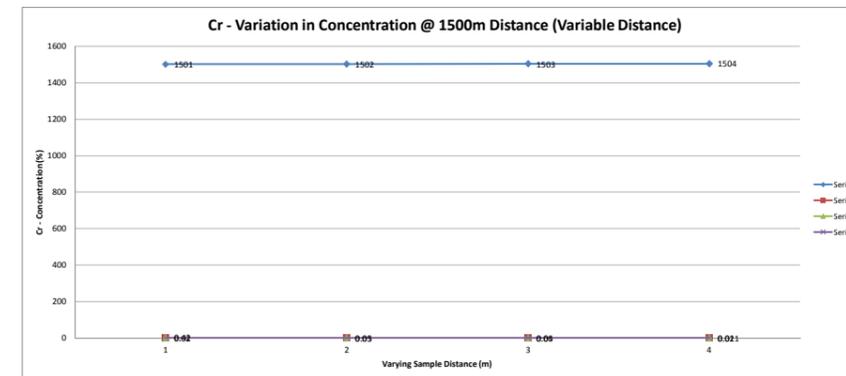
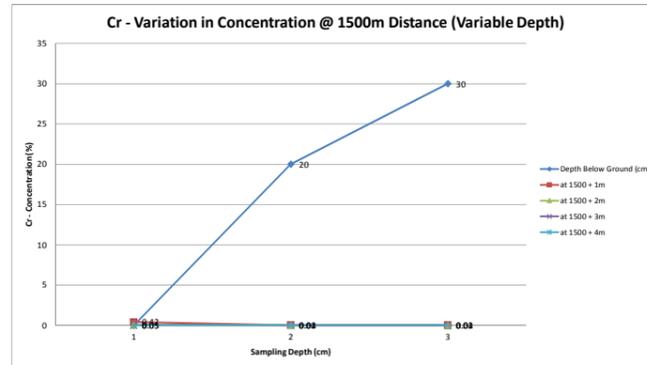
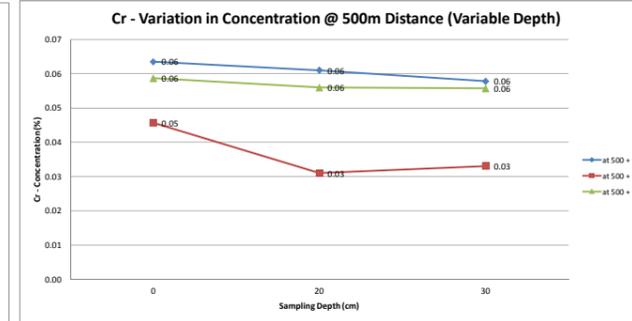
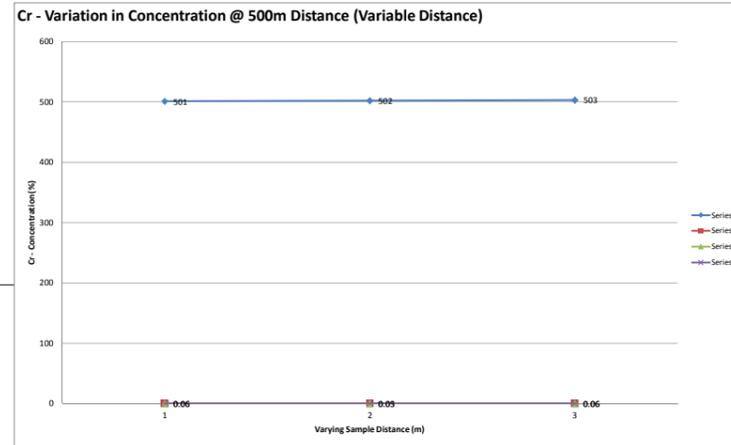
The alternative hypothesis, H_1 , is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = ν_1

$\alpha = 0.05$ (95% probability) thus..... From F-Distribution Table = F = 4.07

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**



Appendix E.4 – STATISTICAL ANALYSIS – Pb

Analysis A: Fixed Distance vs Variable Depth

1. Metal Type **Pb**
 Sample Distance = meters i.e. from Tailings Dam
 n = sample size =
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)			Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 500 + 1m	at 500 + 2m	at 500 + 3m			
Depth Below Ground (cm)	501	502	503			
0	0.00	0.00	0.00	0.00	0.000	0.000
20	0.00	0.00	0.00	0.00	0.000	0.000
30	0.00	0.00	0.00	0.00	0.000	0.000
Mean	0.00	0.00	0.00			
Variance	0.0000	0.0000	0.0000			
Standard Deviation (S.D)	0.000	0.000	0.000			

$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$ $\bar{x} = \frac{\sum x}{n}$ $s.d. = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 0.00161
 Total Mean = $\bar{Xbar} = 0.000$
 Variance for entire samples = 0.000 σ^2
 Total SS = 7.2E-05 SS_{total}

Step 2: SSSys = 1.7E-06
 SSE is found by difference SSE = 7.01244E-05

ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	1.6956E-06	2	8.47778E-07	0.072537711
Errors	7.0124E-05	6	1.16874E-05	
Total	0.00007182	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5% .

Degrees of Freedom = ν_1 Error = ν_2
 thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 0.00161
 Total Mean = $\bar{Xbar} = 0.000$
 Variance for entire samples = 0.000 σ^2
 Total SS = 7.2E-05 SS_{total}

Step 2: SSSys = 0.6E-06
 SSE is found by difference SSE = 6.32578E-05

ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	8.5623E-06	2	4.28111E-06	0.406063374
Errors	6.3258E-05	6	1.0543E-05	
Total	0.00007182	8		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5% .

Degrees of Freedom = ν_1 Error = ν_2
 thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**

1. Metal Type **Pb**
 Sample Distance = meters i.e. from Tailings Dam
 n = sample size = N = population size
 Null Hypothesis, $H_0 = 0$
 $H_1 \neq 0$
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)				Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 1500 + 1m	at 1500 + 2m	at 1500 + 3m	at 1500 + 4m			
Depth Below Ground (cm)	1501	1502	1503	1504			
0	0.01	0.00	0.00	0.00	0.00	0.000	0.000
20	0.00	0.00	0.00	0	0.00	0.000	0.000
30	0.00	0.00	0.00	0.0003	0.00	0.000	0.000
Mean	0.0027	0.0017	0.0020	0.0005			
Variance	0.0000	0.0000	0.0000	0.0000			
Standard Deviation (S.D)	0.000	0.000	0.000	0.000			

$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$ $\bar{x} = \frac{\sum x}{n}$ $s.d. = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 0.00172
 Total Mean = $\bar{Xbar} = 0.000$
 Variance for entire samples = 0.000 σ^2
 Total SS = 0.0002 SS_{total}

Step 2: SSSys = 0.7E-06
 SSE is found by difference SSE = 0.000195206

ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	6.7288E-06	2	3.36438E-06	0.155114782
Errors	0.00019521	9	2.16896E-05	
Total	0.00020194	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5% .

Degrees of Freedom = ν_1 Error = ν_2
 thus..... From F-Distribution Table = F = 4.28

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 0.00172
 Total Mean = $\bar{Xbar} = 0.000$
 Variance for entire samples = 0.000 σ^2
 Total SS = 0.0002 SS_{total}

Step 2: SSSys = 1E-05
 SSE is found by difference SSE = 0.000191753

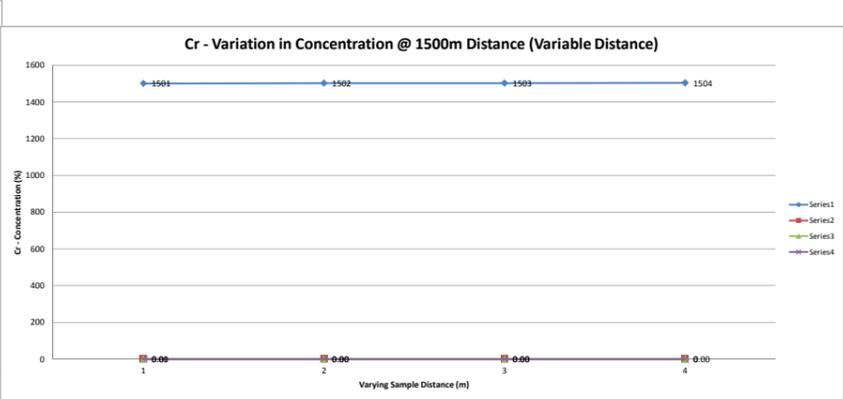
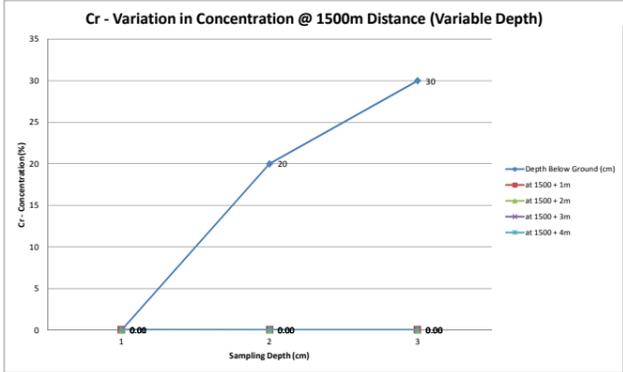
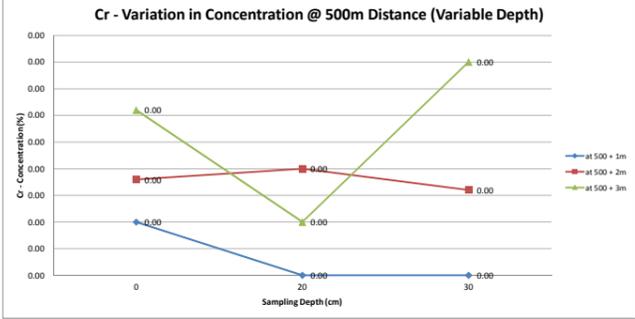
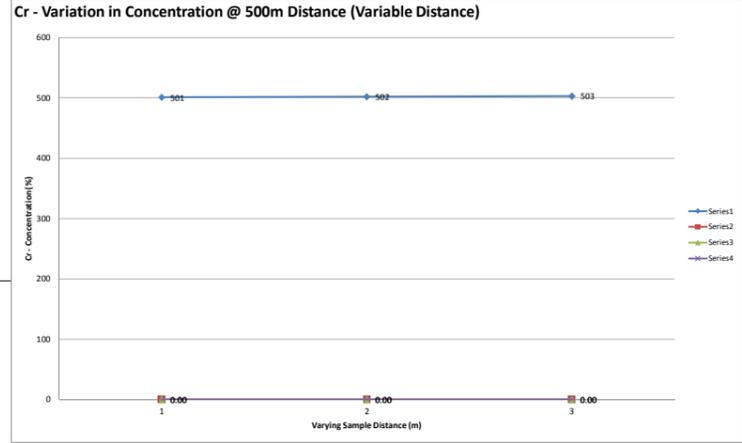
ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	1.0183E-05	3	3.39407E-06	0.141602082
Errors	0.00019175	8	2.39691E-05	
Total	0.00020194	11		

The null hypothesis, H_0 , is that all the group means are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$ (i.e. mean concentration at varying distance are equal)
 The alternative hypothesis, H_1 , is that at least two of the group means are different.
 The significance level is as stated of 5% .

Degrees of Freedom = ν_1 Error = ν_2
 thus..... From F-Distribution Table = F = 4.07

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**



Appendix E.5 – STATISTICAL ANALYSIS – Fe

Analysis A: Fixed Distance vs Variable Depth

1. Metal Type: Fe
 Sample Distance = 500 meters (I.e. from Tailings Dam)
 n = sample size = 3
 Null Hypothesis, H₀ = 0
 H₁ ≠ 0
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)			Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 500 + 1m	at 500 + 2m	at 500 + 3m			
0	8.41	8.46	8.41	8.43	0.001	0.001
20	7.40	6.66	7.76	7.27	0.210	0.458
30	7.54	6.42	7.71	7.22	0.328	0.573
Mean	7.78	7.18	7.96			
Variance	0.10794	0.62687	0.28236			
Standard Deviation (S.D)	0.328	0.792	0.531			

variance = $\frac{\sum (x - \bar{x})^2}{n}$ $\bar{x} = \frac{\sum x}{n}$ s.d. = $\sqrt{\frac{\sum (x - \bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS
 Total Mean = Xbar = 7.64067
 Variance for entire samples = 1.828 σ^2
 Total SS = 16.4476 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 13.67562067
 SSSys = 2.772

Source	S.S	d.f.	M.S.S.	F
Between groups	2.77204667	2	1.38602333	0.608090426
Errors	13.67562067	6	2.279270111	
Total	16.44762533	8		

The null hypothesis, H₀, is that all the group means are equal. H₀: μ₁ = μ₂ = μ₃ = μ₄
 The alternative hypothesis, H₁, is that at least two of the group means are different.
 The significance level is as stated of 5% .
 -Degrees of Freedom = v₁
 -α = 0.05 (95% probability)

thus = $\frac{2}{6}$ Error = v₂ = 6
 From F-Distribution Table = F = 5.14

Accept H₀. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth

ANOVA - F-test (Variation by Distance)

Step 1: Total SS
 Total Mean = Xbar = 7.64067
 Variance for entire samples = 1.828 σ^2
 Total SS = 16.4476 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 15.44478067
 SSSys = 1.00284

Source	S.S	d.f.	M.S.S.	F
Between groups	1.00284667	2	0.50142333	0.194792925
Errors	15.44478067	6	2.574130111	
Total	16.44762533	8		

The null hypothesis, H₀, is that all the group means are equal. H₀: μ₁ = μ₂ = μ₃ = μ₄ (i.e. mean concentration at varying distance are equal)
 The alternative hypothesis, H₁, is that at least two of the group means are different.
 The significance level is as stated of 5% .
 -Degrees of Freedom = v₁
 -α = 0.05 (95% probability)

thus = $\frac{2}{6}$ Error = v₂ = 6
 From F-Distribution Table = F = 5.14

Accept H₀. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance

1. Metal Type: Fe
 Sample Distance = 1500 meters (I.e. from Tailings Dam)
 n = sample size = 3
 Null Hypothesis, H₀ = 0
 H₁ ≠ 0
 No significant change in concentration
 Reject Null Hypothesis
 N = 4 population size

Depth	Concentration (%)				Mean \bar{x}	Variance	Standard Deviation (S.D)
	at 1500 + 1m	at 1500 + 2m	at 1500 + 3m	at 1500 + 4m			
0	7.03	13.33	7.40	4.59	8.09	10.327	3.213
20	4.01	12.78	6.02	4.01	6.71	12.975	2.699
30	3.94	6.60	6.66	4.23	5.36	1.630	1.257
Mean	4.9933	10.9033	6.6933	4.2767			
Variance	2.0748	9.3098	0.3180	0.0572			
Standard Deviation (S.D)	1.440	3.051	0.564	0.239			

variance = $\frac{\sum (x - \bar{x})^2}{n}$ $\bar{x} = \frac{\sum x}{n}$ s.d. = $\sqrt{\frac{\sum (x - \bar{x})^2}{n}}$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS
 Total Mean = Xbar = 6.71667
 Variance for entire samples = 36.692 σ^2
 Total SS = 440.303 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 429.1234542
 SSSys = 11.18

Source	S.S	d.f.	M.S.S.	F
Between groups	11.1799625	2	5.58998125	0.117238596
Errors	429.1234542	9	47.6803838	
Total	440.3034167	11		

The null hypothesis, H₀, is that all the group means are equal. H₀: μ₁ = μ₂ = μ₃ = μ₄
 The alternative hypothesis, H₁, is that at least two of the group means are different.
 The significance level is as stated of 5% .
 -Degrees of Freedom = v₁
 -α = 0.05 (95% probability)

thus = $\frac{2}{9}$ Error = v₂ = 9
 From F-Distribution Table = F = 4.28

Accept H₀. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth

ANOVA - F-test (Variation by Distance)

Step 1: Total SS
 Total Mean = Xbar = 6.71667
 Variance for entire samples = 36.692 σ^2
 Total SS = 440.303 SStotal

Step 2: SSSys
 SSE is found by difference SSE = 334.4946167
 SSSys = 105.809

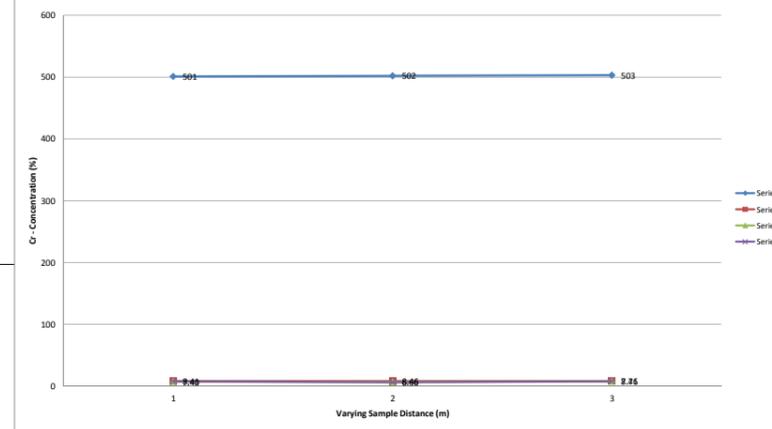
Source	S.S	d.f.	M.S.S.	F
Between groups	105.8088	3	35.2696	0.843531662
Errors	334.4946167	8	41.81182708	
Total	440.3034167	11		

The null hypothesis, H₀, is that all the group means are equal. H₀: μ₁ = μ₂ = μ₃ = μ₄ (i.e. mean concentration at varying distance are equal)
 The alternative hypothesis, H₁, is that at least two of the group means are different.
 The significance level is as stated of 5% .
 -Degrees of Freedom = v₁
 -α = 0.05 (95% probability)

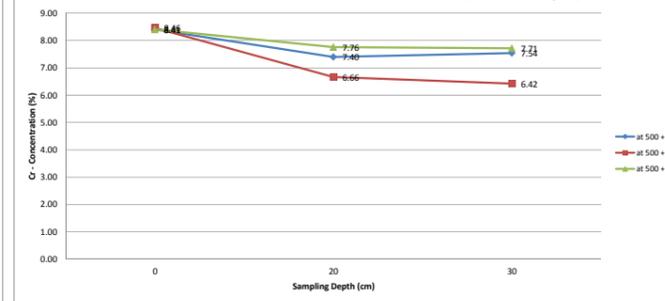
thus = $\frac{3}{8}$ Error = v₂ = 8
 From F-Distribution Table = F = 4.07

Accept H₀. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance

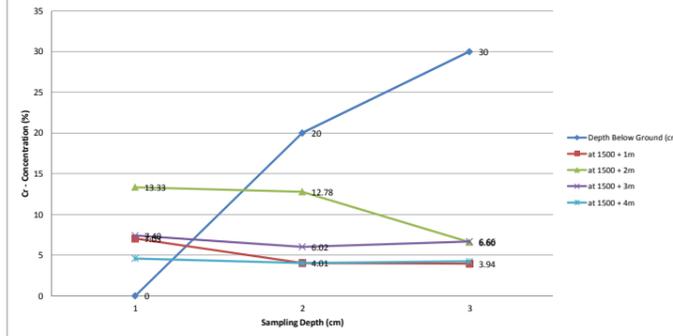
Cr - Variation in Concentration @ 500m Distance (Variable Distance)



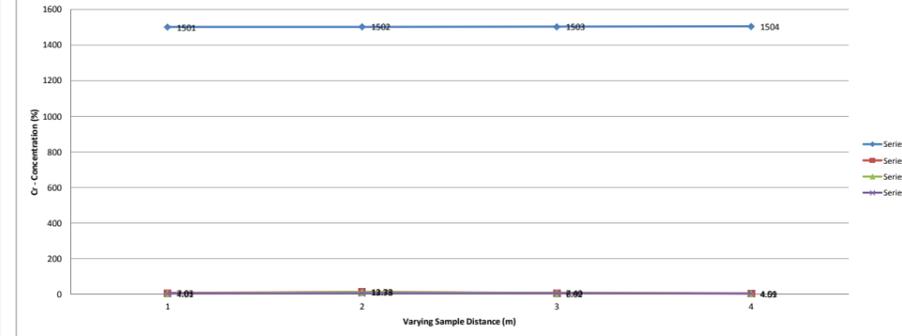
Cr - Variation in Concentration @ 500m Distance (Variable Depth)



Cr - Variation in Concentration @ 1500m Distance (Variable Depth)



Cr - Variation in Concentration @ 1500m Distance (Variable Distance)



Appendix E.6 – STATISTICAL ANALYSIS – Al₂O₃

Analysis A: Fixed Distance vs Variable Depth

1. Metal Type

Al2O3

Sample Distance = 500 meters i.e. from Tailings Dam

n = sample size = 3
 Null Hypothesis, Ho = 0
 H1 ≠ 0
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)			Mean x̄	Variance	Standard Deviation (S.D)
	at 500 = 1m	at 500 = 2m	at 500 = 3m			
Depth Below Ground (cm)	501	502	503			
0	41.02	14.40	14.00	23.14	159.874	12.645
20	13.01	14.01	13.35	13.46	0.172	0.415
30	12.80	13.58	10.23	12.20	2.048	1.431
Mean	22.28	14.00	12.53			
Variance	159.874	0.172	2.048			
Standard Deviation (S.D)	12.645	0.415	1.431			

$$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$$

$$\bar{x} = \frac{\sum x}{n}$$

$$s.d. = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 16.2667
 Total Mean = Xbar = 342.477
 Variance for entire samples = 3082.3
 Total SS = 3082.3 SStotal

Step 2: SSSys = 214.948
 SSE is found by difference SSE = 2867.346667
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	214.948467	2	107.4742333	0.224892723
Errors	2867.34667	6	477.8911111	
Total	3082.29513	8		

The null hypothesis, Ho, is that all the group means are equal. Ho: μ1 = μ2 = μ3 = μ4

The alternative hypothesis, H1, is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = v1

α = 0.05 (95% probability) thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 16.2667
 Total Mean = Xbar = 342.477
 Variance for entire samples = 3082.3
 Total SS = 3082.3 SStotal

Step 2: SSSys = 165.782
 SSE is found by difference SSE = 2916.513333
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	165.7818	2	82.8909	0.170527388
Errors	2916.51333	6	486.0855556	
Total	3082.29513	8		

The null hypothesis, Ho, is that all the group means are equal. Ho: μ1 = μ2 = μ3 = μ4 (i.e. mean concentration at varying distance are equal)

The alternative hypothesis, H1, is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = v1

α = 0.05 (95% probability) thus..... From F-Distribution Table = F = 5.14

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**

1. Metal Type

Al2O3

Sample Distance = 1500 meters i.e. from Tailings Dam

n = sample size = 3
 Null Hypothesis, Ho = 0
 H1 ≠ 0
 No significant change in concentration
 Reject Null Hypothesis

Depth	Concentration (%)				Mean x̄	Variance	Standard Deviation (S.D)
	at 1500 = 1m	at 1500 = 2m	at 1500 = 3m	at 1500 = 4m			
Depth Below Ground (cm)	1501	1502	1503	1504			
0	12.83	14.40	15.10	15.02	14.34	0.831	0.912
20	12.33	13.32	14.74	13.02	13.35	0.771	0.876
30	11.77	13.01	15.05	13.39	13.31	1.374	1.172
Mean	12.3100	13.5767	14.9633	13.8100			
Variance	0.1875	0.3950	0.0254	0.7549			
Standard Deviation (S.D)	0.433	0.628	0.158	0.869			

$$\text{variance} = \frac{\sum (x - \bar{x})^2}{n}$$

$$\bar{x} = \frac{\sum x}{n}$$

$$s.d. = \sqrt{\frac{\sum (x - \bar{x})^2}{n}}$$

ANOVA - F-test (Variation by Depth)

Step 1: Total SS = 13.665
 Total Mean = Xbar = 4.298
 Variance for entire samples = 51.5761
 Total SS = 51.5761 SStotal

Step 2: SSSys = 2.03854
 SSE is found by difference SSE = 49.53754583
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	2.0385375	2	1.01926875	0.185181131
Errors	49.5375458	9	5.504171759	
Total	51.5760833	11		

The null hypothesis, Ho, is that all the group means are equal. Ho: μ1 = μ2 = μ3 = μ4

The alternative hypothesis, H1, is that at least two of the group means are different.

The significance level is as stated of 5%.

Degrees of Freedom = v1

α = 0.05 (95% probability) thus..... From F-Distribution Table = F = 4.28

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by depth**

ANOVA - F-test (Variation by Distance)

Step 1: Total SS = 13.665
 Total Mean = Xbar = 4.298
 Variance for entire samples = 51.5761
 Total SS = 51.5761 SStotal

Step 2: SSSys = 14.2021
 SSE is found by difference SSE = 37.37399444
 ANOVA TABLE 1: FOR VARIATION BY DEPTH

Source	S.S	d.f.	M.S.S.	F
Between groups	14.2020889	3	4.73402963	1.013331264
Errors	37.3739944	8	4.671749306	
Total	51.5760833	11		

The null hypothesis, Ho, is that all the group means are equal. Ho: μ1 = μ2 = μ3 = μ4 (i.e. mean concentration at varying distance are equal)

The alternative hypothesis, H1, is that at least two of the group means are different.

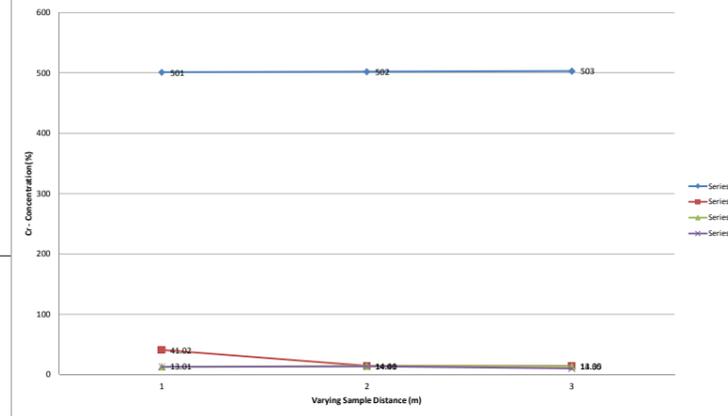
The significance level is as stated of 5%.

Degrees of Freedom = v1

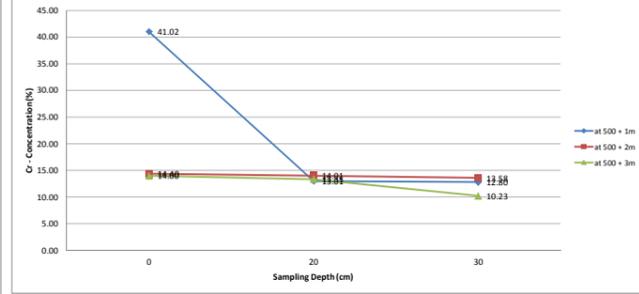
α = 0.05 (95% probability) thus..... From F-Distribution Table = F = 4.07

thus = **Accept Ho. There is no significant difference between the group means. I.e there is no significant difference in the mean concentration when varying by distance**

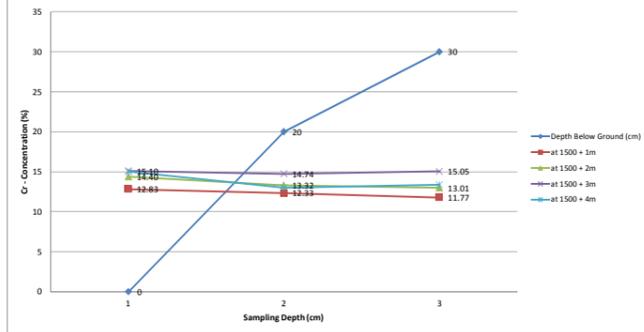
Cr - Variation in Concentration @ 500m Distance (Variable Distance)



Cr - Variation in Concentration @ 500m Distance (Variable Depth)



Cr - Variation in Concentration @ 1500m Distance (Variable Depth)



Cr - Variation in Concentration @ 1500m Distance (Variable Distance)

